SYMPOSIUM A

Amorphous and Heterogeneous Silicon Thin Films-2000

April 24 - 28, 2000

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TUTORIAL

ST A: AMORPHOUS SILICON MATERIALS AND DEVICES FOR LARGE AREA ELECTRONICS

Monday, April 24, 2000 8:30 a.m. - 4:30 p.m. Salon 7 (Marriott)

Hydrogenated amorphous silicon (a-Si:H) is an important technological material for large-area electronics, with applications to solar cells, liquid crystal displays, optical scanners, and radiation imaging. The course describes the growth, material properties, device physics, and large-area array technology of amorphous silicon. The relation between material properties and device performance of a-Si:H is emphasized.

Instructors:

Robert A. Street, Xerox Palo Alto Research Center Michael Hack, Universal Display Corporation

> SESSION A1: AMORPHOUS SILICON GROWTH Chair: Hiroyuki Fujiwara Tuesday Morning, April 25, 2000 Salon 7 (Marriott)

8:30 AM *A1.1 SURFACE MICROCHEMICAL REACTIONS DURING HYDRO-GENATED SILICON GROWTH STUDIED BY IN-SITU ESR TECHNIQUE. <u>Satoshi Yamasaki</u>, Joint Research Center for Atom Technology (JRCAT), Tsukuba, JAPAN.

To address the μc-Si:H and a-Si:H growth mechanism, several groups have reported on the surface morphology and bonding configurations during film growth using real-time spectroscopic ellipsometry, ultrahigh-vacuum scanning-tunneling-microscopy, and infrared absorption reflection spectroscopy. These measurements, however, give us information on the macroscopic change of surface structures. For the growth of μ c-Si:H and a-Si:H, dangling bonds (dbs) in the surface region play a crucial role as reaction sites for precursors to bond to the surface. From this meaning, elementary reactions of the film growth are equivalent to the process of termination, annihilation of and creation of dbs. Therefore, in-situ electron-spin-resonance (ESR) measurements during film growth give us a valuable information to understand growth kinetics. Previously, we have reported that (1) using in-situ ESR technique the dynamic change of Si db during and after deposition has been detected, in addition to the gas-phase ESR signals both of atomic hydrogen and radicals related with silane molecules, (2) the surface region has high db density ($\sim 10^{13}~{\rm cm}^{-2}$) during film growth, (3) the surface db density during film growth is almost independent of the growth temperature in the temperature range below 200°C, (4) the db signal intensity decreases after stopping the deposition due to a structural relaxation, (5) during hydrogen plasma treatments hydrogen atoms create dbs, rather than terminate them, which are spatially distributed within the deeper layers of the film (around 100 nm from the top-surface). In this talk, I show the recent results obtained using the in-situ ESR technique and discuss the surface microchemical reactions during Si:H film growth.

9:00 AM A1.2

FRACTAL ANALYSIS OF TOPOGRAPHY AND SURFACE TRANSPORT DURING AMORPHOUS SILICON GROWTH, AND ITS RELATION TO DIFFUSION STATE ENERGETICS DETERMINED FROM AB-INITIO CALCULATIONS Gregory N. Parsons, Kevin R. Bray, Atul Gupta, Department of Chemical Engineering; Hong Yang, Department of Chemistry, North Carolina State University, Raleigh, NC.

A fundamental understanding of surface reactions in plasma deposited amorphous silicon is critical to improve material properties. A combined approach to this problem, including atomic force microscopy analysis of surface topology and ab-initio calculations of surface reactions and stable configurations is used to gain insight into growth mechanisms. AFM surface topography was compared for samples deposited over a range of temperatures (25 - 150°C) and film thicknesses (20 - 1500 Å). The surface transport mechanism active during deposition can be extracted from the fractal analyses of surface morphology by determining a static scaling coefficient (α). Individual nuclei are observed to coalesce after 15-20 sec deposition, and the static scaling coefficient increases from 0.25 to 1 as deposition time continues upto ~ 60 seconds (corresponding to thickness upto $\sim 50 \text{\AA}$). and saturates near $\alpha = 1$, consistent with surface transport controlled by diffusion. Moreover, the rate of evolution is thermally activated,

with a small activation barrier of 1.6 kcal/mol between 25 and 150°C, suggesting a thermally activated diffusion process. Ab-initio calculations have been used to study reactions between silyl (SiH3) radicals and a-Si:H surface, including adsorption states that could lead to low-barrier surface diffusion. Results show that the H radicals have a lower barrier to H abstraction than H abstraction by SiH3 (~7.2 kcal/mol for H vs. ~12.9 kcal/mol for silyl). Also, the H abstraction process, calculated using multiparent CI and BLYP DFT, shows a distinct saddle-point structure in the potential energy surface, with no evidence for a stable 3-center Si-H-Si bond on the surface. A stable 3-center bond is an important element in deposition models based on adsorbed radical diffusion. The morphology and reaction analysis, however, indicate that some other process is occurring on the surface. For example, the observed growth evolution may be consistent with other stable adsorbed radicals whose hopping rate is determined by the rate of H abstraction.

9:15 AM A1.3

ENHANCEMENT OF THE TRANSPORT PROPERTIES OF a-Si:H PECVD FILMS BY PROPER CONTROL OF THE ION BOMBARDMENT. Hugo Aguas, R. Martins, I. Ferreira, E. Fortunato, Univ. Nova de Lisboa, Faculty of Science and Technology, Dept. of Materials Science, CENIMAT and CEMOP/UNINOVA, Monte da Caparica, PORTUGAL.

In this work we show how it is possible to enhance the transport properties of a-Si:H films while the growth rate of the films is kept constant. To do so, we used a modified PECVD triode reactor. The modification consists in applying a DC voltage to a set of grids placed in front of the r.f. electrode. By doing so, we control the energy of the ions striking the substrate during the film's growth. The films were deposited in large area substrates of 15 cm x 20 cm and presented good uniformity over the substrate area. The results achieved show that as the energy of the ions increase up to 100 eV, the SiH_2 concentration decreases and the refractive index increases, leading to denser films. The films photosensitivity (under AM 1.5 conditions) presents a maximum of 1.3×10^6 when the ion energy is 40 eV. For higher ion energies, the photosensitivity decreases abruptly by about one order of magnitude to increase again linearly and to reach the same photosensitivity at an ion energy of 100 eV. Under this new conditions the films are more dense. These results indicate that in spite of the films microstructure being linearly dependent on the ion energy, the films defects are not. This means that the ion energy influences the Si bonding during the films growth and also implies that when the growth surface sustains a high ion bombardment, a different type of structure is achieved, which exhibits a better film stability. So, with a precise control of the energy of the ions that strike the substrate during the films growth it is possible to grow both dense and high quality films for optoelectronic applications, more stable than the ones produced by conventional r.f. glow discharge techniques.

9:30 AM *A1.4

GROWTH PROCESSES OF a-Si:H. John Robertson, Engineering Dept, Cambridge University, Cambridge, UNITED KINGDOM.

The surface and subsurface processes occurring during the growth of a-Si:H are analyzed to understand the formation of dangling bond defects and weak bonds, particularly at lower deposition temperatures. It is shown that abstraction and addition by SiH_3 radicals cannot account for the temperature dependence of the bulk defect density. We argue that hydrogen elimination to form the Si-Si network is the rate limiting process at lower temperatures, and this is responsible for the creation of weak Si-Si bonds. The dangling bonds form subsequently from weak bonds by a defect pool type process. Additional plasma-driven processes such as ion bombardment also help eliminate hydrogen, and so allow lower weak bond densities to be achieved at lower deposition temperatures.

> SESSION A2: ORDERING AND ORDERING TRANSITIONS Chair: Sigurd Wagner Tuesday Morning, April 25, 2000 Salon 7 (Marriott)

10:30 AM *A2.1

NUCLEATION MECHANISM OF MICROCRYSTALLINE SILICON STUDIED BY REAL TIME SPECTROSCOPIC ELLIPSOMETRY AND INFRARED SPECTROSCOPY. H. Fujiwara, Y. Toyoshima, M. Kondo and A. Matsuda, Thin Film Silicon Solar Cells Super Lab., Electrotechnical Laboratory, Tsukuba, JAPAN.

We have applied real time spectroscopic ellipsometry (SE) and infrared attenuated internal total reflection spectroscopy (ATR), in order to investigate microcrystalline silicon (µc-Si:H) nucleation mechanism in plasma-enhanced chemical vapor deposition using

hydrogen dilution of SiH_4 source gas. The combination of these real time monitoring techniques provides a greater capability to characterize the μ c-Si:H nucleation process and following μ c-Si:H grain growth with sensitivity exceeding monolayer. In a-Si:H layers formed before the μ c-Si:H nucleation at 230°C, we found no significant variation in bulk hydrogen contents for either hydrogen dilution ratios or a-Si:H layer thicknesses. In contrast, a drastic change in SiH_n (n=1-2) bonding modes has been found in a two-monolayer thick sub-surface, and we observed a new peak centered at 1940 cm⁻¹. We assigned this peak to the SiH_n complex that contains one dangling bond in four-fold coordinated Si atom. In the high-dilution deposition conditions, the integrated absorbance of the SiH_n complex increases with increasing film thickness, and reaches maximum just at the onset of the μ c-Si nucleation. Thus, the SiH_n complex within the two-monolayer sub-surface is precursors that lead to the μ c-Si:H nucleation. More importantly, upon H2-plasma treatment of a-Si:H layer, we observed a rapid increase in the SiH_n complex in the a-Si:H sub-surface. Based on the above results, we conclude that the structural relaxation by atomic hydrogen creates the flexible SiH_n complex in the sub-surface, which in turn induces μ c-Si:H nucleation.

11:00 AM $\underline{A2.2}$ STUDY OF THE AMORPHOUS-TO-MICROCRYSTALLINE TRANSITION DURING SILICON FILM GROWTH AT HIGH RATES; EXTENSIONS OF THE EVOLUTIONARY PHASE DIAGRAM. A.S. Ferlauto, P.I. Rovira, R.J. Koval, C.R. Wronski and R.W. Collins, The Pennsylvania State University, Materials Research Laboratory and Center for Thin Film Devices, University Park, PA.

We have studied the effect of plasma power on the amorphous-tomicrocrystalline $(a \rightarrow \mu c)$ transition in silicon thin films prepared by rf plasma enhanced chemical vapor deposition (PECVD) using moderate hydrogen dilution of silane. The nature of initial amorphous layer formation and the subsequent $a \rightarrow \mu c$ transition is elucidated by real time spectroscopic ellipsometry (RTSE). RTSE provides evolutionary phase diagrams for film growth; these diagrams describe the critical thickness d at which microcrystallinity first develops during growth, as a function of the H_2 :Si H_4 gas flow ratio R. We find that for amorphous layer growth on a c-Si substrate at R=10, the initial enhanced smoothening during coalescence/growth, and thus suitability of the resulting films for devices, is not degraded by moderate increases in rf power flux (from 0.08 to $0.3~\rm W/cm^2$, yielding increases in deposition rate from 0.5 to 2 Å/s). Additionally the thickness at which microcrystallinity develops when using an amorphous silicon substrate film (as for the i-layer in a p-i-n solar cell) is not significantly affected by such moderate increases in power. Above a critical power flux of $\sim 1~W/cm^2$, however, both the smoothening and the $a\rightarrow \mu c$ transition are suppressed by plasma and surface effects that may include SiH4 depletion, ion bombardment, or simply kinetic limitations. The suppression of microcrystallinity is a manifestation of a shift in the $a \rightarrow \mu c$ phase boundary to higher R for the high power conditions. Detailed studies of the $a{ o}\mu c$ transition in films deposited at different rates provide insights into the evolutionary forces driving this transition. Finally, consideration of the overall results suggests approaches for high rate i-layer preparation in p-i-n solar cells. As an example, we assess the benefits of a two-step process in which the initial stage of i-layer growth is performed at minimum power, whereas the latter stage is performed at moderate or high power.

DISORDER IN THIN-FILM SILICON. Xiao Liu, SFA Inc, Largo, MD; Christoph L. Spiel, Cornell University, Department of Physics, Ithaca, NY; Richard S. Crandall, National Renewable Energy Laboratory, Golden, CO; R.O. Pohl, Cornell University, Department of Physics, Ithaca, NY.

We have recently shown that low temperature internal friction is a sensitive tool for the detection of disorder in amorphous silicon films containing hydrogen (1). We have now extended these measurements to thin silicon films prepared by PECVD. By increasing the hydrogen dilution of the silane used to prepare these films, their structure is known change from amorphous to micro-crystalline. We have found the unexpected result that the internal friction increased by over one order of magnitude as the crystallinity of the films increased. It is concluded that the micro-crystalline films are highly disordered. We are now exploring the origin of the disorder and the role played by the hydrogen.

(1) Xiao Liu, R.O. Pohl, R.S. Crandall, MRS Conference, San Francisco, April 1999, to appear.

Work supported by NREL under contract Nr AAD-9-18668-12.

11:30 AM A2.4

MEDIUM-RANGE ORDER IN HYDROGENATED AMORPHOUS SILICON MEASURED BY FLUCTUATION MICROSCOPY P.M. Voyles, University of Illinois, Dept of Physics, Urbana, IL and NEC Research Institute; H-C. Jin, J.R. Abelson, University of Illinois, Dept of Materials Science and Coordinated Science Laboratory,

Urbana IL; J.M. Gibson, Argonne National Laboratory, Argonne IL; M.M.J. Treacy, NEC Research Institute, Princeton, NJ.

Fluctuation microscopy is a new electron microscopy technique which is sensitive to medium range order (MRO) in disordered materials at a characteristic length scale of 1-2 nm. We have previously applied this technique to amorphous semiconductor thin films to develop the paracrystalline model of their as-deposited structure and to detect a decrease in the MRO of device-quality sputtered hydrogenated amorphous silicon films with light soaking [J.M. Gibson, et al., Appl. Phys. Letts. 73 3093 (1998)]. Recent advances in experimental technique and data analysis allow us to more accurately compare films deposited by varying means to varying thickness, and to observe smaller differences in the degree of ordering. Here we extend our previous measurements to sputtered films with varying hydrogen content, PECVD films with and without hydrogen dilution of the silane precursor, and hot-wire CVD films.

11:45 AM A2.5

TOPOLOGICAL SIGNATURES OF MEDIUM RANGE ORDER IN AMORPHOUS SEMICONDUCTOR MODELS. M.M.J. Treacy, NEC Research Institute, Princeton NJ; P.M. Voyles, University of Illinois, Dept of Physics, Urbana IL and NEC Research Institute; J.M. Gibson, Argonne National Laboratory, Argonne, IL.

Topological tools are useful for classifying ordering in models of amorphous materials. Based on experimental fluctuation electron microscopy, we have recently introduced the paracrystalline model for the as-deposited structure of amorphous semiconductor thin films. A paracrystalline film is a compact of topologically crystalline grains strongly distorted by strain. Paracrystalline structures have been created by molecular dynamics. In this paper we use two new topo logical methods to analyze these structures and several continuous random networks. A simple concept is that of the topological density ρ_{TD} which is a measure of the average number of nodes (atoms) in coordination shells at large radius k. The number of nodes grows as $N = 3\rho_{TD}k^2$. The topological density is not the same for each atom, and the spread in values provides a signature that is unique to each model. The Schläfli cluster, a topological tool which is particularly sensitive to medium-range topology, is defined by the local circuits for each atom. All small unit cell four-connected crystals have distinct Schläfli clusters, so the Schläfli cluster provides a con-venient method for identifying local topological crystallinity within a model. The length scale of a typical Schläfli cluster is ~ 1 nm, which is a convenient medium range order length scale. We show that this is an important tool for studying paracrystallinity in models.

> SESSION A3: METASTABILITY Chair: Martin Stutzmann Tuesday Afternoon, April 25, 2000 Salon 7 (Marriott)

1:30 PM *A3.1

A STUDY OF THE TIME SCALES OF PROCESSES RESPONSIBLE FOR THE LIGHT-INDUCED DEGRADATION OF a-Si:H BY PULSE ILLUMINATION. Paul Stradins, Michio Kondo, and Akihisa Matsuda, Thin Film Silicon Solar Cells Super Laboratory, Electrotechnical Laboratory, Tsukuba, JAPAN.

We examine the time scales of processes responsible for the metastable Si dangling bond defect creation by degrading a-Si:H with sequences of intense ns laser pulse pairs of variable delay [1]. The defect creation by the second pulse of the pair will be modified by the non-equilibrium species left over from the first pulse. By changing the delay between the pulses, we determine the lifetime of these species We observe that the defect creation efficiency by the 2nd pulse remains strongly affected by the 1st pulse at delays as long as 0.65 microseconds. This phenomenon cannot be explained by the weak thermal effects or by the residual trapped carriers. The numerous recombination events during the intense 2nd pulse erase and reset all the preceding residual carrier populations, as shown by the residual photocurrent transients, so that these are unlikely to affect the defect creation by the 2nd pulse. The weak influence of the residual photocarriers is further demonstrated by applying a microsecond flash bias pulse during the laser pulse degradation. To explain the origin of the observed robust long-living species affecting the defect creation, we suggest that metastable structural precursors are created by the intense bimolecular recombination during the 1st pulse. They survive until the 2nd pulse and affect the degradation efficiency. The possible origins of these precursors are discussed. We expand our study into microsecond and millisecond time domain by applying electronically-controlled Xe flash microsecond pulse pairs and by combining flash and ns laser pulse illumination. The lifetimes of the defect precursors are compared in samples with different H content and a-Si:D. Their dependences on exposure temperature, pulse energy, and defect concentration are also discussed. 1. P. Stradins, M. Kondo, A. Matsuda, ICAMS18 (1999), to appear in J. of Non-Cryst.Solids.

2:00 PM A3.2

SLOW DEFECT INCREASE DURING LOW-INTENSITY PULSED ILLUMINATION OF HYDROGENATED AMORPHOUS SILICON: NEW RESULTS. Stephan Heck and Howard M. Branz, National Renewable Energy Laboratory, Golden, CO.

Illumination of hydrogenated amorphous silicon (a-Si:H) samples with short (e.g., 40 microsecond) pulses of red light produces a smaller metastable absorption increase in the defect region than continuous illumination of the same intensity for the same integrated exposure time. The defect absorption was measured by use of the constant photocurrent method (CPM). This smaller degradation parallels the photoconductivity results we reported previously [1] and suggests that, in addition to electron-hole recombination, there is a second, slower, precursor to the light induced metastable increase of defect density. Careful measurement of the film temperature with a predeposited nickel resistor confirms our previous measurement of internal film temperature: even under continuous illumination, the film temperature rises less than 2°C. The annealing behavior of the pulsed and continuously degraded samples will be reported, along with a detailed study of the pulse- and dark-time dependence. We have observed the slower metastable degradation for pulsed illumination on NREL plasma-enhanced (PE) and hot-wire chemical vapor deposition (CVD) samples, and on University of Chicago and Electrotechnical Laboratory PECVD samples. [1] S. Heck and H.M. Branz, Proc. MRS 1999 Spring Meeting, Symposium A, in press. This research was supported be the U.S. DOE under contract DE-AC36-99GO10337.

2:15 PM A3.3

A CRITICAL TEST OF DEFECT CREATION MODELS IN HYDROGENATED AMORPHOUS SILICON ALLOYS.

Kimon C. Palinginis and J. David Cohen, Department of Physics, University of Oregon, Eugene, OR; Jeffrey C. Yang and Subhendu Guha, United Solar Systems Corporation, Troy, MI.

Recently a new mechanism, known as the "hydrogen collision model", was proposed to explain light-induced degradation of a-Si:H [1]. We have carried out measurements that directly test several predictions of this model. Our approach has been to examine a-Si,Ge:H alloys in the low Ge fraction (2 to 20at.%) regime. The relative fractions of the different defects can be monitored using modulated photocurrent (MPC) spectroscopy which clearly discloses the existence of two bands of majority carrier traps in these alloys. Correlating these with ESR measurements on matched films unambiguously demonstrates that the bands originate from neutral Si and neutral Ge dangling bonds. Somewhat surprisingly, our studies show that all the films (even with 2at.% Ge) exhibit a predominance of neutral Ge dangling bonds in the as-grown state while they are all dominated by neutral Si dangling bonds in their light-soaked states. By monitoring the details of the creation and annealing kinetics of these two types of defects within a single sample we obtain a powerful method to test proposed models of metastability in a-Si:H. Many models explain metastable defect creation via local bond reconfiguration, while others invoke a global mechanism such as, in the case of the H-collision model, a remote center that traps and releases hydrogen. In our sequences of isochronal anneals, for example, we observe that the Si dangling bonds are annealed at a much faster rate than the Ge dangling bonds. While this may suggest that the two annealing processes are uncorrelated and hence local in nature, the changes in the densities in the two defects indicate that they are in direct competition in a manner which agrees with the H-collision model. Other viable models that could explain our experimental data will also be discussed. [1]. H. Branz, Phys. Rev. B59, 5498 (1999).

2:30 PM A3.4

CREATION AND ANNEALING KINETICS OF LIGHT INDUCED DEFECTS BETWEEN 40 K AND 300 K IN INTRINSIC a-Si:H. N.A. Schultz, P.C. Taylor, University of Utah, Physics Dept., Salt Lake City, UT.

Using the technique of electron spin resonance (ESR), we measured the production and annealing kinetics of the light induced deep defects (silicon dangling bonds) in hydrogenated amorphous silicon (a:Si:H) between 25 K and 300 K. These experiments employed an illumination time of 10 hours with approximately 100 mW/cm² of filtered white light (approximately 600 to 3500 nm) from a Xe arc lamp. At approximately room temperature we find the commonly observed light induced degradation, which is generally referred to as the Staebler-Wronski Effect. At low temperatures (T < 100 K) the measurement of silicon dangling bonds is complicated by photoexcited, long-lived, band tail carriers that mask the dangling bond ESR signal. However, after removing most of these long-lived carriers by irradiation with infrared-light, we find a significantly lower concentration of light induced defects created at low temperatures, as

compared to room temperature degradation. By annealing the degraded a-Si:H film to successively higher temperatures we are able to monitor the annealing kinetics of the photoinduced defects. The defects, which were produced at low temperatures, almost entirely anneal out at temperatures around 300 K. The concentration of defects, created at low temperatures and stable at room temperature, is at least a factor of 10 less than the defect concentration created at room temperature. A broad distribution of annealing energies cannot explain this behavior. Although the defects created at low temperatures have the same ESR signal as the defects created at room temperature, the kinetics for growth and annealing are very different.

2:45 PM *A3.5

MECHANISMS OF METASTABILITY IN HYDROGENATED AMORPHOUS SILICON. <u>Rana Biswas</u>, Iowa State University, Dept. of Physics, Microelectronics Research Center, and Ames Laboratory, Ames IA

I will describe recent advances in understanding two types of metastability in a-Si:H. These involve i) local metastability of hydrogen atoms at Si-H sites and ii) metastable dangling bond formation (Staebler-Wronski effect). Recent experiments of light induced degradation find large changes of the network that exceed the low density of metastable dangling bonds. These include changes in infrared absorption, NMR intensities, and photodilation. We find that many of these changes can be explained by the 'H-flip' defect where a H-atom at a monohydride site flips to the backside of the Si-H bond[1]. The dynamic dipole moment increases in the H-flip state leading to larger IR absorption. The model can explain increased intensity of the narrow NMR line after light soaking. In the area of Staebler-Wronski metastability, we will describe new results of the breaking of weak silicon bonds and generation of metastable dangling bonds. Dangling bond formation is accompanied by rebonding in the network. Relations between these two metastabilities will be discussed. Results are based on tight binding molecular dynamics. [1] R. Biswas and Y.P. Li, Phys. Rev. Lett. 82, 2512 (1999). This research is supported by EPRI and U.S. DOE

SESSION A4: HIGH RATE DEPOSITION-MATERIALS AND DEVICES Chair: Robert W. Collins Tuesday Afternoon, April 25, 2000 Salon 7 (Marriott)

3:45 PM A4.1

FAST GROWTH OF AMORPHOUS SILICON LAYERS BY AMPLITUDE MODULATION PECVD. A.C.W. Biebericher, J. Bezemer, W.F. van der Weg, Debye Institute, Interface Physics, Utrecht University, Utrecht, THE NETHERLANDS; W.J. Goedheer, FOM Institute for Plasmaphysics 'Rijnhuizen', Nieuwegein, THE NETHERLANDS.

Plasma enhanced CVD of amorphous silicon by a square wave amplitude modulated RF excitation has been studied by optical emission spectroscopy and plasma modelling. The deposition rate varies with the modulation frequency, depending on the plasma parameters. In the (powder-free) α -regime, the deposition rate is enhanced, up to a factor of three, with respect to the deposition rate in a similar continuously excited (cw) plasma. An optimum is reached at a modulation frequency of about 100 kHz. This behavior is explained by the characteristics of the electron energy distribution, during the periodical onset of the plasma. An overshoot in optical emission at the onset indicates a large production of radicals by high energy electrons. This is confirmed by a one dimensional fluid model of the plasma which has been applied successfully before to the α -regime [1]. The optimum in deposition rate is determined by the decay time of the electron density. We present results on 50 MHz $\mathrm{SiH_4/H_2}$ plasmas. In the γ' -regime the deposition rate is reducedwith respect to the the deposition rate in a similar cw plasma, due to a reduction of powder in the plasma: the deposition rate and the microstructure parameter \mathbf{R}^* decrease, the refractive index increases. In solar cell fabrication, amplitude modulation is not only a useful tool to optimize the growth rate of amorphous silicon. Another advantage is the increase in homogeneity of the layers due to production of radicals in a larger space of the reactor, during the plasma pulse. We found that the variation in thickness over an a-Si:H film can be reduced by a factor of two by using a pulsed plasma. [1] G.J. Nienhuis, W.J. Goedheer, E.G.A. Hamers, W.G.J.H.M. van Sark, and J. Bezemer, J. Appl. Phys. 82(5), 2060 (1997)

4:00 PM <u>A4.2</u>

RELATION BETWEEN GROWTH PRECURSORS AND FILM PROPERTIES FOR PLASMA DEPOSITION OF a-Si:H AT RATES UP TO 100 Å/s. W.M.M. Kessels, A.H.M. Smets, M.G.H. Boogaarts, D.C. Schram and M.C.M. van de Sanden, Dept. of Appl. Physics,

Eindhoven University of Technology, Eindhoven, THE NETHERLANDS.

From a detailed study of the deposition of a-Si:H with a remote silane plasma, it is demonstrated that deposition of device quality a-Si:H with a defect density $< 10^{16}~{\rm cm}^{-3}$ at 100 Å/s is possible under conditions where SiH_3 contributes $\sim 90\%$ to film growth. The SiH_3 flux, created by an intense atomic hydrogen source, is studied by threshold ionization mass spectrometry and cavity ringdown absorption spectroscopy, applied here for the first time for spatially resolved SiH $_3$ measurements. The first, non-optimized p-i-n solar cells with the intrinsic layer deposited at 70 Å/s and at 300°C have revealed an efficiency of 4.1% while the optimum substrate temperature at this deposition rate is 400°C. The optimum substrate temperature decreases for lower deposition rates for conditions where SiH₃ governs film growth and is about 250°C for 2 Å/s. The contribution of radicals other than SiH_3 , and Si_nH_m ⁺ ions to film growth has been studied by mass spectrometry, Langmuir probes and optical emission spectroscopy. No direct correlation between film quality and contribution of ions (less than 9% for all conditions) has been observed except from the fact that the average number of Si atoms in the ions decreases with decreasing deposition rate. The film quality however strongly deteriorates by an increasing contribution of SiH_x (x ≤ 2) radicals. An increasing contribution of these radicals corresponds with an experimentally determined increasing surface reaction probability, starting at ~ 0.3 for almost completely SiH₃ governed conditions, and agrees with an increasing surface roughness and void density. The reaction pathways leading to the different radical and ionic species and their influence on film quality are addressed and implications for depositing device quality a-Si:H at elevated deposition rates are discussed.

4:15 PM <u>A4.3</u>

EFFICIENT 18Å/s SOLAR CELLS WITH ALL SILICON LAYERS DEPOSITED BY HOT-WIRE CHEMICAL VAPOR DEPOSITION. Qi Wang, Eugene Iwaniczko, Yueqin Xu, Wei Gao, Brent P. Nelson, A.H. Mahan, R.S. Crandall and Howard Branz, National Renewable Energy Laboratory, Golden, CO.

We have fabricated hydrogenated amorphous silicon (a-Si:H) n-i-p solar cells with all doped and undoped a-Si:H layers made by hot-wire chemical vapor deposition (HWCVD). On untextured stainless steel (SS), we reached an initial efficiency of 7.46%, eclipsing the previous record of 6.2% for an all-HWCVD cell. This is also the highest untextured-substrate efficiency ever reached in any solar cell that contains HWCVD a-Si:H The increased efficiency results primarily from improvement in the final 60Å of i-layer material, which is nearest the i-p interface. We first mapped H-dilution conditions for the transition from amorphous to microcrystalline Si layer growth on a-Si:H by UV-reflection and Schottky cell open-circuit voltage measurements. We then incorporated 60 Å of this a-Si:H material grown at conditions near the transition to microcrystallinity into the i-p interface cells to obtain a fill factor increase from 0.60 to 0.68. The open-circuit voltage is 0.86V - our best results are with an a-Si:H p-layer grown near the transition to microcrystalline Si. The n-layer is deposited at 11\AA/s , the 3000\AA i-layer at 18\AA/sec , the 60\AA transition layer at 3.6 Å/sec, and the p-layer at 4.6 Å/sec. Cell stability against light-soaking is now under test. Due to improved light-trapping, our earlier n-i-p solar cell recipes yielded over 2% improvement in efficiency when transferred to textured Ag/ZnO-coated SS supplied by United Solar Corp. Preliminary cell fabrications on textured SS with our recipe have already given an all-HWCVD record of 8.7%.

4:30 PM <u>A4.4</u>

FAST DEPOSITION OF MICROCRYSTALLINE SILICON FILM USING THE HIGH-DENISTY MICROWAVE PLASMA UTILIZING A SPOKEWISE ANTENNA. Hajime Shirai, Yoshikazu Sakuma, Saitama University, Faculty of Engineering, Saitama, JAPAN; Hiroyuki Ueyama, Nihon Koshuha Co. Ltd., Midori-ku, Yokohama, JAPAN.

Now, microcrystalline silicon (mc-Si:H) is one of the promising material for thin film solar cell of lower cost, better stability and higher conversion efficiencies more than that of hydrogenated amorphous silicon (a-Si:H). However, several problems remained to be unsolved for further improvement of the characteristics and performance of the device. These include low deposition rate, powder formation and poor crystallinity at the initial growth stage. To overcome these difficulties, we have developed a novel high-density and low temperature microwave plasma without magnetic field utilizing a spokewise antenna for fast and uniform deposition of mc-Si:H.[1] A high deposition rate is achieved up to 47A/s from SiH₄ and Ar without the use of H₂ dilution. I will discuss the generation of high-density microwave plasma and its characteristics including film properties and solar cell performance. [1] H. Shirai et al. Jpn. J. Appl. Phys. 37 (1998) L1078

4:45 PM <u>A4.5</u>

PREPARATION OF MICROCRYSTALLINE SILICON BASED SOLAR CELLS AT HIGH I-LAYER DEPOSITION RATES USING A GAS JET TECHNIQUE. S.J. Jones, R. Crucet, X. Deng, and M. Izu, Energy Conversion Devices, Inc., Troy, MI.

A Gas Jet technique has been used to prepare microcrystalline silicon thin films at high deposition rates. The technique involves the use of a gas jet flow which is subjected to a high intensity microwave source. With this technique, microcrystalline Si films have been prepared at deposition rates as high as 20 Å/s. The best films were made using rates near 16 Å/s. These materials have been used as i-layers for nip single-junction solar cells. The high deposition rates allow for fabrication of the required thicker microcrystalline Si i-layers in a similar amount of time to those used for high quality a-SiGe:H i-layers (rates of 1-3 Å/s). The doped layers for these cells were made using standard PECVD practices and different deposition equipment. Using a 610nm cutoff filter which only allows red light to strike the device, pre-light soaked short circuit currents of 8-10 mA/cm2 and 2.7% red-light efficiencies have been obtained while AM1.5 white light efficiencies are above 7%. These efficiencies on average degrade only by 2% (stabilized efficiencies of 2.6%) after long-term light soaking (1000 hrs.). This small amount of degradation compares with the 15-17% degradation in efficiencies for a-SiGe:H cells subjected to similar irradiation treatments (final light-soaked red light efficiencies of 3.2%). The lower efficiencies for the microcrystalline Si cells are presently due to lower short circuit currents and low open circuit voltages (near 0.50V under AM1.5 white light measurements) due to the low bandgap of the material. The poorer performance could also be partially due to the fact that the doped layers used in these devices were optimized for a-SiGe:H nip solar cells rather than for the microcrystalline Si i-layer and that air break between the microcrystalline i-layer and doped layers deposited in a different system, as required for now, may lead to unoptimized interface layers.

SESSION A5: POSTER SESSION:
GROWTH AND PROPERTIES
Chairs: Brent P. Nelson and Michio Kondo
Tuesday Evening, April 25, 2000
8:00 PM
Salon 1-7 (Marriott)

A5.1

MOLECULAR BEAM EPITAXIALLY DEPOSITED AMORPHOUS SILICON. D.J. Lockwood, Institute for Microstructural Sciences, National Research Council of Canada, Ottawa, Ontario, CANADA; B.J. Fogal, S.K. O'Leary, Faculty of Engineering, University of Regina, Regina, Saskatchewan, CANADA.

We have deposited a novel form of amorphous silicon through molecular beam epitaxy. In particular, by depositing silicon atoms epitaxially onto a relatively cool quartz substrate, we have obtained a silicon based material which lacks the periodicity which characterizes crystalline silicon but nevertheless has 98% of the density. Spectroscopic studies demonstrate that there are only trace amounts of hydrogen and other impurity atoms in this novel form of amorphous silicon, this contrasting dramatically with the case of conventional amorphous silicon. The optical and Raman spectroscopic properties of this form of amorphous silicon are contrasted with those of conventional amorphous silicon, and conclusions regarding the amount of disorder are drawn. Finally, the device implications of this novel form of amorphous silicon are discussed.

A5.2

WIDE BANDGAP ≥1.8eV AMORPHOUS SILICON FOR SOLAR MULTIJUNCTION CELL AND IMAGE SENSOR APPLICATIONS. Andrzej Kolodziej, Pawel Krewniak, Univ of Mining and Metallurgy, Inst of Electronics, Krakow, POLAND.

It is considered the using of wide bandgap a-Si:H for triple junction cell applications. Amorphous silicon were prepared by DC magnetron sputtering under strong hydrogen dilution conditions approaching high incorporation of hydrogen to obtain device quality wide bandgap a-Si:H. Our proposal is to use the special mode of the reactive magnetron sputtering technique to create aforementioned i a-Si:H and $\rm n^+$ a-Si:H layers, particularly in low temperature deposition conditions [1]. Light and dark current-voltage characteristics and internal quantum efficiency characteristics have been investigated in specular TCO/n $^+$ (a-Si:H)/Nickel Schottky barrier cell structures with the wide bandgap a-Si:H. These characteristics were used for analyzing a gap state distribution, which includes charged defects. The studies were carried out on structure with different i layer thickness between 0.2 and 0.5 $\mu \rm m$ after a degraded steady state. There are presented fill factor dependence on light, field, thickness and time. Using AFM, TEM and X-ray small angle spectroscopy we

have confirmed that these samples contain in the case of i layers, single Si microcrystallities embedded in a matrix that is predominantly high quality a-Si and for n⁺ layers more than 40% of the Si microcrystalline phase. At the same time, the comparison between various properties of layers obtained in temperature $250\,^{\circ}\mathrm{C}$ and obtained in temperature 100°C was performed carrying out a number of systematic experiments on Schottky structures made on stainless steel, glass and laminated Cu poliimid foil substrates. Optical characteristics of undoped a-Si:H film and of phosphorus doped n a-Si film have been determinated using transmission and reflectance measurements over a wide range of wavelengths. We also show how operate this type p-i-n photodiodes in 40×40 matrix image sensor made by us. [1] A. Kolodziej, P. Krewniak, R. Tadeusiewicz, Mat. Res. Soc. Symp. Proc. 558 (1999), in press.

MICROSTRUCTURAL CONTROL OF THIN FILM Si USING LOW ENERGY, HIGH FLUX IONS IN REACTIVE MAGNETRON SPUTTER DEPOSITION. J.E. Gerbi, J.R. Abelson, Coordinated Science Laboratories and the Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, IL.

Using plasma growth sources with concurrent particle bombardment, silicon thin films can be deposited with various phases and microstructures. DC Reactive Magnetron Sputtering (RMS) can produce amorphous, paracrystalline, mixed-phase, nanocrystalline, polycrystalline, porous columnar, and epitaxial Si films. In particular, a large flux of low energy, heavy ions strongly affects phase and microstructure, and therefore modifies the quality of the deposited film. RMS is particularly suited for this type of plasma manipulation: we bias the substrate to produce the ion energy of choice, and use an external magnetic field to control the ion/neutral flux ratio, therefore decoupling the parameters of bombardment energy and flux. In this work, we study the influence of slow (< 40 eV), heavy (Ar+) ions in RMS deposition on the formation kinetics and microstructures of nanocrystalline, mixed-phase, and polycrystalline Si films. The analytical methods are in-situ real-time spectroscopic ellipsometry and reflection-IR absorption, as well as post-deposition Raman scattering, SIMS, TEM and photoluminescence. We will show how ion bombardment drives the nucleation of polycrystalline Si on glass at temperatures below $400\,^{\circ}\mathrm{C}$, enhances the bulk crystallinity, and yields extremely smooth surfaces, as well as produces nanocrystalline Si with tailored grain sizes at temperatures below 200°C. There are myriad applications for such films directly deposited onto plastic or glass substrates, for which tailored microstructural growth is extremely valuable. Enhancement of medium range order (the paracrystalline state) is another microstructural product that is of possible interest, particularly for electronically stable solar cells.

IN-SITU MASS SPECTROSCOPY OF ECR SILANE PLASMAS FOR AMORPHOUS AND MICROCRYSTALLINE SILICON GROWTH. Young J. Song, Elena A. Guliants, Wayne A. Anderson, State University of New York at Buffalo, Dept of Electrical Engineering, Amherst, NY.

ECR silane plasmas for the deposition of a-Si:H and uc-Si films were investigated by in-situ mass spectroscopy (MS) using a quadrupole residual gas analyzer. The results showed that the intensities of ionic and neutral species (H, H₂, He, Ar, Si and SiH_n) in the 2% SiH₄/He plasma are strongly dependent on the deposition conditions such as chamber pressure, input power and hydrogen dilution. In all cases, the predomination of Si ions was observed over the SiH, SiH2 and SiH3 ions, suggesting a high decomposition rate of the silane in the plasma. In particular, the population of atomic hydrogen in the plasma seems to play a key role in the properties of both films. For example, the increased intensity of atomic hydrogen, compared to that of molecular htdrogen, resulted in the better quality a-Si:H film, showing a higher photo and dark conductivity ratio (10^5) . The intensity of the hydrogen species was especially sensitive to the chamber pressure. the correlation between MA spectra and film properties will be discussed in detail.

<u>A5.5</u>

 $\overline{\text{SOLAR}}$ -CELL SUITABLE μ c-Si FILMS GROWN BY ECR CVD. M. Birkholz, E. Conrad, K. Lips, B. Selle, I. Sieber, J. Platen, W. Fuhs, Hahn-Meitner-Institut Berlin, Silicium-Fotovoltaik, Berlin, GERMANY; S. Christiansen, Werkstoffwissenschaften, Friedrich-Alexander Universität, Erlangen, GERMANY.

The generation of silane plasmas by virtue of electron-cyclotron resonance (ECR) CVD holds the promise of high rates for Si thin film deposition at low temperatures. The authors report about the preparation of $\mu c\text{-Si}$ films from SiH₄-H₂ mixtures by ECR CVD at deposition temperatures $\leq 400\,^{\circ}\mathrm{C}$ on different substrates. For high hydrogen dilutions optimized deposition conditions could be identified for which Si films with a high degree of crystallinity were grown as

was confirmed by Raman spectroscopy. μ c-Si films exhibiting line widths of the c-Si LO/TO mode at 520 cm⁻¹ as small as 7 cm⁻¹ (FWHM) could be produced by biasing the substrate. In order to investigate the growth mode of ECR-grown films a set of samples with varying thickness was prepared under otherwise unchanged conditions. XRD measurements as performed in grazing incidence geometry by varying the glancing angle revealed the evolution of the (110) fibre texture to be a depth-dependent property of thin μc -Si films. The texture evolved with increasing thickness starting from a random orientation of grains at the first stages of film growth. Grains sizes were identified by TEM investigations to range from 10 - 12 nm. Next to the optimization of crystallinity of Si films several sources of possible contamination during film deposition were identified and restrained. Intrinsic μ c-Si layers could be prepared under these conditions that exhibited a dark conductivity σ_d of 2×10^{-7} S/cm and photosensitivity σ_{ph}/σ_d of 150. We conclude that ECR CVD is capable of producing intrinsic layers with electronic properties as necessary for their use in state-of-the-art p-i-n μ c-Si solar cells.

METHODS OF SUPPRESSING CLUSTER GROWTH IN SILANE RF DISCHARGES. Masaharu Shiratani, Shinichi Maeda, Yasuhiro Matsuoka, Kenichi Tanaka, Kazunori Koga and Yukio Watanabe, Kyushu University, Dept of Electronic Device Engineering, Fukuoka, JAPAN.

Size and density of clusters, which are believed to degrade film quailty, in silane parallel plate RF discharges are measured using a novel double pulse (DP) method and a high-sensitivity photon-counting laser-light-scattering (PCLLS) method. Small neutral clusters of about 1 nm in size and about $10^{10}~{\rm cm}^{-3}$ in density are found to exist over the discharge space even under so-called device quality conditions. In order to suppress such cluster growth, effects of gas temperature gradient, pulse discharge modulation, and hydrogen dilution on growth of clusters below about 10 nm in size are studied. The thermophoretic force due to the gas temperature gradient between the electrodes drives neutral clusters above a few nm in size toward the cool RF electrode which is at room temperature. The pulse discharge modulation is much more effective in reducing the cluster density when it is combined with the gas temperature gradient and clusters above a few nm in size cannot be detected by the PCLLS method even over 2 hours. Hydrogen dilution of a high H₂/SiH₄ concentration ratio above about 5 is also useful in suppressing cluster growth in the radical production region around the plasma/sheath boundary near the RF electrode. The hydrogen dilution is revealed to reduce the cluster growth rate even for small clusters such as $\mathrm{Si}_5\mathrm{H}_x$. Correlation between cluster density and a-Si:H film quality will be presented at the meeting.

- M. Shiratani and Y. Watanabe, Rev. Laser Eng., 26 (1998) 449.
 T. Fukuzawa, et al., J. Appl. Phys., 86 (1999) 3543.
 M. Shiratani, T. Fukuzawa, and Y. Watanabe, Jpn. J. Appl. Phys., 38 (1999) 4542.

Si-NETWORK STRUCTURE AND STABILITY OF He-DILUTED a-Si:H DEVELOPED IN THE γ -REGIME OF RF PECVD. A.R. Middya 1 , S. Hazra 2 , S. Ray 2 , S.N. Sharma 2 , C. Longeaud 3 , J.P. Kleider³, S. Hamma¹, D.L. Williamson⁴; ¹Ecole Polytechnique, FRANCE; ²IACS, INDIA; ³Univ. Paris VI et XI, FRANCE; ⁴Colorado School of Mines, CO.

a-Si:H films deposited in the $\gamma\text{-regime}$ (P $_{r}$ \approx 0.5 to 1.8 Torr) of RF PECVD with helium dilution exhibit very fast kinetics of light-induced degradation, with stabilized mobility-lifetime products (independent of Fermi level positions) which are comparable to that of state-of-the-art materials in the annealed state¹. These materials are reproduced in a different reactor and 10% stable a-Si:H solar cells have been fabricated on glass substrate². Spectroscopic ellipsometry analysis of these materials shows that the experimental curve of the variation of imaginary part of the dielectric function vs. photon energy (eV) cannot be simulated based on effective medium theory. i.e. with the a-Si:H consisting of an a-Si network and voids. Moreover the interference fringes in the low energy portion of the curve can only be reproduced by the inclusion of a fraction of crystalline component (<30%) in the model. However, the amorphous structure of the materials has been verified by Raman and x-ray diffraction (XRD), although the width of the first scattering peak of the XRD systematically decreases with P_r indicating improvement of medium range order (MRO). Consistent with the improvement of MRO, the carrier mobility (by Time Resolved Microwave Conductivity) is found to improve by a factor of 2-3. Small-angle x-ray scattering (SAXS) and flotation density methods reveal undetectable levels of inhomogeneities on the nanoscale (nanovoid density <0.01 vol.%) and compact (density $\thickapprox 2.23\pm0.01~\mathrm{g/cm^3},$ density deficit <4.3%) network structure however a small amount of larger-scale features (>20 nm) exists, which reduces with P_r up to 1.8 Torr. Concomitantly the density of states (by Modulated Photocurrent method) above E_F

decreases and the hole diffusion length (SSPG) increases by 54%. The Si-H IR stretching band appears at 2010 cm⁻¹ (a position generally assign to Si-H bond on c-Si surface), indicating a different environment for the Si-H bonds (H bonded to ordered Si-Si network?) and the bonded H-content is significantly lower (6-8 at%) than that of standard materials. The correlation between improved electronic properties and stability of these materials with its network structure will be presented and future directions to improve further the stability of materials and solar cells will be discussed. ¹A.R. Middya et. al. MRS Proc. Vol. 467, 615 (1997); ²Pere Roac i Cabarrocas et. al. 2nd World Conference PVSEC, Vienna (1998) (in press).

A5.8

STRUCTURE OF Si:H FILMS FABRICATED BY PLASMA-ENHANCED CVD USING HYDROGEN DILUTED PLASMA. F. Edelman, A. Chack, R. Weil, R. Beserman, Solid State Institute, Technion, Haifa, ISRAEL; P.Werner, MPI für Microstrukturphysik, Halle, GERMANY; B. Rech, T. Rosheck, W. Beyer, ISI-PV, Forschungszentrum Jülich, Jülich, GERMANY.

The addition of hydrogen to silane during plasma-enhanced chemical vapordeposition (PECVD) improves the photovoltaic characteristics of intrinsic a-Si:H films. The PECVD process with hydrogen-diluted ${
m SiH_4}$ can also produce microcrystalline Si:H films on glass substrates at temperatures below 200°C. We present results of structure studies of undoped Si:H films deposited by PECVD at high power at an RF frequency of 13.56 MHz over ${\rm SiO_2/(001)Si}$ substrates held at temperatures T_s in the range of 140 to 240° C and employing a hydrogen dilution d (d=SiH₄/H₂%) from 0.8% to 1.5%. The deposition rate was 6 to 9 AA/s. In-situ TEM, high resolution TEM, XRD, Raman spectrometry, infrared absorption and hydrogen effusion methods were used for the Si:H film structure characterization. Using the films, μ c-Si:H thin film solar cells with efficiencies of 7% were produced; incorporated in a-Si/ μ c-Si tandem cells, stable efficiencies of 10% were achieved. The Si:H films deposited at $T_s=140$ °C with strongly diluted SiH₄(d=0.8%) were nanocrystalline (average grain size of 20 nm) in the as deposited state and after vacuum annealing up to 800°C for 1h. For intermediate H₂ dilution (d=1%), a stable mixed amorphous/nanocrystalline structure was observed both for the as-deposited state ($T_s = 140$ °C) and after vacuum annealing up to 600°C for 1 h. Weakly diluted (d=1.5%) Si:H films were found to be amorphous in the as-deposited state, crystallizing at temperatures of 700 and 800°C via the nucleation-growth Avrami mode with an incubation time t_o of about 10 and 1 min, respectively. After 1 h annealing at 800°C these films were microcrystalline, having an average grain size of the order of $1\mu m$. Effusion measurements show release of hydrogen predominantly between 300 and 700°C. Both H effusion spectra and IR absorption measurements show only moderate microstructure in the a-Si:H films and μc-Si:H films. Raman spectroscopy data were used to estimate the amorphous to crystalline ratio.

A5.9

THICKNESS AND INTERFACE LAYER EFFECTS ON THE AMORPHOUS SILICON FILM PROPERTY STUDIED BY VARIOUS PHOTOLUMINESCENCE EXCITATION WAVE LENGTHS. Guozhen Yue, Daxing Han, Dept of Physics & Astronomy, Univ of North Carolina at Chapel Hill, Chapel Hill, NC; Jeffrey Yang, Subhendu Guha; United Solar Systems Corp., Troy, MI.

We have used photoluminescence (PL) as a spectroscopic tool to study the microstructure of hydrogenated amorphous silicon (a-Si:H) films prepared using high hydrogen dilution during film growth. The films were deposited onto stainless steel substrate covered with textured Ag/ZnO with the following three types of structures. Type I consists of $\sim 0.5 \ \mu \text{m}$ a-Si film deposited directly onto substrate, type II has the same structure as type I except that a thin amorphous n-layer was inserted between the substrate and the a-Si film, and type III is the same as type II except that the a-Si film has a larger thickness of $\sim 1.5 \ \mu \text{m}$. These three structures were identical to those recently studied by Guha et al. using X-ray diffraction spectroscopy and a capacitance profiling technique.[Appl. Phys. Lett., 74, 1860 (1999)] They observed that type I film contains partial microcrystallinity in an a-Si matrix, type II film remains fully amorphous, and type III film exhibits partial microcrystallinity toward the top surface. In this study, we used HeCd, ${\rm Ar}^+$ and HeNe lasers to provide excitation beams at 325 nm (3.81 eV), 488 nm (2.54 eV), 514 nm (2.41 eV), and 632 nm (1.96 eV) to probe the film property at the depth of 10 nm, 50 nm, 80 nm and 1 μ m, respectively, from the top surface. The results indicated that the type I and type III have evident microcrystalline components which manifest themselves in the low energy PL peak at \sim 0.9 eV. For type III film, we found that for 325 nm excitation, the PL peak energy is located at 1.39 eV. For 488 and 514 nm excitation, the PL peak is at 1.41 eV. However, by increasing the penetration depth by using 632 nm excitation, the peak is shifted to 1.37 eV. These imply non-uniform electronic states in the growth direction. Detail discussion will be presented in conjunction with PL spectra temperature dependence as well as Raman measurements. The work

at UNC and United Solar, was supported by NREL sub-subcontract under thin film PV partnership, XAK-8-17619-11, ZAK-817619-09, respectively. Yue is partially supported by NSF-Int-9604915.

A5.10

SURFACE CHLORINE TERMINATION OF SILICON FILMS PREPARED UNDER GLOW DISCHARGE PLASMA OF DICHLOROSILANE-HYDROGEN MIXTURE. Yasutake Toyoshima, Michio Kondo, Akihisa Matsuda, Electrotechnical Lab, Tsukuba, JAPAN.

The growing surface of silicon films prepared under glow discharge of dichlorosilane(DCS)-monosilane-hydrogen mixture is investigated using IRRAS (infrared reflection absorption spectroscopy), which is capable of detecting the surface submonolayer coverage. It is surprising that when DCS-hydrogen mixture (no monosilane) is used even at a high dilution condition (DCS/hydrogen = 2/100sccm), no surface hydrogen is detected by IRRAS. Instead, surface chlorine is detected as the absorption band in the frequency of Si-Cl stretching mode. It is noteworthy that surface chlorine coverage is found to be stable to the hydrogen plasma exposure, which phenomenologically explains the dominancy of chlorine at the growing surface in the DCS-hydrogen mixture. When a small amount of monosilane is added to the DCS-hydrogen mixture, surface hydrogen absorptions are appeared. The surface hydrogen signals are increased whereas surface chlorine signal is decreased when monosilane to DCS fraction is increased. The deposited films, which are basically microcrystalline due to the high hydrogen dilution, degrade their crystallinity with this increase of monosilane fraction. However, the crystallinity recovers when no DCS is added to the mixture. This behavior suggests that the coexistence of hydrogen and chlorine at the growing surface is detrimental to the microcrystalline formation.

A5.11

THERMAL OXIDATION OF SI NANOPARTICLES GROWN BY PLASMA-ENHANCED CVD. J. Farjas, D. Das, J. Costa, P. Roura, Grup de Recerca en Materials, Universitat de Girona, Girona, SPAIN; G. Viera, E. Bertran, Dept. de Fisica Aplicada i Optica, Universitat de Barcelona, Barcelona, SPAIN:

The growth of nanostructured thin films of amorphous silicon has a potential interest due to its enhanced properties for photovoltaic conversion. Thin films of silicon nanoparticles embedded into an amorphous Si matrix are currently grown by plasma-enhanced chemical vapor deposition (PECVD). The residence time of the nanoparticles inside the plasma and the plasma conditions determine, among other structural characteristics as crystallinity and size, the hydrogen content which, in turn, plays an important role in the oxidation mechanisms. The oxidation of hydrogenated amorphous Si nanoparticles is studied by thermal analysis (calorimetry and thermogravimetry) and TEM in order to assess the influence of the hydrogen content on the oxidation kinetics. At high hydrogen concentration, the oxidation takes place at temperatures below 300°C in which case the process is not diffusion controlled. The oxidation kinetics slows down when the hydrogen content diminishes. Therefore, at the temperatures where oxidation takes place a simultaneous crystallization is observed. The use of nanoparticles to study the thermal oxidation of amorphous silicon involves a much higher sensibility than with thin films due to its higher specific surface. The first steps of oxidation resulting in very thin oxide layers (<10 nm) can be easily recorded through the related increase of mass. This results can be useful in the technology of amorphous thin films.

> SESSION A6: POSTER SESSION: HOT-WIRE CVD 1 Chair: Qi Wang Tuesday Evening, April 25, 2000 8:00 PM Salon 1-7 (Marriott)

A6.1

Si + SiH₄ REACTIONS AND IMPLICATIONS FOR HOT-WIRE CVD OF a-Si:H: COMPUTATIONAL STUDIES. Richard P. Muller¹, William A. Goddard, III¹, Jason K. Knowles² and <u>David G. Goodwin</u>³; ¹Materials and Process Simulation Center, ²Division of Chemistry and Chemical Engineering, ³Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA.

Gas-phase chemistry is believed to play an important role in hot-wire CVD of amorphous silicon, serving to convert the highly-reactive atomic Si produced at the wire into a less-reactive species by reaction with ambient SiH₄. In this paper, we use quantum chemistry computations (B3LYP density functional theory with the cc-pVTZ(-f) basis) to examine the energetics and rates of possible gas-phase reactions between Si and SiH₄. The results indicate that formation of

triplet disilyne (Si₂H₂) and H₂ is exothermic by 2.01 kcal/mol with a low (≈ 2 kcal/mol) barrier. It does not require collisional stabilization and thus can proceed at the low pressures characteristic of hot-wire CVD. Other singlet species can also play a role but may require collisional stabilization. Possible roles for singlet or triplet disilyne in film growth will also be discussed.

GAS PHASE AND SURFACE KINETICS PROCESSES IN HOT-WIRE CHEMICAL VAPOR DEPOSITION OF Si IN SiH4:He AND H₂ DILUTED SiH₄:He AMBIENTS. <u>J.K. Holt</u>, T. Bistritschan, M. Swiatek, D.G. Goodwin and H.A. Atwater, Thomas J. Watson Laboratories of Applied Physics, California Institute of Technology,

In order to better understand the fundamental gas-phase and surface interactions of importance in hot-wire chemical vapor deposition (HWCVD), numerical simulations of a simplified HWCVD reactor have been carried out, and compared with experimental quadrupole mass spectrometry and film growth rate experiments. These simulations examine, among other questions, the relative roles in film growth of different gas-phase species in various growth regimes, and the effect of hydrogen gas dilution on gas-phase composition and surface morphology. In particular, hydrogen etching simulations predict the transition from net growth to net surface etching that is observed experimentally. Also predicted is the absence of Si_2H_x species (an indicator for gas-phase chemistry) under simulated conditions mirroring those of experiments, implying that atomic Si is the dominant growth species. The simulation used in these studies is a variation of the Direct Simulation Monte Carlo (DSMC) method. It includes 15 species, with 19 reversible gas-phase reactions, and simplified wire and surface chemistries. The reactor geometry is simplified so as to simplify computations and focus on the relevant chemistry and transport issues. Given the computational intensity of DSMC calculations at high pressures with multiple species, a new version of this model is being developed. Near the wire, where transport is ballistic, the Direct Simulation Monte Carlo (DSMC) technique is used, while in the diffusive transport regime further away, a continuum model is used. With this "hybrid method", it is possible to simulate HWCVD experiments using highly dilute silane in helium at pressures up to several hundred millitorr, corresponding to the conditions of experiments being conducted in conjunction with this work. Work is also being initiated in developing a two-dimensional model that incorporates a kinetic Monte Carlo (kMC) surface model; results of these efforts in progress will also be presented.

DRASTIC REVOLUTION IN CATALYTIC CVD USING "CATALYTIC PLATE" INSTEAD OF "HOT WIRE" Atsushi Masuda, Yoriko Ishibashi, Hideki Matsumura, Japan Advanced Institute of Science and Technology (JAIST), Ishikawa, JAPAN.

One of the problems to be solved in catalytic CVD (Cat-CVD), often called hot-wire CVD, is the suppression of heat radiation from catalyzer to substrate or growing surface. Especially, heat radiation should be strictly suppressed for Cat-CVD growth on the transparent conducting oxides, ferroelectric oxides, GaAs, etc. It was found that the simple and easy method to suppress heat radiation is decreasing the catalyzer-surface area. However, the deposition rate is also proportional to the catalyzer-surface area and a decrease in the catalyzer-surface area brings about a decrease in the deposition rate since the decomposition of gas molecules occurs on the catalyzer surface. In order to solve the above trade-off problem, we propose the "catalytic plate" perpendicular to the substrate surface instead of the conventional "hot wire". Since the heat from the catalyzer is radiated in the normal direction of the catalytic plate, heat radiation should be suppressed using the catalytic plate in comparison with the conventional wire in spite of the same catalyzer-surface area. It was found that the deposition rate of 15 A/s for a-Si:H is obtained using the catalytic plate with the area of 27 cm2 at the substrate temperature of 250°C including heat radiation, on the other hand, the substrate temperature is elevated to 340°C due to heat radiation for obtaining the same deposition rate using the conventional wire with the same area of 27 cm². The catalytic plate is expected to be used in near future as an essential technique for low-temperature and high-rate deposition and to bring about drastic revolution in Cat-CVD.

A6.4

EFFECT OF HYDROGEN RADICAL ON PROPERTIES OF HYDROGEN IN HYDROGENATED MICROCRYSTALLINE SILICON. <u>Takashi Itoh</u>, Noriyuki Yamana, Hiroki Inouchi, Hidekuni Harada, Kanta Yamamoto, Katsuhiko Inagaki, Norimitsu Yoshida, Shuichi Nonomura and Shoji Nitta, Dept. of Electrical Engineering, Gifu Univ., Gifu, JAPAN.

Hydrogen radical density is one of the key deposition parameters on the growth of hydrogenated microcrystalline silicon (μ c-Si:H). The effect of the hydrogen radical on the properties of incorporated hydrogen into μ c-Si:H, however, has not been understood yet. The incorporated hydrogen into μc Si:H has been studied using FTIR absorption and gas effusion spectroscopies [1]. We found out the polysilane structure mode near 840cm⁻¹ in IR absorption spectra for the μ c-Si:H [2]. This structure would be related to the electrical properties and the oxidization in the μ c-Si:H. Recently we demonstrated Hot-wire assisted plasma enhanced CVD (HWAPECVD), which consists of PECVD for deposition and Hot-wire for exiting hydrogen, as a new preparation method for μ c-Si:H [3]. The advantage of this method is that the hydrogen radical density is controlled by filament temperature without changing the other preparation conditions. In this report, the effect of the hydrogen radicals on the hydrogen in $\mu c\text{-Si:H}$ has been studied using FTIR absorption spectroscopy and gas effusion spectroscopy. Samples are prepared at 250°C by HWAPECVD from silane highly diluted in hydrogen. RF (13.56MHz) power is ~10W. Filament temperature is varied from room temperature to ~1750°C. The amplitude of the polysilane mode decreases with increasing the filament temperature. This result indicates that the amplitude of the polysilane structure can be controlled by varying the hydrogen radical density. Hydrogen density of the sample decreases with increasing the filament temperature. The decreases in the polysilane mode and the hydrogen density would be caused by hydrogen etching. The mechanism of the hydrogen radicals and the incorporated hydrogen into μ c-Si:H film is discussed with the results of gas effusion spectroscopy and ESR. [1] K. Yamamoto, et al., MRS Symposium Proc., in print. [2] T. Itoh, et al., J. Non-Cryst. Solids, accepted.

[3] H. Harada, et al., Solar Energy Materials and Solar Cells, submitted.

N-TYPE SILICON FILMS PRODUCED BY HOT WIRE TECHNIQUE. I. Ferreira, R. Martins, A. Cabrita, E. Fortunato, P. Vilarinho, Univ Nova de Lisboa, Faculty of Science and Technology, Dept of Materials Science, Monte de Caparica, PORTUGAL.

The role of the deposition pressure and of the types of filaments (tungsten or tantalum) used to produce large area n-type Si:H films by the hot wire technique was investigated under a design system, that allows the definition of highly uniform 10cm-10cm films. The data achieved show that Ta filaments are more adequate to produce large area amorphous or poly-Si films than W filaments. The reason is that the Ta filaments are more resistant than the W filaments, after being used, not leading to any significant contamination, when filament temperatures up to 2200°C are used as the SIMS data reveal. Apart from that, we also noticed that the electro-optical properties of the films produced are highly dependent on the pressure used. In the pressure range from 0.1 Torr to 1.0 Torr, the film's conductivity varies by more than two orders of magnitude, for films produced at same hydrogen dilution and filament temperature, reaching values of about 10 S/cm, at deposition pressures of about 0.4 Torr. On the other hand, high conductive films are produced using specific deposition conditions concerning hydrogen dilution and filament temperature. These data as well the performances of p.i.n devices produced using the improved n-layer deposited by hot wire technique will be presented.

 $\frac{\mathbf{A6.6}}{\mathbf{THE}}$ INFLUENCE OF W FILAMENT ALLOYING ON THE ELECTRONIC PROPERTIES OF HWCVD DEPOSITED a-Si:H FILMS. A.H. Mahan, J. Thiesen, A. Mason, A. Swartzlander-Guest, and A.C. Gallagher*, National Renewable Energy Laboratory, Golden, CO; *JILA, University of Colorado and NIST, Boulder, CO.

In depositing a-Si:H by HWCVD using W filaments, one issue common to this technique is that of filament lifetime. When using undiluted silane as the source gas, a buildup of silicon at the colder ends of the filament is routinely observed, and it is here that filament breakage usually occurs. Less well understood is the effect of alloy formation on a-Si:H electronic properties. As this alloying is usually confined to the filament ends, with proper baffle designs this alloying does not normally affect the growing film surface. However, by using shorter filaments where the growing film surface sees the entire filament length, we can probe this issue. In this work we combine ambipolar diffusion length (SSPG) measurements on consecutively deposited a-Si:H films with sputter Auger depth profiling of the filament Si/W composition to track film electronic properties as a function of the Si buildup on these short filaments. With increased run time, this alloying ('thickened' region) progresses further and further along the filament length, so that at the end of the experiment, approximately half of the filament was alloyed ('thickened'). Further, even the non-thickened central regions contained appreciable Si. This alloying had two major consequences. The decrease in film deposition rate could be quantitatively understood by considering the decreased

fraction of the hot filament length, which accounts for the large majority of film deposition. However, the film electronic properties also deteriorated dramatically with filament run time, as evidenced by the sharp drop in the film SSPG value. We detail the results of these measurements, and suggest that the nature of the filament surface must be carefully considered when optimizing a-Si:H film electronic properties. Finally, we discuss possible ways to minimize this alloying by pre or post deposition treatments, different filament run temperatures, and the possible use of other filament materials.

> SESSION A7: POSTER SESSION: HIGH-RATE DEPOSITION Chair: Hajime Shirai Tuesday Evening, April 25, 2000 8:00 PM Salon 1-7 (Marriott)

 $\underline{\mathbf{A7.1}}$ ION-ASSISTED DEPOSITION OF SILICON EPITAXIAL FILMS WITH HIGH DEPOSITION RATE USING LOW ENERGY SILICON IONS, Lars Oberbeck, Ralf B. Bergmann, Jürgen H. Werner, Univ of Stuttgart, Inst of Physical Electronics, Stuttgart, GERMANY.

Ion-assisted deposition (IAD) enables low-temperature (< 550°C), high-rate ($\leq 0.5 \ \mu \text{m/min}$) epitaxial growth of silicon films. These features make IAD an interesting deposition technique for microelectronic devices and crystalline thin film silicon solar cells on glass substrates. Ion-assisted deposition is based on electron-gun evaporation and subsequent ionization of a small fraction of evaporated silicon atoms. An applied voltage of several 10 V accelerates the silicon ions towards the substrate. This hyperthermal kinetic ion energy allows lower deposition temperatures and higher deposition rates compared to other low-temperature epitaxial growth techniques. In order to evaluate the structural and electrical properties of epitaxial layers we use monocrystalline Si substrates to exclude influences of grain boundaries. The electron and hole mobility of our in-situ doped films reaches values of Cz-Si in the doping range between 10^{16} and $10^{20}~{\rm cm}^{-3}$. The minority carrier diffusion length substantially increases with deposition temperature. Secco etching demonstrates that a decreasing density of extended defects such as dislocations and stacking faults is responsible for the increase of short circuit current density and minority carrier diffusion length of test solar cells with increasing deposition temperature. Structural investigations of epitaxial growth on large and fine grained poly-Si substrates demonstrate the possibility of low-temperature epitaxial growth on arbitrarily oriented grains. Growth on fine grained Si substrates, however, exhibits influences of growth rate anisotropy during epitaxial growth. We apply epitaxial Si layers with in-situ emitter deposited by IAD to microcrystalline seeding layers on glass substrates and study the influence of deposition parameters and hydrogen treatment.

A7.2

A NEW VHF PLASMA SOURCE FOR LARGE AREA PLASMA DEPOSITION OF THIN SILICON FILMS. J. Kuske, U. Stephan, Forschungs- und Applikationslabor Plasmatechnik GmbH Dresden,

The use of VHF for deposition of large-area amorphous silicon films leads to a non-uniformity of the film thickness due to the generation of standing waves and evanescent waveguide modes at the electrode surface. One possibility to process large area substrates with very high frequencies (50...100MHz) is the use of an linear plasma source in combination with a moved substrate. The VHF plasma source is electrically screened to prevent electromagnetic and plasma emissions. Several kinds of power feeding were investigated, e.g. dual power feeding, single power feeding with load resistances, and multiple power feeding. But multiple power feeding is the only way for using VHF at any source length up to 2000mm and more. Using a source of 600mm length, experiments were done with 81.36 MHz at RF power densities of $25...250 mW/cm^2$, nitrogen and silane pressures of 5...100Pa, and flow rates of 10...1000sccm. The measured potential distribution error was $\pm 2\%$. Optical emission spectroscopy delivers discharge intensity errors of $\pm 3...10\%$ in opposition to $\pm 33...100\%$ at a single power feeding. Deposition rates up to $15\mu m/h$ (40 Å/s) and film thickness inhomogeneities less than ±5% were achieved. The best deposition parameters are 16Pa/160mW/cm² at 35mm electrode distance. More experimental results will be discussed in dependence on the deposition parameters.

OPTIMIZATION OF HIGH RATE a-SiGe:H TECHNOLOGY FOR SOLAR CELLS. B.G. Budaguan, A.A. Sherchenkov, A.A. Aivazov, MIET, Materials Science Dept., Moscow, RUSSIA.

For the application of the low band gap a-SiGe:H alloys as an active layer in tandem and triplet solar cells it is necessary to increase the deposition rate and photosensitivity, and decrease substrate temperature to minimize the degradation of the previously fabricated layers. Recently we have shown that 55 kHz PECVD method allows to deposit high photosensitive a-SiGe:H films at the substrate temperature 225°C with optical band gap 1.63 eV and high deposition rate (~1.2 nm/s). For further optimization of this technology we investigated the influence of the substrate temperature on optoelectronic properties and microstructure of a-SiGe:H. The films were deposited by $55~\mathrm{kHz}$ PECVD at substrate temperatures from 175 to $275\,^{\circ}\mathrm{C}$. The low frequency power, the total gas pressure and GeH₄ concentration in the gas mixture with SiH₄ were kept at constant values of 150 W, 70 Pa and 17%, respectively. It was found that the decrease of T_S leads to the decrease of the dark, σ_d , and photoconductivity, σ_{ph} . However, the decrease of σ_{ph} is lower, which cause the high values of photosensitivity, σ_{ph}/σ_d at lower substrate temperatures. To determine the factors controlling σ_{ph}/σ_d IR spectroscopy measurements were carried out. The results showed that E_a was determined by the concentration of Si-H_n configurations. The increase of σ_{ph}/σ_d correlates with the increase of SiH configurations, which decreases with the decrease of T_S . This means that for the investigated range of temperatures and concentration of Ge in the films the passivation of dangling bonds at lower temperatures is connected mainly with Si bonds and recombination centers in 55 kHz a-SiGe:H are mainly determine by Si defects. So, the results showed that photosensitivity of 55 kHz PECVD a-SiGe:H films can be increased by the decrease of substrate temperature and is controlled by Si related defects.

COMPARISON OF STRUCTURAL PROPERTIES AND SOLAR CELL PERFORMANCE OF a-Si:H FILMS PREPARED AT VARIOUS DEPOSITION RATES USING 13.56 AND 70 MHZ PECVD METHODS. <u>S.J. Jones</u>, T. Liu, X. Deng, D. Tsu and M. Izu, Energy Conversion Devices, Inc., Troy, MI; D.L. Williamson, Colorado School of Mines, Golden, CO.

The advantage of using very high frequencies for preparation of a-Si:H materials at high rates (above $\bar{5}$ Å/s) for intrinsic layers of solar cells has been well documented. In an effort to identify structural film properties which may be related to this superior device performance, we have completed a study of the structural properties of films made at various deposition rates between 1 and 15 Å/s using rf frequencies of 13.56 and 70 MHz. The results from the structural properties of the single-layer films have been compared with the performance of nip solar cells whose intrinsic layers were prepared under identical conditions to those for the single-layer films. The film microstructure was characterized using Small-Angle X-ray Scattering (SAXS), Infrared Absorption Spectroscopy, Secondary Ion Mass Spectroscopy (SIMS) and Raman Spectroscopy Analysis. With these techniques, the void content and structure, bonded hydrogen contents and configurations, the unbonded hydrogen contents and the local ordering was characterized. In order to alter the deposition rate, several deposition parameters were altered including the active and dilution gas flows, the chamber pressure, and the applied rf power. Of particular interest is the appearance of a highly oriented columnar-like microstructure for films made using the $13.56~\mathrm{MHz}$ frequency and deposition rates of 5-8 Å/s. This type of microstructure was not detected in any of the films prepared using the 70 MHz even at deposition rates as high as 13 Å/s. For the films made using the 70 MHz frequency, only a small volume fraction of randomly oriented microvoids, which linearly increased as a function of increasing deposition rate, was noted. This linear increase in void content with increasing deposition rate correlated with a small deterioration in the solar cell performance.

GROWTH RATE STUDY OF a-Si:H DEPOSITION USING AN EXPANDING THERMAL PLASMA. A.H.M. Smets, C. Smit, B.A Korevaar, W.M.M. Kessels, D.C. Schram and M.C.M. van de Sanden, Dept. of Appl. Physics, Eindhoven University of Technology, Eindhoven, THE NETHERLANDS.

In order to understand the a-Si:H growth mechanism from a source producing primarily SiH3 and H, a study of the both substrate temperature and growth rate dependence of a-Si:H film properties is undertaken. For this purpose the expanding thermal plasma (ETP) deposition technique is used which enables access to a range of growth rates ranging over two orders of magnitude (2-200 Å/s). The growth rate as determined from in situ ellipsometry and substrate temperature dependence of a variety of film properties have been determined. The hydrogen content as determined from Elastic Recoil Detection Analysis decreases with increasing substrate temperature and at lower substrate temperatures (< 350°C) the hydrogen content increases with increasing growth rate. The band gap (from transmission/ reflection measurements) decreases with increasing temperature and

does not depend strongly on the growth rate and correlates with the hydrogen content. The Urbach edge at $T_{sub} > 100\,^{\circ}\mathrm{C}$ are around 50 meV and defect densities as determined from Dual Beam Photoconductivity measurements for our best samples are below 10^{16} cm⁻³ even at growth rates as large as 25 Å/s. The results indicate that with increasing growth rate the substrate temperature at which we obtain device quality film properties should be increased. The results will be interpreted in an a-Si:H growth model for hydrogen, weak bond and defect incorporation as a function of growth rate and substrate temperature.

A7.6

ROUGHNESS EVOLUTION OF HIGH RATE a-Si:H GROWTH USING AN EXPANDING THERMAL PLASMA. A.H.M. Smets, C. Smit, W.M.M. Kessels, D.C. Schram and M.C.M. van de Sanden, Dept. of Appl. Physics, Eindhoven University of Technology, Eindhoven, THE NETHERLANDS.

The expanding thermal plasma (ETP) deposition technique, developed at the Eindhoven University, combines high growth rate (100 Å/s) with device quality opto-electronic a-Si:H film properties. In this paper we report results on film growth, dominated by silyl (SiH₃) radicals and atomic hydrogen species impinging the growth surface, as studied using single wavelength rotating compensator ellipsometry. An optical growth model is formulated similar to models as proposed by Collins et al. (J. Vac. Sci. Technol. B7 1115 (1989)) to simulate the ellipsometric measurements. This model enables us to monitor the surface roughness evolution, characterized by a roughness toplayer thickness d_{top} in time. Results are presented as function of growth rate (2-120 Å/s) and substrate temperature (100-500°C). The post initial roughness evolution (film thickness > 100 nm) can be described by $d_{top} \sim t^{\beta}$ where β is a scaling exponent being 1/2 for random growth and < 1/2 if a surface smoothening processes during growth is active. For growth rates ≤ 22 Å/s, β decreases with increasing temperature from 0.5 at 100°C. Often the decreasing β values as function of temperature are explained in terms of surface diffusion of weakly adsorbed silyl radicals. In this paper we will argue that β values smaller than 1/2 not necessarily implies that the dominant smoothing mechanism is determined by surface diffusing weakly adsorbed radicals but rather by the ability of surface dangling bonds to preferently reside at surface valleys. Possible mechanisms for dangling bond transport on the a-Si:H growth surface will be discussed.

SESSION A8: POSTER SESSION:
POLYCRYSTALLINE FILMS
Chairs: Norbert H. Nickel and Gregory N. Parsons
Tuesday Evening, April 25, 2000
8:00 PM
Salon 1-7 (Marriott)

A8.1

MODELING OF SILICON CHEMICAL VAPOR DEPOSITION FROM CHLOROSILANES BASED ON QUASI-THERMODYNAMIC APPROACH. Alexander S. Segal, Institute for Fine Mechanics and Optics, Computer Technology Dept, St. Petersburg, RUSSIA; Alexey V. Kondratíyev, Alexander O. Galyukov, Sergey Yu. Karpov, Soft-Impact Ltd, St. Petersburg, RUSSIA; Yuri N. Makarov, Fluid Mechanics Dept, Univ of Erlangen-Nurnberg, Erlangen, GERMANY.

When chlorosilanes (dichlorosilane or trichlorosilane) are used as precursors in CVD of silicon the surface is covered significantly by H and Cl adatoms. The adatoms occupy free surface sites available for adsorption of gaseous reactive species, providing kinetic limitation of the growth rate at moderate temperatures. We employ this idea to develop a model of surface processes, accounting for the kinetic limitation at the stage of species adsorption/desoprtion. It is done in terms of the sticking coefficients related to reactive species or radicals and dependent on the surface coverage with H and Cl adatoms. The rest stages of crystal growth are assumed to proceed under quasi-equilibrium conditions where the atoms in the adsorption layer are nearly in equilibrium with the crystal. Parameters of the model are extracted from the experimental data on low-pressure CVD. Compared to other models, this approach allows one to reduce considerably the number of kinetic rate constants normally poorly known. The developed model of the surface processes is coupled with gas-phase homogeneous chemistry and transport equations to carry out detailed three-dimensional simulation of CVD of Si in a commercial reactor. The growth rate and deposition uniformity depending on the process conditions are studied systematically. The computations revealed high sensitivity of the growth rate to variation of the gas-phase composition and, in particular, to content of HCl. Excess of HCl in the vapor phase can also result in etching of Si surface. The theoretical predictions are found to agree well with available experimental data.

A8.2

LOW TEMPERATURE SELECTIVE SI EPITAXY INTRODUCING THE PERIODIC DEPOSITION AND ETCHING CYCLES USING SiH₄, H₂, AND HCl BY REDUCED PRESSURE CHEMICAL VAPOR DEPOSITION. H.S. Kim, K.W. Shim, J.Y. Kang, Microelectronics Technology Laboratory, Electronics and Telecommunications Research Institute, Taejon, KOREA.

Low temperature selective Si epitaxy is on going issue to be addressed for Si/SiGe heterostructure devices, such as, modulation-doped field effect transistors (MODFETs), metal-oxide-semiconductors (MOSFETs) and heterojunction bipolar transistors (HBTs) applications in Si integrated circuit processing. Impurity diffusion, intermixing at Si/SiGe interface, and relaxation of strain have been observed to deteriorate device performance. To effect the above improvements, selective epitaxy growth temperatures must be reduced to the 700°C and below. Currently, for low temperature selective Si epitaxy, nonchlorinated source gases such as SiH_4 and Si_2H_6 have been used. However, selectivity was lost once a critical epitaxy layer thickness was reached. In this work, to extend the selective si epitaxy layer thickness range at 650-700°C, the periodic deposition and etching cycles were introduced. We present the use of the SiH₄/HCl/H₂ system for deposition and the HCl gas for etching by reduced pressure chemical vapor deposition. The dependence of SiH₄/HCl ratio, SiH₄ and HCl flow rate, and deposition and etching time on the growth rate and selectivity are investigated. While the selectivity was easily lost without the HCl etching process in the temperature range of 650-700 °C, the introduction of HCl etching process following the deposition allows sustaining the selectivity for several tens period.

A8.3

RESISTIVITY AND HALL VOLTAGE INVESTIGATION OF P SEGREGATION IN POLYCRYSTALLINE SIGE THIN FILMS. W. Qin, D.G. Ast, Cornell University, Department of Materials Science & Engineering, Ithaca, NY; T.I. Kamins, Hewlett-Packard Laboratories, Palo Alto, CA.

It is known that n-type dopants, such as P and As, segregated to the grain boundaries in poly-Si, where they become electrically inactive. Our previous STEM microanalysis showed that grain-boundary segregation also takes place in P doped, polycrystalline Si_{0.87}Ge_{0.13} thin films but left the electrically activity of segregated P unresolved. To investigate this issue, the electrical properties of atmospheric-pressure CVD deposited, 300 nm thick, polycrystalline $Si_{0.95}Ge_{0.05}$ and $Si_{0.9}Ge_{0.1}$ thin films, implanted at 80 KeV with 2×10^{18} to 1.5×10^{19} P/cm³, and annealed at 800 C for 1 hr were investigated using a combination of Hall and resistivity measurements. The room temperature resistivity strongly varied with doping and decreased from 1×10^4 to $1\times10^{-1}~\Omega\cdot cm$, as the P concentration was increased from 2×10^{18} to $1.5\times10^{19}~P/cm^3$. In all cases, the resistivity at a given doping level was slightly, but systematically, lower in $\mathrm{Si_{0.9}Ge_{0.1}}$ films. In $\mathrm{Si_{0.9}Ge_{0.1}}$, the activation energy of conduction decreased with doping from 0.38 to 0.035 eV, and in $Si_{0.95}Ge_{0.05}$ films from 0.43 to 0.034 eV. The trap density at grain boundaries, derived from the Seto model, was found to be $4.4\times10^{12}/\mathrm{cm}^2$ in $\mathrm{Si_{0.9}Ge_{0.1}}$ and $3.6\times10^{12}/\mathrm{cm}^2$ in $\mathrm{Si_{0.95}Ge_{0.05}}$. Hall measurement, feasible only in heavily doped films, showed that 29% of dopants in $Si_{0.9}Ge_{0.1}$ and 42% in $Si_{0.95}Ge_{0.05}$ were electrically inactive. The difference between carrier and dopant concentration is attributed to inactive P segregated to grain boundaries.

A8.4

HIGH RESOLUTION ELECTRON MICROSCOPY (HREM) STUDY OF CHEMICAL VAPOR DEPOSITED POLYCRYSTALLINE SiGE THIN FILMS. W. Qin, D.G. Ast, Cornell University, Dept of Materials Science & Engineering, Ithaca, NY; T.I. Kamins, Hewlett-Packard Laboratories, Palo Alto, CA.

Electrical conduction in polysilicon is influenced by both carrier trapping at and dopant segregation to grain boundaries. Both effects, in turn, depend on the atomic structure of the bounday; however, compared to the extensive experimental and theoretical studies of the atomic structure of grain boundaries (GBs) in polysilicon, little is know about the structure of GBs in poly-SiGe. We used high resolution TEM analysis to study the GB structure in Sio.69 Geo.31 thin films and, as a reference, in polysilicon thin films. The SiGe films were deposited by CVD at 600 C from a GeH₄/SiH₂Cl₂ mixture onto a 60 nm polysilicon seed layer. The poly-Si films were deposited from SiH₂Cl₂ at 790 C. Grain size in both film types was similar, with the average grain size being 52 nm in Si_{0.69}Ge_{0.31} and 45 nm in polysilicon. In Si_{0.69}Ge_{0.31} multiple twins with five-fold symmetry were observed. Inspection of all five-fold twin images recorded showed that none of the single crystal region inside these twins exceeded 18 monolayers in size. Theory indicates that this is the maximum number of layers a five-fold symmetric twin can tolerate. While multiple twins were also observed in polysilicon, no twins with five-fold symmetry

could be found. In general, less substructure was seen in the polysilicon reference samples. Consistent with this trend, wider twin bands were observed in polysilicon films than in $Si_{0.69}Ge_{0.31}$ films. Finally, the density of multiple twins was lower in Si. Since the grain size of the two film types is similar, the observed structural differences must reflect the addition of Ge, which being a larger atom, both introduces more local strain (promoting twinning), and by replacing Si atoms under tensile stress, offers the opportunity to lower the strain associated with joining together larger substructures, such as those making up 5 fold twin structures. In the case of the second order symmetric twin boundary, analysis of high resolution images showed that in Si_{0.69}Ge_{0.31} the boundary structure was identical to that reported for the second-order symmetric twin boundary in Si. The structure, again, is based on a zig-zag arrangement of five-membered and seven-membered rings. Within the accuracy of HREM, the repeat length of this boundary in Si_{0.69}Ge_{0.31}, is the same as in Si, A previous STEM microanalysis showed that Ge does not segregate to GBs in $Si_{0.69}Ge_{0.31}$. Thus, the ratio of Si to Ge at GBs is that of the bulk; leading to the conclusion that replacement of about 1/3 of the Si atoms by Ge does not significantly influence the boundary structure of the second order twin boundary.

A8.5

EFFECT OF DEPOSITION CONDITIONS ON THE STRUCTURAL AND MECHANICAL PROPERTIES OF POLY SiGe. Ingrid DeWolf, IMEC, Leuven, BELGIUM, Sherif Sedky, Cairo University, Faculty of Engineering, Dept of Engineering Physics, Giza, EGYPT; Ann Witvrouw, Matty Caymax, IMEC, Leuven, BELGIUM.

In this paper, we analyze the effect of decreasing the deposition temperature of poly SiGe from $650^{\rm o}C$ to $500^{\rm o}C$ on the growth rate, germanium concentration and structural and mechanical properties of the grown films. Poly SiGe has been deposited on eight-inch wafers using chemical vapor deposition (CVD) in an EPSILON I reactor, at atmospheric pressure (AP) or a reduced pressure (RP) of 40 Torr. 10%/90% Germane/Hydrogen has been used as the germanium gas source, whereas, the silicon gas source is either silane or dichlorosilane. The gas flow rate has been adjusted to yield a germanium concentration varying from 20% to 40%, as determined by Rutherford Backscattering Spectroscopy (RBS). The deposition rate of RPCVD poly SiGe decreases from 7.5 nm/min to 4.2 nm/min by reducing the deposition temperature from 600°C to 550°C, for a fixed silane and germane flow rate of 10 and 200 sccm, respectively. For RPCVD poly Ge, the growth rate increases from 0.64 nm/min to 2.8 nm/min by increasing the deposition temperature from 500°C to 580°C. The texture, the transition temperature from amorphous to polycrystalline and the microcrystalline structure of the grown films have been determined by means of X-ray diffraction spectroscopy (XRD) and transmission electron microscopy (TEM). The structure of poly SiGe deposited at atmospheric pressure has been found to be more columnar than that deposited at reduced pressure. Finally, the impact of the deposition temperature, pressure, germanium concentration and annealing temperature on stress is presented. It is shown that as grown RPCVD poly SiGe, deposited at 550°C, has a tensile stress of 118 MPa. Such stress is suitable for micro machining applications. Increasing the deposition temperature to 600°C, the stress is increased to 150 MPa. Stress in RPCVD poly Ge decrease from 257 MPa to 197 MPa by increasing the deposition temperature from 550°C to 580°C.

A8.6

CRYSTALLINE SILICON FILMS GROWN EPITAXIALLY AT LOW TEMPERATURES BY ECR-PECVD. J. Platen, B. Selle, Hahn-Meitner-Institut, Abteilung Silicium-Photovoltaik, Berlin, GERMANY; S. Christiansen, M. Nerding, Universitaet Erlangen-Nuernberg, Institut fuer Werkstoffwissenschaften, Mikrocharakterisierung, Erlangen, GERMANY; M. Schmidbauer, Humboldt-Universitaet, Institut fuer Physik, Berlin, GERMANY; K. Kliefoth, W. Fuhs, Hahn-Meitner-Institut, Abteilung Silicium-Photovoltaik, Berlin, GERMANY.

Homoepitaxial growth on top of laser-crystallized poly-Si seed layers is one important option for realizing polycrystalline Si with large grains for thin-film solar cells. Ion assisted deposition techniques and, in particular, electron cyclotron resonance chemical vapor deposition (ECR-PECVD) have been shown to enable epitaxial growth at low temperatures and with reasonably high deposition rates. Here we report on results obtained with ECR-PECVD using systematic variations of the deposition parameters (substrate temperature, ion energy, gas composition) with crystalline Si-substrates of different orientations. Structural properties of the films are investigated by transmission electron microscopy techniques (TEM), Rutherford backscattering (RBS), and x-ray diffraction (XRD). Highly phosphorus and boron doped films on Si(100) substrates turned out to be of high structural quality with defect densities of less than 10^6 cm⁻² (dislocations). The structural order is inferior in case of undoped Si-films. For Si(100) orientation the crystallinity is

significantly improved with substrate temperature (325 - 500°C). Simultaneously, we observed an enhancement of the lattice strain. Ion energy is varied by applying an additional dc bias V_b to the substrate holder. Negative V_b accelerates the ions which results in enhanced ion damage of the lattice structure and increased surface roughness. In contrast, positive V_b reduces the density of lattice defects by decreasing the ion energy. Under so far optimized conditions we obtain epitaxial growth on differently orientated substrates. However, two-dimensional, extended defects are observed the density of which depends on the substrate orientation. Moreover, we find nanosized interfacial inclusions of material of different orientation with a separation of about 1 μ m. By reducing the hydrogen dilution and adding Ar to the excitation gas the deposition rate increases substantially, but the structural quality is diminished. At present it is not clear as to whether the reason is the higher rate or the enhanced ion bombardment.

A8.7

POLYCRYSTALLINE SILICON THIN FILMS FOR MICRO-ELECTRONIC APPLICATIONS. <u>Elena A. Guliants</u>, Young J. Song and Wayne A. Anderson, SUNY at Buffalo, Dept of Electrical Engineering, Buffalo, NY.

For years, thin Si films grown by Physical Vapor Deposition techniques have been known to be inferior in both structural and electrical properties as compared to those grown by Chemical Vapor Deposition. This study is aimed at restoring the importance of the sputtering technique as a convenient, safe and low-cost method to produce good quality Si films at a high deposition rate. Polycrystalline silicon thin films with thickness of $0.5-5\mu m$ were grown on 5-100nm thick Ni prelayers by d.c. magnetron sputtering from a Si target. In contrast to the conventional sputtering, the use of a thin Ni film on a variety of substrates allowed the production of the high crystallinity silicon at temperatures below 600°C. The Ni disilicide grains formed at the Ni - growing Si film interface are shown to provide sufficient sites for the epitaxial growth of Si. The resulting metal-induced grown Si film exhibits a columnar structure. The cross-sectional diameter of the Si crystals is in the $500-5000\,\mbox{\normalfone}{\normalfone}$ range with length equal to the film thickness. Moreover, the Si crystal size is found to be strongly dependent on the thickness of the Ni film. The Ni-Si interdiffusion kinetics plays a dominant role in the silicide formation and the subsequent silicon growth. The dynamics of the ${\rm Si}$ crystal growth on a Ni prelayer is briefly discussed. The Si films with resisitivity of 10^2 - $10^3\Omega$ -cm possess up to $11\mu s$ carrier lifetime which makes them applicable to various microelectronic devices. The Ni silicide layer at the bottom of the silicon film provides a satisfactory back ohmic contact. As an example, Schottky diodes fabricated on a $0.5\mu m$ thick Si film grown at $525^{\circ}\mathrm{C}$ exhibited a forward-to-reverse current ratio of 10⁷. The results of a detailed investigation of both Schottky and p-n junction diodes will be presented. The influence of such post-deposition techniques as annealing and hydrogenation on the device performance will also be reported.

A8.8

IN-LINE CHARACTERISATION OF THIN POLYSILICON FILMS BY VARIABLE ANGLE SPECTROSCOPIC ELLIPSOMETRY. Steffen Paprotta, Kai Sven Roever, Ruediger Ferretti, Univ Hannover, Dept Elektrotechnik und Informationstechnik, Uwe Hoehne, Jan Dirk Kaehler, Josef Haase, Centrotherm, Blaubeuren, GERMANY.

Up to now an in-line method for parameter determination of deposited polysilicon films is not available. In this paper a method for monitoring the polysilicon deposition process in device manufacturing by variable angle spectroscopic ellipsometry (VASE) is demonstrated. Therefore a wide range of polysilicon films is deposited on silicon wafer (100) with different SiO_2 interlayers. These samples are characterised by VASE in the optical range of 450 - 850 nm. Parameters are determined by simulation using a multilayer model consisting of air, interface layer (surface roughness), polysilicon, SiO₂, and silicon substrate. Different recently used optical models representing properties of polysilicon are tested. The free parameters are the oxide thickness, the composition and the thickness of the interface layer (air, polysilicon), the thickness and the complex refractive index of the polysilicon layer. Results of the spectroscopic analysis are verified by surface profiler, AFM, SEM and TEM measurements. It can be shown that parameters of the deposited polysilicon films, which up to now could only be determined by complex and destructive off-line analysis methods are also accessible by non-destructive in-line VASE measurements.

SESSION A9: POSTER SESSION: CRYSTALLIZATION I Chair: Toshio Kamiya Tuesday Evening, April 25, 2000 8:00 PM Salon 1-7 (Marriott)

A9.1

CHARACTERIZATION OF Si-IMPLANTATION INDUCED a-Si LAYER AND ITS RECRYSTALLIZATION THROUGH THERMAL ANNEALING. Ran Liu, Rich Gregory, Peter Fejes, Zhong Lu, Semiconductor Products Sector, Motorola Inc., Mesa, AZ.

In an effort to develop advanced BiCMOS devices, Si implantation is used to create an a-Si layer to prevent BF2 implant channeling and thus to reduce the base junction width. Information about the crystallinity and thickness of the a-Si layer and the lowest thermal budget needed to re-crystallize this layer after BF2 implantation are of great technological importance. This paper presents the characterization results from samples implanted with different doses of 80 keV Si ions and samples annealed at different thermal budgets using Rutherford Backscattering Spectroscopy (RBS), ion channeling, Transmission Electron Microscopy (TEM), Raman spectroscopy, and spectroscopic ellipsometry. Good agreements on the crystallinity and thickness of the Si-implanted layer were found between different techniques. The results indicate that the thickness of the implanted layer follows a logarithmic relationship with Si ion dose and the crystallinity of the layer is also dose dependent. An implantation with $5 \times 10^{14}~{\rm cm^{-2}}$ Si at 80 keV can only partially amorphize Si surface through 1400 Å. Dose above $5 \times 10^{14}~{\rm cm^{-2}}$ will fully amorphize the Si substrate through 1600 \mathring{A} and greater. Experimental results from the samples after two different Rapid Thermal Annealing (RTA) processes (900°C/15 Sec. And 1000°C/35 Sec.) show evidence of remaining end-of-range defects after the lower-thermal-budget RTA. The higher-thermal-budget RTA was found to be sufficient to recrystallize the implanted layer.

LARGE GRAINED POLYCRYSTALLINE Si (POLY-Si) FILMS OBTAINED BY SELECTIVE NUCLEATION AND SOLID PHASE EPITAXY: POLY-Si AS A TEMPLATE SUBSTRATE. R.A. Puglisi, H. Tanabe, C.M. Chen and H.A. Atwater, Thomas J. Watson Laboratories of Applied Physics, California Institute of Technology, Pasadena, CA.

The formation and properties of large grain polycrystalline silicon films on low-cost substrates such as glass are of prime interest for applications in solar cells devices. Since use of glass constrains process temperatures, our approach to large-grain polycrystalline silicon template formation is selective nucleation and solid phase epitaxy (SNSPE), in which selective crystallization of an initially amorphous silicon film at lithographically predetermined sites enables grain sizes larger than those observed via pure thermal crystallization. Selective nucleation centers were created on undoped 100 nm amorphous silicon films, by masked implantation of Ni islands. During annealing between 500 and 610 C, seeded crystallization begins at the Ni islands and continues via a lateral solid phase epitaxy process, whose rate is enhanced by the presence of nickel silicide precipitates at the amorphous Si - crystal Si interface. Upon 1 hour long annealing, crystallized portions of up to 40-50 microns in diameter are obtained, with a growth rate of about 7 nm/s. Ni-induced crystallization leads to a needle-like subgrain structure of low-angle boundaries, with a length scale of 10-100 nm. The maximum achievable grain size depends on the product of the solid phase epitaxy rate and the incubation time for random crystallization. We have studied, by transmission electron microscopy (TEM) and optical image analysis, the variation of the solid phase epitaxy rate and the incubation time as a function of Ni dose, in the $10^{14}/\mathrm{cm}^2$ - $10^{16}/\mathrm{cm}^2$ regime, and thus find an optimal doping concentration for largest grain size. The crystallized samples were then used as substrates for epitaxial growth of 1 micron thick Si layers. Atomic force microscopy analysis and optical images showed strong correlation between the substrate and the Si over-layer morphology. Further structural and optical characterization by TEM and photoluminesence decay lifetime measurements will be presented.

THIN SINGLE CRYSTAL SILICON ON OXIDE BY LATERAL SOLID PHASE EPITAXY OF AMORPHOUS SILICON AND SILICON-GERMANIUM. B.J. Greene, J. Valentino¹, J.L. Hoyt, and J.F. Gibbons, Solid State Electronics and Photonics Laboratory, Stanford University, Stanford, CA, $^1{\rm Villanova}$ University, Villanova,

Processes to generate single crystal Si on oxide are of interest for the fabrication of multiple layers of Si MOSFETs. One method under investigation is lateral solid phase epitaxy (LSPE) of amorphous Si on oxide, using the Si substrate as a seed. In this work, we characterize the LSPE growth process for amorphous films grown by low-pressure $\,$ chemical vapor deposition at 525°C on oxide-patterned, (001) Si substrates. For sub-50 nm gate length devices, a Si layer thickness on the order of 10 nm will be required. Previous work on LSPE has shown significant faceting and lack of a well defined growth front for Si layer thicknesses less than about 0.5 μ m. Here, we demonstrate the fabrication of 25 nm-thick epitaxial Si regions on oxide, by LSPE of an amorphous $\mathrm{Si/Si_{1-x}Ge_x/Si}$ stacked structure. A thin $\mathrm{Si_{1-x}Ge_x}$ layer (x=0.2) is used as an etch stop. Following LSPE of the $0.53\mu\mathrm{m}$ -thick stack by annealing at $555^{\circ}\mathrm{C}$, the top two layers are selectively removed by wet chemical etching. The resulting structure achieves a 25 nm-thick single crystal Si region on oxide with a lateral epitaxial growth distance of $2.5\mu\mathrm{m}$ from the seed window. In this structure, the Si_{1-x}Ge_x serves as an etch stop layer. However, the addition of Ge to amorphous Si impacts the LSPE process itself. In a separate set of experiments we find that the activation energy for LSPE growth is reduced for 20% Ge alloys compared to that for pure Si. At 555°C, this amounts to an enhancement of roughly a factor of three in the LSPE growth rate, which enables reduced substrate thermal exposure. However, the Ge fraction and anneal temperature must be optimized, as Ge also increases the rate of random crystallization of the amorphous film over the oxide.

 $\frac{ ext{A9.4}}{ ext{VARYING HYDROGEN EVOLUTION TIME IN THE}}$ SOLID-PHASE CRYSTALLIZATION OF a-Si_{1-x}Ge_x:H FILMS. O.H. Roh, J.-K. Lee, Chonbuk National University, Dept of Physics, Chonju, KOREA.

We have investigated the solid-phase crystallization (SPC) of $a-Si_{1-x}Ge_x$:H (x=0,0.21,0.67) films by using electron spin resonance (ESR) and x-ray diffraction (XRD) measurements. The films were deposited on Corning 1737 glass in a plasma-enhanced chemical vapor deposition system using ${\rm SiH_4}$ and ${\rm GeH_4}$ gases. The substrate temperature was 200°C and the r.f. power was 3 W. The film thickness ranged $2.8-3.3\mu m$. The films were then annealed to be crystallized at $600^{\circ}C$ in a N_2 atmosphere. The total spin density first increased with annealing time due to hydrogen evolution, and then rapidly decreased as the film was crystallized. The variation of spin densities due to the annealing was found to be keenly related to the variation of the crystalline fractions in the SPC process. The SPC process was dominated by Ge dangling-bonds rather than Si dangling-bonds for the Ge-rich samples (x = 0.21 and 0.67). Also, it was observed that the H evolution time from the Si-H bond or Ge-H bond was strongly affected by the Ge composition of the films. The H evolution time from Si-H bond for the x=0.67 film was faster than for x=0 or 0.21 film; the H evolution from Ge-H bond for x=0.67film was significantly faster than x=0.21 film. Our results were attributed to the varying Si-H dissociation energy and the Ge-H dissociation energy depending on the Ge composition x of the films. The atomic environments around the H of the Si-H or the Ge-H bond would be varying with the Ge composition of the films.

CONTROL OF AMORPHOUS SILICON CRYSTALLIZATION USING GERMANIUM DEPOSITED BY LOW PRESSURE CHEMICAL VAPOR DEPOSITION. Masato Toita, Asahi Kasei Microsystems, Tokyo, JAPAN; Pranav Kalavade, Krishna C. Saraswat, Stanford University, Dept of Electrical Engineering, Stanford, CA.

Statistical variations in electrical characteristics of polysilicon thin film transistors (poly-Si TFTs) result from random distribution of the grains in devices. The density and location of grain boundaries in the channel region strongly affect transistor's electrical characteristics Therefore, control of grain size and location in a poly-Si thin film is necessary for realizing uniform and scaled TFT's. Germanium seeding is an effective way to achieve such controllability. In this paper, we have studied solid phase crystallization (SPC) behavior of amorphous Si films with and without Ge seeding. Oxidized Si(100) wafers were used as substrates. Ge was deposited by LPCVD from GeH4 at 500°C, 100mtorr on 100nm-thick amorphous Si films that were also deposited by LPCVD. Amorphous Si films without Ge layer (uncovered Si) were also prepared as control samples. Films were annealed at 525°C or 600°C for 30min to 62hr to obtain several degrees of crystallization. TEM observation was done to investigate crystallization behavior of Si films. SEM was also used, in which case, amorphous portion of a film was selectively etched with a HF and HNO₃ based solution to observe crystal grains. Grain population linearly increased with annealing time after an incubation period specific to each annealing temperature. Incubation time for nucleation of Ge-covered Si was about twice as much as uncovered Si. On the other hand, nucleation rate was larger for Ge-covered Si than for uncovered Si. Activation energy for incubation of Ge-covered Si (-3.3eV) was approximately the same as uncovered Si (-3.2eV) However, activation energy for nucleation was significantly lower for

Ge-covered Si (2.3eV) than for uncovered Si (2.7eV). We conclude that, to make LPCVD-Ge an effective seeding agent for spatially controlled crystallization of amorphous Si film, annealing should be started at relatively low temperature (for example, 500°C).

 $\underline{\textbf{A9.6}}$ THICKNESS-DEPENDENT MICRO-RAMAN MEASUREMENT OF POLY-Si FILMS PREPARED BY METAL-INDUCED-CRYSTALLIZATION USING Ni LAYER. Shin-ichi Muramatsu, Yasushi Minagawa, Fumihito Oka, Advanced Research Center, Hitachi Cable, Ltd., Ibaraki, JAPAN; Yoshiaki Yazawa, Central Research Laboratory, Hitachi, Ltd., Tokyo, JAPAN.

This paper presents the thickness-dependent characteristic features of micro-Raman spectra from a cross section of polycrystalline silicon (poly-Si) films prepared by metal-induced-crystallization (MIC) of amorphous silicon (a-Si) films using a thin Ni layer. We found that a 1-nm-thick Ni layer gives the same crystalline volume fraction and the same crystallized depth as a 10-nm-thick Ni layer at an annealing temperature as low as 550°C. A Ni layer thicker than 10 nm also gave the same result. For a solar cell application, relatively thick poly-Si film - from 1000 to 10000 nm - is preferable for light absorption. Using MIC is quite effective to prepare such a thick film, because it allows us to prepare a high-quality film at a high-deposition rate. However, to reduce the metal (Ni) contamination in poly-Si, it needs Ni thickness to a minimum for complete crystallization. Thus, we examined the thickness dependence of the MIC feature by using Raman measurement. A 6000-nm-thick a-Si film was deposited on a glass substrate. Then, 1-nm or 10-nm Ni layer was evaporated on it. After that, samples were annealed in N2 ambient for 10 or 60 min. at 550°C. Micro-Raman spectra were measured at 1000-nm intervals on the cross-section of Si films from Ni/Si interface to glass substrate. Crystallization from the surface advanced 2000 nm in 10 min., and 4000 nm in 60 min. for both samples with the Ni layer of 1 nm and 10 nm. The polycrystalline volume fractions in the crystallized region were also the same for both samples. This means that a few monolayers are sufficient for MIC. These results suggest that the crystallization proceeds as a catalytic reaction. We will also present the crystalline size and orientation at the conference.

EFFECT OF RAMP ANNEALING ON Ni INDUCED LATERAL CRYSTALLIZATION OF AMORPHOUS SILICON. S. Shivani, M.C. Poon, M. Chan, Dept. of Electrical and Electronic Engineering, Hong Kong University of Science & Technology, Sai Kung, HONG KONG.

Nickel Metal-Induced-Lateral-Crystallization (MILC) has been used to enlarge the grain size and improve the quality of poly-silicon (poly-Si) Thin-Film-Transistor (TFT). However, the MILC temperature is still low and the grain size is still small. We have studied the feasibility of forming very large grains (single crystal like) from amorphous silicon (a-Si) by combining MILC on a-Si with ramp annealing. 7000Å of oxide was grown on Si substrate by wet oxidation at 1000°C, followed by the deposition of 1000Å of a-Si at 550°C. A 3000 Å of LTO layer was then deposited at 425 °C, and windows are patterned next to the desired region for crystallization. Thin nickel (Ni) was then deposited and MILC was carried out subsequently by ramp annealing at 600-1000°C in N2 ambient for 0-2 hours. We have found that the grain size after ramp annealing is remarkably enhanced and can reach the order of several tens of microns. The velocity of MILC with ramp annealing is faster than that of MILC with constant annealing. The grain size becomes maximum at around 625°C/2hrs, and saturates at higher temperatures of 625-1000°C. We have also studied the effect of the MILC temperature and time and the other parameters to maximize the grain size and quality. MILC with ramp annealing at 625°C can greatly lower the process time and reduce the need of subsequent annealing to enhance the grain size. The new technology can have numerous novel applications such as providing a low cost alternative to form silicon-on-insulator (SOI) substrates and a breakthrough to high performance TFTs and novel multi-layers SOI like devices and circuits.

> SESSION A10: POSTER SESSION: METASTABILITY AND EQUILIBRATION Chair: Peter A. Fedders Tuesday Evening, April 25, 2000 8:00 PM Salon 1-7 (Marriott)

X-RAY PHOTOEMISSION SPECTROSCOPIC STUDY OF STRUCTURAL CHANGES IN AMORPHOUS SILICON. Shuran Sheng, Edward Sacher and Arthur Yelon, Groupe de Recherche en Physique et Technologie des Couches Minces & Departement de Genie Physique et de Genie des Materiaux, Ecole Polytechnique de Montreal, Montreal, Quebec, CANADA.

It is now recognized that defect creation is not the only light-induced metastable change in a-Si:H: there is now considerable evidence for large light-induced metastable structural changes in a-Si:H in addition to changes in electronic properties. Recently, we reported a preliminary X-ray photoemission spectroscopy (XPS) study of lightand X-ray-induced structural changes in a-Si:H [1]; we observed metastable, simultaneous, identical shifts in both Si2s and Si2p peaks to lower binding energies with light-soaking or X-ray irradiation times. In this contribution, we present detailed XPS investigations of light- and X-ray-induced structural changes in undoped a-Si:H, as well as pure a-Si and c-Si, and their annealing behaviors. The shifts in both the 2s and 2p peaks of a-Si:H, with illumination or X-ray irradiation, were found to follow a stretched exponential time dependence, and to nearly reach saturation after about one hour of exposure at the intensity used. In contrast to the SWE changes in electronic properties, these light- and X-ray-induced shifts are unstable even at room temperature and can be reversed, by annealing, with a lower activation energy (0.6 eV) than that for the SWE (1.1 eV). The absence of metastable XPS changes in pure a-Si suggests that hydrogen is actively involved in the process. Furthermore, visible light produces XPS changes in a-Si:H in a more complicated way, and less efficiently, than X-rays. The shifts in the measured XPS lines, without any change in the line widths, require that the entire network structure change uniformly. In this sense, this effect may present a greater challenge to modeling than do the other observations of structural changes. These structural changes may be an independent phenomenon or a precursor process of the SWE. [1] S.R. Sheng, E. Sacher, A. Yelon, H.M. Branz, and D.P. Masson, Mat. Res. Soc. Symp. Proc. 557, 1999 (in press).

METASTABLE DEFECT FORMATION AND ANNEALING INFLUENCE ON TWO-LEVEL HOPPING CURRENT FLUCTUATIONS IN MESOSCOPIC a-Si BASED STRUCTURES. Natalia Stepina, Andrew Yakimov, Anatolii Dvurechenskii, Institute of Semiconductor Physics, Novosobirsk, RUSSIA.

Two-level hopping current fluctuations (random telegraph noise RTN) have recently been investigated in mesoscopic structures based on a small-area thin layers of a-Si. Amplitude of RTN was an amount of 0.5-100% dependent on the feature size of device. Effective lifetimes in low-conductive (τ_l) and high-conductive states (τ_h) were observed to be independent of the sample sizes and conductivity, and fluctuate by up to 100% from one device to another. Two types of structures were obtained: the first type is characterized by $\sim 70 \%$ fluctuation amplitude value, which was found to reduce with applied voltage. In the second one, the amplitude value is equal to 10% and didn't depends on voltage applied to the sample. Field and light assistant switching acceleration have been observed while the field affects au_h rather than τ_l . Light illumination reduces both lifetimes. Microscopic model involving the unit atomic transitions in hydrogen-related two-level systems (TLS) has been proposed to explain the observed RTN signal. Conductivity of this system was described by mesoscopic carrier transport via 1D chains of localized states. Hopping current switchings were suggested to arise from leading chain rearrangement due to atomic transfer between ground and metastable states in TLS. Having appeared in the vicinity of the leading chain, a new localized state changes the resistance of main hop and transforms system to high-current state with the time τ_h . Metastable defect formation is determined by weak bond breaking followed by hydrogen emission from Si-H bond and its migration to a bond-on state. Initial low-conductive state is recovered through metastable defect annealing during τ_h and depends on hydrogen traps concentration. Voltage rise results in carriers redistribution between dangling bonds in different charge states, with hydrogen traps concentration falling and τ_h droping. We have found that the discrepancy between switching frequency change under light emission and estimated magnitude of photon flux on leading chain area by order of 3. This discrepancy is assumed to arise from the contribution of long-range excitations within the hydrogen diffusion length. Voltage dependence of fluctuation amplitude was demonstrated to determine by whether the new localized state produces an additional hop through the leading chain or creates a new chain and thus depends on leading chain configuration.

 $\overline{I,V}$ CHARACTERISTICS OF a-Si:H P-I-N DIODES WITH UNIFORM AND NON-UNIFORM DEFECT DISTRIBUTIONS. M.A. Kroon, R.A.C.M.M. van Swaaij, and J.W. Metselaar, Delft University of Technology, Lab. of Electronic Components, Technology and Materials - DIMES, Delft, THE NETHERLANDS.

In many generation-recombination models describing the dark current-voltage (I, V) characteristics of a-Si:H p-i-n diodes, a spatially uniform distribution of defect states throughout the intrinsic part of

the junction is assumed. However, according to the defect pool model the density of states is usually higher near the interfaces than in the center of the intrinsic region, when the material is allowed to equilibrate during deposition.

In this work, the I, V-characteristics of lateral p-i-n diodes are presented, which do have a spatially uniform defect distribution. These devices provide an excellent opportunity to study defect equilibration in different materials. Devices have been fabricated by deposition of an i-layer on an insulating substrate, lithographic patterning, and room temperature ion implantation of boron and phosphorus for the p- and the n-region, respectively.

The forward I, V-characteristics of these devices show a clear dependence of the ideality factor on the width of the intrinsic region, W. When W is varied, the internal electric field changes and hence the recombination rate. This width dependence indicates that in these diodes the recombination takes place throughout the bulk of the intrinsic region rather than near the p-i interface. Obviously, the spatial defect distribution in the intrinsic layer is uniform and has not equilibrated during sample fabrication. In conventional layered p-i-n diodes, recombination occurs near the interfaces only. In these regions the band bending is significant, by which the electric field does not depend on W.

After annealing for 15 min. at 240°C, the dependence of the I, V-characteristics on W has almost disappeared, implying that the recombination occurs near the p-i interface. During the anneal treatment, the density of states equilibrates in the intrinsic region and a situation similar to conventional layered p-i-n diodes is obtained. The obtained results are supported by numerical simulations.

A10.4 MODEL FOR STAEBLER-WRONSKI DEGRADATION DEDUCED FROM LONG-TERM, CONTROLLED LIGHT-SOAKING EXPERIMENTS. Bolko von Roedern, Joseph A. del Cueto, National Renewable Energy Laboratory, Golden, CO.

We carried out controlled light-soaking experiments simulating outdoor operating-temperature conditions (about 5 to 60°C device temperature) of amorphous silicon (a-Si) photovoltaic (PV) modules. After consecutive degradation cycles, the stabilized performance declined as the modules were exposed to light at lower and lower temperatures. Depending on the conditions used and the prior exposure history, this additional degradation may be almost completely recoverable, partially recoverable, or almost non-recoverable - there is at least as much additional degradation with 0.5-sun intensity and 5°C conditions, as previously observed for 1-sun intensity and 25°C exposure. Afterwards, little to no recovery occurred when the modules were returned to 1-sun intensity and 25°C conditions. Earlier, we had observed that modules stabilized under 1-sun, $50\,^{\circ}\mathrm{C}$ indoor-exposure conditions degraded an additional 15%when exposed outdoors, which was not recovered by returning to the previous indoor conditions at 50°C. We suggest that the PV parameters are much more sensitive than film properties (e.g., photoconductivity) to changes in light-soak exposure temperature (in the 5 to 60°C range) or to prior exposure history. However, history-dependent (hysteresis) effects and more easily recoverable photoconductivity degradation mechanisms are well documented after light-soaking at very low temperature [1], suggesting that degradation and stabilization is not caused by a single degradation and recovery (annealing) mechanism. We will quantitatively analyze how multiple degradation mechanisms with different time constants and annealing activation energies lead to a given stabilization level depending on the operating condition and history. This information is helpful to predict at which level a module will stabilize for a given exposure history, and how much recovery can be expected with increases in module operating temperature. This will allow to better predict how a-Si PV modules will perform in different climatic environments. [1] P. Stradins, M.Q. Tran, and H. Fritzsche, J. Non-Cryst. Solids 164-166 (1993) 175.

> SESSION A11: POSTER SESSION: RARE EARTH LUMINESCENCE Chair: Daxing Han Tuesday Evening, April 25, 2000 8:00 PM Salon 1-7 (Marriott)

UPS of a-Si:H<Er>: WHAT IS THE ENERGY OF THE Er 4f STATES? <u>Leandro R. Tessler</u>, Cinthia Piamonteze, Ana Carola Iniguez, Abner de Siervo, Richard Landers, IFGW, UNICAMP, Campinas, BRAZIL; Jonder Morais, LNLS, Campinas, BRAZIL.

Erbium in its trivalent state emits characteristic intra-4f level photo and electroluminescence at $1.54\mu\mathrm{m}$ when in silicon hosts. This wavelength is very important because it corresponds to the window of

minimum transmission loss in which conventional silica based optical fibers. One very important problem concerning erbium doped silicon is the electronic structure of the ${\rm Er}^{3+}$ impurities. In particular, it is still not clear if the 4f levels can be treated as frozen core levels or their overlap with s and p states of their neighbors must be considered explicitly. For crystalline Si, the 4f levels have been supposed anywhere between 20 eV below the valence band and within the energy gap. In this paper we report on the first ultraviolet photoemission spectroscopy (UPS) measurements on Er-doped a-Si:H. Samples of a-Si:H<Er> with different Er contents (up to 1 at. % [Er]/[Si]) were prepared by co-sputtering from a Si target partially covered with metallic Er platelets. UPS measurements took place at the Brazilian National Synchrotron Light source (LNLS). The samples were sputter cleaned until the Si 2p line at 102 eV, characteristic of silicon oxide, became undetectable. In order to enhance the Er states relative to the Si states, the excitation energy was 140 eV. At this energy the cross section of the Er 4f and 5p states is more than an order of magnitude higher than the cross section of the Si 3s or 3p states. As the Er concentration increases, a shoulder and then a peak appears at $9.9\pm0.5~\rm eV$ binding energy. This peak is well correlated with the Er $5p_{3/2}$ and $5p_{5/2}$ levels at 24 and 31 eV binding energy respectively. We attribute the peak at $9.9\pm0.5~\rm eV$ binding energy to the Er 4f level. These are the only occupied states which can be related to the presence of Er and can probably be treated as frozen core levels.

A11.2

Er ENVIRONMENT IN a-Si:H<Er> PREPARED BY PECVD. Cinthia Piamonteze, Leandro R. Tessler, IFGW, UNICAMP Campinas, BRAZIL; Helio Tolentino, Maria do Carmo M. Alves, LNLS, Campinas, BRAZIL; Gerhard Weiser, Marburg University, Marburg, GERMANY; E. Terukov, Ioffe Institute, St. Petersburg, RUSSIA.

Er-doped a-Si:H is a material with potential applications in photonics due to the intra-4f level transition of ${\rm Er^{3}}^+$ at $1.54\mu{\rm m}$. This transition is electric dipole forbidden in the free ion and requires a non-centrosymmetric environment to be partially permitted. It is well known that in sputtered a-Si:H, Er³⁺ is surrounded by an oxygen first coordination shell. To obtain material with better electronic properties and high luminescence efficiency, we have prepared Er-doped a-Si:H by PECVD using Er(TMHD)3 as a metallorganic Er precursor. In this molecule, Er is surrounded by a very distorted oxygen octahedron, which is expected to induce dipole moments by large electric field gradients. Such a-Si:H<Er> samples show indeed intense $1.54\mu\mathrm{m}$ photoluminescence in addition to intrinsic luminescence which is absent in sputtered samples. In this work we present the results of a study of the chemical environment of Er in Er(TMHD)₃ and in the PECVD a-Si:H<Er> samples. Extended X-ray Absorption Fine Structure (EXAFS) measurements at the Er L_{III} edge were undertaken in powder $Er(TMHD)_3$ and a thin film of PECVD a-Si:H<Er>, and compared to an Er₂O₃ reference. We observed that: 1) In Er(TMHD)₃ Er is coordinated to oxygen atoms, as expected. We find an average coordination $N=6.5\pm1$, with negative Debye-Waller σ^2 factor and average interatomic distance $r=2.23\pm0.01$ Å, compared with 2.26Å in the $\mathrm{Er_2O_3}$ reference. The negative σ^2 is probably due to the occurrence of different Er sites in Er₂O₃. 2) In the as-deposited a-Si:H<Er> sample Er is also coordinated to oxygen with average coordination $N=7.2\pm1$ and interatomic separation $r=2.27\pm0.01 \mathring{A}$ and $\sigma^2=0.009\pm0.001 \mathring{A}^2$ indicating a disordered Er₂O₃-like Er environment. Annealing at 400°C in vacuum leaves the Er neighborhood essentially undisturbed within experimental error: $N=5.7\pm1$, $r=2.28\pm0.01 \mathring{A}$ and $\sigma^2=0.008\pm0.001 \mathring{A}^2$. For annealing temperatures above 600°C, $r=0.008\pm0.001 \mathring{A}^2$. and σ^2 decrease. The coordination is always 6 within experimental error. The results indicate that the Er environment of Er(TMHD)3 becomes Er₂O₃-like during the deposition. Annealing at moderate temperatures does not affect the Er environment. Higher annealing temperatures relax the disorder around the Er atoms, and decrease the size of the oxygen cages that surrounds them. We conclude that the Er environment in PECVD a-Si:H<Er> is very similar to that of $\mathrm{Er_2O_3}$. The as-deposited first coordination shell has a relatively low free energy and evolves very little upon annealing. The high luminescence efficiency is probably due to a better host quality (lower density of states in the gap) compared to sputtered a-Si:H<Er> rather than the incorporation of Er in more distorted lattice sites due to the metallorganic precursor.

A11.3

ON MICROSCOPIC NATURE OF THE ENHANCEMENT AND STRONG SHARPENING OF THE Er^{3+} CHARACTERISTIC EMISSION AT 1.54μm IN MIXED AMORPHOUS AND NANOCRYSTALLINE Si:H:O FILMS. S.B.Aldabergenova, M. Albrecht, G. Frank, H.P. Strunk, Inst für Werkstoffwissenschaften, Univ Erlangen-Nürnberg, GERMANY; J. Viner, I. Ermakov, P.C. Taylor, Univ of Utah, Salt Lake City, UT; V.G. Golubev, A.A. Andreev, A.F. Ioffe Physical-Technical Inst, RUSSIA.

We report on the very strong $\mathrm{Er^{3+}}$ luminescence at $1.54\mu\mathrm{m}$ and in the visible region at room temperature in essentially amorphous Si:H:O films and their dependencies on annealing treatments. The films are prepared by (DC+HF) magnetron sputttering of Si targets with additional pellets of metallic Er. As grown sample is characterized in structure and luminescence properties, and then is subjected to a careful cumulative anneal programme. After each anneal step the samples are cooled down to room and characterized for the luminescence at 77 K and 300 K and then subjected to a subsequent anneal at a temperature 50°C higher than before. The optimal annealing temperature was 350°C, at which the highest luminescence intensities at $1.54\mu m$ and $0.7-1.0\mu m$ region are obtained. The structure of the films, as revealed by high resolution transmission electron microscopy, remain remarkably stable during annealing, and consists in small Si crystallites (about 2-4nm in diameter) embedded in an amorphous matrix, identified as a-Si by Raman scattering. Already prepared, the films exhibit pronounced luminescence at $1.54\mu\mathrm{m}$ at room temperature. Annealing enhances the PL intensity by 100 at $1.54\mu\mathrm{m}$ and 20 times in the range $0.7\text{-}1.0\mu\mathrm{m}$. Moreover, annealing temperatures beyond $153^{\circ}\mathrm{C}$ cause very marked Stark splitting of the 1.54 \mu m peak at 77K. Above 250-300°C anneal, however, the structure of this characteristic peak smears and practically it is difficult to resolve the fine picture. After 350°C anneal the PL peak at $1.54\mu\mathrm{m}$ is highly broadened and substantially increased in intensity. Since the structure on the nm scale (HRTEM) and local atomic order (Raman) do not change with temperature we shall interpret these prominent changes of the PL spectra with changes brought about in the atomic vicinity of the Er3+ ions during hydrogen outdiffusion.

A11.4

PHOTOLUMINESCENCE OF Eu³⁺ IN Si/SiO₂ NANO-STRUCTURE FILMS. <u>Huimin Liu</u>, Aziz Mahfoud, G. Nery*, Luis F. Fonseca*, Zvi S. Weisz*, O. Resto*, Department of Physics, University of Puerto Rico, Mayaguez, PR. *Department of Physics, University of Puerto Rico, Rio Piedras, PR.

Eu³⁺-doped Si/SiO2₂ nanocomposites were successfully prepared by electrochemical etching of c-Si surfaces. The optical properties were studied using time-resolved laser spectroscopy. Excited by intense picosecond laser pulses with the energy greater than 1GW/cm2 and wavelength at 532nm the observed photoluminescence consists of a rapidly decaying component with the life time of ~1 microsecond and a slowly component with the life time of ~ 2 ms. The former was recognized as coming from Si/SiO2 nanostructures matrix while the latter as coming from the impurity Eu³⁺ ions. With the intense laser excitation a two-photon absorption by silicon matrix occurred, resulting in charge carriers produced in conduction band. A direct recombination gives a weak but fast emission from Si/SiO₂ nanostructure host, creating a large number of nonequilibrium phonon. For ${\rm Eu}^{3+}$ emission a set of $^5{\rm D}_0$ - $^7{\rm F}$ multiplet transitions were identified. In addition to the direct excitation by $532\mathrm{nm}$ the excited state $^5\mathrm{D}_0$ of Eu^3+ ions was also found to be populated by excitation transfer from silicon matrix. The mechanism of phonon-assisted excitation transfer is discussed.

> SESSION A12: POSTER SESSION: AMORPHOUS SILICON DETECTORS AND OTHER DEVICES Chairs: Manuela Vieira and Reinhard Schwarz Tuesday Evening, April 25, 2000 8:00 PM Salon 1-7 (Marriott)

CORRELATION BETWEEN SURFACE/INTERFACE STATES AND THE PERFORMANCES OF MIS STRUCTURES. Hugo Aguas, Elvira Fortunato, Isabel Ferreira, Franco Giuliani, Rodrigo Martins, Materials Science Department, CENIMAT, Faculty of Sciences and Technology, New University of Lisbon, Quinta da Torre, Caparica, PORTUGAL.

Recently hydrogenated amorphous silicon (a-Si:H) has been used in a wide variety of technological applications such as solar cells, image sensors, position sensors and thin film transistors. In all of these applications surface and interface states play an important role in determining the final performances of the devices. In the particular case of a metal-insulator-semiconductor (MIS) structure the incorporation of a thin oxide layer can drastically modify the electrical properties of such interfaces.

In order to understand the kinetics of formation of interface/surface states and its correlation on the final device performances, a detailed study was performed on MIS structures, before and after surface

oxidation, using different oxidation techniques and oxides: thermal (in air), chemical (in hydrogen peroxide) and physical (by SiO2 sputtering).

The devices used in this work are based on a glass/Cr/a-SiH(n⁺)/ a-Si:H(i)/SiO₂/Pd structures, where the amorphous silicon was deposited by a conventional plasma enhanced chemical vapour deposition (PECVD) system. The electrical properties of the a-Si:H MIS structures were investigated by measuring their diode current-voltage characteristics as a function of temperature and the way how oxygen was incorporated by means of infra-red spectroscopy. The surface/interface states will be correlated through an ellipsometric analysis (using a spectroscopic ellipsometer) of the variation of the optical constants, before and after oxidation.

 $\frac{\text{A12.2}}{\text{ITO/a-SiN}_X/\text{a-Si:H PHOTODIODE WITH ENHANCED}}$ PHOTOSENSITIVITY AND REDUCED LEAKAGE CURRENT USING POLYCRYSTALLINE ITO DEPOSITED AT ROOM TEMPERATURE. Q. Ma, S. Tao and A. Nathan, University of Waterloo, Dept of Electrical and Computer Eng, Waterloo, Ontario, CANADÁ

We report a MIS photodiode structure using indium tin oxide/silicon nitride/hydrogenated amorphous silicon (ITO/a-SiN_x/a-Si:H) based on room temperature deposition of optically transparent polycrystalline ITO for applications in large area optical and X-ray imaging. The photodiode exhibits device characteristics with dramatically enhanced photosensitivity and reduced leakage current giving rise to a hundred-fold improvement in dynamic range. This notable improvement in performance stems from reduced oxygen and indium diffusion from the ITO into the a-Si:H layer (thanks to the low deposition temperature of the ITO), and the increased barrier height and reduced surface recombination at the ITO/a-Si:H interface due to presence of the a- SiN_x layer. As a result, the leakage current stemming from both thermionic emission and tunneling is reduced. In this work, the deposition gas ratio of $\mathrm{NH_3/SiH_4}$ for the barrier layer was chosen to be 20 to yield a N-rich film, characterized by a low defect density and high band gap energy. When the thickness of a-SiN $_x$ is increased from 0 to 200 Å, the leakage current decreases by a factor of 5 from 60 pA to 12 pA for a $300\times300~\mu\mathrm{m}^2$ detector with $0.5\mu\mathrm{m}$ thickness a-Si:H. Correspondingly, the photosensitivity is increased by a factor of 50 and the dynamic range (I_{photo}/I_{dark}) from 10 to 1000.

NON LINEAR OPTICAL GAIN IN BULK BARRIER AMORPHOUS SILICON PHOTOTRANSISTOR. D. Caputo, G. de Cesare, A. Nascetti and F. Palma, Dept. of Electronic Engineering, University of Rome 'La Sapienza', Rome, ITALY.

In this work we present a study of the dependence of the optical gain of the bulk barrier amorphous silicon phototransistor with the incident light intensity. Phototransistors provide an output signal current which is greater than the photogenerated current making them suitable for low intensity radiation detection. Conventional devices do not have a wide dynamic range of operation, showing saturation of the output signal under bright illumination. Our work is focused on the possibility to manufacture an imager with a wide dynamic range based on the amorphous silicon n-i-δp-i-n bulk barrier phototransistor. Operation of this two terminal device relies on the modulation of the potential barrier existing in correspondence of the low doped p-type base. Under illumination, carriers photogenerated in the thick intrinsic layer (primary photocurrent) induce a reduction of the potential barrier leading to an increase of the total current (secondary photocurrent) giving rise to the amplification mechanism of this device. Simulations, performed using an analytical model which describes the behavior of the amorphous silicon phototransistor both in dark conditions and under illumination, show that the optical gain decreases with increasing light intensity. The self-adaptive-gain feature allows to emphasize low intensity signal and to properly detect high intensity signals. Experiments have been performed on samples prepared by glow discharge with 75Angstrom thick δ p layer and B_2H_6/SiH_4 equal to $5\cdot 10^{-4}$. First measurements performed at 5V bias voltage under white light illumination are in agreement with model results showing a 25% reduction of optical gain for incident radiation varying of one order of magnitude.

AMORPHOUS SILICON/AMORPHOUS SILICON GERMANIUM NEAR IR PHOTODETECTOR. Yeu-Long Jiang, National Chung Hsing Univ, Dept of Electrical Engineering, Taichung, Taiwan, REPUBLIC OF CHINA; Tzong-Yih Yew, National Tsing Hua Univ, Hsin-Chu, Taiwan, REPUBLIC OF CHINA.

The a-Si:H/a-SiGe:H NIPIN photodetectors are fabricated to block visible light and detect near infrared light. The first I layer is the absorption region of the short wavelength portion and the second I layer is the absorption region of the long wavelength one. The visible light response is suppressed and the infrared light is detected when the first NIP and the second PIN diodes are under forward bias and reverse bias, respectively. The photo to dark current ratios of the device structure with the first I layer (1.42 eV and 2000 A) and the second I layer (1.42 eV and 4000 A) at the bias of -0.05V is about 500. The photo current under the reverse bias larger than 0.5 V is over 1 uA which could satisfy for the requirement of circuit design. The peak response of the device was 790 nm. It could be used for the near infrared light detection

COLOUR CHARACTERISATION OF a-Si:H-BASED THREE-TERMINAL THREE-COLOUR DETECTORS. Janez Krc, Marko Topic, Franc Smole, Faculty of Electrical Engineering, University of Ljubljana, SLOVENIA.

Hydrogenated amorphous silicon (a-Si:H) based colour detectors and arrays may in future have a potential to compete with standard CFA (Colour Filter Arrays) in some areas of colour recognition. Their multi-terminal structure of vertically stacked PIN photodiodes with appropriate spectral responses - determined by optical gaps and layer thicknesses - enables filter-free colour detection omitting Moire effect, which is found to be a relevant drawback of CFAs. The a-Si:H-based detector's spectral responses for three fundamental colour spectra -Red, Green and Blue (RGB) - can be quite well matched with three characteristic responses of standard human eye, but to achieve an exact colour recognition and qualification, a specific transformation from the detector to standard colour space is required. Therefore, we performed colour characterisation of three-terminal three-colour detectors in superstrate glass/TCO/P-I-N-I-P/TCO/P-I-N/Al assembly with either smooth or rough TCO layer. The transformation from the detector space to standard colour space was defined with polynomial functions of different order, using Munsell (64 chips) and Dupont (120 chips) test colour sets. The metameric errors for the detectors with smooth and rough TCO layer, obtained with both test sets will be presented and their deviations discussed. The trade-off between polynomial order and errors will be estimated. Furthermore, the errors will be compared with standard CFAs and other multiterminal devices. Finally, an optimisation criteria - based on minimal metameric errors - for three fundamental spectral responses of detectors will be discussed.

A12.6

TEMPERATURE INDUCED STRESS EFFECTS ON A FLEXIBLE POSITION SENSOR. F. Giuliani, E. Fortunato, I. Ferreira, R. Martins, Material Science Department, CENIMAT, Faculty of Science and Technology of the New University of Lisbon, Caparica, PORTUGAL.

We have developed a working large area flexible a-Si:H position sensor¹ for angular position detection. The effects of mechanical stress due to the different thermal expansion coefficient of the substrate and the sensor itself have been studied. In fact, the chosen flexible substrate (Kapton - polyamide foil) has a thermal expansivity 4 times greater than corning glass and about 7 times greater than a-Si:H. So, when the sensor is extracted from the deposition chamber, it cools down to ambient temperature and becomes strained. If the sample is heated up again, its mechanical stress is released. Photothermal Deflection Spectroscopy and Constant Photocurrent Method (when applicable) have been emploied to estimate the variation in the density of states (DOS) inside the gap of both the single layers and the whole structure.

¹E. Fortunato, I. Ferreira, F. Giuliani, R. Martins, J. Non-Cryst. Solids, in press

LARGE AREA FLEXIBLE THIN FILM POSITION SENSITIVE DETECTORS. Elvira Fortunato, Isabel Ferreira, Franco Giuliani, Rodrigo Martins, Materials Science Department, CENIMAT, Faculty of Sciences and Technology, New University of Lisbon, Caparica, PORTUGAL.

In this paper we present the electro-optical performances of one dimensional (1D) a-Si:H thin film position detector deposited on polymeric substrates (Kapton - polyamide foil) with 2 cm long and 0.5 cm wide. It is also demonstrate that when improved interfaces are produced the back metal contact does not need to cover the entire back area of the sensor to produce the required reference equipotential. The technical and theoretical concepts of large area thin film position sensitive detectors based on the amorphous silicon technology was introduced some years ago [i, ii, iii] where most of the research done was concentrated in the development of devices deposited on rigid substrates, such as glass. Nevertheless, in applications where the device is mounted on a rotating axis of a motor or determination of the angular position of the rotor of a motor is required, it should be of great importance to have a curved sensor with a cylindrical shape. To do so, it is important to have the sensing

element deposited on a flexible substrate with the required position accuracy and reliability, besides having a high enough response frequency.

[i] E. Fortunato, M. Vieira, L. Ferreira, C.N. Carvalho, G. Lavareda, R. Martins, Mat. Res, Symp. Proc. 1993, Vol. 297, p. 981-986 [ii] E. Fortunato, M. Vieira, L. Ferreira, G. Lavareda, R. Martins, J. Non-Cryst. Solids 1993, 164 & 165, 797-800. [iii] E. Fortunato, G. Lavarenda, M. Vieira, R. Matins, Rev. Sci. Instrum. 1994, 65, 3784-3786.

EFFECTS OF BURIED INSULATOR-SENSOR INTERFACE ON THE LATERAL CONDUCTION OF HIGH FILL FACTOR a-Si:H IMAGERS. M. Mulato, F. Lemmi, S.E. Ready, J.P. Lu, R.A. Street J. Ho, R. Lau and J.B. Boyce, Xerox Palo Alto Research Center, Palo

The new high fill factor design for two-dimensional amorphous silicon (a-Si:H) imager arrays is an intrinsic requirement for the achievement of higher sensitivity and resolution for X-ray medical applications, like mammography and also CMOS sensors. The increased performance is achieved by depositing a continuous intrinsic amorphous silicon layer over the surface of the imager, but it is important to minimize lateral image spreading. A buried dielectric is used to insulate the TFT addressing electronics from the sensors. This introduces a parasitic capacitance, which can be reduced by using a thick insulator with a low dielectric constant. We have explored thick dielectric layers and compared the lateral conduction at the interface with a-Si:H with the present silicon-oxynitride (SiON) layers. Arrays with pixel size of $75\mu \text{m}$ were used, as well as separate test structures. Polymer-based resins (PBR) allow thickness up to $\sim 5\mu m$, and epoxy-based photoresists allow thickness of $\sim 50\mu m$. Experimentally, in the case of PBR, image blooming - as determined from line spread function measurements - starts at low illumination intensities, and increases as a function of illumination. In the case of SiON, this blooming is significant only near pixel saturation, being one order of magnitude lower than the PBR case. The blooming is correlated to a lateral leakage current between neighboring pixels, which takes place at the interface of the insulator material and the intrinsic a-Si:H. When PBR is capped with SiON, the arrays characteristics lie in between the previous cases. Analysis of the lateral leakage current as a function of temperature gives nearly the same activation energy of $0.3~\mathrm{eV}$ for the cases of PBR and SiON, which suggests that the conduction mechanism might be the same in both kinds of interfaces. The results are interpreted in terms of band bending at the interface.

a-SiN:H THIN FILM DIODE FOR DIGITAL RADIOGRAPHY. I.A. Popov, G. Van Doorselaer, A. Van Calster, H. De Smet, J. De Baets, ELIS-TFCG/IMEC, Univ. Ghent, Ghent, BELGIUM, F. Callens, E. Boesman, CSSS, Univ. Ghent, Ghent, BELGIUM.

Recent developments in the area of cost effective 2D direct x-ray sensor arrays on the base of a-SiN:H back-to-back Schottky diodes and no switching devices per pixel are presented. Discussion focuses on two major aspects: (i) x-ray sensitivity of the sensor itself; (ii) the overall performance of the sensor array. Comparison with the AM plus x-ray sensor approach is given.

<u>A12.10</u> PHASE TRANSITION IN Cr/a-Si:H/V THIN FILM DEVICES. <u>Jian Hu</u>, Janos Hajto, Napier Univ, School of Engineering, Edinburgh, <u>UNITED KINGDOM</u>; Tony Snell, Univ of Edinburgh, Dept of Electrical Engineering, Edinburgh, UNITED KINGDOM; Mervyn Rose, Univ of Dundee, Dept of Applied Physics and Electronics &Manufacturing Engineering, Dundee, UNITED KINGDOM.

Experimental results on the electronic properties of conditioned Cr/hydrogenated amorphous silicon (a-Si:H)/V thin film devices are presented. The devices under test were electro-formed, and had resistances in the range from several hundred ohms to several kilo-ohms. Further "conditioning was carried out at room temperature by biasing the device using either a dc voltage (< 10V) or a voltage ramp (10 $\sim 20V$, 0.5 $\sim 1V/sec$, 50 - 200 mV steps). During conditioning, the device current initially increased linearly with the bias until the voltage reached a critical value where the current fell by several orders of magnitude. After the conditioning treatment, the electrical properties of the conditioned device had changed. At low biases, the current varied non-linearly with the bias, but exhibited 'jumps' at a threshold voltage (V_{th}) (typically 2-3V), leading to a resistance change of 1-2 orders of magnitude. Above V_{th} the current increased almost linearly with bias, indicating a change in carrier transport from an insulating or semiconducting regime into a more conducting (metallic) state. This was confirmed by ac characteristics of the conditioned devices, which showed a transition from a capacitive to an inductive behaviour at V_{th} . In addition, the current-voltage characteristic of conditioned devices, measured under

constant current conditions, exhibited a distinct negative resistance region at V_{th} , suggesting that the transition at V_{th} involved the creation of conducting filament(s) in which the current density differed from that of surrounding material. It was noted that the threshold voltage for the current jumps decreased with increasing temperature and eventually disappeared at $\sim 340\,K$, but recovered on reducing temperature. We suggest that the observed transition at V_{th} could involve vanadium oxides such as VO_2 , which experiences a phase transition at 340K. It has previously been shown that during the initial forming process some of the top metal is incorporated into the amorphous silicon, presumably by a process of diffusion and/or electro-migration [1], while oxygen is also present in the ambient atmosphere, resulting in thermodynamically favourable conditions for VO_2 formation. It was also generally observed that at the transition the measured conductances G_m had values close to $2ie^2/h$, where i = 1, 2, ..., as reported previously [2]. It is possible that nano-size filament(s) are created as a result of the field-induced conditioning, in which ballistic transport of electrons could occur. References [1] J. Hajto, A.E. Owen, A.J. Snell, P.G. LeComber and M.J. Rose. Chap 14, pp 641-701 in Amorphous and Microcrystalline Semiconductor Devices, Ed: J. Kanicki, Artech House, 1992 [2] J. Hajto, A.E. Owen, S.M. Gage, A.J. Snell, P.G. LeComber, and M.J. Rose, Phys. Rev. Lett, 66, 1918 (1991)

A12.11
THE EMERGENCE OF AN AMORPHOUS-SILICON BASED PHOTONIC TECHNOLOGY OPTICAL MEMORIES TO 3-D PHOTONIC CRYSTALS. C.M. Fortmann, Tokyo Inst. Tech., Dept. Innovative and Engineered Materials, Yokohama, JAPAN; N. Hata, Electrotechnical Laboratory, Tsukuba, JAPAN.

The ability of amorphous silicon to absorb large quantities of impurities combined with its tunable optical parameters make it an ideal base for photonic device patterning. Fortmann and Jaen [1] described how the refractive index of amorphous silicon could be varied by over 50% in some cases by changing the hydrogen content and how in-situ patterning of the amorphous silicon hydrogen content can be used to define photonic devices. Photonic devices include 3-D photonic crystals with features scaled to interact with visible light. Interesting the optical band gap depends on a sub-set of the total hydrogen content which is bonded into Si-H2 sites [2]. More recently Hata et al, [3] described reversible, light induced above gap changes observed at amorphous silicon/glass interfaces. By taking advantage of this effect, for example, a write-read erasable optical memory can be proposed. The memory state (of an annealed sample) is changed by short wavelength above-bandgap illumination. Local heating to 200 C is used for erasing. The amplitude ratio and phase difference of reflected p- and s-polarized light provides the differentiation needed to define an on and an off state. These above gap optical changes were also consistent with at least some degree of structural rearrangement. The tunable and patternable amorphous silicon optical parameters together with a detectable light induced optical parameter change present a rich pallet for photonic engineering. [1] C.M. Fortmann and E.L. Jaen, Proc. Symp. in Photorefractive Fiber and Crystal Devices: Materials, Optical Properties, and Applications V, Francis T.S., Yu, Shizhuo Yin, Eds., Proc. of SPIE 3801, 24 (1999). [2] C.M. Fortmann, Phys. Rev. Lett. 81, 3683 (1998). [3] N. Hata, et al., in 18th International Conference on Amorphous and Microcrystalline Semiconductors Science and Technology (1999)

SESSION A13: POSTER SESSION: HETEROJUNCTION AND HETEROGENEOUS SOLAR CELLS

Chairs: Christopher R. Wronski and Jeffrey C. Yang Tuesday Evening, April 25, 2000 8:00 PM Salon 1-7 (Marriott)

A13.1

RECOMBINATION AND RESISTIVE LOSSES IN AMORPHOUS SILICON/CRYSTALLINE SILICON HETEROJUNCTION SOLAR CELLS. Nils Jensen, Uwe Rau, and Juergen H. Werner, Universitaet Stuttgart, Institut fuer Physikalische Elektronik, Stuttgart, GERMANY.

Production of crystalline silicon (c-Si) solar cells requires usually several high temperature processing steps. The low-temperature formation of heterojunctions between amorphous and crystalline silicon promises a cost saving alternative. In our group, cell efficiencies of 12.5% are reached using p-type single c-Si as a base material and a thin n-type hydrogenated amorphous silicon (a-Si:H) emitter. These results stem from cells that lack high efficiency features such as back surface fields and surface texturing. This contribution systematically investigates the electronic properties of a-Si:H/c-Si solar cells and explains the limitation of open circuit

voltage, short circuit current density, and fill factor. Our device analysis is based on measurements of internal quantum efficiency and temperature dependent current/voltage (I/V) measurements. On the one hand, this modeling reveals carrier recombination within the crystalline silicon base material to be responsible for the limitation of the open circuit voltage. On the other hand, the short circuit current is bound by collection losses in the base material and, in addition, by absorption in the electrically inactive a-Si:H emitter. Resistive losses affecting the fill factor originate from the transport of minority carriers across the interface. The I/V curves measured across the heterojunction reveal a characteristic S-shaped behavior. This interesting phenomenon is the result of carrier transport, which is hindered by the band offset between a-Si:H and the crystalline absorber. We propose a new analytical model which describes this anomal behavior and find a conduction band discontinuity of 500mV-550mV for p-type a-Si:H/n-type c-Si.

CARRIER TRANSPORT AND PHOTOGENERATION IN SILICON HETEROJUNCTION SOLAR CELLS WITH AMORPHOUS P/I INTERFACES. Yu Vygranenko, A. Fantoni, M. Fernandes and M. Vieira, Electronics and Communications Dept, ISEL, Lisbon, PORTUGAL; N. Carvalho, G. Lavareda, CFM, Lisbon, PORTUGAL; R. Schwarz, ISEL and IST, Lisbon, PORTUGAL.

Heterojunctions with a TCO/p+-a-Si:H/i-a-Si:H/n-c-Si/metal configuration were obtained by depositing p-type hydrogenated amorphous silicon on n-type single crystalline silicon substrate. To improve the conversion efficiency an intrinsic thin amorphous layer with different thicknesses (70 Å to 500 Å) has been inserted between the substrate and the amorphous p-type layer. Details concerning material and device characterization, structure and geometry optimization are presented and correlated. Junction properties, carrier transport and photogeneration are investigated from dark and illuminated current-voltage and capacitance-voltage characteristics. The collection efficiency is evaluated from spectral response measurements under different applied bias voltages (in the range of -1 V to 1 V). Both open circuit voltage and fill factor were improved with the increase of the intrinsic amorphous layer thickness, however, the short circuit current presents a decrease as the thickness of the undoped a-Si layer increases. For a 120 $ilde{A}$ i-a-Si:H layer a maximum in the fill factor is obtained. The insertion of the undoped i-layer improves the collection efficiency in the blue range while the interfacial region and depletion width of the substrate are active for the longest wavelengths. The heterojunctions were compared with entirely microcrystalline p-i-n-Si:H solar cells. Additionally, numerical solar cells modeling based on the band discontinuities near the interfaces and/or grain boundary complements the study and gives insight into the internal physical process. Considerations about the drift-diffusion and the generation-recombination are used to explain the correlation between the basic device output (short circuit current, open circuit voltage, fill factor, efficiency), the i-layer characteristics (structure, thickness), the incident radiation intensity and photon ènergy.

A13.3

INVESTIGATION OF CRYSTALLINE SILICON SURFACE TREATMENTS IN AMORPHOUS / CRYSTALLINE HETEROJUNCTION VIA CAPACITACE MEASUREMENTS. M Tucci, R. De Rosa, F. Roca, ENEA Research Centre, Portici, ITALY; D. Caputo, F. Palma, Department of Electronic Engineering University of Rome La Sapienza, Roma, ITALY.

In this work we investigate amorphous-crystalline silicon interface that play the key role in the heterostructure solar cell application. Our devices are based on p-doped textured wafer of < 100 > oriented crystalline silicon on which n-doped films of hydrogenated amorphous silicon are deposited by Plasma Enhanced Chemical Vapour Deposition after plasma treatment of the crystalline surface. These treatments are able to easily clean the crystalline surface but they greatly influenced the electrical properties of the device. In particular we present a systematic study on the effect of hydrogen and $\mathrm{CF_4/O_2}$ plasma dry treatment on the properties of the heterostructure. We used low temperature (20K-300K) capacitance measurement performed in different bias conditions and in a wide range of frequency of signal probe $(1 \mathrm{mHz}\text{-}1 \mathrm{MHz})$. The value of capacitance against the temperature depends on the depletion edge in the device, and, consequently, on the trapped charge activated on the time-scale of the measurements. Differences in the capacitance profile between samples with various plasma dry treatments indicate different defect density profile at interface. With the aid of a finite difference model of the capacitance as a function of temperature, bias voltage and frequency we extract information from the measurements about the defect energy distribution at interface. As a result, the density and the nature of defects at interface will be correlated to the technological parameters as: wafer cleaning procedure, hydrogen plasma treatment, type and concentration of dopants in the buffer layer.

A13.4

AMORPHOUS CRYSTALLINE SILICON HETEROJUNCTION WITH SILICON NITRIDE BUFFER LAYER. G. Claudio, R. De Rosa, F. Roca, M. Tucci, ENEA Research Center Localita, Granatello Portici, ITALY.

Hydrogenated amorphous silicon grown by plasma enhanced chemical vapour deposition is currently used for a large class of photovoltaic applications, in particular for heterojunctions with crystalline silicon. One of the problems involved with these structures is the high recombination rate at the amorphous crystalline interface that significantly degrades the characteristics of the device. The introduction of a thin buffer layer of intrinsic amorphous silicon between the doped materials reduces the recombination of carriers at the interface level, giving an appreciable improvement to the photovoltaic conversion efficiency. In this work we study the possibility to use amorphous silicon nitride, grown by plasma, as an alternative way to realise the buffer layer of a-Si/c-Si heterostructure. We experimented several growing condition for silicon nitride depending on deposition parameters obtaining samples highly transparent and with optical gap varying in the range 2.4 - 5.2 eV. We found evidence that the gap of the material is principally due to the NH₃/H₂ or N₂ ratio. The very low absorption obtainable on this material was successfully utilised to increase the short circuit current density of the device respect to the standard cell with amorphous silicon buffer, particularly in the low wavelength region as confirmed by quantum yield measurements. Dark current voltage characteristic of these devices indicates a decrease of reverse current, confirming a lower recombination rate at interface respect to standard p-n heterojunction. Also capacitance measurements are performed to evaluate the trapping kinetics at the heterojunction.

<u>A13.5</u>

MEASUREMENT OF IMPURITY PROFILES IN MICRO-CRYSTALLINE SILICON SOLAR CELLS BY SIMS. Arup Dasgupta*, Uwe Zastrow, Andreas Lambertz, Oliver Vetterl, Friedhelm Finger, Wolfhard Beyer, Institut fuer Schicht- und Ionentechnik, Forschungszentrum Juelich GmbH, GERMANY. *Permanent Address: Energy Research Unit, Indian Association for the Cultivation of Science, Calcutta, INDIA.

To investigate the influence of impurity contamination on the performance of microcrystalline silicon (µc-Si:H) solar cells prepared by PECVD we have measured the concentration profiles of B, P, Zn, Al, O and C in the active intrinsic (i) μc-Si:H layer and across the various interfaces in nip and pin structures with secondary ion mass spectrometry (SIMS). Sources of contamination in the intrinsic layer are e.g. etching and consequent re-deposition of dopant atoms during the $\mu c ext{-Si:H}$ i-layer deposition under high hydrogen dilution or migration or diffusion of impurities along grain boundaries or through the bulk material. The material was deposited on ZnO(Al) coated glass or Si wafer. The deposition temperature was 200°C. For the $TCO/\mu c$ -p/ μc -i sequences, an apparent B profile extends over several hundred nanometers into the i-layer. Oxygen and carbon concentrations follow the boron profiles. In addition, high levels of Zn and Al can be found in some cases. These B profiles are not affected by annealing at the deposition temperature for 15 h. Therefore a diffusion or migration process is ruled out. These findings are characteristic for the presence of pin holes in the material such that the SIMS probe is able to look directly to the p-layer and in some cases down to the substrate. If instead the SIMS profile is measured away from the p-layer like at μc -p/ μc -i or μc -p/c-Si interfaces, such pin hole effects can be excluded. Indeed the boron profiles at the μc -p/c-Si interface is sharp and extends only a few tenths of nanometers. But for μc -p on μc -i the B-profile still extends about 150 nm into the i-layer. Surprisingly though, it seems not to effect the solar cell efficiencies. It will be discussed in how far these B profiles are an indication for etching and re-deposition during the μc-Si:H layer deposition.

A13.6

MICROSTRUCTURES OF MICROCRYSTALLINE SILICON SOLAR CELLS PREPARED BY VERY HIGH FREQUENCY GLOW-DISCHARGE. J. Dubail, E. Vallat-Sauvain, J. Meier, S. Dubail, L. Feitknecht, U. Kroll and A. Shah, Institut de Microtechnique (IMT), Université de Neuchâtel, Neuchâtel, SWITZERLAND.

A series of undoped microcrystalline hydrogenated silicon samples was deposited on glass substrates, at various silane concentrations in the plasma phase, and studied by Transmission Electron Microscope (TEM) [1]. These TEM investigations show a great variety of microstructures resulting from the sole variation of the dilution parameter (ratio of silane flow to total gas flow of the hydrogen/silane mixture) in the deposition process. The series of samples reveal an evolution of the microstructure from small silicon nanocrystallites embedded in an amorphous matrix to long columnar grains (> 750

nm). The question raised by these observations is to what extent a certain microstructure is better than another w.r.t. the performance of the corresponding microcrystalline silicon (μ c-Si:H) device. For μ c-Si:H solar cells, where transport takes place parallel to the growth direction. It is assumed that columnar grains should be appropriate because of the reduced number of grain boundaries across the electronic transport path. As it is currently becoming clear that the film microstructure is critically substrate-dependent, the authors will address this question on actual solar cell devices fabricated at IMT Neuchâtel [2]. The goal of this study is, thus, to identify the microstructure of entirely μ c-Si:H devices and to correlate the structural results with solar cell performance. A comparison of the microstructure of entirely μ c-Si:H cells with the microstructure found on the film series deposited on glass will be presented and discussed as well. [1] E. Vallat-Sauvain et al., to be publ. in J. Non-Cryst. Solids (ICAMS 18, 1999). [2] J. Meier et al., to be publ. in Solar Energy Mat. and Solar cells (PVSEC-11).

A13.

NEAR INFRARED DETECTORS AND SOLAR CELLS BASED ON MICROCRYSTALLINE SILICON GERMANIUM. Mathias Krause, Helmut Stiebig, Reinhard Carius, Heribert Wagner, Inst. für Schichtund Ionentechnik, Forschungszentrum Jülich GmbH, Jülich, GERMANY.

A highly near infrared (NIR) sensitive pin diode is of great interest for the application either as NIR detector or bottom cell in tandem and triple stacked solar cells. Compared to microcrystalline silicon (μ c-Si:H) microcrystalline silicon germanium alloys (μ c-Si_{1-x}Ge_x:H) show an increasing absorption in the NIR region with increasing germanium content in addition to the shift of the bandgap. Thus these alloys are promising materials for the application as thin absorber layers in thin film devices. In previous investigations we used Si₂H₆ and GeH₄ as source gases which limited microcrystalline growth to alloys with a germanium content to less than 40% due to our deposition conditions. In this study $\mu \operatorname{c-Si}_{1-x} \operatorname{Ge}_x : H$ films and devices with comparable and higher germanium content were prepared by PECVD (210 $^{\circ}$ C, 95.5MHz, 200mTorr, 10W) using SiH₄ and GeH₄ diluted in hydrogen up to 480. For monosilane instead of disilane we find a shift of the transition region from amorphous to microcrystalline growth towards lower hydrogen dilution. Raman ${\it spectroscopy shows a high crystalline\ volume\ fraction,\ good\ structural}$ quality and homogeneous composition. PDS spectra exhibit the expected shift of the bandgap and an increasing sub-bandgap absorption with increasing Ge content. The sub-bandgap absorption is larger in films prepared with SiH_4 than with Si_2H_6 of similar composition which indicates a higher defect density for SiH₄. p-i-n solar cells with μ c-SiGe:H i-layers show an increasing dark current due to a decreasing bandgap and increasing defect density with increasing germanium content. This leads to a decreasing fill factor (FF) and open-circuit voltage (V $_{OC}$) of μ c-SiGe:H diodes. The strong reduction of V_{OC} and FF with increasing Ge content restricts the application of $\mu \text{c-Si}_{1-x} \text{Ge}_x$:H for pin solar cells presently to the low and medium Ge range while NIR detectors can be realized with a high Ge concentration.

A13.8

MICROCRYSTALLINE (Si,Ge) SOLAR CELLS. Vikram L. Dalal, Yong Liu, Iowa State University, Dept. of Electrical and Computer Engr., Ames, IA.

We report on the growth and fabrication of microcrystalline (Si,Ge) solar cells on stainless steel substrates. The devices were grown using remote ECR plasma deposition using H and He dilution. The device structure was ss/n+/n/p+. Graded gap buffer layers were interposed between the middle n microcrystalline layer and the two contact (n+ and p+) layers to improve performance. It was found that the performance of the device depended critically upon the design of the front (p/n) buffer layer. The devices had significant QE beyond 900 nm. Measurements of hole properties in the devices were made and will be reported.

SESSION A14: DETECTORS, SENSORS, AND MEMORIES
Chair: Hiroaki Okamoto
Wednesday Morning, April 26, 2000
Salon 7 (Marriott)

NOTE EARLY START

8:15 AM <u>A14.1</u>

HOT ELECTRON PHOTO-TRANSISTORS IN HYDROGENATED AMORPHOUS SILICON. John M. Shannon, Edmund G. Gerstner, School of Electronic Engineering, IT and Mathematics, University of Surrey, Guildford, UNITED KINGDOM.

It has been shown that useful current gains can be obtained in hot-electron device structures containing very thin a-CrSi2 layers of nanometer dimensions in hydrogenated amorphous silicon [1]. The $a ext{-Si:H}/a ext{-CrSi}_2/a ext{-Si:H}$ device structure made using PECVD and sputtering techniques naturally forms a hot-electron transistor device where the electrons are emitted across a high potential barrier on one side of the silicide and are collected over a low barrier on the other. Recent results [2] have shown that current gains can be in excess of 40 in structures having a-CrSi₂ bases ≈ 1.5 nm thick. Here we outline the relatively simple technology used to make these devices and examine their performance as photo-transistors in which the photo-current is amplified by hot-electron transistor action. Particular attention is paid to the linearity of the output with light intensity and the uniformity of transistor gain over large areas. The speed of response can be maximised by operating the photo-transistor with high electric field across the collector since it is the transit time of the photo-induced carriers that determines the response time. We show that these devices provide a useful new active element for large area amorphous silicon electronics. [1] J.M. Shannon, A. Kovsarian, and J.E. Curran, Electron. Lett. **33**, 2074 (1997). [2] E.G. Gerstner and J.M. Shannon, submitted to IEEE Electron Device Lett.

8:30 AM A14.2

IMPROVED RESOLUTION IN A P-I-N IMAGE SENSOR BY CHANGING THE STRUCTURE OF THE DOPED LAYERS. M. Vieira, J. Martins, M. Fernandes, Yu. Vygranenko, A. Márico and R. Schwarz, Electronics and Communications Dept., ISEL, Lisboa, PORTUGAL.

TCO/μc-pin-Si:H/metal structures can recognise an image contour or a light pattern projected onto the photosensitive surface if a small-signal scanning beam is used to read out the transverse photovoltage. Due to the lateral photoeffect the carriers generated inside the light pattern drift towards the internal dark regions (holes, gaps, lines) behaving like ghost images. Modifications on the gaps, mass) beliaving the ghost mages. Modifications on the transducer configuration are proposed for improving the sensitivity and the spatial resolution of the transducer. Different amorphous to microcrystalline hydrogenated silicon top layers ($10^{-4}~\Omega^{-1}~{\rm cm}^{-1}<<10^{-1}~\Omega^{-1}~{\rm cm}^{-1}$) were deposited. Both n- and p-type layers with varying doping levels were employed. Details concerning sensor characterisation and optimisation of the configuration are presented and discussed. The results show that in all configurations a good representation of the object contour is achieved. When the top layer resistivity increases the spatial resolution is improved. A 50% increase in the spatial resolution was obtained by decreasing the p-layer conductivity three orders of magnitude. A physical model for the transducer supported by an electrical circuit simulation is presented. Simulated results confirm our experimental findings. As the top layer resistivity increases the ratio between the lateral to transverse photocurrents decreases allowing a better thresholding of the transverse photovoltage. By increasing 10³ the ratio between the dynamic lateral resistance (that models the doped layer) and the transverse one (that models the active layer) a 60% increase in the spatial resolution is obtained for the same threshold level. An analysis of the image geometric distortion, restoration, and enhancement is presented. A low level image processing is performed to suppress the noise and to enhance details. Algorithms and tools are proposed for digital image analysis.

8:45 AM A14.3

a-Si:H PHOTODIODE TECHNOLOGY FOR ADVANCED CMOS ACTIVE PIXEL SENSOR IMAGERS. Jeremy A. Theil, Min Cao, Gerrit Kooi, Gary W. Ray, Wayne Greene, Jane Lin, A.J. Budrys, Uija Yoon, Shawming Ma, Hewlett-Packard Laboratories, Palo-Alto, CA

Amorphous silicon photodiode technology is a very attractive option for image array integrated circuits because it enables large die-size reduction and higher light collection efficiency than c-Si arrays. We have developed an photodiode array technology that is fully compatible with a $0.35\mu\mathrm{m}$ CMOS process to produce image sensors arrays with 10-bit dynamic range that are 30% smaller than comparable c-Si diode. The work presented here will discuss performance issues and solutions to lend itself to cost-effective high-volume manufacturing. The various methods of interconnection of the diode to the array and their advantages will be presented. The effect of doped layer thickness and concentration on quantum efficiency (as high as 70% around 560nm), and the effect of a-Si:H defect concentration on diode performance will be discussed.

9:00 AM A14.4

AMORPHOUS SILICON MICROBOLOMETER TECHNOLOGY. A.J. Syllaios, T.R. Schimert, R.W. Gooch, W.L. McCardel, B.A. Ritchey, J.H. Tregilgas, Raytheon Systems Company, Dallas, TX.

This paper will discuss the current status of amorphous silicon (a-Si) for microbolometer infrared detector arrays. Amorphous silicon is an

ideal material for detection of optical radiation from the UV-VIS to the IR spectral range. In the IR part of the spectrum a-Si thin films are used in microbolometer or thermal detector structures. Highly sensitive microbolometer arrays have been developed that take advantage of the high temperature coefficient of resistance (TCR) of a-Si and its relatively high optical absorption coefficient. TCR is an important design parameter and depends on material parameters such as doping concentration. The IR absorptance of the bolometer detectors is enhanced by using quarter wave resonant cavity structures and thin metal absorber layers. Ultra-thin (~2000 Å) SiN/a-Si/SiN membranes with low thermal mass suspended over silicon readout integrated circuits are built using RF plasma enhanced chemical vapor deposition (PECVD) and surface micromachining techniques. To ensure high thermal isolation the microbolometer arrays are vacuum packaged using wafer-level vacuum packaging. Imaging and non-imaging sensor applications of a-Si bolometer arrays will be also discussed. Imaging applications include a 120x160 a-Si bolometer pixel array IR camera operating at ambient temperature. Non-imaging applications are multi-channel detectors for gas sensing systems.

9:15 AM A14.5

NEGATIVE DIFFERENTIAL RESISTANCE CHARACTERISTICS OF SILICON NANOCRYSTAL MEMORY. Seung Jae Baik, and Koeng Su Lim, Department of Electrical Engineering, Korea Advanced Institute of Science and Technology, Taejon, KOREA.

As a new Si nanocrystal forming technology, the method of dry oxidation of μc -Si film was presented. μc -Si film was deposited by photo-CVD, which is very promising method for ultrathin film application due to its fine thickness controllability and defect-free deposition method. $\mu c ext{-Si}$ is oxidized in dry O_2 atmosphere, and then we obtained two dimensional Si nanocrystal array separated by SiO2. This is due to self-limited oxidation property of small particle. By adapting this structure to gate of MOSFET we fabricated nanocrystal memory, which has Electrically Erasable and PROgrammable Memory (EEPROM) structure with nanocrystal layer as floating gate. We observed large threshold voltage shift more than 2 V at low gate bias as low as 2V. And single electron tunneling effect is observed in charging stage. The size of each nanocrystallite is 7nm and 3 electrons are stored in each nanocrystals for 2V threshold voltage shift.In increasing gate bias sweep, negative differential resistance characteristic is observed, this can be explained by Coulomb blockade effect.

SESSION A15: SOLAR CELLS I-FROM MATERIALS TO DEVICES

Chair: Klaus Lips Wednesday Morning, April 26, 2000 Salon 7 (Marriott)

10:00 AM *A15.1 HYDROGENATED MICROCRYSTALLINE SILICON: FROM MATERIAL TO SOLAR CELLS. N. Wyrsch, L. Feitknecht, C. Droz, P. Torres, J. Meier, E. Vallat-Sauvain, A. Shah, Institut de Microtechnique, Université de Neuchätel, Neuchätel, SWITZERLAND.

Microcrystalline hydrogenated silicon (μ c-Si:H) is a very attractive material for the active layer of thin-film solar cells. Efficiencies of up to 8.5% have been demonstrated on entirely microcrystalline p-i-n cells with no sign of light-induced degradation [1]. Despite numerous studies on μ c-Si:H solar cells and on μ c-Si:H layers used as i-layers in these cells, it is yet unclear in which respect the material must be optimised to improve solar cell efficiency. Furthermore, microcrystalline material is not a unique and well defined material, but can exhibit various forms of microstructure [2]; the latter depends critically on the deposition conditions and substrate. Here, the authors will investigate material properties such as ambipolar diffusion length \mathcal{L}_{amb} (deduced from steady-state photocarrier grating), diffusion length L_D (deduced from surface photovoltage), $\mu_0 \tau_0$ products (deduced from photoconductivity and L_{amb}) and defect densities (deduced from the absolute constant photocurrent method a-CPM) measured on series of μ c-Si:H layers deposited under various plasma powers and hydrogen dilutions of silane. The transport properties and their anisotropy (seen in some samples) will be discussed in relation with the microstructure prevailing in these layers. Performance of solar cells incorporating the same layers will also be compared with layer characteristics in order to suggest path for μ c-Si:H material optimisation. [1]J. Meier et al., Proc. of the 2nd World Conf. on Photovoltaic Solar Energy Conversion, Vienna, 1998, 375. [2]E. Vallat-Sauvain et al., Proc. of the ICAMS 18.

10:30 AM A15.2

EFFECTS OF STRUCTURAL PROPERTIES OF μ c-Si:H ABSORBER LAYERS ON SOLAR CELL PERFORMANCE. Oliver Vetterl, Reinhard Carius, Lothar Houben, Andreas Lambertz, Friedhelm Finger, Heribert Wagner, Forschungszentrum Juelich GmbH, Institute of Thin Film and Ion Technology, Juelich, GERMANY

For microcrystalline silicon (µc-Si:H) absorber layers in thin film solar cells a key topic in current research is the link between material properties and the performance of corresponding solar cells. We found that, surprisingly, not the material with the highest crystalline content but the material prepared close to the transition to amorphous growth yields the best solar cell performance - in particular a high open circuit voltage $V_{\mathcal{OC}}$. This is demonstrated for a series of μ c-Si:H nip structures prepared with PECVD at 95 MHz and substrate temperatures of 200°C. The plasma power, source gas composition and absorber layer thickness were varied aiming at high deposition rates with still good solar cell performance. The highest achieved conversion efficiencies for a growth rate of 1.9 Å/s and 5.0 Å/s are 8.1 % and 6.2 %, respectively. Structural properties were investigated by Raman spectroscopy and cross section TEM measurements directly on the solar cell. Employing different laser wavelengths (418 nm - 799 nm) the probe depth of the Raman experiment was varied over a wide range ($\sim 100 \text{ nm} - \sim 3 \mu \text{m}$). For cells produced under growth conditions yielding high crystallinity the Raman spectra are independent of the incident laser wavelength, i.e. the structure does not change during growth of the absorber layer. This finding is supported by the TEM images. In contrast to this, preparation conditions near the transition to amorphous growth result in a gradual decrease of the detected amorphous phase with increasing thickness. Furthermore amorphous phase can be detected even in the surface near volume of several μ m thick solar cells. The results emphasise, that control of the material structure and, possibly, of its evolution with thickness will be required for further improvement of μc-Si:H solar cells.

 $\bf 10:45$ AM $\, \underline{A15.3}$ GROWTH OF HIGH QUALITY, LOW BANDGAP, a-(Si,Ge) MATERIALS AND DEVICES. <u>Vikram L. Dalal</u>, Zhiyang Zhou, Iowa State University, Ames, IA.

We report on the growth of high quality a-(Si,Ge):H materials and devices across the entire range of Ge concentration, from 0% to 100%. The materials and devices were grown using low pressure, reactive ECR plasma deposition. The material and device properties were measured in films, in diagnostic n-i-n devices deposited on stainless steel substrates, and in p-i-n solar cell devices, also on stainless steel substrates. All three sets of measurements indicate that high quality (low Urbach energy, good fill factors, low defect density) materials can be made if one controls the plasma carefully. In particular, it was discovered that low pressure plasmas which produced a high flux of H ions and radicals were important in making good films. By doing experiments which changed either the ion energy or the flux density impinging on the substrate, we discovered that the critical factor determining film and device quality was the radical and ion flux, not the ion energy.

11:00 AM A15.4

AMORPHOUS SILICON ALLOY SOLAR CELLS NEAR THE THRESHOLD OF AMORPHOUS TO MICROCRYSTALLINE TRANSITION. Jeffrey Yang, Kenneth Lord and Subhendu Guha, United Solar Systems Corp., Troy, MI.

A systematic study has been made of amorphous silicon (a-Si) alloy solar cell performance using various hydrogen dilution ratios (R) during the growth of the intrinsic (i) layer. We found that the open-circuit voltage (Voc) of the cells increases as R increases; it then reaches a maximum before it decreases dramatically. This sudden drop in V_{oc} is attributed to the transition of the amorphous silicon network to microcrystalline inclusion in the i layer. We have studied i-layer thicknesses ranging from 1000 to 5000 Å, typically used for solar cells, and found that the transition occurs in all thicknesses investigated. Furthermore, for R values approaching the amorphous-to-microcrystalline transition, the formation of microcrystallites as indicated by V_{oc} can occur within a very small increment (≤ 1000 Å) in the *i*-layer thickness. Based on the study, we have made a-Si alloy p i n solar cells suitable for use in the top cell of a high efficiency triple-junction structure. By selecting an appropriate R value, V_{oc} greater than 1 V can readily be achieved. In fact, we have obtained a V_{oc} value exceeding 2 V in an a-Si/a-Si doublejunction structure, which is believed to be the highest value reported to date for a two-cell configuration.

Solar cells made near the threshold not only exhibit higher initial characteristics but also better stability against light soaking. We have compared top cells made near the threshold with our previous best data, and found that both the initial and stable efficiencies are superior for the near-threshold cells. We have achieved an AM1.5initial efficiency of $\sim 12\%$ in an a-Si/a-Si double-junction device of \sim $0.25~{
m cm}^2$ active area. Light soaking experiments are underway, and we expect a record stabilized efficiency for this structure.

11:15 AM $\underline{A15.5}$ KINETICS OF LIGHT INDUCED CHANGES IN PROTO-CRYSTALLINE THIN FILM MATERIALS AND SOLAR CELLS. R. Koval, L. Jiao, X. Niu, Z. Lu, G. Ganguly¹, J. Yang², S. Guha², R.W. Collins, C.R. Wronski, Center For Thin Film Devices, The Pennsylvania State University, University Park, PA; ¹BP Solarex, Toano, VA; ²United Solar Systems Corp., Troy, MI.

Studies have been carried out on the light induced changes in a-Si:H under conditions that result in "protocrystalline" materials which are amorphous but close to the microcrystalline boundary (1). Detailed characterization of degradation kinetics was carried out on the results obtained on a-Si:H films, as well as Schottky barrier and p-i-n solar cell structures, to a degraded steady state (DSS) with illuminations from 1 to 10 suns and at temperatures from 25 to $100^{\circ}\mathrm{C}$. The effects of improved microstructure on light induced defect states in these materials are clearly indicated by the rates at which the electron mobility-lifetime products change under 1 sun illumination, being distinctly different from the $\rm t^{-0.33}$ dependence associated with materials fabricated without hydrogen dilution of silane. They are also reflected in the large differences in these light induced changes, as well as those of solar cells, at temperatures well below $100^{\circ}\mathrm{C}$. Although the DSS in films and cells is reached in the same time frame, there are significant differences in the form and the temperature dependence of the kinetics for the mobility-lifetime products and the fill factors. There are however strong similarities between the systematic changes in the corresponding DSS with temperature, recovery under illumination, and the dependence of DSS on the intensity of illumination in both films and solar cells. The significance of these results on the characterization of gap state distributions, the densities of metastable defects created by light, and methods used in evaluating the stability of solar cell materials is discussed. (1) R. Koval, et al, Appl. Phys. Lett., 75, 1553 (1999)

11:30 AM <u>A15.6</u>

PROTOCRYSTALLINE SILICON DEPOSITED AT 75°C AND 40°C FOR SOLAR CELL APPLICATION. Christian Koch, Manabu Ito, Markus B. Schubert, Juergen H. Werner, Univ of Stuttgart, Inst of Physical Electronics, Stuttgart, GERMANY.

Inexpensive flexible substrates such as PET (polyethyleneterephtalate)-foils for amorphous silicon (a-Si:H) solar cells limit the deposition temperature to $T_s < 80$ °C. Unfortunately, at such low temperatures a-Si:H by standard plasma enhanced chemical vapor deposition (PECVD) exhibits very poor electronic quality. Our contribution presents a modified PECVD process that results in device quality very low temperature silicon. A systematic investigation of the hydrogen dilution ratio $r_H = [H_2]/[SiH_4]$ at $T_s =$ 75°C and 40°C allows us to identify a process window that yields so-called protocrystalline silicon (pc-Si:H). This material at the edge of crystallinity between amorphous and nanocrystalline silicon (nc-Si:H) exhibits remarkable electronic quality. An extensive electrical (photo carrier mobility-lifetime product, dark conductivity), optical and structural (Urbach energy, crystalline volume fraction) characterization gives us detailed insight into material properties at the transition from amorphous to nanocrystalline silicon. Thermal annealing and light soaking of our a-Si:H, pc-Si:H, and nc-Si:H reveals surprisingly stable material in a narrow (but well-controlled) window of r_H . Apart from investigating films, we fabricate and characterize pin- and nip-solar cells in the regime of amorphous, protocrystalline, and nanocrystalline silicon at $T_s=75^{\circ}\mathrm{C}$ and $40^{\circ}\mathrm{C}$. Quantum efficiency measurements as well as current voltage characteristics of as-deposited, thermally annealed, and light soaked cells show strong correlations to properties of equal single layers and underline the benefit of pc-Si:H for solar cells. Modeling of the n-side and p-side illuminated structures reveals an unexpected behavior: in a certain regime of r_H , we find an effective hole drift length exceeding the electron drift length. This result is in contrast to all previous investigations on either amorphous or nanocrystalline silicon solar cells and an important step towards higher efficiencies.

> SESSION A16: STRUCTURE AND HYDROGEN Chair: Rana Biswas Wednesday Afternoon, April 26, 2000 Salon 7 (Marriott)

1:30 PM A16.1

SELF-INTERSTITIALS HAVE NEVER BEEN OBSERVED DIRECTLY IN CRYSTALLINE Si. HOW ABOUT AMORPHOUS Si? Sjoerd Roorda, Département de physique, Université de Montréal, Montréal, CANADA.

In the early days of point defect studies in electron irradiated crystalline silicon, it was surmised that the Si self-interstitial is highly mobile even at 4 K and escapes direct detection. The existence of

self-interstitials has of course been confirmed through the diffusion behaviour of a range of impurities and the direct observation of larger interstitial-type clusters resulting from the aggregation of a large number of single interstitials. Against this background, the direct observation of self-interstitials in amorphous Si would seem next to impossible. Yet just such an observation may have been made recently. Its basis is a comparison of the high-resolution radial distribution function of pure amorphous Si before and after thermal anneal and that of crystalline Si. These measurements [1] will be reviewed, and their possible interpretation in terms of self-interstitials in amorphous Si, will be discussed. [1] K. Laaziri, S. Kycia, S. Roorda, M. Chicoine, J.L. Robertson, J. Wang, and S.C. Moss, Phys. Rev. Lett. 82, 3460 (1999)

1:45 PM A16.2

SMALL-ANGLE NEUTRON SCATTERING FROM DEVICE-QUALITY a-Si:H AND a-Si:D PREPARED BY PECVD AND HWCVD. D.L. Williamson, D.W.M. Marr, Colorado School of Mines, Golden, CO; B.P. Nelson, E. Iwaniczko, National Renewable Energy Laboratory, Golden, CO; J. Yang, B. Yan, S. Guha, United Solar Systems Corp., Troy, MI.

The heterogeneity of hydrogen and deuterium on the nanometer scale has been probed by small-angle neutron scattering (SANS) from a-Si:H and a-Si:D films. Films were deposited by two techniques, plasma-enhanced chemical vapor deposition (PECVD) and hot-wire chemical vapor deposition (HWCVD) using conditions that yield high quality films and devices, as well as conditions known to yield material with somewhat inferior optoelectonic properties. The SANS measurements were done at the NIST Center for Neutron Research on beamline NG-3. Data were collected over a momentum transfer range from $q=0.05~\mathrm{nm}^{-1}$ to $3~\mathrm{nm}^{-1}$. The four samples made under conditions that yield high quality material (high hydrogen or deuterium dilution in PECVD, and high substrate temperature in HWCVD) were examined in both a light-soaked state (300 h, AM1) and an annealed state (190°C, 1 h) to look for a Staebler-Wronskieffect-induced change in structure as reported in a SANS experiment several years ago¹. No detectable difference in SANS intensity from the two states was observed in the four samples to a precision that could have readily detected the 25% change reported previously¹. We do find significant differences in the heterogeneity of the films grown by PECVD and HWCVD as well as in the samples made by each technique, but under different conditions. ¹A. Chenevas-Paule, R. Bellissent, M. Roth, and J.I. Pankove, J. Non-Cryst. Solids 77&78 (1985) 373.

 $2:00~{\rm PM}~\underline{A16.3}$ DIAMAGNETIC SUSCEPTIBILITY OF MICRON THICK a-Si:H FILMS MEASURED VIA PROTON NMR: A PROBE OF STRUCTURAL DISORDER. Jonathan Baugh, Daxing Han, Chunlei Liu, Yue Wu, University of North Carolina at Chapel Hill, Dept of Physics and Astronomy, Chapel Hill, NC; Qi Wang, NREL, Golden,

Amorphous silicon is known to exhibit a 450% enhancement of its diamagnetic susceptibility relative to the crystalline phase, and this effect is attributed to bond length and bond angle disorder in the amorphous lattice. Further, it has been predicted theoretically that the enhancement increases smoothly with increasing disorder. Therefore, diamagnetic susceptibility may provide a direct probe of the degree of intrinsic disorder in a-Si related materials. We have recently made precise measurements of the bulk magnetic susceptibility of ~ 1 micron thick, ~ 0.5 mg a-Si:H and μ c-Si:H films using the NMR frequency of the incorporated hydrogen as an effective magnetometer. Other means of measuring susceptibility (e.g. SQUID, etc.) require much larger amounts of sample so that the diamagnetic response of the sample holder can be reliably subtracted out. The resolution of this method is enhanced by using a multiple-pulse line-narrowing technique in order to average out the H-H dipolar interaction, achieving linewidths $\sim 1~\mathrm{kHz}$. $\widecheck{\mathrm{A}}$ series of HWC $\widecheck{\mathrm{VD}}$ samples with varying depostion temperature as well as standard PECVD samples have been investigated. Preliminary results will be discussed.

2:15 PM A16.4

ANISOTROPY IN HYDROGENATED SILICON THIN FILMS. John D. Webb, B.P. Nelson, A.H. Mahan, J. Theisen and L.M. Gedvilas, National Renewable Energy Laboratory, Golden, CO.

We investigated spatial and optical anisotropy in hydrogenated silicon thin films using infrared spectroscopy and other techniques. The films ranged in morphology from amorphous to micro-crystalline, as determined by Raman spectroscopy. Structural analysis of the films was carried out using scanning and transmission electron microscopy (SEM, TEM, respectively). We used polarized attenuated total reflection (ATR) measurements together with Fourier transform infrared (FTIR) spectroscopy to investigate anisotropy in the Si-H covalent bonding structure of the films, and also to detect oxide

impurity phases present at certain sites in some samples. The FTIR-ATR measurements were performed using a germanium (Ge) contact microprobe with a 100-micron sampling area, as well as by deposition on standard crystalline Si and Ge ATR substrates. The Ge contact ATR microprobe enabled interference-free measurement of the IR spectra of u-SiH and a-SiH films deposited on conductive substrates such as stainless steel and transparent conductive oxides. This measurement is difficult or impossible using transmission or reflection IR spectroscopy, and is also sensitive to the spatial distribution of potentially lifetime-limiting oxide precipitates in the

2:30 PM A16.5

SURFACE COMPOSITION DURING PLASMA DEPOSITION OF HYDROGENATED AMORPHOUS SILICON STUDIED AS A FUNCTION OF ION FLUX AND SUBSTRATE TEMPERATURE Denise C. Marra, Univ of California Santa Barbara, Dept of Chemical Engineering, Santa Barbara, CA; W.M.M. Kessels, M.C.M. van de Sanden, Eindhoven Univ of Technology, Dept of Applied Physics, Eindhoven, THE NETHERLANDS; Eray S. Aydil, Univ of California Santa Barbara, Dept of Chemical Engineering, Santa Barbara, CA.

We investigate plasma deposition of hydrogenated amorphous silicon films from SiH₄/Ar discharges using in situ multiple total internal reflection Fourier transform infrared spectroscopy (MTIR-FTIR) and spectroscopic ellipsometry (SE). By applying a technique that combines surface-sensitive, attenuated total reflection (ATR-) FTIR and a brief Ar^+ sputtering of the surface hydrides, we report on the surface hydride composition as a function of the substrate temperature. As expected, fewer higher hydrides exist on the surface at elevated deposition temperatures. Based on the IR data, we propose a set of thermally activated surface reactions in which higher hydrides decompose sequentially via reaction with dangling bonds. In our Ar-rich discharge, Ar^+ and ArH^+ are the dominant ions, therefore we manipulate the rate of dangling bond generation through ion sputtering by varying the plasma power. By monitoring the surface species as a function of ion bombardment over a range of substrate temperature, we find a synergy between thermal activation and ion flux. The effect of ion bombardment is shown to be negligible in the limits of high and low substrate temperature. Using MTIR-FTIR, we monitor the bulk hydrogen concentration and, with spectroscopic ellipsometry, the index of refraction of films grown under the various conditions. Thus, we investigate the relation between the dynamics of the surface reactions and the properties of the bulk film, with particular focus on understanding the mechanism of H incorporation into the bulk. Furthermore, hydrogen either at isolated Si-H locations in the films or at Si-Si bond center sites has been detected and is created during Ar plasma exposure of a-Si:H films as well as by application of thermal energy.

SESSION A17: THE MILLENNIUM SESSION Chair: Eric A. Schiff

Wednesday Afternoon, April 26, 2000 Salon 7 (Marriott)

3:15 PM INTRODUCTION TO THE HONORED MILLENNIUM SESSION SPEAKERS. E.A. Schiff

3:30 PM <u>A17.1</u>

EARLY RESEARCH ON AMORPHOUS SILICON: ERRORS AND MISSED OPPORTUNITIES. <u>Hellmut Fritzsche</u>, Energy Conversion Devices, Inc., Troy, MI.

It is instructive to reflect on the past research of an entirely new material, such as hydrogenated amorphous silicon, in order to analyze which impediments lay in the way of reaching our present understanding. What in retrospect appears to be clear and important evidence was often not recognized as such and, therefore, was not incorporated into a coherent picture for a surprisingly long time. One reason for the inability to see and understand is one's mode of thinking, which is conditioned by training and prior experience. Other impediments to progress are some persuasive, but erroneous, views of respected members of the scientific community. A third factor that tends to slow progress is a false sense of competition which, for example, prevents research laboratories from a fruitful exchange of materials and samples. It appears that human faults run neck to neck with nature's intricacies in slowing the pace of our understanding.

3:45 PM A17.2

40 YEARS TRAJECTORY OF AMORPHOUS SEMICONDUCTOR RESEARCH. Yoshihiro Hamakawa, Faculty of Science and Engineering, Ritsumeikan University, Kusatsu, JAPAN.

A review is given on a research trajectory of amorphous and microcrystalline semiconductors and their device applications proceeded in Osaka University and Ritsumeikan University since 1970. In the last half period of 1960s, I had conducted the research on band structure characterization of various semiconductors by the modulation spectroscopy, and also been interested in an electronic activity of lattice defects in semiconductors. A strong motivation to start amorphous semiconductor research was to produce a new kind of synthetic semiconductors having continuous energy gap controllability with valency electron controllability in both chalcogenide and tetrahedrally bonded semiconductors.

The first material we have challenged is Si-As-Te chalcogenide semiconductor which has a very wide vitreous region in Gibb's Triangle. A series of systematic experiments has been carried out in the terrestrial environment since 1971, and also within the TT-500A Rocket experiment in 1980. On the basis of these data, the Spacelab J experiments have been accomplished in the FMPT (First Material Processing Test) project in 1992. In the presentation, some basic technical data on electrical, optical and optoelectronic properties, energy gap and also valency electron controllabilities are demonstrated and discussed.

The second material is hydrogenated amorphous silicon (a-Si:H) and its alloys started in 1976 just after the Garmisch Partenkirchen ICALS-6 where the first report on the valency electron controllability with hydrogen passivation by Prof. Spear's Dundee group. Then, 4.5% efficiency was achieved with p-i-n heteroface junction solar cells in 1978, which triggered high efficiency competition in the a-Si basis solar cells. Our continuous effort to improve the efficiency beared the tandem type solar cells in 1979, and also new products of a-SiC:H and a-SiGe:H in the early period of 1980s. These innovative device structure and materials have been bloomed in the middle of 1980s in R & D phase such as a-SiC/a-Si heterojunction solar cells, a-Si/a-SiGe and also a-Si/poly-Si tandem type solar cells, and industrialized in recent few years. New kind of trials on full-color thin film light emitting devices has also been recently iniciated with wide range of band gap controllability of a-SiC:H.

The third material is microcrystalline silicon (μc -Si) and their alloys, which we have reported firstly in 1984. This class of materials has been utilized mostly as a buffer layer for wide-gap window heterojunction electrodes in the period of 1980s, and also wide-area TFTs for Liquid Crystal Display devices in the recent few years. Quite recently, a tremendous R & D effort has been payed on this material as the bottom cell of the a-Si/ μ c-Si tandem solar cells aimed for the all-round plasma CVD process for the next age thin film photovoltaic devices.

In the final part of presentation, a brief discussion will be given on a technological evolution from "bulk crystalline age" to "multilayered thin film age" in the semiconductor optoelectronics toward 21 century.

4:00 PM A17.3

AN EUROPEAN ADVENTURE IN AMORPHOUS MATERIALS: FROM PAST TO FUTURE. Ionel Solomon, Ecole Polytechnique, Laboratoire PMC, Palaiseau, FRANCE.

The early work on amorphous silicon in Europe was dominated by the activity of the Dundee group, who demonstrated the feasibility of substitutional doping, which was quite a surprise at the time [1]. The publication of the famous curve, showing a variation of resistivity of more than 10 orders of magnitude with small amounts of phosphorus or boron, marked the beginning of a new era in the industry of semiconductors. The role of hydrogen in this new "good" disordered semiconductor, a-Si:H, was not immediately accepted, and the controversy was finally settled by the crucial experiment of post-hydrogenation by D. Kaplan [2]. It is little known that this process of post-hydrogenation, currently used for the improvement of devices, was covered by a patent, which turned out to be quite inapplicable! The high hopes raised by this "new" material, in particular for photovoltaic applications, rendered the field highly competitive. It produced a "pollution by the applications" effect which resulted in some surprising neglect of the basic principles of physics. A striking example is the sweeping under the rug of the effect of band bending at the surface of intrinsic a-Si:H. This effect makes the surface much more conducting than the bulk, rendering a large number of published transport measurements in planar geometry completely meaningless. Research in Europe has been less application-oriented than in USA and Japan. For example, spin-dependent effects in a-Si:H have been extensively studied in France (Ecole polytechnique) and Germany (Marburg): so far no commercial application has been found (yet?). On a small scale, Europe was not completely absent from industrial application to photovoltaics: a spinoff adventure "a la French" will be described. The problem of disordered materials is one of the timely solid-state topics, to become a major subject of material research in the near future. In that respect, amorphous silicon is an exemplary system, and the hydrogen glass picture, pioneered by R.A. Street et al., is an open field of research for the improving of disordered semiconductors. [1] W. E. Spear and P. G. LeComber, Sol. State Comm. Vol 17, 1193 (1975) [2] D. Kaplan, P. A. Thomas, N. Sol and G. Velasco, Appl. Phys. Letters Vol 33, 440 (1978). French patent #17245, June 1977.

4:15 PM PANEL DISCUSSION Moderator: E.A. Schiff

Panel:

H. Fritzsche - Energy Conversion Devices, Inc., Troy, MI Y. Hamakawa - Ritsumeikan University, Kusatsu, JAPAN I. Solomon - Ecole Polytechnique, Laboratoire PMC, Palaiseau, FRANCE.

> SESSION A18: SOLAR CELLS II-CHARACTERIZATION Chair: Subhendu Guha Thursday Morning, April 27, 2000 Salon 7 (Marriott)

NOTE EARLY START

CELL MATERIALS AND DEVICES. R. Carius, J. Klomfass, ISI-PV, Forschungszentrum Juelich GmbH, Juelich, GERMANY.

Thin film silicon solar cells consist of a stack of layers of various materials and thickness. In an amorphous (and/or microcrystalline) silicon thin film solar cell for example, this layers include up to three p-i-n diodes, protective coatings, transparent conductive oxide (TCO) layers and a highly reflecting back contact. The thickness of these layers range from a few nm for the doped layers to about 1 μ m for the textured TCO. Several types of optical spectroscopy are used to provide the data to optimize optical matching and the absorption of the different layers on one hand and information on their structural and electronic properties on the other. Particularly in the spectral range of the fundamental absorption and the absorption tail of the <i>-layers the other layers have to be optimized for low absorption. The application of efficient light trapping schemes for highest solar cell performance means multiple passing of the light wave through the films and therefore requires absorption and reflection measurements which are often far beyond the sensitivity limits of conventional absorption and reflection measurements. It will be shown that by photothermal deflection spectroscopy (PDS) all layers of a thin film solar cell can be characterized giving valuable information for optimization. This includes the determination of defect densities, the identification of thin defect-rich layers in a layer stack, evaluation of absorption losses in scattering media and light trapping structures, as well as reflection losses of high reflecting back contacts. It will also be demonstrated how PDS can be applied to determine all optical and thermal losses of thin film silicon solar cells under operation by a single experiment. Finally, the application of Raman spectroscopy and $\,$ photoluminescence to get information on structural properties such as amorphous and crystalline volume fraction of the films will be briefly discussed.

8:45 AM *A18.2

SPIN-DEPENDENT PROCESSES IN THIN-FILM SILICON SOLAR CELLS. K. Lips, R. Müller, P. Kanschat, W. Fuhs, Hahn-Meitner-Institut, Abt. Silizium-Photovoltaik, Berlin, GERMANY; F. Finger, Institut für Schicht und Ionentechnik, Forschungszentrum Jülich, GERMANY.

Electron spin resonance (ESR) is a unique tool for the identification of the microscopic nature of localized states in semiconductors. Such states are known to largely influence the electronic properties of devices like solar cells. Unfortunately, common device characterization methods like I-V or capacitance measurements only yield macroscopic information and their interpretation has to rely on assumptions of the fundamental transitions which involve such localized states. These limitations can be partly overcome if one combines current measurements with ESR to a technique referred to as electrically detected magnetic resonance (EDMR). EDMR allows to identify the microscopic nature of transport and recombination paths. Since the sensitivity of EDMR is not limited by the absolute number of paramagnetic centers like in the case of ESR, this method can successfully be applied to thin-film devices under operating conditions. In this report we will review the EDMR technique and discuss in detail spin-dependent processes observed in a variety of different types of thin-film silicon solar cells prepared by PECVD and ECR-CVD. The cells under study range from a-Si:H pin and Schottky barrier diodes, microcrystalline silicon (µc-Si:H) pin diodes to solar cells using Si wafers with a-Si:H and epitaxially grown thin film emitters. Within these structures a variety of fundamental transitions can be identified in the dark and photocurrent. These include surface recombination through P_{b0} centers in c-Si devices, recombination through neutral dangling bonds in the bulk of a-Si:H and μc -Si pin diodes or hopping transport in 30 nm thin a-Si:H emitter layers Limitations of the EDMR technique will be critically discussed.

 $9{:}15~\text{AM}~\underline{*A18.3}$ OPEN-CIRCUIT VOLTAGE PHYSICS OF AMORPHOUS SILICON BASED SOLAR CELLS. L. Jiang, J.H. Lyou, <u>E.A. Schiff</u>, Q. Wang, Dept. of Physics, Syracuse University, Syracuse, NY.

The open-circuit voltage $V_{O\,C}$ in amorphous silicon based pin solar cells behaves relatively simply compared to most device parameters. $V_{O\,C}$ varies little with the thickness and the density of deep levels in the undoped absorber layer, and varies essentially one-to-one with changes in absorber layer bandgap. It is crucial to further improvements in V_{OC} and in solar cell efficiency to establish whether V_{OC} in optimized cells is determined solely by absorber layer properties, or is reduced by effects at the pi or ni interfaces. The simplicity of the behavior of V_{OC} suggests that it is determined by equally simple physics. In this paper we summarize V_{OC} measure ments for cells from several laboratories. We present experimental estimates, mainly from electroabsorption, of the built-in potential V_{BI} for a number of amorphous-silicon based solar cells. Typical V_{BI} estimates 1.0 - 1.25 V are sufficiently close to measured open-circuit voltages (up to 1.05 V) to suggest some reduction of Voc by interface effects. Finally we present computer simulations of V_{QC} using the AMPS computer code. These simulations use simplified parameter sets chosen for consistency with drift-mobility and electroabsorption measurements. The results indicate that open-circuit voltages may be reduced about 0.1 V by electron diffusion to (and recombination in) the p-layer. We discuss implications for future improvements in V_{OC} . This research was supported through the Thin Film Photovoltaics Partnership of the National Renewable Energy Laboratory and by the Korea Science and Engineering Foundation.

SESSION A19: HETEROGENEOUS MATERIALS I-GROWTH

Chair: Nicolas Wyrsch Thursday Morning, April 27, 2000 Salon 7 (Marriott)

10:15 AM A19.1

GAS-PHASE AND SURFACE REACTIONS OF DECOMPOSED SPECIES IN CATALYTIC CVD. Namiko Honda, Atsushi Masuda, Hideki Matsumura, Japan Advanced Institute of Science and Technology (JAIST), Ishikawa, JAPAN.

Catalytic CVD, often called hot-wire CVD, is a novel low-temperature and high-rate deposition technique for amorphous silicon films, silicon nitride films, etc. Influence of gas flow on the film uniformity, efficiency of gas use, lifetime of deposition species were clarified using the specially designed tube reactor. Here, gas-phase and surface reactions of decomposed species in catalytic CVD are also clarified using the tube reactor by comparative study on source gases between H₂ diluted SiH₄ and He diluted SiH₄. Deposition rate and crystalline fraction were estimated as a function of the distance from the catalyzer. As a result, the following conclusions were obtained: 1) Most SiH₄ molecules are decomposed on the catalyzer surface and little SiH4 decomposition occurs by the collision with atomic H in gas phase. Therefore both the shape and the surface area of the catalyzer directly determine the deposition rate of Si films. 2) Crystallization of Si films occurs by the exothermic reaction on the growing surface accompanied with the exchange between H bonded to surface and atomic H in gas phase. 3) Not only the deposition rate but also the crystalline fraction are influenced by the gas flow, suggesting that control of the gas flow in the chamber design is important for not only the thickness uniformity but also the crystallinity.

 $10:30~\mathrm{AM}~\mathrm{\underline{A19.2}}$ MANIPULATION AND CONTROL OF NUCLEATION AND GROWTH KINETICS WITH HYDROGEN DILUTION IN HOT-WIRE CVD-GROWTH OF POLY-Si . Maribeth Swiatek, Jason K. Holt, David G. Goodwin, Harry A. Atwater, Thomas J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena, CA.

Hot wire chemical vapor deposition (CVD) is an attractive method for growth of polycrystalline silicon thin films for application in thin film polycrystalline silicon photovoltaics. A key issue is to identify growth conditions that enable the largest possible grain size at a given growth temperature with low intragranular defect density. Hydrogen is known to play a critical role in development of a crystalline microstructure in both amorphous and polycrystalline films grown by hot wire CVD at low temperatures. We systematically explore the relationship between gas-phase kinetics and film microstructure in the hot-wire CVD technique using diluted silane (1% in He) and additional hydrogen. Using a wire temperature of 2000°C, films were grown on Si (100) at 300°C using 1 mTorr SiH₄ and 99 mTorr He at hydrogen pressures from 0-100 mTorr. Transmission electron microscopy and atomic force

microscopy measurements indicated that the resulting microcrystalline films had a columnar grain structure and that grain size increased from 400 \mathring{A} using SiH₄/He to 850 \mathring{A} using Si/He/H₂ with $16:1 H_2:SiH_4$ ratio due to the etching by hydrogen of amorphous silicon. Etching rate measurements using a quartz deposition monitor show that, under the current deposition conditions, a transition from net film growth (2 Å/sec using only SiH_4) to net etching occurs at the addition of 80 mTorr hydrogen. The influence of selective nucleation at nucleation sites defined by metal nanoparticles on grain size in polycrystalline silicon films will also be discussed.

10:45 AM A19.3

INCREASE OF HYDROGEN-RADICAL DENSITY AND IMPROVEMENT OF THE STRUCTURE OF MICRO-CRYSTALLINE SILICON FILMS PREPARED BY HOT-WIRE ASSISTED PECVD METHOD. Norimitsu Yoshida, Takashi Itoh, Hiroki Inouchi, Hidekuni Harada, Katsuhiko Inagaki, Noriyuki Yamana, Kanta Yamamoto, Shuichi Nonomura, Shoji Nitta, Gifu Univ., ERES Div., Dept. of Electronic & Computer Engineering, Gifu,

The importance of the existence of the excited hydrogen (hydrogen radicals) for preparing hydrogenated microcrystalline silicon (μ c-Si:H) films has been studied. For increasing the density of the hydrogen radicals, VHF plasma CVD is one of the key technology. However, it requires complicated instruments for preparing μ c-Si:H with higher crystalline volume fraction at lower hydrogen dilution ratio. We have previously suggested a new method for preparing μ c-Si:H named hot-wire assisted PECVD (HWAPECVD) [I]. This method is constructed by two parts, plasma-enhanced CVD (PECVD) and hot-wire (W filament) [2] for exciting hydrogen. This technique has an advantage that the hydrogen-radical density is controllable without influencing the deposition conditions of the PECVD. Samples were prepared at a substrate temperature of $\sim 250^{\circ}\mathrm{C}$ and an RF (13.56 MHz) power of ~ 10 W. The temperature of the W filament was varied from room temperature to ~ 1750°C. The hydrogen dilution ratio to silane was also varied from ~ 10 to ~ 60. From the Raman spectroscopy and x-ray diffraction, it is found that both the crystalline volume fraction and the crystalline grain size become larger with an increase of the filament temperature at a fixed hydrogen dilution ratio of $\sim 60.$ It is also found that the sample crystallizes at a hydrogen dilution ratio of ~ 10 with a filament temperature of $\sim 1750 ^{\circ} \rm C$, in which the crystalline volume fraction is \sim 60 %. Note that the sample is normally amorphous for the latter deposition condition in the conventional PECVD (without the filament). Also note that the deposition rates for all samples are sim $0.5\ A/$ s. These results directly suggests the importance of hydrogen radicals and the HWAPECVD technique is promising for preparing $\mu \text{c-Si:H.}$ [1] H. Harada et al., submitted. [2] A. Sutoh et al., Jpn.

 $11:00~\mathrm{AM}~\mathrm{\underline{A}19.4}$ COMPARISON OF GROWTH OF Si THIN FILMS ON LOW TEMPERATURE AMORPHOUS SUBSTRATES BY MBE AND PECVD. J.A. Anna Selvan, D. Grutzmacher, E. Muller and J. Gobrecht, Laboratory for Micro- and Nanotechnology, Paul-Scherrer Institute, Villigen, SWITZERLAND.

Hydrogenated microcrystalline and amorphous Si films are of commercial interest because of their potential applications in solar cells, liquid crystal displays, image sensors and printer arrays. The growth technique and mechanisms are of crucial importance for the control of the microstructural properties of these films. A wide-spread method for the growth of Si thin films is PECVD. In this work, we have grown Si films on amorphous substrates by Molecular Beam Epitaxy (MBE) as well as by a new configuration of DC remote PECVD. The growth mechanisms of Si films for both methods are explained and the two techniques are compared. We show that with MBE, one can obtain high quality Si films with grains larger than those obtained by any other known growth method at low temperature. The films exhibit a highly columnar nature with a texture along < 220 > direction and a pronounced surface texture. By DC remote PECVD, we were able to precisely control the microstructural properties of microcrystalline Si films by varying the growth conditions. The optimised films have reduced point defects, passivated grain boundaries with a high growth rate of 6Å/sec. The ratio of the Raman signals corresponding to the crystalline (at 520 cm⁻¹) and amorphous (at 480 cm⁻¹) contents in the films is substantially higher in the Si films grown by MBE than in the films grown by PECVD. The electrical resistivity of the intrinsic Si films grown by both methods is on the order of $10^6~\Omega cm$ when measured along the surface. The mobility perpendicular to the surface increases in samples with highly columnar grains. In MBE grown films, the reflectance shows two prominent maxima at around 3.4 and 4.5 eV due to the high crystallinity of these films.

For large area electronic devices (e.g. solar cells), microcrystalline films with large grains are preferred. We achieved completely columnar, thin film solar cell structures on amorphous substrates

which have very interesting microstructural properties. Analysis of the structural (TEM, X-ray diffraction, Raman spectroscopic), surface (SEM & AFM), electrical (van der Pauw configuration) and optical properties were performed. The mechanisms and regimes of surface texture growth of Si films were identified. Surface texture growth is highly desirable for the purpose of 'light trapping' in thin film solar cells. The formation of point defects, twins, stacking faults and the amorphous tissues in the Si films grown by these two methods were studied. The TEM cross section of Si films grown by MBE shows grains with a width of 750nm and a length of 3 μ m; the largest reported so far for a microcrystalline Si thin film grown at low temperature. For high quality, large area Si films with few defects and large grains, one may grow Si films by MBE, where as for a Si film with passivated grain boundaries and for increased deposition rate, it is advantageous to grow Si films by DC remote PECVD. [1] A. Van der Drift Philips Res.Reports 22, 267-288, 1967 R626 [2] J.A. Thronton, J. Vac. Sci. Tech 11 (1974), 666

11:15 AM A19.5

IMPROVED CRYSTALLINITY OF MICROCRYSTALLINE SILICON FILMS USING DEUTERIUM DILUTION. Susumu Suzuki, Michio Kondo, Akihisa Matsuda, Electrotechnical Laboratory, TFSSCS Lab., Ibaraki, JAPAN.

The role of hydrogen is an important issue in microcrystalline formation but is not well understood. We have deposited microcrystalline silicon films by plasma enhanced chemical vapor deposition(PECVD) at an excitation frequency of 60MHz using hydrogen diluted silane as a source gas, and have studied the role of hydrogen by comparing hydrogen and deuterium dilution. In the present work, it is found that the better crystallinity can be obtained at a same growth rate when using D₂ dilution as compared to H₂ dilution. The ratio of deuterium content C_D to hydrogen content C_H in the film shows an interesting universal correlation with its crystallinity independent of the deposition conditions. Microcrystalline silicon films were deposited at 250°C in a capacitively coupled diode reactor under high- pressure-depletion(HPD) conditions as reported previously[1]. The silane fraction to hydrogen was kept constant at 10%, and the pressure was 2Torr. The input power density was changed from 0.1 to $1.1 \rm W/cm^2$ at an excitation frequency of 60MHz. The Raman crystallinity, the intensity ratio of the Raman= $I(520.5 {\rm cm}^{-1})/I(480 {\rm cm}^{-1})$, as a function of growth rate reveals marked improvement for D_2 dilution in comparison with H_2 dilution. The ratio of number of H and D atoms (C_H/C_D) has a good correlation with the crystallinity, i.e., crystalline phase is observed for the film having ${\rm C_D}/{\rm C_H}{>}0.5$, and this empirical rule is observed universally for different deposition conditions such dilution ratio and power. The improved crystallinity for D_2 dilution is ascribed to lower electron temperature and to more stable surface coverage by D. These characteristics of D arise from heavier mass than hydrogen. The empirical correlation for C_D/C_H to the crystallinity suggests that H-D exchange events on the surface promotes crystal formation above a certain threshold numbers if we assume that atomic deuterium comes from the D2 diluent and that surface hydrogen originating from SiH_x fragment of SiH_4 source gas molecules. [1] L. Guo et al., Jpn. J. Appl. Phys. 37. L1116 (1998).

11:30 AM <u>A19.6</u>

REAL TIME OPTICS OF p-TYPE MICROCRYSTALLINE SILICON DEPOSITION ON SPECULAR AND TEXTURED ZnO-COATED GLASS. P.I. Rovira¹, A.S. Ferlauto¹, Xinwei Niu¹, C.R. Wronski¹ R.W. Collins¹ and G. Ganguly². ¹The Pennsylvania State University, Materials Research Laboratory and Center for Thin Film Devices, University Park, PA; ²BP Solarex, Thin Film R&D, Toano, VA.

Previous real time spectroscopic ellipsometry (RTSE) studies have identified optimum plasma-enhanced chemical vapor deposition (PECVD) processes for the immediate nucleation of p-type microcrystalline silicon (µc-Si:H) layers at high density on H₂-plasma-treated intrinsic amorphous silicon (a-Si:H) using boron trifluoride (BF₃) and trimethyl boron [B(CH₃)₃]doping source gases [1]. Such structures have been designed for incorporation into a-Si:H n-i-p solar cells. In the present study, we explore how these optimum PECVD processes can be adapted for immediate nucleation of μ c-Si:H p-layers on zinc oxide (ZnO) for incorporation in p-i-n solar cells. In this work, we explore p-layer nucleation and growth on two different types of ZnO surfaces: $\sim 2000~\text{Å}$ thick specular ZnO on glass, and textured ZnO/SnO₂ bilayers on glass in which case very thin 200 Å ZnO layers are used. Detailed information is extracted from RTSE including the morphology, thickness, and phase evolution for the μc-Si:H p-layers prepared under different conditions. Such information allows us to adapt effectively the p-layer process to the ZnO surfaces. As a result, we have found that high-density microcrystallite nucleation and a fully-coalesced 100 Å $\mu c\text{-Si:H}$ p-layer can be achieved even on smooth, specular ZnO using the $B(CH_3)_3$ doping source gas and the process optimized for H₂-plasma-treated a-Si:H substrates. In contrast, the nucleation density is much lower for the corresponding

p-layer attempts on specular ZnO using the ${\rm BF_3}$ source. Basic differences between p-layer nucleation and growth on a-Si:H, H₂-plasma-treated a-Si:H, and ZnO substrates are identified and quantified through the use of substrate-dependent deposition phase diagrams that plot the accumulated film thickness at which the amorphous-to-microcrystalline transition occurs versus the H₂-dilution ratio. [1] Joohyun Koh, et al., J. Appl. Phys. 85, 4141

> SESSION A20: DYNAMICS AND HYDROGEN Chair: Howard M. Branz Thursday Afternoon, April 27, 2000 Salon 7 (Marriott)

1:30 PM A20.1

ULTRAFAST DYNAMICS OF PHOTOEXCITATIONS IN HWCVD HYDROGENATED AMORPHOUS SILICON-GERMANIUM ALLOYS. J.E. Young¹, B.P. Nelson², and <u>S.L. Dexheimer</u>¹; $^1{\rm Department}$ of Physics and Materials Science Program, Washington State University, Pullman, WA; $^2{\rm National~Renewable~Energy}$ Laboratory, Golden, CO.

We will present femtosecond studies of carrier dynamics in hydrogenated amorphous silicon and silicon-germanium alloys grown by the recently developed hot-wire assisted chemical vapor deposition (HWCVD) technique, which is promising for producing high-quality device-grade materials. We have used wavelength-resolved femtosecond pump-probe techniques, in which an intense pump pulse excites carriers in the sample and a time-delayed probe pulse measures the resulting change in optical properties as a function of time delay following the pump pulse, to study the dynamics of photoexcitations in these materials. Femtosecond dynamics measurements have been carried out on thin film samples under experimental conditions with varying sensitivity to carriers in extended states or in band tail states. The relaxation dynamics of carriers associated with extended states show a strong dependence on excitation density and follow a bimolecular recombination law, consistent with a number of earlier studies on related amorphous materials. In contrast, measurements sensitive to band tail states reveal significantly altered dynamics, characterized by a marked deviation from simple bimolecular recombination. This work is supported by the US Department of Energy through the National Renewable Energy Laboratory, and the National Science Foundation Division of Materials Research.

1:45 PM *A20.2 DYNAMICS OF Si-H VIBRATIONS IN HYDROGENATED AMORPHOUS SILICON. <u>Jaap I. Dijkhuis</u>, Faculty of Physics and Astronomy, Debye Institute, Utrecht University, Utrecht, THE NETHERLANDS.

We study the vibrational population decay and phase relaxation of Si-H stretching vibrations in a-Si:H. We employ intense subpicosecond pulses from the free-electron laser FELIX for pumping and probing the vibrations. We demonstrate that the vibrations are localized and break up into three Si-H bending vibrations and one phonon, with a distribution of rates determined by the amorphous host. The pure dephasing of the stretching vibrations is single exponential and shown to be governed by elastic phonon collisions. Evidence is obtained for a longevity of high-frequency phonons produced in the decay of the bending vibrations, consistent with pulsed Raman experiments (Scholten et al. Phys. Rev. 47, 13910, 1993). Work in collaboration with M. van der Voort, C.W. Rella, L.F.G. van der Meer, and A.V. Akimov.

2:15 PM A20.3

INFLUENCE OF THE FERMI ENERGY ON Si-H VIBRATIONAL MODES IN AMORPHOUS AND MICROCRYSTALLINE SILICON. N.H. Nickel and P. Lengsfeld, Hahn-Meitner-Institut Berlin, Berlin, GERMANY.

Hydrogenated amorphous (a-Si:H) and microcrystalline silicon (µc-Si:H) films were prepared by rf-glow discharge at a substrate temperature of 230°C. Microcrystalline growth was achieved by diluting silane with hydrogen. Boron doped, phosphorous doped, and compensated samples were prepared by premixing silane with either diborane or phosphine or a mixture of both. The crystalline fraction of μc-Si:H was determined from Raman backscattering data. Information on hydrogen bonding was obtained from Si-H_x stretching local vibrational modes (LVM) at 2000 and 2100 cm⁻¹. In n-type and undoped a-Si:H the LVM's of Si-H at 2000 cm $^{-1}$ and clustered Si-H $_x$ groups at 2100 cm $^{-1}$ can be clearly distinguished. The ratio R=I(2100)/(I(2000)+I(2100)) amounts to $R\approx 0.25$. As the Fermi energy moves towards the valence band R approaches zero indicating that in boron doped a-Si:H all H atoms are accommodated as monohydrides (Si-H). Since the doping source gases were diluted with

H the vanishing of the LVM at 2100 cm $^{-1}$ could be due to a structural change of the samples from a-Si:H to $\mu c\text{-Si:H}$. However, the Raman spectra did not reveal the presence of the TO mode at 520 cm $^{-1}$ but only the broad gaussian peak centered at 480 cm $^{-1}$ characteristic of a-Si:H. On the other hand, $\mu c\text{-Si:H}$ reveals two new LVM's centered around 1920 and 2140 cm $^{-1}$. These lines are also found in poly-Si containing platelets. These new vibrational modes occur with considerable strength even before the TO line at 520 cm $^{-1}$ is detectable. Thus, these LVM's can be used to detect crystalline fractions in material prepared in the protocrystalline regime. The results are discussed in terms of current models for the properties of H in silicon.

2:30 PM <u>A20.4</u>

DEPENDENCE OF H DIFFUSION IN HYDROGENATED SILICON ON DOPING AND THE FERMI LEVEL. W. Beyer and U. Zastrow, ISI-PV, Forschungszentrum Jülich, Jülich GERMANY.

The dependence of hydrogen diffusion in a Si:H and μ c-Si:H on doping and the Fermi level is of considerable importance for H stability. The nature of this effect is not fully understood. The doping effect was first observed in hydrogen effusion experiments of a -Si:H [1] and was also reported for $\mu c\text{-Si:H}$, a-Ge:H as well as Si-rich a-Si alloys with C, O and N. It was studied extensively by hydrogen-deuterium interdiffusion. However, in these experiments the hydrogen concentration c_H which is also known to affect H diffusion [2] was not kept at a fixed level. Here we report on results of H-D interdiffusion studies on doped c-Si:H wafers and (low c_H) μ c-Si:H and a-Si:H films which were post-hydrogenated by hydrogen implantation in the range from less than 1% H to more than 20%. The results show for a fixed doping level that an increasing hydrogen concentration increases the diffusion coefficient (at a fixed temperature) in a-Si:H and µc-Si:H while it decreases the diffusion coefficient in c-Si:H, similar as observed for undoped material [3]. At a fixed hydrogen concentration, the diffusion coefficient (at $T=400\,^{\circ}C$) increases by three orders of magnitude on p-type (boron) doping and by about one order of magnitude on n-type doping with a doping level of 1%. The doping and H concentration dependence of the H diffusion coefficient at fixed temperature as well as of diffusion energies and diffusion prefactors will be discussed in terms of an energy band model of H diffusion. The results suggest that the energy of the hydrogen transport path is changed by doping. W. Beyer and H. Wagner, J. Appl. Phys, 53 (1982) 8745. [2] W. Beyer, in Semicond. and Semimetals, Vol. 61 (Academic Press, San Diego, 1999) 165 [3] W. Beyer and U. Zastrow, Mat. Res. Soc. Symp. Proc. 507 (1998)

[3] W. Beyer and U. Zastrow, Mat. Res. Soc. Symp. Proc. 507 (199 679.

2:45 PM A20.5

A CASE FOR MOLECULAR HYDROGEN BEING THE MOBILE H SPECIES IN a-Si:H. Peter A. Fedders, Washington University, Dept Physics, St. Louis, MO.

The mechanism (or mechanisms) for the transport of hydrogen in a-Si:H is of great intrinsic interest, but is also important for the understanding of a number of phenomena including light induced defects. The standard picture for hydrogen migration is that a hydrogen atom leaves a trap site for a higher energy transport site, migrates among the transport sites, and eventually falls back into a trap site. Presuably the transport sites are bond centered sites and the trap sites are H passifying dangling bonds although other possibilities do exist. We find that the literature includes many calculations for the activation energy for hydrogen diffusion that are at best misleading and often interpreted incorrectly. In this work we exhibit the results of a number of calculations that apply to particles hopping and apply the results to a-Si:H. These calculations coupled with existing estimates of the energy of various hydrogen configurations in a-Si:H show that the standard picture is very likely to be incorrect. However, using past and present molecular dynamics calculations, we show that the mobile species of hydrogen in a-Si:H may well be molecular.

SESSION A21: NOVEL DEVICE STRUCTURES
Chair: Ruud E. I. Schropp
Thursday Afternoon, April 27, 2000
Salon 7 (Marriott)

3:30 PM *A21.1

THIN FILM TRANSISTORS ON FLEXIBLE SUBSTRATES.
Sigurd Wagner, Helena Gleskova, Princeton University, Dept of
Electrical Engineering, Princeton, NJ; Zhigang Suo, Princeton
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Electronics on foil or fabric, electronics on non-planar surfaces, and electronic skin are core development goals of the nascent macro-electronic industry. These products need electronic and photonic

circuits that can withstand elastic or even plastic deformation. Thin-film silicon transistors (TFTs) are central devices in deformable macroelectronics. In three ways TFTs also function as vehicles for exploring the concepts that differentiate flexible electronics from rigid electronics. (1) TFTs are fabricated on substrates that are flexible or deformable, and are compared to benchmark TFTs made on glass. (2) New TFT materials and processes are created or adapted to novel substrates, typically organic polymers or steel. (3) TFTs on foil substrates are evaluated during and after the application mechanical strain. Thin-film transistors on flexible substrates are surprisingly robust. They can be made on steel or plastic despite big differences in coefficients of thermal expansion, can be dropped down several stories, and can be bent to radii of millimeters. Eventually the TFTs fail mechanically, not electrically. Bending experiments and associated design rules focus on the TFT-to-neutral-plane distance, and say that: (a) thinner is more forgiving of bending, (b) a compliant substrate will offload strain from the electronics, and (c) the electronics should lie close to the neutral plane. The last conclusion also guides the choice of substrate and encapsulation by their Young's moduli and thicknesses. Experiments on in-plane strain are more difficult to do than on bending, but the theoretical guidelines appear to be similar. Effects of fatigue remain to be explored. A particularly interesting result is the importance of failure initiation. TFTs fail under tensile strain by crack propagation from defects at the edge of islands. In compression they fail by buckling after delamination. As a result TFTs fail more easily under tension than compression. In consequence, edge passivation may turn out to be more important to flexibility than layer adhesion. This research is supported by DARPA.

4:00 PM <u>A21.2</u>

LOW TEMPERATURE THIN-FILM MICROMACHINING ON PLASTIC SUBSTRATES. M. Boucinha, V. Chu, P. Alpuim, Instituto de Engenharia de Sistemas e Computadores (INESC), Lisbon, PORTUGAL; J.P. Conde, Department of Materials Engineering, Instituto Superior Técnico, Lisbon, PORTUGAL.

Sensors and actuators made using thin film micromachining allows the advantages of low temperature, large area technology to be applied to microelectromechanical systems (MEMS). The cost reduction of this technology, as well as the expansion of the range of materials which can be used as substrates, as compared with MEMS based on crystalline silicon, will be a strong driving force in its further development.

Thin-film surface micromachining techniques are used on low cost plastic substrates (PET) with a maximum processing temperature of 100°C. The structural layers used are a-Si:H, Al or a bi-layer formed by both materials. The sacrificial layer is a commercial photoresist. Acetone is used to selectively remove the photoresist. Bridges and cantilevers are fabricated with comparable dimensions and yields as on glass substrates. Electrostatic actuation of these microstructures is demonstrated. The electromechanical properties of these structures are presented.

The Young's modulus of PET is 2-4 GPa while for Al, it is 70 GPa and for a-Si:H, 150 GPa. On a compliant substrate, when the structural material surpasses a certain thickness, deformation of the substrate rather than the structure itself may occur during the actuation. The extent of this deformation depends on the thickness and elastic properties both of substrate and structural layer, and also on the stress of the structural material. The PET thickness presently used is 125 $\mu \rm m$. Processes for the fabrication of air-gap structures on thinner plastic substrates will be also studied. The main challenge in this process is the control of the stresses imposed by a thick microstructure on a thin substrate. Details of processing technology on plastic substrates, which differ substantially from that on glass substrates, will be discussed. The ability to locally deform a large area plastic membrane is one of the goals of this study.

4:15 PM A21.3

FABRICATION OF MECHANICAL MICROSTRUCTURES USING AMORPHOUS SILICON FILMS ON GLASS SUBSTRATES.
Chingwen Yeh, James B. Boyce, Jackson Ho, Rachel Lau, Xerox
Corporation, Palo Alto Research Center, CA.

Microelectromechanical systems (MEMS) technologies have recently become important in manufacturing various sensors and actuators for many applications, including avionics, biomedicine, data storage, environmental monitoring, space, transportation, and so on. However, using single-crystal silicon substrates in these MEMS technologies is a significant limitation for some applications, where large-area substrates are required. Amorphous silicon on glass substrates provides an approach to broaden MEMS technologies and brings them into the large-area applications. Unlike polycrystalline silicon, amorphous silicon is usually deposited at low temperatures (lower than 400 degree C) in PECVD (Plasma-Enhanced Chemical Vapor Deposition) systems, thus allowing the fabrication of microstructures on glass substrates. In this research, amorphous silicon films have been as the mechanical layer while oxynitride films can be used as the

sacrificial layer. Different generic mechanical microstructures such as cantilever beams, bridges, and membranes have been fabricated by utilizing surface micromachining techniques in MEMS technologies. Several issues regarding film stress and adhesion of amorphous silicon on glass substrates, and stiction problems after structure release will be discussed.

4:30 PM <u>A21.4</u>

NOVEL MICRO-PHOTODIODES FOR RETINA STIMULATION. Martin Rojahn, Markus B. Schubert, University of Stuttgart, Institute of Physical Electronics, Stuttgart, GERMANY.

The retinal layer of photoreceptor cells transforms incoming daylight into electrical pulses, thereby stimulating the ganglion cells as part of the neural visual system. Certain deseases, namely retina pigmentosa, result in degradation of photoreceptor cells whereas all other parts of the neural visual system remain functional. In 1995, a German research program was started to develop an eye implant which would functionally replace the degenerated rod and cone cells. We deposit micro-photodiodes based on amorphous silicon (p-i-n- and n-i-pstructures) at 100°C so that flexible plastic or biodegradable substrate foils may be used. The capacitive coupling of our photodiode's electrodes to the nervous tissue is crucial for the actual electrical stimulation of the ganglion cells. In-vitro experiments [1] with retinae and a variety of micro- electrodes and -photodiodes show that electrical activation of ganglion cells upon illumination requires a potential change of about 2V. Our approach investigates the fabrication of different sizes of micro-photodiodes with photolithography and several lift-off processes. Photodiodes of $200 \times 200 \mu \text{m}^2$ in size show an open circuit voltage of about 1.5V. Laterally series-connected micro-photodiodes of a tandem-structure (p-i-n-p-i-n and n-i-p-n-i-p) enable us to reach the required 2V. However, the performance of our photolithographically structured amorphous cells is still inferior to that of our standard a-Si:H cells using shadow masks for the front- or back-contact. We correlate parameters of our photolithographic process such as the heat resistivity of the photoresist during the deposition of the p-i-n layers, with the current-voltage-characteristics of the cells. At present, a low parallel- and a high series resistance limit the efficiency of our micro-photodiodes. Improved results of our technology we enable us to realize local light induced stimulation of the ganglion cells of the retina in in-vitro experiments. [1] A. Stett et al, Investigative Ophthalmology & Visual Science 40:S736, 1999

4:45 PM A21.5

SELECTIVE AREA CELL ADHESION ON AMORPHOUS SILICON USING PATTERNED SELF-ASSEMBLED ALKYL MONOLAYERS. L.L. Smith, K. Wang, G.N. Parsons, Dept. of Chemical Engineering; R. Hernandez, D.T. Brown, Dept. of Biochemistry, North Carolina State University, Raleigh, NC.

The compatibility of inorganic materials with living cells and tissues is crucial in many areas, including medical diagnostics, biosensors, drug delivery, etc. In this work, we are interested in the interaction of living mammalian cells with semiconductor surfaces for novel thin-film biosensor devices. Amorphous silicon may give advantages over crystalline silicon for some devices because of its large-area, low-temperature compatibility, and its large optical absorption coefficient in the visible spectrum. Amorphous silicon thin films (500Å) deposited on quartz were cleaned using ambient UV/O₃ treatment, leaving the surface largely OH-terminated and hydrophilic. The hydrophilic surface was then exposed to a vapor of octyltrichlorosilane (CH₃(CH₂)₇SiCl₃), creating a molecular layer formation on the surface. XPS confirms that the organic hydrolyzes, leading to a monolayer bound to the oxide surface through Si-O-Si linkages, with the Cl completely removed. The resulting surface is strongly hydrophobic, with advancing contact angles >106°. This organic surface was mask-patterned to reserve areas of uncoated hydrophilic substrate, and placed in a cell culture to observe cell adhesion and proliferation. The cells were baby hamster kidney epithelial (BHK-21) cells in a buffered culture medium of fetal bovine serum. A high degree of cell attachment and spreading was observed on the UV/O3-treated surfaces ($\approx 400~{\rm cells/mm}^2$) compared to $\approx 450/\text{mm}^2$ on the culture dish control surface, indicating cell proliferation and growth. Little cell adhesion occurred on the hydrophobic organic-coated surface (≈40 cells/mm²), and the cells remained round and only minimally attached. On patterned surfaces, the organic-free areas showed dense, well-adhered cell growth while the coated areas showed much fewer and more rounded cells. On all samples as well as control surfaces, cell death was ≪1%. These results suggest a means for selectively controlling cell adhesion to thin film electronic device surfaces, through the patterning of hydrophobic surface coatings

SESSION A22: POSTER SESSION: HOT-WIRE CVD II Chairs: A. H. Mahan and Don L. Williamson Thursday Evening, April 27, 2000 8:00 PM Salon 7 (Marriott)

A22.1 Si-H VIBRATION ONLY AT 2000/cm IN FULLY POLY-CRYSTALLINE SILICON FILMS MADE BY HWCVD. J.K. Rath and R.E.I. Schropp, Utrecht University, Interface Physics, Utrecht, THE NETHERLANDS.

The Si-H vibration in our device quality poly-Si made by hot-wire chemical vapour deposition (HWCVD) at low wire temperature (Tw=1800 degree C) is at 2000/cm in IR spectra whereas in a poly-Si film made at high wire temperature (Tw=1900 degree C) both 2000/cm as well as 2100/cm are observed. On the other hand, the Raman spectra (probing the upper part of the film) of Si-H vibration measured for both these samples show only at 2000/cm. XTEM micrographs of these films show that whereas the low Tw film has a structure made of closely packed crystalline columns; the high Tw film has conical crystalline structures with amorphous regions between them. For the high Tw film, the crystal cones meet each other towards the top of the film and form a closed structure. This is confirmed by Raman spectrum at 520/cm. We attribute the 2100/cm mode to the Si-H bonds at the surface of the cones touching the amorphous regions. The Si-H vibration shifts to 2000/cm when the crystalline cones coalesce with each other, as is the case in the upper part of the film. This explains the existance of both the frequencies in IR spectrum. The Raman spectrum (penetration depth of 514.5 nm laser beam is ~100 nm) essentially detects this Si-H bond in the top region at 2000/cm. For the low Tw film, the Si-H bonds are between closed packed crystal columns throughout the length of the film due to which all the Si-H bonds have vibration at 2000/cm, which explains why IR (bulk) and Raman (top region) have similar stretching mode characteristics. We attribute the Si-H vibration at 2000/cm in our HWCVD poly-Si films to the hydrogen at compact sites which, in addition to XTEM in defocussed condition, is also confirmed by hydrogen effusion and deuterium diffusion experiments.

OPTICAL PROPERTIES OF MICROCRYSTALLINE SILICON THIN FILMS PREPARED BY HOT WIRE CHEMICAL VAPOR DEPOSITION. M. Zhu, Y. Cao, X. Guo, Graduate School, Univ of Science and Technology of China, Laboratory of Semiconductors Materials Science, CAS, Beijing, CHINA.

Undoped microcrystalline Si thin films ($\mu c\text{-Si:H}$) were prepared by HWCVD with different H_2/SiH_4 ratios. The optical properties of the μc-Si:H films were characterized by optical transmission spectra. Raman scattering and Fourier transform infrared spectroscopy (FTIR). The nanocrystalline volume fraction Xc of film was determined by Raman spectra to be 0-0.74 varying with the H dilution ratio. Correspondingly, the optical gap is in the range of 1.80-1.40 eV. The absorption spectra intersect at energy 1.86 eV (Ec). Above Ec, the absorption coefficient decreases with Xc and the opposite behavior was observed below Ec. Raman peak at around 513 1 from the backside incident Raman measurement for films with $\mathrm{Xc} = 0.52$ and 0.62 was observed. Combining the result of TEM, it is $\rm AC=0.32$ and 0.02 was observed. Combining the result of 1 EM, it is suggested that silicon crystallization on the glass substrate occurs in the initial stage of growth in HWCVD. The FTIR data show that the intensities of the 2000 cm⁻¹ stretching modes and 858 cm⁻¹, 889 cm⁻¹ SiH₂ bend modes decrease with increasing Xc and disappear as the Xc > 0.62. While the 2100 cm⁻¹ stretching mode is getting strong with Xc and then splits into two modes at 2098 cm⁻¹ and 2082 cm⁻¹. The ratio of intensity at 2098 cm⁻¹ to 2082 cm⁻¹ promotes with increasing Xe. Cardona has proposed that the stretching modes with increasing Xc. Cardona has proposed that the stretching modes at 2085 cm⁻¹ and 2100 cm⁻¹ are corresponding to the SiH bonds on two different crystallographic surfaces possibly (111) and (110) Combining our observations of a preferential growth orientation along the (111) direction and no trace of the SiH₂ groups in 840 to 900 cm^{-1} as Xc > 0.62, we suggest that the 2098 cm⁻¹ mode is corresponding to the Si-H stretching vibration at the nanocrystalline Si (111) surface in μ c-Si:H.

EFFECT OF GROWTH METHOD ON THE COMPOSITION AND MICROSTRUCTURE OF HYDROGENATED AMORPHOUS SiC ALLOYS. Moon-Sook Lee, Stacey F. Bent, Dept. of Chemical Engineering, Stanford University, Stanford, CA

Amorphous and heterogeneous hydrogenated silicon and its alloys are finding wide use for photovoltaics and flat panel displays. A common growth method for these materials is plasma-enhanced chemical vapor deposition (CVD), but hot-wire CVD is becoming an attractive alternative because it provides a way to generate reactive species such as radicals with less ion-induced damage to the growing film. Here we compare the use of both electron cyclotron resonance (ECR) plasma and hot-wire sources in the growth of amorphous and microcrystalline silicon-carbon alloys. Alkyl-substituted silanes were used as single source precursors in a low pressure regime between 200 and 600 K. In situ multiple-internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy was used to obtain a detailed identification of the hydride bonding in the film, and near-edge X-ray absorption fine structure (NEXAFS) measurements provide supporting information on carbon and silicon bonding. The differences between films grown by the plasma vs hot-wire methods are more apparent at the higher growth temperatures. We show that HW-CVD affords greater control of the film bonding and microstructure. By using hydrogen dilution and varying growth temperature over the range of 200 K to 600 K, the film structure can be varied from poly (methyl)silane and polycarbosilane forms of a-SiC:H, to microcrystalline material. Studies using IR and real-time mass spectrometry point to the role of hydrogen atoms and indicate that the temperature dependence of H atom reactions influences the growth process.

A22.4

NANOCRYSTALLINE UNDOPED SILICON FILMS PRODUCED BY HOT WIRE AND HOT WIRE PLASMA ASSISTED TECHNIQUE. <u>I. Ferreira</u>, R. Martins, A. Cabrita, E. Fortunato, P. Vilarinho, Univ Nova de Lisboa, Faculty of Science and Technology, Dept of Materials Science, Monte de Caparica, PORTUGAL.

One of the main weak points of amorphous or micro/nano-crystalline undoped silicon films produced by the hot wire technique is that the films present a porous like structure with a roughness surface. This type of structure leads to a fast oxidation of the films once exposed to air, which increases with the time of air exposition. On the other hand, the production of polycrystalline undoped silicon films by the conventional plasma enhanced chemical vapour deposition is very difficult it requires the use of high r.f. power and/or high r.f. frequencies. In order to overcome the difficulties and to produce high compact structures at high growth rates with the performances required to device application, we introduce the plasma assisting the hot wire deposition technique. By doying so, we were able to produce high compact structures presenting regular distributed grains with sizes in the range of hundred nanometers, where post-oxidation is prevented. In this work, we show SEM results concerning the morphology of the films produced by hot wire with and without plasma assisting the process. There, it is observed that the films produced by hot wire process present a mulberry like structure while the films produced by plasma assisting the hot wire show a compact granular structure. On the other hand, the IR results show no post-oxidation for the films produced with plasma assisting the hot wire. On the contrary, a strong peak in the range of 1100-1200cm is observed, after tow months of the deposition of the films by the hot wire process. This behaviour is associated to a porous like structure. The influence of hydrogen dilution on the properties of the films was also investigated. The data reveals that hydrogen dilution improves the overall electrical properties of the films. Nevertheless, the films produced by hot wire technique are more porous when hydrogen dilution is used.

A22.5

p-TYPE WINDOW LAYERS FOR a-Si:H BASED SOLAR CELLS BY THE THERMO CATALYTIC CVD. M. Koob, U. Weber, H. Seitz, R.O. Dusane and B. Schroeder, Dept. of Physics and Research Center of Materials Science, University of Kaiserslautern, Kaiserslautern, GERMANY. Indian Institute of Technology, Bombay, INDIA.

We report the results of our investigations on p-type amorphous and microcrystalline silicon window layers deposited by the thermocatalytic chemical vapor deposition (TCCVD) method to be used in the TCO/p-i-n/metal superstrate solar cells. An important consideration in this cell structure is the damage of the TCO/p-layer interface due to reduction reactions of the TCO. An independant study on the effect of the atomic hydrogen present in TCCVD method on TCO revealed that the substrate temperature is important in this regard. So we prepared the p-type silicon carbon alloy (a-Si:C:H:B) using trimethyl boron (TMB) + methane and p-type microcrystalline silicon (µc-Si:H:B) using diborane and TMB independantly at as low substrate temperature as possible. We obtain a-Si:C:H:B layer with band gap 1.9 eV and $10^{-5}~(\Omega~cm)^{-1}$ conductivity which yield an open circuit voltage (V_{oc}) of 850 mV for a cell made on ASAHI TCO. Important correlations between the process parameters and film properties are evolved. For a-Si:C:H layers the carbon incorporation is more sensitive to absolute silane flow than to the silane to methane ratio. From signatures observed in the infrared spectra (Si-CH₂, Si-CH₃) we propose that in TCCVD the hot wire alone is not effective in dissociating the CH₄ in sufficient quantity. Collisions of Si, H or Si-H radicals with CH₄ are needed to obtain C-containing precursors which get incorporated in the alloy film. For the μc -Si:H layers the

filament temperature and pressure play important role in inducing microcrystallinity in the films. Also $\mu\text{c-Si:C:H}$ made with TMB requires larger gas pressure to induce crystallinity compared to that made with diborane. However this increases the atomic hydrogen concentration which damages the TCO/p-layer interface yielding lower V_{oc} in the present TCO/ $\mu\text{c-Si:C:H}$ p/i-n/Al cells. Cells with p-layers made using diborane show comparatively higher V_{oc} . Further understanding of the role of other process parameters is required to obtain high V_{oc} using TCCVD $\mu\text{c-p}$ layers.

A 22.6

N-TYPE AND P-TYPE DOPING OF AMORPHOUS AND MICROCRYSTALLINE SILICON FILMS BY HOT-WIRE CVD AND RF-PECVD AT LOW SUBSTRATE TEMPERATURES ON GLASS AND PLASTIC SUBSTRATES. P. Alpuim, V. Chu, INESC, Instituto de Engenharia de Sistemas e Computadores, Lisbon, PORTUGAL; J.P. Conde, Department of Materials Engineering, Instituto Superior Tecnico, Lisbon, PORTUGAL.

Deposition of amorphous (a-Si:H) and microcrystalline (μ -Si:H) silicon thin films at very low (<150°C) substrate temperatures is motivated by the necessity of using novel substrates, like plastic, to extend existing areas of microelectronics or to make possible entirely new ones (microelectromechanical systems on flexible substrates or integration with organic or biomaterials for biological applications). In this paper, the gas-phase doping of a-Si:H and μ -Si:H deposited at substrate temperatures, T_{sub}, of 25°C and 100°C by hot-wire CVD (HW-CVD) and rf-PECVD on glass and plastic (PET) substrates using hydrogen dilution is studied.

N-type and p-type doped a-Si:H films were obtained by RF using phosphine and trimethylboron as doping gases respectively, at both $\rm T_{\it sub}{=}25^{\circ}C$ and 100°C. While p-type samples showed the same conductivity at both $\rm T_{\it sub}~(\sigma_d{\sim}1{-}2x10^{-7}~\Omega^{-1}~cm^{-1}$ and $\rm E_a{\sim}0.58$ eV), n-type films showed higher σ_d at $T_{sub}=100$ °C than at 25°C and are more conductive than p-type films $(\sigma_d{\sim}8.5{\rm x}10^{-4}~\Omega^{-1}{\rm cm}^{-1}$ and $E_a \sim 0.30$ eV for n-type films at $T_{sub} = 100^{\circ}$ C). Doped μ -Si:H films were obtained at $T_{sub} = 100^{\circ}$ C with similar conductivity and activation energy for n-type and p-type films ($\sigma_d \sim 2 \times 10^{-2} \ \Omega^{-1}$ cm⁻¹ and $E_a \sim 0.10$ eV). Doping of a-Si:H and μ -Si:H films by HW at $L_{sub}^{a}=25^{\circ}\mathrm{C}$ and $T_{sub}=100^{\circ}\mathrm{C}$ has so far been successful only in the case of n-type a-Si:H films. Preliminary work shows that the properties of doped films deposited at low \mathbf{T}_{sub} depend critically on the filament temperature and filament to substrate distance. Raman, XRD and SIMS will be used to study the structure and composition of these films in connection with its transport properties. Diborane (B₂H₆), due to its easier decomposition into fragments by the HW filament, will also be studied as dopant gas. The quality of the doped layers will be tested by incorporation in Schottky and p-i-n diodes made on glass and plastic substrates.

A22.7

PHOTODEGRADATION IN a-Si:H PREPARED BY HOT-WIRE CVD AS A FUNCTION OF SUBSTRATE AND FILAMENT TEMPERATURES. Jing Lin, Guozhen Yue, Dept of Physics & Astronomy, Univ of North Carolina at Chapel Hill, Chapel Hill, NC; Qi Wang, National Renewable Energy Laboratory, Golden, CO; Daxing Han, Dept of Physics & Astronomy, Univ of North Carolina at Chapel Hill, Chapel Hill, NC.

Device quality a-Si:H prepared by hot wire chemical vapor deposition (HWCVD) is attractive because of the high deposition rate and improved stability as compared to the plasma-enhanced CVD (PECVD) materials. The device quality films can be deposited at substrate temperature, $\rm T_s$, range from 280 to 440 °C. However, there was more or less photodegradation effects. In order to optimize deposition conditions for stable materials, we have studied the photosensitivity, activation energy and density of defect as well as the degradation kinetics for two group of films deposited at a temperature range from 280 to 440 °C at filament temperature 1500 and 2000 °C. A MMR micro-probe system with vacuum 10⁻⁴ Torr was used to mount the sample. Light-soaking was performed by a 100 mW/cm² white light through a water filter. The sample temperature was kept at 35 °C during light-soaking. A Keithley 615 programmable electrometer was used to record the current as a function of exposure time. State A was reached after the sample was annealed in a vacuum for two hours at 150 °C; state B was reached after light-soaking of 28 hours. For these two groups of films, the quality varies with substrate temperature obviously. For the samples deposited at $T_s = 280$ °C, the photo/dark current ratio was 103 at State A and decreased a factor of 8 at state B. For the samples deposited at $T_s > 320$ °C, the photo/ dark current ratio was 10⁵ at state A and decreased a factor < 3 at state B. The sample deposited at 360 °C shows the highest photo/ dark current ratio with the lowest defect DOS. Interestingly, for all the films deposited at $T_s > 320$ °C, the Fermi level position was ~ 0.9 eV below conduction band edge at State A and did not move further down or even slightly upwards upon light-soaking. This indicates the defects energy distribution in HW is different from PECVD samples.

The work is supported by NREL sub-subcontract XAK-8-17619-11 and thin film PV partnership. Lin is supported by Chinese Educational Fellowship. Yue is partially supported by NSF-Int-9604915. Han is partially supported by CGP Fund, NSF-Int-9802430. Wang is supported by DOE subcontract DE-AC02-83CH10093.

A22.8
DEVICE QUALITY AMORPHOUS SILICON FILMS GROWN AT RATES UP TO 1 MICRON/MIN BY HOT-WIRE CHEMICAL VAPOR DEPOSITION. Brent P. Nelson, A.H. Mahan, Yueqin Xu, R.S. Crandall, Eugene Iwaniczko, National Renewable Energy Laboratory, Golden, CO.

We grow hydrogenated amorphous silicon (a-Si:H) from silane gas by hot-wire chemical vapor deposition (HWCVD). By using more than one W filament, and decreasing the filament to substrate distance, we are able to increase our deposition rates from our typical singlefilament HWCVD process of < 0.2 nm/s to over 15 nm/s. By optimizing our deposition parameters we are able to grow a-Si:H films with AM1.5 photo responses in excess of 10^5 at deposition rates up to 13 nm/s. This is a significant increase over the 4 nm/s deposition rates we have previously reported for films of the same quality. The main deposition parameters we optimize are the substrate temperature, silane gas flow, chamber pressure, and filament current. The as-grown dark conductivity of these films is between 10^{-10} and 10⁻⁹ S/cm. The photo conductivity of these films all degrade with light exposure to about the same value ($\sim 5 \times 10^{-6}$ S/cm). In this paper, we report other electronic properties of these films as a function of deposition rate. The deep-defect density (obtained by drive-level capacitance measurements) for a deposition rate of 0.7 micron/min is less than $4\times10^{16}~{\rm cm}^{-3}$ after degradation by light, similar to that of the low deposition rate HWCVD a-Si:H.

> SESSION A23: POSTER SESSION: SILICON-CARBON ALLOYS Chair: John Robertson Thursday Evening, April 27, 2000 8:00 PM Salon 7 (Marriott)

 $\overline{\text{STRU}}$ CTURE AND COMPOSITION OF SiC $_x$:H FILMS FORMED BY PLASMA IMMERSION ION IMPLANTATION FROM A METHANE PLASMA. <u>Kerstin Volz</u>, Wolfgang Ensinger, Philipps University, Materials Science Center, Marburg, GERMANY.

Plasma Immersion Ion Implantation (PIII) of silicon in a methane plasma has been used to form ${
m SiC}_x$:H films. PIII can be a low temperature technique if desired (T < 150 °C). During PIII it is possible to coat a complex-shaped object from all sides simultaneously, as the workpiece is immersed into the plasma, which contains the ions to be implanted. From the plasma not only carbon, but hydrogen ions as well are implanted. In order to determine the concentration-depth distribution of the elements Nuclear Resonance Analysis (NRA) has been applied for the H and Rutherford Backscattering Spectrometry (RBS) has been used to depth profile Si and C. It is shown that by using PIII all C/Si ratios of 0 to 1/0 can be obtained. The H depth profile is shown not to be an implantation profile. Rather, the H depth profile is chemically governed by the C depth distribution. SiC with its stoichiometry close to unity can trap by far the most H. Increasing or lowering the C/Si ratio results in a decreasing trapping possibility for H. The chemical bonding in the layer systems is investigated by using vibrational spectroscopic methods. Infrared spectroscopy indicates that the H is mainly attached to C. The microstructure of the films is investigated in dependence on the film preparation conditions by high resolution transmission electron microscopy. The onset of crystallization of SiC is monitored as a function of the implantation temperature, which has been varied for this analysis. Nanocrystalline precipitates with random orientation up to hetroepitaxially growing SiC precipitates are found. The results of the structural analysis are correlated to the different trapping behaviour for H in dependence of the temperature.

SILICON:CARBON ALLOYS DEPOSITED BY ELECTRON CYCLOTRON RESONANCE CHEMICAL VAPOR DEPOSITION. Mark B. Moran and Linda F. Johnson, Naval Air Warfare Center, Weapons Division, Naval Aviation Science and Technology Office, China Lake, CA.

Silicon:carbon (Si:C) alloys were deposited by electron cyclotron resonance chemical vapor deposition (ECR-CVD) using either trichlorosilane (SiHCl3) or tetrachlorosilane (SiCl4) with either

ethylene (C2H4) or tetrachloroethylene (C2Cl4) in a high-density argon (Ar) plasma. Deposition temperatures ranging from 150 to 750°C and plasma powers from 600 to 3000W were used. A Si doped carbon film (C:Si) deposited using SiHCl₃, C_2Cl_4 and Ar at 1200W and a deposition temperature of about 150°C is electrically conductive with a resistivity value of about 0.067 ohm-cm. Electron spectroscopy for chemical analysis (ESCA) shows that the atomic weight percent of Si in the C:Si film is only 3%. A near-stoichiometric ${
m SiC}_x$ film deposited using SiHCl₃, C₂ H₄ and Ar at 3000W and a deposition temperature of about 325°C is electrically insulating. ESCA shows that the C/Si ratio of the SiC_x film is about 0.93 Fourier transform infrared (FTIR) spectroscopy indicates that pi orbital bonding is associated with enhanced electrical conductivity in these Si:C alloys. The intense asymmetric stretching mode for single-bonded Si-C which occurs at about 780cm⁻¹ in the FT: spectra of near stoichiometric SiC_x films is replaced with a "bond-and-a-half" Si-C stretching mode at $1180 \operatorname{cm}^{-1}$ in the spectra of electrically conductive C:Si films. In addition, the electrical conductivity of the C-rich SiC_x films increases as the intensity of the double-bonded C=C stretching mode at $1580\mathrm{cm}^{-1}$ increases. Additional results show that etching of the substrate by the plasma can have a dramatic effect on the microstructure, porosity and moisture stability of ECR-CVD films. Plasmas containing chlorine (C1) etch Si wafers rapidly at powers above 2000W. The C:Si films are much more stable than SiC_x films because they are deposited at lower plasma powers that do not etch the Si substrate. Switching to a more Cl-resistant substrate like sapphire or coating the substrate with Al₂O₃ should improve the microstructure.

<u>A23.3</u>
DEVICE QUALITY SILICON CARBON THIN FILMS. Christian Gemmer, Markus B. Schubert, University of Stuttgart, Institute of Physical Electronics, Stuttgart, GERMANY.

For stacked amorphous silicon based solar cells, high quality material for the top cell is of crucial importance to achieve both high efficiencies and high output voltages. Amorphous silicon carbon having a optical gap of about 2.00 eV meets these prerequisites. Thus, the optical, electrical and structural properties of this alloy are subject of our investigations. The deposition of the samples proceeds in a plasma-enhanced chemical vapor deposition system at a frequency of 54.24 MHz and at a substrate temperature of 150 $^{\circ}\mathrm{C}.$ The hydrogen dilution ratio $r_{\rm H}=([{\rm H_2}]+[{\rm SiH_4}]+[{\rm CH_4}])/([{\rm SiH_4}]+[{\rm CH_4}])$ ranges in our series of intrinsic silicon carbon films from $r_{\rm H}=1$ to $r_{\rm H}$ = 21 whereas all other deposition parameters and the layer thickness retain constant. The optical gap $E_{\rm g}$ drops from $E_{\rm g}$ = 2.20 eV to $E_{\rm g}$ = 2.02 eV as $r_{\rm H}$ rises from $r_{\rm H}=1$ to $r_{\rm H}=21$. We measure the photocarrier mobility-lifetime product $\mu\tau$ under monochromatic illumination (energy E=2.20 eV, photon flux $\phi=2.5 \times 10^{14}$ cm⁻²s⁻¹) and the dark conductivity $\sigma_{\rm d}$. At $r_{\rm H}=10$ the $\mu\tau/\sigma_{\rm d}$ ratio shows a maximum of 1 \times 10⁶ cm³A⁻¹, which originates from a strong increase of $\mu\tau$. The dark conductivity only ranges between $\sigma_{\rm d}=5\times 10^{-11}~\Omega^{-1}{\rm cm}^{-1}$ and $\sigma_{\rm d}=5\times 10^{-10}~\Omega^{-1}{\rm cm}^{-1}$. The electrical properties correlate with the structural findings of silicon carbon: In the low hydrogen dilution range of our series $(r_{\rm H} \le 10)$ Raman measurements reveal no crystalline fraction $X_{\rm c}$ whereas the sample prepared with the highest hydrogen dilution $(r_{\rm H}=21)$ shows $X_{\rm c}$ of 25%. Hence, the transition from amorphous to nanocrystalline phase occurs between $r_{\rm H}=10$ and $r_{\rm H}=21$. These results affirm that analogous to amorphous silicon, device quality silicon carbon grows near the transition from amorphous to nanocrystalline phase.

MICROSTRUCTURE CHARACTERIZATION OF AMORPHOUS SILICON BASED ALLOYS BY INERT GAS EFFUSION STUDIES. W. Beyer, ISI-PV. Forschungszentrum Jülich, Jülich, GERMANY; S. Camargo, Jr., Univ. Federal, Rio de Janeiro, Coppe Inst., BRAZIL; R. Saleh, Universitas Indonesia, Depok, INDONESIA.

One major defect in amorphous silicon-based alloys is an interconnected void structure, as detected e.g. by hydrogen effusion measurements. However, H-effusion measurements give little information about void sizes. In order to obtain knowledge about this important parameter, we implanted inert gas ions and studied out-diffusion by effusion experiments. Since these gas atoms do not react with silicon, their effusion temperature is expected to be related to the size of network spacings and voids. Results for several series of a-Si:C:H and a-Si:O:H samples are presented. The film microstructure was characterized by hydrogen effusion and infrared absorption measurements. While in samples without an interconnected void structure implanted argon and neon atoms effuse at temperatures exceeding 700-800°C, i.e. near or above the crystallization temperature, neon and argon effusion shifts to lower temperature when an interconnected void structure according to H- effusion measurements is present. For plasma-grown a-Si:O:H samples with an oxygen concentration near 20 at%, we find a neon effusion peak near $500^{\circ}\mathrm{C}$ and an argon peak near $800^{\circ}\mathrm{C}$ while standard plasma-grown

a-Si:C:H films of about 20 at% carbon show argon effusion near 500°C, suggesting a larger void size in the latter case. On the other hand, for near-stoichiometric a-Si:C:H films plasma-deposited under conditions of hard carbon, the effusion results suggest the presence of smaller voids similar in size as observed for the void-rich a-Si:O:H samples. In this case, the void size is found to increase on increasing carbon concentration. Limitations of the method and implications on the structure of a-Si-based alloys will be discussed.

A23.5

P-TYPE MICROCRYSTALLINE SILICON CARBON ALLOY FILMS BY VHF-PECVD TECHNIQUE. Tapati Jana, Arup Dasgupta and <u>Swati Ray</u>, Energy Research Unit, Indian Association for the Cultivation of Science, INDIA; Freidhelm Finger and R. Carius, ISI-PV, GERMANY.

P-type μ c-Si:H layer having high conductivity and transparency can effectively replace doped amorphous window layers of the p-i-n solar cells to increase built-in-potential and decrease series resistance. Now the very high frequency (VHF) PECVD technique becomes very much important for the growth of microcrystalline material, leading to high quality material at low power and low deposition temperature with high deposition rate. However, p-type μ c-SiC:H films having high optical transparency than μ c-Si:H material with high conductivity can also be used as the window layer of p-i-n solar cells to improve the conversion efficiency. But till date only a limited work on μ c-SiC:H films by VHF-PECVD have been reported.

The samples were prepared in a capacitively coupled multichamber PECVD system with plasma excitation frequencies between 13.56 to 120 MHz using silane (Si H_4), methane(C H_4), diborane and hydrogen (H_2) gas mixture. The effect of substrate temperature and frequency variation on the optoelectronic and structural properties have been investigated at a low power of 55 mW/cm 2 .

The initial decrease of substrate temperature from 250°C to 200°C at 66 MHz increases the conductivity from 0.57 $\mathrm{S}cm^{-1}$, where as further lowering of substrate temperature decreases the conductivity again. The optical absorption decreases continuously with the decrease of substrate temperature. At higher substrate temperature, hydrocarbon radicals collect H from the growing surface and liberated as CH_4 . Whereas, at sufficiently low substrate temperature (150°C) desorption of H from the surface is low as a result more hydrocarbon radicals may be adsorped at the growing surface. As the substrate temperature decreases from 250°C to 200°C the conductivity increases due to better crystalline structure and the lowering of absorption is accompanied by increase in carbon incorporation as well as improvement in crystallinity as shown. However, further lowering of temperature (180°C to 150°C) suggest that there has been a remarkable increase of carbon content in the film which suppresses increase of absorption due to loss of crystallinity, as a result σ_D dereases. The grain size has been calculated from the TEM micrograph. The diffraction pattern show well defined crystallographic planes of c-Si. The frequency variation at 180° C shows that optimum frequency is 81 MHz having 2.32 Scm^{-1} conductivity and 26 Å/mindeposition rate for an optical gap of 2.00 eV. Whereas, at rf frequency under the same deposition conditions, materials becomes amorphous.

A23.6

Abstract Withdrawn

A23.7

EFFECTS OF THERMAL ANNEALING ON THE PROPERTIES OF PECVD a-SiC LAYERS. <u>L.F. Marsal</u>, J. Pallares, Departament d'Enginyeria Electronica, Universitat Rovira i Virgili, Tarragona, SPAIN; A. Orpella, D. Bardes, J. Puigdollers and R. Alcubilla, Departament d'Enginyeria Electronica, Universitat Politecnica de Catalunya, Barcelona, SPAIN.

Hydrogenated amorphous silicon carbon alloys deposited by Plasma Enhanced Chemical Vapour Deposition (PECVD) are of great interest because they can be deposited at low temperature on large area. Main applications are wide band gap emitter in bipolar transistors, thin film transistors, solar cells, displays, etc. [1] However, amorphous silicon carbon alloys (a-SiC) have a high density of states and high resistivity. One way of improving these properties is to promote crystallites formation in the amorphous film through thermal annealing. Nano or microcrystalline regions within the amorphous network increase the electrical conductivity and reduce the state density [2]. Despite of large number of contributions of amorphous and annealed silicon-carbon films, the knowledge and comparability of the physical properties is difficult because its depend strongly on the preparation conditions and on the particular process used for deposition. We report the structural characterisation of amorphous and annealed silicon carbon alloys layers at different temperatures by using Raman and Fourier Transform Infrared Spectroscopy (FTIR). In addition, the optical properties obtained by Phototermal Depletion (PDS) and Optical Transmission spectroscopy (OTS) are also reported. REFERENCES [1]J. Kanicki, Amorphous and microcrystalline semiconductor devices, Vol. II, Materials and device physics, Artech House, 1992. [2] F. Demichelis, C.F. Pirri and E. Tresso, Philosophical Magazine B, Vol. 66, p. 135, 1992.

SESSION A24: POSTER SESSION: CLUSTERS, NANOCRYSTALS, AND POROUS MATERIALS

Chairs: Arthur Yelon and Reinhard Carius Thursday Evening, April 27, 2000 8:00 PM Salon 7 (Marriott)

A24.1

DEPOSITION OF SILICON CLUSTERS ON SILICON. A MOLECULAR DYNAMICS STUDY. <u>A.M. Mazzone</u>, C.N.R.-Istituto LAMEL, Bologna, ITALY.

The synthesis of nanostructured material is of primary technological importance. Preparation of this material can be achieved by depositing elementary units or already formed units onto a support. This last possibility has stimulated the interest on the physics of cluster deposition and theory and experiments show a wealth of new phenomena. This study presents a molecular dynamics simulation of deposition of silicon clusters on a silicon substrate with a (100) surface. The purpose is to gain insight into cluster-cluster coalescence, cluster fragmentation and cluster-surface interaction and interdiffusion. We are specifically concerned with the structural aspects of these mechanisms and the aim of the simulations is to clarify whether or not crystallinity in the growing film may be sustained by properly selected cluster size and deposition temperature.

A24.

MECHANICAL CHARACTERIZATION OF SIGE ISLANDS AND THIN FILM HETEROSTRUCTURES BY ULTRASONIC FORCE MICROSCOPY. Bryan D. Huey, G. Andrew D. Briggs, Oleg V. Kolosov, Oxford University, Department of Materials, Oxford, UNITED KINGDOM.

The capability to measure nanoscale mechanical properties is vital for the continued miniaturization and hybridization of semiconductor devices, micro-electro-mechanical-systems, chemical sensors, etc. Local elastic properties can be uniquely measured for brittle materials by employing the non-linear detection of oscillating surface forces in an atomic force microscope during ultrasonic sample oscillation (known as Ultrasonic Force Microscopy, UFM). Studies on cleaved cross-sections of $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ (0.1
<x<0.3) islands and multilayers reveal mechanical contrast for films thinner than 5 nm. These experimental results are compared with simulations of various tip-surface mechanical interactions (Hertz, JKRS, Maugis) and experimental parameters (load, cantilever/tip effects). UFM can therefore be used to characterize nanoscale mechanical properties of thin film heterostructures.

A24.

SPECTROSCOPIC ELLIPSOMETRY FOR THE CHARACTERIZATION OF THE MORPHOLOGY OF ULTRA-THIN THERMAL CVD AMORPHOUS AND NANOCRYSTALLINE SILICON THIN FILMS. Sukti Hazra, Mitsuyuki Yamanaka, Isao Sakata, Toshiyuki Tsutsumi, Tatsuro Maeda, Hirohisa Taguchi and Eiichi Suzuki, Electrotechnical Laboratory, Electron Devices Division, Tsukuba, Ibaraki, JAPAN.

Thermal CVD (chemical vapor deposition) a-Si:H films can be dense and have flat surfaces due to the absence of ion bombardment during growth, and thus can be a candidate for a staring material in the fabrication of novel quantum dot memory devices. In the present study we have introduced for the first time spectroscopic ellipsometry (SE) to find out optical functions and structural properties of ultra-thin thermal CVD a-Si:H and to study the formation processes of nanocrystalline Si from a-Si:H by rapid thermal annealing/ oxidation (RTA/RTO) processes. A new parameterization i.e., the combination of Sellmeier law and the four Lorentzian peaks, has been successfully introduced in data analysis. Widths of peaks are directly related with the change of optical functions with the a-Si:H film thickness. It has been clarified that the dense Si matrix with smaller degree of disorder is formed when the film thickness exceeds 8 nm and the films with the thickness less than 3.5 nm becomes voided, which suggests that the coalescence of Si islands takes place around this thickness during growth. It has also been confirmed that ultra-thin thermal CVD a-Si:H films have smooth surfaces as expected. The formation of Si nanocrystallites from ultra-thin thermal CVD a-Si:H films by RTA / RTO processes has also been studied by SE. Three layer model consisting of poly-Si + void, a-Si:H + void, and SiO2 has been adopted to interpret the data. It has been shown that the formation processes of nanocrystalline Si can be systematically

controlled by the morphology of starting a-Si:H films and RTA/RTO conditions

A24.4

TEM AND HREM STUDY OF SILICON AND PLATINUM NANOSCALE ENSEMBLES IN 3D DIELECTRIC OPAL MATRIX. N.A. Feoktistov, V.G. Golubev, D.A. Kurdyukov, A.B. Pevtsov, L.M. Sorokin, Ioffe Physico-Technical Institute, RAS, St. Petersburg, RUSSIA; J.L. Hutchison, J. Sloan, Department of Materials, Oxford University, Oxford, UNITED KINGDOM.

One of the promising methods of nanoscale engineering is based on filling of the dielectric matrix, possessing by a regular void structure, with metals or semiconductors. It allows obtaining regular 3D cluster systems with the cluster size from 1 to 100 nm and density of elements as high as $10^{14} cm^{-3}$. In the present work regular systems of silicon and platinum clusters have been fabricated in a void sublattice of artificial SiO₂ opal. The opal consisted of 250-nm diameter close packed amorphous silica spheres and had the regular sublattice of voids (45-90 nm) up to 26% accessible to filling by other substances. To incorporate silicon into opal voids the thermal CVD technique was used [1]. The fill factor of opal pores was varied by the parameters of the thermal CVD process. The samples were filled with platinum from a solution of platinum tetrachloride in ethanol to fabricate metal contacts to silicon. The detailed TEM and HREM structure study of "opal-Si" and "opal-Pt-Si" composites was carried out using electron microscopes JEM4000EXII and JEM2010EX. The microstructure images both in diffraction contrast and high-resolution modes were taken. It was found that in composites "opal-Si" the silica spheres were covered uniformly with an amorphous-nanocrystalline silicon layer with thickness ranging in 0 - 25 nm. Volume fraction of nanocrystalline silicon was increased up to 50% by thermal annealing and Si monocrystals with linear sizes about 300 nm were fabricated. To form the Pt-Si contact the silica spheres were coated with a uniform 5 nm-thick platinum film before incorporation of silicon. The results obtained demonstrate a possibility of creating 3D multilayer semiconductor electronic structures (p-n junctions, Shottky barriers) on the inner surface of opal voids. [1]V.N. Bogomolov, V.G. Golubev, N.F. Kartenko, D.A. Kurdyukov, A.B. Pevtsov et al., Techn. Phys. Lett., 24, 326 (1998).

A24.5

THERMAL CRYSTALLIZATION OF NANOMETRIC PARTICLES OF SI-C-N PRODUCED BY RF-PLASMA ENHANCED CHEMICAL-VAPOR-DEPOSITION. E. Bertran, G. Viera, M.C. Polo, E. Garcia-Caurel, Universitat de Barcelona, Dept Fisica Aplicada i Optica, Barcelona, SPAIN; D. Das, J. Farjas, Universitat de Girona, Dept Fisica, Girona, SPAIN.

The compatible technology for producing Si-based materials both in the form of thin films and nanometric particles opens new possibilities, as it is the case of heterogeneous thin films based on nanocrystalls of Si-alloys embedded in amorphous matrix, which have potential applications for temperature resistant films, buffer layers, anisotropic thin films or inorganic membranes. Before inserting nanocrystalls in an amorphous matrix, we have carried out a preliminary study, in which nanometric particles of Si, SiN, SiC and SiCN were grown at room temperature in a RF-PECVD process from mixtures of silane, methane and ammonia. Among the diverse conditions for particle formation, we chose moderate low pressure (below 100Pa) and RF-power lower than 200W in all cases. The particle size was controlled by a low frequency square-wavemodulation of the RF-power in order to get a narrow size-distribution in the 2-100nm range. Depending on the conditions used during the plasma process -mainly due to the bombardment and the gas dilution-, we can vary the structure of the nanometric particles from polymeric (amorphous) to crystalline. To study the thermal crystallization process of the particles, the RF-plasma conditions were tuned to have polymeric particles with a high yield. The annealing of these particles at 1400°C during one hour under argon or nitrogen led to different results depending on the composition of the samples as revealed by HRTEM and electron-diffraction analysis. SiCN particles developed nanocrystalls embedded in their amorphous matrix, SiC particles showed a notable internal crystallization and SiN remained amorphous. In the case of Si particles, the results depended strongly on the atmosphere: they resulted fully crystallized in argon, whereas, in nitrogen atmosphere, long whiskers 50-200nm wide of the α -Si₃N₄ phase grew from the particles.

A24.6

AN ARRAY OF SINGLE CRYSTALLINE SILICON DOTS ON CURVED SUBSTRATE FOR OPTICAL IMAGING APPLICATIONS. Hyun-Chul Jin and John R. Abelson, Univ. of Illinois, Dept. of Materials Science and Engineering, Materials Research Laboratory, and the Coordinated Science Laboratory, Urbana, IL; Martin K. Erhardt and Ralph G. Nuzzo, Univ. of Illinois, Dept. of Chemistry and the Materials Research Laboratory, Urbana, IL; Robert S. Sposili

and James S. Im, Columbia University, Materials Science and Metallurgy Program, New York, NY.

We have fabricated an array of single crystalline silicon dots (islands) on a curved glass substrate using soft lithographic patterning and pulsed excimer laser crystallization. The polymer template with an inverted copy of the dots is first patterned on glass using MIMIC (micromolding in capillaries), and a 0.1 μ m thick hydrogen-free amorphous silicon layer is subsequently deposited by dc magnetron sputtering at 125°C. Finally the dots are formed by liftoff, and selectively crystallized by pulsed excimer laser processing with sequential lateral solidification (SLS). In the pulsed excimer laser processing with SLS, the melt/crystallization zone has a defined shape in the plane of the substrate, and is laterally translated to produce a continuous single crystal grain. Soft lithography enables us to fabricate an array of dots on a curved glass substrate without the complicated optical setup which would be required to use projection photolithography. In the soft lithography technique, a polymer template is formed by (i) pressing an elastomer mold against the curved glass and (ii) injecting a pre-polymer into micro-channels on the mold. Upon curing the pre-polymer and removing the mold, this leaves the desired pattern. We produce an array of 50 μ m diameter islands, spaced 200 μ m apart. We characterize the structural and electrical properties of these islands, and will discuss possible application of this structure.

A24.

MULTI-BAND ELECTRON PARAMAGNETIC RESONANCE STUDY OF MICROCRYSTALLINE OR CLUSTER SILICON EMBEDDED IN SiO₂. <u>Takashi Ehara</u>, Ishinomaki Senshu University, School of Science and Engineering, Ishinomaki, JAPAN; Tadaaki Ikoma, Shozo Tero-Kubota, Tohoku University, Institute for Chemical Reaction Science, Sendai, JAPAN.

Dangling bond defects in the silicon grains embedded in SiO₂ have been studied by X- and Q-band electron paramagnetic resonance (EPR) spectroscopy. Cluster and microcrystalline silicon grains in the SiO₂ thin film were prepared by co-sputtering of silicon and SiO₂ followed by thermal annealing. It has been clarified from the Raman spectra that the microcrystalline has been produced at an annealing temperature of 1000°C, while the cluster has been formed after annealing at 600 or 800°C. A broad and unsymmetrical EPR signal with the line width of 13 G and the average g-value of 2.006 was observed in the microcrystalline containing film. The line width observed in the Q-band EPR is 2.6 times of that in the X-band. The signal can be simulated by using the anisotropic g-values of g_{\parallel} 2.0022 and $g_{\perp} = 2.0078$. The g-values obtained are very similar to those of P_b center. The X-band EPR spectra of the cluster samples give an asymmetric signal with the line width of 9 G. The spectra can be interpreted by the superposition of two kinds of signals due to the defects in the silicon clusters and in the SiO_2 . The g-values of the defects in the silicon clusters was determined to be g = 2.0035, and g_{\parallel} = 2.000, g_{\perp} = 2.004 in SiO₂, respectively, in the sample annealed at 600°C by Q-band.

A24.8

OPTICAL AND STRUCTURAL PROPERTIES OF SI NANO-CRYSTAL ARRAYS FORMED BY ULTRA LOW ENERGY SI IMPLANTS INTO THIN GATE OXIDES. S. Coffa, E. Castagna, C. Bongiorno, CNR-IMETEM, Catania, ITALY; D. Patti, STMicroelectronics, Catania, ITALY.

Advanced electronics and opto-electronics devices can be fabricated making use of carrier confinement and Coulomb blockade effects in Si quantum dots. In this work we show that ultra-low energy (< 5 keV) Si implantation into thin (5-40 nm) oxides is a suitable technique for producing a well localized array of small (1-3 nm in diameter) Si nanocrystals with a sharp size distribution. Thermally grown SiO₂ layers were implanted with 0.5-5 keV Si ions to fluences of 5×10^{15} - $5 \times 10^{16} / \mathrm{cm}^2$ and annealed at temperatures of 600-1150°C for times up to 4 hrs. Transmission electron microscopy (TEM) measurements show that, when the Si peak concentration is below 1x10²²/cm³ annealing at T> 1000°C are needed in order to form Si nanocrystals. Their size distribution is critically dependent on the implanted fluence and no significant ripening is observed after their nucleation. Photoluminescence (PL) measurements reveals a strong light emission in the 600-800 nm range which can be unambiguously associated to the recombination of confined excitons. A strong correlation between the grain size distribution and the PL lineshape has been found. When the Si peak concentration exceeds $\sim 3 \times 10^{22} / \text{cm}^3$ a buried policristalline Si layer is formed even at temperatures as low as 900°C. This striking reduction in the thermal budget is due to the coalescence of the high density of small Si aggregates formed at the Si projected range. The depth location of this layer is determined by the Si energy and its width is roughly equal to the straggling of the ions. Post oxidation of these layers in a N2+O2 ambient produces the separation of the Si nanograins and the formation of an array of Si

quantum dots with an extremely sharp size distribution. The advantages of this approach with respect to alternative methods such as chemical vapour deposition or aerosol techniques are elucidated.

A24.9

FTIR SPECTROSCOPY AND SPECTROSCOPIC ELLIPSOMETRY STUDY OF NANOCRYSTALLINE LAYERS FORMED BY HIGH-DOSE HYDROGEN AND DEUTERIUM IMPLANTATION IN SILICON. L.N. Safronov, E.V. Spesivtsev, V.P. Popov, I.V. Antonova, A.K. Gutakovskii, V.I. Obodnikov, Institute of Semiconductor Physics, Novosibirsk, RUSSIA, A.P. Stepovik, V.T. Gromov, Federal Nuclear Center, Snezhinsk, RUSSIA.

Structural study of nc-Si layers formed by high fluence hydrogen or deuterium implantation (up to $5 \times 10^{17}~\rm cm^{-2})$ using high current beams with means of current up to 4 mA/cm² was carried out in the present work. The nc-Si:H(D) silicon films were characterized using FTIR spectroscopy, spectroscopic ellipsometry, transmission electron microscopy and secondary ion mass spectrometry. Hydrogen solubility in crystalline silicon is low but ion implantation allows introducing of $10^{22}~\rm cm^{-3}$ of the hydrogen atoms or even more in thin silicon layer. High defect concentration in combination with the very active hydrogen impurity causes the formation of mixed amorphous and nanocrystalline phases with pores similar to porous silicon produced by electrochemical anodization. The transformation of optical properties of these films during annealing in temperature range of 200-1050°C was investigated. The changes in optical characteristics and number of Si-H or Si-D bonds in the spectra of IR absorption is correlated with the increase in crystalline sizes with a temperature.

A24.10

ELECTROREFLECTANCE STUDY OF LIGHT-EMITTING POROUS SILICON THIN-FILMS. Toshihiko Toyama, Akihito Shimode, Hiroaki Okamoto, Dept of Physical Science, Graduate School of Engineering Science, Osaka University, Toyonaka, JAPAN.

Electroreflectance (ER) spectroscopy is a powerful tool for a precise analysis on optical transitions in nanocrystalline Si (nc-Si) [1]. We have measured the ER spectrum of light-emitting porous Si (LPSi), which is the most intensively studied nc-Si, and found 4 transition bands in the ER spectrum The LPSi thin films were made by anodization in HF aqueous solution (50%HF:DI water = 1:1) from p-type crystalline Si (c-Si) (100) substrates with different resistivities of 0.018, 0.1–1, and 4–10 Ω cm. The anodizing current density was 48.7 mA/cm², and the anodizing time was determined by the LPSi thickness of 50-100 nm (typical 1-3 sec). Visible photoluminescence (PL) ($\lambda_{\rm exc} = 325$ nm) is observed with a peak energy of ~ 1.8 eV, and the PL intensity is increased with an increase in the resistivity of the c-Si substrate. The ER features are observed at 293 K at photon energies of ~ 1.2 , ~ 1.9 , ~ 2.9 , and ~ 3.4 eV. The 1.2-eV ER feature would be attributed to the direct-assisted optical transitions at the fundamental gap of LPSi as found in that of the nc-Si thin films made by plasma-CVD and post-anodization [1]. The 3.4-eV ER feature would arise from direct transitions at the $E_1(E_0{\,}')$ gap of LPSi as found in both the nc-Si thin films and c-Si. Whereas the 1.9-eV and 2.9-eV ER features have been found in neither the nc-Si thin films nor c-Si. The ER signal of LPSi made from $0.018\text{-}\Omega\text{cm}$ substrates is different from those of LPSi made from the substrates with higher resistivities; the 3.4-eV ER features seem to be shifted toward lower energies and the ER signal is quite intense. 1. T. Toyama et al., Appl. Phys. Lett. 74, 3323 (1999), Mater. Res. Soc. Symp. Proc. 557 (in press).

> SESSION A25: POSTER SESSION: CRYSTALLIZATION II Chair: Wolfhard Beyer Thursday Evening, April 27, 2000 8:00 PM Salon 7 (Marriott)

 $\begin{array}{l} \textbf{A25.1} \\ \textbf{AFM AND HREM OBSERVATION OF PULSED LASER} \\ \textbf{INTERFERENCE CRYSTALLIZED a-Si:H/a-SiN}_x:H \\ \textbf{MULTILAYERS. Li Wang, Xinfan Huang, Jian Li, Jun Xu, Qiliang Li, Xiaobo Yin, Wenbin Fan, Wei Li, Jianming Zhu, Mu Wang, Zhiguo Liu, <math>\underline{\text{Kunji Chen}}$ National Laboratory of Solid State Microstructure and Department of Physics, Nanjing University, Nanjing, P.R. CHINA.

Nanometer-sized crystalline silicon (nc-Si) has attracted wide attention due to the possibility of a zero-dimensional quantum size effect. In nc-Si system, the visible photoluminescence (PL) and electroluminescence (EL) have been reported. Although a great progress has been accomplished on the investigation of nc-Si system, some difficulties, such as how to accurately control the size and the

location of nc-Si, are still present in the fabrication and investigation of nc-Si. Based on the previous works on the constrained crystallization of amorphous silicon [1], we employed a KrF excimer pulsed laser source through a phase shifting mask grating to irradiate a-Si:H/a-SiN_x:H multilayers to achieve the control of the size and the location of nc-Si. The a-Si:H/a-SiN $_x$:H multilayers were deposited on silicon or fused quartz substrates by computer-controlled plasma enhanced chemical vapor deposition (PECVD) technique. The sublayer thickness of samples was 5 nm for a-Si:H and 10 nm for a-SiNx:H, respectively. A KrF (λ =248 nm) excimer pulse laser with a 20 ns pulse length and an energy density in the range of 50-300 mJ/cm² was used. The irradiation processes were performed in air at room temperature. AFM images of the irradiated samples show that under all laser energy density used in this paper, the stripes corresponding to the irradiated regions are present on the surfaces of the samples with the same periodicity of the phase-shift grating mask, $2.0 \ \mu \text{m}$. And under higher laser density, $300 \ \text{mJ/cm}^2$, the surfaces of the irradiated samples were seriously damaged. In the micro-Raman spectrum of the irradiated samples, a broad peak attributed to amorphous silicon has been observed in the non-irradiated regions and a weak shoulder attributed to nc-Si is present in the irradiated regions. TEM and HREM observations show that nc-Si are formed and the size of nc-Si is determined by the thickness of a-Si:H sublayer. Moreover, the distribution of nc-Si has the periodicity of 2 μm in transverse direction and 10 nm in longitudinal direction. The visible PL and EL have been also observed in laser interference crystallized $a-Si:H/a-SiN_x:H$ mutlilayers. The origin and difference between PL and EL is briefly discussed in this paper. [1] K.J. Chen, X.F. Huang, J. Xu and D. Feng, Appl. Phys. Letts. 61, 2069 (1992)

A25.2

POLYSILICON THIN FILMS OBTAINED BY CW AND PULSED LASER SOURCES FOR TFT ACTIVE LAYER. C. Privato, M.L. Addonizio, P. delli Veneri, A. Imparato, C. Minarini, E. Terzini, ENEA Research Center, Portici, ITALY.

Polysilicon thin films, obtained by Laser Induced Crystallization, are very promising materials for low cost realization of Thin Film Transistor (TFT) and thin film solar cells. This work reports on the comparison between polysilicon thin films obtained by pulsed Nd:YLF laser and cw ${\rm Ar}^+$ laser crystallization of amorphous silicon. The starting intrinsic and n doped materials have been deposited on Corning 1737 glass by LPCVD technique at a deposition temperature of 570°C. The film thickness range is 50-200 nm. A Q switched diode pumped, frequency-doubled Nd:YLF laser at 523 nm wavelength and a cw ${\rm Ar}^+$ laser, at 514 nm wavelength, having a power of 2 W, have been used for crystallization process. The influence of laser power scanning speed on material properties has been evaluated for both the laser sources. Electrical and optical properties of as-deposited and crystallized films have been determined. SEM analysis of Secco etched crystallized material have been used to evaluate grain size and their distribution. Film structure and crystallite size have been analyzed by XRD spectroscopy. The main results of crystallization by pulsed source is the larger grain size observed in the intrinsic material compared with n type material. Grain size of about 1 μm was obtained on intrinsic material having thickness of 50 nm, utilizing an energy density of 590 $\rm mJ/cm^2$ and an overlapping of 90%. Preliminary data of cw source crystallization realized at different scanning speed and at a power of 550 mW point out a wide distribution of grain size in the 45 - 300 nm range achieved on intrinsic materials with thickness of 100 nm. Further investigation is under way in order to improve the cw laser crystallization process by optimizing the optical system and by heating the substrate during irradiation.

A25.3

EXCIMER LASER RECRYSTALLIZATION OF a-Si EMPLOYING ALUMINUM MASKING WINDOW. Jae-Hong Jeon, Min-Cheol Lee, Sang-Hoon Jung, Min-Koo Han, Seoul National Univ, School of Electrical Engineering, Seoul, KOREA.

Excimer laser recrystallization of amorphous silicon (a-Si) film is widely used for the fabrication of polycrystalline thin film transistors (poly-Si TFTs). In order to improve the characteristics of poly-Si TFT, the number of poly-Si grain boundaries should be reduced by increasing the grain size. It has already been reported that the lateral temperature gradient in molten a-Si film induces the lateral grain growth, so that the grain size could be increased considerably. Recently, we have reported that an employment of the masking window during laser irradiation induces the lateral temperature gradient effectively. Our previous experimental results verified that the lateral grain growth took place near the edge of masking window due to an abrupt temperature difference between molten a-Si and unmelted a-Si. The purpose of our work is to report that a metal masking window, which is directly deposited and patterned on a-Si film, enhances the lateral growth effect because high thermalconductive metal pattern cools down the unmelted solid region so the

lateral temperature gradient becomes more significant. We employed 3000 Å thick aluminum (Al) layer for the masking material. Aluminum exhibits high optical reflectance exceeding 90% at 308nm, the wave length of XeCl excimer laser, so it is suitable for the masking pattern. We examined the grain growth with two types of sample using TEM observation. The one employs an intermediate oxide layer, which is thermally insulating material, between Al masking pattern and a-Si film, and the other has direct contact of Al pattern with a-Si film. After laser irradiation, the sample without the intermediate oxide showed the considerably enhanced grain size in micrometer order near the edge of masking pattern, compared with the sample with the intermediate oxide. This result may be attributed to the enhanced temperature gradient in the sample where a-Si film directly contacts with high thermal-conductive metal pattern. We will also report TFT characteristics fabricated by the proposed method.

THE REGULAR ARRANGEMENT OF ENLARGED POLY-Si GRAINS BY SELECTIVE Si ION-IMPLANTATION AND EXCIMER LASER ANNEALING. Min-Cheol Lee, Jae-Hong Jeon, Jin-Woo Park, Min-Koo Han, Seoul National Univ., School of Electrical Engineering, Seoul, KOREA.

Polycrystalline silicon (poly-Si) film with low defect density and uniform grain size is essential to fabricate the high performance poly-Si TFTs for AMLCD application. To improve the uniformity of poly-Si film, several investigations have been focused on the ion-implantation and high temperature thermal annealing. It is well known that ion-implantation with high acceleration energy may form artificial nucleation seeds in amorphous silicon film. Following thermal annealing at around 600°C could increase the grain size larger than 1 micrometer and arrange the poly-Si grains rather uniformly. However, this technique cannot be applied to the low temperature poly-Si TFTs fabrication on glass substrate due to thermal damage. We propose the new laser annealing method to obtain the reproducible low temperature poly-Si film with low defect density and large grain employing the combination of the selective self ion-implantation and excimer laser annealing. Selective self ion-implantation is utilized to form artificial nucleation seeds in a-Si film prior to excimer laser annealing. Through specifically designed implantation mask, we could control the grain boundary location in poly-Si film and may increase the grain size in micrometer order without any other treatment. We observed the grain boundary distribution in the excimer laser annealed film by TEM and crystallinity of the enlarged grain by TEM diffraction image. In our poly-Si film, we observed well arranged grains in which the size is larger than 1 micrometer. We fabricated poly-Si TFTs successfully employing the proposed excimer laser annealing method and measured the performance of poly-Si TFTs. Our experimental data shows that field-effect-mobility is 5 times higher than that of TFT fabricated by conventional excimer laser annealing method and leakage current of new TFT is 2 order lower than that of the conventional TFT due to low defect density.

SESSION A26: POSTER SESSION: HYDROGEN

Chairs: P. Craig Taylor and Jaap I. Dijkhuis Thursday Evening, April 27, 2000 8:00 PM Salon 7 (Marriott)

HYDROGEN INCORPORATION IN a-Si. AN ab initio SUPERCELL APPROACH. Fernando Alvarez, Ariel A. Valladares, UNAM, Instituto de Investigaciones en Materiales, Mexico DF, MEXICO.

We have carried out an extensive ab initio study of hydrogen incorporation in amorphous silicon supercells that contain at least 64 atoms. Hydrogens were placed evenly distributed throughout the cells, with and without voids, which were then annealed at 300 and 400 K and quenched to 0 K using the Fast Structure Simulated Annealing code of MSI. Results will be presented concerning the dynamics of the hydrogen atoms both as a function of annealing temperatures and the presence of voids. The effect of hydrogen incorporation on the radial distribution functions and the electronic structures of the cells will be reported.

A26.2

T-SITE-TRAPPED MOLECULAR HYDROGEN IN a-Si:H. R.E. Norberg, D.J. Leopold, P.A. Fedders, R. Borzi, P.H. Chan, J. Herberg, N. Tomic, Department of Physics, Washington University, St. Louis, MO.

Proton-²⁹Si double resonance NMR measurements on high quality plasma-enhanced chemical vapor deposition a-Si:H deposited from SiH₄ show that more than one third of the contained hydrogen is present as H₂ molecules residing in the amorphous equivalent of T sites. The NMR signal from these trapped H₂ appears primarily in the narrow 4 kHz proton line, which arises from the less clustered hydrogen population. Very little of the molecular component is in the broad $\sim 24~\mathrm{kHz}$ line, which is mostly comprised of clustered hydrogen tightly bonded to silicon.

 $\overline{
m A~STU}$ DY OF NON-INFRARED ACTIVE HYDROGEN BONDING IN a-Si:H THIN FILM USING COMBINED CALIBRATED TEMPERATURE DESORPTION SPECTROSCOPY AND FTIR. D.J. Santjojo, J.C.L. Cornish, Murdoch University, Dept of Physics and Energy Studies, Perth, AUSTRALIA.

Problems which have not been completely resolved in the a-Si:H based solar-cell arise from the microstructural degradation caused by Staebler-Wronski effect (SWE). Hydrogen concentration and its bonding configuration in the film play a significant role in the stability and performance of the devices. A transmission FTIR technique has been utilized to calculate hydrogen concentration and identify qualitatively the hydrogen bonding in the a-Si:H films. However, some hydrogen trapped in the film structure may not be detected by means of FTIR technique. This phenomenon was observed during light-soaking experiment, where the peak at $630~\rm cm^{-1}$ increases during the first 10 hours. This may be explained if non-IR active hydrogen is present in the film and is converted to active Si-H bonds by photon interactions. This work describes a combined method of FTIR and calibrated TDS to measure quantitatively the hydrogen released from the film. Temperature Desorption Spectroscopy (TDS) as a complementary technique is used to analyze the structure of the film. This technique has previously been a qualitative measurement and has not been used to calculate the hydrogen concentration. The non-infrared hydrogen species will be investigated by analyzing the infrared spectra and the TDS spectra of hydrogen released during the annealing or degassing process in four stages. Samples will be exposed to light and then annealed at 180°C and degassed gradually using a linear temperature ramp (.5°C/s). Each stage corresponds to a temperature at which the hydrogen effusion peaks can be found (≈350°C, ≈450°C, ≈575°C, and ≈750°C). Differences in the amounts of hydrogen obtained from the FTIR spectra and the TDS measurement correspond to the non-IR active occluded hydrogen.

TO STUDY THE HYDROGEN DISTRIBUTION IN THE SURFACE, BULK AND INTERFACE OF a-Si:H FILMS EMPLOYING THE INFRARED SPECTROSCOPY. G. Talukder, J.C.L. Cornish, P.J Jennings, Department of Physics and Energy Studies, School of MPS, Murdoch University, Murdoch, WA, AUSTRALIA.

We present the characterisation of both sputtered and GD samples of a-Si:H through thermal hydrogen desorption and infrared spectroscopies. Both types of samples were deposited onto crystalline silicon substrates held at ~100°C. However, depending on other deposition parameters, the sputtered samples contained, predominantly, the higher hidrides, whereas, the GD samples contained, predominantly, the mono-hydride. In fact, we have studied the effects of thickness on the infrared (ir) spectra and those of annealing on both the thermal effusion (TE) and ir spectra of sputtered a-Si:H samples. From the results obtained and from a comparison of the ir spectra of sputtered and GD samples, we have found the distribution of different configurations of Si and H in the a-Si:H films. Thus, we have demonstrated how we can analyze the infrared absorption spectra (or use the infrared spectroscopy) to get information about the distribution of hydrogen in the surface, bulk and substrate-film interface of a-Si:H films.

 $\frac{\textbf{A26.5}}{\textbf{FAST}}_{\textbf{IN-DIFFUSION OF HYDROGEN AT THE INITIAL STAGE}$ OF HYDROGEN PLASMA TREATMENT ON a-Si:H FILMS OBSERVED BY IN-SITU ESR MEASUREMENTS. Ujjwal Kumar Das, Tetsuji Yasuda, Satoshi Yamasaki, Joint Research Center for Atom Technology, NAIR, Tsukuba, Ibaraki, JAPAN.

Time evolution of Si dangling bonds (dbs) in hydrogenated amorphous silicon (a-Si:H) has been observed during hydrogen plasma treatment using in-situ ESR technique, in which a high diffusion coefficent of hydrogen atoms (D_H) was detected at the very initial stage of hydrogen plasma treatment. A remote H plasma, triggered by a microwave power of 50 W, was used to treat the films inside the ESR cavity. Apart from the db terminating properties of H, it can create dbs as well and eventually some additional dbs (ΔN_s) are observed during H treatment. These additional dbs are not created only at the top surface, but a spatial distribution of ΔN_s is apparent from the film thickness dependence of H treatment study. From the time evolution of dangling bond it is speculated that the atomic H initially diffuses very fast $(D_H>10^{-10}~{\rm cm^2/s}~{\rm compared}~{\rm to}~{\rm th}~{\rm normal}~{\rm D_H}>10^{-16}~{\rm cm^2/s}~{\rm at}~{\sim}~200^{\circ}{\rm C},$ observed by SIMS study after long time deuterium plasma treatment of a-Si:H) into some depth of the

film and reacts with the network to form dbs. The characteristic depth of the db distribution is found to be ~ 30 nm at a H treatment temperature of 200°C. Interestingly, the depth of db distribution increases with the decrease of H treatment temperature and does not depend on the film deposition temperature, varied in the range of $80^{\circ}\text{C}\text{-}200^{\circ}\text{C}$. Such a temperature dependence of db distribution suggests that the spatial variation of db is not controlled by any possible increase in the diffusion coefficient of H with temperature, rather it is determined by the activated type of cross section of the reactions between H and the Si:H network.

A26.6

POST-DEPOSITION HYDROGENATION OF HOT-WIRE DEPOSITED SILICON. <u>A.M. Brockhoff</u>, R.E.I. Schropp, W.F. van der Weg, and F.H.P.M. Habraken, Utrecht Univ, Debye Inst, Section Interface Physics, THE NETHERLANDS.

We have found that hot-wire (HW) deposited amorphous and heterogeneous silicon films can be deuterated to anomalously high concentrations using atomic deuterium as produced by the dissociation of D₂ at a hot wire. Usually, hydrogen in amorphous silicon films can be substituted by deuterium through an exchange reaction. In some cases it seems possible to add a small amount of hydrogen to as deposited samples, which is attributed to hydrogen insertion into strained Si-Si bonds [1]. Remarkably, in HW material we find a substantial supplementary incorporation of deuterium. For instance, HW deposited amorphous silicon with an as deposited hydrogen content of 8 at.% exhibits a deuterium content of more than 12 at.% after hot-wire deuteration at 350°C, while a residual amount of 1 at.% hydrogen is still present. The diffusion coefficient of deuterium at 350°C in this material is measured to be in the order of $10^{-15} \ \mathrm{cm^2/s}$, similar to what is found in glow-discharge deposited amorphous silicon in this temperature regime. Techniques applied are elastic recoil detection (ERD) for hydrogen/deuterium and depth profiling, infrared spectroscopy and Raman spectroscopy. The investigations of the behaviour of hydrogen/deuterium in HW deposited silicon have been carried out since the bonding characteristics and the related microstructure of the material is of crucial importance for its (sometimes) excellent device performance. Specifically, the field-effect stability in transistors based on hot-wire deposited silicon is strikingly good [2]. Our results on HW induced incorporation of hydrogen or deuterium indicate the peculiar character of HW deposited silicon and HW processing. [1] A. von Keudell and J.R. Abelson, J. Appl. Phys. 84 (1), 489 (1998). [2] B. Stannowski, R.E.I. Schropp and A. Nascetti, Appl. Phys. Lett. 75 (23), (1999).

A26.7

 $\overline{\text{DIFFUSION}}$ OF HYDROGEN AND DEUTERIUM IN STACK SYSTEMS OF $Si_xN_yH_z/Si_xN_yD_z$ AND CRYSTALLINE Si. Christoph Boehme, Gerald Lucovsky, North Carolina State University, Department of Physics, Raleigh, NC.

In recent years it was confirmed several times, that post deposition anneal of amorphous $Si_xN_yH_z$ anti reflection coatings increase the efficiency of c - Si solar cells beyond an anticipated improvement through reflectivity changes. This improvement, which is clearly due to an increase of the internal quantum efficiency, was explained by two hypothesis: Bulk passivation, through saturation of crystal defect states by hydrogen that diffuses from the coating into the c - Si bulk. Surface passivation by formation of a thin oxide layer during the anneal. To see which mechanism is actually most responsible for the improvement, the diffusion of hydrogen between crystalline silicon and silicon nitride was investigated by observation of H/D, N-H/D-bond and Si-H/D-bond density changes in stacks of C = Si, different thicknesses of SiO_2 , $Si_xN_yD_z$ and $Si_xN_yH_z$ during rapid thermal anneal. The stacks were grown with remote plasma enhanced chemical vapor deposition (RPECVD). This is a low temperature ($\approx 200^{\circ}C$) reaction of downstream injected ammonia (NH_3) and silane (SiH_4) activated by an upstream injected He-plasma, produced through rf-radiation (13.65MHz). Thermal treatment was executed by ex situ rapid thermal anneal in Arambient. For the measurements of H and D bond densities, FTIR was used while SIMS determined atomic densities of H, D and O in the c - Si/nitride interface region. The experiments showed that Htransport in silicon nitride is determined by several mechanisms including diffusion and dissociation processes where molecular species like ammonia and H_2 can develop. Dissociation is dominant at high Hdensities and leads to a rapid loss of H from the system since molecular species have high diffusivities. At low H densities, dissociation reduces strongly, allowing atomic H diffusion between covalent bonding sites to prevail.

A26.8

ISOTOPE EXCHANGE IN HYDROGENATED SILICON-OXYNITRIDE (SiON) FOR 1.55 μm OPTICAL WAVEGUIDE APPLICATIONS. Jinju Lee, Kangguo Cheng and Joseph W. Lyding, Beckman Institute for Advanced Science and Technology, Urbana, IL; H.W.M. Salemink, IBM Research Division, Zurich Research Laboratory, Ruschlikon, SWITZERLAND.

It has been reported that SiON layers can be used for planar optical waveguides in the 1.55 μm wavelength region. SiON can be made with a relatively high refractive index of 1.50. A structure in which SiON is sandwiched between two silicon-oxide (refractive index of 1.45) cladding layers is an effective waveguide candidate for Si-based opto-electronic integrated circuits. Due to the hydrogenated precursors, the as-deposited SiON layers contain N-H bonds. An intrinsic infrared absorption peak at a wavelength of 1.51 μm and the peaks low-energy tail leads to an unwanted absorption loss in the wavelength region of interest (1.545 to 1.565 μ m). We report a novel way of reducing the unwanted absorption loss by replacing N-H bonds with N-deuterium (D) bonds in an isotope exchange process. D was introduced to SiON layers in an atmospheric D anneal after the deposition of SiON. The propagation loss was measured by a moving prism coupling technique. The deuterated SiON showed a factor of 2 less absorption at 1.51 μm than before the D anneal. The loss in the wavelength region of interest, therefore, is significantly minimized. The annealing temperature varied from 450 to 950°C. There seems to be an onset of thermal activation temperature for D to replace H in these structures. This mechanism is being studied carefully by Fourier transform infrared spectroscopy (FTIR) and secondary ion mass spectrometry (SIMS).

SESSION A27: POSTER SESSION: DEFECTS AND TRANSPORT Chairs: Satoshi Yamasaki and J. David Cohen Thursday Evening, April 27, 2000 8:00 PM Salon 7 (Marriott)

A27.1

TRANSPORT PROPERTIES OF POLYCRYSTALLINE SILICON WITH VARIOUS TEXTURES AND MICROSTRUCTURES.

Toshio Kamiya, Kouichi Nakahata, Atsushi Suemasu, Kazuyoshi Ro, C.M. Fortmann and Isamu Shimizu, The Graduate School, Tokyo Institute of Technology, Midori-ku, Yokohama, JAPAN.

We previously reported that high quality polycrystalline silicon (poly-Si) was grown at low temperatures (<300C) from SiF₄/H₂ gas mixtures using a very high frequency (VHF: 100MHz) plasma enhanced CVD (PECVD). Randomly, (220) or (400) orientation structures were chosen by the selection of SiF₄/H₂ gas flow ratio and their microstructures were found to be a strong function of the orientation structure. In this study, we focused on transport properties of these poly-Si in relation with their orientation and microstructures. Film structure was varied by the selection of substrate temperature and $\mathrm{SiF_4/H_2}$ flow ratio. (220) oriented films were grown at small SiF₄/H₂ ratios (<30/40sccm) and (400) oriented films were grown at larger SiF_4/H_2 ratio of $\sim 60/3$ sccm, VHF power of 20W and reaction pressure of 400mTorr. Film thickness was varied from 200 to 1000nm. Transport properties were evaluated from current-voltage measurements in dark and under 100mW white light illumination for undoped poly-Si, and from Hall measurements for P-doped poly-Si. Intermittent hydrogen treatment was also examined to modify defect-density and transport properties of undoped poly-Si. Film structures were studied by X-ray diffraction, Raman scattering spectrum, scanning microscope (SEM), atomic force microscope (AFM), secondary ion mass spectroscopy and spectral ellipsometer. Large Hall mobility of ~8cm²/Vs for low temperature CVD poly-Si was obtained with 1 μ m-thick (400) oriented P-doped film and this value was larger than that of (220) oriented films $(\sim 6 \text{cm}^2/\text{Vs})$. While undoped (400) oriented film showed high dark conductivity $>10^{-3} \mathrm{S/cm}$ for intrinsic crystal silicon. Intermittent hydrogen treatment successfully produced reasonably low dark conductivity (400) oriented film with the Fermi level located near the middle of bandgap.

A27.2

INFLUENCE OF THE GRAIN BOUNDARY BAND OFFSET ON CHARGE TRANSPORT MECHANISM IN MICROCRYSTALLINE SILICON ANALYSED BY NUMERICAL SIMULATION. A. Fantoni, Electronics and Communications Dept., ISEL and FCT-UNL, Lisbon, PORTUGAL; M. Vieira, J. Martins, DEEC-ISEL, Lisbon, PORTUGAL; R. Schwarz, DEEC-ISEL and IST, Lisbon, PORTUGAL.

Microcrystalline silicon can be considered as a two-phase material. We interpreted its composition as grains of crystalline silicon imbedded in an amorphous silicon tissue, with a high concentration of dangling bonds in the transition regions. The boundary regions between the crystalline grains and the amorphous matrix can be treated similarly

to a heterojunction interface. When the band structure of a solid becomes non-uniform, and material parameters like the dielectric constant, the electron affinity and the energy gap become position dependent within the structure, forces in addition to those from the macroscopic electric field act on the carriers, and the non uniform DOS modifies carrier transport. The non-uniform material composition is described through the introduction of two bandparameters into the standard drift-diffusion transport equations. The results we obtained show the band offset at the grain boundaries to cause the appearance of local electric field peaks. Once the equivalent energy gaps are fixed, these peaks are strongly influenced by the nature of such band offset not only in their intensity but also in direction. A shift of the conduction band offset of about 0.3 eV causes a complete reverse of the local electric field peak sign at the grain boundaries. As the material composition is inhomogeneous a two-dimensional solution of the semiconductor equations is required for a correct description of the device operation. We present here results obtained with one and two dimensional simulations of a μc-Si:H p-i-n junction in short circuit condition. The charge transport mechanism is described in terms of the internal electric configuration (carrier concentrations, electric field and potential distribution, drift and diffusion currents) assumed by the junction in thermodynamic equilibrium and illuminated with different monochromatic radiations. Different configurations of the band offset at the grain boundaries are also considered and related to the transport properties in microcrystalline silicon.

A27.3

DEFECT AND TAIL STATES IN MICROCRYSTALLINE SILICON INVESTIGATED BY PULSED EPR. Peter Kanschat, Klaus Lips, Walther Fuhs, Hahn Meitner Institut, Silicium Photovoltaik, Berlin, GERMANY; Helmut Mell, Philipps Universität, Marburg, GERMANY.

We report on a detailed study on paramagnetic states in microcrystalline silicon (μ c-Si:H) performed by pulsed EPR. In contrast to cw EPR the echo detected field sweep spectra are nearly baseline free and allow the detection of broad resonances with relatively low spin densities. All EPR spectra obtained for a doping series deposited by PECVD are fitted by a unique set of peaks. This set consists of: (i) Two dangling bond like resonances at g=2.0052(2) with a nearly constant density of states distribution (DOS) and g=2.0043(2) centered in the lower half of the gap, respectively; (ii) the CE line at g = 1.997 - 1.998 which is known to correlate with n-type doping; (iii) two hyperfine satellites with a splitting a = 119 G centered at the CE line. Their spin density does not directly correlate with the spin density of the central CE line; (iv) a broad resonance (g = 2.075(10), ΔH_{FWHM} = 230 G) which we find to correlate with B-doping. Further insight into the nature of these states is gained by the study of light induced changes of their population. We demonstrate that both the CE and the broad line are enhanced in undoped and slightly doped samples while they are quenched in case of higher doping. Light induced changes of the hyperfine satellites are found not to correspond to the relative changes of the CE line. From our results we assign the CE and the broad resonance to electrons and holes, respectively, trapped on dopant sites and in tail states of their respective bands. Neither free electrons in the conduction band nor free holes in the valence band are detected in μ c-Si:H. We will discuss our results in terms of a qualitative DOS model for μ c-Si:H.

A27.4

NUMERICAL MODELING OF BETA-CONDUCTIVITY IN TRITIATED AMORPHOUS SILICON. <u>Stefan Costea</u>, Franco Gaspari, Tome Kosteski, Stefan Zukotynski, University of Toronto, Dept of Electrical and Computer Engineering, Toronto, Ontario, CANADA; Nazir P. Kherani, Walter T. Shmayda, Ontario Power Technologies, Toronto, Ontario, CANADA.

Tritiated-hydrogenated amorphous silicon (a-Si:H:T) films were prepared using the saddle-field glow discharge deposition method. The decay of a tritium atom produces beta-particles with a mean energy of 5.7 keV. The energetic beta particles create electron-hole pairs in the film, and a He atom. The He atom diffuses away leaving a dangling bond. We analyze the time evolution of the density of dangling bonds (DBs) in the films in terms of beta-conductivity. A model correlating the change in conductivity with the evolution of different types of gap states is presented.

A27.5

LIGHT INTENSITY EXPONENTS AS SENSITIVE TOOLS FOR THE DETECTION OF IMPURITIES IN a-Si:H. L.F. Fonseca, S.Z. Weisz, University of Puerto Rico, Dept of Physics, Rio Piedras, PR; P. Alpuim, V. Chu, Instituta de Engenharia, Lisbon, PORTUGAL; J.P. Conde, Instituto Superior Technico, Dept. of Materials Engineering, Lisbon, PORTUGAL; R. Naides and I. Balberg, Racah Institute of Physics, The Hebrew University, Jerusalem, ISRAEL.

We have shown recently [1,2] that the temperature dependence of the two carriers phototransport properties can yield information regarding the state distribution in the forbidden gap of semiconductors. Of these properties the light intensity exponents of both, the majority carriers, γ_e , and the minority carriers, γ_h , were found to be very sensitive to the details of the distribution. In particular, noting that sub 1/2 values of the exponents are very unusual we have studied their origin in some a-Si:H materials. Finding experimentely [3,4] such sub 1/2 values of γ_e and of γ_h and running computer simulations, of the recombination processes in a-Si:H, lead us to the conclusion that these low values of the exponents are due to recombination centers which have a discrete level. For example the $\gamma_h < 1/2$ results are associated with acceptor-like centers which have a relatively high capture coefficient for holes. We attribute these centers to the unintentional oxygen doping (to a level of $10^{18}~{\rm cm}^{-3}$) of the sample under study. We will show that the oxygen presence, usually ignored in the discussions of a-Si:H, appears to be, in many cases, the dominant factor in the phototransport properties of "intrinsic" a-Si:H. [1] Y. Lubianiker, I. Balberg and L. Fonseca, Phys. Rev. B 55, R15997 (1997). [2] L. Fonseca, S.Z. Weisz, R. Rappaport and I. Balberg, Mat. Res. Soc. Symp. Proc., (1999) in press. [3] P. Brogueira, V. Chu and J.P. Conde, Mat. Res. Soc. Symp. Proc. <u>377</u>, 57 (1995). [4] R. Rapaport, Y. Lubianiker I. Balberg and L. Fonseca, Appl. Phys. Lett. 79, 103 (1998).

A27.6

IMPROVED HIGH RESOLUTION POST-TRANSIT SPECTROSCOPY FOR DETERMINING THE DENSITY OF STATES IN AMORPHOUS SEMICONDUCTORS. C. Main, S. Reynolds, School of Science and Engineering, Univ of Abertay Dundee, UNITED KINGDOM; R.I. Badran, Dept of Physics, The Hashemite University, JORDAN; J.M. Marshall, Dept of Materials Engineering, Univ of Wales Swansea, UNITED KINGDOM.

Post-transit spectroscopy is a variant of the time-of-flight technique in which excess carriers are created by pulsed illumination in a semiconductor structure (e.g. p-i-n). A high reverse field ensures that any excess carriers emitted from traps will transit the structure, to be collected, before re-trapping can occur. The resulting 'post-transit' photocurrent decay I(t) then simply reflects progress of the rate of release of charge from traps distributed in the semiconductors energy gap, g(E). This situation is clearly simpler than the 'pre-transit' photocurrent case in which re-trapping occurs, and so is relatively easier to model and analyse. In principle, a numerical Laplace inversion of the I(t) data allows g(E) to be found. In practice, a delta function approximation of the release time distribution for any given trap results in the simple expression $g(E) \propto tI(t)$ with energy scale E=kTln(vt) where v is the trap attempt-to-escape frequency. Several authors have reported on using this expression, e.g. [1]. What may not be generally known is that even this simple analysis yields a better energy resolution than the various general purpose Fourier and Laplace - based methods which we and others have recently developed [2]. However, in the present work we show how the resolution can be still further improved, without delta function approximation or numerical transformations, by solution of an implicit equation set, (for a finely discretised g(E) rather than a continuum) needing only a least-squares fitting technique with exponential decomposition, to obtain g(E). We demonstrate the remarkable improvement in energy resolution afforded by this straightforward method, using computed post-transit currents for systems containing discrete levels and distributed traps. [1] A Fejfar, G. Juska and J. Kocka, J. Non-Cryst Solids 200, 190, (1996). [2] C. Main, R. Brueggemann, D.P. Webb, and S. Reynolds, Solid State Comms 83, 401, (1992).

A27.7

ON THE ROLE OF CHARGED DEFECT STATES AND DEEP TRAPS IN THE PHOTOCARRIER DRIFT AND DIFFUSION IN a-Si:H. Paul Stradins and Akihisa Matsuda, Thin Film Silicon Solar Cells Super Laboratory, Electrotechnical Laboratory, Tsukuba, JAPAN.

We re-examine the photocarrier continuity equations used to evaluate the ambipolar diffusion length in various photocarrier-grating technique experiments in a-Si:H [1,2]. In contrast to earlier works, we make a clear distinction between the carriers contributing to the drift and diffusion currents, and carriers captured into deep traps waiting for recombination. Only the carriers in the shallow traps experience multiple trapping and contribute to currents according to their drift mobilities and diffusion coefficients. Numerous photocarriers, however, are in the deep traps (especially in defect states) and remain immobile until recombination. They should be excluded from the currents in continuity equations. Nevertheless, they directly affect the charge balance via the Poisson's equation. Due to the asymmetry of the conduction band and valence band tails, most of the negative charge will accumulate in the Si dangling bond defects compensating for the charge of the valence band tail holes. As a result, the positive charge grating of the VB tail holes is approximately counterbalanced by the

grating of the negatively charged defects, while the modulation of the CB tail electron concentration is much smaller. Attributing the drift mobilities and diffusion coefficients to the whole photocarrier populations [1,2] rather than to their fraction in shallow traps and neglecting the defect states as charge reservoirs may lead to a notable underestimate of the carrier drift mobilities, especially for the majority carriers. We discuss the implications of our considerations on the values of the mobility-lifetime products obtained by the Steady State Photocurrent Grating technique (SSPG) and compare our calculations with the SSPG data in a-Si:H for various defect concentrations and exciting light intensity levels.

1. D. Ritter, E. Zeldov, K. Weiser, Phys. Rev. B38 (1988), 8296;

2. U. Haken, M. Hundhausen, L. Ley, Phys. Rev. B51 (1995), 10579.

A 27.8

DISCRETE LAPLACE TRANSFORM TECHNIQUE FOR DIRECT DETERMINATION OF DENSITY OF ELECTRONIC STATES IN DISORDERED SEMICONDUCTORS FROM TRANSIENT PHOTOCURRENT DATA. M.J. Gueorguieva, C. Main and S. Reynolds, School of Science and Engineering, University of Abertay Dundee, Dundee, UNITED KINGDOM.

A technique for direct determination of the density of electronic states (DOS) in disordered semiconductors is presented. This method involves discrete Laplace transformation of transient photocurrent data I(t) followed by the numerical solution of the system of linear algebraic equations (LAE) obtained from the Fredholm integral of the first kind for a discrete DOS. No approximations are used in the solution, and no prior assumptions as to the form of the DOS are made, i.e. the method is truly spectroscopic. By representing the DOS as a set of closely spaced discrete values the Fredholm integral relating I(t) to the DOS may be rendered as a summation, with a simple mathematical procedure then leading to the LAE system. An appropriate choice of Laplace variable prevents the problem becoming 'ill-posed' and a unique solution, avoiding the simplifications necessary in earlier Laplace transform analyses [1, 2, 3], is obtained. We demonstrate the fidelity of this method in comparison to earlier approximate Laplace (and Fourier) techniques by applying each to computer-simulated I(t) data generated from single-level and continuous DOS profiles. The effects of noise and bandwidth limitations inherent in experimental I(t) data on its operation are also illustrated. [1] T. Nagase, H. Naito, J. Non-Cryst. Solids, 227-230, 824 (1998). [2] H. Naito, T. Nagase, T. Ishii, M. Okuda, T. Kawaguchi, S. Maruno, J. Non-Cryst. Solids, 198-200, 363 (1996). [3] H. Naito, M. Okuda, J. Appl. Phys. 77, 3541 (1995).

A27.9

ELECTRONIC DEFECTS AND INTERFACES IN a-Si:H MULTILAYERS. F. Giuliani, E. Fortunato, I. Ferreira, R. Martins, Material Science Department, CENIMAT, Faculty of Science and Technology of the New University of Lisbon, Caparica, PORTUGAL.

Constant Photocurrent Method (CPM) and Photothermal Deflection Spectroscopy (PDS) are commonly emploied to measure the absorption coefficient arising from intragap states in single layer films. By a simple analysis of this intragap absorption spectrum it is possible to evaluate the defect density. When this method is applied to structures with more layers, only an effective absorption coefficient and no quantitative information about defect density can be obtained. But given the already measured single layer spectra it's possible to simulate the effective absorption spectrum to be expected by a multilayer without interface defect states. Comparison of simulated and real PDS data yields information about such states. If the multilayer structure has an ohmic current-voltage characteristic, it is possible to apply also CPM. Since CPM is not sensitive to surface states, comparison of PDS and CPM data gives a check of the simulation reliability. In order to do such check n-i, i-n and n-i-n structures, along with single layers of a-Si:H, have been deposited and characterized

> SESSION A28: POSTER SESSION: THIN FILM TRANSISTORS Chair: Richard L. Weisfield Thursday Evening, April 27, 2000 8:00 PM Salon 7 (Marriott)

A28.1

SIMULATION AND DESIGN OF AMORPHOUS SILICON THIN FILM TRANSISTORS FOR DRIVING THREE COLOR ATCD DETECTOR. D. Caputo, F. Irrera, F. Palma, Dept. of Electronic Engineering, University of Rome La Sapienza, Rome, ITALY; L. Colalongo, University of Bologna, DEIS, Bologna, ITALY; F. Lemmi, Xerox PARC, Coyote Hill Road, Palo Alto, CA.

Use of Adjustable Threshold Color Detectors (ATCD) in large-area arrays requires periodic readout of the photo-charge stored in the capacitance of the device by a transient technique of sensing. In ATCDs, as in any stacked-junction devices, color information is obtained by the self-biasing process: during the integration time, the three junctions independently lose charge; during the readout pulse, the capacitances of the three junctions in electrical series are re-charged. Equilibrium is reached after a few cycles, when the charge lost in a cycle by each junction is the same, and equals the readout one. The amount of this charge is determined by the reverse biased junction and accounts for the light intensity. Dimensioning the a-Si:H Thin Film Transistor (TFT) used as a pixel switch for the ATCD is a critical part of the project of a color imager. The actual design determines the self-bias process duration of the readout accuracy. The large thickness difference between the ATCD junctions makes the constraints for the switching process extremely demanding: since a greater capacitance is expected in the thinner top junction detecting blue radiation, the on-resistance must be reduced. On the other hand, the front junction does not ensure complete rejection of green and red light, so that a calculation must be performed to extract the information on blue radiation implying a high accuracy in the sensing process. In this work we present a simulation study of the self-bias process. Both a-Si:H TFT and the a-Si:H ATCD are simulated by a finite-elements two-dimensional, which allows to study in detail the timing and the accuracy of the self-bias process. A set of design rules for the TFT is also achieved in terms of on-current design including electrostatic capacitance and trapped charge.

A28.2

HYDROGENATED AMORPHOUS SILICON AND SILICON NITRIDE DEPOSITED AT LESS THAN 100°C BY ECR-PECVD FOR THIN FILM TRANSISTORS. <u>A.J. Flewitt</u>, A.P. Dyson, J. Robertson, W.I. Milne, Engineering Department, Cambridge University, Cambridge, UNITED KINGDOM.

Thin film transistors (TFTs) for active matrix liquid crystal displays use hydrogenated amorphous silicon (a-Si:H) for the channel and silicon nitride (a-SiN) for the gate insulator. Plasma enhanced chemical vapour deposition (PECVD) of these materials usually requires substrate temperatures over 200° C which are too high for plastic substrates. Electron cyclotron resonance (ECR)-PECVD produces a highly ionised plasma (>10 16 m $^{-3}$) with very low ion energies (\sim 10 eV). These ions allow the efficient removal of hydrogen from a-Si:H and a-SiN during growth at <100° C. A systematic study has been made of the growth of both a-Si:H and a-SiN by ECR-PECVD. For a-SiN, helium and nitrogen gases are injected so as to pass through the ECR zone. These highly ionised gases then ionise the silane, which is injected downstream. A gas phase reaction occurs between the silane and nitrogen species. Control of the ratio of silane to nitrogen flow is critical for production of stoichiometric a-SiN Material has been produced at 80° C with a Si:N ratio of 1:1.28, a breakdown strength of $8~{\rm MV~cm^{-1}}$ and a resistivity of ${\rm >}10^{14}~\Omega$ cm. For a-Si:H, helium and hydrogen gases are injected into the ECR zone and silane is injected downstream. Control of the deposition rate and ion energy is critical. a-Si:H has been deposited with a low dark conductivity $\sim \! 10^{-11} \; \Omega^{-1} \; \mathrm{cm}^{-1}$ and a high photosensitivity $> \! 10^{5}$ Preliminary characteristics of TFTs made using these materials will be presented.

A28.3

A PHYSICALLY-BASED SPICE MODEL FOR THE LEAKAGE CURRENT IN a-Si:H TFTS ACCOUNTING FOR ITS DEPENDENCIES ON PROCESS, GEOMETRICAL, AND BIAS CONDITIONS. Peyman Servati, Arokia Nathan, University of Waterloo, Dept of Electrical and Computer Engineering, Waterloo, Ontario, CANADA.

In this work, we have developed a physically-based analytical model of the static current-voltage characteristics of the hydrogenated amorphous silicon (a-Si:H) inverted staggered thin film transistors (TFT) in the reverse (leakage) regime ($V_G < 0, V_D > 0, V_S = 0$). The model adequately describes the dependency of the leakage current on geometrical and bias conditions as well as on processing parameters of the source/drain n⁺ contact layers. Here, the deposition temperature of the contact layer determines the phosphorus diffusion profile in the a-Si:H active layer, which in turn affects leakage characteristics at low V_D . The transport mechanisms underlying the leakage behavior can be viewed in terms of charge generation in the p-n diode in the vicinity of the n⁺ drain contact layer and subsequent charge transport along the p-channel at the a-SiN:H/a-Si:H interface. Because of this diode-like behavior at the drain contact area, the leakage current characteristics of the TFT is determined by the profile of minority carriers (holes) in this region, which in turn is affected by defects induced by the diffusion of phosphorus in the region. The mechanism of current flow along the p-channel to the source end is considered to be hole diffusion dominated. We have studied analytically (based on measurement data) the dependence of the leakage current on process

parameters (e.g. the deposition-temperature-dependent phosphorus diffusion profile in the a-Si:H active layer), geometrical parameters (e.g. a-Si:H thickness, source/drain overlap areas), and operating conditions (e.g. \mathbf{V}_G , \mathbf{V}_D). The derived analytical model is implemented in HSPICE. The simulated and measured results are in good agreement with a discrepancy of less than 5%.

FLOATING BODY INDUCED TRANSIENT CHARACTERISTICS IN POLY-Si TFTS. Y.Z. Xu, F.J. Clough, E.M.S. Narayanan and R. Cross, Emerging Technologies Research Centre, Department of Electrical and Electronic Engineering, De Montfort University, Leicester, UNITED KINGDOM.

The realisation of 'system on glass' flat panel displays requires poly-Si TFT capable of high frequency operation. It is well known that the thin film SOI FET has floating body effect, which results in a current surge in the transient procedure for the partially depleted devices and is a limiting factor for its high frequency operation[1]. Although recent reports have investigated the transient characteristics of poly-Si TFTs[2] and a 'capacitance overshoot' effect[3], the full impact of the floating body effect remains unclear. Therefore it is necessary to investigate the impact of the floating body effect on the transient performance of TFTs. This paper reports, for the first time, the results of the transient behaviour of TFTs induced by the floating body effect. N-channel poly-Si TFTs, fabricated using a glass compatible low temperature process, are investigated. Using a 2D numerical simulator[4], the insights of the mechanism governing the transient procedure are obtained and compared with the single crystal FET. It is found that the floating body effect arises from the defect of states in poly-Si thin film. The differences of transient behaviours between the poly-Si TFTs and SOI FETs suggests that existence of defect states is equivalent to doping of the channel region in SOI FETs. By investigating the transient characteristics at elevated temperature, it is also found that capture rates of defect states have a significant impact on the floating body effect.

References:

[1] H.C. Shin, Ik-Sung Lim, et. Al., IEEE Transaction on Electron Devices, Vol. 43, No. 2, 1996, pp 318-325 [2] Y.Z. Xu, F.J. Clough, E.M.S. Sankara, Y. Chen and W.I. Milne, IEEE Electron device letters, February,1999, pp. 80-82 [3] Simon W.-B. Tam, P. Migliorato, O.K.B. Lui and M.J. Quinn, IEEE transaction on electron devices, Vol. 46, No. 1, January 1999 [4] 'TMA MEDICI 4.0 and Trapped Charge AAM', Technology Modelling Associates Inc. Palo Alto, USA

A28.5
THIN FILM TRANSISTORS MADE OF 950°C POLYSILICON ON STEEL FOIL. Ming Wu and Sigurd Wagner, Princeton University, Department of Electrical Engineering, Princeton, NJ.

Amorphous silicon can be crystallized on steel foil passivated with SiO_2 at temperatures up to 950°C. The resulting polycrystalline films furnish channel material for thin film transistors (TFTs) with good electrical performance. Our motivation for developing this silicon-on-steel process is threefold. (1) The time to crystallization drops from hours at 600°C to seconds at 950°C. (2) Polysilicon on steel foil can provide rugged, flexible backplanes with TFTs for matrix and driver circuits. (3) A TFT on steel foil process may be amenable to manufacture on continuous web. Stainless steel foil substrates are coated with $\sim 0.5 \mu m$ of SiO₂ for planarization and electrical insulation. 200-nm thick a-Si:H films are deposited by PECVD at 150°C and then crystallized by furnace anneal at 600°C to 950°C, for 6 hours to 20 seconds. The films are processed to top gate TFTs with 200-nm PECVD SiO₂ gate dielectric. We use both a non-self-aligned and a self-aligned process. For the former an n⁺ μ c-Si source /drain is deposited at 350 °C, and for the latter P is ion implanted into the source/drain openings and the gate silicon. Thermally evaporated Al is used for source, drain, and gate contacts. The non-self-aligned channel has a width/length of $180\mu m/45\mu m,$ and the self-aligned channel is $50\mu m/50\mu m.$ To date the best TFT performance has been obtained with polysilicon To date the best 1F1 performance has been obtained when performed crystallized at 650°C, where the electron field effect mobility is 64 cm²V⁻¹s⁻¹ in the linear and saturated regimes. The TFTs made from the 950°C polysilicon have $\sim 12~{\rm cm}^2 {\rm V}^{-1}{\rm s}^{-1}$ in both regimes. The OFF current in all TFTs is $\sim 1~{\rm nA}$. These characteristics suggest that contamination from the steel substrate is not important at any of the crystallization temperatures. At the symposium we will report TFT results of current experiments on crystallization and device processing.

ROUGHNESS OF TFT GATE METALLIZATION AND ITS IMPACT ON LEAKAGE, THRESHOLD VOLTAGE SHIFT AND MOBILITY. A. Nathan, R.V.R. Murthy, B. Park, A. Sazonov and S.G. Chamberlain*, Department of Electrical and Computer Engineering, University of Waterloo, Waterloo, Ontario, CANADA. *DALSA Inc., Waterloo, Ontario, CANADA.

A systematic study of the sputter deposition conditions for Al thin films employed as gate metallization is presented. Here, we vary sputtering parameters such as deposition temperature, process pressure, and power, all of which have a strong bearing on the surface roughness of the film. For example, films deposited at low temperature (30°C) and low process pressure (5mTorr), appear to have a significantly reduced roughness with corresponding transistors yielding a low leakage current ($\sim 10 {
m fA}$ at low ${
m V}_{DS}$), an ON/OFF current ratio better than 10^8 , and a mobility of $1.1 {
m cm}^2/{
m Vs}$, values comparable to those reported for Mo or anodized Al gate TFTs. In contrast, films deposited at 150°C and 10mTorr yield a degradation in mobility to 0.77cm²/Vs and an increase in leakage current to 1pA, caused by the high interface roughness due to hillock formation on the Al gate. Also the corresponding shift in threshold voltage is large After one-hour bias stress of +25V applied to the gate, the shift in threshold voltage is ~5V, as compared to the small shift ~2.3V associated with the smoother gate. We attribute this to the (and perhaps even singular) localized electric fields stemming from surface non-uniformity in the channel. The same reasons hold for the increased leakage current, which we believe is due to an electric field dependent Frenkel-Poole type carrier generation in the active region. The field effect mobility in these transistors, retrieved from the associated transfer characteristics, clearly shows the impact of surface roughness on mobility degradation. For comparison, we have also studied a TFT whose Al gate is now capped with 20nm of Mo to minimize propagation of the gate surface roughness to the active channel. SEM cross sectional views show high interface smoothness to yield significantly improved leakage, stability, and mobility.

A28.7

TRANSITION METAL SILICATE ALLOYS - ADVANCED GATE DIELECTRIC MATERIALS FOR HIGH PERFORMANCE THIN FILM TRANSISTORS, TFTs. Bruce Rayner, Robert Therrien, Hiro Niimi and Gerald Lucovsky, North Carolina State University, Raleigh,

In order to meet the year 2010 challenges presented in the SIA National Technology Roadmap for Semiconductors, high-k alternative gate dielectrics are being developed to replace SiO2, and silicon nitride and oxynitride alloys. As TFT technology evolves from hydrogenated amorphous Si, a-Si:H, to poly-crystalline silicon, poly-Si, advances in gate stack technology developed for these scaled c-Si devices can be transported to the poly-Si TFT technology and thereby provide opportunities for enhanced device performance. This paper describes materials and device research performed on two qualitatively different SiO2-transition metal oxides: i) one in which there is a chemically-ordered compound silicate phase: ZrO2-SiO2, and ii) a second in which there is no compound phase: Ta₂O₅-SiO₂ Thin films have been prepared by 300°C remote plasma-enhanced chemical vapor deposition using i) plasma excited O2/He mixtures, and ii) downstream injected alkoxides as source gases for the transition metal alloy constituents, and SiH4 as the source gas for Si. To suppress reactions between the Si surface and the oxygen and metal organic precursors, an ultra-thin passivating layer of nitrided SiO₂ is formed by plasma assisted oxidation and is followed by interface nitridation. Composition, local atomic bonding and film morphology have been determined by Rutherford back scattering, RBS, X-ray photoelectron, spectroscopy, XPS, infrared absorption spectroscopy, IRAS, Raman scattering, X-ray diffraction, XRD, and high resolution transmission electron microcopy, HRTEM. Compositional and structural phase diagrams have been constructed for as-deposited and annealed films. For the ZrO2-SiO2 system, these diagrams are separated into two qualitatively-different regions by the compound composition, $ZrSiO_4$ whereas in the Ta_2O_2 -SiO₂ system, the absence of a compound means that the corresponding diagram is continuous between the end-member oxides. Finally, the paper will present the results of current-voltage, I-V, and capacitance-voltage, C-V, measurements from which dielectric constants, tunneling masses and band offset energies have been determined. Supported by the SEMATECH/SRC FEP center, ONR and AFOSR.

> SESSION A29: POSTER SESSION: HETEROGENEOUS SILICON DEVICES Chair: Domenico Caputo Thursday Evening, April 27, 2000 8:00 PM Salon 7 (Marriott)

MEMORY EFFECTS IN MOS CAPACITORS WITH SILICON RICH OXIDE INSULATORS. S. Lombardo, I. Crupi, S. Coffa, C Spinella, C. Bongiorno, CNR-IMETEM, Catania, ITALY; C. Gerardi, B. Fazio, M. Melanotte, STMicroelectronics, Catania, ITALY.

Crystalline Si dots embedded in SiO₂ show electron transport in the regime of quantum Coulomb blockade at room temperature for grain sizes of the order of a few nanometers. Thus, this composite material and in particular its Si dots have been proposed for the reversible storage of charge in the gate stack of single electron memories characterized by very compact one transistor cells. Such structures have a strong potential for ultra-low power, multi-bit storage, and for capacities above 1 Gb. To form crystalline Si dots embedded in SiO2; we have either deposited thin films of silicon rich oxide (SRO) by plasma-enhanced chemical vapor deposition of SiH4 and O2, or implanted Si ions into thermally grown SiO2. Then the materials have been annealed in N2 ambient at temperatures between 950 and 1100°C. Under such processing, the supersaturation of Si in the amorphous SRO film produces the formation of crystalline Si dots embedded in SiO2. The narrow dot size distributions, analyzed by transmission electron microscopy, are characterized by average grain radii and standard deviations down to about 1 nm. The memory function of such structures has been investigated in MOS capacitors with a SRO film sandwiched between two thin SiO2 layers as insulator and with an n⁺ polycrystalline silicon gate. The operations of write storage, and erase, are clearly detected by measurements of hysteresis in capacitance-voltage characteristics, and they have been systematically studied as a function of bias and temperature in a number of different SRO structures.

A29.2

CAPACITANCE-VOLTAGE CHARACTERISTICS OF POLY-SILICON-POLYSILICON OXIDE-POLYSILICON STRUCTURES FOR THREE-DIMENSIONAL MEMORY. John Lindsey and T.S. Kalkur, Microelectronics Research Laboratories, Department of Electrical and Computer Engineering, University of Colorado, Colorado Springs, CO.

Three-diemsional integration offers a dramatic reduction in chip area required per bit and has long been a research objective. Three-dimensional integration with thin film transistors (TFTs) requires detailed parametric analysis with techniques such as Capacitance-Voltage (C-V) characterization. C-V analysis of polysilicon TFT's uses polysilicon-oxide-polysilicon thin film structures. Most of the C-V analysis involving polysilicon available to date, however, is with polysilicon-oxide-bulk silicon structures. In this paper, we report the results of modeling and measurement of the C-V characteristics of polysilicon-polysilicon oxide-polysilicon for doped and undoped polysilicon. To increase the conductivity of the polysilicon, elevated temperatures were used for measurement. CV measurement matching the theoretical curves were made for these polysilicon films. Oxide thickness, series and shunt resistance were extracted and correlated to process problems and splits.

A29.3

INFLUENCE OF MECHANICAL STRESS ON THE ELECTRICAL PERFORMANCE OF POLYCRYSTALLINE-SILICON RESISTORS. M. Nakabayashi, Mitsubishi Electric Co., Nishigoshi, Kumamoto, JAPAN; H. Ohyama, K. Kobayashi, M. Yoneoka, Kumamoto National College of Technology, Nishigoshi, Kumamoto, JAPAN; E. Simoen, C. Claeys, IMEC, Leuven, BELGIUM; Y. Takami, Rikkyo University, Kanagawa, JAPAN; H. Sunaga, H. Takizawa, Takasake JAERI, Gunma, JAPAN.

Results are presented of a study on the mechanical stress dependence of the resistance of polycrystalline silicon (Poly-Si) films, doped with different atomic species. Two types of Poly-Si films implanted with boron and phosphorus ions were used, respectively. Poly-Si films of 400 nm (to be used for boron doping) and 250 nm (to be used for phosphorus doping) thickness were deposited by LPCVD at 620°C on thermally oxidized silicon wafers. Film doping was done by ion implantation at 50 KeV, with a dose of boron and phosphorus of 2 x 10^{14} and 5.3 x 10^{14} cm⁻², respectively. The samples were annealed in a $\mathrm{H_2}$ ambient at 1000°C for 20 min to activate the implanted atoms. The geometry of the resistors was defined by standard photolithographical and etching processes. The width and length of the resistors were 6 and 60 μ m, respectively. A 600 nm SiO₂ film was deposited by LPCVD at 420°C, and subsequently sintered in a N₂ ambient at 950°C for 30 min. Then the SiO2 film was was etched by RIE to allow contact between the electrodes and the Poly-Si. The metallization patterns were defined using photolithography and RIE etching. A silicon nitride film was deposited at 300°C to a thickness of 750 nm by plasma enhanced CVD and finally a H₂ treatment was performed at 400°C for 30 min. We investigated how mechanical stress affected the conductivity of the Poly-Si film, by measuring the resistance using convex wafer stages with a projection from 0.1 to 1 mm and concave wafer stages with a sag from 0.1 to 1 mm. The resistance of PolyiSi films implanted with boron ions was increased by mechanical stress, while the resistance of Poly Si films implanted with phosphorus remained unchanged. It is concluded that this difference is related to the structural differences between Poly-Si films implanted with boron and phosphorus, respectively.

A29.4

FABRICATION OF PIEZORESISTIVE PRESSURE SENSOR BASED ON POLY-Si. Lim Jae Hong, Seok Jin Yoon, Young Soo Yoon, Korean Institute of Science and Technology, Thin Film Technology Research Center, Seoul, KOREA.

A pressure sensor based on poly-crystalline silicon thin film whose merits are nearly linear change in piezoresistance according to water level and no current leakage over 150° was fabricated. Polysilicon diaphragms with various sizes were fabricated using dry etching and bulk micromaching based on wet etching. In order to compose the diaphragm structure, silicon dioxide, silicon nitride, poly-silicon and silicon nitride are deposited on silicon substrate in order. Those were dry-etched by reactive ion etcher to make a mask pattern. The polysilicon diaphragm was wet-etched by EPW (Ethylenediamine, pyrocatechol, water). The etch rate is 71.109 micrometer/hr(1.185 micrometer/min) at 110°. After making diaphragm, silicon to glass bonding based on anodic bonding technique was conducted to deliver a pressure to opposite surface of the diaphragm. A pressure change induced the change of the polysilicon diaphragm curvature, which made the change the resistance of the patterned polysilicon electrode. The resistance changes were linear at low-pressure level, while a little bit nonlinear at high-pressure level. The result is that the change in piezoresistance is 4.4E-4O/psi. More detail results will be presented.

> SESSION A30: POSTER SESSION: AMORPHOUS SOLAR CELLS Chairs: Vikram L. Dalal and Scott J. Jones Thursday Evening, April 27, 2000 8:00 PM Salon 7 (Marriott)

A30.1

DEPENDENCE OF PHOTOVOLTAIC PROPERTIES OF HYDROGENATED AMORPHOUS SILICON P-I-N DEVICES ON THE DENSITY OF DEFECTS IN THE INTRINSIC LAYER.

Tome Kosteski, Franco Gaspari, Stefan Costea, Stefan Zukotynski, University of Toronto, Dept of Electrical and Computer Engineering, Toronto, Ontario, CANADA; Nazir P. Kherani, Walter T. Shmayda, Ontario Power Technologies, Toronto, Ontario, CANADA.

Tritiated-hydrogenated amorphous silicon (a-Si:H:T) was used for the intrinsic (i-) layer of a p-i-n hydrogenated amorphous silicon photovoltaic device. The bonded tritium atom decays into a beta particle and He leaving behind a dangling bond. The photovoltaic properties of the device, namely the short circuit current (Isc), open circuit voltage (Voc) and fill factor (FF), were measured as a function of time. The decrease in Isc, Voc and FF were correlated with the increase in the dangling bond density of the intrinsic layer which manifests itself by decreasing the lifetime of carriers in the intrinsic region and also increasing the effective series resistance of the device.

A30.2

CORRELATION BETWEEN FILM AND CELL PROPERTIES FOR DC PLASMA DEPOSITED AMORPHOUS SILICON.

<u>Jennifer Heath</u>, Yoram Lubianiker, J. David Cohen, Univ. of Oregon, Dept. of Physics, Eugene, OR; Gautam Ganguly, BP Solarex, Toano, VA.

We have carried out measurements to try to correlate amorphous silicon film properties with companion solar cell device performance. The films and devices were deposited at Solarex in a double-load lock research reactor using dc plasma decomposition. The films were i-layers deposited onto p $^+$ -type crystalline Si substrates and the device structure was glass/TCO/p/i/n/ZnO/Al. For the devices only the i-layers were varied to match the growth conditions of the corresponding films. In some cases, a thin pure silane buffer layer was deposited prior to the deposition of the a-Si:H layers to ascertain its effect upon subsequent growth. Cell performance was explored in both the as-grown and light-soaked states. Cell efficiency decreased from a maximum of 8.5% to 7.5% as the i-layer growth rate was increased by a factor of 3 by increase of the plasma power, while the relative degradation of efficiency after 1000h of light soaking remained about 20%. The film properties in the corresponding annealed and degraded states were determined using drive-level capacitance profiling (DLCP) and transient photocapacitance spectroscopy. The DLCP technique was used to establish quantitative values of the deep defect densities in the films as well as the spatial uniformity of their electronic properties. Defect densities of annealed samples ranged from 1 to 3 \times 10¹⁵ cm⁻³, and degraded by about a factor of 10 upon light scaling , and degraded by about a factor of 10 upon light soaking. The photocapacitance method provided a sub-band-gap spectra of each film. These indicated Urbach energies of 49±1 meV and optical gaps of 1.81±0.05 eV. Because these thin film characterization methods employ a sandwich device structure very similar to the

working solar cell devices, the material properties and cell parameters are more likely to exhibit clear correlations across the wide range of growth conditions employed. Distinct correlations are indeed observed in several regards and will be discussed.

COMPARATIVE STUDY OF a-SiGe SOLAR CELLS AND MATERIALS DEPOSITED USING DIFFERENT HYDROGEN DILUTION. H. Povolny, P. Agarwal, S. Han and X. Deng, Univ of Toledo, Dept of Physics and Astronomy, Toledo, OH.

Although the correlations between amorphous silicon based solar cell device performance and a variety of intrinsic layer (i-layer) materials properties have been studied broadly, somewhat conflicting findings in terms of the existence of a reliable correlation have been reported, partially due to the different ways used for depositing these materials. In this paper, we report our study on the light soaking degradation of amorphous silicon germanium solar cells and the corresponding intrinsic i-layer materials deposited using different hydrogen dilution R, hydrogen flow/(germane+disilane flows). a-SiGe n-i-p solar cells with i-layer deposited with a germane to disilane ratio of 0.72 and R values of 1.7, 10, 30, 50 and 120 are deposited on stainless steel substrates without the use of a back-reflector. This germane to disilane ratio represents what we use for the bottom cell of our standard triple-junction solar cells. Solar cell I-V and quantum efficiency were measured for these devices. Light soaking test has been performed for these devices under 1 sun light intensity at 50 C. While device with R=30 shows the highest initial efficiency (6.8%), the device with R=120 exhibit the highest stabilized efficiency (6.1%) after 100 hours of light soaking. Single-layer a-SiGe films deposited under the same conditions as the i-layer of these devices were deposited on a variety of substrates including crystalline silicon, 7059 glass, and stainless steel for the measurements of IR, Raman, refractive index, bandgap, dark- and photo-conductivity, and hydrogen effusion. It is interesting to note that the bandgaps of a-SiGe with R=10 to 50 were around 1.48 eV while the bandgaps of a-SiGe with R=1.7 and 120 were both higher, at around 1.515 eV, most likely due to the increased amount of H incorporated in these films. We think that the additional H atoms in these two films are bonded to the Si network structurally differently. Detailed comparative study of the light induced degradation of solar cell performances and the structural and optoelectronic properties of the corresponding films will be reported at the conference.

MODIFICATION OF ZnO WORK FUNCTION BY H OR O3 EXPOSURE AND EFFECTS ON a-Si:H SOLAR CELL PERFORMANCE. John F. Kaeding, John R. Abelson, University of Illinois, Department of Materials Science and Engineering, Urbana, IL; Tianming Bao, BP Solarex, Toano, VA.

The existence of a potential barrier at the interface between n-type transparent conductive oxide (TCO) and p-type a-Si,C:H layers is thought to reduce the efficiency of p-i-n photovoltaic devices. In previous work using an in situ Kelvin probe (contact potential) method, we showed that the work function of ZnO can be reversibly cycled by as much as 1 V using sequential surface treatments by atomic hydrogen and ozone.* Measurements during deposition of the p-type a-Si,C:H and undoped a-Si:H films indicated that the reduction in interface potential barrier was stable. In this work, we report how changes in the work function of ZnO films modify the efficiency of p-i-n photovoltaic devices deposited at the BP Solarex Thin Film Division and analyze the effect in terms of potential barrier, carrier recombination rate, and TCO conductivity. * A. Nuruddin and J. R. Abelson, In-Situ Kelvin Probe Analysis of the p+/i Interface Potential, spring MRS meeting (1196).

SUPRESSION OF PLASMA DAMAGE ON SnO2 BY MEANS OF A DIFFERENT SURFACE CHEMISTRY USING DICHLOROSILANE. T. Nakashima, M. Kondo, Y. Toyoshima, A. Matsuda, Thin Film Silicon Solar Cells Super Laboratory, Electrotechnical Laboratory, Ibaraki, JAPAN.

The fabrication process of a p-i-n solar cell with a superstrate structure includes the deposition of a p-layer on a transmittance conductive oxide (TCO) coated substrate such as SnO2. In this process, SnO₂ is damaged by plasma due to reduction by atomic hydrogen in plasma enhanced chemical vapor deposition (PECVD). This reduction causes the darkening of SnO₂ because of the appearance of metallic Sn, and is more significant at higher substrate temperatures, which limits the process temperature of the solar cells. Very recently it was found that surface coverage during the deposition of thin film silicon using dichlorosilane/hydrogen source gas is not hydrogen but chlorine[1]. In this paper, we report the effect of the different surface chemistry of chlorine on the reduction of SnO2. Amorphous silicon was deposited on a SnO₂ coated substrate

(ASAHI-U) using RF-glow discharge decomposition of SiH₂Cl₂ diluted by H₂. Substrate temperature was 100-250°C, and pressure is 20-300mtorr. We evaluate the degree of the damage by a ratio of transmittance with and without a-Si:H layers in the IR-region where a-Si:H is transparent, but presence of Sn decreases the transmittance. At 180°C which is a usual a-Si:H solar cell process temperature, the transmittance for a-Si:H deposited from SiH2Cl2 shows higher transmittance than that from SiH₄. This result is explained in terms of chemical reaction of chlorine at the interface which prevents from reduction of SnO₂ by atomic hydrogen. [1] L. Guo, Y. Toyoshima, M. Kondo and A. Matsuda, Appl. Phys. lett.75.(1999) in press

A30.6

LIGHT TRAPPING BY PERIODICALLY STRUCTURED TCO IN THE SUB-MICROMETER REGIME. C. Eisele, C.E. Nebel, M. Stutzmann, Walter Schottky Institut, TU-München, GERMANY.

The efficiency of thin film solar cells strongly depends on light trapping effects as the solar cells are generally thinner than the required thickness to absorb visible and near IR light. Amorphous solar cells are therefore grown on textured TCO which shows a random roughness with about one micrometer periodicity. Whether this is the optimized geometry of light trapping structures for a-Si:H solar cells has up to now not been discussed. In this paper we present optical properties of solar cells deposited on well defined light trapping geometries. We use planar TCO (Al doped zinc oxide) which is covered by photoresist (spin-on-process). The photoresist is illuminated by an interfering laser beam to generate micro- and submicrometer masks on TCO. As etchant HCl is used. The period of the structures, determined by atomic force microscopy (AFM), varies between 400 nm and 2 micrometer with rectangular or pyramidal geometries. The optical properties of these TCOs and the solar cells grown on top of theses structures are measured by conventional transmission reflection experiments (macroscopic) and by spatially resolved optical experiments (microscopic properties) with a lateral resolution of about 0.8 micrometer. These experiments show that optimal light trapping is achieved for periods smaller than one micrometer and amplitudes in the range of about 100 nm. By tuning the geometry, scattering governs the absorption of visible light and diffraction the IR-part of the solar radiation. A detailed discussion of the optical properties of these periodic light trapping structures will be given.

 $\overline{ ext{MODE}}$ LLING THE OPTICAL QUANTUM EFFICIENCY OF THIN FILM AMORPHOUS SILICON SOLAR CELLS. Sally-Anne F Rowlands, John Livingstone, University of Western Australia, Dept Electrical and Electronic Engineering, Perth, AUSTRALIA; Chris P. Lund, Murdoch University, Dept Physics and Energy Studies, Perth, AUSTRALIA.

The optical quantum efficiency and spectral response of p-i-n thin film (a-Si:H) amorphous silicon solar cells have been modelled using software based on optical admittance analysis. The optical constants of a-Si:H and ITO thin film layers have been measured by Variable Angle Spectroscopic Ellipsometry (VASE) and used as inputs into the optical admittance analysis program in order to model cells constructed from these films. Amorphous silicon (a-Si:H) thin films and p-in assemblies have been deposited by Glow Discharge and Reactive Sputtering techniques. The optical constants were determined by VASE, the hydrogen content of the films has been determined by FTIR spectroscopy, and the thickness of the films verified by Scanning Electron Microscopy studies. The optical constants of commercially available transparent conducting oxide (TCO) coated substrates have been determined by VASE. The experimental UV/vis transmission spectra of p-i-n assemblies are compared with those predicted by the model. Results of modeling different a-Si:H solar cell structures using these materials are presented, including a study of the optimal TCO layer thickness for p-i-n a-Si:H solar cells.

A30.8
OPTICAL MODELING OF AMORPHOUS SEMICONDUCTOR SOLAR CELLS: ANALYTICAL EXPRESSIONS FOR THE COMPONENT LAYER OPTICAL FUNCTIONS. R.W. Collins, A.S. Ferlauto, P.I. Rovira, G.M. Ferreira, Lihong Jiao, and C.R. Wronski, Materials Research Laboratory and Center for Thin Film Devices, The Pennsylvania State University, University Park, PA

Calculating the spectroscopic reflection losses and absorption profiles for amorphous silicon-based multijunction solar cells is a necessary first step in performance modeling. Likewise, obtaining accurate spectra in the index of refraction n and absorption coefficient α over the full solar spectrum for the component layers of the cell is an important first step in optical modeling. We have applied ex-situ transmission and reflection spectroscopies, dual beam photoconductivity, and ex-situ and real-time ellipsometric and Stokes

vector spectroscopies to extract the optical functions of the component layers used in multijunction solar cells, including intrinsic amorphous semiconductor layers of variable optical bandgap, microcrystalline doped layers 100 Å in thickness, transparent conducting oxides in textured and specular forms, and metallic back reflectors. For such layers, we have developed analytical expressions for the optical functions, using a minimum number of physicallymeaningful parameters. For the i-layers, as an example, our expression for the dielectric function ε is Kramers-Kronig-consistent and is valid on a logarithmic scale. It includes an Urbach tail at low energies, a parabolic band-to-band region at intermediate energies (applying a constant dipole matrix element), and a Lorentz oscillator extending to high energies. Using this expression for ε , we can fit experimental data in $[n, \log(\alpha)]$ over the full solar spectrum, obtaining a set of seven parameters. For optimum i-layers of solar cells, these parameters are found to be polynomial functions of the optical gap. As a result, $[n, \log(\alpha)]$ spectra can be generated for amorphous semiconductors having arbitrarily-assigned optical gaps. Furthermore, the effects of material characteristics such as disorder and density deficits on the reflection and absorption characteristics of the solar cell can be computed explicitly. Finally, we present absorption profiles for multijunction solar cells that demonstrate the utility of our analytical expressions.

> SESSION A31: FROM MATERIALS TO TFTs Chair: Isamu Shimizu Friday Morning, April 28, 2000 Salon 7 (Marriott)

8:30 AM <u>A31.1</u>

A JUNCTION FIELD EFFECT TRANSISTOR BASED ON HYDROGENATED AMORPHOUS SILICON. D. Caputo, G. de Cesare, V. Kellezi, A. Nascetti, F. Palma, University of Rome La Sapienza, Dept. of Electronic Engineering, Rome, ITALY.

An hydrogenated amorphous silicon junction field effect transistor suitable for analog and digital applications is presented. The device is constituted by a $p^+ - i - n$ junction, with the drain and source contacts patterned on the n-doped layer and the gate electrode patterned on the p^+ doped layer. As in the crystalline case, the device is a voltage-controlled resistor, and its drain-source resistance can be varied, with a voltage applied to the gate electrode, by modulating the width of the depletion layer extending into the n-type channel. The doping value of this layer has been chosen to ensure an ohmic contact between the semiconductor and the evaporated aluminum layer, the highest value of channel conductivity resulting from our deposition system and a relatively low defect density in the material. The manufactured device, with $W/L = 5000/200 \,\mu\text{m}$, shows the typical current-voltage curves of a JFET, where the pinch-off and the triode regions are well distinguished. In particular, the JFET saturates for drain/source voltage, V_{ds} , higher than 20V and 10V at gate/source voltage V_{gs} equal to 0V and \sim 10V respectively. At lower V_{ds} , the current presents the linear behavior of the triode zone, where the JFET operates as a linear resistance whose value is controlled by the gate voltage. Regarding its application in linear circuit, first results are very encouraging, since we have achieved transconductance values of 10^{-6} V/A, which are comparable to those of state of the art TFT.

8:45 AM A31.2

THIN FILM TRANSISTORS WITH ELECTRON MOBILITY OF 36 cm²V⁻¹s⁻¹ MADE FROM DIRECTLY DEPOSITED INTRINSIC MICROCRYSTALLINE SILICON. I-Chun Cheng and Sigurd Wagner, Princeton University, Department of Electrical Engineering, Princeton, NJ; Marcelo Mulato, Xerox Palo Alto Research Center, Palo Alto, CA.

Microcrystalline silicon (μ c-Si:H) with the electrical conductivity of intrinsic silicon, $\sim 10^{-8}$ to 10^{-7} S·cm⁻¹, can be deposited from a glow discharge in the presence of chlorine. This low conductivity translates to a low off current in μ c-Si:H thin film transistors (TFTs). Because the deposition temperature for this μ c-Si:H is as low as that of hydrogenated amorphous silicon (a-Si:H), it has become of particular interest upon the recent demonstration of p-channel operation and of an integrated CMOS inverter. These devices suggest the potential for a full-fledged, ultra-low temperature silicon technology, competitive with polycrystalline silicon made on glass at 600°C. We report on top-gate n channel μ c-Si:H TFTs with electron mobility up to 36 cm²V⁻¹s⁻¹ and ON/OFF ratio up to 10^6 . The μ c-Si:H was

up to $36~{\rm cm^2V^{-1}s^{-1}}$ and ON/OFF ratio up to 10^6 . The $\mu c\text{-Si:H}$ was grown from silane, dichlorosilane, and hydrogen. The glow discharge was excited at a frequency of 80 MHz to raise the growth rate above that achievable with $13.56~{\rm MHz}$. Deposition temperatures were $230^{\circ}{\rm C}$ for the i-layer and $280^{\circ}{\rm C}$ (the highest temperature in the process) for the n⁺ source and drain layer. The TFTs were fabricated on 340-nm thick $\mu c\text{-Si:H}$ films, and with a 300-nm gate insulator of plasma deposited ${\rm SiO}_2$.

For TFTs with channel width/length of $180\mu\text{m}/45\mu\text{m}$ we obtain off currents in the 10^{-10} A range and on currents in the 10^{-4} A range. In 23 samples the linear electron mobility averages at 16 ± 6 cm²V⁻¹s⁻¹, and the saturated mobility at 23 ± 10 cm²V⁻¹s⁻¹. High threshold voltages of 15 to 25 V reflect an immature device fabrication technology. At present we are modifying the deposition of the $\mu\text{c-Si:H}$ film as well as the device process, and will report the results at the symposium.

9:00 AM <u>A31.3</u>

LOW TEMPERATURE POLY-SI LAYERS DEPOSITED BY HOT WIRE CVD YIELDING A MOBILITY OF 4.0 cm²/Vs IN TOP GATE THIN FILM TRANSISTORS. R.E.I. Schropp, J.K. Rath, B. Stannowski, C.H.M. van der Werf, Utrecht University, Debye Institute, THE NETHERLANDS; Y. Chen, S. Wagner, Princeton University, Princeton, NJ.

For better resolution, larger size, and integration of drive electronics in display applications, low-temperature TFT technology is currently under development. Usually, excimer laser annealing and/or furnace pre- and postannealing steps are needed to produce high mobility top-gate TFTs. In contrast, the Hot Wire Chemical Vapor Deposition (HWCVD) method has the potential to deliver as-deposited poly-Si with high electronic quality, due to the native passivation of grain boundaries at the low (T < 500 C) processing temperatures used. For the first time we have fabricated high-performance poly-Si TFTs using poly-Si that is directly deposited by the HWCVD method. This material was deposited at Utrecht University in the Poly2 regime, leading to very compact, purely intrinsic polysilicon, that does not require any further annealing, crystallization and/or passivation treatments. After deposition of the polysilicon layer (at a deposition rate of 0.55 nm/s), top gate TFTs were fabricated at Princeton University. The field-effect electron mobility in the saturation regime was 4.0 cm²/Vs. The TFTs also have a remarkably low OFF current (< 1E-10 A at Vd = 10 V), which we attribute to the low concentration of oxygen and other impurities, leading to the intrinsic properties of the polysilicon bulk material. These poly-Si TFTs have the potential to be made uniformly on large glass backpanes with large throughput. Their performance already is high enough for high resolution pixel switching and integrated drive circuitry.

9:15 AM *A31.4

LASER PROCESSING OF AMORPHOUS SILICON FOR POLY-SILICON DEVICES AND CIRCUITS. J.B. Boyce, R. Fulks, J. Ho, J.P. Lu, P. Mei, R.A. Street, and Y. Wang; Xerox Palo Alto Research Center, Palo Alto, CA.

Pulsed excimer-laser processing of amorphous silicon on non-crystalline substrates is an important processing technology for large-area polysilicon electronics, such as flat-panel displays and two-dimensional imaging arrays. It allows for the fabrication of high-quality polysilicon thin-film transistors (TFTs) and for the integration of amorphous silicon and polysilicon devices on the same low-temperature substrate. It also provides procedures for doping self-aligned amorphous silicon TFTs. In addition, laser-crystallized polysilicon exhibits some interesting materials properties, such as, large lateral grain growth with a corresponding enhancement in the electron mobility. These relationships between laser processing conditions and materials and device properties will be reviewed along with the conditions that yield good devices. Under these optimized processing conditions, excellent polysilicon TFTs with high mobilities, sharp turn on, and low off-state leakage currents (2fA/micron) can been achieved. These improved parameters, particularly the low off-state leakage currents, enable not only displays but also the more-demanding flat-panel imaging arrays to be fabricated using polysilicon. In addition, the application of laser processing to the doping of self-aligned polysilicon source/drain contacts for amorphous silicon TFTs allows devices with reduced source/drain parasitic capacitance to be fabricated. Excimer laser processing for both polysilicon TFTs and self-aligned amorphous silicon TFTs will be discussed along with the application of these technologies to flat panel imagers.

9:45 AM <u>A31.5</u>

HIGH PERFORMANCE 200nm SINGLE GRAIN TFT'S FABRICATED USING A SELF-ALIGNED GERMANIUM SEEDING TECHNOLOGY. <u>Pranav Kalavade</u>, Amol R. Joshi, Vivek Subramanian and Krishna C. Saraswat, Stanford University, Department of Electrical Engineering, Stanford, CA.

Sub-micron poly-Si TFTs exhibit performance variations caused by statistical variation in the number and location of grains within the channel. Recent advances in seeded lateral crystallization technology allow control over grain location, thereby increasing uniformity and performance of TFTs. Use of Ge seeding for lateral crystallization is especially attractive due to its CMOS compatibility. All Ge-seeding techniques demonstrated to date have required the use of additional

masking steps, increasing process complexity and cost. We report on 200nm TFTs fabricated using a self-aligned Ge seeding technology requiring no additional masks. Ge-seeded TFTs were fabricated using a conventional planar TFT process. After gate stack patterning, an oxide spacer was formed. Processing upto this point was performed at low temperature (≤500°C) to prevent random nucleation in the amorphous silicon channel. Ge was deposited selectively on the S/D regions and the films were then crystallized. The main advantage of this technique is that the seeding is self-aligned, requiring no additional lithography step. This was followed by S/D implants and back-end processing. Seeded devices were seen to have a substantially higher performance than unseeded devices. Seeded device drive currents were $\sim 100 \mu A/\mu m$ (NMOS) and $\sim 40 \mu A/\mu m$ (PMOS). compared to unseeded device drive currents of $\sim 10 \ \mu \text{A}/\mu \text{m}$. To determine the quality of crystallization, hydrogenation was carried out by implanting hydrogen ions into the channel region of the devices, followed by a 375°C forming gas anneal. Seeded devices showed little improvement after hydrogenation, indicating good crystalline quality within the channel. Unseeded devices, on the other hand, showed a 3x drive current improvement, from $10\mu A/\mu m$ to $30 \mu A/\mu m$. This implies that seeded devices are relatively defect free as compared to the unseeded devices. Ge-seeding is thus seen to be effective as it ensures the absence of grain boundries within the channel region, thereby resulting in high performance TFTs.

10:00 AM A31.6

Yokohama, JAPAN.

EFFECT OF NICKEL IN LARGE GRAIN POLY-Si FILM FORMED BY NICKEL INDUCED LATERAL CRYSTALLIZATION AND NEW GRAIN ENHANCEMENT METHOD. A.M. Myasnikov, M.C Poon, M. Chan, Hong Kong Univ of Science and Technology, Dept of Electrical and Electronic Engineering, Kowloon, HONG KONG.

Large grain poly-silicon film (poly-Si) with high material quality and uniformity can have numerous novel applications such as providing a low cost alternative to form silicon-on-insulator (SOI) substrates and a breakthrough technology to ultra-dense 3-dimensional multi-layer SOI like devices and circuits. Nickel Induced Lateral Crystallization (NILC) of amorphous Si (a-Si) has been studied intensively, yet the grains are still small ($\sim 1 \mu m$). Recently, we have reported a novel method by combining NILC and a new annealing (at above 900°C) to form poly-Si film with very large grains ranging from 10 to 100 μ m. The film has good quality and the TFTs formed are highly comparable to SOI TFTs. This work further reports the effect of Ni to the new large grain poly-Si film. 3000 Å thermal oxide was formed on 20 Ω cm p-Si. 1000 Å of a-Si was formed on the oxide by LPCVD at 550°C, and followed by $3000~\mbox{\normalfont\AA}$ of LTO. Windows were then patterned and 50 \mathring{A} of Ni was deposited onto the a-Si using an electron beam evaporator. NILC of a-Si film was then performed at 560°C for 20 hr. in N2. The Ni and LTO were then removed. A special annealing at 1000°C for 2 hours was then used to enhance the grains. SIMS results show that Ni is around 100 to 1000 ppma under the Ni, 10 ppma in the NILC region, and negligible in the oxides. While size of Ni film and amount of Ni affect greatly the Si grain size, quality and uniformity, the effect to TFT performance is not significant. The other effects of Ni to the quality of the poly-Si grains, the gate oxide underneath the poly-Si, the oxide grown on the poly-Si, and the quality of the fabricated TFTs, will be further reported and discussed.

> SESSION A32: HETEROGENEOUS MATERIALS II-STRUCTURE AND TRANSPORT Chair: James B. Boyce Friday Morning, April 28, 2000 Salon 7 (Marriott)

10:45 AM *A32.1 DEPOSITION OF HETEROGENEOUS SILICON THIN FILMS -STRUCTURE AND ELECTRIC STATES. Isamu Shimizu, The Graduate School, Tokyo Institute of Technology, Midori-ku,

Heterogeneous Silicon Thin Films (HFTS) prepared by PE-CVD on glass at low temperature has been accumulated a great attention for its potential to improve the performances of large area devices such as solar cells or TFT. In practice, conversion efficiency higher than 10% was achieved so far in the microcrystalline silicon solar cells with pin structure.[1] In addition, a TFT with the mobility of more than 30 cm²/Vs was successfully made using polycrystalline silicon thin film prepared by PE-CVD from a gaseous mixture of SiF₄+H₂+SiH₄.[2] However, the structural factors i.e., volume fraction, size and microstructure of crystallites, specific textures and grain boundaries which offer great influences on electrical and optical properties depend markedly on the preparation methods. In this work, we reviewed some specific trends for controlling these structural factors in making HSTF by PE-CVD from fluorinated sources in comparison with from silane. In particular, we address on the effective parameters in respective

processes; (1) formation of neclei on glass, (2) growth and control of crystalline textures and (3) impurities' doping and passivation of defects in view of controlling chemical reaction on growing surface or sub-surface. In addition, the optical and electrical properties, viz. carrier transport and its anisotropy or light scattering related to these structural factors are discussed as well. [1] K. Yamamoto, M. Yoshimi, T. Suzuki, Y. Tawada, Y. Okamoto, and A. Nakajima: Mat. Res, Soc. Symp. Proc. 507 (1998) 131. [2] T. Nagahara, K. Fujimoto, N. Kohno, Y. Kashiwagi, and H. Kakinoki: Jpn. J. Appl. Phys. 31 (1992) 4555.

11:15 AM A32.2

BARRIER-CONTROLLED TRANSPORT IN DOPED MICROCRYSTALLINE SILICON. Stephan Brehme, Peter Kanschat, Klaus Lips, Walther Fuhs, Hahn-Meitner-Institut, Berlin, GERMANY.

Thin microcrystalline films are grown at 325°C on glass substrates by electron cyclotron resonance chemical vapor deposition (ECR-CVD). Films are doped in situ either with PH_3 or B_2H_6 , and structural and electronic properties are studied as a function of doping levels. Typical grain sizes are in the range 15 - 40 nm. Resistivity and Hall effect data obtained from van der Pauw measurements reveal carrier concentrations between $3\times10^{17}~{\rm cm^{-3}}$ and $2.7\times10^{20}~{\rm cm^{-3}}$ and mobility values in the range 0.5 - $3~{\rm cm^2/Vs}$ at room temperature. The mobilities decrease with decreasing temperature in the entire temperature range investigated (20 K - 450 K). From a detailled investigation of the ESR signal related to conduction band electrons an in-grain mobility can be determined which is found to be much higher than the Hall mobility. These findings suggest that the electrical transport is limited by potential barriers at grain boundaries. By analyzing the temperature dependence of Hall mobility data we obtain barrier heights in the range 30 - 65 meV. The results are discussed in terms of a simple barrier-limited model (J. Y Seto, J. Appl. Phys. 46 (75) 5247) which assumes effective interface trap densities (IFTD) being independent from doping level. However, in our mc-Si films the effective IFTD increases with increasing doping level following a power law for both p and n-type doping. The results will be discussed in an extended Seto model including the temperature and doping level dependences of the Fermi level position E_F .

11:30 AM <u>A32.3</u>

TEMPERATURE DEPENDENT TRANSPORT IN MICRO-CRYSTALLINE SILICON PIN DIODES. Torsten Brammer, Helmut Stiebig, Andreas Lambertz, Wilfried Reetz, Heribert Wagner, Institut für Schicht- und Ionentechnik, Forschungszentrum Jülich GmbH, Jülich, GERMANY,

The optoelectronic behavior of microcrystalline silicon (μ c-Si:H) diodes deposited by PECVD (95MHz, 50-80mW/cm², 300mTorr, 200°C) with pin and nip deposition sequence were investigated for silane concentations ([SiH₄]/([SiH₄]+[H₂])) from 2% to 8%. The open-circuit voltage $V_{\it OC}$ of the cells increased from 450mV to 550mV with increasing silane concentration and the FF showed a maximum of above 70% for silane concentations between 4% and 6%. The purpose of this work was to correlate device characteristics with μ c-Si:H inherent material properties. Therefore, dark and light I(V) curves and quantum efficiencies (QE) were measured at temperatures ranging from 250K to 350K and compared with numerical simulations. The dark I(V) curves and, therefore, the Voc behavior of this series was dominated by the bulk properties of the i-layer (equilibrium carrier concentration) as shown by numerical modelling. The temperature dependent QÉ of nip and pin diodes allowed to distinguish between interface and bulk effects. Interface effects dominated the temperature dependent blue response of pin diodes. The gain in blue response increased with temperature and silane concentration by up to 200%which revealed transport limiting material properties in the vicinity of the p/i-interface. This behavior was attributed to the nucleation region extending deeper into the i-layer for higher silane concentrations. For nip diodes the nucleation region is located at the i/n-interface. Consequently, the temperature dependent blue response of nip cells was mainly controlled by bulk effects, the dominant being a negative mobility temperature coefficient. For temperatures above 300K the blue response decreased uniformly and the increase of the QE for longer wavelengths due to the optical band gap shift was partly compensated. The simulated results were in good agreement with the experiments. The negative mobility temperature coefficient also explained the temperature dependence of FF which was more pronounced for smaller silane concentration.

 ${\bf 11:45~AM}~{\underline{A32.4}}$ RESPONSE TIME MEASUREMENTS AND FLYING SPOT TECHNIQUE IN MICROCRYSTALLINE SILICON SOLAR CELLS. Schwarz, P. Sanguino, and S. Koynov, Dept. Physics, IST, Lisboa, PORTUGAL; M. Fernandes, A. Macarico, M. Vieira, Electronics and Communications Dept., ISEL, Lisboa, PORTUGAL

We used two complementary methods, the Flying Spot Technique (FST) and Transient Photoconductivity (TPC), to measure essential

thin film solar cell parameters like carrier recombination lifetime and ambipolar diffusion length. Transverse charge collection in a p-i-n structure based on microcrystalline silicon (μ c-Si:H) and lateral transport in a coplanar structure were analyzed using the flying spot technique FST and transient photoconductivity TPC, respectively. The FST technique has been successfully applied to solar cell structures based on hydrogenated amorphous silicon for the determination of minority carrier diffusion length. In this contribution we extend the study to the promising, however complex material of hydrogenated microcrystalline silicon prepared by the cyclic CVD technique. Using the FST technique we found an ambipolar diffusion length, L_{amb} , to be around 200 nm and recombination time, $\tau_{rec} =$ $24 \mu s$. It is an advantage of the FST method that both a complete p-i-n device and a simple Schottky barrier metal contact can be employed. Care has to be taken to reach a sufficient large time resolution, which is obtained when working in short-circuit current mode and/or under additional bias light. In TPC measurements we used two Cr contacts evaporated on top of a n i-layer, that is also used in p-i-n solar cell structures. The light source was a high power Nd:YAG laser of 5 ns pulse duration (5 MW/cm² power density, green line at 532 nm). The initial photocurrent decay is characterized by a decay time constant of 4 μ s, whereas at longer times the decay slows down to values of about 15 μ s. This shows that photocurrent decay strongly depends on the carrier density present at a given moment. A large number of trap states is assumed to be responsible for the large response times. Optoelectronic parameters of minority and majority carriers in microcrystalline silicon thin films obtained from this study allow one to identify necessary steps for improvement of solar cell device performance.