# SYMPOSIUM A

# Amorphous and Heterogeneous Silicon-Based Films—2002

April 1 - 5, 2002

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### TUTORIAL

ST A: AMORPHOUS AND POLYSILICON MATERIALS AND DEVICES FOR LARGE-AREA ELECTRONICS Monday, April 1, 2002 8:30 a.m. - 4:30 p.m. Salon 5/6 (Marriott)

Hydrogenated amorphous silicon (a-Si:H) and micro- or polycrystalline silicon ( $\mu$ c-Si, poly-Si) are important technological materials for large-area electronics, with applications to thin film solar cells, active matrix liquid crystal displays (AM-LCDs), optical scanners, and radiation imaging. The course describes the growth and preparation, basic material properties, device physics and state-ofthe-art processing issues of modern large-area-array technology based on amorphous or heterogeneous thin silicon films. Special emphasis will be on the relation between material properties and device performance.

#### Instructors:

Robert A. Street, Xerox Palo Alto Research Center Ping Mei, Hewlett-Packard Laboratories

> SESSION A1: HYDROGEN Tuesday Morning, April 2, 2002 Golden Gate B2 (Marriott)

### 8:00 AM \*A1.1

MOLECULAR HYDROGEN IN AMORPHOUS SILICON. D.J. Leopold, P.A. Fedders, and R.E. Norberg, Washington University, Department of Physics, St. Louis, MO.

Proton NMR studies performed on hydrogen in numerous plasma deposited a-Si:H thin film samples over many years have established that there are primarily two dipolar broadened lines, representing different distinct degrees of proton clustering involving most of the contained hydrogen. In addition, both of these configurations were thought to be hydrogen tightly bonded to silicon. However, deuteron magnetic resonance established long ago that a substantial fraction of the hydrogen (deuterium) population was a weakly bonded species, very different than the silicon bonded hydrogen typically seen in infrared measurements. Deuteron magnetic resonance can easily distinguish bond strength because deuterons have spin 1, an electric quadrupole moment, and are sensitive to electric field gradients. The much weaker deuteron dipolar coupling results in NMR line shapes and widths that are determined by distributions of electric field gradients and angular averages about the applied magnetic field direction. The primary features of the deuteron line shape are a sharp powder-pattern Pake doublet attributed to the tightly silicon bonded species and a broad central Gaussian component originally interpreted as a weakly bound component, but now recognized as molecular D2 and HD trapped in the amorphous equivalent of T-sites. This latter result is confirmed by spin-echo double resonance experiments using H and Si nuclides, which reveal a very appreciable population of molecular hydrogen in T-like sites. These results also indicate that the majority of this species resides in the less clustered hydrogen phase. Some possible implications of this molecular component on a-Si:H optoelectronic properties will be discussed.

INTERACTIONS OF ATOMIC DEUTERIUM WITH HYDRO-GENATED AMORPHOUS SILICON THIN FILMS: AN IN SITU STUDY USING ATTENUATED TOTAL REFLECTION FOURIER TRANSFORM INFRARED SPECTROSCOPY. Sumit Agarwal, Saravanapriyan Sriraman, Department of Chemical Engineering, University of California, Santa Barbara, CA; Akihiro Takano, Fuji Electric Corporate Research and Development, Ltd., JAPAN; M.C.M. van de Sanden, Department of Applied Physics, Eindhoven University of Technology, THE NETHERLANDS; Dimitrios Maroudas, and Eray S. Aydil, Department of Chemical Engineering, University of California, Santa Barbara, CA.

Atomic hydrogen plays a significant role in the deposition of hydrogenated amorphous silicon (a-Si:H) from silane containing discharges. In order to isolate the effect of H atoms from those of other radicals impinging onto the growth surface during deposition, as-deposited a-Si:H films were exposed to a  $D_2$  plasma. Subsequent compositional and structural changes in the film were studied using in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and spectroscopic ellipsometry. The a-Si:H thin films were deposited in an inductively coupled plasma reactor at 200°C. The deposited films were exposed to a series of one-second D<sub>2</sub> plasma pulses at different substrate temperatures. The use of D

generated by the plasma and the deconvolution of the infrared absorption regions allowed us to observe the occurrence of both surface H abstraction and insertion reactions on the films surface and in its bulk. In situ ATR-FTIR was used to observe the changes in the film after each pulse. Peak assignments were made and the IR data was deconvoluted for both the  $SiH_x$  and  $SiD_x$  regions of the spectrum. We determined that surface H abstraction is barrierless and proceeds through an Eley-Rideal mechanism, in agreement with our atomistic calculations. In contrast, the modification of the bulk film through abstraction and insertion reactions is limited by D diffusion. Moreover, we found that a thin sub-surface region (<30 Å) exists that is rich in silicon di- and trihydride species and strained Si-Si bonds. a-Si:H films deposited and exposed to a  $D_2$  plasma at substrate temperatures of  $300^{\circ}$ C show stretching modes of bond-centered hydrogen and deuterium at  $1945~{\rm cm}^{-1}$  and  $1423~{\rm cm}^{-1}$ , respectively. In agreement with this finding, our molecular-dynamics simulations predict that bond-centered hydrogen forms in the a-Si:H films during their exposure to H and mediates the amorphous-to-nanocrystalline structural transition of these films.

#### 8:45 AM A1.3

ENERGETICS OF INTERSTITIAL HYDROGEN IN REALISTIC a-Si:H SUPERCELLS. P.A. Fedders, Washington University, Dept of Physics, St. Louis, MO.

Both recent and past energy calculations have shown that it is very unlikely that H in a-Si:H migrates via bond centered sites. The bond centered site energy levels lie far too high above the dangling bond levels. Here we report on recent calculations of the energetics of interstitial H, which is a viable alternative. These calculations pertain to the site energies and energy barriers to migration. We find that there are many interstitial sites at or near the amorphous analogue of T sites in crystalline Si. Some of these sites are very near the "center" of the T-like sites and some are off-center where the H is weakly bonded to a Si atom. Both of these types of sites have a spread of energies that lie lower that the energy of BC sites by several tenths of an eV. Further the barriers from one interstitial site to a neighboring one are considerably less than the 0.5 eV associated with BC to BC migration. The combination of the lying lower and the reduced mobility barrier yields a the difusion activation energy to that approximately measured in diffusion experiments. Thus all three charge states (0, +1, and -1) are excellent candidates for the transport sites of H in a-Si:H.

9:00 AM  $\underline{A1.4}$  ABSENCE OF A STEADY STATE IN HYDROGEN DILUTED SILANE PLASMAS DUE TO MASS DEPENDENT GAS PUMPING SPEEDS AND ITS CONSEQUENCES. G. Ganguly, J.N. Newton, S. Liu, M. Gleaton, G. Wood, D.E. Carlson and R.R. Arya, BP Solar, North America Technology Center, Toano, VA.

A great deal of work has gone into characterizing silane plasmas and the amorphous silicon thin film during growth. Several models have been proposed to understand the growth process and many of these assume steady state processes. Spectroscopic Ellipsometry [1] and Scanning Tunnelling Microscopy [2] have been used to show that the surface roughness of plasma deposited amorphous silicon films increases with film thickness/deposition time. We have observed using a mass spectrometer the hydrogen, silane, disilane and trisilane related signals during the i-layer deposition process in a reactor that processes 1ft<sup>2</sup> modules. We find that the latter three signals increase continuously relative to the hydrogen signal with increasing i-layer deposition time. This has been verified using different flow rates, discharge currents, deposition systems and dilution ratios. In order to understand this observation we have measured the pressure in the chamber using equal flows (calibrated using pressure increase rate) of hydrogen and argon. There are clear differences in the pumping rate of these two gases using our mechanical pump. This implies that the observed increase in the silane to hydrogen signal using the mass spectrometer could be attributed to differences in pumping speed for silane and hydrogen. Therefore, all experimental results that observe differences as function of time are dubious. In particular, increase of roughness with thickness can occur due to the increase in the relative concentration of higher silane species. [3] Other implications and possible ways to compensate for the lack of a steady state will be discussed at the meeting. [1] J. Koh, A.S. Ferlauto, P.I Rovira, R.J. Kovaal, C.R. Wronski, and R.W. Collins, J. Non-cryst. Solids 266-269 (2000) 43. [2] A.J. Flewett, J. Robertson and W.I. Milne, J Non-cryst. Solids 266-269 (2000) 74. [3] A. Matsuda, Proc. 25th IEEE PVSC (1996) 1029.

9:15 AM  $\underline{*A1.5}$  THE ROLE OF HYDROGEN IN DISORDERED SILICON. N.H. Nickel, Hahn-Meitner-Institut Berlin, Berlin, GERMANY.

The properties of hydrogen in disordered silicon are of great importance since it is readily incorporated during sample growth or post-hydrogenation experiments. Hydrogenated amorphous silicon (a-Si:H), microcrystalline silicon ( $\mu$ c-Si), and polycrystalline silicon (poly-Si) owe their success to the beneficial properties of hydrogen. The use of these materials in devices such as solar cells, thin-film transistors, flat panel displays, and two-dimensional x-ray scanners is possible only because hydrogen minimizes the concentrations of deep defects leading to high quality electronic material. On the other hand, the presence of hydrogen also gives rise to the formation of new defects. The most prominent defect creation mechanism is the so called "Staebler-Wronski" effect [1]. Although the microscopic origin of the Staebler-Wronski effect is still an unsolved problem the participation of hydrogen in this effect was established previously [2]. This presentation will give an overview of recent developments regarding the beneficial and deleterious properties of hydrogen in disordered silicon. [1] D.L. Staebler and C.R. Wronski, J. Appl. Phys. 51, 3262 (1980). [2] N.H. Nickel, W.B. Jackson, and N.M. Johnson, Phys. Rev. Lett. 71, 2733 (1993).

# SESSION A2: ELECTRONIC STRUCTURE AND TRANSPORT

Tuesday Morning, April 2, 2002 Golden Gate B2 (Marriott)

### 10:15 AM <u>A2.1</u>

ULTRAFAST CARRIER THERMALIZATION IN HYDRO-GENATED AMORPHOUS SILICON. J. Liu $^a$ , C.P. Zhang $^a$ , J.E. Young $^a$ , B.P. Nelson $^b$ , and <u>S.L. Dexheimer</u> $^a$ ,  $^a$ Department of Physics, Washington State University, Pullman, WA;  $^b$ National Renewable Energy Laboratory, Golden, CO.

We present detailed studies of the initial relaxation processes of photoexcited carriers in hydrogenated amorphous silicon. We have carried out time-resolved measurements of the photoexcited carrier response in HWCVD a-Si:H thin films using 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. Measurements of the transient optical absorbance as a function of the density of excited carriers and as a function of sample temperature reveal a fast carrier thermalization process that occurs prior to bimolecular recombination. We find that the photoexcited carriers relax via interaction with the lattice on a time scale of  $\sim 250$  fs. This work is supported by the National Renewable Energy Laboratory and the National Science Foundation Division of Materials Research.

10:30 AM A2.2 MONTE-CARLO SIMULATION OF GENERATION - RECOM-BINATION NOISE 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, Zaqar, JORDAN.

We compare the predictions of several analytical models [1 - 3] for conductivity fluctuations in a homogeneous semiconductor containing discrete and distributed traps, with a Monte-Carlo simulation of the relevant multi - trapping transitions. The simulation directly embodies the statistical features associated with such processes, in a simple "model - independent" approach, free of approximations and assumptions. We compare the results with those of several analytical approaches. In one [1], the noise spectrum is assumed to reflect separately, the characteristic individual release time constants of the various trapping centres in the material. In another [2], the trapping time into the ensemble of electron traps is taken to be the dominant time constant, and hence, in a material such as a-Si:H, where the trapping time into tail sates is of order 1ps, this is taken to imply that this component of the conductivity noise spectrum is unobservable in practice. Our own analytical approach [3], incorporates coupling (albeit weak) between traps, which necessarily communicate via the extended states. Preliminary results of the simulation support our thesis, and verify that the same information is contained in the real part of the modulated photoconductivity (MPC) spectrum. The 'full Monte' - Carlo simulation incorporating all gap states and spatial inhomogeneities is now a priority. [1] F.Z. Bathaei and J.C. Anderson, Philos. Mag. B55, 87, (1988). [2] P. Verleg, "Noise spectroscopy of hydrogenated amorphous silicon", PhD thesis, University of Utrecht (1997). [3] C. Main, S. Reynolds and M.J. Rose, J. Non-Cryst. Solids 227-230, (1998) 233.

# 10:45 AM \*A2.3

MAGNETIC RESONANCE PROBES OF BAND TAIL STATES AND DEFECTS IN TETRAHEDRALLY COORDINATED AMORPHOUS SEMICONDUCTORS. P.C. Taylor, University of Utah, Department of Physics, Salt Lake City, UT.

I will review recent nuclear magnetic resonance (NMR) and electron spin resonance (ESR) results relating to (1) recombination processes for optically excited electrons and holes in tetrahedrally coordinated amorphous semiconductors and (2) microscopic properties of metastable defects (dangling bonds associated with the Staebler-Wronski effect) in these semiconductors. With regard to recombination processes, ESR measurements have been performed over a wide range of excitation intensities (nW/cm2 to W/cm2) on hydrogenated amorphous silicon (a-Si:H) and hydrogenated amorphous germanium (a-Ge:H). The kinetics can be studied down to carrier densities as low as 10<sup>14</sup> cm<sup>-3</sup>. The long-time decay curves show that at large carrier separation (1) the random distribution of optically excited electrons and holes is subject to the condition of charge neutrality, and (2) the decays are universal and independent of the densities of localized, band-tail states. At decay times shorter than 1s, the ESR results can be directly compared with those inferred from NMR measurements (dipolar echos) on the same samples. With regard to the metastable defects in a-Si:H, the kinetics of the production and thermal annealing of silicon dangling bonds has been measured at temperatures between 25 and 480 K using ESR. Below about 150 K the measurement of the dangling bonds is masked by long lived, band tail carriers that accumulate with time. The production rate for silicon dangling bonds decreases with decreasing temperature and is nearly temperature independent below approximately 100 K. Defects created by 10 hours of irradiation below 100 K anneal almost completely at 300 K. In a-Ge:H, the first measurements of metastable germanium dangling bonds have been made. Very recent NMR experiments on light-soaked and annealed samples of a-Si:H from BP Solar have shown that a metastable hydrogen "doublet" appears only in the light-soaked samples with a density between  $10^{16}~\rm and~10^{18}~cm^{-3}$  .

### 11:15 AM A2.4

RECOMBINATION OF OPTICALLY EXCITED CARRIERS IN a-Si:H AT LOW TEMPERATURES AND INTERMEDIATE TIMES. J. Whitaker, T. Su, R. Plachy, and P.C. Taylor, Department of Physics, University of Utah, Salt Lake City, UT.

The discovery in 1989 by Shklovskii et al. [1] that the simultaneous diffusion and recombination of electron-hole pairs in amorphous semiconductors is a universal property that does not depend on the densities of localized band-tail states has prompted renewed interest in the low temperature recombination processes in hydrogenated amorphous silicon (a-Si:H). At short times, diffusion of the carriers plays the major role in recombination, and at long times recombination via tunneling is the only important process. Short times (t < 1 ms) have been probed in photoluminescence (PL) or photoconductivity (PC) experiments [2] while long times (t > 10 s have been probed in optically excited electron spin resonance (LESR) experiments [3]. We have studied the LESR on time scales in between the previously published PL and LESR results. This regime allows us to examine the cross over between diffusion- and tunneling-dominated recombination to understand better the localized band-tail states in a-Si:H. These data also increase our understanding of the kinetics of the recombination processes in a-Si:H. In addition, these data can be directly compared in the same sample with NMR data on the dipolar spin-lattice relaxation of the bonded hydrogen [4]. In the NMR experiments the light inducted electrons and holes are responsible for dipolar relaxation of bonded hydrogen. Therefore, the direct comparisons between the LESR and NMR experiments provide a stringent test of the interpretation of the NMR measurements. 1. B.I. Shklovskii, H. Fritzsche, and S.D. Baranovskii, Phys. Rev. Lett. 62, 2989 (1989); E.I. Levin, S. Marianer, and B.I. Shklovskii, Phys. Rev. b45, 5906 (1992). 2. See, for example, R.A. Street, Hydrogenated Amorphous Silicon (Cambridge University Press, Cambridge, 1991). 3. B. Yan, N.A. Schultz, A.L. Efros, and P.C. Taylor, Phys. Rev. Lett. 84, 4180 (2000). 4. T. Su, S. Chen, P.C. Taylor, R.S. Crandall, and A.H. Mahan, Phys. Rev. B 62, 12849 (2000).

### 11:30 AM A2.5

MEDIUM RANGE ORDER AND 1/F NOISE IN HYDROGENATED SILICON THIN FILMS.  $\underline{T. James Belich}$ , J. Kakalios, School of Physics and Astronomy, University of Minnesota, Minneapolis, MN.

Conductance fluctuations (1/f noise) in hydrogenated amorphous silicon (a-Si:H) have been interpreted as reflecting the dynamics of inhomogeneous current filaments, believed to arise from medium range (1-10 nm) structural disorder. The non-Gaussian statistics which characterize the 1/f noise are reflected in measurements of the second spectra, obtained by Fourier transforming the time-dependent fluctuations of the 1/f noise spectral density. The second spectra in a-Si:H films may also display a 1/f frequency dependence, reflecting electronic correlations between different current microchannels. We report here measurements of the second spectra for a series of n-type doped a-Si:H films for which the deposition conditions are systematically varied. The non-Gaussian character of the noise is found to decrease with decreasing deposition temperature. Previous measurements in our lab have correlated lower deposition

temperatures with both an increase in the silicon-dihydride content (from FTIR studies) and an increase in the difference between the conductivity and thermopower activation energies (the Q-function). The sensitivity of the second spectra and Q-function to variations in the medium and long-range disorder are also observed in plasma deposited a-Si:H films with increasing microcrystalline content, and Hot Wire deposited films with a deliberately high density of microvoids. This research is supported by NREL/AAD-9-1866-13.

# 11:45 AM A2.6

GENERATION-RECOMBINATION NOISE IN a-Si:H STUDIED BY DEVICE SIMULATIONS. <u>Jeroen Bakker</u><sup>a</sup>, Boris Fine<sup>b</sup>, Jaap Dijkhuis<sup>a</sup>, <sup>a</sup>Debye Institute, <sup>b</sup>Spinoza Institute, Department of Physics and Astronomy, Utrecht, THE NETHERLANDS.

Generation-recombination (g-r) noise spectra of a-Si:H in an n-i-ndevice have a characteristic frequency, thermally activated with an energy 0.83 eV [1]. The activation energy differs markedly from that of the electrical conduction and is explained by thermally activated electron-hole recombination. In an earlier paper [2], we described computer simulations using the one-dimensional device simulation program AMPS-1D [3] to calculate the lifetime of the majority carriers (electrons) and compared the results to the temperature dependence of the noise spectra. We found quantitative agreement between the exponential lifetime and the characteristic noise frequency for a specific location in the device. We examine this by analyzing the noise intensity in terms of a sum of Lorentzian spectra, each corresponding to an exponential recombination lifetime. Band bending near the interfaces naturally produces a distribution of electron lifetimes in the device and leads to a phenomenological, position dependent weight factor. The weight factor determined from the noise data taken at 434 K is found to peak at the position where the computed activation energy exactly coincides with the measured activation energy of the characteristic noise frequency. This suggests that the characteristic frequency observed in the noise spectra corresponds to a dominant spatial region in the device. Experimental g-r noise intensities do not change much under illumination. The computed electron lifetime, however, undergoes a drastic change. If we assume a constant weight factor in space, and using the calculated electron lifetimes, we can account for the g-r noise spectra under illumination. The noise contributions to the experimentally accessible frequency range originate from the region near the n-i interface. [1] P.A.W.E. Verleg and J.I. Dijkhuis, Phys. Rev. B 58 (1998) 3904 [2] J.P.R. Bakker, B.J. van der Horst and J.I. Dijkhuis, J. Non-Cryst. Solids, accepted for publication [3] http://www.psu.edu/dept/AMPS

### SESSION A3: THIN-FILM TRANSISTORS Tuesday Afternoon, April 2, 2002 Golden Gate B2 (Marriott)

# 1:30 PM <u>A3.1</u>

THIN-FILM TRANSISTORS ON PET AT 100°C. J.P. Condea, P. Alpuim<sup>a,b</sup> and V. Chu<sup>b</sup>, <sup>a</sup>Department of Materials Engineering, Instituto Superior Técnico, Lisbon, PORTUGAL; Microsystems and Nanotechnologies, Lisbon, PORTUGAL.

Amorphous silicon thin-film transistors (TFTs) fabricated on inexpensive, transparent substrates are the basic components of circuits for application in disposable electronics, bioelectronics, sensitive skins, and textile electronics. In this paper, we report on the fabrication of TFTs on polyethylene terephthalate, using a maximum processing temperature of 100°C. Two main issues are addressed in this work: (1) the optimization, at 100°C, of the individual films which make up the TFT; and (2) details of device processing on a flexible substrate.

The semiconductor and dielectric films to be incorporated in the devices were individually optimized for deposition at and below 100°C: amorphous silicon, intrinsic and doped, and doped microcrystalline silicon, deposited by hot-wire CVD and RF PECVD, and silicon nitride, deposited by RF PECVD and ECR PECVD. The characteristics of the optimized films and their preparation conditions will be described. At such low temperatures, much more hydrogen dilution is needed to obtain device quality films than is required for standard temperatures of >200°C. Fabrication of TFTs on compliant substrates, such as thin plastics, requires careful stress management of the individual films, and chemical compatibility between the fabrication procedure and the substrate. The process modifications needed to fabricate devices on plastic substrates will be discussed. Both bottom and top-gate TFTs were fabricated on PET, with the best device characteristics to date obtained for a bottom-gate, inverted-staggered RF a-Si:H TFT, which has a mobility of  ${\sim}0.03$  cm $^2V^{-1}s^{-1}$ ,  $I_{ON}/I_{OFF}/\sim{5}{\rm x}10^5$ , and a subthreshold slope of  ${\sim}2.5$ V/decade. It was necessary to perform a post-fabrication anneal at 100°C to improve and stabilize the device properties. The relatively large subthreshold slopes in these devices indicates a high defect

density at the interface suggesting that device performance can be improved by further improvements in the dielectric material. These improvements will also be discussed.

 $1:\!45$  PM  $\underline{A3.2}$  FABRICATION AND CHARACTERIZATION OF ULTRA-SMALL POLYCRYSTALLINE SILICON ISLANDS FOR ADVANCED DISPLAY AND MICROSENSOR APPLICATIONS. Dominik Schmidt, Frank Shi, and Piero Pianetta, Stanford Linear Accelerator Center, Stanford University, Menlo Park, CA.

Polycrystalline silicon (polysilicon) is a key component of integrated circuit technology, micromechanical systems and displays. Highmobility polysilicon thin-film transistors are replacing amorphoussilicon transistors in advanced active-matrix displays, and are also vital to the emerging fields of microsensors and microactuators. In this study, the deposition processes (LPCVD) of polysilicon thin films were carefully studied and the basic film kinetics were analyzed. The films were patterned into submicron islands and the relation of the deposition temperature to the crystallinity of polysilicon islands was observed. A threshold deposition temperature for polysilicon crystals larger than 0.35 mm was found. The relationship of polysilicon crystal size to the annealing temperature and the annealing duration was also systematically studied. Polysilicon islands of ~0.1 mm lateral dimensions were successfully fabricated by ebeam lithography and various annealing cycles were performed to increase micro-crystal size, with the goal of creating single-crystal high-mobility islands. Theoretically, transistors built from such islands should match the performance of state-of-the-art bulk CMOS devices. The crystal size was initially measured using TEM and AFM analysis. Additionally, EXAFS (Extended X-ray Absorption Fine Structure) measurements at SSRL (Stanford Synchrotron Radiation Lab) were employed to study the crystalline quality of the polysilicon islands and the correlation between the absorption curves, the thin-film electrical properties and the polysilicon grain sizes.

### 2:00 PM A3.3

GROWTH OF HIGH QUALITY FLUORINATED SILICON DIOXIDE FOR THIN FILM TRANSISTORS, Roger Keen. Vikram L. Dalal, Iowa State University, Dept. of Electrical and Computer Engr., Ames, IA.

Thin Film Transistors in microcrystalline and amorphous Si need stable, high quality oxides deposited at low temperatures. In this paper, we describe the fabbrication of high quality oxides on Si at low temperatures (~300-400°C) using ECR plasma CVD process. The oxides were grown using in-situ plasma oxidation in the presence of Fluorine. The source gases for oxidation were oxygen and Fluorine, diluted in He. MOS capacitors were made using this oxide, and the interface defect density calculated from capacitance spectroscopy.It was found that the use of F in the plasma reduced the defect density to  $\sim 2E10/\ cm^2$ , comparable to the defect density found in the best oxides grown at high temperatures (>800°C) using dry oxidation technniques. When F was not used, the interface density was >1E11/cm<sup>2</sup>. Too much F was found to degrade the interface properties. No post-deposition annealing was needed to achieve the low defect density.

### 2:15 PM \*A3.4

EFFECTS OF MECHANICAL STRAIN ON a-Si:H THIN-FILM TRANSISTORS. <u>Helena Gleskova</u> and Sigurd Wagner, Princeton University, Department of Electrical Engineering, Princeton, NJ.

Novel display applications, such as electronic paper, smart labels, and displays for vehicles, require flexible TFT backplanes. Future sensor skins and electrotextiles also will be based on flexible circuits Because bending and draping will induce strain in these circuits, understanding the electrical performance of TFTs when under mechanical strain becomes essential. We fabricated a-Si:H TFTs on  $\sim$ 50  $\mu$ m thick polyimide foil and studied their electrical performance under externally applied, uniaxial, compressive or tensile strain of up to 2%. The test devices were a-Si:H TFTs with inverted staggered structure. The gate electrode was made of Ti/Cr and the source-drain contacts of Al. The  $SiN_x$  gate dielectric was  $\sim 360$  nm thick, the a-Si:H channel layer 100-200 nm, and the (n)a-Si:H contact layer 50 nm. Some TFTs had back-channel etch structure, others were passivated with 150 nm of  $SiN_x$ . All processes were optimized to provide good electrical performance and to minimize mechanical stress in the as-fabricated devices. Uniaxial strains of defined magnitude are developed by bending individual TFTs around cylinders of a range of radii. Inward bending causes compressive strain and outward bending tensile strain. In separate experiments, measured uniaxial tension is introduced by stretching the TFT between two jaws of a microstrain tester while the strain is measured independently. In compression, the TFT electron mobility decreases linearly with increasing strain. Eventually, the TFTs fail by mechanical fracture due to the buckling and consequent cracking of the TFT layers. Good adhesion between

the TFT structure and the substrate is essential to preventing failure. Our TFTs are able to sustain compressive strain of up to 2% without failing. In tension, the electron mobility increases linearly with applied strain. The TFTs fail by crack formation at a strain of about 0.5%. This work is supported by DARPA, NSF, and NJCST.

SESSION A4: SENSOR AND IMAGING ARRAYS Tuesday Afternoon, April 2, 2002 Golden Gate B2 (Marriott)

# 3:15 PM <u>\*A4.1</u>

LARGE AREA ELECTRONICS FOR FLAT PANEL IMAGERS - PROGRESS AND CHALLENGES. J.P. Lu, K. Van Schuylenbergh, J. Ho, Y. Wang, J.B. Boyce, and R.A. Street, Xerox Palo Alto Research Center, Palo Alto, CA.

The technology of large area electronics, which until recently has been limited to active matrix switching networks using amorphous Si, has made significant progress in recent years. This has been driven by the need for integrated peripheral drive circuits on glass substrates and the need for more complex circuits at the pixel, such as analog pixel drivers for OLED displays and low-noise pre-amps for flat panel imagers. Poly-silicon Thin Film Transistors (TFTs) with performance beyond that of amorphous-Si devices have been developed to achieve these advanced functions. Excimer-Laser Annealing (ELA) has become the major processing technology for fabricating these large-area compatible, high performance TFTs. In this talk, we will review the progress of large area electronics enabled by the ELA process, and will report on the status of developing high performance flat panel imagers using these new technologies. Both the integration of on-glass peripheral drivers to reduce the complexity of interconnection and the implementation of pixel level electronics to improve the sensitivity of flat panel imagers will be discussed. The large off-state leakage current of ELA-processed poly-Si TFTs was a major concern in building full poly-Si flat panel imagers previously. Recent improvements in poly-Si TFT leakage currents achieved by either novel TFT structure or process optimization have reduced the leakage currents to an acceptable level  $(<2 \text{ fA}/\mu\text{m})$ . This progress has enabled us to build prototype imagers with 384×256 pixels, with on-glass drive electronics, namely, multiplexers on the data lines and shift registers and drivers on the gate lines. In addition, we have demonstrated imagers with pixel-level amplifiers. Acceptable image quality, good uniformity, and excellent noise performance as low as 1200 eRMS have been achieved with these pixel amplifiers. The principle of pixel-amplified imagers, the origin of the dominated noise process, as well as the need and the challenges for further improving TFTs and imagers will be discussed.

### 3:45 PM A4.2

AMORPHOUS SILICON ACTIVE PIXEL SENSOR READOUT CIRCUIT ARCHITECTURES FOR MEDICAL IMAGING. Karim S. Karim, <u>Arokia Nathan</u>, University of Waterloo, Dept of Electrical and Computer Engineering, Waterloo, CANADA; John A. Rowlands, Sunnybrook and Women's College Health Sciences Centre, Toronto, CANADA.

Amorphous silicon active matrix flat-panel imagers have gained considerable significance in digital diagnostic medical imaging applications. The most widely used pixel architecture in these imagers is a passive pixel sensor (PPS) where the pixel consists of a detector and an a-Si:H thin-film transistor readout switch. While the PPS has the advantage of being compact, reading the low PPS output signal requires costly, bulky column charge amplifiers, which also add a large noise component to reduce the minimum readable sensor input signal. Therefore, it is beneficial to have a pixel architecture that can perform input signal amplification inside the pixel. The amplified output signal reduces performance requirements of low noise from external amplification circuitry in addition to increasing the dynamic range of the pixel This paper presents different active pixel sensor (APS) readout circuit architectures that perform on-pixel input signal amplification. Unlike conventional PPS systems with one TFT switch per pixel, the APS has three TFTs per pixel. The large number and sizes of a-Si:H TFTs make pixel design and integration challenging. Therefore, in an effort to optimize fill factor, the feasibility of embedding TFTs beneath the sensor will be examined. This approach to provide high fill factor imaging systems is based upon the idea of previously reported continuous layer sensor architectures. Theoretical calculations and experimental results indicating the feasibility of the APS for low-noise, real time imaging applications (e.g. fluoroscopy) are presented. Specifically, signal gain, dynamic range, readout rate and noise of the APS are examined. Lastly, a discussion on the APS threshold voltage stability is also included.

# 4:00 PM <u>A4.3</u>

TAILORED PINPIN a-SiC:H DEVICE FOR IMAGE

RECOGNITION AND COLOUR SEPARATION. <u>M. Vieira</u>, M. Fernandes, P. Louro, A. Fantoni, R. Schwarz, Electronic and Communications Dept., ISEL, Lisbon, PORTUGAL; M. Schubert, Institut für Physikalische Electronik, GERMANY.

Studies on the use of glass/ITO/p /i /n /metal structures as Laser Scanned Photodiode (LSP) image sensors have recently shown its potential capability. Those sensors are based on single large area p-i-n sensing element and a scanning reader. They can detect an optical image with a spatial resolution of 20  $\mu m$  in a flux range of two orders of magnitude and present a sensitivity of 6.5  $\mu W \cdot cm^{-2}$ . This work intends to study the use of a similar imaging method for colour recognition. For this purpose a two terminal wavelength-optimised pinpin stacked structure is proposed. No optical filters are used. The image is projected onto the front part of the sensing element and the reader scans the device through the rear part of the structure. Red, green and blue scanners are used during the read-out of the photogenerated carriers and give information on the spectral region. The first p-i-n photodiode confines the carriers at the illuminated regions while the second one driven by the scanner gives information on where the carriers where generated. Glass/ZnO:Al/p (SiC:H)/i (Si:H)/n (SiC:H)/p (SiC:H)/i (SiC:H)/n (SiC:H)/ZnO:Al stacked devices were produced by PECVD at low temperature (100°C). The front a-Si:H i-layer is thick enough (>500 nm) to absorb all the light incoming from the image and the rear one is thin (<100 nm) and based on a-SiC:H in order to enhance light transmission from the scanner. Junction properties, carrier transport and photogeneration are investigated from dark and illuminated current-voltage characteristics and bias dependent spectral response. The effects of material properties (layer composition, optoelectronic properties and thickness) and read-out parameters (applied voltage, scanner modulation, and wavelength) on the reading process of pinpin LSP colour sensors are analysed. Preliminary results show the possibility to tailor a-SiC:H stacked heterostructures in order to optimise the LSP as an image and colour recognition sensor.

> SESSION A5: POSTER SESSION STRUCTURAL AND ELECTRONIC PROPERTIES OF AMORPHOUS SILICON Tuesday Evening, April 2, 2002 8:00 PM Salon 1-7 (Marriott)

A5.1 MICROSTRUCTURE CHARACTERIZATION OF a-Si BASED ALLOYS BY EFFUSION OF IMPLANTED HELIUM. Wolfhard Beyer and Friedhelm Finger, IPV, Forschungszentrum Jülich, Jülich, GERMANY.

Recently we demonstrated that the effusion of implanted helium is a useful technique for the structural characterization of amorphous and microcrystalline Si:H films. As a function of temperature, helium was found to effuse in two stages. The first (low temperature (LT)) stage was associated with the out-diffusion of He from network sites and the second (high temperature (HT)) stage was attributed to the effusion of He precipitated in isolated voids [1,2]. Here, we report on results of a structural characterization of various series of plasma-deposited a-Si based alloys by this method. The results show for wide bandgap alloys of silicon with oxygen, nitrogen and carbon already for low alloy concentrations a negligible HT helium effusion and a gradual decrease of the LT helium effusion temperature with rising alloy content. The first effect can be explained by the formation of interconnected voids at the expense of isolated voids; the second effect points to a general decrease in material density. The results are compared with effusion data of implanted Ne and Ar [3], which show higher effusion temperatures in agreement with the larger atomic radii, but similar shifts of the effusion peaks with changing alloy concentration. The relation of this shift to the changing incorporation and bonding of hydrogen will be discussed. The a-SiGe alloy films investigated show two He effusion stages similar to the corresponding a-Si:H films. Decreased LT He effusion temperatures demonstrate the presence of microstructure effects in this material, visible also in hydrogen effusion spectra.

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- 2. W. Beyer and U. Zastrow, Proc.  $19^{th}$  ICAMS, Nice, 27.-31.08.2001 3. W. Beyer, S.S. Camargo Jr. and R. Saleh, MRS Symp. Proc. 609 (2000) A23.4

### A5.2

TEMPERATURE-DEPENDENT TRANSIENT GRATING MEASUREMENTS (TG) IN a-Si:H. M. Niehus, P. Sanguino, S. Koynov, R. Schwarz, Physics Department, Instituto Superior Tecnico, IST, Lisbon, PORTUGAL.

Several groups have measured ambipolar photocarrier diffusion in amorphous hydrogenated silicon (a-Si:H) by transient grating (TG) experiments and found a diffusion coefficient D of about  $10^{-2}$  cm<sup>2</sup>/s, which is a factor of 100 higher than the value induced from ambipolar diffusion length measurements done under steady-state condition and under low injection. In this contribution we have looked at the temperature dependence of carrier mobility and photocarrier response time with the TG method in the temperature range of 280 to 470 K using 5 ns pulses from a frequency-doubled Nd:YAG laser at 532 nm. For read-out we passed the first-order diffracted beam from a HeNe laser to a photomultiplier through an quartz glass fiber for electronic background noise suppression. Pulse energy densities reached values up to 150 mJ/cm<sup>2</sup>/ where permanent gratings started to be burnt in. Below this limit, zero-order reflection was used to monitor transient sample heating. An intriguing observation was the inversion of the first-order diffracted beam signal that appeared once a permanent grating was partially burnt in. This effect may occur when the permanent grating pattern and the transient light pattern are off-set by half the grating period. If mobility were independent of temperature we would expect the diffusion coefficient D to increase linearly with temperature due to the Einstein relation. Mobility itsself would deacrease with a power law with an exponent of -1.5 when caused by phonon scattering at elevated temperatures. In amorphous silicon, however, due to the wide distribution of electronic states in the band gap, mobility should be increasing at low carrier injection due to trap filling. Our results show a sublinear decrease of D with temperature which indicates that transport measured with the TG method at high carrier density is already approaching transport properties of crystalline silicon.

#### $\underline{\mathbf{A5.3}}$

Abstract Withdrawn.

#### A5.4

CHARGE MODULATED INFRARED SPECTROSCOPY OF DEFECTS IN PHOSPHORUS-DOPED AMORPHOUS SILICON. Kai Zhu, E.A. Schiff, Department of Physics, Syracuse University, Syracuse, NY; G. Ganguly, BP Solar, Toano, VA.

We present infrared charge-modulation absorption spectra on phosphorus-doped amorphous silicon (a-Si:H:P) with doping levels between 0.17% - 5.0%. We find two distinct spectral lines that change systematically with the phosphorus doping level; their behavior suggests a very different perspective on doping at concentrations beyond 1.0% than would be inferred from prior work done primarily at lower concentrations.

At our lower doping levels (0.17%-1.0%) we find a single peak in the modulation spectrum near 0.8 eV with a width of 0.2 eV. We attribute this peak to optical transition involving the (0/-) level of a dangling bond. This peak deepens by about 0.1 eV as the doping level increases, suggesting that the (0/-) level lies deeper in more heavily doped material. Although the possibility of this effect has been noted previously, these data appear to be the first clear spectroscopic evidence for it.

At higher doping levels (1.0%-5.0%) we find an additional, sharper spectral line near 0.75 eV with a width of 0.1 eV. We attribute this second line to the internal optical transitions of a complex incorporating fourfold coordinated phosphorus and a dangling bond.<sup>2,3</sup> There is essentially no trace of the second line at a doping level of 0.5% or below, while this line is nearly fully developed at 1.0%. This suddenness in the onset is very surprising to us, and is suggestive of a phase transition.

This research was supported by the Thin Film Photovoltaics Partnership of the National Renewable Energy Laboratory.

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 M.P. Pétkov, M.H. Weber, K.G. Lynn, R.S. Crandall, V.J. Ghosh, Phys. Rev. Lett. 82, 3819 (1999).

### A5.5

TEMPERATURE COEFFICIENT OF RESISTANCE OF AMORPHOUS SILICON. A.J. Syllaios, T.R. Schimert, W.L. McCardel, R.W. Gooch, J.H. Tregilgas, Raytheon Commercial Infrared, Dallas, TX.

An important application of amorphous silicon (a-Si) is in microbolometer infrared detector arrays. Highly sensitive microbolometer arrays have been developed that take advantage of the high temperature coefficient of resistance (TCR) of a-Si. The temperature dependence of the electrical conductivity and TCR of Boron doped thin ( $\sim 2000~\text{Å}$ ) a-Si suspended membranes passivated with a-SiN was measured and analyzed. The a-Si test structures were prepared by RF plasma enhanced chemical vapor deposition (PECVD) and surface micromachining techniques. It was found that for certain growth conditions that are used in a-Si microbolometer array fabrication the conductivity is thermally activated,  $\sigma =$ 

 $\sigma_o \exp(-E/kT)$ , and its exponential prefactor,  $\sigma_o$ , is temperature independent. The activation energy, E, is also temperature independent and the temperature coefficient of resistance follows the relation TCR=-E/kT<sup>2</sup>. TCR generally increases for lower Boron doping.

#### A5.6

RECOMBINATION OF PHOTOCARRIERS AT FRONTAL INTERFACE AND ITS EFFECT ON a-Si:H SOLAR CELL PERFORMANCE. A. Kosarev<sup>a,b</sup>, A.S. Abramov<sup>b</sup>, Y. Poissant<sup>c</sup>, P. Roca i Cabarrocas<sup>c</sup>; <sup>a</sup>Electronics Dpt, Puebla, Pue., MEXICO; <sup>b</sup>Solid State Electronics Dpt., St.-Petersburg, RUSSIA; <sup>c</sup>LPICM (UMR 7647 CNRS), Palaiseau, FRANCE.

Little is known about recombination at interfaces in p-i-n (n-i-p) a-Si:H solar cells and even less about photo-induced changes in electronic properties of the interfaces. Recombination velocity of photoelectrons,  $\%S_n$ , or photo-holes,  $S_p$ , at the interface is the main electronic characteristic of the interfaces. Advances in crystalline silicon processing has reduced S from  $10^5$  to 0.1 cm/s and to 600sm/s in amorphous/crystalline hetero-junctions. This work is addressed to experimental study of surface recombination velocity at the frontal interface in p-i-n (n-i-p) a-Si:H structures. Photo-induced changes of the surface velocity under intensive light  $(\%1.5W/cm^2)$ soaking were also studied. The samples were fabricated by plasma enhanced CVD (PE CVD) at frequencies f = 13.5 and 56~MHz. During fabrication of p-i-n (n-i-p) structures we used ion bombardment or different deposition temperatures or buffer layer to change recombination at the frontal interface. The structures were studied in three states: as grown(A), light soaked (B) and annealed (C). Standard current-voltage diode characteristics were measured in the samples. Defect concentration in intrinsic layer was measured by constant photocurrent method. The recombination velocity was measured by method proposed in ref.[1]. Among the samples studied two structures were selected and kinetics of  $S_n$ ,  $S_p$  photo-induced changes were measured. To vary interface properties intrinsic layer prior deposition frontal p (or n) doped layer was treated by different ways: Ar, H ion bombardment, increasing ion energy by biasing. In A-state S was in the range of  $2.8x10^3$  to  $2x10^5$  sm/s, less magnitude was observed for n-i interface. In B-states all structures demonstrated larger S magnitudes by factor of 2 to 10. In annealed C-states S magnitudes returned either to the initial values (A-state) or to slightly less values and n-i interfaces again had lower S values. To understand the results obtained we performed computer modeling, considering the interface as 5-10 nm layer with different surface state concentration. This modeling revealed that not only parameters of the interface layer are important, but also occupation of states in the vicinity of the interface.

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SESSION A6: POSTER SESSION AMORPOUS AND MICROCRYSTALLINE SOLAR CELLS Tuesday Evening, April 2, 2002 8:00 PM Salon 1-7 (Marriott)

A6.1
PROTOCRYSTALLINE Si:H p-TYPE LAYERS FOR MAXIMIZATION OF THE OPEN CIRCUIT VOLTAGE OF a-Si:H n-i-p SOLAR CELLS. R.J. Koval, Chi Chen, G.M. Ferreira, A.S. Ferlauto, J.M. Pearce, P.I. Rovira, C.R. Wronski, and R.W. Collins, Materials Research Institute, Center for Thin Film Devices, and Department of Physics, The Pennsylvania State University, University Park, PA.

In early pioneering research, it was proposed that hydrogenated amorphous silicon (a-Si:H) n-i-p solar cells are significantly improved by incorporating p-type layers fabricated from microcrystalline silicon (μc-Si:H) [1]. Such a proposal was offered, however, before it was widely recognized that the phase of the Si:H (a vs.  $\mu$ c) deposited at high H<sub>2</sub>-dilution ratios R=[H<sub>2</sub>]/[SiH<sub>4</sub>] is extremely sensitive to the substrate material and the accumulated film thickness [2]. We have revisited the issue of p-layer optimization in a-Si:H solar cells, motivated by more recent work that has questioned the strategy of adopting single-phase  $\mu c\text{-Si:H}$  p-layers. Working with p-layer gas mixtures of  $H_2/SiH_4/BF_3$  in rf PECVD, we find that the maximum open circuit voltage (Voc) in n-i-p solar cells is obtained using p-layers prepared with the maximum R just before the transition from the a-Si:H growth regime to the mixed-phase  $(a+\mu c)$ -Si:H growth regime for the  $\sim 200$  Å layers. As a result, single-step p-layers are optimized in a manner similar to the i-layers, i.e., by operating in the so-called protocrystalline growth regime. Such a conclusion is reached by comparing deposition phase diagrams obtained by ex situ and real time spectroscopic ellipsometry (SE) with solar cell performance.

Deposition phase diagrams reveal that with increased doping gas flow ratio D=[BF<sub>3</sub>]/[SiH<sub>4</sub>], the amorphous-to-(mixed-phase microcrystalline) transition [denoted a $\rightarrow$ (a+ $\mu$ c)] shifts to higher R, thus opening up a wide regime in R (up to R=150) within which p-type a-Si:H can be obtained on an untreated R=10 a-Si:H substrate layer. In this regime, V<sub>oc</sub> increases with increasing R up to the a $\rightarrow$ (a+ $\mu$ c) transition, and shows a rapid decrease as R increases above the transition. [1] S. Guha, J. Yang, P. Nath, and M. Hack, Appl. Phys. Lett. 49, 218 (1986). [2] J. Koh, A.S. Ferlauto, P.I. Rovira, C.R. Wronski, and R.W. Collins, Appl. Phys. Lett. 75, 2286 (1999).

#### A6.2

LIFETIME AND  $\mu\tau$  PRODUCT OF MICROCRYSTALLINE SILICON ABSORBERS IN HIGHLY EFFICIENT THIN-FILM SOLAR CELLS. Torsten Brammer, Helmut Stiebig, Institute of Photovoltaics, Forschungszentrum Juelich GmbH, Juelich, GERMANY.

The optoelectronic properties of absorber layers in microcrystalline Si solar cells deposited with different silane concentrations (SC=1.5%-8%) were investigated by a comparison of experimental data with results obtained by numerical simulations. All the previous reported features [1] are well reproduced. The maximum in solar cell efficiency is not found in the highly crystalline growth region at small SC but in the transition region to amorphous growth (SC=5%-6%) The improvement in efficiency is correlated with the decreasing dark current and the consequential increase in open-circuit voltage and fill factor. Numerical simulations are applied to extract the defect density, recombination lifetime and mobility-lifetime product and the results are compared with analytic approaches. Evaluation of the dark reverse saturation current of the pin diodes indicates an increase of the recombination lifetime in the absorber material when SC is increased. The extraction efficiency of photogenerated carriers as a function of the forward bias applied to the pin diode is used to determine the mobility-lifetime product  $(\mu\tau)$ . A comparison of the experimental data for different SC with results of numerical device simulations shows that  $\mu\tau$  also increases when the amorphous growth regime is approached. Additionally, the peak in  $\mu\tau$  coincides with the maximum efficiency within the SC-series and equals 2E-7 cm<sup>2</sup>V This confirms earlier work [2], where, however,  $\mu\tau$  was determined on single layers and parallel to the layer surface. Combining the seperately determined recombination lifetime and  $\mu\tau$  product, it can be concluded that the mobility is almost independent of SC as long as transport in crystalline regions dominates (SC≤6%) [1] O. Vetterl et al, Solar Energy Materials and Solar Cells 62 (2000)

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### A6.3

SEMICONDUCTING POLYMER-AMORPHOUS SILICON INTERFACE IN SOLAR CELLS DEVICES. A.R. Middya, E.A. Schiff, Syracuse Univ, Dept of Physics, Syracuse, NY.

We have been investigating a semiconducting polymer as a window layer of amorphous silicon solar cells because of its several advantages over the inorganic counterpart, namely low-cost, large-area processing and compatibility with flexible substrates. A p-type, highly conducting, environmentally stable polymer blend poly(3,4-ethylenedioxythiophene) polysterene disulphonate (PEDOT:PSS) have been painted or spin-coated (at room temperature) on top of the intrinsic amorphous silicon (a-Si:H) layer of n/i structure on stainless steel or TCO-coated glass substrates. The device acts as a solar cell. We shall present our systematic studies on effect of surface treatment of a-Si:H by hydrofluoric acid (HF) before polymer was put down and subsequent curing procedure which control the performance of entire solar cells devices. We also investigated the metal/polymer interface to reduce the contact resistance, when thin gold layer was evaporated on top of polymer, Voc did not improve, however the short-circuit current improves by a factor of 10. In our effort to develop polymer/a-Si:H solar cells, so far we achieved around 750mV open-circuit and 1-2 mA/cm<sup>2</sup> short-circuit (J<sub>2</sub>) both on stainless steel and TCO coated glass substrates when electrical contact is taken directly from polymer. The low value of  $J_{sc}$  can easily be increased using thin gold or other metal contacts. We speculate that the limitation to  $V_{oc}$  is related to the low bandgap (1.6 eV) of PEDOT:PSS. We plan to investigate other commercially available high bandgap p-type conducting polymers to enhance Voc of a-Si:H solar cells using the technology developed for PEDOT:PSS. We shall discuss our present understanding about the device performance as well as the physics of semiconducting polymer/amorphous silicon interface. This research was supported through the Thin Film Photovoltaics Partnership of the National Renewable Energy Laboratory.

### A6.4

OPTICAL PROPERTIES OF I-LAYERS AS FUNCTION OF GROWTH RATE IN CORRELATION TO THE PERFORMANCE

OF a-Si:H SOLAR CELLS. <u>Keda Wang</u>, Jessica M. Owens, Jennifer Weinberg-Wolf, Daxing Han, <u>Univ of North Carolina at Chapel Hill</u>, Dept of Physics & Astronomy, Chapel Hill, NC; Lynn Gedvilas, National Renewable Energy Laboratory, Golden, CO; Gautam Ganguly, BPSolar, Toano, VA.

We studied two groups of a-Si:H samples prepared by DC-PECVD with a growth rates of 1, 3, and 10 Å/s. One group was intrinsic films the other group was correlated p-i-n solar cells. IR, Raman, PL and EL spectroscopies were used to study the i-layer properties in relation to the solar cell performance. 1. Raman shows an identical TO mode for all the samples, which indicates the local silicon-bonding configuration does not change with the growth rate from 1 to 10 Å/s. 2. IR absorption shows that the hydrogen configuration is monohydride Si-H bond characterized by the wagging mode at 630 cm<sup>-1</sup> and the stretching mode at 2000 cm<sup>-1</sup> for all the three films. The hydrogen content obtained from the 630 cm<sup>-1</sup> peak is 12-13 at %. Whereas, the oscillator strength for the stretching mode at 2000 cm<sup>-1</sup> becomes a two times stronger when the growth rate is \*3  $\rm \AA/s$ . The peak energy positions of the EL spectra at 80 K show correlation with the values of V  $V_{\rm OC}$ . Whereas, the peak energy positions of the PL spectra do not. This indicates that the value of the  $V_{\rm OC}$  depends on not only the optical gap of the i-layer but also the carrier transport. Although both the Si-H vibration absorption and the electronic density of states were varied with the film growth rate, the devices all had similar performance (>7% energy conversion efficiency) with i-layers having similar bandgaps ( ${\sim}1.7~{\rm eV}$ ). We were able to reproduce the same quality of the cells using the same conditions. The variation of the overall performance of the solar cells was about 2-4%. This work at UNC and BPSolar is supported by NREL thin film PV partnership under sub-subcontract XAK-8-17619-11 and ZAK-8-17619-02, respectively. L. Gedvilas is supported by the U.S. DOE under Contract No. DE-AC36-99GO10337.

#### A 6.

HYDROGENATED AMORPHOUS AND MICROCRYSTALLINE SILICON SOLAR CELLS USING AN EXPANDING THERMAL PLASMA. B.A. Korevaar, C. Smit, A.M.H.N. Petit, R.A.C.M.M. van Swaaij, Delft University of Technology, DIMES, Delft, THE NETHERLANDS; I. Houston, W.M.M. Kessels, M.C.M. van de Sanden, Eindhoven University of Technology, Eindhoven, THE NETHERLANDS.

A cascaded arc expanding thermal plasma is used to deposit intrinsic hydrogenated amorphous silicon at growth rates between 2 and 30  $\mathring{A}/s$ . Incorporation into a single junction p-i-n solar cell resulted in an initial efficiency of 6.7%, whereas all the optical and initial electrical properties of the individual layers are comparable with RF-PECVD deposited films. In this cell the intrinsic layer was deposited at 8.5  $\mathring{A}/s$  and at a deposition temperature of 250°C, which is the temperature limit for growing the p-i-n sequence. The cell efficiency is limited by the fill factor that can be increased by using a buffer layer at the p-i interface deposited with RF-PECVD at low growth rate. The increase in fill factor is achieved by a better initial defect density near the p-i interface then obtained with the expanding thermal plasma, resulting in better charge carrier collection. To use larger growth rates, while maintaining the material properties, higher deposition temperatures are required. To go to higher deposition temperature the cells are deposited in the n-i-p sequence, because a microcrystalline n-type layer can be made temperature resistant up to at least 400°C. Results will be presented on n-i-p deposited solar cells and on modelling work used to determine the optimal bandgap of intrinsic material in such solar cells. The latter work was carried out because the combination of larger growth rate and higher deposition temperature will decrease the optical gap of the material. In addition to a-Si:H also μc-Si:H can be made with a cascaded arc expanding thermal plasma. For the deposition of  $\mu$ c-Si:H also high growth rates up to 37 Å/s are achieved. Material properties will be shown indicating that the present challenge is to get dense material at these growth rates. Also preliminary results on cells with a microcrystalline intrinsic layer will be presented.

### $\underline{\mathbf{A6.6}}$

HYDROGENATED AMORPHOUS SILICON WITH HIGH GROWTH RATE, GAS UTILISATION AND HOMOGENEOUS DEPOSITION BY AMPLITUDE MODULATED VHF-PECVD FOR SOLAR CELL APPLICATION. J.K. Rath, A.C.W. Biebericher, W.F. van der Weg, Utrecht University, Debye Institute, Interface Physics, Utrecht, THE NETHERLANDS; W.J. Goedheer, FOM Institute for Plasma Physics, Nieuwegein, THE NETHERLANDS.

Hydrogenated amorphous silicon samples have been deposited by very high frequency plasma enhanced chemical vapour deposition (VHF PECVD), using a square-wave amplitude-modulated radio-frequency excitation. The increase in deposition rate compared to a continuous-wave plasma under the same conditions by using amplitude modulated plasmas gives rise to an improvement of the gas-utilisation efficiency.

Moreover, it is observed that the gas-utilisation efficiency improves by a considerable amount when amplitude modulation is combined with a reduction in the gas flows. Using a conventional 50MHz SiH4/H2 plasma with gas flows of 30 sccm, both for SiH4 and H2 at a pressure of 0.2 mbar, the gas-utilisation efficiency is about 8%. It increases up to 50%, by modulating the amplitude of the radio-frequency excitation signal and reducing both gas flows to 10 sccm, keeping the pressure constant. In this case, the deposition rate amounted to 0.55 nm/s. The combination of amplitude modulation and gas flow reduction gives rise to sufficient ion bombardment and hydrogen dilution at low flows. Device-quality opto-electronic properties are obtained under these conditions. The refractive index at 2 eV is about 4.25 and the microstructure parameter has a value around 0.02. The photo-to-dark-conductivity ratio is on average more than 1E6 after annealing for 60 minutes at 443 K. The material exhibited a low defect density (CPM) which is in the order of 1E15-1E16 per cubic centimetre. The Urbach energy amounted to 52 meV on the average. N-i-p solar cells (a number of cells of size 0.16 /square centimetre deposited on 10cmx10cm stainless steel (SS) substrate) in the configuration SS/n-a-Si:H/i-a-Si:H/p-microcrystalline-Si with i-layers made under conditions of a gas-utilisation efficiency 50% and a deposition rate of 0.55 nm/s, had a good Voc of 0.85 V on the average and an average fill factor of 0.7.

#### A6.7

INFLUENCE OF ZnO/p+a-Si:H AND Al/ZnO/n+a-Si:H MICROCRYSTALLIZATION ON PIN a-Si:H SOLAR CELLS PERFORMANCE. Andrzej Kolodziej, Pawel Krewniak, Stanislaw Nowak, Univ of Mining and Metallurgy, Dept of Electronics, Krakow,

The research described in the paper is intended to prepare the technological groundwork for Al/ZnO/n+/i a-Si:H and ZnO/p+/i a-Si:H junctions based on layers obtained by reactive magnetron sputtering (RMS) of Si:B, Si:P, Al, Zn:Al targets, but where the "i" layer is a protocrystalline RFCVD layer. Thanks to special magnetron source and magnetron-sample configuration the microcrystalline process of the bottom layers can be perfectly controlled and stimulated by surface temperature of the substrate and hydrogen content in the chamber. These single layers as well as respective structures are studied mainly using Grazing Incidence X Ray Analyzes, High Resolution Cross Section TEM and AFM spectroscopy. Particularly microcrystallization, thickness, roughness and chemical composition profile (by vacuum X ray fluorescence) of the films have been studied. Optical transmission and reflection measurements were used for indication of the light flux which reaches the "i" layer. We found out the experimentally observed angular distribution of scattered light in transmittance through glass/rough ZnO/p+ silicon junction. We discovered that the bottom  $0.03\mu m$ single phase crystalline p<sup>+</sup> layer forced crystallization of the protocrystalline "i" layer not far as  $0.08\mu\mathrm{m}$  thickness. In contrary, this effect was not observed in the case of  $0.03\mu\mathrm{m}$  middle range ordered p+ layer. Thus, the light reaching "i" layer is limited by the  $0.08\mu\mathrm{m}$  crystallized film. Additionally, the phase diagrams of amorphous-to-microcrystalline transition for the p+ on ZnO and n+ on ZnO silicon layers were presented. The optoelectronic properties of glass/ZnO/pin a-Si:H/ZnO/Al and glass/Al/ZnO/pin a-Si:H/ZnO cells are examined by systematic research of their I-V characteristics before and after steady-state conditions. This is supported by our modeling studies, which showed that the lowered gap, absorption loses and defects at the p/i interfaces hamper the efficiency of the cells. Various interface treatments have been studied and state of the art results were presented.

A6.8
NEW TRENDS IN SILICON PHOTOVOLTAICS. Francesco Roca, ENEA CR Portici-Naples, ITALY; Julio Carabe, CIEMAT-Espana.

Materials such as GaAs, CuInSe2, CdTe play an important role in photovoltaic conversion of solar energy but silicon is by far the reference material in photovoltaics. About 80% of the solar-cell world production has its origin in monocrystalline- and multicrystallinesilicon-wafer technology. Most of the remaining 20% is dominated by thin-film silicon (amorphous, microcrystalline, nanocrystalline, etc.) Experience has induced the conviction that crystalline-silicon technology must progress in the direction of lowering costs, mainly by investigating new growth processes leading to cheaper silicon of an acceptable quality. In parallel, the quality of thin-film silicon will be increased, including crystallinity and simultaneously thickness and growth rate. These two research lines seem to give excellent opportunities for synergy in amorphous/crystalline silicon heterojunction solar cells. There are reasons to think that the future of photovoltaics is marked by this convergence. The state of art in European Union on silicon photovoltaics and amorphous/crystralline heterojunction is analysed and described, with particular reference to the activities of two laboratories who hold a mutual collaboration both directly and through their involvement in EC-funded projects.

The most recent research results obtained in several field like emitter growth, cSi surface conditioning, new architectures, innovative optical-electrical characterization of stacked amorphous/crystalline silicon structures are depicted.

MODELING OF THE BANDGAP PROFILE IN THE INTRINSIC LAYER OF THE a-SiGe:H MATERIAL APPLICATION IN SOLAR CELL. R. Jimenez Zambrano, F.A. Rubinelli<sup>a</sup>, J.K. Rath, R.E.I. Schropp Utrecht University, Debye Institute, Physics of Devices, THE NETHERLANDS; <sup>a</sup>INTEC, Universidad Nacional del Litoral, ARGENTINA.

A series of systematic studies are being made on the optimum design of high efficiency a-Si:H/a-SiGe:H double-junction solar cell. It has been found that although the current of the top cell and the bottom cell are matched, the low fill factor of the bottom cell can limit the global characteristics of the double-junction. The a-SiGe:H alloy, constituent of the bottom cell, shows poor optoelectronic properties due to the high defect concentration of essentially dangling bonds of Ge. The design of the bandgap profile of this single junction can help to reduce the recombination losses since the electric field inside the i-layer is increased by the redistribution of the space charge Through computer simulations with the program D-AMPS, we have studied the influence of the shape of the front and back grading on the efficiency of the a-SiGe:H single junction under red light illumination. Our results show an appreciable improvement in open circuit voltage, fill factor and efficiency using an exponential profile instead of a linear profile. At the same time, the exponential grading maintain the short circuit current (the main issue in other profiles, like V-shape profile). The band bending produced by the exponential profile in the middle region of the i-layer induces a high electric field in the bulk (better carrier collection) together with a high optical absorption (more generated carriers).

Different a-SiGe:H single junction have been deposited by PECVD following the profile designs obtained by computer simulation. The profiles are monitored using Rutherford backscattering spectrometry (RBS). In the initial state, the exponential-shape profile shows the improvement with respect to the U-shape profile and the V-shape profile predicted by the computer simulations. Studies in the degradation behaviour are being carried out.

> SESSION A7: POSTER SESSION TFT's SENSORS AND NOVEL DEVICES Tuesday Evening, April 2, 2002 8:00 PMSalon 1-7 (Marriott)

 $\frac{A7.1}{C}$  TFA IMAGE SENSORS FOR LOW LIGHT LEVEL DETECTION. Juergen Sterzel, Frank Blecher, Matthias Hillebrand, Frank Muetze, Bernd Schneider, Markus Böhm, Universität-GH Siegen, Institut für Halbleiterelektronik (IHE), Siegen, GERMANY; Silicon Vision AG, Siegen, GERMANY.

The coating of ASICs with amorphous silicon based photo detectors, named TFA-technology (Thin Film on ASIC), opens new areas of application for CMOS image sensors. A higher sensitivity in the visible spectrum using amorphous silicon detectors has been demonstrated earlier. Now we focus on the lower detection threshold value for this technological structure. Image sensor pixels for low light levels, for example star sensors, have to handle photo currents in the femtoampere range and below. The concept which has been developed is based on a photo current of 0.8 fA. With an optics f-number of 1.2 this is comparable to the brightness of stars with a visible magnitude mv = 4.55. The noise behavior of the detector and that of the following circuit, besides the dark current, establish the detection limit. An early amplification of the photo current in every pixel reduces the influence of ASIC noise components on the signal. The pixel amplifier is realized as an inverter circuit. A pixel amplifier and a source follower readout has been designed in a 0.8  $\mu$ m-CMOS-SOIprocess in combination with an amorphous detector. With this approach and an optimized amplifier a noise equivalent current of 140 e has been reached at a working temperature of 280 K. The calculated conversion gain is 27 uV/e with a non-linearity of 0.5% and a dynamic range of 55 dB. Using a resistor for pixel readout the gain rises up to 106 uV/e compared to the source follower readout above The resistor readout results in a non-linearity of about 10%, while the noise equivalent charge is significantly reduced.

A NOVEL CONCEPT FOR AN AMORPHOUS SILICON UV DETECTOR. Matthias Hillebrand, Frank Blecher, Bernd Schneider, Jürgen Sterzel, Markus Böhm, Universität-GH Siegen, Institut für Halbleiterelektronik (IHE), Siegen, GERMANY.

A novel amorphous silicon UV detector for wavelengths between 180nm and 380nm without scintillator for future high resolution imagers is presented. UV imagers are widely used in chemical industry, in medical and in security technology. The concept is based on a coplanar configuration of the electrodes, similar to measurement structures to determine material characteristics of amorphous layers, e.g. for the constant photocurrent method (CPM). After passing a thin transparent passivations layer, the incident radiation is directly absorbed in the intrinsic a-Si:H material. Using this layout, absorption losses are avoided, as they occur in conventional photodetectors like pin diodes in near surface doped semiconductor layers. In contrast to CPM measurements, no ohmic contacts are required, but Schottky barriers. Here one Schottky contact is biased in forward direction and the other one in reverse direction. The two contacts of one detector pixel can be placed on top or below the photoactive layer or in a mixed configuration. The arrangement of the contacts may be varied according to the requirements, e.g. for one-dimensional or twodimensional sensor arrays. The surface dangling bond density is a crucial factor for the quantum efficiency. The surface defect density highly depends on the production process and the material of the passivation. A first test structure has been fabricated with sputtered chromium contacts on top of a  $0.7\mu m$  thick i-layer. A carbonized i-layer was deposited without using additional hydrogen. The distance between the Schottky contacts is  $3\mu m$ . With this simple coplanar structure a quantum efficiency of already 10% at 200nm wavelength was reached. The application of the new UV detector in the TFA technology (Thin Film on ASIC) is discussed, under consideration of the downscaling of ASIC feature sizes. The coplanar structure offers a small pixel capacity and therefore a high voltage sensitivity.

ANALYSIS OF THE BIAS DEPENDENT SPECTRAL RESPONSE OF a-SiC:H p-i-n PHOTODIODE. Yu. Vygranenko, P. Louro, M. Fernandes, R. Schwarz, M. Vieira, Electronics Telecommunications and Computer Dept, ISEL, Lisbon, PORTUGAL.

Up to now the physics of amorphous hydrogenated silicon-carbon p-i-n heterostructures is not completely understood. Experimental analysis combined with comprehensive numerical simulation are the tools used to develop a physical model for the dominant transport mechanism inside the heterostructures. To achieve unambiguous results it is useful to concentrate on peculiarities of the device, such as the bias voltage dependent spectral response and the current-voltage (I-V) characteristics under different light bias conditions. A series of large area single layers and heterojunction cells in the assembly glass/ZnO:Al/p (Si $_x$ C $_{1-x}$ :H)/i (Si:H)/n (Si $_x$ C $_{1-x}$ :H)/Al (0<x<1) were produced by PE-CVD at low temperature. The structural and optoelectronic properties of the single layers were determined through infrared and visible spectroscopy, temperature-dependent conductivity and complemented by CPM measurements. Junction properties, carrier transport, photogeneration and collection efficiency are investigated from dark and illuminated current-voltage characteristics and spectral response measurements, with and without additional background illumination and under different light bias conditions. The bias voltage dependent spectral response (with and without bias light) and the I-V dependence has been simulated and compared to experimentally obtained values. Results show that in the heterostructures the bias voltage influences the field and the diffusion part of the photocurrent differently. The interchange between primary and secondary photocurrent (i. e. between generator and load device operation) is explained by the interaction of field- and diffusion components within the photocurrent. A field reversal that depends on the light bias conditions (wavelength and intensity) explains the photocurrent reversal. The field reversal leads to the collapse of the diode regime (primary photocurrent) launches surface recombination at the p-i and i-n interfaces leading to a double-injection regime (secondary photocurrent). Considerations about conduction band offsets, electrical field profiles and inversion layers will be taken into account to explain the optical and voltage bias dependence of the spectral response

REDUCTION OF DARK CURRENT UNDER REVERSE BIAS IN a-Si:H p-i-n PHOTODETECTORS. Scott Morison, MVSystems Inc, Golden, CO; Peyman Servati, Arokia Nathan, Department of Electrical & Computer Engineering, University of Waterloo, Waterloo, Ontario, CANADA; Arun Madan, MVSystems Inc, Golden, CO.

Applications involving low-level light conditions impose stringent requirements in terms of the dark current in the photodetector. For example, using amorphous silicon (a-Si:H) p-i-n photodetectors, the dark current density under reverse bias must be reduced to the  $10^{-12}$ A/cm<sup>2</sup> range without compromising the photoresponse of the detector. The dark current of these devices is significantly affected by two important factors: the quality of the p-i interface and the band-gap of the p-type material. We addressed the latter by

employing a p-type a-SiC:H layer as a large band-gap (2.23eV) material so as to increase the built-in potential at the junction and thus reduce the dark current. At the same time, the large band gap (compared to a-Si:H) leads to a band-gap discontinuity, which can degrade the integrity of the interface. Thus, a graded layer is introduced at the p-i interface to provide a smooth and continuous transition of energies over a few monolayers. In addition, a thin insulating silicon carbide p-layer is introduced prior to deposition of the heavily doped p-region to further reduce the dark current. Initial test of the photodiode structures fabricated using these techniques exhibit dark current densities on the order of  $10^{-12}~\mathrm{A/cm^2}$  at a bias of ?0.8 volts. Optimization of both material and device structure for further improvement of the dark current will be discussed.

A NEW SELF-ALIGNED POLY-Si TFT EMPLOYING A PRE-PATTERNED AI MASK LAYER BY BACKSIDE EXPOSURE TECHNIQUE. Woo-Jin Nam, Min-Cheol Lee, Kee-Chan Park, Jae-Hoon Lee and Min-Koo Han.

Polycrystalline silicon thin film transistors (poly-Si TFTs) fabricated by excimer laser crystallization of amorphous Si film have attracted considerable interest for various display applications. The characteristics of poly-Si TFT are critically dependent on the grain qualities such as lateral grain size in the active channel and the defect density in the in-grain or grain boundaries. We have already reported the simple crystallization method using a pre-patterned aluminum (Al) layer on PECVD a-Si film (280°C). The pre-patterned Al layer behaves as a laser beam mask due to its high UV-reflectance so that the lateral grain is grown up to  $1.6\mu\mathrm{m}$  by inducing the large temperature gradient during excimer laser crystallization. However, with the Al pre-pattern which defines the channel and source/drain region beforehand, this method has a problem that the self-alignment technique cannot be easily employed in the gate formation. We propose a process technique using pre-patterned Al layer which not only induces the lateral grain growth in active channel region but also implement the self-aligned poly-Si TFT. In order to use the Al layer as a photolithography mask for the gate pattern, backside UV-exposure of photo-resist (AZ5214E for negative PR) through the active channel is required. We deposited a-Si film by IBS (ion-beam sputtering, 250°C) as a gate material and crystallized the film by excimer laser irradiation in order to improve the UV transparency. By employing this proposed method, a self-aligned poly-Si TFT with a single grain boundary within the  $2\mu m$  channel was successfully fabricated and high on/off current ratio ( $\sim 1 \mathrm{x} 10^7$ ) was obtained in our experiment.

A7.6
DEFECT CREATION AND ANNEALING AT SOURCE/DRAIN JUNCTION OF EXCIMER LASER ANNEALED POLYCRY-STALLINE THIN FILM TRANSISTOR. Kee-Chan Park, Jae-Shin Kim, Woo-Jin Nam, Min-Koo Han, Seoul National Univ, School of Electrical Engineering, Seoul, KOREA.

Low temperature polycrystalline silicon thin film transistors (LTPS-TFT) have attracted much attention for their possible application to the driving circuitry of active-matrix liquid crystal displays and organic light emitting diode displays. However the electrical characteristics of the LTPS-TFT such as carrier mobility, subthreshold swing and leakage current are easily degraded by electrical stress. Several factors such as poor interface characteristics between the gate insulator and the poly-Si channel and the high defect density in the poly-Si channel layer are reported to be responsible for the poor stability of the LTPS-TFT. Recently crystalline defects in the poly-Si channel layer at source/drain junction are suspected to be one of the major reasons of the stability problem by some researchers. The source/drain region of the LTPS-TFT is amorphized during the ion implantation for source/drain doping and recrystallized by excimer laser annealing. The junction defects are supposed to be generated due to insufficient laser activation energy at the source/ drain junctions of the poly-Si film because the laser beam can not reach the recessed poly-Si region at the gate pattern edge due to prominent gate electrode. However no evidence have been reported about the existence of the junction defects until now. The purpose of our work is to investigate the existence of the junction defects of the LTPS-TFT and the effects of various activation methods such as furnace annealing and laser annealing with various laser energy densities on the residual junction defects. The junction defect region at the source/drain of the LTPS-TFT investigated by the high-resolution transmission electron microscopy (HR-TEM) exhibited very short-range order (about ten nanometers) of silicon atom arrangement and very high defect density. The TEM results also showed that the length of the junction defect region was shorter than 100nm for the laser activation energy density of 160mJ/cm<sup>2</sup> and decreased as the laser energy increased. We successfully observed the junction defects at the source/drain of LTPS-TFT and investigated the effects of the laser energy density by HR-TEM for the first time.

#### A7.7

DEPENDENCE OF THE LATERAL PHOTOEFFECT IN a-Si:H P-I-N STRUCTURES ON THE MATERIAL CHARACTERISTICS STUDIED BY MEANS OF A NUMERICAL SIMULATION. Alessandro Fantoni, Miguel Fernandes, Manuela Vieira, Electronic and Cumminication Dept., ISEL, Lisboa, PORTUGAL.

When an a-Si:H p-i-n structure is locally illuminated by a light spot, the non uniformity of light causes the appearance of a gradient in the carrier concentration between the illuminated and the dark zone. Carrier start to flow in agreement with such gradients, and when equilibrium is reached, the lateral diffusion process is counterbalanced by the appearance of a lateral component of the electric field vector in addition to the transverse usual one. The lateral fields act as a gate for the lateral flow of the carriers and small lateral currents appears at the transition region between the illuminated and the dark zone. Known as lateral photoeffect, this phenomena depends on the incident light wavelength, light intensity and on the applied bias. Anyway, its intensity can be, depending on the foreseen application, alternatively enhanced or reduced by correct device engineering. We have used the 2D numerical simulator ASCA to analyze the behavior of a-Si:H p-i-n structures under local illumination with the goal of observing the appearance of the lateral components of the electric field and current density vectors. The dependence of the lateral potential redistribution on the doping density, density of defects in the intrinsic layer, and layer thickness have been analyzed. This study aims to show how material properties and device geometry can be combined in order to control the lateral photoeffect.

#### A7.8

SHORT CHANNEL POLY-SI TFT WITH SINGLE GRAIN BOUNDARY BY EXCIMER LASER ANNEALING ON Al-MASKED a-SI LAYER. Sang-Hoon Jung, Jae-Hong Jeon, Jae-Hoon Lee and Min-Koo Han.

Polycrystalline silicon thin film transistors (poly-Si TFTs) processed at low temperature (below 450°C) with excimer laser annealing (ELA) of amorphous silicon (a-Si) film are devices of great importance in a large area flat panel display. The characteristics of poly-Si TFT are critically dependent on the grain size and the number of grain boundaries in the channel. Various efforts have been made in order to increase the grain size such as sequential lateral solidification (SLS). However SLS requires a rather sophisticated beam scan process. Recently, we have reported that the excimer laser irradiation on PECVD a-Si with pre-patterned aluminum (Al) mask induces the lateral grain growth effectively. The laser irradiation on a-Si film with the Al pattern results in the selective melting of a-Si due to its high UV-reflectance. The large temperature gradient between the liquid and solid regions causes the nucleation to be initiated preferentially at the edge of Al pattern and the lateral grain size increases up to  $1.6\mu m$ . Our method does not require any additional accurate motion controllers and is carried out by a single pulse. We report short channel poly-Si TFTs with a single grain boundary fabricated by the proposed excimer laser annealing. The Al patterns have been allocated on the source and drain. After the excimer laser irradiation for the recrystallization of the channel layer, the nucleation is initiated at both the edges of the source and drain. We fabricated short channel TFTs with the channel length of  $3\mu m$ , which have only single grain boundary in the channel by proposed method. The electrical characteristics of the proposed poly-Si TFT have been improved considerably due to the lowered grain boundary density. The proposed short channel poly-Si TFT with single grain boundary exhibits high mobility as  $222 \mathrm{cm}^2/\mathrm{Vsec}$  and large on/off current ratio exceeding  $1 \times 10^8$ .

# A7.9

TEMPERATURE DEPENDENCE OF HIGH-MOBILITY POLY-Si TFT WITH SINGLE GRAIN BOUNDARY. In-Hyuk Song, Cheon-Hong Kim, Min-Koo Han.

XeCl excimer laser crystallization (ELC) has become a key technology to fabricate high performance polycrystalline silicon (poly-Si) thin film transistors (TFTs). Recently, various efforts have been reported in order to control the SLG (super lateral growth) phenomenon artificially with the final objective to fabricate the poly-Si TFTs with one or no grain boundary perpendicular to the current path. We have already reported a new ELC method to enlarge the grain size by employing a selectively floating amorphous silicon (a-Si) thin film with a thin air-gap [1]. Large lateral grains exceeding 4 microns have been grown due to the lateral thermal gradient caused by the low thermal conductivity of the air. We have fabricated n-type self-aligned TFTs by the proposed laser crystallization method and a high mobility of 331cm<sup>2</sup>/Vsec was obtained because the device has only one grain boundary perpendicular to the current path in the channel. We have investigated temperature dependence of drain current in high-mobility TFTs with large lateral grains. The drain current was measured in the temperature range from 25°C to 110°C. It is well

known that the driving current of poly-Si TFTs is increased with increasing temperature due to the activated mobility property resulted from potential barrier height. However, drain current of the proposed TFT is decreased as temperature increases, which results in a negative activation energy of -0.025eV at  $\rm V_{DS}=0.1V$  and  $\rm V_{GS}=20V$ . The mobility is also decreased with increasing temperature. Because the proposed device has large lateral grains in the channel, the lattice scattering inside the grain would be dominant, which is similar to single crystal Si MOSFETs.

#### A7.10

ELECTRICAL CHARACTERIZATION OF PHOTO-OXIDIZED  $\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y$  FILMS. Peter J. Bjeletich, Jeff J. Peterson, Charles E. Hunt, Department of Electrical and Computer Engineering, University of California at Davis, Davis, CA; Jun-Ying Zhang, Ian W. Boyd, Electronic and Electrical Engineering, University College-London, London, UNITED KINGDOM; McDonald Robinson, Lawrence Semiconductor Research Laboratory, Tempe, AZ.

MOS capacitors were fabricated from uncapped thin film  $\mathrm{Si}_{1-x-y}\mathrm{Ge}_x\mathrm{C}_y$  (SiGeC) layers of various compositions using a novel photo-enhanced oxidation procedure. Previous work on silicon has shown that photo-oxidation yields a high quality oxide, comparable to thermal oxidation, without using high temperatures. This low-temperature oxidation technique enables oxide growth without the germanium segregation associated with thermal oxidation of SiGeC, eliminating the need for a silicon cap layer. In order to evaluate the electrical quality of the oxides produced, Capacitance-Voltage (CV) measurements are extracted from the MOS capacitors. Both low frequency and high frequency CV curves are taken to determine the interface state density and the fixed oxide charge associated with the various SiGeC compositions. This information helps to determine the oxides usefulness as gate dielectrics in SiGeC MOSFETs. Combining these data with previously obtained mobility data allows for the design of high performance SiGeC devices.

SESSION A8: POSTER SESSION NANOCRYSTALLINE SILICON AND QUANTUM DOTS Tuesday Evening, April 2, 2002 8:00 PM Salon 1-7 (Marriott)

### A8.1

LOW PRESSURE CHEMICAL VAPOR DEPOSITION OF Si NANOCRYSTALS FOR NON-VOLATILE MEMORIES. R. Rao, K. Scheer, G. Malyavanatham, R. Muralidhar, X.-D. Wang, J. Hooker, J. Kulik, B.-Y. Nguyen, and B. White, Advanced Process Development and External Research, Motorola SPS, Austin, TX.

Si nanocrystal based non-volatile memories are increasingly attracting more research effort due to their low voltage operation, long retention and fast write times. A critical technology issue in the fabrication of these devices is the uniform deposition of a high density (of the order of  $10^{12}/\mathrm{cm}^2$ ) of Si nanocrystals without inducing coalescence. Such a high density of Si nanocrystals is not easily achieved on SiO<sub>2</sub> substrates. Numerous efforts have focussed on obtaining a high density of nanocrystals through a variety of deposition techniques including aerosol technique, sol-gel technique, ion-implantation, low pressure chemical vapor deposition (LPCVD), molecular beam epitaxy and cluster beam evaporation. We have grown Si nanocrystals on  $SiO_2$  and  $Si_3N_4$  substrates by LPCVD and characterized the size and density of these nanocrystals using atomic force microscopy, scanning electron microscopy and transmission electron microscopy This paper will explore the nucleation and growth mechanisms of Si nanocrsytals deposited by LPCVD on dielectric surfaces. Specifically, the nucleation curves from incubation to coalescence will be compared on different substrate surfaces. The influence of precursor gas partial pressure and substrate temperature on the nucleation and growth characteristics will be investigated in terms of the size and density of the Si nanocrystals. Furthermore, the use of different precursor and carrier gases will also be compared.

### A8.2

LOW TEMPERATURE SYNTHESES OF NANO-CRYSTALLINE SILICON FILMS AND SI NANORODS BY HOT-WIRE CVD. Te-Chi Wong, Jih-Jen Wu, National Cheng Kung University, Department of Chemical Engineering, Tainan, TAIWAN.

Low temperature growth of nano-crystalline silicon films and silicon nanorods by hot-wire chemical vapor deposition (HWCVD) using  $\mathrm{SiCl_4/H_2}$  gases are reported here. Nano-crystalline Si film was deposited at a filament temperature of  $1800^{\circ}\mathrm{C}$  and a substrate temperature of  $150^{\circ}\mathrm{C}$ . The crystallinity of the film characterized by Raman spectroscopy was 77%. While the filament temperature

lowered to 1700°C, Si nanorods with an average diameter size of 60 nm were obtained as the substrate temperatures were lower than 200°C. Raman analyses indicated that the Si nanorods were amorphous. The distribution of gas phase species (e.g.  $\mathrm{SiH}_x\mathrm{Cl}_y\bullet$ ,  $\mathrm{H}\bullet$ ) that were produced under different filament temperatures could play a key role on the Si nanostructures growth.

#### A8.3

NUCLEATION AND GROWTH MECHANISMS OF Si NANOCRYSTALS VIA PHYSICAL AND CHEMICAL VAPOR DEPOSITION PROCESSES. T. Leach, G. Malyavanatham, Jianhong Zhu and J.G. Ekerdt, Dept of Chemical Engineering, University of Texas, Austin, TX; R. Rao, K. Scheer, R. Muralidhar, B.-Y. Nguyen, and B. White, Advanced Process Development and External Research, Motorola SPS, Austin, TX.

The control of silicon nanocrystal density and size is crucial in silicon nanocrystal based electron devices such as single electron transistors and nanocrystal floating gate memories. The atomistic nucleation and growth of Si nanocrystals on structureless substrates like silicon dioxide and silicon nitride occurs via a Volmer/Weber island growth mechanism that exhibits (a) an incubation phase where the adatom concentration in surface builds up, (b) a rapid nucleation phase where stable clusters are formed, (c) a saturation phase where the density of nanocrystals remains constant but increase of size occurs and (d) a coalescence phase where growing nanocrystals begin to touch each other. In this paper, we focus on the first two stages via physical vapor deposition (PVD) achieved via cracking of reactant to form silicon and UHVCVD/LPCVD with the objective of understanding the roles of gas phase transport, surface reaction and surface diffusion of adatoms. In physical vapor deposition, the nanocrystal density is dependent on two time scales, a) arrival of Si atoms on the surface and b) surface diffusion. In chemical vapor deposition, there can be three timescales: a) arrival of chemisorbing species on the surface, b) surface reaction including by-product desorption and c) surface diffusion of Si adatoms. This is particularly so when incoming adsorption sites potentially block the chemisorbing species. Experimental results as a function of reactant type and reactant partial pressure, surface temperature and type of adsorbing surface will be used to delineate the differences between PVD and CVD methods. A first principles model accounting for adatom formation, surface diffusion and clustering will be used to interpret the results. This work attempts to delineate for the first time the differences between PVD and CVD on saturation density of nanocrystals.

#### A8.4

COMBINATORIAL FABRICATION AND STUDIES OF LUMINESCENT SI NANOPARTICLES EMBEDDED IN AMORPHOUS SiO<sub>2</sub> THIN FILMS. O. Resto, L. Fonseca, and S.Z. Weisz, Department of Physics and Materials Research Center, University of Puerto Rico, San Juan, PR; F. Laabs, and S. Chumbley, Ames Laboratory - USDOE and Department of Materials Science and Engineering, Iowa State University, Ames, IA; T.C. Wong, C.S. Lee, and S.T. Lee, Department of Physics and Materials Science, City University of Hong Kong, Kowloon, HONG KONG; J. Shinar, Ames Laboratory - USDOE and Department of Physics and Astronomy, Iowa State University, Ames, IA.

Linear combinatorial arrays of luminescent Si nanoparticles embedded in an amorphous  $\mathrm{SiO}_2$  film are described. The arrays were fabricated by rf sputtering a target composed of a 6" diameter  $\mathrm{SiO}_2$  disk and a 7.0 cm<sup>2</sup> rectangular Si wafer, which was placed at the edge of the SiO<sub>2</sub> disk, in 20 mtorr of Ar at an rf power of 220 W. The substrate was a strip of 14.0cm x 1cm quartz positioned along the line connecting the centers of the SiO<sub>2</sub> and Si targets. Following deposition of the 8 micron-thick films, they were annealed for 30 minutes at  $1100^{\circ}$  C. The resulting dependence of the photoluminescence (PL) of each section of the film on its position on the strip is consistent with a film containing a size and concentration gradient of luminescent Si nanoparticles embedded in a SiO2 matrix, as implied by a noncombinatorial rf sputter deposition of such films from a SiO2 target covered with sections of a Si wafer [1]. In the current study the section of the strip which was over the Si wafer the PL was strongest and peaked at ~760 nm. In the sections farthest from the Si wafer, the PL was the weakest and peaked at ~600 nm. The behavior of the PL under varying deposition and annealing conditions, its dependence on the temperature, and its relation to the film morphology, as revealed by transmission electron microscopy (TEM) measurements, will also be discussed. Ames Laboratory is operated by Iowa State University for the USDOE under Contract W-7405-Eng-82. [1] S. Hayashi, T. Nagareda, Y. Kazawa, and K. Yamamoto, Jpn. J. Appl. Phys. 32, 3840 (1993); Q. Zhang, S.C. Bayliss, and D.A. Hutt,

### A8.5

1-D ORDERING OF SELF-ASSEMBLED Ge DOTS ON

Appl. Phys. Lett. 66, 1977 (1995).

PHOTOLITHOGRPHICALLY PATTERNED Si (001) STRIPES. B. Yang, A.R. Woll, P. Rugheimer and M.G. Lagally, University of Wisconsin-Madison, Madison, WI.

We report a novel way to achieve controlled one-dimensional (1-D) self-assembled Ge quantum dots arrays on several microns wide Si (001) stripes patterned via conventional photolithography and plasma etching. Flashing at 1200°C is used to narrow down the stripes; then CVD growth is performed at 650°C. The self-assembled quantum dots, characterized after growth by atomic force microscopy (AFM) are about 250 nm wide and 50 nm high on the average after about 25 ML Ge deposition. They are well aligned along the narrow ridges of the stripes and form diamond-shaped rings at the cross of the stripes. The process avoids complicated lithography that is generally necessary to achieve alignment at these dimensions. Our studies show that the self-alignment of Ge quantum dots is dependent on the stripe width. Low-energy electron microscopy (LEEM) is used in situ just prior to the growth to monitor the width of the stripes and the alignment of the quantum dots. Because of the stress anisotropy of the Si (001) 2x1 reconstruction, LEEM is sensitive to morphology-induced variations of the surface strain on the stripes. Combining LEEM and AFM, we will discuss the use of varying the stripe height, width, and flashing time to probe the effects of surface morphology and strain on Ge quantum dots nucleation and self-alignment. Supported by ONR and NSF.

### SESSION A9: POSTER SESSION RARE-EARTH DOPED MATERIALS Tuesday Evening, April 2, 2002 8:00 PM Salon 1-7 (Marriott)

#### A9.1

EVOLUTION OF THE ERBIUM ENVIRONMENT IN SILICON NANOCRYSTALS UNDER THERMAL TREATMENT. <u>L.R. Tessler</u>, UNICAMP, Instituto de Física "Gleb Wataghin", Campinas, SP, BRAZIL; J. Coffer, J. Ji, R. Senter, Texas Christian University, Dept of Chemistry, Fort Worth, TX.

Erbium-doped silicon nanocrystals can be prepared by the pyrolysis of Si<sub>2</sub>H<sub>6</sub> diluted in a carrier gas in the presence of an appropriate Er carrier compound, Er(tmhd)<sub>3</sub>. By controlling the reactor geometry, samples can be prepared in a variety of sizes (3 to 30 nm average diameter) either with a homogeneous distribution of Er (H-Er) or with a pure Si core and an Er-rich surface (S-Er). While H-Er samples emit  ${\rm Er}^{3+}$  photoluminescence at 1.54  $\mu {\rm m}$  as prepared, S-Er samples need to be annealed at high temperatures to present  ${\rm Er}^{3+}$  luminescence. In previous work we have shown that in the luminescent H-Er samples the Er environment is very similar to that found in a-Si:H. Low Er coordination provides a low symmetry environment which is favorable to Er<sup>3+</sup> luminescence. In the present work we report on the evolution of the Er environment with annealing temperature for a set of S-Er samples with an average diameter of 26.7 nm. The Er environment was determined by EXAFS at the  $L_{III}$  edge. In all samples Er is coordinated to oxygen. In the as-prepared samples Er is overcoordinated, having 7 first neighbors on average. This may be a consequence of water adsorption in the precursor, which often presents Er over-coordination in EXAFS measurements. The average coordination number decreases with annealing temperature, reaching 5.3 for treatment at 815°C. The Er-O separation also decreases with annealing, going from 2.31±0.01Å in the as deposited samples to 2.23±0.01Å for the 815°C annealed material. In luminescent H-Er the interatomic separation is  $2.19\pm0.01$ Å and in Er<sub>2</sub>O<sub>3</sub> it is 2.26Å.

### A9.2

TEMPERATURE INDEPENDENT  $\mathrm{Er^{3+}}$  PHOTOLUMINESCENCE LIFETIME IN a-SiO $_x$ :H<Er>. L.R. Tessler, D. Biggemann, UNICAMP, Instituto de Física "Gleb Wataghin", Campinas, SP, BRAZIL.

The photoluminescence (PL) lifetime of  $\rm Er^{3+}$  in a-Si:H<Er> and a-SiO\_x:H<Er> was measured between 15 and 300K for a set of samples containing ~1 at. % Er and up to ~10 at. % O. The samples were prepared by RF co-sputtering from a Si target partially covered by metallic Er platelets. The oxygen content in the samples was controlled by introducing a small (up to  $5 \times 10^5$  mbar) O<sub>2</sub> partial pressure in the deposition chamber. Photoluminescence spectra were obtained by exciting with the 514nm line of an Ar<sup>+</sup> laser. The room temperature PL intensity increased and the temperature quenching decreased with O content. The maximum PL intensity at 15K, however, is obtained from samples with no intentional oxygen added. The PL lifetimes were measured by two different techniques: Quadrature Frequency Resolved Spectroscopy (QFRS) and direct observation of the PL decay in a fast digital oscilloscope after a 5 ns excitation pulse (532 nm, doubled Nd:YAG laser). The QFRS signal is well fitted supposing two lifetimes, a fast decay in the 20 - 150  $\mu$ s

range and a slow decay in the 200 - 830  $\mu s$  range. Both lifetimes increase with the O content. The QFRS measurements are confirmed by the direct observation of the PL decay. Only in samples with no intentional oxygen added the lifetimes decrease with temperature. For all other samples both fast and slow lifetimes do not depend on the temperature within experimental incertitude. From the results we can conclude that there are at least two different lattice sites for Er<sup>3+</sup> in a-Si:H<Er> and a-SiO<sub>x</sub>:H<Er>, consistently with previous EXAFS measurements. Moreover, the de-excitation rate of the Er<sup>3+</sup> ions by multiple phonon emission is negligible in this class of materials, making them good candidates for active media in optical devices.

#### A9.3

INTERRELATION BETWEEN MICROSTRUCTURE AND OPTICAL PROPERTIES OF ERBIUM DOPED NANO-CRYSTALLINE SILICON THIN FILMS. Maria Losurdo, MariaMichela Giangregorio, Giovanni Bruno, Plasma Chemistry Research Center-CNR, Bari, ITALY; M.F. Cerqueira, Departamento de Fisica, Universidade do Minho, Braga, PORTUGAL; M.V. Stepikhova, Institute for Physics of Microstrucutres RAS, Novgorod, RUSSIA.

Nanocrystalline silicon (nc-Si) thin films also Er-doped have been attracting enormous scientific and technological interest for applications in Si-based optoelectronic devices, such as the realization of integrated Si-based visible and infrared light emitters and detectors. Specifically, nc-Si:H,Er,O films take on special significance for optical communication systems due to the emission line at 1.54  $\mu m$  (originating by the intra-4f transitions of Er<sup>3+</sup> ions), which corresponds to the absorption minimum of silica-based glass optical fibers. The idea is based on the band-gap widening of nanometer size Si, which consequently results in reducing the thermal quenching of Er photoluminescence (PL). On the other hand, Si nanocrystals, that are well known to emit in the visible range, due to the recombination of confined excitons within the nanostructure, may act as efficient sensitizers for the erbium ions. However, photoluminescence properties of the Er<sup>3+</sup> ions ions and/or of Si-nanocrystallites is strongly influenced by the complex nanostructure of films, i.e. the nanocrystalline volume fraction and crystallite size, and by the impurity content (mainly oxygen and hydrogen). Hence, it is important a detailed investigation of the "anatomy" of the nc-Si:Er,O films, i.e. the layered structure, the non homogeneous distribution of the nc-Si and a-Si phases, the in-depth distribution of the SiO phase, and of the role of nc-Si/a-Si/SiO interfaces, which are strongly dependent on the growth conditions. In the present contribution the effect of the deposition conditions (temperature, hydrogen dilution, plasma configuration) on nanostructure of nc-Si films obtained by PECVD from  $SiH_4$ - $H_2$  plasmas and co-sputtering is investigated. In addition, the correlation between nanostructure of nc-Si:H films also Er-doped and the photoluminescence properties is studied. The peculiarity of this study is the use of spectroscopic ellipsometry to elucidate any correlation between the PL efficiency and the matrix, i.e., the silicon nanocrystallite volume fraction and size, and the SiOx composition. The role of the nanostructure on the competition between PL fron nanocrystals in the visible and PL from  ${\rm Er^{3+}}$  ions at 1.54  $\mu {\rm m}$  is discussed. Ellipsometric and PL data are corroborated with XRD, Raman and RBS measurements.

### A9.4

SUPERSONIC-FREE-JET CVD GROWTH OF DY-DOPED SILICON FILMS FOR 1.3 MICRON LED. S. Kawai, K. Matsutake, F. Watanabe, and <u>T. Motooka</u>, Kyushu University, Dept of Materials Science and Engineering, Fukuoka, JAPAN.

Silicon-based optoelectronics is of great importance for a breakthrough in future silicon microelectronics technologies threatened by an "interconnection bottleneck." Although extensive studies have been carried out to develop Er-doped silicon light-emitting diodes (LEDs) for 1.54  $\mu m$  fiber optic communications, little work has been done to develop silicon photonic devices with 1.3  $\mu$ m luminescence which gives rise to minimum chromatic dispersion of silica-fiber. We have investigated epitaxial film growth of dysprosium (Dy)-doped silicon for fabrication of 1.3  $\mu m$  LED based on chemical vapor deposition using supersonic free jets of Si<sub>2</sub>H<sub>6</sub> and Dy(C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>)<sub>3</sub> gases combined with transmission electron microscopy and secondary ion mass spectroscopy (SIMS) measurements as well as electrical and optical characterization. Epitaxial and polycrystalline films with thickness 80-400 nm were grown on n<sup>+</sup>, p, and p<sup>+</sup>-Si(100) substrates at 800°C for 90-150 min. SIMS measurements revealed that Dy was primarily distributed near the surface region with the peak concentration up to 10<sup>19</sup> cm<sup>-3</sup>. Based on current-voltage and capacitance-voltage measurements, we have found that Dy introduces donor states in silicon and the concentration of Dy related donors saturates at  $\approx 10^{17}$  cm<sup>-3</sup>. Electroluminescence measurements at room temperature using reverse-biased diodes composed of n-type Dy-doped films on p<sup>+</sup>-silicon substrates are currently under way.

#### SESSION A10: POSTER SESSION SILICON NITRIDE AND OTHER NITRIDES Tuesday Evening, April 2, 2002 8:00 PM Salon 1-7 (Marriott)

#### A10.1

THE ELECTRONIC STRUCTURE AND OTHER PROPERTIES OF AMORPHOUS SILICON NITRIDE INVESTIGATED WITH DENSITY FUNTIONAL THEORY. <u>Peter Kroll</u>, Institute of Inorganic Chemistry, RWTH Aachen, GERMANY.

Structural models of amorphous silicon nitride, a-Si<sub>3</sub>N<sub>4</sub>, consisting of 112-448 atoms, were studied using density functional methods. We used continuous random alternating networks with well-defined topology for the representation of chemical order in the material and compared them to "ab initio derived" models obtained from quenching a hypothetical melt. The chemical order, the absence of like-atom bonds such as Si-Si and N-N bonds in a-Si<sub>3</sub>N<sub>4</sub>, and the almost ideal coordination of all atoms is maintained in the network models even after Car-Parrinello molecular dynamic (CPMD) simulations at elevated temperatures for several pico-seconds, in sharp contrast to "ab initio derived" models. Structures of a-Si<sub>3</sub>N<sub>4</sub> we constructed have densities between 2.6 and 3.2 g/cm<sup>3</sup> and have very few topological defects, e.g. the percentage of trigonal-planar three-connected Si is below 1%, while the two-connected N is more likely to occur. To avoid the energetically unfavorable three-connected defect-state, Si tends to build up very long Si-N bonds up to 2.2 Å. Although low-density structures typically contain cavities and pores, there is hardly a detectable trend of total energy or average connectivity with density. The elastic properties, however, decrease with decreasing density. We furthermore discuss the properties of the material after alloying elements such as H, B, C, and O, especially their effect of stabilizing internal surfaces and low-density structures.

#### A10.2

HIGH HYDROGEN CONTENT SILICON NITRIDE FOR PHOTOVOLTAIC APPLICATIONS DEPOSITED BY HOT-WIRE CHEMICAL VAPOR DEPOSITION. J.K. Holt, M. Swiatek, D.G. Goodwin, and Harry A. Atwater, Thomas J. Watson Laboratories of Applied Physics, California Institute of Technology, Pasadena, CA.

Hot-wire chemical vapor deposition has been widely used for the growth of hydrogenated amorphous and polycrystalline silicon. It was recently demonstrated by Sato et al. [1] that the technique can also be applied to the growth of silicon nitride for gate dielectric applications compatible with ULSI technology. Another application for hot-wiregrown silicon nitride lies in surface passivation and antireflection coating of silicon solar cells. We have succeeded in growing silicon nitride layers of 200 nm thickness on lightly-doped p-type (350 Ω·cm), double-side polished, float-zone silicon wafers at a substrate temperature of 280  $^{\circ}\mathrm{C}$  . The gas mixture used for film growth consists of 16.0 sccm of 1% SiH $_4$  in He and 8.7 sccm of NH $_3$ , at a total pressure of 20 mTorr; the large NH<sub>3</sub>/SiH<sub>4</sub> flow ratio (~50) is believed to be critical to obtaining stoichiometric  $(\mathrm{Si}_3\,\mathrm{N}_4)$  films. Measurements of the decomposition kinetics of NH3 (via threshold ionization mass spectrometry) on the tungsten wire used in the reactor suggest that this may be related to the low decomposition probability of NH3 relative to  $SiH_4$  (factor of 100 less). It is notable that the decomposition reaction of NH3 at the wire to produce NH2 appears to be catalyzed, with an apparent activation energy of 31 kcal/mole (compared with the N-H bond dissociation energy of 93 kcal/mole) The as-grown silicon nitride films were analyzed ex-situ with a number of techniques. Ellipsometry measurements indicate a refractive index of 1.8 (at 633 nm), which is tunable with changes in the NH<sub>3</sub>/SiH<sub>4</sub> flow ratio. X-ray Photoelectron Spectroscopy was performed on the as-grown silicon nitride and a reference sample deposited via plasma enhanced chemical vapor deposition. Chemical shifts in the oxygen signal and a ratio of Si/N>1 suggest the presence of an oxide at the surface in both samples (thicker in our sample). The nitrogen signal of the reference sample is consistent with Si<sub>3</sub>N<sub>4</sub> while that of our sample indicates non-stoichiometric silicon nitride. Fourier Transform Infrared transmission spectra were collected on as-grown samples, revealing the presence of H-N and N-Si bonds, with a negligible amount of H-Si; the low Si-H to N-H bond concentration is characteristic of low index films such as these [2]. The total bonded hydrogen content is approximately  $1.8 \times 10^{22}$  cm<sup>-3</sup> ( $\sim 22$  atomic %), consistent with the low growth temperatures used. A series of annealing treatments were performed to evaluate the ability to hydrogenate the underlying substrate. At the highest annealing temperature used (800°C), a factor of 7 reduction in the bonded hydrogen content of the silicon nitride film was observed. Thus, we can incorporate a large fraction of H in the as-grown silicon nitride film (without a post-deposition hydrogen treatment) and deliver a significant amount to the underlying substrate. These results suggest hot-wire silicon nitride is an excellent candidate for a silicon solar cell passivation coating.

[1] H. Sato, A. Izumi, H. Matsumura, Appl. Phys. Lett. 77 (17), 2752 (2000).

[2] T. Lauinger, J. Moschner, A. Aberle, and R. Hezel, *J. Vac. Sci. Technol.* A 16(2), 530 (1997).

#### A10.3

TOW TEMPERATURE FORMATION OF SILICON NITRIDE FILM; COMBINATION OF CATALYTIC-NITRIDATION AND CATALYTIC-CVD. A. Izumi, A. Kikkawa and H. Matsumura, JAIST (Japan Advanced Institute of Science and Technology), Ishikawa, JAPAN.

Silicon nitride  $(SiN_x)$  films prepared at low temperatures are widely applicable such as gate dielectric films of thin film transistors (TFT) of liquid crystal displays (LCD). In this work,  $SiN_x$  films are formed by combination of direct nitridation (catalytic-nitridation) and catalytic-CVD at low temperature around 300°C. In this method, catalytic-nitridation is performed by irradiation to the Si substrate of activated nitrogen-related species, which are generated by NH3 catalytic cracking reactions with a heated tungsten catalyzer placed near substrates, and so that ultra-thin  $SiN_x$  films below 5 nm are formed. Thicker  $SiN_x$  films are deposited on them by catalytic-CVD succeedingly. The electrical properties of the  $SiN_x$  film are investigated. It is found that, 1) Inserting the nitridation layer, injection-type hysteresis of C-V curve is drastically reduced from 6 V to 0.2 V for 40 nm-thick  $SiN_x$ . 2) High performance insulators are obtained. The leakage current and breakdown electric field are  $6 \times 10^{-9}$ A/cm<sup>2</sup> at 1 MV and 9 MV/cm, respectively. These results show that catalytic-nitridation layer is very important to form good interface of  $SiN_x/Si$ , and the usefulness of catalytic-CVD  $SiN_x$  films as gate insulator material for TFT.

#### A10.4

 $\overline{\text{HIGH}}$  RATE DEPOSITION OF SILICON NITRIDE FOR MULTICRYSTALLINE SILICON SOLAR CELLS USING AN N<sub>2</sub>/SiH<sub>4</sub> AND NH<sub>3</sub>/SiH<sub>4</sub> EXPANDING THERMAL PLASMA. J. Hong, W.M.M. Kessels, F.J.H. van Assche, and M.C.M. van de Sanden, Dept. of Applied Physics, Eindhoven Univ. of Technology, Eindhoven, THE NETHERLANDS.

The efficiency of multicrystalline silicon (mc-Si) solar cells can be significantly improved by applying amorphous silicon nitride (a-SiN $_x$ :H) as a functional layer. The a-SiN $_x$ :H serves not only as anti-reflection coating (ARC) but also provides a source of hydrogen for the passivation of defects in mc-Si. The expanding thermal plasma (ETP) technique is an interesting candidate for high throughput production of solar cells (ultimately 1 wafer/cell per second) as it can reach deposition rates up to 20 nm/s. By using  $N_2/SiH_4$  and  $NH_3/SiH_4$  plasmas, a-SiN $_x$ :H films have been deposited with different N/Si ratios and hydrogen concentrations. Compositional and optical properties of the a- $SiN_x$ :H have been investigated by elastic recoil detection, spectroscopic ellipsometry, and infrared spectroscopy. It has been revealed that the film properties are mainly determined by their N/Si ratio ranging from Si-rich to near-stoichiometric a-Si<sub>3</sub>N<sub>4</sub>:H. Mc-Si solar cells have been produced from both  $N_2/SiH_4$  and NH<sub>3</sub>/SiH<sub>4</sub> plasmas and the ARC performance of the films has been optimized by tuning the optical parameters by in-situ ellipsometry. From internal quantum efficiency analysis, hydrogen bulk passivation has clearly been observed by an enhanced red response of the cells with respect to cells with a non-passivating ARC. The films deposited from N<sub>2</sub>/SiH<sub>4</sub> have a significant absorption in the blue spectral range. This is induced by Si-Si bonds in the films that appear to be more Si-rich than films with the same refractive index deposited from  $\mathrm{NH_3/SiH_4}$ . This can be understood from the film growth mechanism. A detailed study of the plasma processes and the plasma radical composition has revealed the dominant creation of  $SiH_3$  radicals which deposit an a-Si:H-like top layer. This top layer is subsequently nitrided into a- $SiN_x$ :H by very reactive N radicals from the plasma as corroborated by real time attenuated total reflection infrared measurements.

### A10.5

INFLUENCE OF GAS COMPOSITION ON THE PROPERTIES OF AMORPHOUS SILICON NITRIDE FILMS DEPOSITED BY MC-PECVD. G. Lavareda, E. Fortunato, Dep. Ciencia dos Materiais, FCT/UNL, PORTUGAL; C. Nunes de Carvalho, A. Amaral, Centro de Fisica Molecular, IST/UTL, Lisboa, PORTUGAL; R. Ramos, ITN, Sacavem, PORTUGAL.

The study of the gas composition influence on the electrical, optical and chemical characteristics of amorphous silicon nitride (a-SiNx) thin films is presented. The films were deposited by Magnetically Confined PECVD at 350°C. This technique allows the use of low rf power densities, keeping high growth rates and reducing the deposition on the chamber walls. The study covers a gas flow ratio [SiH4] ranging from 10% SiH4 (90% NH3) to pure silane. Electrical characterisation consisted of conductivity, dielectric constant ("e") and critical electric

field measurements (Ec), all measured at  $27^{\circ}\,\mathrm{C}$ . While conductivity shows a continuous increase with [SiH4], the Ec values showed a maximum for [SiH4]=30%. The dielectric constant was measured at 9 Hz and 9990 Hz, in order to observe localised state carrier contribution to "e" values. Both frequencies lead to an increase of e with [SiH4], but while the "e" (9990Hz) varies from 6.5 to 10.5, the "e" (9990Hz) ranges from 6.5 to 18.5. The optical properties measured were the refractive index (n) which increases almost linearly and the optical gap (Eop) which presents an abrupt decay from [SiH4]=10% to 40%. The chemical characteristics consisted in measuring the N/Si ratio by RBS, showing a decrease from 1.85 to 0 when [SiH4] varies from 10% to 100%. Those results combined with the growth rate data allow the process manipulation towards the application specificity.

#### A10.6

LOW TEMPERATURE OXYNITRIDATION OF SiGe IN NO/N<sub>2</sub>O AMBIENTS. Anindya Dasgupta, Christos G. Takoudis, University of Illinois at Chicago, Department of Chemical Engineering, Chicago, IL.

Silicon germanium alloys have recently received considerable attention due to its tunable band gap, enhanced hole mobility, improved high frequency behavior, and ease of integration with existing silicon technology. Conventional high temperature thermal oxide growth has been shown to result in undesirable Ge rich layer below the oxide which leads to high interface state density, high fixed charges of SiGe based metal-oxide-semiconductors.

X-Ray photoelectron spectroscopy (XPS), secondary ion mass spectroscopy (SIMS) and spectral ellipsometry have been used to study sub 3.5 nm low temperature oxynitrides of SiGe. The oxynitridations steps have been performed at 550°C and 650°C, while the oxynitridation gases have been preheated to 900°C and 1000°C before entering the reaction zone. At the oxynitridation temperatures, XPS and SIMS data suggests that NO assisted oxynitridation incorporates more nitrogen than N2O oxynitridation while there is minimal amount of Ge segregation towards the dielectric/substrate interface in both oxynitridation processes. SIMS data suggests that the nitrogen is distributed all along the film in contrast to high temperature Si oxynitridation where there is nitrogen incorporation near the dielectric/substrate interface. Spectral Ellipsometry have been used to measure the final thickness of the oxynitrides film. These results will be discussed in the context of an overall mechanism of the oxynitridation of SiGe.

#### A10.7

PECVD SILICON NITRIDE FOR DAMASCENE APPLICATIONS. Nagarajan Rajagopalan, <u>Albert Lee</u>, Maggie Le, Bok Heon Kim, Hichem M'saad, Applied Materials Inc., Dielectric Systems and Modules Product Business Group, Santa Clara, CA.

Copper dual damascene schemes with fluorinated silicate glass (FSG) as the dielectric and silicon nitride as the etch stop and copper barrier are fast becoming the industry norm for production of next-generation semiconductor devices. The silicon nitride layer deposited immediately following a copper oxide removal treatment prevents copper diffusion into FSG. While many PECVD nitride films are available, the Damascene Nitride<sup>TM</sup> film described here was developed to meet specific damascene requirements. This paper examines the film properties and presents data demonstrating its capability to successfully address the issues inherent to damascene integration. The Damascene Nitride film is deposited in a PECVD chamber with a hollow cathode faceplate using silane and ammonia as precursor gases. Various characterization techniques (FTIR, RBS-HFS, SIMS, TDS and BTS) were used to characterize the structure, composition and electrical properties of the film for both 200mm and 300mm silicon substrate sizes. FTIR analysis indicates that Damascene Nitride is very similar to a high density plasma (HDP) nitride film, and RBS analysis indicates that the film is nitrogen rich with no oxygen, resulting in enhanced film density. HFS analysis shows the film's hydrogen content to be 13%, about 6% less than other PECVD nitride films, leading to a 10% improvement in etch selectivity to FSG. SIMS analysis shows that Cu diffusion is very low and is confined within the nitride, and very low leakage current (1e-10 Amp) is confirmed through BTS testing. Integration results demonstrate excellent film adhesion to Cu and FSG with a large fluorine window. Superior electrical properties including line-to-line leakage and via-chain resistance were also observed. Additionally, the Damascene Nitride film, developed with an in-situ CuO removal treatment, has the lowest cost-of-ownership when compared to  $\operatorname{HDP}$ nitride and other PECVD nitride films.

> SESSION A11: METASTABILITY Wednesday Morning, April 3, 2002 Golden Gate B2 (Marriott)

8:00 AM \*A11.1 MICROSCOPIC MODEL FOR CREATION AND REMOVAL OF METASTABLE DANGLING BONDS IN a-Si:H. Martin J. Powell and and Steve C. Deane, Philips Research Laboratories, Redhill, UNITED KINGDOM; Ralf B. Wehrspohn, Max-Planck-Institute of Microstructure Physics, Halle, GERMANY.

A major problem with microscopic models for dangling bond defect creation in hydrogenated amorphous silicon is reconciling the role of hydrogen with ESR experiments, which show that the dangling bond is well separated from any hydrogen atoms. Previous models, generally end with at least one of the dangling bonds close to a hydrogen atom, irrespective of whether carriers cause the breaking of Si-H bonds or Si-Si bonds. Branz proposed a hydrogen collision model to try and resolve this problem (1). In this paper, we discuss a new alternative model (2), where Si-Si weak bonds are broken and stabilised by short range hydrogen motion. This is a local model for defect creation. We resolve the apparent conflict with ESR data, by recognising that the energetically favoured site for a hydrogen atom in a SiHD (an intimate Si dangling bond and Si-H bond) is in the  $T_d$  site and not in the BC site. The distance between the dangling bond and the H atom, in the  $T_d$  site, is in the range 4-5  $\mathring{A}$ , which is in complete agreement with ESR data. The microscopic process for defect creation requires only relatively short range, low energy, H motion, which can proceed by a process of bond switching between neighbouring  $T_d$  sites and Hflips, from BC to  $T_d$  sites. The whole process is fairly localised, requiring H motion over relatively short distances. In contrast, the microscopic process for defect removal, during thermal annealing, involves re-equilibration of H in the a-Si:H network and is a global process involving a large fraction of H atoms. Removal of metastable defects cannot occur at room temperature and annealing activation energies are similar to long range hydrogen diffusion. The ratelimiting step for this process is Si-H bond breaking and this accounts for the maximum activation energy of up to  $1.5 \mathrm{eV}$ . We present a revised hydrogen density of states diagram, in line with this process. (1) H.M. Branz, Phys Rev B 59 5498 (1999). (2) M.J. Powell, R.B. Wehrspohn and S.C. Deane, ICAMS-19 Proceedings (2001).

### 8:30 AM A11.2

<sup>1</sup>H NMR EVIDENCE FOR A CHANGE IN THE LOCAL HYDROGEN ENVIRONMENT OF SITES ASSOCIATED WITH THE STAEBLER-WRONSKI EFFECT IN a-Si:H. <u>T. Su</u>, R. Plachy, P.C. Taylor, Univ of Utah, Dept of Physics, Salt Lake City, UT; S. Stone, G. Ganguly, D.E. Carlson, BP Solar, Toano, VA.

It has been widely speculated that hydrogen is involved in the dominant metastable light-induced effect (Staebler-Wronski effetct) in a-Si:H. However, there is no experimental evidence for a correlation between changes in the local environments of a limited number of hydrogen sites and the Staebler-Wronski effect. Using Jeener-Broekaert three-pulse sequence, we study the  $^1\mathrm{H}$  NMR line shapes of a series of a-Si:H samples: 1) as grown, 2) light-soaked for 600 hours, and 3) light-soaked followed by annealing at different temperatures. At T = 7 K, the NMR line shape of the sample after light-soaking exhibits an additional doublet compared to that of the sample as grown. This doublet is an indication of closely paired hydrogen doublet. The peak-to-peak width of this doublet is about 25 kHz, corresponding to a distance between the two hydrogen atoms of about  $(1.5 \pm 0.5)$  Å. This distance is about twice that in molecular hydrogen. We estimate that the concentration of hydrogen sites with this configuration is between 10<sup>16</sup> and 10<sup>18</sup> cm<sup>-3</sup>. This doublet disappears after the sample is annealed at 200°C for 4 hours. ESR measurements show that the defect density increases by at least a factor of three after light-soaking, and is reduced on annealing as is commonly observed. Photoluminescence (PL) measurements show that the PL intensity is reduced by about one order of magnitude after light-soaking, and returns to about the same initial level after annealing.

### 8:45 AM <u>A11.3</u>

NATURE OF CHARGED METASTABLE DEFECTS IN NETWORK REBONDING MODEL. <u>R. Biswas</u>, B.C. Pan, Dept. of Physics and Microelectronics Research Center & Ames Lab, Iowa State University, Ames IA

We have recently developed a new model of metastability in a-Si:H [1] using molecular dynamics simulations. In this network rebonding model of the Staebler-Wronksi effect, weak silicon bonds are broken creating dangling bond-floating bond pairs. The floating bonds then migrate and annihilate by various recombination processes. We present consequences of this model of Staebler-Wronksi degradation for experiment. The light soaked defects consist of multiple species of dangling bonds including mostly neutral D0 and a smaller density of positively charged D+. Results for the annealing of these metastable defect species will be presented. We find that such charged defects can account for the hysteresis observed in recent mu-tau product measurements during light-soaking and annealing. The light-soaked configurations consisting of metastable dangling bonds will be shown, including their energy difference from the initial configuration.

Kinetics of the process show  $t^{(1/3)}$  defect creation power law with saturation at long times. It is found that at low temperatures when electron-hole driven creation term is not valid, the kinetics can lead to power law growth of defects with an exponent between 0.3 and 0.4. Supported by the American Chemical Society through the Petroleum Research Fund. [1] R. Biswas, B.C. Pan, Y. Ye, to be published.

### 9:00 AM <u>A11.4</u>

LIGHT-INDUCED DEGRADATION IN SOLAR CELLS WITH HYDROGENATED AMORPHOUS SILICON-SULFUR ACTIVE LAYERS. Wei Xu, P.C. Taylor, Department of Physics, University of Utah, Salt Lake City, UT.

The group VI element, sulfur, acts as a very inefficient donor in hydrogenated amorphous silicon (a-Si:H). In the silicon-sulfur alloys an effect exits, which produces changes in the dark and photo-conductivities that are opposite to those produced in the Staebler-Wronski effect. The interpretation of this effect is that light excites a portion of hydrogen-passivated sulfur donors, rendering them electrically active<sup>1,2</sup>. These results suggest that the incorporation of sulfur in the active layers of a-Si:H based solar cells might improve the stability. Previous experiments on a a-SiS $_x$ :H solar cell with low conversion efficiency exhibited less light-induced degradation than undoped cells of similar thickness. We have made a series of a-SiS $_x$ :H based solar cells, with a pin structure, in a mutichamber plasma enhanced chemical vapor deposition (PECVD) system. The sulfur concentration ranges from zero to  $6 \times 10^{-6}$ , in terms of H<sub>2</sub>S/SiH<sub>4</sub> gas flow ratios. The initial conversion efficiency of cells in this series without sulfur is approximately 7%. The degradation study is performed at room temperature using 100 mW/cm<sup>2</sup> white light. Generally, low concentrations of sulfur (ratios  $\leq 2 \times 10^{-7}$ ) in the active layers do not influence the initial conversion efficiency or the deleterious Staebler-Wronski effect. Experiments at higher sulfur concentrations will be discussed.

#### 9:15 AM \*A11.5

STABILIZATION OF AMORPHOUS SILICON BY CROWN-ETHER CYANIDE TREATMENT. Hikaru Kobayashi, Naozumi Fujiwara, Osamu Maida, Masao Takahashi, Osaka University and CREST, Japan Science and Technology Corporation, Osaka, JAPAN.

The most important problem to be solved for large scale employment of amorphous silicon (a-Si) solar cells has been the light-induced degradation. This degradation is generally believed to be caused by the photo-generation of defect states in the a-Si band-gap. In the present study, a method of passivating defect states in a-Si has been developed in order to prevent light-induced degradation and to increase initial conversion efficiencies. In this method, a-Si is immersed in a KCN solution of xylene containing 18-crown-6 molecules, and a positive bias voltage is applied to the a-Si with respect to a counter electrode. This crown-ether cyanide treatment is performed in order to form Si-CN bonds by the reaction of CN- ions with defect and defect precursor states. An 18-crown-6 molecule possesses a hole 2.7 A in diameter and a K ion of 2.66 A diameter is effectively captured by six oxygen atoms pointing toward the hole. Therefore, the inclusion of 18-crown-6 in a KCN solution effectively prevents contamination of a-Si by K ions. The positive bias enhances the migration of CN- ions into the a-Si. With no treatment, the photocurrent density of the <Al/intrinsic (i)-a-Si/TCO> specimens greatly decreased with the irradiation time, indicating that light-induced degradation occurred within the i-a-Si films. The dark current density also greatly decreased with the irradiation time. With the crown-ether cyanide treatment, on the other hand, a decrease in the photocurrent density did not occur at all, showing that light-induced degradation has been prevented. In this case, the dark current density was constant. When crown-ether cyanide treatment was performed on pin-junction a-Si solar cells, the photovoltage increased and the magnitude of light-induced degradation decreased.

> SESSION A12: NOVEL DEVICES Wednesday Morning, April 3, 2002 Golden Gate B2 (Marriott)

# 10:15 AM A12.1

 $\begin{array}{l} {\bf AMORPHO\overline{US~SILICON~HIGH~FREQUENCY~INFRARED}\\ {\bf SOURCE.~\underline{A.J.~Syllaios},~W.L.~McCardel,~R.W.~Gooch,~T.R.~Schimert,\\ {\bf Raytheon~Commercial~Infrared,~Dallas,~TX}. \end{array}$ 

An amorphous silicon infrared radiation emitter array will be described that is capable of producing infrared radiation modulating at high frequency. Each emitter array element includes a low-thermal-mass amorphous silicon resistive membrane that is suspended by long thermal isolation arms over a substrate such that a resonant emitting cavity is formed between the membrane and the substrate. The low-mass, thermally isolated membrane design maximizes the

temperature change induced by Joule heating of the resistive membrane and allows the emitted infrared radiation to be modulated at high frequencies on the order of 100 Hz to 1 kHz. In addition to temporal modulation the emitter arrays can also be spatially modulated, to generate infrared scenes. The effect of material properties such as the temperature coefficient of resistance (TCR) of amorphous silicon has been investigated and will be discussed. These IR source arrays can be used in MID infrared spectroscopic sensor applications, and infrared signal or pattern generation.

### 10:30 AM A12.2

SWITCHING IN THIN FILM Cr/a-Si/Ag DEVICES WITH HYDROGENATED AMORPHOUS SILICON BY HOT-WIRE CVD. Jian Hu, Howard M. Branz, Richard S. Crandall, Graig Perkins, Scott Ward and Qi Wang, National Renewable Energy Laboratory, Golden, CO.

We fabricate the first metal/a-Si/metal thin film switches which incorporate hot-wire chemical vapor deposition (HWCVD) Si layers. A H-diluted gas mixture is used to grow the B-doped, 1000 Å, hydrogenated amorphous silicon (a-Si:H) layers at about 10 Å/s When a voltage pulse or DC current bias is applied, device resistance changes by up to five orders of magnitude. This irreversible switching effect is useful for memory devices and is thought to be due to formation of a metallic filament current path [1]. We study the switching time, and the delay time before switching, using voltage pulses. We also use various micro-scale probes to image the switching area, including electron-beam induced current (EBIC), optical reflectivity through a microscope, and scanning-Auger microscopy. Our devices switch at about 14 V, and the delay time (200 ns - 50 ms) and switching times (20 ns - 10  $\mu$ s) depend upon forming power, rather than voltage or current alone. EBIC and optical reflection both show a 1-2  $\mu$ m spot which is created during switching; this region of high conductivity through the sample must include the formed filament. We also compared a c-Si( $p^+$ )/a-Si:H(p)/Ag (single-Schottky barrier) structure to our Cr/a-Si:H(p)/Ag (double-Schottky) devices. With current flowing into either device through a positive metal contact, switching occurs at about 4 mA/cm<sup>2</sup>. In contrast, we are unable to switch the single-Schottky device even with as much as 1000 times more current (4 A/cm<sup>2</sup>) flowing from the positively biased p<sup>+</sup> c-Si. This shows that a reverse-biased Schottky junction is essential to switching. [1] J. Hajto, A.E. Owen, A.J. Snell, P.G. LeComber, and M.J. Rose, Amorphous and Crystalline Semiconductor Devices, Ed: J. Kanicki, Artech House, 1992, See also references cited therein.

# 10:45 AM \*A12.3

THIN-FILM SILICON MEMS.  $\underline{V.~\mathrm{Chu}^a}$ , J. Gaspar<sup>a,b</sup> and J.P. Conde<sup>b</sup>; <sup>a</sup>INESC Microsystems and Nanotechnologies, Lisbon, PORTUGAL; <sup>b</sup>Department of Materials Engineering, Instituto Superior Técnico, Lisbon, PORTUGAL.

This paper presents the fabrication and characterization of MEMS

structures on glass and flexible plastic substrates using thin film silicon technology and surface micromachining. The technology developed to process bridge and cantilever structures as well as the electromechanical modeling of these structures will be discussed in detail. This technology can enable the expansion of MEMS to applications requiring large area and/or flexible substrates This paper will present in detail the processing technology developed to fabricate MEMS devices on large area substrates such as glass and plastic. Focus will be placed on the characterization of electrostatic actuation in two excitation regimes: (1) low frequency (quasi-DC), low deflection; and (2) resonance frequency. The structures are characterized using electrostatic actuation and optical detection of movement. Experimental results will be discussed and compared to predictions from electromechanical modeling. The main results for the characterization of the movement of the structures are as follows: (1) in the quasi-DC regime and at low applied voltages, the response is linear with the applied dc voltage. Using an electromechanical model which takes into account the constituent materials and geometry of the bilayer, it is possible to extract the deflection of the structures. This estimate suggests that it

11:15 AM A12.4

CARRIER GENERATION IN THIN FILM POLYSILICON.

<u>Bill Eccleston</u>, Department of Electrical Engineering and Electronics,
University of Liverpool, Liverpool, UNITED KINGDOM.

is possible to control the actuation of these structures to deflections

MHz have been measured on a-Si:H bridge structures with quality

factors (Q) of 70-100 in air. The frequency depends inversely on the

square of the structure length, as predicted by the mechanical model.

on the sub-nanometric scale; and (2)  $\underline{\text{resona}}$ nce frequencies of up to 20

Polycrystalline materials are important for a range of devices including active matrix displays. There is a need to analyse carrier generation and flow[1][2][3] in such materials. Polysilicon TFTs are used to test a model based on generation in grain boundaries. When

the generation is stimulated by the depletion of the material, due to field effect, carriers are drawn to the surface and move along it by a process akin to diffusion. At some gate voltage the supply of carriers to the channel is insufficient to maintain the current flow. This leads to an increased reverse bias across the drain junction. It is proposed that carrier generation occurring mainly near to the drain is more likely to be stimulated by increases of drain rather than gate voltage. The temperature dependence of currents at the current minimum, and at current saturation, of the transfer characteristic are described and are used to justify the model for generation and current flow.

#### 11:30 AM A12.5

TEMPERATURE AND FREQUENCY DEPENDENCE OF CHARGING AND DISCHARGING PROPERTIES IN MOS MEMORIES BASED ON NANOCRYSTALLINE SILICON DOTS. Shaoyun Huang, Souri Banerjee, and Shunri Oda, Tokyo Institute of Technology, Research Center for Quantum Effect Electronics, Tokyo, JAPAN.

Electrons charging into or discharging from nanocrystalline silicon (nc-Si) dots embedded in  $\mathrm{SiO}_2/\mathrm{nc}\text{-Si}/\mathrm{SiO}_2$  sandwich structure has been widely investigated to further understand the retention mechanism of single electron memory (SEM) device. A weak temperature dependence of memory retention time implied that effects of interface/deep defects could be ignored [1]. In this work, direct methods like Capacitance-Voltage (C-V) and Conductance-Voltage (G-V) measurements were employed to investigate the contribution of defects, which manifest not only in temperature but also in frequency dependent behaviors. The SiO<sub>2</sub>/nc-Si/SiO<sub>2</sub> sandwich Metal-Oxide-Semiconductor (MOS) diode was prepared on < 100 > n-type silicon wafer with an ultra-thin tunnel dioxide layer, a layer of nc-Si dots of 8 nm in diameter deposited by remote PECVD technique and a comparatively thicker control gate oxide. Clockwise hysteresis was observed at various temperatures and frequencies in both C-V and G-V characteristics before and after dots were charged. A conductance peak was close to the flat band voltage, which could be attributed to one electron trapping per nc-Si dot. A very small negative voltage shift in C-V and G-V curves was found with increasing temperature or decreasing frequency, which could result from the change in trapped charge in the defect. A detailed analysis of G-V characteristics at different temperatures yielded a negligible thermal activation. Time dependent discharging behavior in capacitance of the device indicated that the charge-loss rate decreased slightly as temperature was decreased from 300K to 77K at a fixed frequency. These results suggest that the thermal activation is not dominant for the charging or discharging behaviors in our devices. A repulsive electrical field created and controlled by charge loss in nc-Si dots is adopted to explain the device characteristics as well as long-term retention time. [1] B.J. Hinds, T. Yamanaka and S. Oda, to appear in J. Appl. Phys., 90 (11), (2001).

### 11:45 AM <u>A12.6</u>

AMORPHOUS SILICON VERTICAL THIN FILM TRANSISTOR FOR HIGH DENSITY INTEGRATION. <u>Isaac Chan</u> and Arokia Nathan, Dept. of Electrical and Computer Engineering, Univ. of Waterloo, Waterloo, Ontario, CANADA.

The vertical thin film transistor (VTFT) in amorphous silicon (a-Si:H) technology appears to be a highly attractive structural alternative to improve the switching performance of the TFT. The VTFT lends itself naturally to scaling down of the channel length into sub-micron dimensions, without being limited by photolithographic resolution. From a geometrical standpoint, arranging the various layers and active components in a vertical orientation also offers considerable savings in device area, compared to that achievable using conventional (lateral) TFT structures. For example, in applications where high device/pixel packing density is required, VTFTs have a pronounced advantage in terms of the pixel size and fill factor. This paper reports a fabrication process for 1- $\mu$ m channel VTFTs, which yield an ON/OFF ratio higher than  $10^5$  and a leakage current of the order of  $10^{-13}$ A. Further improvement in device characteristics can be achieved by improving the dry etch process. The sidewall for the vertical channel in the structures reported here shows significant undercutting due to the isotropy of the dry etch process. This serves to undermine the structural integrity and the electrical performance of the VTFT. Optimized dry etch processes have been developed using a  $\mathrm{CF_4/20\%\,H_2}$  gas mixture, which appears to yield a sharp vertical sidewall profile for the channel region. Details of process optimization will be presented along with results of TFT characterization based on the new processes.

> SESSION A13: AMORPHOUS SILICON SOLAR CELLS Wednesday Afternoon, April 3, 2002 Golden Gate B2 (Marriott)

#### 1:30 PM <u>A13.1</u>

HIGH VOLTAGE AMORPHOUS SILICON SOLAR CELLS BY HOT-WIRE CHEMICAL VAPOR DEPOSITION. Qi Wang and Eugene Iwaniczko, National Renewable Energy Lab., Golden, CO.

We have achieved the best open-circuit voltage ( $V_{oc} = 0.94 \text{ V}$ ) to-date in hydrogenated amorphous silicon (a-Si:H) photovoltaic cells deposited entirely by hot-wire chemical vapor deposition. The fill factor (FF=0.74) remained high and a current of 8-9 mA/cm² with about 180 nm i-layer was obtained in our n-i-p cells on untextured stainless-steel substrates. The  $V_{oc}$  improvement of about 60 mV in compared to our previous best  $V_{oc}$  was obtained by incorporating materials grown with H-dilution close to the phase transition from amorphous to microcrystalline silicon in the i-layer and at the p-i interface. A low substrate temperature of 150°C for the i-layer was also essential, most likely to widen the bandgap of the i-layer. A brief atomic H-treatment after grown the i layer increases the Voc further by improving the p-i interface. The last 6 nm of the i-layer before p-layer is extremely close to the transition to microcrystallinity, though it remains mainly amorphous. Our p-layers are also close to the phase transition. These results contribute to a growing body of work that suggests amorphous silicon is improved by incorporation of amorphous silicon with enhanced medium range order.

### 1:45 PM A13.2

EFFECT OF INCREASING GROWTH RATES ON FILM PROPERTIES AND DEVICE PERFORMANCE FOR DC GLOW DISCHARGE AMORPHOUS SILICON. J.T. Heath, J.J. Gutierrez, and J.D. Cohen, Department of Physics, University of Oregon, Eugene, OR; G. Ganguly, BP Solar, Toano, VA.

We have examined the electronic properties of intrinsic amorphous silicon films as a function of deposition rate, and compared these with the performance of companion solar cell p-i-n devices. Both the films and devices were deposited at BP Solar using dc plasma decomposition. Films were deposited onto either p<sup>+</sup>-type crystalline Si or ZnO coated glass substrates. The device i-layers were deposited under identical conditions to the films, in a glass/SnO2/p/i/n/ZnO/Al structure in which only the i-layer deposition parameters were varied. By varying the dc plasma power and the degree of hydrogen dilution of the silane, the growth rate for the intrinsic a-Si:H layer was varied from 0.65~Å/s to 6.0~Å/s. Films and devices were characterized in their initial and their light degraded states. For the devices we determined the fill factors, open circuit voltages, short circuit currents and the device efficiencies. The degraded device efficiencies and fill factors were found to decrease monotonically with growth rate. To evaluate the deep defect densities of the films we used drive-level capacitance profiling. We also utilized transient photocapacitance and photocurrent spectroscopy to obtain values for the Urbach energy, and also estimate minority carrier mobilities. In contrast to the cell performance, we did not find any clear correlation between deep defect densities or the deduced hole  $\mu\tau$  products with growth rate. However, we did discover a strong correlation between the Urbach energies and the observed decrease in fill factor of the companion devices, and hence with growth rates. Such a correlation has not been reported previously. It may indicate that there exists a direct effect of the network disorder, exacerbated by the increasing growth rate, on the ultimate solar cell device performance. This effect seems to be much stronger than any effects that can be directly attributable to the deep defects in these films. Possible mechanisms for these effects will be discussed.

# 2:00 PM <u>A13.3</u>

EXPERIMENTAL INVESTIGATION AND MODELLING OF LIGHT SCATTERING IN a-Si:H SOLAR CELLS DEPOSITED ON GLASS/ZnO:Al SUBSTRATES. Janez Krc, Miro Zeman<sup>a</sup>, Oliver Kluth<sup>b</sup>, Franc Smole and Marko Topic, Faculty of Electrical Engineering, University of Ljubljana, SLOVENIA; <sup>a</sup>Delft University of Technology - DIMES, THE NETHERLANDS; <sup>b</sup>Institute of Photovoltaics (IPV), Forschungszentrum Juelich GmbH, GERMANY.

To enhance light absorption in active layers of hydrogenated amorphous silicon (a-Si:H) solar cells rough interfaces are introduced in the solar cell structures. At rough interfaces a part of the incident light is scattered leading to a better light confinement and an increased absorption in the solar cell. For investigation and understanding of the complex process of light scattering in solar cells we developed a semi-coherent optical model that takes both, interference effects of non-scattered light and multi-directional spreading of scattered light into account. The input parameters of the model are the descriptive scattering parameters, which are the haze and the angular distribution function. We have determined haze and angular distribution function of textured glass/ZnO:Al substrates with different roughnesses of ZnO:Al transparent conductive oxide layer using total integrating scattering measurements and angular resolved scattering measurements, respectively. The scattering parameters of the glass/ZnO substrates will be presented. In order to

verify our optical model, we carried out the simulations of a series of p-i-n a-Si:H solar cells which were deposited on the textured glass/ZnO:Al substrates. In the simulations the experimentally determined scattering parameters of the rough ZnO:Al interfaces were used. In the simulated external quantum efficiencies, QE, an experimentally observed trend of a suppressed interference pattern and an enhancement of the quantum efficiency in the long-wavelength region by increasing the interfaces roughness are reproduced. We shall demonstrate that the simulated QEs are in good agreement with the measured QE of the solar cells, confirming the applicability of our

 $2:15~\mathrm{PM}~\underline{*A13.4}$  LIGHT INDUCED CHANGES IN PROTOCRYSTALLINE AND AMORPHOUS SILICON MATERIALS AND THEIR SOLAR CELLS. J.M. Pearce, R.J. Koval, A.S. Ferlauto, J. Koh, R.W. Collins, and C.R. Wronski, Center For Thin Film Devices, The Pennsylvania State University, University Park, PA.

It is well established that hydrogenated amorphous silicon (a-Si:H) materials and solar cells fabricated with hydrogen dilution exhibit higher stability than those deposited without hydrogen dilution. In the case of diluted materials protocrystalline Si:H can be obtained, whose evolving microstructure during growth undergoes transitions from a purely amorphous phase into a mixed phase (amorphous + nanocrystallite) and then to a microcrystalline phase (1). This paper reviews studies carried out on the light induced changes in protocrystalline Si:H thin films and solar cells deposited with sufficiently low hydrogen dilution as to ensure amorphous growth throughout the i layers of the p-i-n cells studied. The results presented include the degradation kinetics of both cells and corresponding i layer films at different temperatures obtained under 1 sun illumination to clearly defined and reproducible degraded steady states (DSS). These results are then compared with those obtained on undiluted material and cells whose high quality is indicated by the high fill factors in the annealed state. The results obtained have allowed for the first time direct correlations to be established between solar cell properties and those of the corresponding i layer thin films. They also clearly point to the presence of multiple light induced defects with kinetics for their creation and annealing that are different (2). Although no quantitative analysis of the results is made, the similarities and differences in the kinetics of the diluted and undiluted materials and cells offer new insights into the nature and densities of these defects. (1) R.J. Koval, J. Koh, Z. Lu, Y. Lee, L. Jiao, R.W. Collins and C.R. Wronski, Mat. Res. Soc. Symp. Proc. 557 pp 263-268 (1999). (2) L. Yang and L. Chen, Appl. Phys. Lett. 63 (3) pp 400-402 (1993).

### SESSION A14: ELECTRONIC AND NETWORK STRUCTURE Wednesday Afternoon, April 3, 2002 Golden Gate B2 (Marriott)

# 3:15 PM \*A14.1

STRUCTURE AND ELECTRONIC PROPERTIES OF AMORPHOUS SILICON: RESULTS FROM RECENT FIRST PRINCIPLES CALCULATIONS. David Drabold, Ohio University, Dept of Physics and Astronomy, Athens, OH.

In this talk I describe recent theory work on a-Si. I begin with a short review of the current understanding of the deep defects in a-Si. Then I discuss the band tails and the character of the Anderson transition. This will include some results on phonon-driven hopping obtained from integrating the time dependent Schrödinger (Kohn-Sham) equation (e.g. by explicitly computing the time development of excess electron or hole packets in the presence of thermal disorder). As time permits, I will briefly describe our recent simulation of a first order amorphous to amorphous (insulator to metal) phase transition.

# 3:45 PM A14.2

ENTROPY CHANGES FOR ELECTRON AND HOLE EMISSION FROM METASTABLE DEFECTS IN P-TYPE HYDROGENATED AMORPHOUS SILICON. <u>Richard S. Crandall</u>, National Renewable Energy Laboratory, Golden, CO.

Measurements of capacitance transients due to electron and hole emission from metastable defects are used to make the first determination of the defects entropy changes during charge emission. For appropriate injection pulse conditions in B doped hydrogenated amorphous silicon (a-Si:H) n/p junction structures, electrons and holes are simultaneously trapped in the p layer. By measuring charge emission rates (r) between 313 and 480 K, I determine that the enthalpy changes for hole and electron emission are 0.94 and 0.51 eV, respectively. The straight lines in a plot of ln(r) versus 1/temperature, used to determine these enthalpies, cross at 350 K. This crossing unambiguously determines the isokinetic temperature (Tiso) for the

Meyer-Neldel rule for p-type a-Si:H. Tiso is the temperature (350 K) at which the change in Gibbs free energy for the hole and electron emission are identical. Thus defect reactions in p-type a-Si:H obey the Meyer-Neldel rule. The entropy changes for hole and electron emission are 31 and 16 Boltzmann constants, respectively. Below Tiso electrons are emitted faster than holes and above Tiso the reverse is true. These relative changes in emission rates are a direct consequence of the large entropy changes in the reactions. Tiso, within experimental error, is the same as the H glass equilibration temperature measured by others in p-type a-Si:H, suggesting that the defect reactions measured here are those involved in H glass equilibration. Activation and deactivation of B atoms with accompanying charge emission and trapping likely govern both processes.

MEDIUM RANGE ORDER IN AMORPHOUS, POLYMORPHOUS, AND NANOCRYSTALLINE Si:H FILMS EVALUATED BY FLUCTUATION MICROSCOPY. Lakshminarayana Nittala, John R. Abelson, University of Illinois, Dept of Materials Science & Engineering, Urbana, IL.

The fluctuation electron microscopy (FEM) technique is directly sensitive to 3- and 4-body atomic correlation functions in amorphous materials, and therefore, to medium-range order (MRO). We previously showed that device quality a-Si:H samples deposited by different techniques (PECVD, HWCVD, reactive magnetron sputtering) all contain significant and rather similar quantities of MRO. We developed a molecular dynamics model for MRO in a-Si which consists of topologically crystalline grains, 1-2 nm in diameter, joined by an amorphous grain boundary phase. We showed that strain effects so distort the grains that coherent diffraction is NOT observable. We refer to such grains, which give no diffraction signature, as paracrystallites. Here, we systematically compare the MRO in the as-deposited state and following many cycles of light-soaking and annealing, for films deposited by PECVD with pure silane, hydrogen diluted silane, the "polymorphous" regime (in which nanometer size Si particulates from the plasma are incorporated into the growing film), and the nanocrystalline limit of the polymorphous regime. The samples were supplied by the USSC and Ecole Polytechnique groups. In previous work, both hydrogen-diluted and polymorphous materials had greater stability against the Staebler-Wronski effect, and more network ordering was proposed as the explanation. Our data thus far do not indicate a major difference in the MRO of these materials. However, the dilute population of larger grains - nanocrystallites detectable by diffraction - does vary. We will report the variation of MRO in these materials after cycles of light-soaking and annealing.

> SESSION A15: GROWTH PROCESSES Thursday Morning, April 4, 2002 Golden Gate B2 (Marriott)

# 8:00 AM \*A15.1

SURFACE SCIENCE ASPECTS OF a-Si:H GROWTH. M.C.M. van de Sanden Department of Applied Physics, Eindhoven University of Technology, Eindhoven, THE NETHERLANDS.

Studying the growth mechanism of hydrogenated amorphous silicon during PECVD requires the simultaneous study of both the plasma state as well as the nature of the a-Si:H surface. Since the growth under these non-equilibrium growth conditions is kinetic in nature, identification of the various silane radicals and ions by means of a variety plasma diagnostics is needed. In line with previous speculations we have established that indeed the silyl radical, which is unreactive in the gas phase, dominantly contributes to growth of good quality a-Si:H in a remote generated Ar/H2/SiH4 plasma. By means of the newly developed time dependent cavity ring down absorption spectroscopy, the reaction probability of SiH3, which depends on the a-Si:H surface, is determined. Under these conditions of dominantly  ${
m SiH_3}$  and atomic hydrogen fluxes, detailed well defined surface studies of a-Si:H growth become feasible. For example, in situ, surface studies are undertaken to measure the hydrogenation of the a-Si:H surface. With Fourier transform infrared attenuated total reflection spectroscopy, the different hydrides present on the a-Si:H surface are identified as function of the substrate temperature. Based on this data, a tentative hydrogen incorporation model is proposed which could explain the observed small activation energy for hydrogen incorporation from a SiH3 flux. A new surface diagnostic to measure the dangling bonds on the surface and which is based on the cavity ring down principle, will be presented. First results indicate a low surface dangling bond concentration, in line with previous in situ ESR measurements by Yamasaki et al. The connection between these observations and surface roughness development, surface diffusion of weakly adsorbed SiH3 and of hydrogen and dangling bonds on the amorphous silicon surface will be emphasized.

8:30 AM  $\underline{\text{A15.2}}$  A SURFACE HYDRIDE-DEPENDENT PRECURSOR DIFFUSION MODEL FOR LOW TEMPERATURE AMORPHOUS SILICON DEPOSITION.  $\underline{G.N.\ Parsons},\ A.\ Gupta$  and K. Bray, Dept. of Chemical Engineering, NC State University, Raleigh, NC.

A new quantitative kinetic model for low temperature hydrogenated amorphous silicon deposition has been developed. The model is based on SiH<sub>3</sub> radical adsorption, diffusion, and surface incorporation, with provision for surface H abstraction and radical insertion into strained Si-Si bonds. This model differs from previous kinetic models of Matsuda, Perrin, Robertson, and others in the following important ways: 1) it includes a surface valence balance in addition to a site balance, to account explicitly for Si-Si bond formation and SiH3 insertion; 2) it does not rely on a specific physisorption bonding geometry for the silyl radical; and 3) it includes a new hypothesis that the precursor surface diffusion rate depends on the nature of the surface physisorption site, where diffusion rate for precursors physisorbed on di- and tri-hydride sites is impeded relative to those on mono-hydride sites. This hypothesis enables surface diffusion barrier to be smaller than the barrier for hydrogen abstraction, but still produces an apparent diffusion activation barrier that is >0. This helps resolve an important inconsistency in previous models where the surface diffusion barrier had to be larger than the abstraction barrier in order to achieve a positive apparent barrier for precursor surface diffusion. All modeled growth parameters are consistent with experimental data, including: 1) mono- di- and tri-hydride surface coverage vs. temperature (consistent with results of Kessels et.al.); 2) precursor surface reaction probability and incorporation probability independent of substrate temperature (consistent with experiments of Matsuda and Perrin): 3) film growth rate independent of temperature but strongly dependent on precursor flux; and 4) an apparent activation energy of ~0.2eV for precursor surface diffusion under typical growth rate conditions, also consistent with experiments. The model furthers our understanding of fundamental processes occurring in plasma deposition, with implications for advancing predictive capability in low temperature thin film growth.

### 8:45 AM <u>A15.3</u>

SURFACE DIFFUSION OF SiH<sub>3</sub> RADICALS ON a-Si:H AND THE GROWTH MECHANISM OF a-Si:H AND uc-Si. R. Dewarrat and J. Robertson, Engineering Department, Cambridge University, Cambridge, UNITED KINGDOM.

The growth of a-Si:H requires that the growth species SiH<sub>3</sub> physisorbs to the a-Si:H surface and diffuses over it. However, previous calculations have found no binding. Using local density pseudopotential calculations, we find that the growth radical  $\mathrm{SiH}_3$  does bind to the hydrogen terminated (111)Si surface. The bound site is not the three-centre Si-H-Si bridging site previously assumed. Instead, it has a direct Si-Si bond between the  $\mathrm{SiH}_3$  and the surface Si, and the terminal hydrogen has been displaced to a bond centre site of a lateral surface Si-Si bond. The bound site validates conventional models of the growth of hydrogen amorphous silicon (a-Si:H), in which a mobile growth species is needed to give the observed surface loss probability, growth scaling exponent and smooth surfaces.

# 9:00 AM <u>A15.4</u>

REAL-TIME MEASUREMENT OF STRESS EVOLUTION DURING DEPOSITION OF AMORPHOUS GROUP IV THIN FILMS AND MULTILAYERS. Jerrold A. Floro and Sean J. Hearne, Sandia National Laboratories, Surface and Interface Sciences Dept,

We use sensitive real-time measurements of wafer curvature to investigate stress evolution during ultra-high vacuum evaporation of amorphous Si, Ge, and SiGe alloys on oxidized Si substrates. Generically, the stress evolves from compressive (in the earliest stages of growth) to tensile (upon island coalescence), and then back into net compression once the film becomes fully continuous. This behavior is commonly observed in polycrystalline metal and semiconductor films that grow initially in the Volmer-Weber mode, i.e., as non-epitaxial three dimensional islands. For thicker films or lower homologous temperatures, another stress reversal into net tension is observed. Growth interrupts show that for low homologous temperature, the generic stress evolution does not arise from time-dependent processes such as bulk defect annihilation or surface structural evolution. At slightly higher temperatures, relaxation of discontinuous films is observed, most likely due to island coarsening, whereas continuous films exhibit little or no relaxation. The origins of compressive and tensile stresses in continuous amorphous films are poorly understood; we will examine the strengths and shortcomings of several current models for stress generation. Finally, we will show preliminary results for the complex stress evolution of multilayer amorphous Si/Ge/SiGe films, where the stress of the composite structure may be tailored towards zero.

### 9:15 AM \*A15.5

INTERMEDIATES AND REACTION MECHANISMS IN AMORPHOUS AND MICROCRYSTALLINE SILICON FILM GROWTH. HaiLan Duan, Gillian A. Zaharias, and Stacey F. Bent, Dept of Chemical Engineering, Stanford University, Stanford, CA.

Together with ionic interactions, radical adsorption and reaction are among the most prevalent gas-surface steps in semiconductor materials processing. In both plasma and hot-wire chemical vapor deposition of amorphous (a-Si:H) and microcrystalline ( $\mu$ c-Si) silicon, gas phase radicals can influence reaction pathways, reaction rates, and product distributions. I will discuss advances in detection capabilities that allow us to probe these radical species as well as the surface intermediates in the growth of a-Si:H and  $\mu$ c-Si from silane. In our laboratory, we are using multiple internal reflection infrared spectroscopy to obtain real-time information on the composition and bonding in films deposited by hot-wire CVD. Free-radicals in the gas phase are detected using single-photon ionization (SPI) spectroscopy. We have identified Si, SiH3 and Si2H6 in the gas phase at low pressure, indicating the formation of these species directly from the filament or from secondary wall reactions. We are beginning to obtain new understanding of how different process variables - such as chamber history, filament temperature, and filament material influence the radical concentrations. This molecular-level information in turn is providing new information on the reaction mechanisms in the CVD of these thin films.

> SESSION A16: MICROCRYSTALLINE SILICON Thursday Morning, April 4, 2002 Golden Gate B2 (Marriott)

### 10:15 AM A16.1

FABRICAT $\overline{\text{ION}}$  AND CHARACTERIZTION OF POLYCRY-STALLINE SILICON THIN FILMS BY REACTIVE THERMAL CVD WITH  $\text{Si}_2\text{H}_6$  AND  $\text{F}_2$ .  $\underline{\text{J.W. Lee}}$ , K. Shimizu and J. Hanna, Tokyo Inst of Technology, Yokohama, JAPAN.

Recent demand for high quality poly-Si thin films is increasing in the large-area electronic devices such as LCDs and solar cells more and more, which require large-area uniformity and low cost production simultaneously. We have investigated to fabricate the device-grade poly-Si films by Reactive Thermal Chemical Vapor Deposition (RTCVD) techniques, in which the chemical reactions of source gases allow us deposit the poly-Si films at low-temperature less than 500°C. We selected Si<sub>2</sub>H<sub>6</sub> and F<sub>2</sub> for the source gases. In order to establish the film deposition condition, total pressure, gas flow rates of  $\mathrm{Si}_2\mathrm{H}_6$  $F_2$  and helium (He) as a carrier gas, and residence time,  $\tau$ , are tuned. As we expected, the poly-Si films having the high uniformity and its reproducibility are deposited by decomposing disilane (Si<sub>2</sub>H<sub>6</sub>) in the presence of small amount of fluorine (5%-F2,) on glass substrate at 450°C, when the  $\tau$  was appropriately chosen, e.g., 31.6[sec] in the different pressure. The growth rate is 3.2-4.2[nm/min] and film uniformity is within  $\pm 6.5\%$ . The average grain size is around 100-200[nm] even in 300nm-thick-films. A sharp peak at 520[cm<sup>-1</sup>] of Raman shift is observed, and its full width at half maximum (FWHM) is 6-8[cm<sup>-1</sup>] in higher flow rate of helium. The high crystallinity even at the early stage of film growth is confirmed by a sharp Raman peak of c-Si observed on the back surface of the sample as well as Si-matrix just on glass surface by transmission electron microscopy (TEM) According to XRD spectra of the films, all the films us are oriented to the (220) plane with the FWHM of 0.2-0.3[degree]. The conductivity and activation energy is on the order of  $10^{-5}$ - $10^{-6}$ [S/cm] and 0.45[eV], respectively. These poly-Si films are promising for TFTs and solar cells, because of high crystallinity on glass substrate.

### 10:30 AM A16.2

QUANTITATIVE STUDY OF TRAP DANGLING-BOND RECOMBINATION IN MICROCRYSTALLINE SILICON.

Christoph Boehme, Klaus Lips, Hahn-Meitner-Institut Berlin, Berlin, GERMANY.

In the study presented, time domain measurement of spin–dependent recombination (TSR) was used for a systematic quantitative study of the trap dangling–bond recombination probability of charge carriers in hydrogenated microcrystalline silicon ( $\mu$ c-Si:H). TSR is based on the selective enhancement of distinct spin–dependent recombination pathes by electron spin resonant excitation and is therefore related to electrically detected magnetic resonance methods (EDMR). However, in comparison to EDMR, much shorter mirrowave pulses with higher intensities are used, which allow the quantitative determination of the recombination coefficients. The information is extracted from the time evolution of the sample current after the microwave pulse is turned off. For the data presented, TSR was carried out on a 2.7 $\mu$ m thick

film of  $\mu$ c-Si:H deposited by electron cyclotron resonance chemical vapor deposition. The experiments were performed at various light exposures of the sample and thus at various quasi fermi levels in the temperature range between T=5K and T=150K. The results are discussed in a tunneling recombination model where pair dissociation occurs through tunneling between shallow trap states.

# 10:45 AM \*A16.3

DEFECTS IN MICROCRSTALLINE SILICON PREPARED WITH HOT WIRE CVD. F. Finger, S. Klein, T. Dylla, A.L. Baia Neto and R. Carius, Institut für Photovoltaik, Forschungszentrum Jülich, Jülich, GERMANY.

Hot Wire (HW) - or Catalytic Chemical Vapour Deposition (CVD) has attracted attention for the fabrication of microcrystalline silicon (μc -Si:H) solar cells. High deposition rates and grain size dimensions, usually not found with competing PECVD techniques, have triggered this interest. However, up until recently, solar cells with  $\mu c$  -Si:H prepared by HW-CVD have shown poor performance. Now a major breakthrough was achieved by reduction of the deposition temperature, accompanied by control of the wire temperature and wire arrangement. Under such conditions material with excellent opto-electronic properties and solar cell efficiencies of 9.4% are obtained. This improvement is linked to a reduction of the defect density, which in turn is related to hydrogen passivation of grain boundaries. Investigation of these defects by means of electron spin resonance (ESR) is the topic of the present paper.  $\mu$ c-Si:H was prepared at four substrate temperatures  $(T_S)$  between  $185^{\circ}C$  and  $450^{\circ}C$ . For each  $T_S$  the silane-hydrogen process gas mixture (SC) was varied to obtain material with different structure composition i.e. different contents of crystalline and disordered phase. All samples show a single ESR line at g = 2.0048 - 2.0054. The spin densities decrease by up to three orders of magnitude within the investigated  $T_S$  range, and in addition, for a given  $T_S$  the spin densities decrease with increasing SC, confirming earlier findings for PECVD-material. It is proposed that hydrogen etching and thermal desorption of hydrogen lead to poor grain boundary passivation at low SC and high temperature, respectively. This is supported by results on hydrogen bonding and hydrogen content in the material. We conclude that optimum  $\mu c$  -Si:H solar cell material, both from HW-CVD and from PECVD, is not necessarily obtained with largest grain sizes and apparent highest crystalline content, but rather by a material prepared under conditions which yield a compact morphology with an effective grain boundary passivation.

### 11:15 AM <u>A16.4</u>

LARGE-GRAIN POLYSILICON FILMS WITH LOW INTRAGRANULAR DEFECT DENSITY BY LOW-TEMPERATURE SOLID-PHASE CRYSTALLIZATION. Xiang-Zheng Bo, Nan Yao<sup>a</sup>, and J.C. Sturm, Center for Photonics and Opti-Electronic Materials, Department of Electrical Engineering, Princeton University, Princeton, NJ; <sup>a</sup>Princeton Materials Institute, Princeton University, Princeton, NJ.

Polysilicon films crystallized from amorphous silicon are active layers in thin film transistors (TFTs) used in active matrix liquid crystal displays (AMLCD) and silicon-on-insulator (SOI) technologies for three-dimensional integrated devices. The electrical characteristics of polysilicon TFTs are strongly dependent on the polysilicon microstructure. Larger-grain polysilicon films with fewer intragranular defects at low temperature have been a continual goal [1,2]. In this paper, we studied 600°C solid phase crystallization (SPC) of hydrogenated amorphous silicon deposited by PECVD in a cantilever structure, where underlying silicon oxide was removed prior to furnace anneal. Transmission electron microscopy and Raman spectroscopy were used to measure the structure of polysilicon films. The grain size of polysilicon in the cantilever film increased to 3.0  $\mu$ m, compared with a size of 0.6  $\mu$ m in the polysilicon film with underlying oxide. By examining the microstructure as a function of time, we observed that the grain growth rate increased by a factor of two and the grain nucleation density decreased by a factor of five, when the underlying oxide was removed. Both factors contributed to the larger grain size. Furthermore, the intragranular defect density was reduced by one order of magnitude, from  $10^{11}~{\rm cm^{-2}}$  to  $10^{10}~{\rm cm^{-2}}$ , corresponding to an increase of a defect-free area between microtwins within grains from 25 nm to 100 nm in diameter. The lower nucleation rate is thought to be due to the removal of the a-Si/SiO2 interface, which has been thought to be the preferred nucleation site for a-Si SPC. The removal of underlying oxide also leads to an easier silicon atomic rearrangement at the a-Si/SiO2 interface and easier macroscopic release of the tensile stress which normally accompanies the amorphous to crystalline phase transition. This reduction in stress was confirmed by Raman spectroscopy, and is thought to be a cause of the increased grain growth rate and the reduced intragranular References

[1] L. Haji, P. Joubert, J. Stoemenos, and N.A. Economou, J. Appl.

Phys. 75, 3944 (1994). [2] Y. Morimoto, Y. Jinno, K. Hirai, H. Ogata, T. Yamada, and K. Yoneda, J. Electrochem. Soc. 144, 2495 (1997).

#### 11:30 AM A16.5

THE USE OF SEED LAYERS IN HOT WIRE CHEMICAL VAPOR DEPOSITION OF MICROCRYSTALLINE SILICON FILMS. G.A. Zaharias\*, A.H. Mahan, R.E.I. Schropp\*, Y. Xu, D.L Williamson\*, M.M. Al-Jassim, K.M. Jones and L.M. Gedvilas, National Renewable Energy Laboratory (NREL), Golden, CO; \*Dept. of Chemical Engineering, Stanford Univ., Stanford, CA; \*Utrecht Univ., Debye Institute, Utrecht, THE NETHERLANDS; \*Dept. of Physics, Colo. School of Mines, Golden, CO.

The use of thin seed layers as the initial layers in the deposition of thick hydrogenated microcrystalline silicon (mc-Si:H) films is investigated by XRD, FTIR, SEM and cross sectional TEM, Hot-wire chemical vapor deposition (HWCVD) from silane and hydrogen is used for both the low growth rate seed layer and the subsequent, high growth rate bulk layer, using higher deposition rates than previously attempted in HWCVD of mc-Si:H. Bulk layers are also deposited without seed layers to examine the effects of the seed layers on subsequent film growth. The growth conditions used for the seed layer greatly affect the nature of the bulk film deposited subsequently. When the seed layer is made highly crystalline by using high H dilution (H2:SiH4 100:1), the amorphous incubation layer typical of mc-Si:H growth is virtually eliminated. The seed layer also allows the use of bulk layer deposition conditions that would otherwise produce highly amorphous material. SEM shows improved compactness and uniformity of grains in the composite films. When the seed layer consists of a mixed phase material, deposited using a lower H dilution (10:1), the small crystallites contained within the seed layer again facilitate immediate nucleation in the bulk film, enabling the formation of larger grains in the subsequent layer. In concurrence with other results, filament temperature is shown to be a crucial parameter for both stages of the profiled deposition. Lowering the filament temperature from 2000C to 1750C for both layers results in significant improvements in film compactness, photoresponse and grain size, while maintaining a high crystalline fraction. On selected films we compare different methods (XRD, Raman, cross sectional TEM) for determining the crystalline volume fraction. The use of mc-Si:H layers in high deposition rate solar cells is also discussed.

## 11:45 AM <u>A16.6</u>

APPLICATION OF IMPEDANCE SPECTROSCOPY TO POLYCRYSTALLINE SI PREPARED BY EXCIMER LASER ANNEALING. Jinha Hwang, K.H. Jang, W.P. Lee, C.S. Kim, T.S. Kim, H.D. Kim, and H.K. Chung, Samsung SDI, Corporate Research & Development Center, Suwon, KOREA.

Polycrystalline Si (polysilicon) TFTs have opened a way for the next generation of display devices, due to their higher mobility of charge carriers relative to a-Si TFTs. The polysilicon TFT applications extend from the current Liquid Crystal Displays to the next generation Organic Light Emitting Diodes (OLED) displays. In particular, the OLED devices require a stricter control of properties of gate oxide layer, polysilicon layer, and their interface. The polysilicon layer is generally obtained by annealing thin film a-Si layer using techniques such as solid phase crystallization and excimer laser annealing. Typically laser-crystallized Si films have grain sizes of less than 1 micron, and their electrical/dielectric properties are strongly affected by the presence of grain boundaries. Impedance spectroscopy allows the frequency-dependent measurement of impedance and can be applied to interface-controlled materials, resolving the respective contributions of grain boundaries, interfaces, and/or surfaces. Impedance spectroscopy was applied to laser-annealed Si thin films, using the electrodes which are designed specially for thin films. In order to understand the effect of grain size on physical properties, the amorphous Si was exposed to different laser energy densities, thereby varying the grain size of the resulting films. The microstructural characterization was carried out to accompany the electrical/dielectric properties obtained using the impedance spectroscopy. The correlation will be made between Si grain size and the corresponding electrical/dielectric properties. The ramifications will be discussed in conjunction with active-matrix thin film transistors for Active Matrix OLED

> SESSION A17: HOT WIRE CVD Thursday Afternoon, April 4, 2002 Golden Gate B2 (Marriott)

# 1:30 PM A17.1

AMORPHOUS TO MICROCRYSTALLINE TRANSITION IN THICKNESS-GRADED HOT-WIRE CVD SILICON FILMS.

Qi Wang, John Perkins, Helio Moutinho, Bobby To, Brent Nelson and Howard M. Branz, National Renewable Energy Laboratory, Golden, CO.

We have studied the amorphous to microcrystalline silicon phase transition in hot-wire chemical vapor deposition hydrogenated amorphous silicon (HWCVD a-Si:H) by depositing a series of unique, thickness-graded, samples on a glass substrate at 200°C. By inserting or withdrawing a motor-driven shutter during growth, we make samples that vary from 20 to about 200 nm thick across each 5-cm along stripe. Each stripe is grown at a different dilution ratio of hydrogen to silane in the source gas (R between 0 and 20). The phase composition at various locations was determined by Raman spectra, ultraviolet-reflectivity and spectroscopic ellipsometry. We construct an evolutionary phase diagram as a function of H-dilution and thickness for HWCVD Si and find that it is qualitatively similar but quantitatively quite different from the diagram obtained for plasma-enhanced (PE) CVD [1]. In HWCVD, as in PECVD, low H-dilution and thin films favor amorphous growth, while high H-dilution and thick films favor microcrystalline silicon growth. We characterize the transition by focusing on those stripes that span the phase transition and include large top surface areas of the transitional "edge" material. For example, for the stripe grown at R=2.3, atomic force microscopy (AFM) images of topology reveal that the surface changes from a rather smooth a-Si phase to more granular microcrystalline-Si (rms roughness increases from 1.0 to 4.7 nm) However, in the 90 to 150 nm in thickness region, Raman and reflectivity show a mixed amorphous/crystalline phase, but the AFM shows a smooth surface (1.6 nm) across this range, with relatively constant feature sizes (about 50 nm); resembling the surface of the amorphous region. This surprising result suggests that the mixed-phase growth condition is quite stabilized for an extended period (in thickness). 1. Joohyun Koh, et al., JNCS, 266: 43-47, Part A MAY 2000.

### 1:45 PM A17.2

CHARACTERIZATION OF MICROCRYSTALLINE TRANSITION FROM AMORPHOUS SILICON AS A FUNCTION OF SUBSTRATE TEMPERATURE OF HOT-WIRE CVD. Keda Wang, Haoyue Zhang, Jian Zhang, Jennifer Weinberg-Wolf, Jessica M. Owens, Daxing Han, Univ of North Carolina at Chapel Hill, Dept of Physics & Astronomy, Chapel Hill, NC; Lynn Gedvilas and Brent Nelson, National Renewable Energy Laboratory, Golden, CO.

We have reported the properties of transition films from amorphous to microcrystalline silicon as a function of hydrogen-dilution ratio,  $R=H_2/SiH_4$  prepared by hot-wire CVD at substrate temperature  $T_s$ = 240 °C. We found the transition occurs at 2 <R <3. Since device-quality films can be prepared at a broad substrate temperature range by the hot-wire CVD technique, we studied the transition films made with varied substrate temperature (Ts) from 150 to 550°C at R=3. The characterizations were carried out using IR, Raman and PL spectroscopies. The Raman results indicate that the crystalline volume fraction is negligible at  $T_s \leq 200$  °C and reaches a maximum of ~42% at  $250 \le T_s \le 300^\circ$  C, then slightly decreases to 33% at  $350 \le T_s \le 550^\circ$  C. There is a sudden change from a- to  $\mu$ c-Si at  $T_s = 250^\circ$  C. The total H content decreases when the  $T_s$  increases. The Si-H stretching mode shows a dual-peak feature at 2000 and 2090 cm $^{-1}$  for all the six films. Interestingly, the relative intensity of the 2090 cm $^{-1}$  peak shows a sudden increase at  $T_s=250^{\circ}\mathrm{C}$  consistent with the sudden increase of crystallinity. Whereas, the intensity of the 850-900 cm<sup>-1</sup> SiH<sub>2</sub> bending mode was not correlated with either the 2090 cm<sup>-1</sup> peak or the crystallinity. Therefore, we attribute the 2090 peak to Si-H stretching absorption at c-Si gain-boundaries but not to the SiH2 stretching mode. The PL features also indicate a sudden change from amorphous to microcrystalline silicon at the same student change from anti-photos to infectly stainer show at the same temperature of  $T_s = 250^{\circ}\text{C}$ . Whereas, at  $T_s \geq 250^{\circ}\text{C}$  we observed a gradual change of the PL lineshape and its total intensity. The low energy PL from grain boundaries becomes dominant and the PL total intensity decreases as  $T_s$  increases.

### 2:00 PM A17.3

REAL TIME SPECTROSCOPIC ELLIPSOMETRY OF HIGH DEPOSITION RATE AMORPHOUS SILICON GROWN BY HOT-WIRE CVD. <u>Brent P. Nelson</u>, A. Harv Mahan, Yueqin Xu, Eugene Iwaniczko and Dean Levi, National Renewable Energy Laboratory, National Center for Photovoltaics, Golden, CO.

We use real-time spectroscopic ellipsometry (RTSE) for in-situ characterization of the optical properties and surface roughness (Rs) of hydrogenated amorphous silicon films (a-Si:H) grown by HWCVD with varying deposition rates (0.4 to 10 nm/s). Early time evolution of the Rs during film growth is remarkably similar for all deposition rates. During the first few nm of growth, there is a sharp increase in Rs as the film nucleates in separate islands. This is followed by a reduction of Rs as these areas coalesce into a bulk film, which is coalesced by an average thickness of 10 nm. After another  $\sim\!10$  nm of smooth growth the Rs starts increasing again. Beyond this thickness Rs rises to a stable value that is dependent upon growth conditions. For example, we observe low deposition rate conditions producing  $\sim\!2$ 

nm Rs while films grown at over 10 nm/s have an Rs of almost 20 nm. However, the material properties are not unique for a given deposition rate. Increasing deposition rates by increasing silane flow produces films of superior quality to those grown by increasing the pressure. While there is a general tendency for both the surface roughness and optical gap to increase with increasing deposition rate, films grown under high silane flow and low pressure have a better photo-response and a lower Rs than films grown at the same deposition rate but with low silane flow and high pressure. We observe a strong monotonic decrease in photo-response, and linear increase in optical gap, with

 $2:15~\mathrm{PM}~\frac{*\mathrm{A17.4}}{\mathrm{PROGRESS}}$  IN INDUSTRIAL APPLICATIONS OF CAT-CVD (HOT-WIRE CVD). Atsushi Masuda, Akira Izumi, Hironobu Umemoto, Hideki Matsumura, School of Materials Science, Japan Advanced Institute of Science and Technology (JAIST), Ishikawa, JAPAN.

Rapid progresses are achieved in catalytic CVD (Cat-CVD), often called hot-wire CVD, in the past 3-years NEDO national project in Japan. Cat-CVD technology presents many advantages in thin-film formation processes; high-efficiency of gas use, large-area deposition, no ion bombardment and low-temperature deposition even below 200°C. All of the elemental techniques for the industrially applicable Cat-CVD apparatus, such as the suppression of the metal contamination, the precise control of the substrate temperature, the life extension of the catalyzer, 1-m size uniform deposition and the chamber cleaning, have been completely developed. Sophisticatedly designed substrate holder with electrostatic chuck and showerhead equipped with catalyzers are both key technologies for these achievements. High reproducibility for film properties is also obtained by controlling the reaction between high-density radicals and chamber walls. Quite high stability in both thin-film transistors and solar cells using amorphous Si films by Cat-CVD is achieved. Prototype mass-production apparatus for SiNx passivation films in GaAs devices has been already developed and this will be probably the first application of Cat-CVD in industry. These recent movements appear to promise the drastic revolution in semiconductor industry by introducing Cat-CVD in very near future.

> SESSION A18: GERMANIUM ALLOYS Thursday Afternoon, April 4, 2002 Golden Gate B2 (Marriott)

 $3:15~\mathrm{PM}~*A18.1$  GROWTH AND CHARACTERIZATION OF AMORPHOUS AND MICROCRYSTALLINE SILICON-GERMANIUM FILMS. S. Miyazaki, H. Takahashi, M. Sagara and M. Hirose<sup>a</sup>, Department of Electrical Engineering, Graduate School of Advanced Sciences of Matter, Hiroshima University, Hiroshima, JAPAN; aAdvanced Semiconductor Research Center, AIST, Ibaraki, JAPAN

The microcrystallites formation from RF glow plasma of H2-diluted SiH<sub>4</sub>+GeH<sub>4</sub> has been systematically studied by the combination of in-situ Fourier transform infrared attenuated-total reflection (FT-IR-ATR) and ex-situ surface-sensitive Raman scattering measurements. The temporal changes in hydrogen bonding features on reacting film surfaces during a layer-by-layer process, in which the deposition of a few nm-thick film and its exposure to a  $H_2(\text{or }D_2)$ plasma were alternately repeated at 200°C, were monitored with submonolayer sensitivity by means of the FT-IR-ATR technique. The evolution of microcrystallites with progressive film growth was examined in the temperature range from 100 to 350°C by surface sensitive Raman Scattering measurements. For the Si-rich film growth, a significant rate reduction in the incorporation of Si-hydrides with progressive film growth and the appearance of the sharp IR absorption bands due to surface Si-hydride are good indications for the microcrystallites formation as in the case of microcrystalline ( $\mu$ c-)Si:H growth. And we found that higher Si-hydrides existing on as-grown surface are selectively etched away by hydrogen plasma treatment and subsequently hydrogen termination of surface Ge atoms are promoted. For the Ge-rich film growth, the slow time evolution of Si- and Ge-hydrides reflects the onset of the microcrystallization although no significant spectral change in the IR absorption bands is observable during the film growth. Even in the case, the ATR spectra taken during hydrogen plasma treatment shows clearly the narrowing of the IR absorption bands due to surface Ge-hydrides in the beginning of microcrystallization. Raman spectra indicate that, in the substrate temperature range of 200-300°C, the nucleation and grain growth of microcrystallites are promoted markedly. In addition, we found that, in continuous film growth, the incubation layer thickness prior to the microcrystalline formation on quartz becomes large significantly with increasing Ge content (~5nm for  $\mu$ c-Si:H and  $\sim$ 20nm for  $\mu$ c-Si<sub>0.4</sub>Ge<sub>0.6</sub>:H).

3:45 PM A18.2 STRUCTURAL, ELECTRICAL, AND OPTICAL PROPERTIES OF PECVD DEPOSITED GERMANIUM FILMS. William B. Jordan, Sigurd Wagner, Princeton University, Dept of Electrical Engineering, Princeton, NJ.

We report the results of a study of some basic properties of germanium films, which are attracting interest for possible use in low gap solar cells due to their low optical gap and high optical absorption. We discovered that the structure of germanium thin films is a strong function of temperature. The films grew  $microcrystalline~(\mu c)$  in the vicinity of 200°C, amorphous around 300°C, and microcrystalline again near 400°C. We provide an overview of the optoelectronic properties of the Ge films throughout their microcrystalline/amorphous/microcrystalline phase range. We grew thin films of  $\mu$ c-Ge:H on 1737 glass substrates by RF (13.56 MHz) plasma enhanced chemical vapor deposition (PECVD) using GeH<sub>4</sub> and H<sub>2</sub> source gases. The GeH<sub>4</sub> flow rate, hydrogen dilution, deposition pressure, substrate temperature, and RF power were varied and their effects on the crystallinity, optical absorption, optical gap, dark and photo conductivities, thermal activation energy, carrier mobility and concentration, surface roughness, and growth rate were measured. Crystallinity was determined by UV/visible reflectance, x-ray diffraction, and Raman spectroscopy. The optical absorption was measured by photothermal deflection spectroscopy (PDS). The surface roughness was characterized by atomic force microscopy (AFM) and field emission scanning electron microscopy (SEM). The carrier mobility, concentration, and sign were determined by Hall measurements. The dark and photo conductivities and thermal activation energy were measured under vacuum as a function of temperature. Dark conductivity ranged from 0.01 to 10 S/cm for  $\mu$ c-Ge:H at 400°C, and was as low as  $10^{-5}$  S/cm for amorphous material. Growth rate increased with mass flow and power, and decreased with hydrogen dilution. The optical gap varied from  $0.7~\mathrm{eV}$ to 1.0 eV. Surface roughness and conductivity of  $\mu$ c-Ge:H increased with film thickness. At deposition temperatures nearing 400°C μc-Ge:H was found to be p-type. This work is supported by EPA and NSF

# 4:00 PM <u>A18.3</u>

 $\operatorname{HYDROG}\overline{\operatorname{EN}}$  BONDING AND ELECTRONIC PROPERTIES OF AMORPHOUS SILICON GERMANIUM ALLOYS. Vikram Dalal, Yong Liu, Iowa State University, Dept. of Electrical and Computer Engineering, Ames, IA.

We report on the growth of high quality a-(Si,Ge) materials and devices fabricated using a low pressure ECR discharge with hydrogen or helium dilution. High growth rates could be achieved in a-(Si,Ge) by combining He and hydrogen dilutions. The H bonding in the materials was related to the plasma conditions employed during growth. By inducing significant ion bombardment during growth, one could achieve strong Ge-H bonding and at the same time, reduce deleterious Si-H2 bonding which is commonly observed in a-(Si,Ge) films. Defect densities were measured using space charge limited currents and were found to be in the 1-2E16/cm3-eV range.Good devices at 5 A/sec could be made across the entire range of bandgaps, from 1.1 to 1.7 eV by using a combination of He and H dilutions. The device properties could be improved by using chemical annealing with

> SESSION A19: POSTER SESSION GROWTH: NEW METHODS AND FUNDAMENTALS Thursday Evening, April 4, 2002 8:00 PM Salon 1-7 (Marriott)

AMORPHOUS SILICON FILMS AND SUPERLATTICES GROWN BY MOLECULAR BEAM EPITAXY. D.J. Lockwood, J.-M. Baribeau, G.I. Sproule, Institute for Microstructural Sciences National Research Council of Canada, Ottawa, Ontario, CANADA; M. Noël, J.C. Zwinkels, Institute for National Measurement Standards, 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 produce a novel form of amorphous silicon through ultrahigh-vacuum molecular beam epitaxy. By depositing silicon atoms onto a fused quartz substrate at temperatures between 100 and 335°C, we obtain a silicon-based material that lacks the characteristic periodicity of crystalline silicon but nevertheless has 98% of its density. The impurity content of this material is studied through infrared and secondary ion mass spectroscopies, particular attention being given to the dependence of this impurity content on the growth

temperature. The primary impurity found is oxygen, at levels of the order of 1 atomic %, with hydrogen and carbon atoms also being found at trace levels (i.e., at less than 0.1 atomic %). Deposition parameter optimization is explored, with the aim of producing higher quality films. We also use this molecular beam epitaxy method to fabricate a number of amorphous silicon superlattices, comprised of thin layers of amorphous silicon separated with even thinner layers of  $\mathrm{SiO}_2$ . The optical properties of the films and superlattices are examined and conclusions are drawn regarding the nature of the disorder and the role of quantum confinement.

#### A19.2

COMPUTATIONAL MODELING OF HOMOGENEOUS NUCLEATION AND PARTICLE GROWTH DURING CHEMICAL VAPOR DEPOSITION OF SILICON FILMS FROM SILANE PLASMAS. Upendra Bhandarkar, Uwe Kortshagen, Steven Girshick, Dept of Mechanical Engineering, University of Minnesota, Minneapolis, MN.

It is well known that gas-phase nucleation of particles occurs in silane plasmas under certain conditions. This phenomenon is now of interest for the growth of amorphous hydrogenated silicon films with nanometer-sized crystalline inclusions. These films have been shown to exhibit improved medium-range order and enhanced stability against light-induced defect formation. To help understand the process of gas-phase particle formation we have developed a computational model for particle nucleation and growth in capacitively-coupled silane plasmas. This model includes a detailed chemical kinetic mechanism for the growth of silicon hydride clusters. Both plasma chemistry and neutral chemistry are considered. Because anions are trapped in the plasma we include both neutral and anion clusters. The model is zero-dimensional, time-dependent, but species diffusion of neutrals is included in an approximate way as a sink term in the species equations. Electron concentrations are found from plasma quasi-neutrality, and the electron temperature is obtained from the electron energy equation, for an assumed Maxwellian electron energy distribution. The clustering model is coupled to an aerosol dynamics model, that solves for single-particle growth by surface reactions, and for particle charging and coagulation. Results are presented for various operating pressures and power levels, and are compared to experimental observations. The clustering chemistry, particle dynamics, and plasma behavior are found to be strongly coupled to each other. The model predicts the particle charge distribution as a function of particle size. Very small particles are predominantly neutral, whereas for diameters larger than about 10 nm the particles are predominantly negatively charged. A non-negligible fraction of positively charged particles is predicted. This may have important implications for film growth, because positively-charged particles are accelerated into the film by the field across the plasma sheath, whereas neutral particles deposit by Brownian diffusion (and, possibly, thermophoresis), while negatively-charged particles are repelled.

### A19.3

EXPANDING THERMAL PLASMA DEPOSITION OF SILICON DIOXIDE-LIKE FILMS FOR MICROELECTRONIC DEVICES.

M. Creatore, M.F.A.M. van Hest, M.C.M. van de Sanden, Department of Applied Physics, Eindhoven University of Technology, THE NETHERLANDS.

Silicon dioxide plays a fundamental role in all the devices based on Si technology: it is used as insulator between metal layers in multilevel metal systems, as gate oxide and capacitor dielectric in MOS devices, as mask against diffusion and implantation, as passivator and as sacrificial film in MEMS. The deposited films must exhibit uniform thickness and composition, low chemical contamination and pinhole density, and good adhesion to the substrate. Plasma Enhanced-Chemical Vapour Deposition can successfully meet these requirements, beside allowing low process temperatures. The expanding thermal plasma (ETP) technique, when compared to more conventional plasma systems, leads to a simplified optimisation of the process and facilitates studies of plasma reactions and film growth mechanism, because of the separation between the plasma source and the deposition chamber. The plasma generated in a dc cascaded arc (0.2-0.6 bar) expands through a nozzle into the chamber (0.1-0.3 mbar) where the deposition precursor gases (injected by means of a ring) are dissociated/ionised by the reactive species coming from the arc. The effects of the plasma source parameters (arc current, Ar flow rate), the feed gas composition (hexamethyldisiloxane/oxygen mixture), the substrate temperature and bias (applied to the substrate holder) were investigated. In order to correlate the plasma species density with the deposited film chemistry, a multi-diagnostics approach was carried out. The in situ film growth was monitored by means of Ellipsometry and IR Reflection Absorption Spectroscopy, adapted to our fast deposition process (tenths of nm/s). The plasma phase was investigated by means of Mass Spectrometry and Cavity Ring Down Spectroscopy, used for the determination of the radicals density. The tailoring of the deposition process through the above

mentioned diagnostic tools has lead to carbon-free films with very low silanol content (SiOH is primarily responsible for the increase in refractive index and dielectric constant).

#### A19.4

SURFACE ROUGHNESS EVOLUTION OF PECVD CATHODIC AND ANODIC a-Si:H. George Dalakos, General Electric Corporate Research and Development, Niskayuna, NY; Joel Plawsky, Rensselaer Polytechnic Institute, Dept of Chemical Engineering, Troy, NY; Peter Persans, Rensselaer Polytechnic Institute, Dept of Physics, Troy, NY.

Surface or interface roughness can impact optical, electronic, and MEMS applications of thin a-Si:H films. Deposition at lower temperatures can be advantageous for some applications of a-Si:H, but lower temperature deposition generally leads to rougher films. We have found that the evolution of surface roughness growth can be modified substantially by ion bombardment due to the self-bias of the plasma during Plasma-Enhanced Chemical Vapor Deposition (PECVD). Notable differences in the surface roughness evolution and deposition rate are shown for films deposited in "cathodic" versus "anodic" mode - where the substrate is placed on the powered and grounded electrode respectively. Suppression of surface roughness growth of a-Si:H can be achieved under conditions of relatively high ion bombardment even at deposition temperatures as low as 75°C Atomic force microscopy (AFM) was used to measure the relative surface roughness profile as a function of deposition time. Analysis of the power spectral density of the roughness yielded important statistical surface parameter information. Based on these observations, insight is given into growth mechanisms under the two deposition conditions.

#### A19.5

GERMANIUM DAMASCENCE PROCESS BY SELECTIVE LPCVD AND SURFACE SMOOTHENING TECHNIQUE. Chi On Chui, and Krishna C. Saraswat, Stanford University, Dept. of Electrical Engineering, Stanford, CA.

Highly compatible with the silicon-based technology, Ge offers some superior material qualities like higher carrier mobilities and broader absorption spectrum for opto-electronic applications. In addition, the lower processing temperature with Ge makes it an attractive material for post-metallization fabrication of transistors and photodetectors in the upper layers for 3-D ICs. Unfortunately, the water-soluble germanium native oxide rinses off during processing. In this presentation, a damascene scheme for Ge growth by selective LPCVD with LTO (low-temperature SiO<sub>2</sub>) barriers is discussed to avoid germanium post-deposition water exposure. On a substrate with both silicon and LTO, pure Ge is deposited by the pyrolysis of GeH<sub>4</sub> in a LPCVD system. Simultaneously,  $GeH_4$  would also etch off native  $SiO_2$ and LTO through a reduction reaction. Since the density of surface adsorption sites, for pyrolysis of GeH<sub>4</sub>, on SiO<sub>2</sub> surface is negligibly small compared to silicon, the process of nucleation and growth for  ${\rm Ge}$ film on SiO2 is more difficult, which explains the selectivity in deposition. However, at some processing conditions, enhanced deposition on SiO2 can occur. In this study, we try to explain this phenomenon and establish a process window for selective depositions, the corresponding incubation time and the critical Ge film thickness Contrasting any UHV systems, the finite oxygen contamination in these common LPCVD furnaces would tend to react with the residual  $\mathrm{GeH_4}$  gas to form intermediate  $\mathrm{GeO}_x$  on the Ge surface right after deposition. From both AFM and SEM, hillock structures are observed on the deposited Ge surface, mainly composed of  $GeO_x$  as confirmed with EDS analysis. After coating and stripping of photoresist on the surface, almost all the hillocks disappear. The surface RMS roughness also reduces from 35.5nm to 2.8nm, which is similar to the post-CMP polysilicon films for TFT applications.

### A19.6

CHARACTERIZATION OF ECR PLASMA USED FOR GROWING AMORPHOUS SILICON, SILICON-GERMANIUM AND SILICON-CARBON ALLOYS. Marsela Pontoh, <u>Vikram Dalal</u>, Neha Gandhi, Iowa State University, Dept. of Electrical and Computer Engr., Ames, IA.

We report on the characterization of ECR plasmas used for depositing a-Si and a-(Si,Ge) alloy films and devices. The plasma was characterized using in situ mass-sectrometery, Langmuir probes and optical emission spectroscopy. The ECR plasma was used in a remote mode, with diluting gases (Hydrogen and Helium) introduced in the plasma zone, and the feedstock gases (silane, germane, methane and ethylene) introduced near the substrate. The substrate coud be biased using a dc voltage source. A grounded grid could be placed in front ofthe substrate, thereby converting the plasma into a triode ECR plasma. It was found that the presence of the grid had a significant influence on the plasma properties reaching the substrate. Without the grid, changing the dc bias on the substrate led to significant

changes in all the plasma properties (OES, ion energy, flux etc.), but with the grid present, only the energy was changed. This result points out that the usual assumption regarding biasing of a substrate, namely that it only changes the ion energy, is wrong. We also observed systematic variation in the flux density of neutral H radicals as the pressure and power were changed, with higher radical fluxes at low pressures. The addition of even small amounts of hydrogen to a He plasma significantly changed the ion flux, electron temperature and ion energies. From this, we can deduce that the addition of H to a plasma reduces the growth rate not because of etching of the film, but primarily because of changes in the plasma properties. An excellent correlation was observed between growth rates and plasma properties, such as OES spectra.

MICROWAVE PLASMA ASSISTED VHF-PECVD OF MICROCRYSTALLINE SILICON. Wim Soppe, Corinne Droz, Urs Graf, Ulrich Kroll, Johannes Meier, Arvind Shah, Institute of Microtechnology (IMT), Neuchatel, SWITZERLAND

Growth of intrinsic microcrystalline silicon layers by means of a VHF-PECVD, assisted by an additional remote microwave (MW) plasma has been investigated. The aim of the microwave plasma is to enhance the deposition rate by the introduction of extra excited hydrogen and Ar atoms in the VHF deposition zone. For this purpose a remote microwave plasma source was constructed in which a H<sub>2</sub>/Ar plasma is generated in a 20 mm diameter tube of dielectric material. A gas-shower has been constructed for homogeneous distribution of the flow of excited gas species from the microwave source into the deposition zone of the VHF-PECVD reactor where the dissociation of silane takes place. At high microwave power (> 500 W) and undiluted hydrogen in the MW source, an increase of the deposition rate of silicon by 20% with respect to pure VHF deposition was observed. The silicon layers grown with MW assistance had a high oxygen content as a result of a strong reduction of the quartz tube by the hydrogen plasma. In a second series of experiments, the quartz tube was replaced by an alumina tube and Ar dilution and reduced MW power were used to eliminate the effect of etching of the tube by the microwave hydrogen plasma. In this series of experiments an increase of the growth rate of micro-crystalline silicon by about 15% due to assistance of the microwave plasma was found. Optical emission spectroscopy indicates that in these experiments - the main mechanism for the increased dissociation of silane is through a reaction with atomic hydrogen (hydrogen abstraction) and not by electron impact.

MICROWAVE PECVD OF MICROCRYSTALLINE SILICON. Wim Soppe, Camile Devilee, ECN Solar Energy, Petten, THE NETHERLANDS; Harry Donker, Laboratory for Inorganic Chemistry, Delft University of Technology, Delft, THE NETHERLANDS; Jatin Rath, Debye Institute, Utrecht University, Utrecht, THE NETHERLANDS.

The deposition of intrinsic micro-crystalline silicon by means of PECVD with a new linear microwave plasma source is investigated. This plasma source already has successfully been introduced in the large scale production of multi-crystalline Si solar cells for the deposition of passivating silicon nitride layers. Advantages of the linear plasma source are high deposition rates and the large area (up to 80 cm width, no length limitations) on which a homogeneous deposition can be achieved. Since this source has not been applied for deposition of micro-crystalline silicon before, we had to explore a large parameter space (substrate temperature, pressure, MW-power, gas flow rates), in order to find optimum growth conditions. It is observed that with this microwave source it is possible to grow micro-crystalline layers at significantly higher silane/hydrogen ratios and deposition rates than for conventional RF PECVD. In this paper, structural properties of the silicon layers, as investigated by Raman and FTIR spectroscopy, XRD and SEM measurements are discussed.

EFFECTS OF SUBSTRATE TEMPERATURE AND ATOMIC HYDROGEN FLOW ON THE MIRCOCRYSTALLINITY OF EVAPORATED HYDROGENATED SILICON FILMS. A.J. Stoltz, Whitney Mason, J.D. Benson, J.H. Dinan, Night Vision & Electronic Sensors Directorate, Ft. Belvoir, VA; K. McCormack, Institute for Defense Analysis, Alexandra, VA; A. Kaleczyc, E-OIR Measurements, Inc., Spotsylvania, VA.

There has been a long standing interest in amorphous/microcrystalline silicon due to its applications in solar cells and thin film transistors. More recently these films have found application in uncooled infrared detectors. Traditionally amorphous/microcrystalline silicon has been deposited by a variety of methods including plasma enhanced chemical vapor deposition (PECVD), hot-wire chemical vapor deposition, and sputtering. There have been few reports of the

properties of films deposited by evaporation. There has been increasing interest in microcrystalline hydrogenated silicon. We used physical vapor deposition (PVD) to form Si films and examined their crystalline and chemical characteristics. E-beam evaporation was carried out in an ultra high vacuum chamber that contained an atomic hydrogen effusion cell. The effects of hydrogen flux and substrate temperature on crystallinity and hydrogen concentration were measured. Films were deposited on (100) Si wafers coated with either silicon nitride or evaporated titanium. Raman Spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), Secondary Ion Mass Spectroscopy (SIMS), and Spectrographic Ellipsometry (SE) were utilized to characterize the films. Raman spectra for unhydrogenated films deposited at 24, 200, and 400°C exhibit a broad peak at approximately 480 cm<sup>-1</sup> whose intensity increases with temperature. This feature has been previously associated with the amorphous phase of Si. In contrast, the sample grown at  $600^{\circ}\mathrm{C}$  shows a sharp feature at approximately  $520~\mathrm{cm}^{-1}$ , characteristic of crystalline Si. FTIR spectra show a strong dependence of hydrogen concentration on both substrate temperature and atomic hydrogen. SIMS data show that hydrogen concentration can be varied from the detection limit of SIMS to a value in excess of  $10^{21}$  atoms/cc.

EPITAXIAL GROWTH IN DISLOCATION-FREE STRAINED ALLOY FILMS. Zhi-Feng Huang, Rashmi C. Desai, Univ of Toronto, Dept of Physics, Toronto, CANADA.

The morphological and compositional instabilities in the heteroepitaxial strained alloy films have attracted intense interest from both experimentalists and theorists. To understand the mechanisms and properties for the generation of instabilities, we develop a nonequilibrium, continuum model for the dislocation-free and coherent film systems. The early evolution process of surface profiles for both growing and postdeposition (non-growing) thin alloy films are studied through stability analysis. We consider the coupling between top surface of the film and the underlying bulk, as well as the combination and interplay of different elastic effects caused by film-substrate lattice misfit, composition dependence of film lattice constant (compositional stress), and in particular, composition dependence of both Young's and shear elastic moduli. The interplay of these factors as well as the growth temperature and deposition rate leads to rich and complicated stability results. For both the growing film and non-growing alloy free surface, we determine the stability conditions and stability diagrams of the system, showing the joint stability or instability for film morphology and compositional profile, as well as the asymmetry between tensile and compressive layers. The kinetic critical thickness for the onset of instability during film growth is also calculated, and its scaling behavior with respect to misfit strain and deposition rate determined. Our results are applied to some real alloy growth systems such as SiGe and InGaAs, and compared with recent experimental observations.

PHOTOCONDUCTIVITY STABILITY IMPROVEMENT IN HYDROGENATED AMORPHOUS SILICON BY ULTRAVIOLET ILLUMINATION. Howard M. Branz, Yueqin Xu, Stephan Heck, Qi Wang, Richard S. Crandall, Brent Nelson and Wei Gao, National Renewable Energy Laboratory, Golden, CO.

We observe improved photoconductivity stability against light-soaking in hydrogenated amorphous silicon thin films as a result of an ultraviolet illumination and etch treatment. Device quality plasmaenhanced CVD films on pre-deposited Cr contacts are treated for 1 hour to 4 days by 330±40 nm ultraviolet (UV) illumination. After treatment, the damaged top surface layer is removed with an NaOH etch and then the red photoconductivities are monitored during 1 sun red light soaking. Although the UV-etched sample begins with photoconductivity inferior to that of a control sample which is only etched, after less than an hour of light-soaking the photoconductivity of the etched-only control falls below that of the UV-etch treated sample. For optimized treatments, photoconductivity more than 35%higher than the control is observed after a 60 hr light soak. We observe no corresponding improvement of defect optical absorption by constant photocurrent method (CPM) spectroscopy. Although the UV photons are absorbed in the top 10 to 20 nm, damage goes deeper because of electron-hole diffusion. A study of the dependence on post-UV etch depth reveals that 100 nm must be removed to obtain the greatest improvements; this is the depth of damge by photocarrers. Still deeper etching reduces the improvement; we conclude that the region of photoconductivity stability improvement extends 200 to 400 nm into the bulk. We speculate that mobile hydrogen produced during UV illumination is penetrating the film and improving stability. Anneal experiments show that much of the difference between etch-only control samples and the UV-etch sample disappears with 90°C annealing.

SESSION A20: POSTER SESSION FUNDAMENTAL PROPERTIES OF MICROCRYSTALLINE SILION Thursday Evening, April 4, 2002 8:00 PM Salon 1-7 (Marriott)

### A20.1

OPTICAL PROPERTIES OF MICROCRYSTALLINE SILICON DETERMINED BY SPECTROSCOPIC ELLIPSOMETRY AND PHOTOTHERMAL DEFLECTION SPECTROSCOPY. Kyung Hoon Jun, Helmut Stiebig, Reinhard Carius, Forschungszentrum Juelich GmbH, Institute of Photovoltaics, Juelich, GERMANY

The effect of the microstructure and hydrogen bonding on the optical properties of microcrystalline films (µc-Si:H) was investigated by Spectroscopic Ellipsometry (SE) and Photothermal Deflection Spectroscopy (PDS) for photon energies between 1.0 eV and 3.2 eV. Variation of the microstructure was achieved by using different silane concentrations in the gas phase. Measurements were performed on samples as deposited and after annealing at 600°C for 60 min. Removal of the surface layer and flattening the surface by mechanical polishing was essential for accurate data analysis of the bulk properties by SE. Samples with a high crystalline volume fraction (fc)exhibit a significant higher absorption coefficient for  $\mu c ext{-Si:H}$  than c-Si in the energy range between 1.5 eV and 3.2 eV. Annealing affects the optical properties of samples with high fc only in the vicinity of the band gap of c-Si (0.9 - 1.3 eV) where the increase of  $\alpha$  can be attributed to a higher defect density. The higher absorption in the  $\mu$ c-Si:H films between 1.5 eV and 3.2 eV in the as deposited and annealed state can neither be explained by a contribution of the amorphous phase, nor by internal scattering. We suggest strain and local disorder as possible reasons for the enhancement of  $\alpha$  and we will discuss the results taking into account the Raman spectra. For the films with low crystalline volume fraction, we extracted the optical properties of the disordered part which change drastically after annealing. This is attributed to the variation of density of states, defects, and strained bonds in the amorphous and crystalline phase. To study the disordered part in more detail, the variation of the Tauc-Lorenz parameters will be discussed.

LIFETIME REGIME IN THE ELECTRICALLY-DETECTED TRANSIENT GRATING METHOD APPLIED TO MICRO-CRYSTALLINE SILICON. P. Sanguino, M. Niehus, S. Koynov, P. Brogueira, R. Schwarz, Departamento de Fisica, Instituto Superior Tecnico, IST, Lisbon, PORTUGAL; J.P. Conde, Departamento de Materiais, Instituto Superior Tecnico, IST, Lisbon, PORTUGAL; and V. Chu, INESC Microsystems and Nanotechnologies, Lisbon,

Thin silicon films deposited by hot-wire chemical vapor deposition (HW-CVD) near the amorphous-to-microcrystalline transition appeared to be ideal candidates to study the interplay between carrier recombination and dielectric response by the electrically-detected transient grating method (EDTG). We have previously followed the change in secondary photocurrent response time  $\tau_R$  in this region and found that  $\tau_R$  increased from sub-microseconds to some hundred  $\mu_{S_1}$ while the Fermi level remained near midgap [1]. If  $\tau_R$  is dominant with respect to the dielectric relaxation time  $\tau_{diel}$  then the simple ambipolar approach should apply. Here we show that by modifying the ambipolar description of the carrier grating build-up and decay we can obtain a good agreement between analytical calculation and experimental results. The main ingredient is that we allow the internal electric fields to be switched on and off exponentially in time with the time constant  $\tau_{diel}$ , corresponding to the time evolution of the interference terms in the EDTG formalism [2]. Apart from some uncertainty due to the clearly non-exponential decay of the transients we have obtained an experimental tool to monitor the dielectric relaxation which is a combined effect of majority and minority carrier transport. The transition from the lifetime dominated behavior to the dielectric relaxation time regime can be studied also in one given film by increasing recombination losses either through reduction of carrier lifetime by measuring at higher light intensity, or, more efficiently, by fast annealing of the samples with high power laser pulses from the green line (532 nm) of a Nd:YAG laser. [1] P. Sanguino, R. Schwarz, T. Murias, J.P. Conde, P. Brogueira, and V. Chu, Mat. Res. Soc. Symp. Proc. 507 (1998) 193. [2] F. Wang and R. Schwarz, "The Electrically Detected Transient Photocarrier Grating Method", Appl. Phys. Lett. 65 (1994) 884.

# A20.3

Abstract Withdrawn.

RAMAN SPECTROSCOPY OF HEAVILY DOPED POLYCRYSTALLINE AND MICROCRYSTALLINE SILICON. P. Lengsfeld, S. Brehme, and N.H. Nickel, Hahn-Meitner-Institut Berlin, Berlin, GERMANY.

Polycrystalline silicon (poly-Si) thin films were prepared by excimer laser crystallization of a-Si:H deposited by PECVD. Microcrystalline silicon ( $\mu c$ -Si) films were deposited by PECVD and ECR-CVD using hydrogen diluted silane. Doping of a-Si:H (and thus of poly-Si) and of μc-Si:H was achieved by mixing silane with phosphine or diborane. The free carrier concentration of the samples was determined by Hall effect measurements. Raman spectroscopy was performed with a standard micro-Raman setup equipped with a HeNe laser. The Raman spectra of heavily B and P doped laser crystallized poly-Si revealed asymmetrical broadenings of the LO-TO phonon line [1]. These changes of the phonon line shape are well know to occur in heavily doped c-Si and are caused by the Fano effect [2]. The precondition for the occurrence of the Fano effect for Raman scattering in silicon is degenerate doping, i.e. the Fermi energy has to reside in the conduction or valence band.

In case of  $\mu c$ -Si:H both B and P doped films revealed free carrier concentrations on the order of  $> 8 \times 10^{19} \sim cm^{-3}$  independent of temperature in the range 12-300K. These two facts indicate that the films are degenerately doped. Thus the precondition for the occurrence of the Fano effect is met. However, the Raman measurements did not give any conclusive evidence for the Fano effect. It will be discussed, how the differences in the material properties between  $\mu c$ -Si and poly-Si can explain the experimental observations. [1] N.H. Nickel, P. Lengsfeld and I. Sieber, Phys. Rev. B 61, 15558

[2] F. Cerdeira, T.A. Fjeldy, and M. Cardona, Phys. Rev. B 8, 4734 (1973).

### A20.5

PARAMAGNETIC CENTERS IN MICROCRYSTALLINE SILICON.  $\underline{M.M.}$  de Lima Jr. and P.C. Taylor, Department of Physics, University of Utah, Salt Lake City, UT; S. Morrison and A. LeGeune, MV Systems, Golden, CO; F.C. Marques, Departamento de Fisica Aplicada, Instituto de Fisica "Gleb Wathaghin", Universidade Estadual de Campinas, Unicamp, Campinas, SP, BRAZIL.

Hydrogenated microcrystalline silicon is a material that has attracted attention recently for possible application in solar cells and other electronic devices. Using dark and light-induced electron spin resonance (ESR) we investigate paramagnetic centers in high quality intrinsic microcrystalline silicon. The characteristic dark ESR signal can be explained by means of only one center. From powder pattern lineshape simulations, we suggest that this center may be due to vacancies in the crystalline phase. The g values obtained empirically from these simulations are g(parallel) = 2.0096 and g(perpendicular)= 2.0031. During illumination at low temperatures an additional ESR signal appears. This signal is best described by two powder patterns indicating the simultaneous production of two centers. One center is asymmetric [g(parallel) = 1.999, g(perpendicular) = 1.996] while the other is characterized by large unresolved broadening such that unique g-values cannot be obtained. The average g value for this center is 1.998. The light-induced signal, which we interpret as carriers trapped in the band tails at the crystalline grain boundaries, remains for at least several minutes after the light is turned off. The decay curves are qualitatively the same for samples prepared by different techniques, and they can be fitted using the assumption of distant-pair recombination via tunneling between localized states. However, the time scales of the decays are very different in the two samples studied. The decay is much faster for the sample with the best electronic properties.

 $\frac{\mathbf{A20.6}}{\mathbf{STRUCTURAL}}$  AND ELECTRICAL CHARACTERIZATION OF B-DOPED MICROCRYSTALLINE SILICON THIN FILMS. R. Saleh, Jurusan Fisika, Fakultas MIPA, Universitas Indonesia, INDO $\overline{\rm NESIA};$ and N.H. Nickel, Hahn-Meitner-Institut Berlin, Berlin, GERMANY.

B-doped microcrystalline silicon films have been grown on quartz substrates by plasma-enhanced chemical vapor deposition (PECVD) using a mixture of silane and hydrogen as reaction gases and diborane was chosen as dopant gas. The hydrogen dilution and substrate temperature were fixed at 99% and  $230^{\circ}\,C$ , respectively, while the diborane dilution was varied from 100 to 5000 ppm. Structural and electrical properties of the films were studied as a function of diborane dilution using Raman spectroscopy, hydrogen effusion, and dark conductivity measurements.

Results of Raman studies showed that the crystal volume fraction decreased as the diborane dilution is increased from 100 to 5000 ppm. Raman spectra also show two peaks at 2000 and 2100cm characteristic of Si-H stretching mode. The intensity ratio of these two lines  $I_{2100}/I_{2000}$  decreases with increasing B doping level indicative of increasing number of isolated Si-H bonds in the films. The hydrogen concentrations were determined from hydrogen effusion measurements. We found that the peak in the hydrogen effusion rate

are shifted to lower temperature as compared to an undoped film. To understand the electron transport mechanism on our B-doped series of films, temperature dependence of dark conductivity has been measured in the range of 150 to 440 K and giving rise to the calculation of activation energy  $E_A$ . The dark conductivity as well as  $E_A$  initially increased rapidly to a maximum, followed by reduction at high diborane dilution. The relationship between structural and transport properties in these materials will be discussed.

STUDY OF AMORPHOUS TO MICROCRYSTALLINE SILICON TRANSITION FROM ARGON DILUTED SILANE. N. Dutta Gupta, P.P. Ray and P. Chaudhuri, Energy Research Unit, Indian Association for the Cultivation of Science, Jadavpur, Calcutta, INDIA.

We have studied the changes in structural morphology of Si:H materials prepared at various power densities in PECVD of argon diluted silane. Emitting species like  $SiH^*$  and  $Ar^*$  in the plasma were monitored by OES. During the evolution from amorphous to microcrystalline mixed phase significant changes in the structural heterogeneity in the material has been reported [1]. We have discussed the role of heterogeneity in the growth of microcrystalline mixed phase. At low rf power densities ( $< 82 \text{ } mW/cm^2$ ), the material is amorphous with low structural heterogeneity as measured by SAXS. With the increase in power void fraction initially increases. FTIR measurements show a decrease of H-content and change in bonding configuration predominantly from SiH to  $SiH_2$  type.  $2030~cm^{-2}$ mode, occurring due to hydrogen present in platelet like void [2], has been observed to increase with power. Sharp increase in SAXS intensity, in accordance with tilt measurements at a higher power density indicates columnar morphology in the microcrystalline sample formed in this transition region (mixed phase microcrystallinity). With further increase in power density, decrease in heterogeneity in the sample may be due to transition to single-phase microcrystallinity due to coalescence of these columns. In this region both 2030 cm mode and void fraction decreases in while TEM pictures indicate formation of large microcrystalline grains. Elimination of the hydrogen from the platelets will result in collapse of the platelets with the formation of strong Si-Si bonds [3]. These regions will facilitate microcrystalline growth. The bombardment of  $Ar^*$  from the plasma in mediating these transitions and in the nucleation of microcrystalline grains by strain relaxation in the material has been discussed. References: [1] Cabarrocas et al, J. Non-Cryst. Solids, **198-200**, (1996) 871. [2] von Keudell et al, J. Appl. Phys., **84**, (1998) 489. [3] Jackson et al, Phys. Rev.B **45**, (1992) 6564.

<u>A20.8</u> PHOTOLUMINESCENCE PEAKS IN MICROCRYSTALLINE SILICON FILMS GROWN FROM HYDROGEN DILUTION OF SILANE. Jong-Hwan Yoon, Kee-Tae Lee, Kangwon National University, Department of Physics, Chunchon, Kangwon-do, KOREA.

It is well known that hydrogenated microcrystalline silicon films (μc-Si:H) reveal a photoluminescence (PL) band with a peak located within 0.8 - 1.0 eV, depending on growth conditions. However, it is unclear why the peak position of the PL band is changed by growth conditions. In this work we present experimental results that the PL band basically arises from a superposition of several subbands whose intensities strongly depend on deposition conditions, and that the position of the PL peak is determined by the intensity of dominant subband. The  $\mu$ c-Si:H films studied in this work were grown by a conventional plasma-enhanced chemical vapor deposition (PECVD) excited at 13.56 MHz using hydrogen diluted SiH4 gas. A series of μc-Si:H films was grown by changing either the hydrogen dilution or rf power. The dependences of the PL on H<sub>2</sub> dilution ratio, plasma RF power, and measurement temperatures have been measured and analyzed. It is observed that there are at least four subbands the peaks of which are located at energies of 0.81 eV, 0.87 eV, 0.92 eV, and 0.99 eV, whose intensities strongly depend on deposition conditions. It is found that RF power significantly affects the intensities of subbands, while H<sub>2</sub> dilution ratio has little influences in the intensities of subbands. It is also observed that subband with lower energy peak is dominant at higher temperature, while subband with higher energy peak is rather dominant at lower temperature. From the results it is suggested that the PL band in the  $\mu$ c-Si:H films is attributed to a complex of luminescences originated from several material factors, such as crystallites, grain boundaries, and defects in amorphous phase.

# A20.9

ELECTRON SPIN RESONANCE AND ELECTRONIC CONDUCTIVITY IN MODERATELY DOPED N-TYPE MICROCRYSTALLINE SILICON AS A PROBE FOR THE DENSITY OF GAP STATES. T. Dylla, R. Carius, F. Finger, Institut für Photovoltaik, Forschungszentrum Jülich, GERMANY

Electron spin resonance (ESR) accompanied by conductivity

measurements in n-type microcrystalline silicon ( $\mu$ c-Si:H) with different Fermi level (E<sub>F</sub>) positions has been applied for the study of the density of gap states and the influence of these states on charge carrier density. The material was deposited with VHF-PECVD at silane concentrations SC=2-7% for ESR, Raman and conductivity measurements. We studied doping concentrations close to the defect density where the doping induced  $E_F$  shift is determined by compensation of gap states. In earlier prepared undoped material the spin densities decrease from  $N_S{=}7{\times}10^{16}{\rm cm}^{-3}$  at SC=2% to  $1{\times}10^{16}{\rm cm}^{-3}$  at SC=5-6%. If  $N_S$  represents the majority of defect states, the necessary doping concentrations are in the range of a few (1, 5, 10) ppm which was obtained by admixture of phosphine to the process gas. All samples show clear doping effects in ESR and conductivity starting at the lowest doping level which supports the assumption that the spin density represents the major part of the defect density in  $\mu$ c-Si:H. The conductivity increases by several orders of magnitude at SC=6% i.e. the low  $N_S$  material, while the  $E_F$  shift is less pronounced for the SC=2% sample with its higher  $N_S$ . In ESR the characteristic CE resonance at g=1.998 is found in both the highly crystalline material and also in material where very little Raman intensity of crystalline structure is found (SC=6-7%) and where the undoped sample shows only the a-Si:H dangling bond signal at g=2.0055. Apparently also for crystalline grains strongly diluted in the amorphous matrix, a low level doping  $(10^{16} {\rm cm}^{-3})$  can shift  ${\rm E}_F$ into conduction band tail states of the crystalline phase and activate a stable CE resonance. This is in accordance with the earlier suggestion of a significant conduction band offset between the amorphous and crystalline regions in  $\mu$ c-Si:H.

> SESSION A21: POSTER SESSION TRANSPORT PROPERTIES OF MICROCRYSTALLINE SILICON Thursday Evening, April 4, 2002 8:00 PMSalon 1-7 (Marriott)

ANALYSIS OF POST-TRANSIT CURRENT-TIME DATA BY APPLICATION OF TIKHONOV REGULARISATION. M.J. Gueorguieva, C. Main and S. Reynolds, School of Science and Engineering, Univ. of Abertay Dundee, Dundee, UNITED KINGDOM.

In 1989 Seynhaeve et al [1] showed that in the post-transit regime of the time of flight experiment, the density of states at an energy E =kT ln (nu\*t) is approximately proportional to the product t\*I(t Subsequently, the present authors developed a method [2] capable of improved resolution based on the least-squares fitting of the post-transit data to an exact solution of the rate equations. However, this method is subject to a broadening of spectral features inherent in the fitting process. Here, we present a novel post-transit analysis, in which Tikhonov regularisation [3] is used to solve the Fredholm integral equation in the time domain. This approach obviates the need for Laplace transformation and is found to yield a highly accurate solution when applied to simulated post-transit or post-recombination I(t) data from discrete levels or distributions of states. The method is also shown to perform favourably in comparison with the above methods when applied to experimental data. [1] G.F. Seynhaeve, R.P. Barclay, G.J. Adriaenssens and J.M. Marshall, Phys. Rev. B 39, 10196 (1989). [2] C. Main, S. Reynolds, R.I. Badran and J.M. Marshall J. Appl. Phys. 88, 1190 (2000). [3] J. Weese, Computer Physics Communications 69, 99 (1992).

TRANSIENT PHOTOCURRENTS IN MICROCRYSTALLINE SILICON FILMS. Steve Reynolds, Vlad Smirnov, Charlie Main, School of Science and Engineering, Univ of Abertay Dundee, Dundee, UNITED KINGDOM; Reinhard Carius, Friedhelm Finger, Forschungzentrum Jülich, IPV, Jülich, GERMANY.

Transient photoconductivity in microcrystalline silicon thin films prepared by VHF PECVD over a range of [silane] : [silane + hydrogen] concentrations (3 - 6.3%) has been measured as a function of temperature (150 K - 380 K) and laser pulse density ( $10^{15}$  -  $10^{18}$ cm<sup>-3</sup>). Raman spectroscopy shows that all films are highly crystalline except at the highest silane concentration (6.3%) where a small contribution from the amorphous phase is observed. PDS and spin density measurements reveal a low subgap absorption and spin density  $(<5 \times 10^{16} \text{ cm}^{-3})$ , respectively, which is highest at low (3%)silane concentration and decreases at higher concentrations. The transient photodecays fall broadly into two categories which appear to reflect the above. At low silane concentrations there is a gradual fall in the photocurrent (typically  ${\bf t}^{-0.7}$ ), followed by a more rapid fall at times >1 ms (typically t<sup>-2</sup>). At higher concentrations the rapid fall is less pronounced. However, interpretation in terms of the density of states distribution is found not to be straightforward. The DOS profiles obtained for the same microcrystalline sample at different

temperatures cannot be brought into good agreement by varying the attempt to escape frequency over a realistic range. In contrast, for amorphous silicon a reasonable correspondence is obtained, at least separately over the tail or the defect states. Also, a fall in photocurrent at typically  $10^{-7}$  s of two to three orders is observed at high excitation density, whereas in amorphous silicon a similar but less pronounced feature appears at low excitation. These differences in behavior are discussed by taking into account the inhomogeneous microstructure of  $\mu$ c-Si:H.

### A21.3

TRANSIENT PHOTOCURRENT DECAY FROM THE STEADY STATE IN MICROCRYSTALLINE SILICON FROM PECVD AND HWCVD. Rudolf Brüggemann, Fachbereich Physik, Carl von Ossietzky Universität Oldenburg, Oldenburg, GERMANY; Steve Reynolds, School of Science and Engineering, University of Abertay Dundee, Dundee, SCOTLAND, UK; Charlie Main, School of Science and Engineering, University of Abertay Dundee, Dundee, SCOTLAND, UK.

We measured the time-dependent photocurrent decay from the steady state in microcrystalline silicon ( $\mu c$ -Si) from plasma-enhanced chemical vapor deposition and hot-wire chemical vapour deposition. Measurements were made over a wide range of steady-state photogeneration rates. We detail the variation with photogeneration rate of the decay time, at which the initial photocurrent has dropped to 50% or 1/e of its initial value. We studied samples exhibiting a range of photoconductive properties in terms of both the majority and minority carrier mobility-lifetime products. For our samples the shape of the transient photocurrent versus time shows power-law behavior with different power-law parameters. Interestingly, samples with a short steady-state photocarrier lifetime show a long decay time, together with a distinctly different power-law behavior when the decay time is plotted versus photogeneration rate. We relate the slow decay process to the much larger density of localized states in the band gap in the poor-quality samples. Trapped carriers are released, undergo emission and trapping processes and eventually recombine in these samples, on a much longer time-scale than in the high-quality samples. We also critically examine the estimation of drift mobilities from our decay experiments.

THE MEYER-NELDEL RULE IN CONDUCTIVITY OF MICROCRYSTALLINE SILICON. Sanjay K. Ram, Satyendra Kumar, Dept of Physics, Indian Institute of Technology, Kanpur, INDIA; P. Roca i Cabarrocas, LPICM, UMR 7647 - CNRS - Ecole Polytechnique, Palaiseau Cedex, FRANCE.

The dark conductivity  $(\sigma_d)$  has been measured from 300 to 440K on undoped hydrogenated microcrystalline silicon ( $\mu$ c-Si:H) films having different thicknesses. The  $\mu$ c-Si:H films were prepared by standard rf glow discharge plasma CVD technique using a mixture of SiF<sub>4</sub>, Ar and H<sub>2</sub> at 200°C. The carrier transport is found to be thermally activated with single activation energy in all the samples. The conductivity prefactor  $(\sigma_0)$  is found to depend on the activation energy  $(E_a)$  as  $\sigma_0 = \sigma_{00}$  exp  $GE_a$ . This behavior, known as Meyer-Neldel rule (MNR), is found to explain a variety of temperature activated phenomena in disordered materials. The MNR parameter G is reciprocal of the Meyer-Neldel characteristic energy often denoted as  $E_{MN}$ . This energy is a measure for the dependence of the temperature coefficient  $\gamma_f$  of the Fermi level position in the gap and  $\sigma_{00}$  is a constant. We calculated the value of  $E_{MN} \approx 55.6$  meV and  $\sigma_{00} \approx 0.02~\Omega^{-1} \cdot cm^{-1}$ . With an increase in film thickness, activation energy decreases. The inhomogeneity in the film growth as a function of thickness is revealed from the in-situ spectroscopic ellipsometry, Raman scattering and X-ray diffraction measurements. The activation energies can be explained if we consider the carrier transport in  $\mu$ c-Si:H as limited by grain boundaries (GB). In case of thicker samples, the material becomes relatively defect free with larger grains.  $\mathbf{E}_a$  represents the GB barrier height between the columnar crystallites. The height of the GB barrier decreases as the free carrier concentration in the columnar island increases. Thus change in Ea with the film thickness is directly related to the density of localized states at the Fermi level in GB. Therefore varying the film thickness and, hence, the exponential density of states induces a statistical shift of Fermi level which gives rise to the origin of observed MNR.

> SESSION A22: POSTER SESSION CRYSTALLIZATION Thursday Evening, April 4, 2002 8:00 PM Salon 1-7 (Marriott)

INFLUENCE OF THE BEAM IRRADIATION CONDITION WITH

OBLIQUE INCIDENCE ON CRYSTALLIZATION OF A SILICON FILM BY A LINEARLY POLARIZED PULSE LASER. Yasunori Nakata, Hirokazu Kaki and Susumu Horita, Japan Advanced Institute of Science and Technology, Ishikawa, JAPAN.

The periodic temperature distribution on a material surface irradiated by a linearly polarized laser beam is spontaneously generated without additional optical components and processes. By applying this phenomenon to melt-crystallization of Silicon(Si) film, we made the grain boundaries aligned in paralleled one another with the width of laser beam wavelength and obtained stripe large grains on a glass substrate. In order to enlarge the periodic width of strip crystallized grain, we increased the incident angle  $\theta_i$  to 25°, from which the periodic width is calculated to be 920 nm according to Rayleghs diffraction condition. In this meeting, we present the influence of beam irradiation condition with large  $\theta_i$  on crystallization of an Si film on a glass substrate. A 60-nm-thick amorphous Si film deposited on a Pyrex glass substrate at 350°C was irradiated by a Nd:YAG pulse laser beam at 220°C in the ultra high vacuum chamber. The wavelength, beam fluence, pulse number and incident angle of the laser beam were 532 nm, 0-225 mJ/cm², 1-100 and 25°, respectively. Although, at only 1 pulse, the grain boundaries are generated randomly, the periodic grain boundaries appear step by step increasing the pulse number. This tendency can be explained by a positive feed loop between the periodic modulated intensity of the laser beam and the periodic rough surface on the crystallized film. However, further increasing the pulse number, the periodic boundaries disappear gradually because the crystallized film is damaged and the film surface is too rough. Therefore, we have an optimum pulse number for controlling grain boundary. Also, this optimum number decreases with higher laser fluence because the period ic surface roughness is formed earlier with higher fluence. Furthermore, we found that the optimum pulse depends on the film thickness, which is complicated behavior. The details will be discussed in the meeting.

LOW TEMPERATURE LATERAL CRYSTALLIZATION OF AMORPHOUS SILICON ON GLASS. Leila Rezaee, Arash Akhavan, S. Shamsoddin Mohajerzadeh, Ebrahim Asl Soleimani, Thin Film Lab., Dept of Elect. & Comp. Eng, University of Tehran, Tehran, IRAN.

Low temperature lateral growth of amorphous silicon films has been achieved on thin flexible glasses using ultra-violet assisted metal-induced crystallization technique.  $125\mu m$  ordinary glass substrate is sputter-coated with a  $1500 \AA$  chromium and a  $1000 \AA$  SiN layer, respectively. 1000Å Si film was deposited using e-beam evaporation at a temperature of 350°C. A 50Å Ni film was e-beam deposited and patterned to form equally spaced circles with  $20\,\mu\mathrm{m}$ diameters. These circular nickel pads were used as seed of crystallization of a-Si layer. After silicide formation at  $350\,^{\circ}\mathrm{C}$ , the crystallization is accomplished in the presence of ultra-violet exposure with an intensity of 15mW/cm<sup>2</sup> measured at a wavelength of 360nm. The energetic UV photons impart energy to the silicon atoms, enhancing the chance of crystallization at reduced temperatures. This post-treatment step has been carried out at substrate temperatures ranging from 350°C to 450°C. Crystallinity of the samples was studied using XRD, SEM and TEM. Study of crystallization after various annealing times (from 16 to 70 hours) shows the gradual progress of lateral growth. The XRD spectra show clearly the emergence of  $\langle 111 \rangle$ ,  $\langle 110 \rangle$  and  $\langle 100 \rangle$  peaks of the silicon layer. Also two other peaks are discernible due to the chromium under-layer and nickel-silicide areas. Optical microscopy was used to monitor the lateral growth at different annealing times. For SEM study, samples have been developed in a crystallographic etchant (called as Sirtl) containing CrO<sub>3</sub> and HF with equal concentrations Based on SEM results, a lateral growth rate of  $2\mu$ m/hr is obtained at a temperature of 380°C. Also TEM confirms the polycrystallinity of the silicon film. The lateral growth has been exploited in making thin film transistors. P-type TFT's have been successfully fabricated showing a hole mobility of 50 cm<sup>2</sup>/Vs.The effect of accumulated strain in the crystallized region is studied. Also growth of Si-Ge alloys is being investigated.

POLYCRYSTALLINE Si FILMS ON Mo COATED GLASS GROWN BY PULSED DC MAGNETRON SPUTTERING. M. Nerding, S. Christiansen, Institute of Microcharacterization, Univ. Erlangen, GERMANY; P. Reinig, F. Fenske, W. Fuhs, Hahn-Meitner-Institute, GERMANY; H.P. Strunk, Institute of Microcharacterization, Univ. Erlangen, GERMANY.

Using transmission electron microscopy (TEM) we analyze undoped, polycrystalline Si films grown by pulsed dc magnetron sputtering at high deposition rates (r = 86 nm/min). A comparison between the growth development on glass and Mo coated glass substrates by cross-sectional and plane-view TEM analysis reveals significant

differences in the film microstructure. Growth on Mo coated glass results in direct formation of a polycrystalline seeding layer. After initial vertical overgrowth of most grains in the incubation layer, growth proceeds columnar. In this columnar growth region, the grains have lateral sizes of up to 300 nm. In contrast, growth on glass results in a typical initial amorphous layer with subsequent cone-shaped growth of crystalline grains, which is well known from low-temperature CVD deposition techniques. As soon as neighbouring grains impinge, columnar growth starts. The grains show heavy intra-grain twinning. According to XRD analysis (and confirmed by TEM) the structural differences correspond to differences in the surface normal of the grains. The films deposited on glass show a predominant (110) surface normal orientation, whereas films deposited on Mo coated glass show a preferential (001) surface normal orientation.

#### A22.4

SINGLE-CRYSTAL SI FORMED ON AMORPHOUS SUBSTRATE AT LOW TEMPERATURE BY LITHOGRAPHY-CONSTRAINED SINGLE SEEDING IN NICKEL INDUCED LATERAL CRYSTAL-LIZATION. Jian Gu, Stephen Y. Chou, Princeton Univ, Dept of Electrical Engineering, Princeton, NJ; Nan Yao, Henny Zandbergen, Princeton University, Princeton Materials Institute, Princeton, NJ; Jeffrey K. Farrer, TSL/EDAX, Draper, UT.

Amorphous silicon film on silicon dioxide substrate was patterned into nanoscale lines, and then crystallized by nickel-induced lateral crystallization (Ni-ILC). Single-crystal silicon has been achieved in all the lines with a width of 50 nm to 200 nm. Transmission electron microscope (TEM) study shows that line width affects the silicon grain formation significantly. For lines with a width above 250 nm, single-crystal silicon can still form. However, competitive grain growth (CGG) could happen at the beginning of the lateral crystallization. For a 3- $\mu$ m-wide line, polycrystalline silicon formed with a longitudinal grain structure. In situ TEM observation has been used to study the crystallization process. Lithography-constrained single seeding (LICSS) is proposed to explain the single-crystal silicon formation.

# <u>A22.</u>5

NUMERICAL ANALYSIS FOR LATERAL GRAIN GROWTH OF POLY-SI THIN FILMS CONTROLLED BY LASER-INDUCED PERIODIC THERMAL DISTRIBUTION. <u>Hirokazu Kaki</u>, Yasunori Nakata and Susumu Horita, Japan Advanced Institute of Science and Technology, Ishikawa, JAPAN.

The pulse laser annealing (PLA) method is effective to produce the polycrystalline silicon (poly-Si) films with the high carrier mobility on a glass substrate. In order to obtain the large grain and to control the location of grain boundary, it is necessary to make the temperature distribution in the melted Si film to be suitable for grain growth. Then, we proposed to use periodic thermal distribution spontaneously induced by a linearly polarized laser beam. This period spacing is formulated by Rayleigh fs diffraction condition. In fact, by using a linearly polarized laser beam, we obtained a grain as large as the wave length of the laser beam. So, in this meeting, by using numerical analysis, we show the lateral grain growth of poly-Si film from molten Si whose temperature distribution is sinusoidaly periodic. The crystallization process was analyzed by two-dimensional finite element computer simulations of the heat transport and the phase transitions during laser crystallization. The typical irradiation conditions are as follows: The poly-Si film thickness was 60 nm, the substrate temperature was 500 K and the laser fluence was 200  $\mathrm{mJ/cm^2}$ . From this numerical analysis, we found following results. Even if the pulse width is increased up to 20ns, the temperature distribution at surface hardly changes. The amplitude of periodic temperature distribution induced by laser beam with the wave length of 308 nm is larger than that with 532 nm because the absorption coefficient of 308nm is much larger than that of 532 nm. However, the crystalline quality of Si film crystallized by 308 nm is poor since its laser energy penetration depth is small. In the meeting, we will show the other analysis results of dependence of lateral grain growth on the poly-Si film thickness, the laser fluence, the substrate temperature, and so on.

### A22.6

MICROSTRUCTURAL EVOLUTION OF NICKEL INDUCED CRYSTALLIZATION OF AMORPHOUS SILICON. Kyu Ho Park, Young Woo Jeong, Hyun Ja Kwon, Jeong Soo Lee, LG Electronics Institute of Technology, Materials Characterization Lab., Seoul, KOREA; Binn Kim, Hae Yeol Kim, Hyun Sik Seo, LG Philips LCD Research Center, Process Technology Gr., Anyang, KOREA.

The Ni silicide-mediated phase transformation of amorphous to crystalline silicon(c-Si) was investigated using transmission electron microscopy. Amorphous silicon(a-Si) films coated with very thin Ni layers ( $\sim 10^{-1}$  Å) were annealed at various temperatures. Randomly oriented NiSi<sub>2</sub> precipitates were observed in Ni deposited amorphous

silicon (a-Si) film annealed at 420°C. The nucleation of the epitaxial crystalline silicon has occurred on the  $\{111\}$  faces of the octahedral NiSi2 precipitate at  $430^{\circ}$ C. The octahedral shape of NiSi2 precipitate was distorted just after the Si nucleation. From the selected area diffraction patterns and bright field images, it was revealed that the growth rate of c-Si on the center of {111} NiSi2 faces was faster than that on the edges of NiSi<sub>2</sub> {111}. Further annealing induces the migration of NiSi2 precipitates through the a-Si matrix leaving a trail of c-Si. It was found that the c-Si had a fan-like shape at the initial growth stage. During the growth of the c-Si fan at higher temperatures, the thin NiSi<sub>2</sub> precipitate in the leading edge of c-Si happened to meet a stationary NiSi2 precipitate in a-Si. It was found that the collision between those two precipitates splitted one c-Si fan into two. The more collisions of a migrating precipitate with stationary precipitates in the a-Si changed the fan shape of c-Si into c-Si needles. The collisions also led to the growth of additional needles on the sides of two initial needle along the variants of the < 111 > direction. The migration of the NiSi2 precipitates and the subsequent growth of Si needles throughout the a-Si film resulted in the crystallization of the entire a-Si layer.

#### A22.7

MICROSAMPLE X-RAY ANALYSIS FOR QUANTIFICATION OF Ni AT THE PPB LEVEL ON AMORPHOUS SILICON. Hyun Ja Kwon, Kyu Ho Park, Jeong Soo Lee, LG Electronics Institute of Technology, Materials Characterization Lab., Seoul, KOREA; Binn Kim, LG Philips LCD Research Center, Process Technology Gr., Anyang, KOREA.

Nickel induced crystallization of amorphous Si (a-Si) has been used to lower the annealing temperature for the cost-effective manufacturing of low-temperature poly-silicon TFTs. Recently, it has been reported that electric field enhances Si crystallization even with the infinitesimal amount of Ni addition. In order to use this process for large area display applications, it is important to precisely determine the concentration and uniformity of Ni at the ppb level. Microsample X-ray analysis (MXA) based on X-ray fluorescence (XRF) is an alternative method to characterize the concentration of metal at the ppb level because of its high peak-to-background ratio. Since the MXA is also a rapid and economical tool, it is very useful for the quantification of various metal contaminants on Si. However, the MXA method has a limitation; the metals should be able to be dissolved by suitable etching solutions for microsampling. We surveyed the etching solution in order to quantify the concentration of Ni on a-Si using the MXA method. The concentration and uniformity of Ni deposited on large area a-Si films were investigated as a function of sputtering power. Among the various candidates for Ni etching, the HF:H2O2 solution showed the best result and its dissolution efficiency was estimated to be over 98%. The MXA indicated that the concentration of Ni deposited on a-Si films varied from  $3.9\times10^{13}$  to  $2.0\times10^{14}$  atoms/cm² with sputtering conditions. The MXA data were compared with those measured by TOF-SIMS. The Ni atoms were distributed on  $35\,\mathrm{cm} \times 30\,\mathrm{cm}$  a-Si films with the uniformity of  $3{\sim}5\%$ from the considerations of instrument and method precisions of the MXA measurement.

### A22.8

HIGH PRECISION PHYSICAL MODEL FOR NICKEL MILC. C.F. Cheng, W.M. Cheung, M.C. Poon, M. Chan, Hong Kong Univ of Science and Technology, Dept of Electrical and Electronic Engineering, HONG KONG.

Recently, Nickel (Ni) Metal-Induced-Lateral-Crystallization (MILC) has been studied as a high potential method to form large grain poly-silicon (poly-Si) film and high quality TFT. In this paper, a high precision and robust physically-based model is proposed. The model incorporates the initial Ni content, MILC annealing temperature and time, Ni diffusion and segregation, Ni traps, and other effects/parameters. The model has been used to generate different simulated Ni profiles in the MILC poly-Si. The simulated results are in good match with the experimental SIMS Ni profiles and MILC poly-Si regions under different MILC process conditions. Furthermore, the effects of the nickel profile on the MILC poly-Si formation, growth rate and grain size can also be predicted.

# A22.9

ATERAL DIFFUSION OF BORON IONS IMPLANTED IN THE AMORPHOUS SI FILM DURING EXCIMER LASER IRRADI-ATION. Min-Cheol Lee, Soo-Jeong Park, Kook-Cheol Moon and Min-Koo Han.

Dopant diffusion by thermal heating in MOSFET has been widely investigated and diffusion constant of dopant ions in solid-state material are widely known. Recently, the excimer laser is widely used to fabricate polycrystalline silicon TFT. In the TFT fabrication based on amorphous Si film, dopants may be diffused vertically and laterally by excimer laser irradiation, however, the lateral diffusion distance

during laser irradiation with various laser energy densities has not been investigated yet. The purpose of this work is to investigate the lateral diffusion of boron ions implanted in the amorphous silicon film during XeCl (l = 308nm) excimer laser irradiation. We employed a selective chemical etching employing HF/HNO3 solutions in order to delineate doping concentration. The boron ions (5  $\times$  10  $^{15})$  were selectively implanted on the PECVD a-Si film deposited on oxidized Si wafer and the excimer laser irradiation with various laser energy densities was followed. During the laser irradiation, boron ions may diffuse as long as Si film remains in the liquid phase. In our experiment, we delineated the boron concentration of  $5 \times 10^{18}/\text{cm}^3$ using chemical etching and observed it using SEM. In the low laser energy density (~200 mJ/cm<sup>2</sup>), the boron diffusion distance was less than 1000 Å when the laser pulse duration was 30 ns. The remained Si patterns of which boron concentration is less than  $5 \times 10^{18}$  were shrunk about  $1000\,\text{Å}$  at the both sides of pattern. However, in the laser energy density of  $300\,\text{mJ/cm}^2$ , remained Si patterns were widen compared with the implantation mask width, which indicates that the high density implanted boron ions were rapidly diffused into undoped Si region during laser irradiation so that the density of ion at the edge of implanted region was less than with  $55 \times 10^{18}$ 

METAL-FREE GERMANUIM-INDUCED CRYSTALLIZATION OF AMORPHOUS-Si ON GLASS. Arash Akhavan, Leila Rezaee, Jaber Derakhshandeh, Shamsoddin Mohajerzadeh and E. Asl. Soleimani, Thin Film Lab., Dep. of Elect. & Comp. Eng, University of Tehran, Tehran, IRAN.

Achievement of a-Si crystallization with the aids of Ge seed at temperatures less than 480°C in the presence of ultra-violet light on thin glasses is reported. A 1000 Å chromium layer sputter deposited on a  $125\mu$ m ordinary glass substrate and coated with  $500 \text{\AA}$  SiN layer, deposited by RF-sputtering. Then  $1000\mbox{\normalfont\AA}$  Si and  $40\mbox{\normalfont\AA}$  Ge layers are consecutively deposited by e-beam evaporation at 400°C. The crystallization process accomplished on a hot plate at temperatures ranging from 430 to 480°C while exposed to UV light with  $25\,\mathrm{mW/cm^2}$  at a wavelength of  $360\,\mathrm{nm}$ . We believe the energetic UV photons decrease the activation energy of process, consequently lowering the temperature of crystallization. The samples' crystallinity with annealing times extended from 3 to 24 hours was investigated using XRD and SEM analyses. Preliminary study shows < 110 > Si peak in XRD spectra. The < 111 > orientation is not quite discernible in the XRD results, which could be due the orientation preference occurred during crystallization. This event needs more thorough investigation. To study the lateral crystallization. Ge was patterned. forming  $20\mu\mathrm{m}$  diameter circles with  $140\mu\mathrm{m}$  spacing. Two crystallographic etchants as Sirtl (CrO  $_3,~\mathrm{HF}$  and  $\breve{\mathrm{H}}_2\mathrm{O})$  and Secco (K2Cr2O7 and HF in water) solutions were used. Exposure the sample to these etchants leads to the formation of surface features as observed using SEM, further indicating the crystallization. A value of  $0.8\mu\mathrm{m/hr}$ is extracted for the lateral growth. Also during crystallization, the conductivity of the sample increases by a factor of 70, reflecting the improvement in the carrier mobility. We speculate that the germanium seed imposes considerable strain on the neighboring silicon atom, enhancing the chance of lateral crystallization at reduced temperatures. Using this technique, one is able to avoid metal contamination, a deleterious effect observed in MIC techniques. Further study of this technique to make Si TFT's is in progress.

ON MECHANISM OF NICKEL DIFFUSION DURING METAL INDUCED LATERAL CRYSTALLIZATION OF AMORPHOUS SILICON. A.M. Myasnikov, Inst of Semiconductors Physics Novosibirsk, RUSSIA; M.C. Poon, P.C. Chan, W.Y. Chan, M.S. Chan, S. Singla, C.Y. Yuen Hong Kong Univ of Science and Technology, Dept. of Elec, HONG KONG.

During metal induced lateral crystallization (MILC) of amorphous silicon (a-Si) the size and quality of obtained film depend on nickel penetration and it is very important to know about nickel diffusion at recrystallization process. For this purpose the samples have been studied, having layers of a-Si with thickness 1000 - 3000  $\mathring{A}$  on oxidized silicon substrate. Nickel islands with thickness from 50 Å to 1000 Å were used as seeds. Temperature, T, and time, t, of recrystallization were varied from 500°C to 640°C and from minutes to 100 hours. The sizes of MILC regions, L, were in the range from some microns to 200  $\mu$ m. Diffusion coefficient for different temperatures was defined by a ration of  $L^2/t$ . It was shown, that diffusion coefficient at MILC should be approximated by equation  $D_0 \times e^{(-\Delta E/kt)}$ , where  $D_0 = 4 \times 10^5$  $cm^2/s$ ,  $\Delta E = 2.45$  eV, k- Boltzmann's constant, T - temperature in K. It was found that all values of diffusion coefficient for different temperatures of MILC are upto 5 orders less than the diffusion coefficient in single crystal silicon. And at the same time the diffusion coefficient at MILC is two orders higher than the diffusion coefficient in a-Si. A comparison of diffusion coefficients in single crystal silicon  $(2\times10^{-3}\times e^{-0.47})$ , on surface of single crystal silicon

 $(2.4x10^{-3}xe^{-3.2})$ , in a-Si  $(2.9\times10^{-3}\times e^{-1.3})$ , with a value obtained by us is allowed to make a conclusion that in the temperature range from 500°C to 640°C the mechanism of nickel diffusion has intermediate character. During annealing the nickel has penetrated on surface of a-Si inducing the recrystallization process, which has changed the mechanism of diffusion on surface of a-Si to the mechanism of diffusion on surface of single crystal silicon and in single crystal silicon. Also the effect of thickness of nickel and a-Si film are discussed.

> SESSION A23: POSTER SESSION HOT-WIRE CVD Thursday Evening, April 4, 2002 8:00 PM Salon 1-7 (Marriott)

PROTON NMR HOLE-BURNING IN HOT WIRE a-Si:H. J. Herberg, P.A. Fedders, D.J. Leopold, R.E. Norberg, Department of Physics, Washington University, St. Louis, MO; R.E. Schropp, Debye Institute, Utrecht University, Utrecht, THE NETHERLANDS.

Proton NMR near 200 MHz has been used to examine the dynamics  $\,$ of hole-burning in a HW a-Si:H film deposited from  $SiH_4$ . Radiofrequency hole-burning is a tool to distinguish inhomogeneous broadening from homogeneous broadening. The 3 kHz FWHM resonance line from T-site-trapped  $H_2$  molecules shows a hole burn behavior similar to that found for PECVD a-Si:H films, as does the 24 kHz FWHM line from clustered silicon-bonded hydrogens. However the ~80 kHz FWHM superbroad line varies with tip angle uniformly across the line for hole burns applied at any location within  $\pm 50~\mathrm{kHz}$ from the resonance center. The superbroad line is homogeneously broadened and thus apparently arises from four-fold super-close SiH clusters with inter-proton distances considerably less than 2 Å. The spin lattice relaxation times for all three components are similar.

HOT-WIRE CHEMICAL VAPOR DEPOSITION FOR EPITAXIAL SILICON GROWTH ON LARGE-GRAINED POLYCRYSTALLINE SILICON TEMPLATES. Maribeth Swiatek, Claudine Chen, and Harry Atwater, Thomas J. Watson Laboratory of Applied Physics, California Institute of Technology, Pasadena, CA.

We investigate the low-temperature (<600°C) epitaxial growth of thin silicon films by hot-wire chemical vapor deposition (HWCVD) on polycrystalline silicon template layers formed by selective nucleation and solid phase epitaxy (SNSPE). Previously, we showed that direct deposition by HWCVD on SiO<sub>2</sub> produced small grains (~40-80 nm) even with the addition of H<sub>2</sub> to a diluted silane mixture (1% in He) [1]. SNSPE layers formed by the use of nickel nanoparticles as nucleatiion sites for the solid-phase crystallization of phosphorusdoped amorphous silicon on SiO2 display grain sizes on the order of  $100 \mu m$ , and have been successfully used as seed layers for epitaxial growth by molecular beam epitaxy at 600°C [2,3]. HWCVD has recently been shown to be a promising method for fast, low-temperature epitaxy [4]. We will discuss the microstructural and electrical properties of epitaxial films grown on the template layers and discuss their suitability for thin-film photovoltaics applications. [1] M. Swiatek, J.K. Holt, D.G. Goodwin and H.A. Atwater, Mat. Res. Soc. Symp. Proc. 609, 2000.

[2] C.M. Chen, Ph.D. thesis, California Institute of Technology, 2001. [3] R.A. Puglisi, H. Tanabe, C.M. Chen and H.A. Atwater, Mat. Sci. Eng. B 73, 2000.

[4] J. Thiesen, E. Iwaniczko, K.M. Jones, A.H. Mahan, and R. Crandall, Appl. Phys. Lett. 75, 1999.

THE EFFECT OF AGING ON TUNGSTEN FILAMENT SURFACE KINETICS IN HOT-WIRE CHEMICAL VAPOR DEPOSITION OF SILICON. J.K. Holt, M. Swiatek, D.G. Goodwin, and Harry A. Atwater, Thomas J. Watson Laboratories of Applied Physics, California Institute of Technology, Pasadena, CA.

The process of filament aging during prolonged exposure to silane is well documented in the Hot-Wire Chemical Vapor Deposition (HWCVD) literature. This aging may take the form of a silicon-tungsten alloy (WSi<sub>2</sub>, W<sub>5</sub>Si<sub>3</sub>) as well as free silicon deposition. It has been previously demonstrated [1] that filament alloying has deleterious effects on film deposition rate and electronic properties (SSPG diffusion length), and the underlying cause has been speculated as the difference in radical chemistry between alloyed and new filaments. We have observed profound differences in radical desorption kinetics and wire surface morphology and composition upon filament aging. In particular, the aged filaments exhibit radical desorption activation energies between 80-120 kcal/mole (3.5-5.2 eV), as compared with the low activation energy of 8 kcal/mole (0.4 eV) observed for SiH<sub>3</sub> desorption from a new filament. The activation

energies determined with the aged filament are characteristic of the bond breaking energies of the particular species, and thus suggest that the aging process has reduced, if not eliminated, the catalytic effect of the filament. At the wire temperatures commonly used for film growth (>1800°C), Si is the predominant species desorbing from both new and aged filaments. The primary difference in radical chemistry between new and aged filaments lies in the transition temperature above which Si becomes the predominant desorbed species. For a new filament, this transition temperature is ~1200°C (below which SiH<sub>3</sub> becomes significant), while for an aged filament, the temperature is much higher at  $\sim 1700$  °C (below which both SiH and SiH<sub>2</sub> become important). It has been determined that silicon diffusion into the wire occurs to an appreciable extent, with a measurable Si radical signal observed in a silane-free ambient. Auger Electron Spectroscopy was performed on aged filaments, revealing a Si content of up to 2% at a depth of  $50\mu m$ , also suggesting that diffusion of Si into the filament occurs. Surface Si concentrations ranged from 12-15% Si, suggesting a two-phase equilibrium between a silicide (W5Si3) and W at a silicon solubility of 4%. Finally, the surface morphology of various filaments was characterized via Scanning Electron Microscopy. Heat-treated filaments exhibit a smooth surface morphology as compared with the striations evident in new filaments. Upon the introduction of SiH4, however, the filaments develop a rough, irregular surface morphology, consistent with the buildup of Si at the surface. This buildup would be expected to lower the growth rate, due to a reduction in the effective catalyzer surface area. These observations are consistent with previous filament surface characterization by Mahan et al. [1]. [1] A.H. Mahan, A. Mason, B.P. Nelson, and A.C. Gallagher, Mat. Res. Soc. Symp. Proc., Vol. 609, Spring MRS Meeting 2000.

#### A23.4

EFFECT OF FILAMENT MATERIALS ON THE HOT WIRE CVD OF AMORPHOUS SILICON. <u>H.L. Duan</u>, Gillian A. Zaharias, Stacey F. Bent, Stanford University, Dept of Chemical Engineering, California, CA.

Filament material plays a critical role in hot wire CVD of amorphous and microcrystalline silicon films. In this study, vacuum ultraviolet laser single photon ionization (SPI) spectroscopy is utilized to probe the gas phase free radicals produced from silane decomposition by different filament materials, including W, Ta, Re and Mo. In addition, corresponding film depositions are detected in situ by multiple internal reflection infrared spectroscopy. Radical profiles as a function of wire temperature show differences in Si production for different filament materials. The concentrations of Si increase at different rates from W, Ta and Mo before leveling off at high temperature for all three metals. However, the Si profile from Re shows similar behavior to W. The apparent activation energies of Si from Ta and Mo are found to be higher than those of W and Re. IR measurements are used to estimate the growth rate of a-Si:H deposited on a Ge substrate. The results indicate that the growth rate deviates from the Si profile, suggesting other radicals such as hydrogen also play a role in the growth. The role of the filament material in determining the radical generations and growth rates will be discussed.

### A23.5

GAS PHASE CHEMISTRY STUDY DURING DEPOSITION OF AMORPHOUS AND MICROCRYSTALLINE SILICON FILMS BY HWCVD USING QUADRUPOLE MASS SPECTROMETRY. Samadhan B. Patil, Alka A. Kumbhar, R.O. Dusane, Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology, Bombay, Powai, Mumbai, INDIA.

a-Si:H and  $\mu c$ -Si:H films were deposited by HWCVD for various parameters and the gas phase chemistry was studied by Quadrupole Mass Spectrometry during deposition. Structural properties of deposited films were correlated with gas phase chemistry during deposition. Interestingly, unlike in PECVD, partial pressure of H2 was higher than any other species during deposition of a-Si:H as well as μc-Si:H. Effect of hydrogen dilution was studied on film properties and on concentration of individual species in gas phase. For low hydrogen dilution (H2 flow rate/SiH4 flow rate) from 0 to 1 (where SiH<sub>4</sub> flow is 10 sccm), all films deposited are perfectly amorphous with photoconductivity gain of  $\sim 10^6$ . During deposition of these amorphous films SiH<sub>2</sub> was dominant in gas phase after H<sub>2</sub>. Important observation noted was [Si]/[SiH2] ratio increases from 0.4 to 0.5 with dilution varied from 0 to 1. This fact projected that [Si]/[SiH<sub>2</sub>] ratio can increase further to its value more than 1 with higher hydrogen dilution leading to [Si] dominance. This was confirmed during deposition of  $\mu c$ -Si:H films, deposited at high hydrogen dilution with dilution ratio 20. As expected atomic Si was dominating in gas phase during deposition of  $\mu$ c-Si:H films with [Si]/[SiH<sub>2</sub>] value above 2. Role of hydrogen mediation was clearly seen for films deposited with and without hydrogen dilution, for 1 sccm silane flow at low filament temperature ~1600°C. Films deposited without hydrogen dilution show less microcrystalline fraction with SiH2 dominance in gas phase whereas films deposited with hydrogen dilution show higher

microcrystalline fraction with atomic Si dominating in gas phase. This shows that hydrogen fraction in gas ambient is crucial parameter to decide chemistry in HWCVD, finally deciding growth of amorphous or microcrystalline films.

# SESSION A24: POSTER SESSION ALLOYS OF SILICON WITH CARBON OR GERMANIUM

Thursday Evening, April 4, 2002 8:00 PM Salon 1-7 (Marriott)

#### A24.1

ELECTRONIC TRANSPORT STUDY OF a-SiC:H BY THE MICROWAVE PHOTOMIXING TECHNIQUE. M. Boshta<sup>a</sup>, R. Braunstein<sup>a</sup>, and G. Ganguly<sup>b</sup>; <sup>a</sup> Department of Physics and Astronomy, University of California, Los Angeles, CA; <sup>b</sup>BP Solar, Toano, VA.

The electronic transport properties of a-SiC:H alloys across the range of C content (0-40%) prepared by DC-Plasma Enhanced Chemical Vapor Deposition technique (PECVD) have been investigated in detail by employing the microwave photo-mixing technique. Strong evidence for the existence of long-range potential fluctuations in a-SiC:H alloys has been found from the measurements of electric field dependence of the drift mobility. Through the drift mobility field dependence, the depth and range of the potential fluctuations as a function of alloy composition are determined, and subsequently the charged defect density. It was observed that the film transport properties degrade with increasing C content, where the strongest potential fluctuations occur as a result of a significant increase in the charged defect density. It is the potential fluctuations whose effect are enhanced by adding C to the alloy system that result in deterioration of the transport properties of a-SiC:H alloys.

#### A24.2

IN-SITU N-TYPE DOPING OF CLOSE TO STOICHIMETRY a-SiC:H FILMS OBTAINED BY PECVD. Marcelo N.P. Carreno, Alessandro R. Oliveira and Ines Pereyra, Departamento de Engenharia de Sistemas Eletronicos, Escola Politecnica, Universidade de Sao Paulo, BRAZIL.

Hydrogenated amorphous silicon carbon alloys (a-SiC:H) grown by plasma enhanced chemical vapor deposition (PECVD) have been widely investigated for a variety of electronic devices, mainly as window layer in solar cells, as insulator layer in thin film transistors and as an active layer in light emitting diodes. These investigations have always explored the possibility of tuning the materials optical gap. Aiming to improve the properties of those films, we have studied the conditions to obtain close to stoichiometry samples of  $\text{a-Si}_{1-x}\mathbf{C}_x\text{:H}$  (x 0.5) having a chemical and structural order similar to that of c-SiC. We have also studied n-type and p-type electrical doping of these stoichiometric films through impurity ion implantation. The stoichiometric a-SiC:H films were deposited at  $350\,^{\circ}\mathrm{C}$  in a conventional capacitively coupled PECVD system from appropriated mixtures of methane, silane and hydrogen. In this work we explore in-situ n-type doping utilizing nitrogen as a doping gas. We investigated the effect of adding different concentrations of nitrogen to the gas mixture, with and without hydrogen dilution, on the electrical, structural and optical properties of the a-SiC:H films. Our previous results indicated that the N concentration is critical, becoming difficult to maintain the nitrogen incorporation at doping levels. Still, the results indicate a considerable improvement of the doping efficiency in samples grown with H2 dilution.

### A24.3

LARGE-AREA PULSED LASER DEPOSITION OF SILICON CARBIDE FILMS. Dongfang Yang, Lijue Xue, Integrated Manufacturing Technologies Institute, National Research Council of Canada, London, Ontario, CANADA; Claire M. Mccague, Peter R. Norton, Department of Chemistry, University of Western Ontario, London, Ontario, CANADA.

Silicon carbide thin films are attractive for a wide range of applications ranging from microelectronic and opto-electronic devices to protective and tribological coatings. In this paper, we will demonstrate that silicon carbide films can be successfully deposited by pulsed laser deposition (PLD) technique over large areas, with good uniformity in thickness, composition, and functional properties. Silicon carbide films were grown on silicon wafers of 75-mm diameter using a KrF excimer laser at a wavelength of 248 nm and a repetition rate of 100 Hz. The laser beam was focused onto a 90-mm diameter SiC target to induce its ablation in vacuum. The large-area coverage was obtained by rastering the laser beam over the radius of the rotating target, while the substrate was rotated simultaneously. The

uniformity of film composition over the 75-mm wafers was characterized by Auger Electron Spectroscopy (AES), while the crystallinity of films was investigated by X-ray Diffraction (XRD). The morphology and particulate contamination of the films were examined using Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The thickness of the coatings along the wafer radii was evaluated optically using a spectrophotometer. The index of refraction (n) and the extinction coefficient (k) of the silicon carbide films were measured by the spectrophotometer in the wavelength region of 220 - 860 nm. The morphology, structure, composition, as well as mechanical properties of the coatings were also investigated as functions of the substrate temperatures.

#### A24.4

NOVEL CARBON SOURCE (1,3-DISILABUTANE) FOR THE DEPOSITION OF P-TYPE a-SiC. Shuhei Yagi, Katsuya Abe, Takashi Okabayashi, Akira Yamada, Makoto Konagai, Tokyo Institute of Technology, Dept of Physical Electronics, Tokyo, JAPAN.

In this paper, we proposed a new carbon source, 1,3-disilabutane (H<sub>3</sub>SiCH<sub>2</sub>SiH<sub>2</sub>CH<sub>3</sub>:1,3-DSB), to grow hydrogenated amorphous silicon carbide (a-SiC:H) films by mercury-sensitized photochemical vapor deposition (photo-CVD) and plasma-CVD. The 1,3-DSB contains two silicon and two carbon which form a Si-C-Si-C skeleton. Thus, we are expecting that the carbon can easily occupy the substitutional site and that the carbon cluster can be hardly formed in the films, resulting in the improvement of film quality. For both methods, the a-SiC:H films were deposited on Corning 7059 glass substrates using a gas mixture of silane, hydrogen and 1,3-DSB. The 1,3-DSB, which is liquid under atmospheric pressure at room temperature, was reserved in a cylinder and introduced into the reaction chamber with a hydrogen carrier gas. The total gas pressure and the substrate temperature were maintained at 0.5 Torr and 200°C, respectively. As a primary experience, we fabricated undoped a-SiC:H. The optical band gap  $E_g$  was changed from 2.2 eV to 2.9 eV by controlling a flow rate ratio of silane/1,3-DSB. The highest  ${\rm E}_g$  of 2.9 eV was obtained by plasma-CVD with a 1,3-DSB flow rate of 2 sccm and a hydrogen flow rate of 20 sccm.  $E_g$  decreased with increasing the silane/1,3-DSB ratio from 0 to 5. The undoped a-SiC:H showed a darkconductivity of  $5 \times 10^{-8} \text{ Scm}^{-1}$  and we tried the p-type doping using a diborane gas by photo-CVD. The darkconductivity of  $8\times10^{-8}~{\rm S\,cm}^{-1}$  was obtained at the E $_g$  of 2.2 eV with a diborane/(silane 1,3-DSB) ratio of 0.042%.

#### A24.5

CHARACTERIZATION OF a-SiC<sub>x</sub>:H FILMS FOR c-Si SURFACE PASSIVATION. <u>M. Vetter</u>, I. Martin, A. Orpella, C. Voz, J. Puigdollers and R. Alcubilla, Departament d'Enginyeria Electrónica. Universitat Politécnica de Catalunya, Barcelona, SPAIN.

Amorphous intrinsic silicon carbide (a-SiC<sub>x</sub>:H(i)) films and amorphous phophorous doped silicon carbide  $(a-SiC_x:H(n))$  films deposited by plasma enhanced chemical vapor deposition (PECVD) from silane/methane mixtures have been shown to provide excellent electronic passivation of p-type c-Si [1, 2, 3]. Effective surface recombination velocities  $(S_{eff})$  lower than  $23 \text{ cm s}^{-1}$  have been reported for a-SiC<sub>x</sub>:H(i) films and S<sub>eff</sub> < 11 cm s<sup>-1</sup> for a-SiC<sub>x</sub>:H(n) films deposited on 3  $\omega$  cm p-type c-Si. From the analysis of the injection level dependency of  $S_{eff}$  determined by the quasi-steady-state photoconductance method [4] results that the good electronic passivation is due to field-effect passivation created by a strong band bending at the c-Si surface. We have extended this study by investigating the passivation properties of these films deposited on n-type c-Si e.g. resulting in  $S_{eff} < 40~{\rm cm~s}^{-1}$  for a-SiC<sub>x</sub>:H(i) films deposited on 2  $\omega$  cm n-type Si. To further characterize these films, in this work we will report on structural, compositional and electrical properties of the a-SiC  $_x$ :H films based on optical and I.R. spectroscopy and the dependency of conductivity on temperature. [1] I. Martín, M. Vetter, A. Orpella, J. Puigdollers, A. Cuevas, R. Alcubilla, Appl. Phys. Lett. 79, 2199 (2001). [2] I. Martín, M. Vetter, A. Orpella, J. Puigdollers, C. Voz, L.F. Marsal, J. Pallarés, R. Alcubilla, Thin Solid Films to be published. [3] I. Martín, M. Vetter, A. Orpella, C. Voz, J. Puigdollers and R. Alcubilla, presented at the 17th Europ. Photovoltaic Solar Energy Conf., Munich, Oct. 2001. [4] A. Cuevas, M. Stocks, D. Macdonald, R. Sinton, Proc. 2nd World Conf. Exh. Photovoltaic Solar Energy Conv. (Viena) 1998, p. 1236.

### A24.6

ROLE OF THE MAGNETIC FIELD ON LARGE-AREA CARBON FILM GROWTH ON SILICON IN A HOLLOW-ANODE ARC PLASMA PROCESS. R. Hyde, P. Mukherjee, and S. Witanachchi, Laboratory for Advanced Materials Science and Technology (LAMSAT), Department of Physics, University of South Florida, Tampa, FL.

This paper presents results on a novel growth process for the deposition of carbon and diamond-like carbon films on Si as a

precursor to the deposition of diamond coatings on Si for tribological and MEMS applications. Sources of metallic ions play an important role in the fabrication of coatings with high density, enhanced adhesion and crystallinity. We have developed a pulsed hollow-anode plasma process that generates a highly ionized plume of cathode material. A low-pressure ambient gas, such as argon, assists the removal of material from the cathode via sputtering. Carbon plasmas generated in this process by using carbon electrodes are ideally suited for the growth of diamond and diamond-like carbon films. The hollow-anode plasma system consists of a cylindrical carbon anode and a solid carbon rod as the cathode placed concentrically inside the hollow-anode. A pulse-forming network that produces an 80J electrical pulse of 5 ms duration is connected across the electrodes Argon gas is flown through the hollow electrode to maintain an ambient pressure of 15-30 mT. A CO<sub>2</sub> laser pulse focused on the cathode triggered the discharge to generate a particulate-free highly ionized transient carbon plasma plume. Application of an axial magnetic field within the hollow-anode guides the carbon ions out of the hollow electrode and accelerates them towards the Si substrate The dynamics of the carbon ions in the transient plasma have been studied by spectrally resolved ICCD imaging. The effect of magnetic field on the film growth rate, radial distribution of carbon ions, and film morphology will be presented.

#### A24.7

OPTIMIZATION OF P-TYPE DOPING IN STOICHIOMETRIC a-SiC:H OBTAINED BY PECVD. <u>Alessandro R. Oliveira</u>, Marcelo N.P. Carreno and Ines Pereyra, Dept de Engenharia de Sistemas Eletronicos, Escola Politecnica, Universidade de Sao Paulo, Sao Paulo, BRAZII.

In recent years, there has been a growing interest in hydrogenated amorphous silicon carbide thin films (a-SiC:H) for device applications as light emitting diodes, photodiodes, and sensors. The investigations have generally explored the possibility of controlling, through carbon and silicon incorporation, the optical band gap of the a-SiC:H films. Therefore, aiming to obtain a material that is a real amorphous counterpart of the crystalline SiC and that preserves at least part of its properties, we have studied the deposition conditions to obtain a-Si<sub>1-x</sub>C<sub>x</sub>:H samples close to stoichiometry (with x  $\sim$ 0.5). Recently, we have investigated a-SiC:H having a chemical and structural order similar to that of c-SiC. We have also studied the n-type and p-type electrical doping of these close to stoichiometry a-SiC:H films through the ion implantation of impurities, with promising doping levels. Here, we performed a systematic study to optimize the p-type doping utilizing boron and aluminum as acceptor impurities, by boron ion implantation and aluminum thermal diffusion as doping techniques. The samples of a SiC:H were grown by PECVD at 350°C from appropriated gas mixtures of methane and silane diluted and non-diluted in H<sub>2</sub>. Boron ion implantation experiments were performed at multiple energies in the 10 to  $65~\rm keV$  range and the doping profile was simulated by the SRIM-TRIM software. The aluminum doping was accomplished by thermal diffusion, in the 550-950°C temperature range, which can be considered low temperature processes if compared to the required for thermal diffusion in c-SiC (greater than 1800°C). Preliminary results show improved doping efficiency for samples grown in H<sub>2</sub> dilution. The films presented small variations in the optical band gap and small activation energy, suggesting that good doping efficiency has been obtained. The results indicate that aluminum doping is more efficient than boron, in accordance to observation in crystalline SiC materials.

### A24.8

LOW-ENERGY ELECTRON MICROSCOPY: A NEW TOOL FOR STUDYING STRAIN RELAXATION IN Si-BASED THIN FILM. A.R. Woll, E.M. Rehder, B. Yang, T.F. Keuch and M.G. Lagally, University of Wisconsin-Madison, Madison, WI.

We demonstrate the use of low-energy electron microscopy (LEEM) as a tool for studying dislocation formation in low-Ge-content SiGe films on Si(001) and SOI. Compared to TEM, sample preparation for LEEM consists only of a conventional surface cleaning procedure. Yet, because of its sensitivity to local variations in surface strain, LEEM can detect dislocations at the earliest stages of strain relaxation, long before cross-hatch becomes visible in AFM. For identically prepared SiGe films, the typical dislocation extends over the entire viewable region of several hundred microns in SiGe/Si, but is less than 100 microns in SiGe/SOI. In addition, dislocation cross-slip and threading segments are common in SiGe/SOI, but virtually non-existent in SiGe/Si. We have also observed dislocation formation in real-time during high temperature annealing. Preliminary results appear to demonstrate dislocation multiplication and blocking at a perpendicular glide plane. The applicability of LEEM to strain relaxation in other Si-based systems will be discussed.

### SESSION A25: MIXED PHASE AND EDGE ${\bf MATERIAL}$

Friday Morning, April 5, 2002 Golden Gate B2 (Marriott)

### 8:00 AM A25.1

ATOMISTIC MODELS OF HETEROGENEOUS EDGE MATERIALS. B.C. Pan, R. Biswas, Dept. of Physics and Microelectronics Research Center, Iowa State University, Ames, IA.

The "edge" materials grown at the phase boundary between amorphous and microcrystalline growth are known to have superior performance and higher stability than traditional a-Si:H materials. This mixed phase material consists of crystallites embedded in an amorphous matrix. With an aim to understanding the properties of such edge materials we initiated simulations using molecular dynamics techniques. We have generated models of mixed phases consisting of a silicon nanocrystallite embedded in a matrix of hydrogenated amorphous silicon. In one simulation method, a c-Si cell was used as the starting configuration with an interior seed crystal kept fixed. The remainder of the cell was melted and annealed to generate an amorphous matrix around the crystallite. H was introduced within the amorphous matrix to reduce defect concentrations. Cell sizes from 2.1 to 4 nm containing 500-4000 atoms will be considered. The structure of the mixed phases was characterized by radial distribution functions, structure factors, bond-angle and dihedral angle distributions. The calculated X-ray diffraction intensity contains signatures of the crystallites and compares well with measurements of mixed phase material. The distribution of H in these mixed phases and the nature of the interfacial region will be discussed. The electronic density of states and vibrational spectra will be presented. Supported by an NREL subcontract.

 $8{:}15\ AM\ \underline{A25.2}$  MAPPING THE PHASE-CHANGE PARAMETER SPACE OF HOT-WIRE CVD Si:H FILMS USING IN-SITU REAL TIME SPECTROSCOPIC ELLIPSOMETRY. <u>Dean H. Levi</u>, Brent P. Nelson, John D. Perkins, and Helio R. Moutinho, National Renewable Energy Laboratory, National Center for Photovoltaics, Golden, CO.

In-situ real-time spectroscopic ellipsometry (RTSE) provides detailed information on the evolution of the structural and optical properties of Si:H films during film growth. We use in-situ RTSE to characterize the film morphology and crystallinity of hot-wire CVD (HW-CVD) Si:H films as a function of hydrogen dilution  $R=[H]/[H_2+SiH_4]$  and substrate temperature  $T_S$ . The surface roughness  $R_S$  of the film provides a real-time indicator of changes in film morphology during growth. All films exhibit qualitatively similar  $R_S$  behavior. There is a rapid initial increase in  $R_S$  as nucleation occurs, followed by a rapid decrease in R<sub>S</sub> as the nucleation sites coalesce to form a continuous film. In single-phase films, the surface roughness then gradually increases to an equilibrium value, whereas in films that undergo a phase change during growth we observe secondary peaks in  $R_S$  versus time, corresponding to nucleation of microcrystalline Si:H (uc-Si:H) layers on the base amorphous (a-Si:H) layer. Films that nucleate as uc-Si:H exhibit much larger initial peak values of R<sub>S</sub> than those that nucleate at a-Si:H. We have corroborated these results using Raman scattering and atomic force microscopy to measure crystallinity and surface roughness, respectively. The growth parameter space we have studied includes dilution ranging from 2 to 12, and temperature ranging from 100°C to 500°C. We have put particular emphasis on characterizing the transition region between a-Si:H and uc-Si:H.

# 8:30 AM A25.3

TRANSPORT PATH IN HYDROGENATED MICROCRYSTALLINE SILICON. Nicolas Wyrsch, Luc Feitknecht, Corinne Droz, Arvind Shah, Institut de Microtechnique, Universitè de Neuchâtel, Neuchâtel, SWITZERLAND.

Microcrystalline hydrogenated silicon ( $\mu$ c-Si:H) is at present the subject of intensive research activities. While  $\mu \text{c-Si:H}$  has been successfully introduced for solar cells, an important enigma persists concerning electronic transport in this material. More precisely, it is still not clear which part of the material (amorphous phase. microcrystalline phases or grain boundaries) controls electronic transport in  $\mu$ c-Si:H. If grain boundaries do not play a role, then transport should only be determined by the ratio of amorphous and microcrystalline phases. In this case, if this ratio is increased (starting from a pure amorphous phase), one should detect a percolation threshold in conductivity. However, such a percolation threshold is not observed in device-grade material, neither in layers deposited by the Jülich group [1] nor in layers deposited at our institute. This indicates that the validity of a the simple two-phases transport model (crystallites embedded into an amorphous tissue), as proposed recently for the simulation of transport in  $\mu c$ -Si:H [2], is questionable. Here, the authors will investigate series of layers deposited across the transition regime from amorphous to microcrystalline growth, by

Raman and conductivity measurements and look at the existence of percolation signatures in the transport properties. The effect of the presence of an amorphous incubation layer or of a change in the crystalline content along the growth axis will also be analysed. Results of this study should be able clarify the role of grain boundaries on the transport in  $\mu \text{c-Si:H.}$  [1] O. Vetterl et al., ICAMS 19, to be published in J. of Non-Cryst. Sol. [2] A. Feijfar et al., MRS Proc. 664 (2001) A16.1.1

### 8:45 AM <u>A25.4</u>

IN-SITU TRANSMISSION ELECTRON MICROSCOPY OF AMORPHOUS SILICON GROWTH. Mark Yeadon, IMRE, Singapore and Dept of Materials Science, National Univ of Singapore, SINGAPORE; J. Murray Gibson, Argonne National Laboratory, Argonne, IL; Michael M.J. Treacy, NEC Research Institute, Princeton, NJ; Jinhua Yu, Dept of Materials Science, National Univ of Singapore, SINGAPORE; Christopher B. Boothroyd, Dept of Materials Science, Univ of Cambridge, UNITED KINGDOM.

Extensive work on the structure of amorphous silicon using "fluctuation electron microscopy" has shown that the as-grown material typically has a "paracrystalline" structure (1). We have speculated that this structure originates from crystalline nucleation during growth, which is frustrated by a high density of nucleation. To confirm this hypothesis we have performed some preliminary experiments on in-situ evaporation of amorphous silicon in an ultra-high vacuum transmission electron microscope (MERLION) at the Institute for Materials Research and Engineering in Singapore. Images were taken with bright-field high-resolution microscopy, and analyzed using a variant on the FEM technique which will be described. 1) P.M. Voyles, J.M. Gibson and M.M.J. Treacy, Phys. Rev. Lett. Vol 86, 5514 (2001).

### 9:00 AM A25.5

ATOMIC-SCALE ANALYSIS OF THE H-INDUCED DISORDER-TO-ORDER TRANSITION IN PLASMA-DEPOSITED SILICON THIN FILMS. Saravanapriyan Sriraman, Sumit Agarwal, Eray S. Aydil, and Dimitrios Maroudas, Department of Chemical Engineering, University of California, Santa Barbara, Santa Barbara, CA.

Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasma deposition from SiH<sub>4</sub>/H<sub>2</sub> containing discharges are widely used in photovoltaic and flat-panel display technologies. The structure of a-Si:H films undergoes a transition from amorphous to nanocrystalline when the SiH<sub>4</sub> feed gas is heavily diluted with H<sub>2</sub>, or when as-deposited a-Si:H films are exposed to H atoms from an H2 plasma Though several hypotheses have been proposed, the fundamental mechanism behind this transition still remains unclear. We have studied the H-induced crystallization of a-Si:H thin films and revealed the structural transition mechanism using molecular-dynamics (MD) simulations and in situ infrared spectroscopy. Thin films of a-Si:H were grown by MD through repeated impingement of individual SiH3 precursors on an initial H-terminated Si(001)-(2×1) surface. MD simulations of repeated H atom impingement on these a-Si:H films were used to elucidate the nanoscopic mechanism of the amorphousto-nanocrystalline transformation. The evolution of the films Si-Si radial distribution function during exposure to H atoms showed the appearance of peaks corresponding to coordination shells of the crystalline Si structure, indicating that the amorphous film undergoes a disorder-to-order transition upon exposure to H atoms. The features of the nanocrystalline Si matrix that emerges after the exposure of the a-Si:H film to the H flux were obtained through detailed computational structural characterization. Analysis of the MD trajectories showed that H atoms diffuse into the a-Si:H film and insert into strained Si-Si bonds to form bond-centered H (Si-H-Si) The existence of bond-centered H(D) in a-Si:H films exposed to H(D)atoms from an H<sub>2</sub>(D<sub>2</sub>) plasma was experimentally verified through in situ infrared spectroscopy. We conclude that H-induced crystallization of a-Si:H films is mediated by insertion of H into strained Si-Si bonds, which results in structural relaxation and transformation of the amorphous Si network

# 9:15 AM <u>A25.6</u>

GROWTH STUDIED BY ADVANCED PLASMA AND IN SITU FILM DIAGNOSTICS. W.M.M. Kessels, J.P.M. Hoefnagels, I.J. Houston, P.J. van de Oever, and M.C.M. van de Sanden, Dept. of Applied Physics, Eindhoven Univ. of Technology, Eindhoven, THE NETHERLANDS

The transition of hydrogenated amorphous silicon (a-Si:H) to microcrystalline silicon ( $\mu$ c-Si:H) has been studied in the remote expanding thermal plasma setup. The absolute densities of  $SiH_x$ radicals have been determined from cavity ring down absorption spectroscopy revealing that SiH3 is dominant in the plasma for both cases but that the contribution of Si and SiH to film growth becomes relatively much more important under the  $\mu$ c-Si:H conditions. This

higher contribution of lower silane radicals can be attributed to sequential hydrogen abstraction reactions from  $\mathrm{SiH_4}$  and its radicals under strong H<sub>2</sub> diluted conditions. The radicals contribution to film growth has been calculated from the radicals density and their surface reaction probability as determined by the newly-developed timeresolved cavity ring down experiment. The latter technique has also revealed that Si in the gas phase is very reactive with SiH4 while SiH3 is completely unreactive in the gas phase. The bulk and surface hydrogen has been investigated by in situ attenuated total reflection infrared spectroscopy during the deposition of the amorphous and microcrystalline silicon films. The silicon hydride stretching and bending modes have been monitored as a function of deposition time/film thickness and a comparison has been made between a-Si:H and  $\mu$ c-Si:H conditions. The transition to  $\mu$ c-Si:H is characterized by narrow, well-separated surface-like absorption peaks. The experimental data will be combined with in situ spectroscopic ellipsometry measurements and will be compared with (ex situ determined) structural and opto-electronic film properties.

#### 9:30 AM A25.7

SILICON NANOCRYSTALLITES IN AMORPHOUS HYDRO-GENATED SILICON MATRIX: PROPERTIES MEASURED ON NANOSCALE. S.B. Aldabergenova, M. Albrecht, G. Frank, M. Becker and H.P. Strunk, Erlangen-Nürnberg University, Institute for Materials Science, Erlangen, GERMANY.

Very small (1-5nm) silicon crystallites embedded in an amorphous hydrogenated silicon matrix with volume fraction of about several %are prepared by the conventional plasma enhanced chemical vapor deposition under strong hydrogen dilution conditions. However, Raman spectroscopy does not show any traces of the crystallites and a broad TO phonon band centered around  $480~{\rm cm}^{-1}$  dominates the spectra. On the other hand, these crystallites manifest themselves prominently since they act like quantum dots. We investigate the structure of these small crystallites with different techniques with a high spatial resolution: high resolution transmission electron microscope imaging, electron energy loss spectroscopy and cathodoluminescence. We report on lattice parameter measurements, the changes in the plasmon spectrum as a function of the diameter and on local measurements of the light emitted from these nanocrystallites.

### SESSION A26: MICROCRYSTALLINE SOLAR CELLS Friday Morning, April 5, 2002 Golden Gate B2 (Marriott)

10:15 AM \*A26.1 CORRELATION OF LIGHT-INDUCED ENHANCEMENT IN THE OPEN-CIRCUIT VOLTAGE AND STRUCTURAL CHANGE OF HETEROGENEOUS. Jeffrey Yang, Kenneth Lord, Baojie Yan, Arindam Banerjee, and Subhendu Guha, United Solar Systems Corp, Troy, MI; Daxing Han and Keda Wang, Dept of Physics and Astronomy, Univ of North Carolina, Chapel Hill, NC.

We have carried out a systematic study on the light-induced effect of thin-film heterogeneous silicon solar cells whose intrinsic (i) layer consists of a mixture of amorphous and microcrystalline phases. Surprisingly, we observe a large enhancement in the open-circuit voltage (V<sub>OC</sub>) after subjecting the solar cells to one-sun light soaking at 50°C for 150 hours. The change in  $V_{OC}$  ( $\Delta V_{OC}$ ) is found to at 50°C for 150 hours. The change in  $V_{OC}$  ( $\Delta V_{OC}$ ) is found to depend on the initial  $V_{OC}$  value, the i layer thickness, and the light-soaking intensity. For cells in either the predominantly amorphous ( $V_{OC} \geq 1$  V) or microcrystalline ( $V_{OC} \leq 0.5$  V) phase, light soaking causes a small reduction in  $V_{OC}$ . For cells in the mixed phase, the enhancement in  $V_{OC}$  shows a symmetric shape with respect to  $V_{OC}$ . The largest  $\Delta V_{OC}$  is centered near  $V_{OC} = 0.75$  V, a value midway between 1 V and 0.5 V and representing the most heterogeneous structure. We also find that solar cells with thicker ilayers exhibit larger  $\Delta V_{OC}.$  In addition, a 2-hour intense (30-sun) light soaking resulted in a dramatic 150 mV increase in  $V_{OC}.$ Light-induced  $\Delta V_{OC}$  can be substantially reversed upon annealing at 150°C for 2 hours. We use photoluminescence (PL) spectroscopy to investigate whether the effect is associated with any structural change in the material. We find that for the mixed phase cells, the intensity of the PL peak associated with the amorphous component increases after light soaking, strongly suggesting that the volume fraction of the amorphous phase is increased. We conclude that the most heterogeneous material shows the largest light-induced structural change.

 $\bf 10:45~AM~\underline{A26.2}$  HIGH EFFICIENCY THIN FILM SOLAR CELLS WITH INTRINSIC MICROCRYSTALLINE SILICON BY HOT WIRE CVD. Stefan Klein, Friedhelm Finger, Reinhard Carius, Bernd Rech, Forschungszentrum Jülich, Institut für Photovoltaik, Jülich, GERMANY; Martin Stutzmann, TU München, Walter Schottky Institut, Garching, GERMANY.

The Hot Wire (HW) or Catalytic Chemical Vapour Deposition (CVD) has attracted much attention for the preparation of microcrystalline silicon (µc-Si:H) due to the high deposition rates and large grain sizes attained by this method. However, the performance of the material in solar cells was poor up to now. We have shown previously that the material quality improves substantially by reducing the substrate temperature  $(T_S)$  below  $300^{\circ}C$ , i.e. low spin densities, low subgap absorption, high photosensitivities and high hydrogen contents were obtained. Using this improved material the highest conversion efficiency of  $\eta = 9.4\%$  for a single junction solar cell with a  $\mu$ c-Si:H i-layer prepared with HW-CVD was obtained ( $\eta = 10.8\%$  for a micromorph tandem cell with HW i-layers). We will report a detailed investigation of  $\mu_{c-Si:H}$  solar cells prepared with HW-CVD at  $T_S = 285^{\circ}C$  and  $185^{\circ}C$ , with various silane concentration (SC), and various i-layer thicknesses in both pin and nip configuration, on  $10 \times 10 \ cm^2$  substrates with an area of  $1 \ cm^2$ . The variation of SC in both cases leads to results very similar to cells prepared by PECVD, i.e. the maximum efficiency is obtained close to the transition from microcrystalline to amorphous growth. In particular a very high  $V_{oc}$  of  $590\,mV$ , a short circuit current density  $I_{sc}=20.4\,mA/cm^2$ , fill factor FF=72%, efficiency  $\eta=8.6\%$  was achieved for a  $0.65\,\mu m$  thick cell with highly crystalline i-layer material. With further increase of the i-layer thickness the maximum efficiency of 9.4% is obtained, mainly by an increase of  $I_{sc}$ , while FFand  $V_{oc}$  decrease with increasing i-layer thickness, which again is very similar to earlier findings for PECVD material. The decrease of  $V_{oc}$  is reflected in the corresponding dark j-V curves. The observed increase of the diode quality factor n from n = 1.3 to n = 1.65indicates that bulk recombination becomes increasingly effective in the thicker cells, thus reducing  $V_{oc}$ .

# 11:00 AM <u>A26.3</u>

MICROCRYSTALLINE SILICON FOR SOLAR CELLS AT HIGH DEPOSITION RATES BY HOT WIRE CVD. R.E.I. Schropp, Utrecht University, Debye Institute, Physics of Devices, Utrecht, THE NETHERLANDS; Y. Xu, National Renewable Energy Laboratory (NREL), Golden, CO; G.A. Zaharias, Chem. Engineering Dept. Stanford University, Stanford, CA; A.H. Mahan, National Renewable Energy Laboratory (NREL), Golden, CO.

We have explored which deposition parameters in Hot Wire CVD have the largest impact on the quality of microcrystalline silicon ( $\mu c\text{-Si}$ ) made at deposition rates (Rd) >10 Å/s for use in thin film solar cells. Among all parameters, the filament temperature (Tfil) appears to be crucial for making device quality films. Using two filaments and a filament-substrate spacing of 3.2 cm,  $\mu$ c-Si films, using seed layers, can be deposited at high Tfil (~2000°C) with a crystalline volume fraction >70-80% at Rd's higher than 30 Å/s. Although the photoresponse of these layers is high (>100), they appear not to be suitable for incorporation into solar cells, due to their porous nature. n-i-p cells fabricated on stainless steel with these i-layers suffer from large resistive effects or barriers, most likely due to oxidation of the silicon layer. This porosity is evident from FTIR measurements showing a large oxygen concentration at ~1050 cm<sup>-1</sup> and is correlated with the 2100 cm<sup>-1</sup> signature of most of the Si-H stretching bonds. Using a Tfil of 1750°C, however, the films are more compact, as seen from the absence of the 2100 cm<sup>-1</sup> SiH mode and the disappearance of the FTIR Si-0 signal, while the high crystalline volume fraction (>70-80%) is maintained. Presently we obtain an efficiency of 4.9% for cells with a Ag/ZnO back reflector and 4.0% for cells on bare stainless steel, with an i-layer thickness of only 0.7 - 1.0  $\mu$ m. High values for the quantum efficiency extend to very long wavelengths, with values of 40% at 800 nm and 20% at 900 nm. Such values are unequalled by a-SiGe:H alloys. The Rd of these i-layers is >10 Å/s. Such rates are the highest to date obtained with HWCVD for microcrystalline layers used in cells with near 5% efficiency.

### 11:15 AM A26.4

HYDROGENATED MICROCRYSTALLINE SILICON SOLAR CELLS MADE WITH MODIFIED VERY-HIGH-FREQUENCY GLOW DISCHARGE. Baojie Yan, Kenneth Lord, Jeffrey Yang, and Subhendu Guha, United Solar Systems Corp., Troy, MI.

Hydrogenated microcrystalline silicon ( $\mu$ c-Si:H) solar cells are made using modified very-high-frequency (MVHF) glow discharge at deposition rates  $\sim 3-5$  Å/s. In this paper, we report material properties characterized by electrical conductivity, optical absorption, X-ray diffraction, infrared and Raman spectroscopies. We also present data on solar cell performance and stability and correlate those with the material properties. Key techniques such as hydrogen dilution, ion bombardment and use of strong etchant gases will be described. By controlling the bias on the substrate, we successfully control the ion bombardment and improve the material quality. We also find that the solar cells made under certain unoptimized conditions show degradation in air without intentional light soaking. The short circuit drops significantly within a few days after deposition, and then

stabilizes. The open circuit voltage and fill factor also degrade, but these changes are small. The ambient degradation is suppressed at low temperatures and/or by storing the samples in a dry nitrogen box. The top indium-tin-oxide electrode accelerates the degradation. We identify post-deposition oxygen diffusion along the grain boundaries or cracks as being the origin of the ambient degradation. The  $\mu c$ -Si:H solar cells made under optimized conditions do not show such ambient degradation. We believe that the unstable behavior of  $\mu c$ -Si:H material made under the unoptimized conditions is due to columnar structures and porosity in the grain boundary regions. Preliminary cell results show an initial active-area efficiency of 5.9% for a  $\mu c$ -Si single-junction cell and an initial active-area efficiency of 11.7% for an a-Si/ $\mu c$ -Si double-junction cell having a total short circuit current density of 26 mA/cm<sup>2</sup>.

#### 11:30 AM A26.5

HIGH RATE DEPOSITION OF MICROCRYSTALLINE SILICON SOLAR CELLS USING 13.56 MHZ PECVD - PREREQUISITES AND LIMITING FACTORS. <u>Tobias Roschek</u>, Tobias Repmann, Oliver Kluth, Joachim Müller, Bernd Rech, Heribert Wagner, Institut für Photovoltaik, Forschungszentrum Jülich GmbH, Jülich, GERMANY.

In this paper we present a comprehensive study of microcrystalline silicon (μc-Si:H) p-i-n solar cells prepared by PECVD using 13.56MHz excitation frequency. The study was performed in p-i-n cells directly, due to the high sensitivity of the solar cell even to small variations of the i-layer material properties. We investigated the role of the deposition parameters pressure, rf-power, electrode distance, substrate temperature as well as pulse frequency and duty cycle in case of pulsed plasma excitation during i-layer growth. For each parameter variation the hydrogen dilution was adjusted to maintain  $\mu c ext{-Si:H}$ growth close to the transition to amorphous growth [1], which was confirmed to be a necessary prerequisite for high cell performance. Solar cell efficiencies above 8% ( $V_{OC} \ge 500 \,\mathrm{mV}$ ) were achieved at deposition rates of 5-6Å/s only by using high deposition pressures above 8Torr. Upon further increasing the deposition rates up to 10 Å/s, we observed only a slight decrease in cell performance (e.g.  $\eta=7.9\%$  at  $9\text{\AA/s}$ ), however, we did not succeed in pushing the deposition rates significantly above  $10\text{\AA/s}$ . At even higher pressures (20 Torr) we investigated pulsed plasma excitation to reduce powder formation. High cell efficiencies (8.4% at 5Å/s) were obtained, but we found no increase in growth rate or cell performance as compared to continuous plasmas. We will discuss the experimental results in view of an up-scaling to larger areas. As an intermediate step towards an industrial application, the results were successfully up-scaled to our 30x30cm<sup>2</sup> PECVD reactor. Applying improved substrates, efficiencies of 9.0% and 12.5% were achieved for  $\mu$ c-Si:H single and a-Si:H/  $\mu$ c-Si:H tandem junction cells, respectively. In both cases the  $\mu$ c-Si:H i-layer was prepared at a deposition rate of 5Å/s. [1] O. Vetterl et al., Solar Energy Materials & Solar Cells 62, 97-108 (2000).

### 11:45 AM A26.6

AMORPHOUS AND MICROCRYSTALLINE SILICON SOLAR CELLS GROWN BY PULSED PECVD TECHNIQUE.
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The Pulsed PECVD technique involves modulating the standard 13.56 MHz RF plasma, in the kHz range. This allows an increase in the electron density during the "ON" cycle, while in the "OFF" cycle neutralizing the ions responsible for dust formation in the plasma. The technique has been shown to increase the deposition rate without an increase in the particulate count in the plasma, which is an important factor in determining the yield of commercial products such as solar cell modules. In this work, we report the increase of i-layer growth rate and silane gas utilization rate (GUR) for amorphous Si p-i-n solar cells grown in a large area (30 cm × 40 cm) single chamber deposition system. The i-layer growth rate of 5.3 Å/sec with a GUR of >15% has been achieved, which shows a device efficiency of 8.3% (same as of our conventional PECVD grown a-Si:H solar cell with i-layer growth rate of 1 Å/sec). For microcrystalline silicon solar cells to be a viable approach for photovoltaic applications, one of the critical technical issues that need to be addressed is the deposition rate of the i-layer. Several techniques have shown promise in depositing  $\mu c\text{-Si}$  at higher deposition rates (>5 Å/sec), including VHF-PECVD and Hot Wire CVD. We deposited microcrystalline Si p-i-n devices via the Pulsed PECVD technique. The crystallite orientation of the films changes from a random orientation to a (220) orientation near the amorphous-to-microcrystalline transition. The observed change in orientation (220 vs. 111) is correlated with solar cell performance, with the best efficiency seen for (220) oriented i-layers. The role of ion bombardment and grain boundary interfaces on the solar cell performances are also investigated. An efficiency of 4.8% for single junction  $\mu$ c-Si:H p-i-n device has been achieved for the i-layer thickness of 0.9  $\mu$ m.