

# SYMPOSIUM A

## Amorphous and Nanocrystalline Silicon-Based Films-2003

April 21 – 25, 2003

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## TUTORIAL

### ST A: AMORPHOUS AND POLYSILICON MATERIALS AND DEVICES FOR LARGE-AREA ELECTRONICS

Monday, April 21, 2003

8:30 a.m. - 4:30 p.m.

Salon 5/6 (Marriott)

Hydrogenated amorphous silicon (a-Si:H) and micro- or polycrystalline silicon ( $\mu\text{c-Si}$ , 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-of-the-art processing issues of modern large-area array technology based on amorphous or polycrystalline thin silicon films. Special emphasis will be on the relation between material properties and device performance.

#### Instructors:

Sigurd Wagner, Princeton University

Joao Pedro Conde, Instituto Superior Tecnico, Lisbon

#### SESSION A1: NANOCRYSTALS AND PHOTONICS

Tuesday Morning, April 22, 2003

Salon 5/6 (Marriott)

##### 8:30 AM \*A1.1

#### SILICON NANOCRYSTAL ELECTRONICS AND PHOTONICS.

Harry A. Atwater, R.J. Walters, J.S. Biteen, T. Feng, J. Caspersen, California Institute of Technology, Pasadena, CA; and Harvard University, Cambridge, MA; and A. Polman, FOM Institute for Atomic and Molecular Physics, Amsterdam, NETHERLANDS.

The interplay between the photophysics and electronic properties of silicon nanocrystals and nanocrystal arrays is a rich arena for physics and device applications, and is currently yielding interesting surprises. In this talk, I will compare and contrast the optoelectronic properties of arrays of isolated silicon nanocrystals passivated by hydrogen or oxide termination with the properties of the continuous films of nanocrystalline silicon that are more familiar to the thin film silicon photovoltaics community. I will discuss the dependence of nanocrystal luminescence on electronic charge state, and survey potential applications for silicon nanocrystal arrays in nonvolatile memory devices, photodetectors, novel optical memory devices, and future possibilities for silicon nanocrystals in photovoltaic devices.

##### 9:00 AM A1.2

PHONON CONFINEMENT IN Ge NANOCRYSTALS IN SILICON OXIDE MATRIX. Y.X. Jie, A.T.S. Wee, C.H.A. Huan and Z.X. Shen, Department of Physics, National University of Singapore, SINGAPORE.

Well-dispersed spherical Ge nanocrystals in silicon oxide thin film on Si substrate have been synthesized with different sizes and crystallinity using RF magnetron sputtering. Significant Raman shift and broadening have been observed from the samples annealed under different conditions. Several phenomenological phonon confinement models have been compared with our experimental data. The observed size-dependent shift and broadening is found to be well depicted by the RWL phonon confinement model combined with a Gaussian weighting function and the isotropic TO2 phonon dispersion relation introduced by Sasaki *et al.* The Raman shift and broadening are described by  $L^{-1.44}$  and  $L^{-1.75}$  power laws respectively. A three-peak fitting method of obtaining Ge nanocrystal size and crystallinity is introduced.

##### 9:15 AM A1.3

PREPARATION OF  $\text{SiO}_x/\text{SiO}_2$  SUPERLATTICES FOR ORDERED Si NANOCRYSTALS. L.X. Yi, J. Heitmann, R. Scholz, and M. Zacharias, Max-Planck-Institute of Microstructure Physics, Halle, GERMANY.

The preparation of ordered arranged Si quantum dots using a superlattice approach and reactive evaporation of SiO powder is presented. By this method, an independent size and density control is possible for Si nanocrystals [1]. The different stages of phase separation and crystallization are studied in detail by infrared absorption (IR), photoluminescence (PL), and TEM as a function of annealing temperature from 300 to 1100°C [2]. IR spectra show a continuous shift of the Si-O-Si asymmetric stretching mode to 1080  $\text{cm}^{-1}$  as a signature of Si and  $\text{SiO}_2$  phase separation. Three PL bands are distinguished correlated to the three stages of phase separation. A band centered at 560 nm is present in as-prepared samples and

vanishes for annealing above 700°C. The second band shifting from 760 nm to 890 nm is detected for annealing temperatures between 500°C and 900°C. A strong red luminescence is observed for annealing above 900°C. The origin of the different IR and PL bands related to different stages of phase separation of the ultra thin  $\text{SiO}_x$  layers will be discussed in detail. Our results show that the different and seemingly contradicting PL observations in literature can be understood as different states of network reorganization during the phase separation and crystallization processes. After crystallization, the strong PL shows a blue shift with decreasing SiO layer thickness from 980 to 740 nm due to quantum confinement. The deviation of temperature and power dependence of the strong room temperature PL is discussed in comparison to bulk crystalline Si. [1] M. Zacharias, J. Heitmann, R. Scholz, U. Kahler, M. Schmidt, J. Blsing, Appl. Phys. Letter 80 (2002) 661. [2] L.X. Yi, J. Heitmann, R. Scholz, M. Zacharias, Appl. Phys. Letter in press.

##### 9:30 AM A1.4

THE FORMATION OF  $\text{Si}_{1-x}\text{Ge}_x$  NANOCRYSTALS AND CONTROL GATE OXIDE THROUGH THE OXIDATION OF THIN AMORPHOUS  $\text{Si}_{0.7}\text{Ge}_{0.3}$  LAYER AND ITS ELECTRICAL PROPERTIES. Tae-Sik Yoon, Seoul National University, Research Institute of Advanced Materials, School of Materials Science and Engineering, Seoul, KOREA; Hyun-Mi Kim, Ki-Su Kim, Ki-Bum Kim, Seoul National University, School of Materials Science and Engineering, Seoul, KOREA.

It is necessary to form nanometer size quantum dots embedded in the oxides in order to fabricate a flash-type single electron memory device. In this talk, we propose a novel scheme to form  $\text{Si}_{1-x}\text{Ge}_x$  nanocrystals and the control gate oxide (upper oxide), simultaneously, through the oxidation of the thin as-deposited amorphous  $\text{Si}_{0.7}\text{Ge}_{0.3}$  layer. Firstly, a 5 nm-thick amorphous  $\text{Si}_{0.7}\text{Ge}_{0.3}$  layer is deposited by LPCVD on  $\text{SiO}_2$  substrate. Secondly, this layer is oxidized by the dry oxidation process at 600°C for 20 minutes. During this second step, not only the oxidation of  $\text{Si}_{1-x}\text{Ge}_x$  layer occurs but also, the remaining  $\text{Si}_{1-x}\text{Ge}_x$  layer forms an uniform nanometer size crystals. It is identified that the average size of nanocrystals is  $3.7 \pm 0.9$  nm with a density of  $5.43 \times 10^{11}/\text{cm}^2$  and the thickness of upper oxide was measured as 4 nm. C-V characteristics were measured by fabricating Al-gate(200nm)/4nm-thick  $\text{SiO}_2/\text{Si}_{1-x}\text{Ge}_x$  nanocrystal/ $\text{SiO}_2$ (100nm)/p-Si structure both before and after programming with negative bias on Al-gate. The plateau of flat-band voltage shift ( $\Delta V_{FB}$ ) was clearly observed at room temperature with a magnitude of 0.223 V due to the electron charging in nanocrystals.

##### 9:45 AM A1.5

POTENTIAL APPLICATION OF PHOTONIC CRYSTALS TO PHOTOVOLTAICS. J.G.Fleming and S.Y. Lin, Sandia National Laboratories, Albuquerque, NM.

Photonic crystals are the photonic analogues of semiconductors. The photonic band structure results when light encounters a well-defined repeating arrangement of materials with differing refractive indexes. This behavior is independent of the electronic properties of the material making up the crystal, as long as it does not strongly adsorb. Advances in silicon processing technology, have resulted in rapid progress in this field. We have recently demonstrated tungsten-based photonic crystals, using silicon, back end of the line processing. In the course of our work we have found that these metallic photonic crystals demonstrate thermal emission properties that deviate significantly from the behavior predicted by the normal derivation of Planck's law. In particular, when heated, they show anomalous thermal emission in a relatively narrow band of wavelengths at the higher energy band edge. We have observed that the bulk of the energy emitted by the structures is contained in this relatively narrow band and that the intensity of emission at these wavelengths is close to an order of magnitude greater than that emitted by a black body. The peak emission wavelength also does not blue shift at the materials are heated. We believe that this behavior arises from the significant modification of the photonic density of states associated with these structures. We propose that it may be interesting to consider the integration of such a photonic crystal emitter with a band edge in the near infrared with a concentrator and adsorber system. The aim of this would be the conversion of a high fraction of the solar radiation into heat and subsequently into a narrow band of wavelengths targeted at the bandgap of a semiconductor. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000.

#### SESSION A2: DEFECT SPECTROSCOPIES

Tuesday Morning, April 22, 2003

Salon 5/6 (Marriott)

##### 10:30 AM \*A2.1

METASTABLE DEFECTS IN THE AMORPHOUS SILICON-

In this talk I will first briefly review some of the early studies that established some of the salient features of light-induced degradation in a-Si<sub>x</sub>Ge<sub>1-x</sub>H. I will then examine a couple of complicating issues that came to light more recently; namely, the possibility that charged defects play a more central role in the alloys, and that both Si and Ge metastable dangling bonds may be involved, even up to levels above 20at.% Ge. I will then discuss some of the most recent studies carried out by members of my laboratory that have been focusing on the details of degradation in the low Ge fraction alloys to gain insight into the fundamentals of degradation of amorphous silicon materials in general. Finally, I will conclude with an overall assessment of the level of our understanding of degradation in the a-Si<sub>x</sub>Ge<sub>1-x</sub>H alloys and where some key issues are still remaining to be resolved.

**11:00 AM A2.2**  
TEMPERATURE DEPENDENCE OF THE DECAY OF OPTICALLY EXCITED CHARGE CARRIERS IN AMORPHOUS SILICON. J. Whitaker and P.C. Taylor, Department of Physics, University of Utah, Salt Lake City, UT.

Modeling of the eventual recombination of optically excited electrons and holes in amorphous silicon at low temperatures ( $T < 40$  K) involves two distinct processes, the hopping down in energy via tunneling of each individual carrier (diffusion) and recombination of electrons and holes via tunneling. At short times the hopping down process dominates, and at long times the recombination process dominates. On shorter time scales ( $t < 1$  s) and at low temperatures the two processes compete: quantum tunneling by a single carrier to a lower energy state, and recombination of an electron and a hole via tunneling [1]. At finite temperature where excitations that increase the energy are possible, a third mechanism, namely variable range hopping of the charge carriers, must be considered. The optically induced electron spin resonance (ESR) signal of amorphous silicon at low temperatures has been well studied for time scales greater than about 1 s [2]. The photoluminescence (PL) signal, which is related to the ESR, in amorphous silicon has also been well studied for time scales less than about 1 ms [3]. We have studied the temperature dependence of the growth and decay of the ESR on short and long time scales ( $10^{-3}$  s  $< t < 2500$  s) in between the previously published photoluminescence and the ESR data. In addition, we have examined the saturated density of charge carriers as a function of temperature and excitation intensity. These measurements lead to a better understanding of the band tail structure of amorphous silicon as well as the kinetics of the excitation and recombination processes. 1. B.I. Shklovskii, H. Fritzche, and S.D. Baranovskii, Phys. Rev. Lett. 62, 2989 (1989). 2. J. Whitaker, T. Su, and P.C. Taylor, Mat. Res. Soc. Symp. Proc. 715, 275-281 (2002). 3. R.A. Street, Hydrogenated Amorphous Silicon (Cambridge University Press, Cambridge, 1991).

**11:15 AM A2.3**  
ELECTRON SPIN RESONANCE INVESTIGATION OF LASER CRYSTALLIZED POLYCRYSTALLINE SILICON. K. Brendel, Hahn-Meitner-Institut Berlin, Berlin, GERMANY.

Polycrystalline silicon (poly-Si) produced by excimer laser crystallization is a promising candidate for electronic devices such as TFTs and solar cells. An attractive way to produce high quality poly-Si is laser crystallization of amorphous silicon. We investigated electronic properties of doped and undoped laser crystallized poly-Si with electron spin resonance (ESR) measurements. Hydrogenated amorphous silicon was deposited in a PECVD process. A step-by-step crystallization procedure was performed on the samples. In fully crystallized films a hydrogen concentration of about 5 - 10 at.% is still remaining in the film. The spin density,  $N_S$ , in fully crystallized films amounts to about  $6\% \times 10^{18}$  cm<sup>-3</sup>. The remaining hydrogen can be activated by a simple vacuum anneal and reduces the defect density. A 1h anneal at 400°C results in a decrease of  $N_S$  by a factor of 2. From the temperature dependence of the change of the spin density,  $\Delta N_S$ , an activation energy of  $E_A \approx 0.2$  eV was estimated. The number of passivated defects depends on the hydrogen concentration in the initial amorphous layer. Phosphorous and boron doping concentrations up to 100 ppm do not result in a decrease of  $N_S$ . For phosphorous concentrations larger than 10 ppm the resonance of the conducting electron (CE) emerges with a  $g$ -value of about 1.9985. The  $g$ -value decreases with increasing temperature and increasing phosphorous doping concentration. Temperature dependent ESR measurements reveal that in highly doped samples nearly all electrons show Pauli paramagnetism. For lower doping concentrations a mixture of Curie and Pauli paramagnetism can be observed. This is similar to results observed in single crystal silicon. The linewidth,  $\Delta H_{PP}$ , increases with increasing doping concentration and increasing temperature.  $\Delta H_{PP}$  is about a factor 2 smaller than in microcrystalline silicon, but it exceeds the value reported for single crystal silicon by about a factor of 4.

**11:30 AM A2.4**  
TIME-RESOLVED SWITCHING STUDIES IN a-Si:H AND RELATED FILMS. P. Stradins, W.B. Jackson<sup>†</sup>, H.M. Branz, J. Hu, C.L. Perkins, and Qi Wang, National Renewable Energy Laboratory, CO; <sup>†</sup>Hewlett Packard Laboratories, Palo Alto, CA.

We report time-resolved studies of switching in hydrogenated amorphous silicon (a-Si:H), microcrystalline Si ( $\mu$ c-Si:H), and a-Si<sub>x</sub>H layers sandwiched between two metallic layers. Two distinct types of switching kinetics are characterized by studying the dependence of switching characteristics on the switch layer material, its doping, the contact metal, and switching temperature over a wide range of applied voltage pulse amplitudes. In a-Si:H and  $\mu$ c-Si:H, we normally see Type I switching characterized by a latency time ( $\tau_L$ ) followed by a sudden switching event. During the latency time, the sample current  $I_s$  exhibits telegraphic noise ("pre-switching") which may be a precursor of a permanent switching and filament formation. These preswitching changes in  $I_s$  for  $t < \tau_L$  are reversible but may persist for as long as milliseconds at room T after terminating the voltage pulse. At  $t \approx \tau_L$ , sample switches permanently to a highly conductive state. The values of  $\tau_L$  follow random statistics and vary over a wide range depending on the applied voltage. Once the final switching event begins, it typically completes in subnanoseconds. Scanning micro-Auger microscopy confirms that Type I switching is normally accompanied by the formation of a single submicron-diameter metallic filament connecting the metallic contacts. In a-Si<sub>x</sub>H switched with sufficient voltage, we normally observe Type II switching in which  $I_s$  increases gradually from  $t = 0$ . By interrupting the pulse, a continuum of stable final states with gradually variable high conductance can be reached. The switched conductance saturates only at long pulse times. Both the sudden and gradual switching times depend exponentially on the applied voltage pulse amplitude with characteristic times that depend on the contact material. Trapped charge accumulation, nonlinear effects of current-induced heating, and field dependent conductivity are investigated as possible causes of the two types of switching and their voltage dependences.

**11:45 AM A2.5**  
ADSORPTION AND OXIDATION EFFECTS IN MICROCRYSTALLINE SILICON. T. Dylla<sup>a,b</sup>, F. Finger<sup>a</sup>, R. Carius<sup>a</sup>; <sup>a</sup>Institut für Photovoltaik, Forschungszentrum Jülich, Jülich, GERMANY; <sup>b</sup>Department of Physics, Syracuse University, Syracuse, NY.

The development of microcrystalline silicon ( $\mu$ c-Si:H) for solar cells has made good progress with efficiencies, and these are significantly larger than for comparable amorphous silicon devices. However, in-diffusion of atmospheric gases can affect the electronic transport and the stability of  $\mu$ c-Si:H devices. We investigated such adsorption or oxidation effects in  $\mu$ c-Si:H with different crystalline volume fractions and various degrees of porosity by electron spin resonance and conductivity measurements. The material was deposited with PECVD at silane concentrations SC=2-8%. The material structures can be classified in three categories as (i) highly crystalline, very porous material at SC=2%, (ii) very crystalline, compact material between SC = 3-5% and (iii) crystallites diluted in an amorphous phase at SC = 6-7%. The samples were stored and annealed (80°C) in different environments (*air*, *O<sub>2</sub>*, *H<sub>2</sub>O*, *Ar*). Spin density  $N_S$  and electronic conductivity are clearly influenced by adsorption and oxidation effects. When stored in water or air,  $N_S$  of highly crystalline, porous material increases by up to a factor of three. Annealing in *Ar* completely restores the original  $N_S$ . These changes in  $N_S$  affect only the resonance at  $g=2.0052$ , while the second resonance at  $g=2.0043$  is not affected. These results indicate that the resonances represent defects in different environments of the material. With decreasing porosity the changes in  $N_S$  are less pronounced, and they are not observed at all for material with a large amorphous phase contribution. The conductivity measurements suggest that adsorption leads to a strong Fermi level shift. If, on the other hand, the material is annealed in pure oxygen atmosphere, a non-reversible increase of  $N_S$  with the appearance of an additional resonance is observed. Such behaviour can have severe consequences on the stability of  $\mu$ c-Si:H devices and should be considered when investigating spin densities of  $\mu$ c-Si:H of different structure compositions.

SESSION A3: SOLAR CELLS I  
Tuesday Afternoon, April 22, 2003  
Salon 5/6 (Marriott)

**1:30 PM \*A3.1**  
HIGH EFFICIENCY THIN FILM SILICON SOLAR CELL AND MODULE. Kenji Yamamoto, Akihiko Nakajima, Masashi Yoshimi, Toru Sawada, Susumu Fukuda, Katsuhiko Hayashi, Takashi Suezaki, Mitsuru Ichikawa, Yohei Koi, Masahiro Goto, Hironori Takata, and

An initial efficiency of 14.5% ( $J_{sc}=14.4\text{mA}/\text{cm}^2$ ,  $V_{oc}=1.41\text{V}$ ,  $FF=71.9\%$ ) has been achieved for a-Si:H / transparent inter-layer / microcrystalline Si solar cell (total area of  $1\text{cm}^2$ ). Both a-Si and microcrystalline Si films were fabricated by plasma chemical vapor deposition at low temperature. The short circuit current ( $J_{sc}$ ) was enhanced by the introduction of transparent interlayer without increasing the thickness of a-Si:H layer. It was also found that total spectral response is enhanced by both selecting and adjusting the appropriate materials and preparation conditions of above mentioned transparent inter-layer. An initial aperture efficiency of 13% has been achieved for  $910\times 455\text{mm}^2$  a-Si / microcrystalline Si thin film integrated large area solar cell module.

#### 2:00 PM **A3.2**

**BANDTAIL LIMITS TO SOLAR CONVERSION EFFICIENCY IN AMORPHOUS SILICON BASED SOLAR CELLS.** K. Zhu<sup>†</sup>, J. Yang<sup>‡</sup>, W. Wang<sup>†</sup>, E.A. Schiff<sup>†</sup>, J. Liang<sup>†</sup>, and S. Guha<sup>‡</sup>;

<sup>†</sup>Department of Physics, Syracuse University, Syracuse, NY; <sup>‡</sup>United Solar Systems Corp., Troy, MI.

We have measured the electrical properties of amorphous silicon based solar cells in their initial, non-light-soaked state, and we conclude that in some cases these properties can be understood without reference to deep levels such as dangling bonds. Such studies are valuable because they provide relatively unambiguous information about the most fundamental aspects of the cells: the electrical bandgaps and the bandtail densities-of-states of their intrinsic layers.

In particular, we have measured the temperature-dependent properties of these cells under uniformly absorbed laser illumination (685 nm) over the range 230 K - 350 K. We have applied an analytical model primarily based on valence bandtail trapping. We find that this model explains the measurements well for cells thinner than 500 nm. For these samples we obtained estimates for the electrical bandgap  $E_G = 1.75\text{ eV}$  and for the valence band effective density-of-states  $N_V = 10^{21}\text{ cm}^{-3}$ . The bandgap is somewhat smaller than has been inferred previously from internal photoemission measurements on similar material. Only very rough bounds on  $N_V$  have been made prior to the present work. The valence bandtail model failed for thicker cells and also (as expected) for light-soaked cells. Using these parameters as inputs for computer modeling, we are able to predict the initial solar conversion efficiencies for simply engineered cells (no texturing or back reflectors). A narrowing of the bandtail width from 50 meV to 40 meV increases the initial efficiency from 7% to 9% in an optimized cell; there is fragmentary experimental evidence that such a narrowing may be feasible in practice. This research was supported by the Thin Film Photovoltaics Partnership of the National Renewable Energy Laboratory.

#### 2:15 PM **A3.3**

**NANOMETER RESOLUTION SPECTROSCOPY OF n/i INTERFACES IN AMORPHOUS SILICON SOLAR CELLS.** K. Zhu, E.A. Schiff, Department of Physics, Syracuse University, Syracuse, NY; G. Ganguly, BP Solar, Toano, VA.

We have studied defect and doping levels at the interfaces of amorphous silicon solar cells using a charge modulated infrared spectroscopy. The fundamental idea is to monitor the change of the infrared transmittance signal as we electrically charge and discharge states near n/i and p/i interfaces. Here we describe the spectra observed for interfaces between intrinsic amorphous silicon and (i) n-type amorphous silicon or (ii) n-type microcrystalline silicon. The results are far more complex than expected in the context of the "standard" doping model for amorphous silicon. More broadly, they illustrate how this spectroscopy may be used to unravel the electronic structure of device interfaces.

Strongly microcrystalline silicon n-layers give a rather weak spectrum, which is consistent with the weakness of the free carrier absorption cross-section in crystalline materials. For amorphous silicon n-layers, we find three distinct spectral features in various samples. The simplest is a broad spectrum of magnitude  $10^{16}\text{ cm}^2$ ; this is consistent with the standard doping model of a fourfold coordinated phosphorus atom with an electron energy level close to the conduction bandedge. A second, more striking feature is a sharp spectral line near 0.75 eV, which we believe is due to an internal optical transition of a complex incorporating a fourfold coordinated phosphorus and a dangling bond. In one series of samples, this line was absent for doping levels below 0.5%, and was nearly fully developed for levels greater than 1.0%. These measurements suggest the possibility of a phase transition in the structure of phosphorus doped a-Si for sufficiently large phosphorus concentrations. We have not yet identified a third, bipolar spectrum with peaks at 0.9 and 1.2 eV; it is, of course, tempting to identify this spectrum with dangling bond levels within the doped material.

This research was supported by the National Renewable Energy Laboratory.

#### 2:30 PM **A3.4**

**CARRIER TRANSPORT AND RECOMBINATION IN A-Si:H P-I-N SOLAR CELLS IN DARK AND UNDER ILLUMINATION.**

Jingdong Deng, Joshua M. Pearce, Vasilios Vlahos, Robert W.

Collins, and Christopher R. Wronski, Center for Thin Film Devices, The Pennsylvania State University, University Park, PA.

To gain a better understanding of the carrier transport and recombination mechanisms both in dark and under illumination, the dark current density - forward bias characteristics ( $J_D - V$ ) and light short circuit current density - open circuit voltage ( $J_{sc} - V_{oc}$ ) obtained over a wide range of light intensities have been investigated for hydrogenated amorphous silicon (a-Si:H) p-i-n solar cells. These were carried out on p(a-SiC:H)/i(a-Si:H)/n( $\mu\text{c-Si}$ ) (superstrate) solar cell structures with different a-Si:H intrinsic layers and a-Si:H buffer layers at the p/i interface. Results are presented and discussed which exhibit superposition between  $J_D - V$  and the  $J_{sc} - V_{oc}$  over extended regions of voltage and illumination. In these cell structures the contributions from interface and bulk recombination to the dark currents are identified and separated. It is found that the superposition is not affected by the interface recombination. However, it depends on both carrier injection from the p and n contacts and the defect densities in the bulk i-layers. Both first principle arguments and computer simulations are presented showing that the superposition observed experimentally here is valid until the bulk defect densities exceed about  $2\times 10^{17}\text{ cm}^{-3}$ . This can explain the absence of such superposition of  $J_D - V$  and  $J_{sc} - V_{oc}$  characteristics previously reported in studies on a-Si:H solar cells.

#### 2:45 PM **A3.5**

**NANOMETER-SIZE STRUCTURE MODULATED SOLAR CELL IN AMORPHOUS-Si/MICROCRYSTALLINE-Si HETEROGENEOUS MATERIAL.** Manabu Ito, Norikatsu Myojin, Michio Kondo, Akihisa Matsuda, TFSSC, AIST, Tsukuba, JAPAN; Masaharu Shiratani and Yukio Watanabe, Kyushu University, Department of Electronic Device Engineering, Fukuoka, JAPAN.

Controlling nanometer-size structure is quite crucial in making high performance Si thin film solar cell. In this study, we have applied nanometer-size structural modulation technique in a-Si/ $\mu\text{c-Si}$  heterogeneous material and demonstrated its validity by showing performance of the solar cells. As for a-Si based solar cell, degradation by light-soaking has been a biggest obstacle in achieving high conversion efficiency. It has been reported that inclusion of nano-sized crystallites into a-Si decreases light-induced degradation. In order to obtain this structure homogeneously in the film growth direction,  $\text{SiH}_4$  flow rate was periodically varied from low hydrogen dilution ratio to high hydrogen dilution ratio and thus a-Si and nc-Si layers are stacked one by one with each layer thickness of few nm. Compared with standard a-Si solar cells whose degradation ratio is around 15%, degradation ratio of our nanometer-size structure modulation silicon solar cells is extremely low, less than 5%. Although their initial efficiencies are not as high as standard a-Si solar cells, their after-light-soaked efficiencies (6.3%) exceed that of a-Si one (6.0%). Nanometer-size structural modulation can also be applied to p/i interface of the  $\mu\text{c-Si}$  solar cells. For achieving high efficiency in  $\mu\text{c-Si}$  solar cell, it is essential to get high open circuit voltage ( $V_{oc}$ ) and fill factor (FF), especially in a-Si/ $\mu\text{c-Si}$  tandem type solar cell. Substrate type solar cells were prepared at  $140^\circ\text{C}$  onto flat substrate with i-layer thickness of  $1\mu\text{m}$ . Two kinds of the buffer layer were examined; one is a-Si single layer with a thickness of 5 to 30nm and the other is a-Si/ $\mu\text{c-Si}$  multilayers. By inserting a single 5nm thick a-Si layer,  $V_{oc}$  increases from 0.472V to 0.530V and FF increases from 70.5% to 74.3%. Although the short wavelength response decreases slightly, efficiency increases from 6.13% to 6.35%. Furthermore, we examined a-Si/ $\mu\text{c-Si}$  superlattice structure at p/i interface and demonstrate  $\mu\text{c-Si}$  solar cell with FF of 75.3%. These are attributed to reduction of the diode saturation current by the insertion of wide band gap material which acts as a barrier.

SESSION A4: SOLAR CELLS II

Tuesday Afternoon, April 22, 2003

Salon 5/6 (Marriott)

#### 3:30 PM **\*A4.1**

**HYDROGENATED MICROCRYSTALLINE SILICON SINGLE-JUNCTION AND MULTI-JUNCTION SOLAR CELLS.** Baojie Yan, Gouzheng Yue, Jeffrey Yang, and Subhendu Guha, United Solar Systems Corp., Troy, MI.

We present results on hydrogenated microcrystalline silicon ( $\mu\text{c-Si:H}$ ) solar cells and their application in various multi-junction solar cells. Two glow discharge techniques have been used in this study. Conventional RF glow discharge is used to deposit intrinsic  $\mu\text{c-Si:H}$

layer in multi-junction solar cells at a low rate to achieve high efficiencies. We have achieved initial active-area efficiency of 13.0% and 11.8% with a-Si:H/ $\mu$ c-Si:H double-junction and a-Si:H/a-SiGe:H/ $\mu$ c-Si:H triple-junction structures, respectively. Although the efficiency of the triple-junction cell is lower than that of the double-junction cell due to the complexity of cell structure, we believe the triple-junction cell will have a better chance to achieve higher stable efficiency by optimizing the cell structure and deposition conditions. In order to obtain a lower cost than that for the current a-Si:H/a-SiGe:H/a-SiGe:H triple-junction technology, we need to reduce the deposition time. For this purpose, modified VHF glow discharge is used to deposit intrinsic  $\mu$ c-Si:H at high deposition rates of  $\sim 3$ -10 Å/s. The best a-Si:H/ $\mu$ c-Si:H double-junction cell with an initial active-area efficiency of 12.3% has been achieved with a  $\mu$ c-Si:H deposition time of 50 minutes. We will also address several fundamental issues. Controlling the plasma parameters in order to produce compact  $\mu$ c-Si:H layers and suppress post-deposition impurity diffusion is key for high rate deposition. We have successfully solved this problem by optimizing deposition conditions. SIMS analyses of  $\mu$ c-Si:H layers deposited under different conditions revealed the correlation of ambient degradation and impurity diffusion. The low open-circuit voltage ( $V_{oc}$ ) is another drawback of  $\mu$ c-Si:H solar cells. The thickness dependence of cell performance showed the non-uniform growth of crystallites along the growing direction. This could contribute to the lower  $V_{oc}$ . Therefore, controlling the crystallite distribution by profiled H<sub>2</sub> dilution should be an effective method of improving cell performance.

#### 4:00 PM A4.2

**ELECTRONIC PROPERTIES OF MICROCRYSTALLINE SILICON INVESTIGATED BY PHOTOLUMINESCENCE SPECTROSCOPY ON FILMS AND DEVICES.** Reinhard Carius, Tsvetelina Merdzhanova, Friedhelm Finger, Institute of Photovoltaics, Forschungszentrum Jülich GmbH.

Plasma enhanced chemical vapour deposition (PE-CVD) is at present the most prominent method for preparation of microcrystalline silicon ( $\mu$ c-Si:H) as this technique is well established for manufacturing device grade amorphous silicon films. Recently, a significant progress in the material and device quality prepared by HW-CVD has been achieved by lowering the substrate temperature to values typically used in PE-CVD processes. Microcrystalline solar cells with this material as intrinsic layer show similar efficiencies as for PE-CVD material. Moreover, very similar electronic and device properties are observed, such as the decrease (increase) of the dark conductivity ( $V_{oc}$ ) with decreasing crystalline volume fraction. These effects are not understood and particularly the high  $V_{oc}$  of more than 590 mV obtained for a HW-CVD cell at a still high fill factor and current density is of current interest. These issues have been addressed by careful investigation of the states at the band edges by photoluminescence spectroscopy (PL) on well characterized samples. In particular we investigated the effect of these states on the splitting of the quasi-Fermi-level by monitoring  $V_{oc}$  and the photoluminescence energy ( $E_{PL}$ ) as a function of temperature and generation rate. We find a simultaneous increase of  $V_{oc}$  and  $E_{PL}$  with increasing ratio of photo- to dark current density for all HW- and PE-CVD samples. The results are consistent with a reduced defect density and reduced density of tail states due to hydrogen passivation and structure relaxation for microcrystalline silicon prepared close to the transition to amorphous growth irrespective of the preparation method.

#### 4:15 PM \*A4.3

**AMORPHOUS AND MICROCRYSTALLINE SILICON SOLAR CELLS ON TEXTURED ZINC OXIDE: FROM LABORATORY CONCEPTS TOWARDS LARGE AREA MODULES.** Bernd Rech, Joachim Müller, Tobias Repmann, Oliver Kluth, Tobias Roschek, Helmut Stiebig, Wolfgang Appenzeller, Institute of Photovoltaics, Forschungszentrum Jülich, Jülich, GERMANY.

Microcrystalline silicon ( $\mu$ c-Si:H) combines the advantages of amorphous Si (a-Si:H) and its technology with the stability and long wavelength spectral sensitivity of crystalline Si. In view of a cost-effective mass production of solar cells incorporating  $\mu$ c-Si:H films, high deposition rates and scalability to large areas have to be demonstrated. Moreover, adapted light trapping schemes are essential prerequisites. We present a comprehensive study of  $\mu$ c-Si:H single junction and a-Si:H/ $\mu$ c-Si:H stacked solar cells prepared by plasma-enhanced chemical vapour deposition (PECVD) at 13.56 MHz excitation frequency. As a first step cell development was performed in a small area PECVD reactor showing the relationship between deposition process and resulting solar cell performance. Subsequent up-scaling to a substrate area of 30x30 cm<sup>2</sup> confirmed the scalability to large area reactors. For an efficient light trapping we focus on textured ZnO:Al films prepared by sputtering and post deposition wet chemical etching. These films were optimised with respect to conductivity, transparency and film structure, the latter one controlling the surface texture obtained after etching. Applied in solar

cells these substrates introduce excellent light trapping and high open-circuit voltages are maintained. The ZnO development was initially performed on small areas using rf-sputtering from ceramic targets. For the up-scaling to 30x30 cm<sup>2</sup> we additionally investigated high rate mf-sputtering from metallic Zn targets in dynamic mode. A-Si:H/ $\mu$ c-Si:H tandem cells developed on textured ZnO coated glass yielded stable efficiencies up to 11.2% (cell area: 1 cm<sup>2</sup>). First solar modules were prepared completely in-house (including laser scribing) and yielded initial module efficiencies of 10.6% and 9.2% for aperture areas of 64 cm<sup>2</sup> and 676 cm<sup>2</sup>, respectively.

#### 4:45 PM A4.4

**MICRO-RAMAN MEASUREMENTS OF MIXED-PHASE HYDROGENATED SILICON SOLAR CELLS.** Jessica M. Owens and Daxing Han, Dept of Phys & Astronomy, Univ of North Carolina at Chapel Hill, Chapel Hill, NC; Baojie Yan, Jeffrey Yang, Kenneth Lord, and Subhendu Guha, United Solar Systems Corp., Troy, MI.

The open-circuit voltage ( $V_{oc}$ ) of mixed-phase hydrogenated-silicon solar cells has been found to increase after light soaking; microstructural change has been proposed to account for the light-induced  $V_{oc}$  enhancement. However, recent studies by Raman Spectroscopy and X-Ray Diffraction found no observable change before and after light soaking. In this study, we used micro-Raman to further investigate the mixed-phase solar cells. A low laser power was used to avoid possibility of laser-induced crystallization. The measurements were made using a laser beam of 3  $\mu$ m in diameter on solar cells with an area of 0.25 cm<sup>2</sup>. For a cell with  $V_{oc} = 0.981$  V, four scans on different locations of the cell showed typical broad Gaussian lineshapes around 480 cm<sup>-1</sup> for amorphous material. A cell with  $V_{oc} = 0.674$  V showed a sharp Lorentzian peak around 516 cm<sup>-1</sup> for most scans, indicative of a large microcrystalline volume fraction. However, for the cells with  $V_{oc} = 0.767$  and 0.748 V, one of the eight scans exhibited both a broad Gaussian lineshape around 480 cm<sup>-1</sup> and a sharp peak around 516 cm<sup>-1</sup>, indicating a mixed-phase material. The cell with  $V_{oc} = 0.767$  V was further systematically scanned in steps of 600  $\mu$ m for a total of 20 different positions. Most spectra showed a typical Gaussian lineshape around 480 cm<sup>-1</sup>, several spectra showed a hint of a microcrystalline shoulder around 512 cm<sup>-1</sup>, and one spectrum showed a distinct microcrystalline peak. From the study, we find that the crystallite distribution in the mixed-phase material is very non-uniform even within a mm dot. This result and other new findings provide further insight into the light-induced phenomenon of the mixed-phase solar cells.

SESSION A5: POSTER SESSION  
GROWTH I  
Tuesday Evening, April 22, 2003  
8:00 PM  
Salon 1-7 (Marriott)

#### A5.1

**HELIUM VERSUS HYDROGEN DILUTION OF SILANE IN THE DEPOSITION OF POLYMORPHOUS SILICON FILMS : EFFECTS ON THE STRUCTURAL AND TRANSPORT PROPERTIES.** O. Saadane, S. Lebib, A.V. Kharchenko, V. Suendo, C. Longeau and P. Roca i Cabarrocas.

Hydrogen dilution of silane has been widely used for the deposition of thin silicon films. When the plasma is operated under conditions close to powder formation, hydrogen-silane mixtures gives hydrogenated polymorphous silicon films (pm-Si:H). However, when incorporating the material in PIN devices, hydrogen reduces the tin-oxide substrate and makes electronic defects at the P/I interface. This is why the effect of helium dilution on the structural and transport properties of pm-Si:H layers were studied and compared to those of pm-Si:H samples prepared by the decomposition of a silane-hydrogen mixture. Plasma diagnostics were achieved during deposition of the layers to determine the role of hydrogen versus helium in the dynamics of cluster formation. We found that helium dilution drastically reduces the RF power needed to achieve the same deposition rate as in hydrogen dilution. IR spectroscopy and hydrogen effusion experiments shown that hydrogen bonding and content are quite different in each process. The films produced from He-dilution have a lower hydrogen content, which we try to link to the nature of the clusters and crystallites produced in the plasma. Transport properties were investigated by means of steady state photoconductivity and steady state photocurrent grating techniques. The density of states was estimated from MPC and CPM measurements. These properties were measured in the as-deposited, light-soaked and annealed states of the samples. Interestingly enough, despite of their higher deposition rate, the films produced from silane-helium mixtures present similar optoelectronic properties as the films produced from silane-hydrogen. On the other hand, we have observed different behaviours of the evolution of the transport properties of the layers (He or H<sub>2</sub> diluted) upon LS/annealing cycles. In this contribution we aim to draw a

detailed picture of the properties of pm-Si:H films based on the correlation between plasma diagnostics, structural and transport properties.

#### **A5.2**

**MICROCRYSTALLINE SILICON GROWN BY ELECTRON CYCLOTRON RESONANCE CHEMICAL VAPOUR DEPOSITION AT 80 DEGREE CELSIUS.** Ian Y.Y. Bu, A.J. Flewitt, C. Ducati, J. Robertson, University of Cambridge, Dept of Engineering, Cambridge, UNITED KINGDOM; M. Powell, Phillips Research Lab, Redhill, UNITED KINGDOM; and W.I. Milne, University of Cambridge, Dept of Engineering, Cambridge, UNITED KINGDOM.

Microcrystalline silicon thin films were deposited using a ECR plasma at 80 degree celsius. These films are suitable for the production of TFTs on plastic substrates. Films were characterised using Raman spectroscopy, high-resolution transmission electron microscopy and conductivity measurements. The results show that thin film properties are strongly dependent on the deposition conditions, chamber pressure, hydrogen dilution and RF power.

#### **A5.3**

**CHARACTERIZATION OF NANOCRYSTALLINE SILICON FILM GROWN BY LEPECVD FOR PHOTOVOLTAIC APPLICATIONS.** S. Binetti, M. Bollani, M. Acciarri, A. Arcari, S. Pizzini, INFN and Dept. of Material Science, Università di Milano-Bicocca, Milano, ITALY; H. Von Känel, INFN and Dept. of Physics, Politecnico di Milano, Como, ITALY.

Crystalline silicon is one of the most extensively used photovoltaic (PV) materials, but its high cost still limits terrestrial applications. One way to overcome this problem is to reduce the material cost, using, for instance, thin silicon films deposited on low cost substrates. This is a viable option only, however, if the quality of the deposited material is such that solar cells with reasonably high efficiency can be obtained. The deposition procedure should hence be able to provide films with the requested features at a low cost. Plasma enhanced chemical vapor deposition (PECVD) has been extensively used for the deposition of thin films. Its major advantage is the ability to deposit good quality layers at reasonable rates and at low substrate temperatures, as required for PV applications. In this work we have grown thin films of nanocrystalline (nc) silicon for solar cell applications using a new PECVD process based on an arc discharge plasma with inherently low ion energies, called LEPECVD (Low energy PECVD). This process permits to increase the intensity of the plasma discharge in the growth region and thus to achieve higher growth rates and while avoiding any ion-induced damage of films. The electrical properties of the LEPECVD grown films were studied as a function of the deposition parameters (substrate temperature, growth rate, hydrogen dilution), by Hall effect, resistivity and surface photovoltage measurements, while the optical ones were investigated by photoluminescence spectroscopy. The influence of process parameters on the structure of nc-Si films have been evaluated by Raman Spectroscopy and SEM analysis. The results of this work allowed us to identify the process requirements suitable for the growth of nc-grains in an amorphous matrix on both an oxidized silicon and on a zinc oxide covered glass substrate. The electrical and optical properties of these films are promising for PV applications.

#### **A5.4**

**INFLUENCE OF SUBSTRATE TEMPERATURE AND DILUTION RATIO ON THE PROPERTIES OF MICROCRYSTALLINE SILICON THIN FILMS GROWN BY HOT-WIRE CHEMICAL VAPOR DEPOSITION.** H.R. Moutinho, C.-S. Jiang, B. Nelson, Y. Xu, J. Perkins, K.M. Jones, M.J. Romero, and M.M. Al-Jassim, National Renewable Energy Laboratory, Golden, CO.

Microcrystalline silicon (mc-Si) has been receiving special attention at present because it is much cheaper to produce than crystalline silicon, and do not present the degradation problems as amorphous silicon (a-Si). Furthermore, because of its bandgap, it can be used in tandem cells with a-Si. Among the deposition methods, hot-wire chemical vapor deposition (HWCVD) has the advantage of higher deposition rates when compared to other conventional techniques, such as plasma-enhanced CVD. In the present work, we deposit mc-Si films at different temperatures (200° - 400°C) and dilution ratios between hydrogen and silane (10-100 sccm), and study the relation between these two parameters, and their influence on the properties of the films. We also study the effects of a very thin seed layer, deposited with high concentration of hydrogen, and the use of different substrates (Si and glass). The films are characterized using several techniques, such as: atomic force microscopy, grazing-angle incidence X-ray diffraction, Raman spectroscopy, and transmission and scanning electron microscopy. We will correlate the growth conditions with properties such as crystallinity, surface morphology, ratio between crystalline and amorphous phases, and development of the microstructure from the interface film/substrate to the film surface.

#### **A5.5**

**STRUCTURAL AND DEPOSITION CHARACTERISTICS OF AMORPHOUS AND MICROCRYSTALLINE Si:H FILMS DEPOSITED AT LOW TEMPERATURE WITH Si-H, Si-H-He AND Si-H-F CHEMISTRY.** Young-Bae Park, Harvard University, Applied Physics Dept, Cambridge, MA; Dong-Wha Park, Dept of Chemical Engineering, Inha University, Incheon, KOREA; Shi-Woo Rhee, Department of Chemical Engineering, Pohang University of Sci. and Technol., Pohang, KOREA.

Silicon films with the nanometer-scale microstructure are widely used as the active and contact layers in thin film transistor (TFT) and solar cell applications. The Si:H, Si:H(He) and Si:H:F films deposited on c-Si, Corning 7059 glass, thermally-grown SiO<sub>2</sub>, and SiN<sub>x</sub>:H at low temperatures (25 - 450°C by remote plasma enhanced chemical vapor deposition (RPECVD) from SiH<sub>4</sub>-H<sub>2</sub>/He and Si<sub>2</sub>H<sub>6</sub>-SiF<sub>4</sub>-H<sub>2</sub> gas mixtures were characterized using quadrupole mass spectrometer (QMS) and optical emission spectroscopy (OES) for the gas phase composition and atomic force microscopy (AFM), high resolution transmission electron microscopy (HRTEM), Raman spectroscopy, X-ray diffractometer (XRD), UV-visible spectrometer, and FT-IR for the thin film characterization, respectively. The Si:H and Si:H:F films were found to be a mixture of amorphous and nanocrystalline phases while most Si:H(He) films had the amorphous phase. The polycrystalline fraction of the as-deposited films was ranged from 0 to 85% depending on gas phase chemistry. The microcrystalline phase exhibited the columnar structure with needle-like grains. The grain size was ranged from 2 to 50 nm. The effects of substrates and deposition parameters on crystallinity, grain shape, size, preferred orientation, and polycrystalline fraction have been studied. The roles of hydrogen, helium and fluorine were elucidated to explain low temperature crystallization and grain boundary passivation processes. The grain sizes measured by different characterization techniques were also compared.

#### **A5.6**

**STRUCTURAL CHANGES IN NANOCRYSTALLINE SILICON.** Wonsok Kim, Jongmin Lee, Janghee Lee, Jong H. Lyou, Korea Univ, Dept of Applied Physics, Graduate School of Natural Science, Seoul, KOREA; Eui-Kwan Ko, Korea Basic Science Institute, Seoul, KOREA.

We have measured structural and optical properties for nanocrystalline silicon thin films deposited by rf-magnetron sputtering and characterized the microstructure of the films with the measurements of scanning electron microscopy, transmission electron microscopy, x-ray diffraction, and Raman scattering. Amorphous and nanocrystalline silicon thin films have been widely deposited with plasma enhanced chemical vapor deposition, hot-wire chemical vapor deposition, and reactive magnetron sputtering (RMS). Especially, the RMS method is useful for the deposition of nanocrystalline silicon, because it requires a low level of reactive gas pressure for the deposition to produce few columns in the microstructure. We have controlled nanocrystals with hydrogen content: we recognize that the nanocrystals are first formed when the ratio (Ar : H<sub>2</sub>) is 1. We determine size and fraction of nanocrystals in nanocrystalline silicon: the size of nanocrystals is about 6 to 8 nm and the fraction is about 70%. The nanocrystalline silicon consists of not only nano-sized crystallites but also amorphous states. The fraction of nanocrystals is measured with Raman scattering and estimated with a two-component Lorentzian plot. Meanwhile, the microstructure of nanocrystalline silicon is understood with scanning electron microscopy. Combined results of SEM micrographs with Raman scattering spectra identify columns appeared on the micrographs with amorphous networks. The results also indicate that the columns regularly disappear with increasing hydrogen content for the deposition of nanocrystalline silicon films. Thus we oversee that the hydrogen dilution helps the amorphous networks removed, but high density of reactive gas molecules makes the microstructure of nanocrystalline silicon to a columnar structure. We conclude that the hydrogen dilution employed with the level of less reactive gas molecules relaxes the amorphous networks in which grain boundaries as well as amorphous tissues and islands are incorporated.

#### **A5.7**

**ELECTRICAL PROPERTIES OF PHOSPHORUS-DOPED AND BORON-DOPED NANOCRYSTALLINE GERMANIUM THIN FILMS.** William B. Jordan and Sigurd Wagner, Princeton Univ, Dept of Electrical Engineering, Princeton, NJ.

The structure (nanocrystalline vs. amorphous) of doped germanium thin films is a strong function of both temperature and source gas ratios. Intrinsic films grow *nanocrystalline* between 150-250°C, *amorphous* around 250-300°C, and *nanocrystalline* again above 300°C. The doped films generally followed this same temperature dependence of phase transition, although high doping concentrations

cause films to grow amorphous. We provide an overview of the electrical and structural properties of the doped Ge films throughout their nc/a/nc phase range, and over varied dopant concentrations. We deposited thin films of nc-Ge:H on Corning 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 source gases used for the p- and n-type dopants were B<sub>2</sub>H<sub>6</sub> and PH<sub>3</sub>, respectively. The GeH<sub>4</sub> and H<sub>2</sub> flow rates were held constant, while the dopant gas flow rates and the substrate temperature were varied and their effects on the growth rate, crystallinity, dark conductivity, and thermal activation energy were measured. Crystallinity was determined by UV/visible reflectance. The H, B, and P concentrations in the films were measured by secondary ion mass spectroscopy (SIMS). The thickness of the doped nc-Ge:H films was approximately 500 Å. Growth rates for the intrinsic and doped films, mostly a function of the hydrogen dilution, ranged between 0.20 and 0.30 Å/sec. Dark conductivity of the intrinsic nc-Ge:H films deposited between 150-200°C was approximately 1E-4 S/cm, while the dark conductivity of the n- and p-doped films was approximately three to four orders of magnitude higher. A Fermi level swing of approximately 500 meV between the n-doped and p-doped films deposited at 150-200°C is inferred from the electrical conductivity data. At deposition temperatures above 310°C, intrinsically-grown nc-Ge:H films were found to be very strongly p-type, with an electrical conductivity of approximately 10 S/cm and a thermal activation energy of about 0.040 eV.

#### A5.8

Abstract Withdrawn.

#### A5.9

PECVD OF SILICON THIN FILMS FOR SOLAR CELLS USING ALTERNATIVE SILICON SOURCES. R. Terasa, M. Albert, J.W. Bartha, TU Dresden, Institut fuer Halbleiter- und Mikrosystemtechnik, Dresden, GERMANY; A.I. Kosarev, SSE Department, A.F. Ioffe Physical-Technical Institute, St.-Petersburg, RUSSIA.

Whereas usually silane (SiH<sub>4</sub>) is used for the plasma deposition of amorphous and microcrystalline silicon thin films for solar cells, our aim is to replace the toxic, highly flammable and relatively expensive gas silane by a less dangerous and cheaper silicon source. We concentrate on two silicon sources silicon tetrachloride (SiCl<sub>4</sub>) and tetramethylsilane (Si[CH<sub>3</sub>]<sub>4</sub>), which are liquid at room temperature but can be easily converted into the gas phase. While Beyer et al.[1] found results relatively similar to the silane process using SiCl<sub>4</sub>/H<sub>2</sub> or SiH<sub>2</sub>Cl<sub>2</sub>/H<sub>2</sub> mixtures in a high pressure regime (p ~200 Pa) - regarding deposition rates, microcrystalline/amorphous silicon transition, doping efficiency - the present experiments using SiCl<sub>4</sub>+H<sub>2</sub> in a low pressure, low temperature regime (p ~20-50 Pa, T ~400...480 K) surprisingly show decreasing growth rates for microcrystalline silicon with increasing SiCl<sub>4</sub> concentrations in the gas mixture. For all used substrate temperatures a silicon deposition could not be realized when the SiCl<sub>4</sub> concentration was higher than 10%. Using the Raman spectroscopy, all deposited films showed crystalline fractions between 30 and 60%. A significant dependence of the crystallinity in relation to the silicon tetrachloride partial pressure in the feed gas was not detected. TEM investigations showed the absence of an amorphous incubation layer at the substrate/film interface, which would make this process attractive for the deposition of very thin microcrystalline films. Furthermore, a completely amorphous layer could not be deposited under the current process conditions. XPS and SIMS measurements of the deposited films showed chlorine concentrations < 3% within the silicon structure. First results for silicon deposition from (Si[CH<sub>3</sub>]<sub>4</sub>)/H<sub>2</sub> mixtures will be presented. [1] W. Beyer et al., PV in Europe - From PV Technology to Energy Solutions, Rome 2002.

#### A5.10

EVOLUTION OF CRYSTALLINITY IN MIXED-PHASE (a+μc)-Si:H AS DETERMINED BY REAL TIME SPECTROSCOPIC ELLIPSOMETRY. A.S. Ferlauto, G.M. Ferreira, R.J. Koval, J.M. Pearce, C.R. Wronski, and R.W. Collins, Materials Research Institute, Center for Thin Film Devices and Department of Physics, Pennsylvania State University, University Park, PA; M.M. Al-Jassim and K.M. Jones, National Renewable Energy Laboratory, Golden, CO.

In the rf plasma-enhanced chemical vapor deposition (PECVD) process, the optimum hydrogenated amorphous silicon films (a-Si:H) for the intrinsic layers of solar cells are obtained at the *maximum* possible value of the H<sub>2</sub>-dilution ratio  $R=[H_2]/[SiH_4]$  sustainable without entering the mixed-phase amorphous + microcrystalline [(a+μc)-Si:H] film growth regime. Furthermore, it appears that the optimum μc-Si:H i-layers for solar cells are deposited using the *minimum* possible R value while maintaining predominantly μc-Si:H, in other words without entering the (a+μc)-Si:H film growth regime. Owing to the critical importance of Si:H deposition near the boundaries defining the (a+μc)-Si:H growth regime, the development

and application of in situ, real time techniques that can provide the phase evolution of such films is of critical importance. We have adopted real time spectroscopic ellipsometry (RTSE) in the rotating compensator configuration for this purpose. Using a novel virtual interface analysis approach, RTSE spectra on Si:H thin films that cross the a→(a+μc) and (a+μc)→μc transitions during growth can be interpreted in detail to extract the bulk layer thickness at which the microcrystallites first nucleate from the amorphous phase [the a→(a+μc) transition], as well as the thickness at which evolving microcrystallites make contact and coalesce [the (a+μc)→μc transition]. In addition, the volume fraction of crystallites  $f_{μc}$  within the top ~30Å of the film can be deduced as a function of bulk layer thickness; as a result, a depth profile in  $f_{μc}$  for the final film can be obtained. The outcome of such RTSE analyses, expressed succinctly in terms of the nucleation densities and cone angles for the preferential growth of crystallites, is in excellent agreement with direct structural measurements. The origin of the "delayed" crystallite nucleation, in which nucleation occurs from the bulk a-Si:H film after a critical thickness (rather than directly from the substrate) remains an important issue that will also be addressed in this paper.

#### A5.11

P- AND N-TYPE MICROCRYSTALLINE SiC FABRICATED BY RF PLASMA CVD WITH ETHANE GAS. T. Toyama, Y. Nakano, T. Kosuge, A. Asano, H. Okamoto, Osaka Univ, Dept of Physical Science, Graduate School of Engineering Science, Toyonaka, JAPAN.

P- and n-type microcrystalline Si<sub>1-x</sub>C<sub>x</sub> (μc-SiC) films with x ≥ 0.1 are fabricated by a conventional rf (13.56 MHz) plasma CVD method with a use of a new carbon source of C<sub>2</sub>H<sub>6</sub> at low substrate temperatures on a glass substrate. Highly conductive p- and n-type μc-SiC is one of the most promising material for optoelectronic devices such as thin-film solar cells [1] and light-emitting diodes [2]. The μc-SiC were formerly developed by electron cyclotron resonance (ECR) plasma CVD with a CH<sub>4</sub> gas source [1,2], however, μc-SiC deposited by ECR plasma CVD has some disadvantages especially significantly slow deposition rate of ~0.01 nm/sec or less. On the other hand, some trials have been performed for fabrication of μc-SiC films by conventional rf (13.56 MHz) plasma CVD with a mixture of SiH<sub>4</sub> and CH<sub>4</sub> gases. However, they have not shown an excellent results because the crystalline volume fraction of SiC films made by rf plasma CVD markedly decreases with an increase in carbon content of the SiC film even if the carbon content is as low as or slightly over 3 at.% [3]. Here we will demonstrate the results on p- and n-type μc-SiC fabricated by rf plasma CVD with a new carbon source of C<sub>2</sub>H<sub>6</sub> gas [4]. Typical substrate temperature was 230°C. The deposited μc-SiC with a carbon content of over 10 at.% shows high conductivities of on the order of 10<sup>-3</sup> Scm<sup>-1</sup> as well as an optical energy gap, E<sub>04</sub>, of more than 2.0 eV. Additionally the deposition rate is ~0.1 nm/sec or higher. [1] Y. Hattori et al., Proc. 19th IEEE PVSC (1987) p.25. [2] D. Kruangam et al., J. Non-Cryst. Solids, 97 & 98 (1987) 293. [3] T. Wada et al., Sol. Energy Mat. & Sol. Cells, 74 (2002) 533. [4] T. Itoh et al., J. Non-Cryst. Solids, 299-302 (2002) 880.

#### A5.12

HIGH-RATE (> 1 NM/S) MICROCRYSTALLINE SILICON FILM GROWTH STUDIED BY IN SITU SPECTROSCOPIC ELLIPSOMETRY AND ATTENUATED TOTAL REFLECTION INFRARED SPECTROSCOPY. I.J. Houston, J. Hong, P.J. van den Oever, W.M.M. Kessels, and M.C.M. van de Sanden, Dept. of Applied Physics, Eindhoven Univ. of Technology, Eindhoven, THE NETHERLANDS.

The growth of μc-Si:H deposited using the expanding thermal plasma (ETP) technique has been extensively studied using in situ spectroscopic ellipsometry (SE). Previous investigations using X-ray diffraction (XRD) and Raman spectroscopy have shown that this technique is capable of producing material with a crystalline fraction of over 60% at growth rates of over 2 nm/s. In situ spectroscopic ellipsometry was used to monitor the evolution of the bulk thickness and surface roughness of the material, as well as the optical properties of the film. The results from this were verified using atomic force microscopy (AFM). SE has also been used to investigate the occurrence of an amorphous incubation layer which forms on the surface prior to μc-Si:H growth. This has been done for various conditions where the hydrogen dilution R (= [H<sub>2</sub>]/[SiH<sub>4</sub>]) was varied. In particular, SE has shown that no significant incubation layer is present for depositions using an R value of 200. This has been confirmed by transmission electron microscopy (TEM) which shows that any amorphous incubation layer in this case (which results in our most crystalline material) is limited to a few nanometers. Depth-profiling by means of in situ attenuated transmission reflection Fourier transform infra-red (ATR-FTIR) spectroscopy has also been applied to study the manner in which hydrogen is bonded within the bulk and on the surface of the material. ATR-FTIR has shown that surface-like SiH<sub>x</sub> modes occur within the bulk of the μc-Si:H material and this is indicative of the characteristic columnar growth associated

with microcrystalline material. These new results confirm that the ETP technique is capable of producing microcrystalline material with different microcrystalline fractions (ranging from entirely amorphous material up to almost polycrystalline material) at high growth rates which is comparable to material that is grown using other techniques.

#### **A5.13**

**POLYMORPHOUS SILICON FILMS PRODUCED IN LARGE AREA REACTORS BY PECVD AT 27.12 MHZ AND 13.56 MHZ.**  
H. Aguas, L. Raniero, E. Fortunato, R. Martins, Univ Nova de Lisboa, Fac de Ciencias e Tecnologia, Dep de Materiais, Caparica, PORTUGAL; P. Roca i Cabarrocas, LPICM, Ecole Polytechnique, Palaiseau, FRANCE.

Polymorphous silicon has gradually earned the attention of the scientific community due to their improved transport properties and stability when compared to the standard amorphous silicon material. In spite of this growing interest, electronic grade material was obtained only at very small growth rates ( $< 1 \text{ \AA/s}$ ), using an excitation frequency of 13.56 MHz. This work presents a study performed concerning the deposition of polymorphous silicon at excitation frequency of 27.12 MHz in a large area PECVD reactor. Apart from that, large area films produced at 13.56 MHz were also investigated, aiming to compare their performances with the ones of the films produced at 27.12 MHz. The plasma was characterised by impedance probe measurements, aiming to identify the plasma conditions that lead to produce polymorphous films, under quasi-isothermal conditions. The films produced were characterised by spectroscopic ellipsometry, infrared and Raman spectroscopy and hydrogen exodiffusion experiments, which are techniques that permit the structural characterisation of the polymorphous films and to study the possible differences between the films deposited at 27.12 MHz and 13.56 MHz. Conductivity and density of states measurements were also performed to determine the transport properties of the films produced. The set of data obtained show that by using the 27.12 MHz excitation frequency the hydrogen dilution needed to produce polymorphous films can be reduced by more than 50%, and the power density has also to be reduced, otherwise the films obtained are microcrystalline. Apart from that growth rates above  $3.1 \text{ \AA/s}$  were obtained using deposition pressures of 240 Pa, being the films more dense and chemical stables, with improved transport properties than the usually ones obtained with the standard 13.56 MHz.

#### **A5.14**

**SURFACE ROUGHNESS STUDY OF LOW-TEMPERATURE PECVD a-Si:H.** George T. Dalakos, General Electric Global Research Center, Niskayuna, NY; Joel L. Plawsky, Department of Chemical Engineering, Rensselaer Polytechnic Institute Troy, NY; Aleksey Filin, Peter D. Persans, Department of Physics, Rensselaer Polytechnic Institute, Troy, NY.

Surface topology of a-Si:H thin films, deposited at  $75^\circ\text{C}$  by Plasma-enhanced Chemical Vapor Deposition (PECVD) has been examined using rare gas(He and Ar)/silane feedstock mixtures under different substrate bias conditions. Notable differences in the surface roughness evolution are shown for films deposited in cathodic versus anodic mode where the substrate is placed on the powered and grounded electrode respectively. Smooth and apparently featureless surfaces result from deposition on the RF powered electrode, upon which a self-bias induces high-energy ion bombardment. Rougher surfaces result from films deposited on the anode. These anodic films show that, after a transition period, surface roughness linearly grows with processing time, exhibiting mounded-type growth as evidenced by power spectral density functions of surface height measurements. Growth of this nature has not been previously reported for a-Si:H. Mounded growth as a linear function of time is not predicted by growth models that assume directional deposition conditions and sticking coefficients less than one. We will discuss our observations on terms of shadow growth assuming the film precursor sticking coefficient of one and random angle approach of film precursor species.

#### **A5.15**

**STRUCTURAL CHARACTERIZATIONS OF MICROCRYSTALLINE SILICON SOLAR CELLS FABRICATED BY CONVENTIONAL RF-PECVD.** Liwei Li, Roland A. Levy, New Jersey Institute of Technology, Department of Physics, Newark, NJ; Yuan-Min Li, J.A. Anna Selvan, Alan E. Delahoy, Energy Photovoltaics, Inc., Lawrenceville, NJ.

While  $\mu\text{-Si}$  materials and solar cells have recently received much attention, there has been a relative lack of direct structural characterizations of  $\mu\text{-Si}$  i-layers (absorbers) on actual  $\mu\text{-Si}$  solar cells as opposed to stand-alone films prepared on substrates other than textured TCO. To help understand and optimize the  $\mu\text{-Si}$  i-layer growth process (and the resulting device performance), we have undertaken a detailed study on the micro-crystallinity of the i-layers ( $\mu\text{-Si}$  or mixed-phase Si absorbers) of a series of p-i-n type single

junction solar cells made under a wide range of deposition conditions. The  $\mu\text{-Si:H}$  i-layers (along with p and n layers) were deposited by glow discharge of silane diluted by hydrogen in a single chamber, batch process type, conventional RF-PECVD system. These solar cells were grown on commercial grade  $\text{SnO}_2/\text{sodalime-glass}$  superstrates at low temperatures ( $< 200^\circ\text{C}$ ). Raman scattering spectroscopy with near-infrared laser as light source and x-ray diffraction (XRD) micro-structural investigations were carried out on these  $\mu\text{-Si:H}$  solar cells (without the Al back contact). The overall crystallinity was presented in terms of the ratio ( $I_c/I_a$ ) of intensities of Raman shift at around  $520$  and  $480 \text{ cm}^{-1}$ , respectively. We find that the crystallinity signatures of  $\mu\text{-Si:H}$  i-layers are strongly correlated with growth conditions and device parameters. In particular, structural data reveal the critical importance of the initial nucleation process, on an amorphous-Si alloy surface, in determining the subsequent growth and properties of the bulk of i-layer and its device performance, including device stability against light soaking (as mixed-phase cells suffer severe light-induced degradation). Our data support the notion that stable, high quality  $\mu\text{-Si}$  i-layers are grown near the "edge" of microcrystalline-to-amorphous phase transition. Such optimal solar cells exhibit moderate Raman  $I_c/I_a$  values. We also show the utility of Raman data in exploring deposition non-uniformity issues over the  $12''\times 15''$  substrates.

#### **A5.16**

**HOLLOW EFFECT ENHANCED RF GLOW PLASMA AND ITS APPLICATION TO THE FAST DEPOSITION OF MICROCRYSTALLINE SILICON.** Toshihiro Tabuchi, Masayuki Takashiri, Yasumasa Toyoshima, Hiroyuki Mizukami, Komatsu Ltd, Research Division, Electronic Material Research Department, Kanagawa, JAPAN.

A hollow effect enhanced RF glow plasma excitation technique has been newly developed. In this technique, the reactor is divided into a capacitively-coupled RF glow discharge space and processing space by the anode electrode, which has a hollow structure and is placed between the cathode and the substrate. After introducing hydrogen gas into the chamber and applying RF power to the electrode, high intensity plasma emission is observed near and inside the hollow structure attached to the anode electrode. The application of this discharge type for semiconductor processing has been studied in the case of plasma enhanced chemical vapor deposition (PECVD) of hydrogenated microcrystalline silicon thin films. High crystallinity, photo-sensitivity and a maximum deposition rate of  $4.9 \text{ nm/s}$  can all be achieved at a plasma excitation frequency of 13.56MHz and a temperature of  $300^\circ\text{C}$ . Properties of this plasma are investigated by observation of the plasma emission pattern, optical emission spectral analysis and plasma potential. Comparative studies of plasma characteristics were carried out between our reactor and a normal PECVD reactor. In our apparatus, both the intensity of  $\text{SiH}^*$  and the plasma potential are higher than that of normal PECVD. The hollow anode enhanced RF glow plasma excitation technique is also shown to be promising for fast processing of device grade hydrogenated microcrystalline silicon thin films. Furthermore, by using hollow cathode excitation in addition to the hollow anode technique, plasma emission is further enhanced and fast deposition can be achieved under lower RF power compared to the hollow anode technique alone. **KEYWORDS:** hollow anode, plasma CVD, RF glow discharge, high-density plasma, microcrystalline silicon, thin film, photo sensitivity, fast deposition, low temperature, hollow cathode.

#### **A5.17**

**DEPOSITION OF AMORPHOUS AND MICROCRYSTALLINE SILICON FILMS USING LADDER-SHAPED ELECTRODE.** Tatsuyuki Nishimiya, Hiroshi Sonobe, Yoshiaki Takeuchi, Matsuhei Noda, Akira Yamada, Hiromu Takatsuka, Nagasaki Research & Development Center, Mitsubishi Heavy Industries, Ltd., Nagasaki, JAPAN.

We have succeeded in getting high-deposition rate and high quality for preparing hydrogenated amorphous silicon (a-Si:H) films, as well as micro-crystalline silicon (mc-Si) films, by Very-high-frequency (VHF) plasma CVD using a ladder-shaped electrode. Recently, VHF plasma CVD technique has become one of the topics in the field of the fabrication of solar cell and thin film transistors, because its high plasma density enables high-speed deposition. However, in the large area deposition, which is needed in the application of commercial production, the effective gas flow rate fed into the plasma region limits the deposition rate and the film qualities because the gas depletion condition leads to the degradation of the film quality. We have developed a VHF plasma CVD device using the ladder shaped electrode, which has an advantage over a conventional parallel-plate electrode in the controllability of the gas flow. The experiments were performed using a ladder-shaped electrode consisted of stainless-steel rods about  $550 \text{ mm} - 450 \text{ mm}$  in external dimension. The material gases were introduced into the plasma region between each rod of the electrode. By using the VHF-SiH<sub>4</sub> plasma at the frequency of 60MHz,



we got a-Si:H film at the averaged deposition rate of 0.7 nm/s  $\pm$  15.2% on 570x420 substrate with the ratio of photo conductivity/dark conductivity of 106. We also applied this electrode to fabricate the mc-Si film and succeed high-speed of 1.1 nm/s  $\pm$  13.2% using the plasma of SiH<sub>4</sub> diluted with H<sub>2</sub> at the frequency of 60 MHz. Furthermore, we employed this technique for fabricating the a-Si/mc-Si tandem solar cell of about 10% efficiency. It was demonstrated that this electrode is highly suitable for the production.

#### **A5.18**

**AMORPHIZATION OF ALPHA-QUARTZ CRYSTAL BY FAST ELECTRONS.** Ju-Yin Cheng, Department of Material Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY; Michael Treacy, NEC Laboratory USA, Inc., Princeton, NJ; Pawel Koblinski, Department of Material Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY.

We study the phase transition of alpha-quartz crystal using transmission electron microscopy. The single-crystalline phase of alpha quartz can be transformed into a completely amorphous phase by electron irradiation. However, the transformation is mediated with some topological crystalline state, which loses the long-range order of the parent crystalline phase. We monitored the dependence of the structure transition on electron dose in the microscope. Our results are based on the analysis of image variance in dark field. This study is a prerequisite of doing fluctuation electron microscopy for amorphous silica in high-angle dark field, since the first sharp diffraction peak (FSDP) for amorphous silica is located around 15-18 nm<sup>-1</sup>.

SESSION A6: POSTER SESSION  
GROWTH II  
Tuesday Evening, April 22, 2003  
8:00 PM  
Salon 1-7 (Marriott)

#### **A6.1**

**THE RELIABILITY OF MEASUREMENTS ON ELECTRON ENERGY DISTRIBUTION FUNCTION IN SILANE RF GLOW DISCHARGES.** Kuixun Lin, Xuanying Lin, Lingfei Chi, Chuying Yu, Yunpeng Yu, Department of Physics, Shantou University, Shantou, CHINA.

Plasma enhanced chemical vapor deposition in parallel-plate silane radio frequency glow discharges is the most widespread method in deposition of silicon-based thin films. To a large extent, the relation between plasma properties and material properties is still unknown. Electron energy distribution function (EEDF) in silane rf glow discharges is a key parameter for studying the spatial reaction process in a plasma and the surface reaction process on the substrate. EEDF is directly proportional to the second derivative of the probe I-V characteristics. Because of an amplifying effect of the unavoidable noises in the experimental probe I-V curves on the second derivative of the probe characteristics, it is very difficult to measure the EEDF accurately and relatively. It is the first time, so far as we know, to measure the EEDF parameters simultaneously by means of both the numerical and circuit derivative methods under the same discharge conditions on the same discharge equipment. The deviation between two groups of mean electron energy (E) and electron density (n<sub>e</sub>) obtained by the above different methods is within about 7%. This apparently improves the reliability of the measurements on the EEDF parameters.

#### **A6.2**

**HIGH RATE GROWTH OF MICROCRYSTALLINE SILICON BY VHF-PECVD FOR SOLAR CELLS.** Xiaodan Zhang<sup>a</sup>, Guofu Hou<sup>a</sup>, Feng Zhu<sup>a</sup>, Wenjuan Xiong<sup>a</sup>, Huidong Yang<sup>a,b</sup>, Chunyu Wu<sup>a</sup>, Junming Xue<sup>a</sup>, Ying Zhao<sup>a</sup>, Xinhua Geng<sup>a</sup> and Shaozhen Xiong<sup>a</sup>; <sup>a</sup>Institute of Photoelectronic Thin Film Device and Technology, Nankai University, Tianjin, CHINA; <sup>b</sup>Institute of Thin Films and Nano-materials, Wuyi University, Guangdong, CHINA.

High rate growth of hydrogenated microcrystalline silicon (mc-Si:H) thin films for solar cells is crucial for cost reduction. In this paper, very-high frequency plasma-enhanced chemical vapor deposition (VHF-PECVD) was employed to deposit microcrystalline silicon in order to increase the deposition rate. The relatively high pressure was combined with the relatively high excitation frequency to further improve the deposition rate. It was found that the photoelectronic properties and the deposition rates of the samples, under the condition of 60MHz and 180Pa, depended on the plasma power and hydrogen dilution ratio of silane. As a result, with the increase of silane concentration SC ([SiH<sub>4</sub>]/[SiH<sub>4</sub> H<sub>2</sub>]), the deposition rate varied from 1.5 A/s to above 20 A/s, accordingly crystalline fraction increased from 30% to 60%. The phase transition from a-Si to mc-Si was observed when the silane concentration was around 7%. In

addition, the dependence of the deposition rate and photo-electronic properties of the samples on working pressure were studied. The material properties of a series of microcrystalline silicon films were analyzed by Raman scattering, x-ray diffraction (XRD) and atom force microscopy (AFM), respectively. Thin film solar cells using microcrystalline silicon materials deposited at high deposition rate were also fabricated. Some interesting results were discussed in detail.

#### **A6.3**

**HIGH RATE DEPOSITION OF STABLE HYDROGENATED AMORPHOUS SILICON IN TRANSITION FROM AMORPHOUS TO MICROCRYSTALLINE SILICON.** Guofu Hou, Xinhua Geng, Ying Zhao, Xiaodan Zhang, Junming Xue, Huizhi Ren, Jian Sun, Dekun Zhang Institute of Photoelectronics, Nankai University, Tianjin, P.R. CHINA.

It is well known that the diphasic films, prepared in the region adjacent to the phase transition from amorphous to microcrystalline state, can gain both high photosensitivity as conventional hydrogenated amorphous silicon (a-Si:H) and high stability as hydrogenated microcrystalline silicon (mc-Si:H). Now this diphasic films have drawn much attention. In this paper, high rate deposition of high quality and stable a-Si:H films were performed near the threshold of amorphous-to-microcrystalline phase transition using a very high frequency plasma enhanced chemical vapor deposition (VHF-PECVD) method combined with a high working pressure. The deposition parameters included a plasma excitation frequency of 60MHz, a working pressure of 180Pa and a substrate temperature of 250°C. It was found that under the high pressure this kind of a-Si:H films could be deposited over a large range of glow power. Besides, the phase transition depended on not only hydrogen dilution but also glow power and substrate temperature. A series of high quality and stable a-Si:H films were obtained at deposition rates above 20 A/s by changing power density, substrate temperature and silane concentration (SiH<sub>4</sub>/ SiH<sub>4</sub>+H<sub>2</sub>) from 15% to 3%. The hydrogen-bond configurations, microstructure and phase state of the a-Si:H films, deposited in the phase transition region (i.e. crystalline volume fraction X<sub>c</sub>=0~30%), were investigated by the infrared absorption spectroscopy, Raman scattering spectra and constant photocurrent method (CPM). The experiment results were also discussed in detail.

#### **A6.4**

**GROWTH AND PROPERTIES OF MICROCRYSTALLINE (Ge,C):H MATERIALS AND SOLAR CELLS.** Xuejen Niu, Vikram Dalal, Iowa State University, Dept. of Electrical and Computer Engr., Ames, IA.

We report on the growth and properties of microcrystalline (Ge,C):H materials and solar cells using mixtures of germane, ethylene and hydrogen. The use of ethylene allows for a higher C:Ge ratio in the solid than the use of methane under similar growth conditions. The materials and cells were grown using a remote ECR plasma apparatus. Hall mobilities in the material were measured using a specially designed high-resistance Hall apparatus, and were found to be in the range of ~5 cm<sup>2</sup>/V-sec. Both p and n type materials could be grown using appropriate doping with diborane or phosphine. Raman and x-ray measurements indicated crystallinity in the material. Spectral photo-conductivity also revealed a crystalline type absorption coefficient. Grain sizes were in the 20-50 nm range. Solar cells were made in the p/i/n configuration on steel substrates, and used amorphous interfaces between both n and i layers and p and i layers to obtain better results. The open circuit voltages were found to increase as the bandgap of the material increased. Subgap QE measurements confirmed that as ethylene content was increased, the bandgap also increased. Both Raman measurements on cells and the QE spectrum indicated that the i layers were indeed microcrystalline and not amorphous.

#### **A6.5**

**STRUCTURAL EVOLUTION OF NANOCRYSTALLINE GERMANIUM THIN FILMS WITH FILM THICKNESS AND SUBSTRATE TEMPERATURE.** William B. Jordan, Eric D. Carlson, Todd R. Johnson, Sigurd Wagner, Princeton Univ, Dept of Electrical Engineering, Princeton, NJ.

Nanocrystalline germanium (nc-Ge:H) has attracted interest for possible use in low gap solar cells or photodetectors due to its low optical gap and high optical absorption. The crystallinity of Ge thin films is a strong function of both deposition temperature and hydrogen dilution. At high hydrogen dilutions, Ge films grow *amorphous* at room temperature, *nanocrystalline* between 80-250°C, *amorphous* around 250-300°C, and *nanocrystalline* again above 300°C. Varying the hydrogen dilution maintains the same phase sequence, but at different transition temperatures. We measured the growth rate, crystallinity, and surface roughness of the Ge films throughout their a/nc/a/nc phase range, and as a function of film thickness, substrate temperature, and hydrogen dilution. We deposited thin films of nc-Ge:H on Corning 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 deposition pressure, power, and GeH<sub>4</sub> flow rate were held constant, while the film thickness, hydrogen dilution, and the substrate temperature were varied. The substrate temperatures ranged from 30°C to 310°C, while the hydrogen dilution ratio ranged from 20 to 600. Crystallinity was determined by UV/visible reflectance and Raman spectroscopy. The surface roughness was characterized by atomic force microscopy (AFM) and field emission scanning electron microscopy (SEM). The thickness of the Ge films ranged from approximately 250 Å to 1600 Å, while the growth rates for both the temperature series and the thickness series ranged between 0.20 and 0.30 Å/sec. The surface roughness of the Ge films increased with film thickness and substrate temperature, and decreased with hydrogen dilution. The nc-Ge:H films developed a fully nucleated surface at a thickness of 250 Å. This work is supported by EPA and NSF.

**A6.6**  
**INFLUENCE OF FILAMENT AND SUBSTRATE TEMPERATURES ON STRUCTURAL AND OPTOELECTRONIC PROPERTIES OF NARROW GAP a-SiGe:H ALLOYS DEPOSITED BY HWCVD.** Yueqin Xu, Brent P. Nelson, D.L. Williamson<sup>a</sup>, Lynn M. Gedvilas, and Robert C. Reedy, National Renewable Energy Laboratory, Golden, CO; <sup>a</sup>Department of Physics, Colorado School of Mines, Golden, CO.

We have found narrow band gap {1.25 < Tauc Gap < 1.50 eV} amorphous silicon germanium (a-SiGe:H) alloys grown by HWCVD can be improved by lowering both the substrate temperature and filament temperature. We systematically study films deposited with a tungsten filament temperature (T{filament}) decreased from our standard temperature of 2150°C down to 1750°C, fixing all other deposition parameters. By decreasing T{filament} at a fixed substrate temperature of 180°C, the hydrogen bonded to Ge increases from 30% to 45% of the total hydrogen, while the Si-H2 content decreases from 22% to zero. Films with more Ge-H bonding and less Si-H2 have improved photoconductivity up to one order of magnitude higher. For this series of films, the germane gas fraction was fixed at 35%, but the energy where the optical absorption is 1x10<sup>4</sup> (E04) drops from 1.54 to 1.41 eV with decreasing T{filament}. This is attributed to a combination of an increasing Ge content, decreasing H content, and an improved compactness due to significant microvoid reduction. We also studied a series of films grown by decreasing the substrate temperature (T{substrate}) from our previous standard temperature of 350°C down to 125°C, fixing all other deposition parameters including T{filament} at 1800°C. By decreasing T{substrate}, the fraction of hydrogen bonded to Ge, which preferentially existing as Ge-H bonding, increased from 27% to 42%, while the Si-H2 content is not measurable in the T{substrate} range from 300-200°C. The E04 increases from 1.40 to 1.50 eV as T{substrate} decreased from 350 to 125°C, mainly due to increased H content. At the same time the photo-to-dark conductivity ratio increases almost three orders of magnitude over this range of T{substrate} at the fixed T{filament}.

**A6.7**  
**PROCESS PARAMETERS FOR POLY-SILICON DEPOSITION AT A HIGH GROWTH RATE (1-7 nm/s) BY HOT-WIRE CHEMICAL VAPOUR DEPOSITION.** J.K. Rath, A.J. Hardeman, C.H.M. van der Werf, P.A.T.T. van Veenendaal, M.Y.S. Rusche, and R.E.I. Schropp, Utrecht University, SID-Physics of Devices, Utrecht, THE NETHERLANDS.

Lack of ions and a high density of atomic hydrogen in the gas phase are considered to be the advantages of Hot-wire chemical vapour deposition (HWCVD) (also called Cat-CVD) compared to PECVD for poly-silicon growth. We have already reported that compact polysilicon films can be made at a high deposition rate of 0.5 nm/s, which is already comparatively high, and solar cells implementing this truly polycrystalline material (with no amorphous phase) have shown 4.4% efficiency [1]. This paper probes into a high growth rate regime (>1nm/sec), facilitated by a changed filament assembly. High silane to hydrogen flow ratios and optimum wire temperatures are the key process parameters to achieve high growth rate HWCVD poly-silicon films using a four-wire hot-wire assembly. Four tungsten wires, 4 cm apart from each other, were used as filament. Growth rates higher than 7nm/s has been achieved at a substrate temperature of ~530°C. The increase of deposition rate was accompanied by deterioration of two physical properties i.e., decrease in photoresponse and increased oxygen incorporation in the film, which is attributed to high porosity in the material that is commonly observed in these high growth rate materials. The process conditions to incorporate high hydrogen content into the material for passivation of defects and donor states have been identified as high hydrogen dilution and lower wire temperature. With these procedures poly-Si films deposited at 1.3nm/s showed high ambipolar diffusion length of 132nm. Incorporating such poly-Si films as i-layer, n-i-p solar cell on stainless steel substrate (without back reflector) showed an efficiency of 4.4%

and a high open circuit voltage of 0.58V, which is attributed to effective passivation of defects and donor states by incorporated hydrogen [2]. [1]. J.K. Rath, F.D. Tichelaar, R.E.I. Schropp, Solid State Phenomena, 67-68, 465 (1999). [2] Y. Nasuno, M. Kondo, A. Matsuda, Appl. Phys. Lett., 78 (2001) 2330.

**A6.8**  
**HIGH TEMPERATURE n- AND p-TYPE DOPED MICROCRYSTALLINE SILICON LAYERS DEPOSITED BY VHF PECVD LAYER-BY-LAYER DEPOSITION.** A. Gordijn, J.K. Rath, and R.E.I. Schropp, Utrecht University, Debye Institute, SID-Physics of Devices, Utrecht, THE NETHERLANDS.

Due to the high temperatures used for high deposition rate microcrystalline ( $\mu$ c-Si:H) and polycrystalline silicon, there is a need for compact and temperature stable doped layers. In this study we report on films grown by the layer-by-layer method (LbL) using VHF PECVD. Growth of an amorphous silicon layer is alternated by a hydrogen plasma treatment. In LbL, the surface reactions are separated time-wise from the nucleation. We observed that it is possible to incorporate dopant atoms in the layer, without disturbing the nucleation. Even at high substrate temperatures (up to 400 degrees C) doped layers can be made microcrystalline. At these temperatures, in the continuous wave case, the crystallinity is hindered, which is generally attributed to the out-diffusion of hydrogen from the surface and the presence of impurities (dopants). We observe that the parameter window for the treatment time for p-layers is smaller compared to n-layers. Moreover we observe that for high temperatures, the nucleation of p layers is more adversely affected than for n-layers. Thin, doped layers have been structurally, optically and electrically characterized. The best n-layer made at 400 degrees C, with a thickness of only 31 nm, had an activation energy of 0.056 eV and a dark conductivity of 2.7 S/cm, while the best p-layer made at 350 degrees C, with a thickness of 29 nm, had an activation energy of 0.11 V and a dark conductivity of 0.1 S/cm. The working of these high temperature n-layers has been demonstrated in a nip microcrystalline silicon solar cell with an unoptimized  $\mu$ c-Si i-layer deposited at 250 degrees C.

**A6.9**  
**THE PROPERTIES OF MICROCRYSTALLINE SILICON FILMS DEPOSITED BY HOT WIRE CVD AT CONSTANT DEPOSITION RATES USING DIFFERENT FILAMENT TEMPERATURES.** A.H. Mahan, Y. Xu, E. Iwaniczko, L.M. Gedvilas, B.P. Nelson, NREL, Golden, CO; D.L. Williamson, Physics Department, Colorado School of Mines, Golden, CO.

The recent success in microcrystalline silicon solar cell performance, with the i-layers deposited by hot wire chemical vapor deposition (HWCVD), has to date only been achieved by using low filament temperatures (<1800C). In particular, microcrystalline silicon i-layers deposited at higher filament temperatures have been found to be very porous, allowing for rapid uptake of atmospheric contaminants (1), and it has only been by using lower filament temperatures that "compact" HWCVD microcrystalline silicon has been deposited (2), and viable device efficiencies achieved. However, the use of these lower filament temperatures means not only a reduction in film deposition rates, but in addition filament lifetime becomes an issue, particularly for W, as filament alloying becomes significant. Since the porous microcrystalline silicon films have typically been deposited, using the higher filament temperatures, at considerably higher deposition rates, the question arises as to whether this porosity is due to the higher film deposition rates or to a different mix of radical species evaporating from a "virgin", high temperature filament as opposed to that from an alloyed, lower temperature filament. By varying the substrate to filament distance while using the same H dilution and substrate temperature, we deposit microcrystalline silicon films using different filament temperatures at constant deposition rate (~10 angstrom/s) on top of a thin, highly microcrystalline seed layer. We deposit these composite films on c-Si, glass, and SS substrates, and from XRD, infrared, and conductivity measurements, establish a detailed correlation between the film crystallinity, porosity, and electronic quality as a function of filament temperature at constant film deposition rate. As the film crystallite orientation has been observed to change with filament alloying when low filament temperatures were used (3), we also deposit films at each filament temperature, using identical deposition conditions, as a function of filament lifetime, and report on any structural changes that may occur. (1) G.A. Zaharias, A.H. Mahan, R.E.I. Schropp, Y. Xu, D.L. Williamson, M.M. Al-Jassim, M.J. Romero, and L.M. Gedvilas, MRS Symp. Proc. 715, A16.5 (2002). (2) J.K. Rath, R. E. I. Schropp, and W. Beyer, J. non-Cryst. Sol. 266-269, 190 (2000). (3) E. Iwaniczko, Y. Xu, R.E.I. Schropp, Q. Wang, and A.H. Mahan, NREL Extended Abstract CP-520-30476 (2002).

**A6.10**  
**INFLUENCE OF HYDROGEN DILUTION ON PROPERTIES OF**

**SILICON FILMS PREPARED BY THE SADDLE-FIELD GLOW-DISCHARGE METHOD: OBSERVATION OF NANOCRYSTALLINITY.** T. Allen<sup>a</sup>, F. Gaspari, N.P. Kherani, T. Kostas, K. Leong, I. Milostnaya, D. Yeghikyan, S. Zukotynski, Univ of Toronto, Dept of Electrical and Computer Engineering, Toronto, CANADA; <sup>a</sup>Univ of Tennessee at Chattanooga, Dept of Physics, Geology, and Astronomy, Chattanooga, TN.

Microcrystalline Si is a prospective material for photovoltaics applications. It can improve stability against light degradation in solar cells and provide for more effective doping than amorphous Si. We report observation of microcrystalline Si obtained by the d. c. saddle-field glow discharge deposition method [1]. The films have been deposited on pyrex, corning glass, and fused silica substrates. The source gas was a mixture of silane and hydrogen, with silane concentration varying from 100% to 1%. Substrate temperature was 250°C. The presence of microcrystallinity was confirmed by Raman spectroscopy by observing a peak at 510-517 cm<sup>-1</sup> [2]. The deposition conditions leading to microcrystallinity have been identified. Detailed studies of film properties, as a function of hydrogen dilution, done by Raman spectroscopy, SEM, TEM and High Resolution TEM microscopy will be presented.

**A6.11**  
**REACTIVE PULSED LASER DEPOSITION OF MICROCRYSTALLINE Ge-BASED THIN FILMS.** Matthew Wills and Alan Constant, Dept. of Materials Science and Engr.; Ruth Shinar, Microelectronics Research Center, Iowa State University, Ames, IA.

Reactive pulsed laser deposition (PLD) was used to grow microcrystalline thin films of Ge and germanium-carbon alloys (Ge:C) with various Ge:C ratios on fused quartz substrates at substrate temperatures between 25 and 325°C. The alloys were prepared by ablating a Ge target in a methane atmosphere. Using PLD, which is an extremely non-equilibrium deposition technique, enabled growth of microcrystalline, metastable Ge:C films using methane and hydrogen as the reactive gases. The films were analyzed structurally using x-ray diffraction (XRD), chemically using Auger, XPS, and SIMS, optically, and electrically with four-point probe measurements. The XRD results indicated a varying degree of crystallinity, with the best samples obtained at temperatures above 150°C. The resistivity decreased with increasing temperature, displaying a sharp decrease for Ge films deposited at 230°C. The growth mechanism associated with the unique PLD process as well as the effects of Ts, methane and hydrogen partial pressures, and growth rate on film properties will be discussed.

**A6.12**  
**GROWTH OF a-(Si,Ge):H FILMS USING COMBINED HOT WIRE-ECR DEPOSITION.** Matt Ring, Vikram Dalal, Iowa State University, Dept. of Electrical and Computer Engr., Ames, IA.

We report on a novel growth technique for growing high quality a-(Si,Ge):H alloys. The technique embraces using a hot wire system to decompose silane and germane while simultaneously subjecting the growing films to ion bombardment from an ECR plasma. Careful diagnostic experiments show that over 90% of the growth of the film can be attributed to the hot wire, with only about 10% of growth being contributed by radicals generated by the plasma. However, the influence of ions on film growth is found to be profound. Both He and H ions were used in the experiment, and it was discovered that ion bombardment significantly improved film properties such as photo conductivity, electron mobility-lifetime products, mid-gap defect densities and Urbach energies of valence band tails. Low Urbach energies (~45 meV) were obtained when ion bombardment was present. Studies of H content revealed that there was significant amount of deleterious dihydride-type bonding when no ion bombardment was present. Ion bombardment reduced the amount of dihydride bonds significantly. Growth rates of ~5 Å/sec were obtained with good properties even in a-(Si,Ge):H alloys. The results indicate the profound importance of low energy ion bombardment on the properties of the (Si,Ge) alloy materials.

**A6.13**  
**NANOVoid FORMATION DURING GROWTH OF AMORPHOUS Si AND Ge.** J.A. Floro and P. Kotula, Sandia National Laboratories, Albuquerque, NM; D.J. Srolovitz, Princeton University, Princeton Materials Institute and Dept. of Mechanical and Aerospace Engineering, Princeton, NJ.

We investigated the formation of nanovoids in amorphous Si and Ge thin films using cross-section transmission electron microscopy and in situ stress measurement during deposition. Nanovoid formation is observed to occur during ultrahigh vacuum evaporative deposition of amorphous Si at room temperature. Relatively small increases in deposition temperature strongly suppress void formation in Si. In amorphous Ge films, however, nanovoid formation is largely

suppressed even at room temperature. We used a marker layer technique, combined with annular dark field microscopy (for Z contrast), to show that nanovoid formation is intimately related to the development of high-aspect ratio surface roughness during deposition. Nanovoids are found to align in tracks perpendicular to the growth direction and the onset of void formation produces tensile stresses in the amorphous Si films as large as 0.5 GPa. These observations strongly suggest that nanovoids are produced via elastic bridging of cusps in the surface. The cusps themselves arise due to nanoscale surface roughening associated with limited adatom mobility. We will present a simple model for the stresses associated with void formation, and we will discuss the possibility of using marker-layer measurements of roughening to estimate the activation energy for adatom diffusion. This work was supported in part by the Division of Materials Science and Engineering, Office of Science, U.S. Department of Energy. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-ACO4-94AL85000.

**A6.14**  
**HOT-WIRE CHEMICAL VAPOR DEPOSITION FOR EPITAXIAL SILICON GROWTH ON LARGE-GRAINED POLYCRYSTALLINE SILICON TEMPLATES.** M.S. Mason, C.M. Chen, and H.A. 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 Si (100) and polycrystalline silicon template layers formed by selective nucleation and solid phase epitaxy (SNSPE). SNSPE layers formed by the use of nickel nanoparticles as nucleation sites for the solid-phase crystallization of phosphorus-doped amorphous silicon on SiO<sub>2</sub> display grain sizes on the order of 100 μm, and have been successfully used as seed layers for epitaxial growth by molecular beam epitaxy at 600°C [1,2]. HWCVD has recently been shown to be a promising method for fast, low-temperature epitaxy [3]. We have grown 300 nm epitaxial films at 300°C on Si (100) substrates at an H<sub>2</sub>/SiH<sub>4</sub> ratio of 70:1; the films are epitaxial but highly twinned and display a periodic array of stacking faults. We will discuss the substrate temperature and hydrogen dilution conditions for epitaxial growth on Si (100), as well as the microstructural properties and photoconductive decay lifetimes of undoped layers grown on SNSPE templates and the suitability of these films for thin-film photovoltaics applications.

[1] C.M. Chen, Ph.D. thesis, California Institute of Technology, 2001.

[2] R.A. Puglisi, H. Tanabe, C.M. Chen and H.A. Atwater, Mat. Sci. Eng. B 73, 2000.

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

**A6.15**  
**ELECTRICAL AND OPTICAL PROPERTIES OF HYDROGENATED AMORPHOUS AND MICROCRYSTALLINE SILICON FILMS DEPOSITED BY THE SADDLE FIELD GLOW DISCHARGE METHOD.** I. Milostnaya, F. Gaspari, N.P. Kherani, T. Kostas, D. Yeghikyan, S. Zukotynski, University of Toronto, Dept of Electrical and Computer Engineering, Toronto, ON, CANADA; T. Allen, University of Tennessee at Chattanooga, Dept of Physics, Geology, and Astronomy, Chattanooga, TN.

Hydrogenated amorphous (a-Si:H) and microcrystalline (μc-Si:H) silicon films have been obtained using the DC saddle field glow discharge deposition method [1,2]. The structural nature of the films was verified by Raman spectroscopy [3], FTIR spectroscopy and TEM. The main deposition parameters influencing the onset of micro-crystallinity were: (i) the silane to hydrogen dilution ratio (R ≤ 1:20), (ii) the gas pressure (P ~ 200 mTorr), and (iii) the substrate holder bias (30 < V<sub>s</sub> < 100V). The opto-electronic characteristics of both a-Si:H and μc-Si:H were investigated using UV/VIS spectroscopy, conductivity and photoconductivity measurements. Boron and phosphorus doping of a-Si:H and μc-Si:H films was also investigated. The Tauc gaps for a-Si:H were in the range 1.7-1.85 eV, while μc-Si:H films exhibited gaps in the range 2.0-2.4 eV. Dark conductivity measurements of undoped films indicate that both a-Si:H and μc-Si:H films are highly resistive (σ<sub>dark</sub> = 10<sup>-7</sup>-10<sup>-8</sup> Ω<sup>-1</sup>.cm<sup>-1</sup>). Dark conductivity measurements of doped films show a higher doping efficiency of μc-Si:H films with respect to a-Si:H films. On the other hand, photoconductivity measurements of undoped films indicate a higher photosensitivity of a-Si:H films (σ<sub>photo</sub>/σ<sub>dark</sub> = 10<sup>4</sup>) than that of μc-Si:H films (σ<sub>photo</sub>/σ<sub>dark</sub> = 10-100). The possible use of both types of material for devices (solar cells) is discussed. References: 1. Kruzelecky, R.V., Zukotynski, S., Materials Science Forum 140-142 (1993) p.89. 2. Zukotynski, S., Gaspari, F., Manage, D., Pletnev, V., Sagnes, E., Mat. Res. Soc. Symp. Proc. 595 (2000) p.239. 3. T. Allen, F. Gaspari, N.P. Kherani, T. Kostas, K. Leong, I. Milostnaya, D. Yeghikyan, S. Zukotynski, (MRS 2003).

#### A6.16

COMBINED PLASMA AND HOT-WIRE CVD: INNOVATION IN PLASMA PROCESSING OF  $\mu\text{-Si:H}$  THIN FILMS. A.R. Middy, Department of Physics, Syracuse University, NY.

In spite of the fact that PECVD  $\mu\text{-Si:H}$  thin-film solar cells emerged as viable cost-effective technology as the bottom junction of a-Si-based tandem solar cells, however, slow growth rate of intrinsic layer and relatively low efficiency of a-Si:H/ $\mu\text{-Si:H}$  tandem solar cells, limit the potential of commercialization of this type of technology. Since the first report of synthesis of micro/poly-Si thin films with high growth rate ( $> 5 \text{ nm/s}$ ) by hot-wire CVD, materials fabrication technology has been progressed significantly<sup>1</sup>. However, fabrication of solar cells or TFT by hot-wire CVD appear to be tricky, particularly controlling interfaces. We propose combined plasma and hot-wire CVD technique to fabricate  $\mu\text{-Si:H}$  thin films materials and devices with high growth rate by taking advantage of both the techniques. With proper control of inter-linked process parameters, we expect to create the environment near the substrates, high density atomic hydrogen, low ion energy, simultaneously high flux of Si atoms and Si-related radicals, which should, in principle, favors nucleation and fast growth of  $\mu\text{-Si:H}$  films having low defect density. Based on this idea, we have modified our plasma CVD reactors to a combined plasma and hot-wire CVD system, where an array of tungsten filament, mounted on an innovatively designed filament holder placed on the ground electrode. The specialty of the filament holder and the reactor geometry and the critical issues to sustain the plasma will be discussed. We have fabricated  $\mu\text{-Si:H}$  films under PECVD condition by decomposing silane diluted with hydrogen, the dark conductivity and the photoconductivity under monochromatic light ( $\lambda > 670 \text{ nm}$ ) of the best film are  $7.75 \times 10^{-9} \text{ Scm}^{-1}$  and  $3.20 \times 10^{-8} \text{ Scm}^{-1}$  respectively. We are in the process of optimizing the deposition parameters of combined plasma and hot-wire CVD to synthesize  $\mu\text{-Si:H}$  films. A comparison of structural and electronic properties of the  $\mu\text{-Si:H}$  films prepared by PECVD and combined plasma and hot-wire CVD will be presented. The results on the defect density studies on two types of  $\mu\text{-Si:H}$  films, analyzed by photocapacitance spectroscopy, particularly in the amorphous-to-microcrystalline transition regime, will be reported. Growth mechanism of  $\mu\text{-Si:H}$  films prepared by combined plasma and hot-wire CVD will be discussed. 1. A.R. Middy, A. Lloret, J. Perrin, J. Huc, J.L. Moncel, J.Y. Parey and G. Rose, MRS Symp. Proc. 377 (1995) p. 119.

#### A6.17

AMORPHOUS SILICON SOLAR CELLS DEPOSITED USING TRISILANE. W. Du, X. Yang and X. Deng, Dept of Physics and Astronomy, Univ of Toledo, Toledo, OH.

We explored the deposition of hydrogenated amorphous silicon (a-Si:H) using trisilane gas as the silicon precursor in a plasma enhance CVD process, to better understand the growth chemistry and the dependence of a-Si:H on precursors. The deposition using trisilane is compared with that using disilane in the same chamber under otherwise identical conditions. Four a-Si:H films, Samples TS, DS, TSH, DSH, are deposited using Si<sub>3</sub>H<sub>8</sub> (=0.67sccm), Si<sub>2</sub>H<sub>6</sub> (=1sccm), Si<sub>3</sub>H<sub>8</sub>/H<sub>2</sub> (=0.67sccm/100sccm) and Si<sub>2</sub>H<sub>6</sub>/H<sub>2</sub> (=1sccm/100sccm), respectively. Different Si<sub>3</sub>H<sub>8</sub> and Si<sub>2</sub>H<sub>6</sub> flows are used in this study so that the same number of Si atoms would flow through the chamber for both types of precursors. Samples TSH and DSH both show a deposition rate of 0.4 Å/s. Sample DS, deposited without H dilution, shows ~1.5 times higher deposition rate than Sample TS, suggesting that the actual flow rate of precursor molecules rather than the number of silicon atoms in these molecules affect the deposition rate. The Tauc bandgaps of both Samples TSH and DSH are around 1.93 eV, while the Tauc bandgaps of both Samples TS and DS are around 1.85 eV. Photoconductivity measurements reveals that photosensitivity of trisilane-deposited samples are approximately a factor 2 higher than the disilane counterparts, with the H diluted samples show much higher photosensitivity. Amorphous Si:H n-i-p single-junction solar cells with 200nm thick i-layer is deposited using conditions as in Sample TSH. Solar cells deposited on bare stainless steel without using a back-reflector show I-V performance of Voc=0.984V, Jsc=10.5 mA/cm<sup>2</sup>, FF=71.1 and efficiency of 7.3%, similar to the start-of-the-art single-junction a-Si cells deposited using disilane in the same system. Further study is in progress and the result will be reported at the conference. Work supported partially by NREL Thin Film Partnership Program. Trisilane gas was produced and supplied by Voltaix, Inc.

SESSION A7: POSTER SESSION  
SOLAR CELLS  
Tuesday Evening, April 22, 2003  
8:00 PM  
Salon 1-7 (Marriott)

#### A7.1

HOLE DRIFT MOBILITY MEASUREMENTS IN

CONTEMPORARY AMORPHOUS SILICON. S. Dincă<sup>†</sup>, G. Ganguly<sup>‡</sup>, E. A. Schiff<sup>†</sup>; <sup>†</sup>Syracuse University, Dept. of Physics, Syracuse, NY; <sup>‡</sup>BP Solar, Inc., Toano, VA.

Hole drift mobilities are very low in amorphous silicon, and until about 1995 it appeared that these low values were fundamentally limited by the amorphous structure. Hole drift mobilities varied remarkably little between laboratories and between alloys prepared with varying concentrations of germanium and carbon. However, since 1995 there have been several, fragmented reports of improved hole drift mobilities in amorphous silicon prepared using innovative techniques (hot-wire, triode plasma, hydrogen-diluted plasma, and remote expanding thermal plasma).

In this paper we show that similar improvements in the hole drift mobility have been realized under conditions used in commercial manufacturing of amorphous silicon solar cells; in particular, for structures prepared at BP Solar, Inc., we have measured hole drift mobilities that are about six times larger (under standard conditions) than the 1994 baseline value. We address whether this improvement is a consequence of the now widespread use of hydrogen-diluted silane in plasma deposition of amorphous silicon. It is plausible, but as yet unproven, that hole drift mobilities are increasing as the amorphous structure approaches the phase transition to the nanocrystalline form; this conclusion would be qualitatively consistent with hole mobility estimates in p-type microcrystalline silicon.

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

#### A7.2

RECOMBINATION IN N-I-P (SUBSTRATE) a-Si:H SOLAR CELLS WITH SILICON CARBIDE AND PROTOCRYSTALLINE P-LAYERS. Vasilios Vlahos, Joshua M. Pearce, Jingdong Deng, Randy J. Koval, Robert W. Collins and Christopher R. Wronski, Center for Thin Film Devices, The Pennsylvania State University, University Park, PA.

Carrier recombination has been investigated in hydrogenated amorphous silicon (a-Si:H) n-i-p (substrate) solar cells with different p-layers. The 4000 Å i-layer cells deposited at 200°C consisted of either 200-250 Å a-Si:C:H or 200 Å protocrySTALLINE Si:H p-layers and 350 Å n-Si:H layers. The protocrySTALLINE p-layers were deposited with hydrogen dilution ratio  $R = [\text{H}_2]/[\text{SiH}_4]$  from 100 to 200 and doping ratio  $D = [\text{BF}_3]/[\text{SiH}_4]$  from 0.1 to 0.3, while the a-Si:C:H p-layers were deposited with a constant doping ratio of  $D = [\text{B}(\text{CH}_3)_3]/[\text{SiH}_4] = 0.005$  and with  $Z = [\text{CH}_4]/[\text{SiH}_4] = 1$ . Indium tin oxide (ITO) contacts were deposited onto the p-layers at 170°C. Short circuit current - open circuit voltage characteristics over a wide range of illumination intensities as well as dark current - voltage characteristics were utilized in the studies on carrier transport. The recombination and its contributions to the magnitude and stability of the open circuit voltage ( $V_{oc}$ ) was evaluated for 1 sun illumination. In order to minimize shunting in the low current region small areas (0.02cm<sup>2</sup>) were isolated in protocrySTALLINE cell structures with a combination of chemical etching of the ITO and reactive ion etching (RIE) of the protocrySTALLINE p-layer. In order to minimize series resistance in the far forward bias region a four-point probe technique was utilized in measuring the forward bias current - voltage characteristics. Results on the recombination identified for different p/i interfaces and their role in determining  $V_{oc}$  are presented and discussed. In addition, the relative sensitivity of the a-Si:C:H and protocrySTALLINE p/i interfaces to vacuum breaks such as used in studies of materials from different laboratories in cell structures is also discussed.

#### A7.3

NANOCRYSTALLINE SILICON (NC-Si) IN SOLAR CELLS. Z.B. Zhou, R.Q. Cui, G.M. Hadi, Solar Energy Institute, Department of Physics, Shanghai Jiaotong University, Shanghai, CHINA; C.Y. Jin and G. Li, Instrumental Analysis Center, Shanghai Jiaotong University, Shanghai, CHINA.

Based on a small set of selected publications on the using of nanocrystalline silicon films in solar cell from 1999 to 2001, this paper reviews the application of nc-Si films as intrinsic layers in p-i-n solar cells. The new structure of nc-Si films deposited at high chamber pressure and high hydrogen dilution have characters of nanocrystallites of only 2-3 atoms embedded in matrix of amorphous tissue and a high volume fraction of crystallinity (60-80%). The new nc-Si material have optical gap of 1.89 eV. The efficiency of this single junction solar cell is 8.7%. This nc-Si layer can be used not only as an intrinsic layer and as a p-type layer. Also nanocrystalline layer may be used as a seed layer for the growth of polycrystalline Si films at a low temperature. We use PECVD and ion beam sputtering methods to synthesized nanocrystalline silicon films successfully. The films were characterized with the technique of Hall effect measurements, laser Raman, spectroscopic ellipsometry and electron spin resonance spectrometer (ESR). Photoconductivity gains of the materials are obtained in our recent investigation.

**A7.4**  
CORRELATION OF MATERIAL PROPERTIES AND OPEN-CIRCUIT VOLTAGE OF a-Si:H and a-SiGe:H ALLOY SOLAR CELLS. Baojie Yan, Jeffrey Yang, Gaozhen Yue, and Subhendu Guha, United Solar Systems Corp., Troy, MI.

Correlation of hydrogenated amorphous silicon (a-Si:H) alloy material properties and solar cell characteristics was studied experimentally and by computer simulation. Simulation results show that all three solar cell parameters, short-circuit current density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ) and fill factor (FF), decrease with an increased defect density. For a given intrinsic layer thickness, a larger band gap ( $E_g$ ) leads to a higher  $V_{oc}$ , but a lower  $J_{sc}$ , and a linear relation between  $V_{oc}$  and band gap is obtained. However, FF does not depend on band gap. This allows us to distinguish the effect of change in band gap from that in defect density on the variation in  $V_{oc}$ . For solar cells with good interface characteristics, a linear relation  $FF = \alpha V_{oc} + \gamma$  was obtained, where  $\alpha$  is around  $2.5 \text{ V}^{-1}$  and  $\gamma$  depends mainly on the band gap. Comparing cells made with high  $\text{H}_2$  dilution to no  $\text{H}_2$  dilution, we found that a 58 mV enhancement in  $V_{oc}$  with  $\text{H}_2$  dilution is due to both the widening of band gap and reduced defect density. Simulation results also show that a narrower valence band tail causes a higher  $V_{oc}$ . However, optical measurements found no observable change in band tail absorption with different  $\text{H}_2$  dilution ratios. Based on this study, we conclude that band gap and density of defect states are the two major parameters that affect the  $V_{oc}$ .

**A7.5**  
SIMULATIONS OF BUFFER LAYERS IN a-Si:H THIN-FILM SOLAR CELLS DEPOSITED WITH AN EXPANDING THERMAL PLASMA. A.M.H.N. Petit<sup>a,b</sup>, M. Zeman<sup>a</sup>, R.A.C.M.M. van Swaaij<sup>a</sup> and M.C.M. van de Sanden<sup>b</sup>; <sup>a</sup>Delft University of Technology, DIMES-ECTM, Delft, THE NETHERLANDS; <sup>b</sup>Eindhoven University of Technology, Department of Applied Physics, Eindhoven, THE NETHERLANDS.

With a cascaded arc expanding thermal plasma (ETP), solar grade amorphous silicon can be deposited at high deposition rate ( $\geq 2 \text{ nm/s}$ ) and high temperature ( $\geq 300^\circ\text{C}$ ). The initial layer grown with ETP appears to have a higher defect density than the rest of the bulk. Therefore we aim to analyze, by the means of simulations, the influence of a thin defect-rich layer when moved from the p-i towards the i-n interface as a function of its thickness. We observe that the increase of the defective layer thickness results in a reduction of the solar cells performance. However, close to the i-n interface, the thickness of the defective layer does practically not affect the open circuit voltage and the short circuit current. We also demonstrate the effect of a buffer layer in between the p- and the i-layers on the density of states and the internal electric field of the solar cell, as well as the consequent improvements of the external parameters. The presence of a buffer layer increases the electric field near the p-i interface, which leads to a higher collection of free charge carriers at the interface, although the electric field is then diminished deeper in the bulk. Therefore we have an optimum for the buffer-layer thickness and it appears that 10 nm is sufficient to improve the performance. In case no buffer layer is applied, recombination losses at the p-i interface diminish the performance of the solar cell.

**A7.6**  
MICROCRYSTALLINE (Si,Ge):H SOLAR CELLS. Jianhua Zhu, Vikram Dalal, Iowa State University, Dept. of Electrical and Computer Engr., Ames, IA.

We report on the properties of microcrystalline (Si,Ge):H solar cells prepared using ECR plasma growth conditions. p/i/n cells were deposited on steel substrates with light incident from the p side. Ge:Si ratios in the cell were changed by changing the Germane/silane ratios in the gas phase. All cells were prepared using high hydrogen dilution. It was found that much more hydrogen dilution was needed to crystallize Ge-rich cells than was needed for crystallizing Si-rich cells. Cells were made across the entire bandgap range from Si to Ge. Si/Ge ratios were measured using EDAX. Degree of crystallinity was determined using Raman and x-ray diffraction. Fill factors, in the 60+% range were obtained in the cells, with Si cells exhibiting 70% fill factors, indicating good carrier collection. The quantum efficiency extended out to infrared range as the Ge content increased. Quantum efficiency spectroscopy was used to determine minority carrier diffusion lengths, and they were found to be high,  $\sim 2\text{-}3$  micrometer.

**A7.7**  
INVESTIGATION OF THE CAUSES AND VARIATION OF LEAKAGE CURRENTS IN AMORPHOUS SILICON P-I-N DIODES. T. Johnson<sup>†</sup>, G. Ganguly, G. Wood, and D.E. Carlson, BP Solar, North American Technology Center, Toano, VA; <sup>†</sup>Princeton University, NJ.

Shunting (excess leakage currents under reverse bias) and curing (spontaneous reduction of the excess leakage currents under reverse bias) in amorphous silicon, single junction p-i-n type solar cells were investigated to understand its physical origins as well as to determine the causes of differences between zinc oxide versus tin oxide front contacts. Before curing, shunting was observed in  $\sim 70^\circ\text{C}$  of cells on zinc oxide front contact versus  $\sim 40^\circ\text{C}$  on tin oxide, and of these cells only  $\sim 30^\circ\text{C}$  were curable for the former versus  $\sim 80^\circ\text{C}$  for the latter. This difference in curing could be due to the thermal properties of the two materials. Using seamed glass, the shunting frequency on zinc oxide was improved to that on tin oxide while the curing rate appeared to be unaffected. The seaming of glass before deposition decreased the debris that flaked off the edges and adhered to the glass surface. This debris can then fall off after deposition of the zinc oxide and amorphous silicon to create low-resistance shunt paths through the aluminum that fills the pinhole left behind. Leaving cells to sit in darkness for over 100 hours caused an increase in leakage currents of  $\sim 0.5\%$  while light soaking under  $100 \text{ mW/cm}^2$  illumination at  $\sim 50^\circ\text{C}$  caused an additional  $0.5^\circ\text{C}$  increase in leakage currents. When subjected to both, sitting in the dark and under illumination, the cells exhibited an increase in leakage current of  $\sim 1^\circ\text{C}$ , regardless of the order suggesting that they are independent factors. Models for the distribution of shunt-causing defects within a given cell area were considered. Comparing the measured frequency of shunting using cells of varying area ( $1$  to  $25 \text{ mm}^2$ ) to the models predictions indicates a distribution of point defects separated by relatively large average distances that are slightly larger for tin oxide ( $\sim 5\text{-}6 \text{ mm}$ ) than for zinc oxide ( $\sim 4 \text{ mm}$ ).

**A7.8**  
HOT WIRE CVD MICROCRYSTALLINE-SILICON SOLAR CELL PERFORMANCE VERSUS W FILAMENT TEMPERATURE AND FILAMENT LIFETIME. E. Iwaniczko, Y. Xu, B.P. Nelson, P. Stradins, and A.H. Mahan, National Renewable Energy Laboratory, Golden, CO.

The recent success in microcrystalline silicon solar cell performance, with the i-layers deposited by hot wire chemical vapor deposition (HWCVD), has coincided with the use of lower filament temperatures. Indeed, record HWCVD efficiencies for single junction microcrystalline silicon cells (9.4%) have been achieved in a p-i-n cell configuration by using two  $1650^\circ\text{C}$  Ta filaments (1), with the i-layer deposited by HWCVD, and by using two  $1750^\circ\text{C}$  W filaments in an all-HWCVD deposited n-i-p cell (6.6%) (2). However, the use of these lower filament temperatures means not only a reduction in film deposition rates, compared to that using higher filament temperatures with the same deposition conditions, but in addition filament lifetime becomes an issue, particularly for W, as filament alloying becomes significant with usage. Rather surprisingly, recent results have shown that, when using identical deposition conditions, the crystallite orientation changes with filament usage, and that the highest efficiencies occur with the use of an aged filament (2). We re-examine the issue of whether viable HWCVD microcrystalline silicon solar cells can be fabricated using a higher filament temperature, resulting in the i-layer being deposited at higher deposition rates with a filament exhibiting less alloying, and thus a longer lifetime. In this work, we use two W filaments with a constant filament-substrate spacing, and identical gas flow conditions for the i-layer, and deposit all doped layers in a separate, load-locked HWCVD chamber. In between all i-layer depositions, a  $\text{H}_2$  filament treatment is performed (3), which aids device reproducibility. In addition, a thin highly microcrystalline seed layer is used between the a-n+ and microcrystalline silicon i-layers, which aids nucleation at the beginning of the i-layer growth. We report device performance, i-layer deposition rate, and filament lifetime by tracking all-HWCVD n-i-p solar cell performance during the lifetime of the filament as a function of filament temperature. All cells are deposited onto Ag/ZnO textured SS back reflectors kindly provided by United Solar. (1) S. Klein, F. Finger, R. Carius, B. Rech, L. Houben, M. Luysberg, and M. Stutzmann, MRS Symp. Proc. 715, A26.2 (2002). (2) E. Iwaniczko, Y. Xu, R.E.I. Schropp, Q. Wang, and A.H. Mahan, NREL Extended Abstract CP-520-30476 (2002). (3) K. Ishibashi, Thin Solid Films 395, 55 (2001); A. Masuda and H. Matsumura, Thin Solid Films 395, 112 (2001).

**A7.9**  
ROOM TEMPERATURE RECOVERY OF LIGHT INDUCED CHANGES IN AMORPHOUS SILICON SOLAR CELLS. G. Ganguly, D.E. Carlson, M. Bennett, F. Willing and R.R. Arya, BP Solar, North American Technology Center, Toano, VA.

Light induced changes in a-Si:H thin films and solar cells have been found to anneal back at temperatures ranging from  $60$  to  $200^\circ$ . Deposition conditions, light intensity, illumination temperature as well as applied field have been shown to influence the activation energy distribution. We have looked for changes of performance of a-Si:H, a-SiGe:H single junction cells and a-Si:H/a-SiGe:H tandem cells after 600h light soaking at  $50^\circ\text{C}$  under light intensity of  $\sim 100 \text{ mW/cm}^2$

from sodium vapor lamps. We have also looked for changes in the performance of cells prepared with deliberate inclusion of impurities like carbon, boron, phosphorus and air, as well as cells prepared under conditions known to induce light induced degradation in excess of those observed for standard cells prepared under optimized conditions. We find that tandem cells that degrade about 11% after light soaking do not exhibit any recovery in 20 days but recover about 10% of the loss after 3 months and about 35% after 12 months at open circuit. a-Si:H single junction cells that degrade about 20% after light soaking recover about 7% of the loss in 1 month and about 17% in 1 year. However, when these single junction cells are made under non-optimal conditions of gas flow and/or temperature, they degrade 30 to 60% and the recovery increases to as much as 25 to 35% after 1 year. Similarly, adding 3-10% C also increases the degradation to 70-80% and its recovery at room temperature to 22 to 35% after 2 years. We are in the process of looking at the kinetics of the recovery process, and how it is influenced by temperature and illumination using both optimized and non-optimized devices. Since even optimized devices exhibit some recovery suggests that there is room for further optimization of the process conditions to reduce light induced degradation.

**A7.10**  
TOWARD UNDERSTANDING THE DEGRADATION WITHOUT LIGHT SOAKING IN HOT-WIRE a-Si:H THIN FILMS AND SOLAR CELLS. Qi Wang, National Center of Photovoltaic, National Renewable Energy Laboratory, Golden, CO; Keda Wang and Daxing Han, Dept of Phys & Astronomy, Univ of North Carolina at Chapel Hill, Chapel Hill, NC.

The degradation without light soaking has been observed in both thin films and solar cells fabricated using the hot-wire CVD technique. For solar cells, a 9.8% initial efficiency became 9.2% after a few weeks of being stored in the dark. The degradation mainly comes from the fill factor (FF) and can be as much as 4-6%. For the intrinsic layers, we also find that the properties of the films change without light soaking; for example, activation energy (E<sub>a</sub>) of conductivity decreases from an initial 0.9-1.0 eV to 0.85-0.9 eV after being stored in the dark for a few weeks. We suggest that the degradation of both materials and solar cells may share the same origin. It comes from the intrinsic layer the upward shift of the Fermi-energy position. In the other words, as the time passed by, the material became more n-type from its initial deposition. To explore whether the source of the slow degradation is the structural relaxation or the gas absorption from the air, we are studying the gas absorption effect of hot-wire films with and without gas-resistive top layer and results will be reported.

**A7.11**  
MATERIAL ASPECTS OF REACTIVELY MF-SPUTTERED ZINC OXIDE FOR TCO APPLICATION IN SILICON THIN FILM SOLAR CELLS. Jürgen Hüpkens, Oliver Kluth, Joachim Müller, Hildegard Siekmann, Chitra Agashe, Bernd Rech, Institut für Photovoltaik, Forschungszentrum Jülich, Jülich, GERMANY; Hans-Peter Boehm, Institut für Schicht- und Grenzflächenforschung, Forschungszentrum Jülich, Jülich, GERMANY; Matthias Wuttig, I. Physikalisches Institut, RWTH Aachen, Aachen, GERMANY.

Silicon thin film solar cells in the p-i-n (superstrate) structure require a transparent conductive oxide (TCO) film, which has to combine low series resistance, high transparency and an adequate surface texture. Magnetron sputtered and texture-etched ZnO:Al films fulfill these requirements. However, for industrial applications high rate sputtering techniques are required and the results obtained on small areas have to be transferred to these techniques. This paper addresses the material properties of medium-frequency (mf)-sputtered ZnO:Al films which were prepared in an in-line sputtering system using dual magnetron cathodes with a length of 750 mm. The ratio between oxygen and argon gas flow during the reactive sputtering process from metallic Zn:Al targets was controlled by plasma emission monitoring. The films were prepared in dynamic or static mode (static print of the magnetrons) with static deposition rates of ~200 nm/min. The electrical film properties were investigated by four point probe and hall measurements. XRD was used to determine the film structure. All films prepared for this study showed low resistivities (<5x10<sup>-4</sup> Ω·cm) and excellent transparency. After etching in diluted hydrochloric acid SEM and AFM measurements revealed different surface textures depending on the sputtering process parameters and, in case of static deposition, on the substrate position of the film relative to the two dual cathodes. Three characteristic positions could be distinguished: The position between the two cathodes, the position directly opposite to the eroded part (racetrack) of the target and the position opposite to the center of each target. A-Si:H pin solar cells prepared on texture etched ZnO coated glass substrates at these different positions show variations in the short-circuit current densities of up to 2 mA/cm<sup>2</sup>. The experiments clearly reveal the strong influence of the magnetron configuration on film structure and resulting surface texture obtained after etching.

SESSION A8: POSTER SESSION  
TRANSPORT  
Tuesday Evening, April 22, 2003  
8:00 PM  
Salon 1-7 (Marriott)

**A8.1**  
STUDY ON ATOMIC STRUCTURE OF CAT-CVD AND PECVD AMORPHOUS SILICON FILMS BY USING REVERSE MONTE CARLO SIMULATION. Norikazu Tabuchi, Hideki Matsumura, JAIST, School of Material Science, Ishikawa, JAPAN; Toshio Kawahara, Jun Morimoto, NDA, Dept of Materials Science and Engineering, Kanagawa, JAPAN.

Structure of amorphous-silicon (a-Si) films are studied by conventional and small-angle X-ray diffraction technique and successive simulation by reverse Monte-Carlo method based on such experimental data. As initial stage, by based on uniform film model, atomic location in the a-Si film is calculated from structural factors derived from X-ray diffraction data. The Si-Si-Si bond angle distribution and the Si-Si bond length distribution are evaluated and these structural parameters are compared for Cat-CVD (often called Hot-Wire CVD) a-Si, PECVD a-Si and vacuum evaporated a-Si. And additionally, to obtain further realistic structural model, non-uniform micro-structure of a-Si observed in small angle X-ray diffraction is considered in initial trial structural function and the above model is modified and improved. This method has potential to clear the unique properties of Cat-CVD a-Si, which is stable for the stress from light soak or electric current. From these studies, it is found that; 1) Si-Si bond length distribution and Si-Si-Si bond angle distribution of a-Si are likely to spread as hydrogen (H) contents in the films increases. 2) The ratio of the short range order of a-Si structure decreases as the dilution ratio by H<sub>2</sub> to SiH<sub>4</sub> increases, and 3) 60 degree and 90 degree Si-Si-Si bond angles are observed. They might originate from three-membered rings and four-membered rings of Si atoms. In Cat-CVD a-Si, H content inside film is a few atomic %. The structural order of a-Si is hardly changed depending on H content. These results reveal the unique structure of Cat-CVD a-Si films.

**A8.2**  
LOCALIZED STATES IN MICROCRYSTALLINE SILICON PHOTOVOLTAIC STRUCTURES STUDIED BY POST-TRANSIT TIME-OF-FLIGHT SPECTROSCOPY. Vlad Smirnov, Steve Reynolds, Charlie Main, Univ of Abertay Dundee, Sch of Computing and Advanced Technologies, Dundee, UNITED KINGDOM; Friedhelm Finger, Reinhard Carius, Forschungszentrum Juelich, IPV, Juelich, GERMANY.

Much interest continues to be shown in the optimization of microcrystalline silicon for use as the absorber layer in solar cells. Factors such as RF power and silane concentration are known to have a strong influence on cell efficiency, and optimum performance has been correlated with preparation conditions close to the transition to the amorphous growth regime. In a previous study of coplanar microcrystalline silicon films using transient photoconductivity (TPC) [1], we showed that transitional films appear to have a higher defect density and a broader conduction band tail than optimized amorphous silicon films, and also that the shallow position of the Fermi level in highly crystalline material gives rise to behaviour similar in character to that seen in n-type amorphous silicon. We have now extended our work to include a study of pin solar cells using post-transit time-of-flight spectroscopy. This method has the advantage of being applicable to device structures, and is thus potentially more useful, but is unable to probe to such shallow energies as TPC. Higher dark currents and steeper decays are also encountered. However, despite these limitations, we have obtained data that suggest a flat density of defect states exists between 0.3 and 0.7 eV over a range of silane dilutions, in contrast to the TPC results. It is suggested that such differences in behaviour may arise from the anisotropic nature of the films. [1] S Reynolds, V Smirnov, C Main, R Carius and F Finger, Mat. Res. Soc. Symp. Proc. 715, A21.2.1-A21.2.6. (2002).

**A8.3**  
FEMTOSECOND FAR-INFRARED STUDIES OF CARRIER DYNAMICS IN HYDROGENATED AMORPHOUS SILICON AND SILICON-GERMANIUM ALLOYS. A. V. Vasudevan Nampoothiri<sup>a</sup>, B.P. Nelson<sup>b</sup>, and S.L. Dexheimer<sup>a</sup>; <sup>a</sup>Department of Physics, Washington State University, Pullman, WA; <sup>b</sup>National Renewable Energy Laboratory, Golden, CO.

We present femtosecond time-resolved studies of the photoexcited carrier response in the far-infrared spectral range in PECVD a-Si:H and a-SiGe:H thin films. The experiments are carried out using an optical pump / terahertz (THz) probe technique, in which a femtosecond pump pulse excites carriers in the sample and a time-delayed probe pulse measures the resulting change in the far-infrared optical properties as a function of time delay following the

excitation. These measurements are sensitive to carrier processes at low energy, corresponding to a range of approximately 0.5 - 12 meV, a key energy scale in these materials. We find that the observed photoexcited carrier dynamics are consistent with rapid carrier trapping on a picosecond time scale. This work was supported by the National Renewable Energy Laboratory and by the National Science Foundation under grant DMR-9973615.

SESSION A9: GROWTH I: MECHANISMS  
Wednesday Morning, April 23, 2003  
Salon 5/6 (Marriott)

**8:30 AM \*A9.1**

COMBINATORIAL APPROACH TO THIN-FILM SILICON MATERIALS AND DEVICES. Qi Wang, Leandro R. Tessler<sup>a</sup>, Helio Moutinho, Bob To, John Perkins, Daxing Han<sup>b</sup>, and Howard M. Branz, National Renewable Energy Laboratory, Golden, CO; <sup>a</sup>Instituto de Física 'Gleb Wataghin', Unicamp, Campinas, SP, BRAZIL; <sup>b</sup>Department of Physics & Astronomy, University of North Carolina at Chapel Hill, Chapel Hill, NC.

We apply the powerful combinatorial approach to thin-film Si materials and devices research. We fitted our hot-wire chemical vapor deposition chamber with xyz substrate translations, motorized shutters, and shadow masks to implement many combinatorial methods. For example, we have explored, in detail, the transition region of thin Si changes from amorphous to microcrystalline silicon. This transition is very sensitive to deposition parameters such as hydrogen-to-silane dilution, chamber pressure, and substrate temperature. A material library on just a few substrates led to a three-dimensional map of the transition as it occurs in our deposition system. This map guides our scientific studies and enabled us to use several distinct transition materials in our optimized solar cells research. We also grew thickness-graded wedge samples spanning the amorphous-to-microcrystalline Si transition. These single stripes that map the temporal change of thin silicon phase onto a single spatial dimension. With these wedges, the structural, optical and electrical properties can easily be studied through the continuous phase transition. We have examined the nature of the phase change with Raman spectroscopy, atomic force microscopy, extended x-ray absorption fine structure, x-ray absorption near-edge spectroscopy, variable angle spectroscopic ellipsometry, ultra-violet reflectivity and other techniques. Combinatorial techniques also accelerate our device research. In solar cells, for example, it has significantly accelerated the optimization process of p-, i-, n-, and buffer layers through wide exploration of the complex space of growth parameters in only a few deposition runs. It has also been useful to correlate the materials properties of single layers in a device to their performance in the device. Not only has the combinatorial approach greatly increased the rate of materials and device experimentation in our laboratory, it has also been a powerful tool leading to a better understanding of structure-property relationships in thin-film Si.

**9:00 AM A9.2**

SiH<sub>3</sub> DIFFUSION AND GROWTH PROCESSES OF a-Si:H. P. Vigneron, P.W. Peacock, J. Robertson, Engineering Dept, Cambridge University, Cambridge, UNITED KINGDOM.

We have studied a variety of microscopic surface processes on the hydrogen-terminated Si:H surface using total energy pseudopotential calculations, in order to understand the growth mechanism of a-Si:H. Surface diffusion is known to be needed to allow valley-filling and give the observed smooth surface. The question is - what diffuses, a weakly bound SiH<sub>3</sub> (silyl) radical, or some other species. We showed previously that the silyl radical can bind weakly to the fully hydrogen-terminated a-Si:H surface. Here, we find that the silyl can diffuse more easily between nearest neighbor Si-H surface groups than between second-neighbor surface Si-H groups, ie across a (110):H-like surface than over a (111):H-like surface. Diffusion allows the silyl to create a surface dangling bond (DB) by abstracting H, and a second silyl to then add to the DB to give a bound SiH<sub>3</sub> group. In the standard picture, this bound SiH<sub>3</sub> does not need to diffuse, it is the first stage of film growth. In this picture, a metastable adsorbed species does the diffusing. An alternative picture is that the H abstraction is an Eley-Rideal reaction, occurring wherever an incident H or silyl hits the surface, without any diffusion, to create the DB. The second silyl then comes along and adds to the DB to give the bound SiH<sub>3</sub> group, and it is this species which could diffuse. In this picture, a fully bound SiH<sub>3</sub> would need to diffuse. We show that this is less likely. Thus, the calculations support the conventional model of growth. Finally, the effects of different hydrogen surface terminations are shown to be deleterious to surface diffusion, showing why low temperature deposition without H dilution gives poor material.

**9:15 AM A9.3**

THE a-Si:H GROWTH MECHANISM: TEMPERATURE STUDY OF

THE SiH<sub>3</sub> SURFACE REACTIVITY AND THE SURFACE SILICON HYDRIDE COMPOSITION DURING FILM GROWTH.

W.M.M. Kessels, Y. Barrell, P.J. van den Oever, J.P.M. Hoefnagels, and M.C.M. van de Sanden, Dept. of Applied Physics, Eindhoven Univ. of Technology, THE NETHERLANDS.

Although the efforts on constructing a growth model for a-Si:H have been fruitful and have contributed greatly to the understanding of the a-Si:H deposition process, there are several issues in the growth mechanism of a-Si:H that are still not completely unraveled. The interaction of SiH<sub>3</sub> radicals with the a-Si:H surface under different surface conditions (as e.g., determined by the substrate temperature) is one particular unresolved issue for which there is still insufficient experimental data. Therefore we have carried out dedicated experiments under SiH<sub>3</sub> dominated film growth conditions and in the absence of ion bombardment in the expanding thermal plasma. The SiH<sub>3</sub> surface reactivity has been determined from time-resolved cavity ringdown spectroscopy experiments for substrate temperatures in the range of 50 - 450°C. This has revealed a temperature independent surface reactivity for SiH<sub>3</sub> of 0.30±0.03. The fact that also the Si growth rate is temperature independent has direct consequences for possible recombination and/or desorption reactions of the SiH<sub>3</sub> radicals at the surface. A temperature independent surface reactivity for SiH<sub>3</sub> is furthermore striking because the chemical state of the a-Si:H surface during growth changes drastically. From the combination of *in situ* attenuated total reflection infrared spectroscopy and argon ion-induced desorption of surface hydrogen, it has been found that the dominant silicon hydrides on the a-Si:H surface change from -SiH<sub>3</sub> to -SiH<sub>2</sub> to -SiH for increasing substrate temperature. The implications of these observations for the a-Si:H growth mechanism will be addressed and the growth model will be refined using simulations and theoretical calculations reported in the literature.

**9:30 AM A9.4**

MODELING RADICAL-SURFACE INTERACTIONS AND H-INDUCED CRYSTALLIZATION IN PLASMA-DEPOSITION OF SILICON THIN FILMS. Saravanapriyan Sriraman, Sumit Agarwal, Eray S. Aydil, and Dimitrios Maroudas<sup>a</sup>, Department of Chemical Engineering, University of California, Santa Barbara, CA; <sup>a</sup>Department of Chemical Engineering, University of Massachusetts, Amherst, MA.

Hydrogenated amorphous silicon (a-Si:H) and nanocrystalline silicon (nc-Si:H) thin films grown by plasma deposition from SiH<sub>4</sub>/H<sub>2</sub> discharges are widely used in photovoltaic and flat-panel display technologies. Understanding the atomic-scale physicochemical surface processes during film deposition is crucial for controlling the film structural and electronic properties. Toward this end, we have developed an atomic-scale computational analysis of the plasma-surface interactions in a-Si:H deposition. This approach combines classical molecular-dynamics (MD), molecular-statics, and Monte Carlo simulations with quantum mechanical density-functional-theory calculations of surface reaction energetics. Growth of a-Si:H on initially H-terminated crystalline Si (c-Si) substrate surfaces is modeled by MD simulations of repeated impingement of SiH<sub>3</sub>, SiH<sub>2</sub> and SiH radicals, separately, as precursors. In this presentation, surface chemical reactions during film growth will be discussed, as well as the evolution of the films' structure, surface morphology and roughness, surface reactivity, and surface composition. The role of Si-Si bond strains in mediating SiH<sub>3</sub> precursor surface diffusion in the valley-filling mechanism leading to smooth film surfaces will be emphasized. The fundamental mechanism of H-induced crystallization of a-Si:H also is analyzed through MD simulations of repeated H atom impingement on a-Si:H films. Detailed structural analysis of the H-exposed a-Si:H film revealed the formation of nanocrystalline regions embedded within the amorphous Si matrix. The MD simulations showed that H atoms diffuse into the a-Si:H film and insert into strained Si-Si bonds to form intermediate bridging and bond-centered H (Si-H-Si) configurations. The existence of bond centered H(D) in a-Si:H films exposed to H(D) atoms from a H<sub>2</sub>(D<sub>2</sub>) plasma was experimentally verified through *in situ* infrared spectroscopy. The insertion of H into strained Si-Si bonds results in structural relaxation and rearrangement of the Si matrix, thus leading to crystallization.

**9:45 AM A9.5**

EFFECTS OF EXCITATION FREQUENCY AND H<sub>2</sub> DILUTION ON CLUSTER GENERATION IN SILANE HIGH-FREQUENCY DISCHARGES. Masaharu Shiratani, Atsushi Harikai, Takanori Ogata, Kazunori Koga, Yukio Watanabe, Kyushu Univ, Dept of Electronics, Fukuoka, JAPAN.

Previously we have shown that the microstructure parameter of a-Si:H films decreases below 0.003 with decreasing the cluster amount in SiH<sub>4</sub> RF discharges by using the cluster suppressed plasma CVD method.<sup>[1]</sup> In order to clarify the conditions under which we can realize a low amount of clusters incorporated in a-Si:H films, effects of

excitation frequency and H<sub>2</sub> dilution on the cluster generation are studied by using the double pulse discharge method<sup>[2]</sup> which realizes *in situ* measurements of size and density of clusters in a size range from sub-nm to a few tens nm. The cluster amount normalized by the deposition rate for a discharge frequency  $f = 60$  MHz is more than one order of magnitude low compared to that for  $f = 13.56$  MHz. Both small clusters of 0.5 nm in size and large clusters above a few nm in size coexist for SiH<sub>4</sub>(100%), while small clusters are detected for SiH<sub>4</sub>(50%)+ H<sub>2</sub> and SiH<sub>4</sub>(20%)+H<sub>2</sub>. Moreover, the cluster amount normalized by the deposition rate for SiH<sub>4</sub>(20%)+H<sub>2</sub> is two order of magnitude low compared to that for SiH<sub>4</sub>(100%). These results suggest that the deposition of high quality a-Si:H films at a high rate can be realized by the cluster suppressed plasma CVD method together with the 60 MHz SiH<sub>4</sub>(20%)+ H<sub>2</sub> discharges. We will present performance of a Schottky solar cell of a-Si:H films deposited by the method.

<sup>[1]</sup> Y. Watanabe, et al., Pure & Appl. Chem. 74 (2002) 483.

<sup>[2]</sup> K. Koga, et al., Appl. Phys. Lett. 77 (2000) 196.

SESSION A10: GROWTH II: MECHANISMS  
Wednesday Morning, April 23, 2003  
Salon 5/6 (Marriott)

**10:30 AM \*A10.1**

APPLICATION OF DEPOSITION PHASE DIAGRAMS FOR THE OPTIMIZATION OF a-Si:H-BASED MATERIALS AND SOLAR CELLS. R.W. Collins, A.S. Ferlauto, G.M. Ferreira, Chi Chen, R.J. Koval, J.M. Pearce, and C.R. Wronski, Materials Research Institute, Center for Thin Film Devices and Department of Physics, Pennsylvania State University, University Park, PA.

Real time spectroscopic ellipsometry has been applied to establish deposition phase diagrams that can guide optimum fabrication of hydrogenated silicon (Si:H) thin films by plasma-enhanced chemical vapor deposition (PECVD) at low temperatures (<300°C) for highest performance in solar cells. The simplest phase diagram incorporates a single transition from the amorphous growth regime to the mixed-phase (amorphous + microcrystalline) growth regime versus the accumulated film thickness [designated the a→(a+ $\mu$ c) transition]. In such a diagram, the a→(a+ $\mu$ c) transition thickness is plotted versus a key deposition variable that can be used to control the Si:H phase (amorphous vs. microcrystalline) in the deposition process, most often R, the flow ratio of H<sub>2</sub> to SiH<sub>4</sub>. These simple phase diagrams have demonstrated that optimization of intrinsic (i) layers by rf PECVD at low rates for a-Si:H-based solar cells is achieved using so-called "protocrystalline" Si:H. Such material is deposited at the maximum possible R value sustainable while remaining within the a-Si:H growth regime, and thereby avoiding the (a+ $\mu$ c)-Si:H regime. The latter regime inevitably occurs for thicknesses greater than the desired value used for the optimum material in the device structure. More recently, our research has suggested that a similar "protocrystalline" Si:H deposition strategy is appropriate for optimization of p-type Si:H:B thin films for application in both p-i-n and n-i-p cell configurations. Finally, the simple phase diagrams have been extended to include, in addition, two other microstructural and phase transitions: (i) a roughening transition such that the film is purely amorphous on both sides of the transition [designated the a→a transition], and (ii) a smoothing transition in the (a+ $\mu$ c)-Si:H growth regime after which single-phase  $\mu$ c-Si:H grows [designated the (a+ $\mu$ c)→ $\mu$ c transition]. It is proposed that optimization of a-Si:H in higher rate rf PECVD processes requires the maximum possible thickness onset for the a→a roughening transition, as this reflects the longest adsorbed radical diffusion in the deposition process.

**11:00 AM A10.2**

FABRICATION OF THE HYDROGENATED AMORPHOUS SILICON FILMS CONTAINING LESS HYDROGEN AT MODERATE SUBSTRATE TEMPERATURES. Satoshi Shimizu, Hiroomi Miyahara, Makoto Shimosawa, Michio Kondo and Akihisa Matsuda, National Institute of Advanced Industrial Science and Technology, Ibaraki, JAPAN.

It has been reported that the light-induced degradation of hydrogenated amorphous silicon (a-Si:H) films correlates with hydrogen concentrations, especially with Si-H<sub>2</sub> bond densities.<sup>[1]</sup> The Si-H<sub>2</sub> densities markedly increase with deposition rates, resulting in serious light-induced degradation. It has been reported that the higher deposition temperatures are beneficial for reducing the Si-H<sub>2</sub> densities in the films prepared at higher deposition rates.<sup>[1]</sup> However, the lower processing temperatures are appreciated for device applications to p-i-n type solar cells. In this study, we attempt to reduce the Si-H<sub>2</sub> densities at lower substrate temperatures. The a-Si:H films were deposited by adopting a mesh into a conventional parallel electrode (diode) plasma enhanced chemical vapor deposition system. The mesh is placed between a cathode and a substrate. Silane plasma is confined between the cathode and the mesh. With increasing the distance

between the mesh and the substrate, the deposition rate decreases and correspondingly, the Si-H<sub>n</sub> (n = 1, 2) densities decreases even at temperatures lower than 300°C, e.g., Si-H = 4.5 at.%, Si-H<sub>2</sub> ≈ 0 at.% (≈ 5 × 10<sup>20</sup> cm<sup>-3</sup>) at 250°C. These values are almost half of those observed in the films prepared using a diode system. In those films, higher stabilities against light soaking are observed both in electron spin resonance measurements and the I-V characteristics of Schottky diodes. The mechanism of the Si-H<sub>2</sub> densities reductions at lower deposition rates is discussed in terms of hydrogen elimination reactions, Si-H<sub>2</sub> incorporation process from deposition precursors and so on. 1) T. Nishimoto, M. Takai, H. Miyahara, M. Kondo and A. Matsuda: J. Non-Cryst. Solids, 299-302 (2002) 1116.

**11:15 AM A10.3**

THE ROLE OF SURFACE DIFFUSION AND ITS RELATION TO THE HYDROGEN INCORPORATION DURING HYDROGENATED AMORPHOUS SILICON GROWTH. Arno Smets, Erwin Kessles and Richard van de Sanden, Department of Applied Physics, Eindhoven University of Technology, Eindhoven, THE NETHERLANDS.

In this contribution a systematic study of the role of surface diffusion and its relation to hydrogen incorporation during hydrogenated amorphous silicon (a-Si:H) growth from a SiH<sub>3</sub> dominant plasma beam is presented. It will be demonstrated that the growth rate and substrate temperature dependence of the surface roughness evolution and of the hydrogen-, vacancy- and void-incorporation into the a-Si:H network during growth are signatures of surface diffusion processes occurring during growth. *In situ* single wavelength ellipsometry (SWE) and ex situ atomic force (AFM) measurements have been used to study the roughness evolution, whereas ex situ infrared (IR) absorption measurements on a-Si:H films have been used to study the hydrogen-, vacancy- and void-incorporation. Void incorporation with hydrogen bonded at void surfaces are a result of a limited activated surface diffusion process, whereas the m-vacancy (m=1-3 missing silicon) incorporation, i.e. the incorporation of a compact cluster of monohydrides, happens at a site where cross-linking between two Si-H bonds has not occurred. The cross-linking step is activated with 0.21 ± 0.02 eV in agreement with previous studies [1]. The SWE and IR absorption studies provide independent verification that the lowest activated surface diffusion state has an activation energy within the range of 0.8 to 1.1 eV. This rules out the possibility that the diffusing weakly adsorbed radical is responsible for the surface smoothing. Possible surface diffusing candidates responsible for the surface smoothing will be discussed. [1] W.M.M. Kessels, A.H.M. Smets, D.C. Marra, E.S. Aydil, D.C. Schram and M.C.M. van de Sanden, Thin Solid Film 383, 154 (2001).

**11:30 AM A10.4**

EFFECT OF TEMPERATURE AND TEMPERATURE UNIFORMITY ON PLASMA AND DEVICE STABILITY. G. Ganguly, M. Bennett, D.E. Carlson, and R.R. Arya, BP Solar, North American Technology Center, Toano, VA.

A great deal of work has gone into understanding the relationship between silicon thin film growth and its effect on light induced degradation. Hydrogen dilution of silane has been observed to reduce light induced degradation. Increasing the growth temperature is widely used as a means of improving stability. This is especially true under conditions required for increasing growth rates that exacerbate the generation of higher silane related radicals. Increasing the temperature has been suggested to reduce the exothermic reactions that generate the higher silanes. We have recently shown that the cathode potential in DC discharges of silane is sensitive to the density of negatively charged ions. Real time monitoring of the cathode potential has also been used to detect gradual changes in silane to hydrogen ratio in the plasma that discernibly influences the stability of a-Si:H single junction cells. Here, we have compared the cathode voltage trends during the deposition of the i-layers of a-Si:H single junction cells. As the growth rate is increased from 1 to 10 Å/s, the cathode potential is observed to become unstable. When the substrate temperature is increased from 200 to 250°C, the cathode potential for the lower growth rate plasmas remain almost the same while a large increase is observed for the higher growth rate plasmas and the fluctuations disappear. This is consistent with increased temperature reducing higher silane generation and in turn, particle formation. [3] However, when we modified the heater assembly to obtain a more uniform temperature distribution over the electrode area of our small area (30cmx35cm) reactors, fluctuation in cathode potential did not occur at 200°C, and increasing the temperature to 250°C did not cause any change in the cathode potential for the higher growth rate plasmas. Concurrently, the light induced degradation of a-Si:H single junction devices improved from ~25 to ~20%.

**11:45 AM A10.5**

HYDROSILYLATION OF SILICON SURFACES: CRYSTALLINE VERSUS AMORPHOUS. Andrea Lehner, Florian Kohl, Martin S. Brandt, Martin Stutzmann, Walter Schottky Institut, Technische



Universitaet Muenchen, Munich, GERMANY; Claudia Dahmen and Horst Kessler, Institute for Organic Chemistry and Biochemistry II, Technische Universitaet Muenchen, Munich, GERMANY.

Hydrosilylation is a common starting process for the functionalization of silicon surfaces. Residual oxide layers on silicon have a negative influence on the degree of hydrosilylation achievable. For crystalline silicon surfaces, oxidation can be minimized by proper treatment, but never completely avoided. On the other hand, formation of a natural oxide on the surface of hydrogenated amorphous silicon is much slower, therefore providing a better starting point for a complete hydrosilylation. In the present study, we have investigated in a systematic way the kinetics of natural oxide formation on hydrogen-terminated crystalline and amorphous silicon surfaces and the influence of this oxide layer on subsequent hydrosilylation by octadecene. The structural and chemical properties of the different surfaces have been studied by AFM and X-ray Photoelectron Spectroscopy. In addition, changes in the surface recombination velocity have been monitored by photoconductivity measurements with strongly absorbed light and by surface photovoltage. Optimized conditions for the hydrosilylation of crystalline and amorphous silicon with a minimum density of structural and electronic defects will be discussed.

SESSION A11: THEORY OF AMORPHOUS MATERIALS

Wednesday Afternoon, April 23, 2003  
Salon 5/6 (Marriott)

1:30 PM \*A11.1

NUMERICAL STUDIES OF THE DYNAMICS OF AMORPHOUS SILICON: STRUCTURE, NUCLEATION AND ENERGY LANDSCAPE. Normand Mousseau, Université de Montreal, Dept de Physique and GCM, Montreal, Quebec, CANADA.

Using various simulation techniques, such as molecular dynamics, the activation-relaxation technique and bond-switching algorithms, we are slowly developing a consistent picture of the dynamical properties of amorphous silicon. For example, results of an extensive search for the activated events surrounding a single minimum, in a well-relaxed model represented by a modified Stillinger-Weber potential, confirm that barrier height at the transition point, for activated mechanisms, is determined essentially by the binding energy of a single bond and not the details of the mechanism. We will discuss these results in detail as well as recent simulations of nucleation in liquid and amorphous silicon. This work was performed in collaboration with Francis Valiquette, Philippe Beaucage. It is funded in part by NSERC (Canada) and FCAR (Quebec). NM is a Cottrell Scholar of the Research Corporation.

2:00 PM A11.2

DETECTING MEDIUM RANGE ORDER IN AMORPHOUS SILICON FILMS WITH THEORETICAL MODELING AND FLUCTUATION TRANSMISSION ELECTRON MICROSCOPY. S.V. Khare, S.M. Nakhmanson, Paul Voyles, J.R. Abelson.

The fluctuation transmission electron microscopy (FEM) technique [1] yields information about the three- and four- body atomic correlation functions of a disordered material such as amorphous silicon (a-Si), via the statistical variance of the dark field image intensity  $V$  as a function of the scattering vector  $k$  and real-space resolution  $0.61/Q$ . To date all a-Si and a-Ge samples for which the FEM signal has been measured have shown peaks in  $V(k)$  which cannot be explained by the continuous random network (CRN) model. The paracrystalline (PC) model [2], consisting of 1-3 nm crystalline Si (c-Si) grains embedded in a CRN matrix, explains these features quantitatively. We have constructed many different realizations of the PC model using a modified Barkema-Mousseau bond-switching algorithm, which yields physically realistic network statistics. We have varied (i) the number of c-Si grains present, (ii) the volume fraction of the grains, and (iii) their size distribution. We have calculated the expected FEM signatures using a modification of the image generation code by Kirkland [3]. The close match between these simulations and experimentally obtained FEM data provides strong support for the PC model. Our simulations show that a fluctuation map, consisting of FEM data as a function of both  $k$  and  $Q$ , can be used to distinguish the contributions of effects (i)-(iii) in the nano-scale structure. [1] J.M. Gibson et al., *Ultramicroscopy* 83, 169 (2000). [2] S.M. Nakhmanson et al., *Phys. Rev. B* 63, 235207 (2001). M.M.J. Treacy et al., *J. Non-Cryst. Sol.* 231, 99 (1998). [3] E.J. Kirkland (unpublished).

2:15 PM A11.3

MEASURING MEDIUM RANGE ORDER IN AMORPHOUS MATERIALS. P. Keblinski, R.K. Dash, Material Science and Engineering Department, Rensselaer Polytechnic Institute, Troy, NY; P. Voyles, Bell Laboratories, Murray Hill, NJ; M. Gibson, Advanced

Photon Source, Argonne National Laboratory, Argonne IL; M.M. Treacy, NECI, Princeton, NJ.

We have examined simulated transition electron microscopy (TEM) images of model atomic structures of paracrystalline amorphous silicon. The variance of the simulated image intensity from these models shows qualitative agreement with the results of fluctuation electron microscopy experiments on amorphous silicon and germanium. Such agreement is not found in simulations from continuous random network models. In addition to the variance, we analyze spatial correlations of the image intensity and demonstrate that they provide a direct measurement of the size of the paracrystalline grains in the model. The associated correlation length is determined by the interplay between the actual physical size of the paracrystals and the microscope resolution. At resolutions equal and smaller than the paracrystal size, the correlation length directly measures the extent of the paracrystal. At much larger resolution, the correlation length is primarily determined by the microscope aperture. Comparison of our findings with experimental TEM results will be also presented.

This research was supported by the NSF grand DMR-0074273.

2:30 PM A11.4

ATOMISTIC CHARACTER OF NANOCRYSTALLINE SILICON.

Rana Biswas, Iowa State University; Bicaï Pan, Iowa State University.

Materials grown close to the phase boundary of amorphous and microcrystalline growth have the best electronic properties for solar cells. Systematic molecular dynamics methods have been employed to generate such nanocrystalline silicon, which consists of a mixed phase of nano-crystallites in an amorphous matrix. We find the embedding method to be the most efficient where nano-crystallites are embedded in a background of amorphous material. An excess density of H resides on the surface of the nano-crystallites. The structure of this heterogeneous phase will be characterized by structural distributions and diffraction. The X-ray diffraction from the crystallites has been calculated and the width of the X-ray spectrum related to the size of the nano-crystallite. The heterogeneous matrix is found to have high and low density regions and the findings will be related to experiment. The electronic band structure of smaller models of nanocrystalline silicon will be presented and the band edges will be studied as a function of the strain. We will discuss ways to reduce the strain of such heterogeneous materials and improve the quality of the material. Supported by NREL.

2:45 PM A11.5

ON THE STRUCTURE OF "RAMAN-AMORPHOUS" SILICON.

S.B. Aldabergenova, G. Frank, M. Nerding, M. Becker, M. Albrecht, H.P. Strunk, Erlangen-Nurnberg Univ, Dept of Material Science and Engineering VII, Erlangen, GERMANY.

Silicon films deposited by different methods have been identified by Raman measurements to be "purely amorphous". The microstructure of these films was then studied by high-resolution transmission electron microscopy and electron energy-loss spectroscopy. Extended analysis of dark-field micrographs and of the observed diffraction ring patterns yield clear evidence that extremely small Si crystallites (about 1nm in diameter) are embedded in the amorphous matrix. We shall discuss the reasons of the disagreement between Raman scattering data and results of electron microscopy. We conclude that Raman measurements become ambiguous in the discrimination between amorphous and crystalline states when the crystals assume sizes of about 1 nanometer.

SESSION A12: METASTABILITY

Wednesday Afternoon, April 23, 2003  
Salon 5/6 (Marriott)

3:30 PM A12.1

NEW PHYSICS IN NEW RATE EQUATIONS FOR THE CREATION AND ANNEALING OF LIGHT INDUCED DEFECTS IN a-Si:H INCLUDING Ge ALLOYS. P.A. Fedders, Dept. of Physics, Washington University, St. Louis, MO; J.D. Cohen, Dept. of Physics, University of Oregon, Eugene, OR.

Although hundreds of experimental studies and dozens of ball and stick type models have been published on the subject of light induced defects in a-Si:H, there is no consensus on what actually causes the generation and/or annealing of such defects. It is not even clear how hydrogen participates, if at all. Motivated by recent experiments with unanticipated results on the generation and annealing of light induced defects on Si and Ge sites in a-Si:H with small amounts of Ge, we have considered the consequences of a number of equations describing the effects. This work eschews a detailed or microscopic analysis but instead focuses on classes of theories and important questions independent of any detailed mechanism. Thus we investigate questions

concerning the interaction or interference between potential dangling bond sites on Si and Ge atoms and the competition for a limited facilitating entity (such as hydrogen) in the annealing out of such defects. In this analysis it is imperative to at least try to come to grips with the observed "stretching out" of time scales observed in all annealing experiments. That is, the annealing data described by a simple rate equation can only be fit by greatly stretched exponentials which implies a very broad (and almost certainly unphysical) distribution of rates. We show that some classes of rate equations need a far narrower distribution of rates than other classes in order to fit the same data.

#### 3:45 PM A12.2

KINETICS OF LIGHT-INDUCED EFFECTS ON THE HETEROGENEOUS SILICON SOLAR CELLS. Guozhen Yue, Jeffrey Yang, Baojie Yan, Kenneth Lord and Subhendu Guha, United Solar Systems Corp., Troy, MI.

We have recently observed a significant light-induced increase in the open-circuit voltage ( $V_{oc}$ ) of mixed-phase hydrogenated silicon solar cells. We proposed that this increase is associated with a light-induced structural change. In addition, light soaking under reverse bias and forward current injection experiments suggest that the  $V_{oc}$  increase has the same origin as the Staebler-Wronski effect (SWE). In a-Si:H cells, SWE typically results in a decrease in  $V_{oc}$ . In mixed-phase solar cells, however, structural change and SWE would affect  $V_{oc}$  in opposite directions. In this paper, we investigate the kinetics of the light-induced effect on mixed-phase solar cells. The values of  $V_{oc}$  and fill factor (FF) for the cells with different initial  $V_{oc}$ 's were frequently recorded during light soaking. For the cells with a low initial  $V_{oc}$  (less than 0.8 V), the increase in  $V_{oc}$  was slow and did not saturate for the experimental time of up to 16 hours. For the cells with medium initial  $V_{oc}$  (0.8 - 0.95 V), the  $V_{oc}$  increased rapidly and then saturated. Cells with high initial  $V_{oc}$  (0.95 - 0.98 V) showed an increase in  $V_{oc}$  in the beginning, followed by a  $V_{oc}$  decrease. All the light-soaked cells exhibited a decrease in FF. The observed behavior of  $V_{oc}$  is consistent with our mixed phase model. The SWE appears to be more pronounced in the cells with high  $V_{oc}$  and low crystal volume fraction than those with low  $V_{oc}$  and relatively high crystal volume fraction. Based on our analysis, we believe that the reduction of crystal volume fraction or grain size may not be the only mechanism for the observed  $V_{oc}$  increase. Degradation of microcrystallite quality, such as increased defects near the grain boundary, can also result in the  $V_{oc}$  increase.

#### 4:00 PM A12.3

MRO MODULATIONS IN a-Si:H FILMS UPON LIGHT INDUCED DEGRADATION. Lakshminarayana Nittala, Yeonwoong Jung, John R. Abelson, Department of Materials Science & Engineering, University of Illinois, Urbana, IL.

In disordered materials, structural information at the nanoscale (2-4 nm) can be observed using Fluctuation Electron Microscopy (FEM), which is sensitive to the 3- and 4-body atomic correlation functions. The FEM technique involves calculation of the statistical variance in dark field image intensities as a function of the scattering vector and the microscope resolution. Previous FEM studies have shown the presence of considerable medium range order (MRO) in as-deposited amorphous silicon and germanium thin films, which do not match the predictions of a covalent random network model. The increased MRO is ascribed to the presence of ~2 nm sized crystalline grains which are heavily strained and therefore invisible to diffraction measurements; to distinguish this special situation, they are called paracrystallites. Previous FEM studies on a-Si have examined very thin (~20 nm) vapor-deposited samples. We have shown that the MRO modulations in these films are small (but definitely non-zero) when the films are subjected to light soaking and thermal annealing treatments [1]. However, changes in MRO may be thickness dependent: surface and interface recombination of e-h pairs can suppress the Staebler-Wronski Effect (SWE), and the presence of a surface oxide retards the effects of thermal annealing. Light soaking of ~0.5  $\mu\text{m}$  thick films avoids these effects and is better representative of the absorber layer in solar cells. In this study, we perform FEM on the central portion of device quality a-Si:H films which are first subjected to light soaking and/or annealing treatments, then chemically thinned from both sides to the ~20 nm thickness required for FEM analysis. The observed changes in MRO are correlated with the SWE and explained in terms of changes in the paracrystalline structure. [1] P.M. Voyles and J.R. Abelson, "Medium Range Order in Amorphous Silicon Measured by Fluctuation Electron Microscopy", accepted by Solar Energy Materials (2002).

#### 4:15 PM A12.4

TEMPERATURE DEPENDENCE OF A HYDROGEN DOUBLET SITE IN LIGHT-SOAKED a-Si:H FROM  $^1\text{H}$  NMR. T. Su, A. Allen, P.C. Taylor, University of Utah, Dept. of Physics, Salt Lake City, UT; G. Ganguly, and D.E. Carlson, BP Solar, Toano, VA.

From  $^1\text{H}$  NMR at 7 K on as-grown, light-soaked, and annealed

samples of a-Si:H an additional doublet signal appears only after light soaking. This doublet indicates a closely spaced pair (approximately 2.3 Å apart) of hydrogen atoms that are considerably further away from other hydrogen atoms. The concentration of these doublets is between  $10^{17}$  and  $10^{18}$   $\text{cm}^{-3}$  and is generally consistent with ESR measurements of the defect density after light soaking [1]. We report the temperature dependence of this doublet from 7 to 20 K. Above about 10 K the signal disappears in a manner that is consistent with local motion of the hydrogen atoms. Details of the local motion will be discussed. 1. T. Su, P.C. Taylor, G. Ganguly, and D.E. Carlson, Phys. Rev. Lett. 89, 015502 (2002).

#### 4:30 PM A12.5

EVIDENCE FOR A TRAP-INDUCED INSTABILITY IN a-Si:H. Vikram Dalal, Puneet Sharma, and Aziz Ahmed, Iowa State University, Dept. of Electrical and Computer Engr., Ames, IA.

We have studied the early time degradation kinetics and CPM spectra of a-Si:H films. We find that at the earliest times (<100 s), the kinetics follow a time and intensity dependence that can be explained assuming a mono-molecular carrier capture event. The intensity dependence is such that the time required to achieve a given dangling bond density is inversely proportional to the intensity, as predicted from mono-molecular kinetic equations. We also find, by measuring the entire alpha vs. energy spectrum during both early (1 min- 10 min) and longer term (1-30 hours) degradation, that there is a decrease in gap state density in the energy region around 1.3 eV below the conduction band, and an increase in the gap state density in the region around 1.0 eV. The decrease at ~1.3 eV, the mono-molecular kinetics of this early decay, and the intensity dependence of degradation, all fit the charged trap to dangling bond conversion model proposed by David Adler in 1984. We have also studied the isothermal annealing behavior of this second kind of defect, and it anneals out much faster than the normal dangling bond defect. When the inverse of photo-conductivity is plotted vs. the normal ~1.0-1.1 eV dangling bond defect, a hysteresis is observed during both degradation and annealing, as would be the case if there were two distinct types of defects present in the material. To make sure that surface effects were not involved, we also made samples with passivated surfaces, using a graded gap a-(Si,C) layers to drive both electrons and holes away from the surface. The results were essentially the same for both surface passivated and unpassivated samples. Based on the spectroscopic and kinetic evidence, we propose that the so-called fast states in a-Si may be Adler-type charged defects. The importance of this new type of defect on stability of solar cells will be discussed in the paper.

#### 4:45 PM A12.6

EVOLUTION OF CHARGED GAP STATES IN a-Si:H UNDER LIGHT EXPOSURE. M. Zeman, V. Nadazdy, R.A.C.M.M. van Swaaij, J.W. Metselaar, Delft University of Technology, DIMES, Delft, THE NETHERLANDS; R. Durny, Slovak University of Technology, Bratislava, SLOVAKIA.

Inherent to hydrogenated amorphous silicon (a-Si:H) are the reversible changes in electronic properties of a-Si:H under light exposure, known today as the Staebler-Wronski effect (SWE). It is generally accepted that light soaking leads to the creation of additional dangling-bond defects. We present experimental results from charge deep-level transient spectroscopy (Q-DLTS) that reveal a surprising behavior of the band-gap states in a-Si:H during light soaking. The Q-DLTS experiments show that prior to the creation of defect states around midgap there is an initial decrease of the density of gap states located above midgap. This observation indicates that in the early stage of light soaking, annihilation of some type of defects takes place. We propose microscopic atomic configurations that introduce charged states in the band gap of a-Si:H. The positively charged states above midgap, normally assigned to positively charged dangling bonds, are related to a charged complex formed by a Si dangling bond and a hydrogen molecule. The dissociation of this complex in the early stage of light exposure supplies mobile hydrogen. The origin of the negatively charged states below midgap is attributed to floating bonds and not to negatively charged dangling bonds. Having identified the origin of the charged gap states we propose a comprehensive model that describes the processes of the SWE. In this model the major contributions of present microscopic models for SWE defect creation are integrated. Using the evolution of gap states during light soaking as predicted by our model we obtained a good agreement between the simulated and measured non-monotonous changes in the dark conductivity of light-soaked a-Si:H.

SESSION A13: GROWTH III: HWCVD AND nc-Si:H  
Thursday Morning, April 24, 2003  
Salon 5/6 (Marriott)

#### 8:30 AM \*A13.1

PRESENT STATUS OF HOT WIRE CHEMICAL VAPOR

In this review, the latest achievements in Hot Wire CVD technology will be presented and illustrated by the performance of silicon thin film devices. In the last few years, tremendous progress has been made: (1) It has been shown that there are no fundamental limitations in HWCVD with respect to substrate area. Using a periodic configuration of multiple short wires, good uniformity ( $\pm 7.5\%$ ) has been demonstrated by Anelva over an area of  $96 \text{ cm} \times 40 \text{ cm}$ . (2) High quality microcrystalline Si can be produced. Solar cells in the n-i-p configuration are currently better than those made by PECVD. At Jlich, the efficiency of such cells is 9.4%, and Utrecht has recently made the first HWCVD multibandgap triple junction solar cells, (3) HWCVD offers the potential of ultra high deposition rates. At NREL, a-Si:H has been deposited at rates in excess of  $12 \text{ nm/s}$ , and at Utrecht University  $\mu\text{-Si:H}$  rates are in excess of  $1 \text{ nm/s}$ . (4) New applications have been demonstrated. Thin film transistors (TFTs) with mobilities in excess of  $1 \text{ cm}^2/\text{Vs}$  with an a-Si:H channel have been shown to be stable and  $\mu\text{-Si:H}$  TFTs have been made (at Sony) with mobilities in excess of  $40 \text{ cm}^2/\text{Vs}$ . (5) The efficient production of atomic H in HWCVD is beneficial in passivation processes, for instance in HIT cells; but it can also be applied in etching processes. (6) Alloys of Si with various functions can be made, such as  $\text{SiN}_x$  for antireflection and passivation coatings. Remarkably, all of the above results have been achieved without detailed knowledge about the primary reactions at the filament, the gas phase reactions, and the reactions with the growing film. The choice of filament material and its operation temperature have a large influence on the production of various reaction species and thus, on the structure of the resulting film. HWCVD is basically an ion-free deposition technique, which is an advantage for many kinds of thin films. Polymer deposition and nanotube formation are other areas in which HWCVD has proven its feasibility.

**9:00 AM A13.2**

PROPERTIES OF HIGH QUALITY p-TYPE MICROCRYSTALLINE-Si PREPARED BY CAT-CVD. Hideki Matsumura, Kouichi Katouno, Masaya Itoh and Atsushi Masuda, JAIST, Tatsunokuchi, Ishikawa, JAPAN.

Cat-CVD (Catalytic Chemical Vapor Deposition), often called Hot-Wire CVD, is a new method to prepare device quality a-Si, micro-crystalline ( $\mu\text{c}$ -Si) and poly-Si films. Particularly, a-Si and  $\mu\text{c}$ -Si were already used as i-layer in p-i-n solar cells and the cell efficiency of about 10% was achieved in spite of much higher deposition rates than PECVD. Thus, it is valuable to know the properties of p-type  $\mu\text{c}$ -Si films as a transparent window layer for improving the efficiency of full Cat-CVD solar cells. Here, the properties of  $\mu\text{c}$ -Si films, which are obtained by using large  $\text{H}_2$  diluted  $\text{SiH}_4$  gas, are extensively studied along with the properties of boron doped p-type films. So far, it is found that 1) by H-dilution of  $\text{SiH}_4$ , films of a thickness of only 20 nm or less become  $\mu\text{c}$ -Si on both glass and ITO of Asahi-U without a-Si incubation layer, 2) by making  $\mu\text{c}$ -Si, transparency is much more improved than that of a-Si particularly at the region of short wave length light, for instance, the absorption coefficient is decreased by one order of magnitude at wave length of 550 nm and becomes enough as window layers, and 3) by boron doping, the conductivity as large as  $0.3 \text{ Scm}^{-1}$  can be obtained keeping transparent properties. The results demonstrate the feasibility of Cat-CVD  $\mu\text{c}$ -Si as a new window material for solar cells.

**9:15 AM A13.3**

HIGH-RATE DEPOSITION OF MICROCRYSTALLINE SILICON THIN FILMS FOR P-I-N SOLAR CELLS. Takuya Matsui, Michio Kondo, Akihisa Matsuda, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, JAPAN.

High rate deposition technique of intrinsic microcrystalline silicon ( $\mu\text{c}$ -Si:H) thin films is essentially required for solar cell fabrication in view of future industrial mass production. We have demonstrated that high-pressure and  $\text{SiH}_4$ -depletion (HPD) conditions in plasma-enhanced chemical vapor deposition (PECVD) process are effective to provide high quality  $\mu\text{c}$ -Si:H films at high deposition rates in excess of  $20 \text{ \AA/s}$  [1]. We have also found that HPD plasma can suppress ion-bombardment and gas-phase reaction even when higher discharge power is used in the higher  $\text{SiH}_4$  flow rate regime. Here we present the results on  $\mu\text{c}$ -Si:H p-i-n solar cells grown at  $20 \text{ \AA/s}$  by 100 MHz-PECVD using HPD technique. In such high rate regime, we found that the deposition pressure plays a dominant role in determining short circuit current ( $J_{sc}$ ) of solar cells. With an increase in deposition pressure from 3 to 6 Torr,  $J_{sc}$  increases by 50% due to a large improvement in long wavelength response, while deposition rate is almost unchanged. From the relationship between  $J_{sc}$  and crystallographic structure of i-layers, we attribute the increase in  $J_{sc}$  to the structural evolution of  $\mu\text{c}$ -Si:H toward the larger crystallites

with (220) preferential orientation. Further improvement in  $J_{sc}$  is achieved at a deposition pressure of 7 Torr by applying a higher discharge power. As a result, we have obtained an 8.1% conversion efficiency of  $\mu\text{c}$ -Si:H solar cell ( $J_{sc}=22.3 \text{ mA/cm}^2$ ,  $V_{oc}=0.52 \text{ V}$ ,  $FF=0.7$ ) with a  $2 \text{ \mu m}$ -thick i-layer grown at  $20 \text{ \AA/s}$ . The above results offer the advantages of the use of HPD technique for the fabrication of high efficiency solar cells at high deposition rates. [1] M. Kondo et al. J. Non-Cryst. Solids, 84, 266-269 (2000).

**9:30 AM A13.4**

INVESTIGATIONS ON THE REAL-TIME MONITORING OF THE CRYSTALLINITY OF HYDROGENATED MICROCRYSTALLINE SILICON FILMS. Christoph Ross, Friedhelm Finger, Reinhard Carius, Institute of Photovoltaics (IPV), Research Centre, Juelich, GERMANY.

Transitions between microcrystalline and amorphous silicon as a function of growth parameters have attracted a lot of interest during the last years (1). For microcrystalline silicon a growth near the transition results in best material properties for devices such as solar cells (2). However, the growth in this regime very critically depends on the substrate. Therefore, a real-time control of the crystallinity is desired. We present a method for monitoring the evolution of crystallinity during the growth by using in situ spectroscopic ellipsometry. The crystallinity is gained from the analysis of the shape of ellipsometric spectra by using only a few spectral points in the near UV. For the present system this results in a sampling rate of up to 6 scans per minute. Hence, if the film grows with a rate of  $0.1\text{-}0.2 \text{ nm/s}$  the crystallinity can be measured at intervals of  $1\text{-}2 \text{ nm}$ , which is an order of magnitude smaller than the probe depth. Results are shown for (i) microcrystalline silicon grown on silicon seed layers with different crystalline volume fractions and for (ii) microcrystalline silicon absorber layers grown on p-type silicon. It turns out that evolutions of crystallinity can be monitored successfully. The crystallinity of selected films is in good agreement with the crystalline volume fraction measured by Raman spectroscopy. Further improvements of the system are discussed. The method turns out to be well suited for a process control. - References: (1) A.S. Ferlauto, R.J. Koval, C.R. Wronski, and R.W. Collins, Appl. Phys. Lett. 80 (2002) 2666. (2) O. Vetterl, F. Finger, R. Carius, P. Hapke, L. Houben, O. Kluth, A. Lambertz, A. Mueck, B. Rech, H. Wagner, Solar Energy Materials and Solar Cells 62 (2000) 97.

**9:45 AM A13.5**

TOWARDS MICROCRYSTALLINE SILICON N-I-P SOLAR CELLS WITH 10% CONVERSION EFFICIENCY. Luc Feitknecht, Xavier Niquille, Joelle Guilet, Corinne Droz, Julien Bailat, Evelyne Vallat, Arvind Shah, Institute of Microtechnology (IMT), University of Neuchatel, SWITZERLAND.

High-performance microcrystalline and amorphous silicon solar cells are the key elements for a successful combination to form the "micromorph" tandem cell. Here, the authors report on the successful realisation of a single-junction microcrystalline silicon n-i-p solar cell by the VHF PE-CVD deposition process; the cell has a conversion efficiency exceeding 9% ( $V_{oc}=520 \text{ mV}$ ,  $FF=73\%$ ,  $J_{sc}=24.2 \text{ mA/cm}^2$ ) and was deposited at a rate of  $2.6 \text{ \AA/sec}$ . This milestone was achieved by a successful combination of three elements:

(1) fine-tuning of the silane concentration (SC) in the silane + hydrogen source gas used for deposition of the intrinsic  $\langle i \rangle$  absorber layer; (2) incorporation of an optimised back-reflecting substrate into the cell; (3) the methodical development of p- and n-type doped films. For in-situ control of the critical i-layer deposition, OES is shown to be an useful process-control tool. On the other hand, a complete posterior microstructure characterisation of this cell will be discussed i.e. based on Raman and TEM data.

Above cell performances could be obtained by a substantial increase in  $V_{oc}$  while maintaining reasonable  $J_{sc}$ -values. Earlier, systematic investigations had revealed a trade-off between those two values in function of SC used for i-layer deposition. The authors now show that a variation in SC as used for deposition of i-layers in n-i-p solar-cells does not influence current generation in the long-wavelength region (above 900nm), provided suitable light-diffusing back-reflectors are employed. In this wavelength region, a saturated absorption value is obtained, independently of the SC used. The fabrication of a micromorph stacked cell integrating such  $\mu\text{c}$ -Si:H bottom cell is under way.

SESSION A14: GROWTH IV: HWCVD AND nc-Si:H  
Thursday Morning, April 24, 2003  
Salon 5/6 (Marriott)

**10:30 AM \*A14.1**

ROLE OF H FOR MICROCRYSTALLINE SILICON NUCLEATION. Hiroyuki Fujiwara, Michio Kondo and Akihisa Matsuda, AIST, Ibaraki, JAPAN.

Nucleation of microcrystalline Si ( $\mu\text{-Si:H}$ ) from the hydrogenated amorphous Si (a-Si:H) phase has been studied by applying real-time spectroscopic ellipsometry (SE) and infrared attenuated total reflection spectroscopy (ATR). We have demonstrated that a high intrinsic stress in the a-Si:H phase is essential for  $\mu\text{-Si:H}$  nucleation. In plasma-enhanced chemical vapor deposition using high hydrogen dilution,  $\mu\text{-Si:H}$  nucleation was observed only when compressive stress inside a-Si:H exceeds 750 MPa, regardless of deposition temperature [1]. As the result of alternating a-Si:H deposition and  $\text{H}_2$ -plasma treatment, we confirmed that the high compressive stress in a-Si:H originates from H inserted into the a-Si:H network. The high compressive stress in a-Si:H was found to enhance the formation of the  $\text{SiH}_n$  ( $n=1-2$ ) complex that has been proposed to be a precursor for  $\mu\text{-Si:H}$  nucleation [2]. The process of  $\mu\text{-Si:H}$  nucleation, however, shows a large substrate effect. In the  $\mu\text{-Si:H}$  growth performed on ZnO substrate at high hydrogen dilution, a porous interface layer having a large amount of  $\text{SiH}_2$  bonds (16 at.%) is formed at the  $\mu\text{-Si:H/ZnO}$  interface. We find a significant increase in the interface-layer thickness with increasing hydrogen dilution ratio. Detailed analyses showed that the chemical reduction of ZnO by H suppresses the chemical reactivity on the ZnO surface and induces the porous interface-layer formation. Based on the above results, we review the role of H for  $\mu\text{-Si:H}$  nucleation. [1] H. Fujiwara, M. Kondo, and A. Matsuda, *Jpn. J. Appl. Phys.* 41, 2821 (2002). [2] H. Fujiwara, M. Kondo, and A. Matsuda, *Surf. Sci.* 497, 333 (2002).

#### 11:00 AM A14.2

**MECHANISM AND ENERGETICS OF H INSERTION INTO Si-Si BONDS IN HYDROGENATED AMORPHOUS SILICON FILMS.** Saravanapriyan Sriraman, Mayur S. Valipa, Eray S. Aydil, and Dimitrios Maroudas<sup>a</sup>, Department of Chemical Engineering, University of California, Santa Barbara, CA; <sup>a</sup>Department of Chemical Engineering, University of Massachusetts, Amherst, MA.

Understanding the mechanism of chemically induced disorder-to-order structural transitions is important for synthesizing various technologically important materials, including nanocrystalline (nc-Si:H) silicon thin films that are used in solar cells and flat panel displays. Thin hydrogenated amorphous silicon (a-Si:H) films crystallize at temperatures much lower than those required for thermal annealing when exposed to a flux of H atoms from an  $\text{H}_2$  plasma, or when the  $\text{SiH}_4$  feed gas is heavily diluted with  $\text{H}_2$ . Although several hypotheses have been proposed in the past, the fundamental mechanism behind this transition has remained under debate. The atomic-scale processes that govern this structural transition are analyzed through molecular-dynamics (MD) simulations of repeated H atom impingement on computationally generated a-Si:H films. We showed recently that H-induced crystallization was mediated by insertion of H atoms into strained Si-Si bonds through the formation of intermediate bridging and bond-centered (BC) configurations as the H atoms diffused through the a-Si:H film. This presentation focuses on the analysis of the mechanism and energetics of these H insertion pathways. Prior to insertion, diffusing H atoms are observed to bond to one Si atom of the Si-Si bond; upon insertion, a bridging configuration forms when the H atom bonds to both of the Si atoms that are bonded. After H insertion, a Si-Si bond is further strained or broken, or it may relax restoring the Si-Si bond closer to the equilibrium c-Si bond length, after the H atom leaves the bridging configuration. On the other hand, when a diffusing H atom occupies the bond-centered (BC) location between two Si atoms that are not originally bonded, a Si-Si bond forms after the H atom diffuses away. The energetics of H insertion into strained Si-Si bonds, its correlation with bond strain, and its implications in the structural relaxation of the amorphous phase are discussed.

#### 11:15 AM A14.3

**EXPERIMENTAL STUDIES OF MEDIUM RANGE ORDER IN NANOSTRUCTURED HYDROGENATED SILICON THIN FILMS.** S. Thompson, Department of Mechanical Engineering; T.J. Belich, School of Physics and Astronomy; C.R. Perrey, Department of Chemical Engineering and Materials Science; U. Kortshagen, Department of Mechanical Engineering; C.B. Carter, Department of Chemical Engineering and Materials Science; and J. Kakalios, School of Physics and Astronomy, The University of Minnesota, Minneapolis, MN.

Thin films of hydrogenated amorphous silicon with nanocrystalline inclusions (a/nc-Si:H) (sometimes also referred to as "polymorphous silicon") have attracted considerable attention recently due to reports of superior electronic properties combined with improved resistance to light induced defect creation. We report experimental studies of a/nc-Si:H films synthesized via rf capacitively coupled plasma discharge using a dilute mixture of silane in helium and hydrogen, operated at pressures above 1000 mTorr at the boundary of powder formation. Plasma conditions are monitored through analysis of RF current and voltage harmonics that are sensitive to particle growth in the plasma. Images of nanocrystallites in these films, with crystallites

as small as 3.2 nm being resolved, are obtained using high resolution transmission electron microscopy (HRTEM). Electron energy loss spectra acquired in the HRTEM confirm the presence of silicon in the crystallites. The optical absorption spectra, measured using the constant photocurrent technique, indicates that both the Urbach slope and mid-gap defect density are lower in the a/nc-Si:H films than in conventional a-Si:H. Despite a lower midgap defect density, the magnitude of the decrease in the dark conductivity following light exposure is comparable in the a/nc-Si:H films to that seen in more defective a-Si:H. The dependence of the a/nc-Si:H film properties as the plasma discharge conditions (gas pressure, silane dilution ratios, temperature gradient between deposition electrodes) are systematically varied will be described. This research supported by NSF under IGERT grant DGE-0114372. TJB and JK primarily supported by NREL/AAD - 9 -18668 - 13. ST, TJB, JK and UK acknowledge partial support by the NSF MRSEC DMR-0212302. C. Nelson (NCEM, NBNL) is acknowledged for assistance with the CM-200 TEM.

#### 11:30 AM A14.4

**CROSS-SECTIONAL TRANSMISSION ELECTRON MICROSCOPY INVESTIGATION OF THE MICROSTRUCTURE OF AMORPHOUS HYDROGENATED Si AND SiGe SOLAR CELL MATERIALS.** Eli Sutter and Don Williamson, Colorado School of Mines, Department of Physics, Golden, CO.

There is a continuous drive for improving a-Si:H and a-SiGe:H materials as intrinsic layers for use in solar cells with recent interest focussed on depositing good quality materials at higher deposition rates. Cell performance and light-induced degradation in these materials seem to depend critically on the microstructure of the films and the presence of heterogeneities, such as microvoids, H-rich areas, reduced density areas, and Ge composition fluctuations in the alloy films. Although such features have been inferred from small-angle X-ray and neutron scattering studies, more direct and detailed knowledge of the microstructures and linking of particular structures to the deposition conditions could lead to improvements in stability and performance of solar cells. Here we use cross-sectional transmission electron microscopy (XTEM) to investigate the microstructure of a-Si:H and a-SiGe:H films prepared by both plasma-enhanced and hot-wire chemical vapor deposition. The XTEM studies show the presence of spherical-like and highly elongated microvoids in device quality a-SiGe:H, as well as in hot-wire a-Si:H grown at high deposition rates. The direct XTEM imaging allows us to follow the evolution of the structural inhomogeneity with increasing the thickness of the films. Investigation of the microstructural properties of a-Si:H prepared near the edge of microcrystallinity which show a lot of promise regarding improved stability will be presented as well.

#### 11:45 AM A14.5

**OPTICAL FUNCTIONS OF TRANSPARENT CONDUCTORS AND THEIR IMPACT ON COLLECTION IN AMORPHOUS SILICON SOLAR CELLS.** G.M. Ferreira, Chi Chen, Ihsin An, C.R. Wronski, R.W. Collins, Materials Research Institute, Center for Thin Film Devices and Department of Physics, Pennsylvania State University, University Park, PA; G. Ganguly, BP Solar, Toano, VA; Joong Hwan Kwak and Koeng Su Lim, Korea Advanced Institute of Science and Technology, Daejeon, KOREA.

We have established procedures for determining the optical functions of textured transparent oxide (TCO) thin films used as contact layers in amorphous silicon-based thin film solar cells. These procedures combine (i) *multichannel Mueller matrix spectroscopy* using a dual rotating-compensator spectroscopic ellipsometer in reflection from the top surface of the TCO film, which provides spectra in the index of refraction  $n$  versus photon energy  $E$ , and (ii) *multichannel transmission spectroscopy* through a double-thick TCO sandwich contacted with index-matching fluid, which provides spectra in the extinction coefficient  $k$  versus  $E$ . These techniques have been designed to extract accurate  $n(E)$ ,  $k(E)$  spectra with essentially full rejection of the scattered light that arises due to macroscopic roughness. The resulting spectra for doped  $\text{SnO}_2$  samples have been fitted using a Kramers-Kronig consistent expression that combines three components: (i) a Drude characteristic for intraband absorption, (ii) a Tauc-Lorentz characteristic for interband absorption, and (iii) a Sellmeier characteristic for additional dispersion. These three components represent "electronic oscillators" with resonant frequencies (i)  $\omega_0=0$ ; (ii)  $\omega_0$  in the near ultraviolet, accessible to the spectroscopies; and (iii)  $\omega_0$  well above the accessible range, respectively. A procedure that fits data from the ellipsometric and transmission spectroscopies iteratively has been most successful in this analysis. Among the primary optical losses in a-Si:H solar cells include absorption by the TCO film [as controlled by  $k(E)$ ] and reflection from the TCO/p-layer interface [as controlled by  $n(E)$ ]. In this paper, we characterize such optical losses in detail through modeling the solar cell optical quantum efficiency and demonstrate the extent to

which microscopic roughness at the TCO/p-layer interface can serve as an "anti-reflection layer" for enhanced collection.

SESSION A15: GROWTH V: LOW TEMPERATURE  
AND HIGH RATE  
Thursday Afternoon, April 24, 2003  
Salon 5/6 (Marriott)

**1:30 PM \*A15.1**

**VERY HIGH INTEGRITY THIN FILM FORMATIONS AT VERY LOW TEMPERATURES.** Tadahiro Ohmi, Akinobu Teramoto, Hiroaki Tanaka, and Masaki Hirayama, New Industry Creation Hatchery Center, Tohoku University, Sendai, JAPAN.

It is usual understanding that the film quality is improved by increasing the substrate temperatures and decreasing the film growth rate for the ultra clean process environment free from various contaminants. On the other hand, recent progresses of semiconductor industry and flat panel display industry essentially require the very high speed film growth at very low temperatures with keeping the very high quality of thin films. In order to establish this very essential requirement, following four new technologies must be completely implemented to the process equipment such as Radical Reaction Based Processings Instead of Current Molecule Reaction Based Processings, Ultra Clean Process Environments Free From Various Contaminants Where Process Gas Flow Rate, Contamination and Composition Must Be Completely Controlled at Scheduled Value, Respectively, Ultra Clean Wafer Surface Free From Various Contaminants Such As Particles, Metals, Organic Molecules, Moisture Molecules and Native Oxide With Keeping Atomic Order Surface Flatness and Hydrogen Termination Particularly for Base Silicon Surface, and Completely Regulated Ion Bombardment onto the Wafer Surface to Promote Very High Integrity Thin Film Growth by Activating the Wafer Surface Where the Bombardment Ion Energy Are Regulated Less Than the Critical Value Giving Rise To Surface Damages and Greater Than the Critical Value Giving Rise To Sufficient Surface Activation to Promote Very High Integrity Thin Film Growth, Respectively. Thus, very high integrity single crystal Si, SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> film have been obtained at 300-400.

**2:00 PM A15.2**

**REACTION CONTROL IN AMORPHOUS SILICON FILM DEPOSITION BY HYDROGEN CHLORIDE.** Akihiro Takano, Takehito Wada, Shinji Fujikake, Takashi Yoshida, Tokio Ohto, Fuji Electric Corporate Research and Development, Ltd., Yokosuka, JAPAN; Eray S. Aydil, Department of Chemical Engineering, University of California, Santa Barbara, CA.

HCl was added to SiH<sub>4</sub> containing plasmas to grow a-Si:H(Cl) films aiming at an alternative dangling bond terminator. Bulk and surface infrared spectra, film thickness and optical band gap were in situ examined by multiple total internal reflection Fourier transform infrared spectroscopy and spectroscopic ellipsometry. SiH<sub>2</sub>Cl<sub>2</sub> was also used as a conventional Cl source for referential a-Si:H(Cl) film deposition experiments. In the conventional SiH<sub>2</sub>Cl<sub>2</sub>/SiH<sub>4</sub> system, the deposition rate increases significantly as already reported. The increase in the deposition rate introduces a monotonous decrease in refractive index and an optical band gap widening. Cl concentration is typically limited to below 10<sup>20</sup> cm<sup>-3</sup> in order to avoid the optical band gap widening for an application to solar cells. In these a-Si:H(Cl) films, Cl is not a major dangling bond terminator. In contrast, the introduction of HCl, which does not affect the deposition rate significantly, changes top surface compositions of growing films drastically from higher silicon hydride to chlorinated lower hydride. The surface reaction control eliminates unfavorable higher hydride bonding structures (SiH<sub>2</sub> and/or SiH in voids) in the deposited bulk films. The a-Si:H(Cl) films deposited from the mixture of SiH<sub>4</sub> and HCl do not show significant optical band gap widening in spite of containing over 10<sup>21</sup> cm<sup>-3</sup> Cl atoms, a concentration that is comparable to that of hydrogen. A competition between Cl and H for surface bonding sites is reflected on the Cl concentration increasing at the expense of decreasing H concentration with the increase in HCl partial pressure in the gas phase. The new a-Si:H(Cl) material from the HCl/SiH<sub>4</sub> system, in which Cl acts as a major dangling bond terminator together with H without optical band gap widening, is expected to be a promising material for amorphous solar cells.

**2:15 PM A15.3**

**MATERIAL STRUCTURE OF MICROCRYSTALLINE SILICON DEPOSITED WITH AN EXPANDING THERMAL PLASMA.** C. Smit<sup>a,c</sup>, D.L. Williamson<sup>b</sup>, M.C.M. van de Sanden<sup>c</sup>, and R.A.C.M.M. van Swaaij<sup>a</sup>; <sup>a</sup>Delft University of Technology, DIMES-ECTM, Delft, THE NETHERLANDS; <sup>b</sup>Colorado School of Mines, Department of Physics, Golden, CO; <sup>c</sup>Eindhoven University of Technology, Department of Applied Physics, Eindhoven, THE NETHERLANDS.

In solar cell technology much research effort is directed towards the high-rate deposition of microcrystalline silicon, because the optical band gap of this material is ideally suited for the intrinsic layer of the bottom cell in a tandem solar cell in combination with a hydrogenated amorphous silicon (a-Si:H) top cell. Furthermore, the charge transport properties and the stability against light soaking are better than that of a-Si:H. With expanding thermal plasma chemical vapour deposition (ETP CVD) high deposition rates have been achieved for the deposition of a-Si:H (around 0.7 nm/s successfully applied in solar cells). Here we apply this technique for the deposition of microcrystalline silicon films with varying crystalline fraction at rates of about 1 nm/s. We used several techniques to characterise the material, in particular the material structure. The crystalline fractions as obtained from Raman spectroscopy as well as from X-ray diffraction (XRD) vary from 0 to 58%. The average particle sizes vary from 6 to 17 nm as estimated from the (111) XRD peak using the Scherrer formula. Small angle X-ray scattering (SAXS) and flotation density measurements indicate void volume fractions of about 6%. However, void volume fractions of about 30% are obtained when the Bruggeman effective medium approach is applied using the far-infrared refractive index. This contradiction is not yet understood. When the samples are tilted the SAXS signal is lower than for the untilted case, indicating elongated objects parallel to the growth direction in the films. These objects can also be seen in high-resolution transmission electron microscopy (HRTEM) images of one of the samples, in which elongated structures in the growth direction are visible.

SESSION A16: CRYSTALLIZATION  
Thursday Afternoon, April 24, 2003  
Salon 5/6 (Marriott)

**3:00 PM \*A16.1**

**HIGH-QUALITY POLY-Si BY SILICIDE MEDIATED CRYSTALLIZATION OF AMORPHOUS SILICON.** Jin Jang, Department of Physics and TFT-LCD National Lab., Kyung Hee Univ., Dongdaemoon-ku, Seoul, KOREA.

A super-grain polycrystalline silicon can be obtained by the metal induced crystallization of amorphous silicon. The optimization of the metal density used for the metal induced crystallization and the crystallization procedure are key factors for the growth of large-grain polycrystalline silicon on glass. We carried out the various approaches to get high-quality poly-Si by silicide-mediated crystallization (SMC) of amorphous silicon. The metal density, heating methods, electric field, amorphous silicon precursor have been varied in the present work. The crystalline properties were studied through TEM, SEM, EBSD and AFM. We found that the orientation of grains are different even in one sample, however, the most of grains have only one orientation in one grain. The crystallization mechanism of SMC and the approach to improve the quality of the poly-Si will be discussed on the basis of our experimental results. The performances of thin-film transistors using SMC poly-Si will be discussed in relation with the crystalline properties. The field-effect mobility of higher than 250 cm<sup>2</sup>/Vs has been obtained with the SMC poly-Si on glass.

**3:30 PM A16.2**

**STRESS EFFECTS ON NANOCRYSTAL FORMATION BY NICKEL-INDUCED CRYSTALLIZATION OF AMORPHOUS SILICON.** Yaocheng Liu, Michael D. Deal, Mahmooda Sultana<sup>†</sup>, and James D. Plummer, Center for Integrated Systems, Stanford University, CA; <sup>†</sup>Department of Chemical Engineering, University of Southern California, CA.

Metal-induced crystallization (MIC) of amorphous Si is gaining increased interest because of its potential use for low-temperature fabrication of integrated circuits. In this work, the MIC technique was used to make Si nanocrystals and the effects of stress on the crystallization were studied. Amorphous Si films were deposited onto the Si substrate with thermal oxides on top by low-pressure chemical vapor deposition (LPCVD) and then patterned into nanoscale pillars by electron beam lithography and reactive ion etching. A conformal low-temperature oxide (LTO) layer was deposited to cover the pillars, followed by an anisotropic etch back to form a spacer, leaving only the top surface of the pillars exposed to the 5 nm Ni sputtering deposition afterwards. An HF dip for different times was used to partially remove the LTO spacers on the pillars, leading to different LTO thicknesses on different samples. These samples were then annealed to crystallize the amorphous Si pillars, forming Si nanocrystals. Transmission electron microscope (TEM) observations after anneal found a clear dependence of the crystallization rate on the pillar size as well as the LTO thickness. The crystallization rate was lower for pillars with thicker LTO spacers, while for the same LTO thickness the crystallization rate was lower for pillars with narrower width. A model based on the stress in the pillars is proposed to explain this dependence. This model suggests some methods to control the MIC process and achieve high quality Si nanocrystals.

**3:45 PM A16.3**

FIELD-AIDED GERMANIUM-INDUCED CRYSTALLIZATION OF AMORPHOUS SILICON ON GLASS. Jaber Derakhshandeh, Shams Mohajerzadeh, Negin Golshani, Ali Khakifirooz, Univ of Tehran, Inst of Electrical and Computer Engineering, Tehran, IRAN; Michael Robertson, University of Acadia, Wolfville, NS, CANADA.

A low temperature metal-free field-aided Ge-induced Si crystallization on glass is reported. E-beam deposition of 1000Å Si followed by 100Å Ge layers form the active film at a substrate temperature of 400°C on 120µm thick ordinary glasses. A 100Å SiO<sub>2</sub> layer is used for the passivation of Ge film. 1cm-apart contact pads are used to apply external voltage onto the Si/Ge bi-layer through windows in the oxide layer during post treatment at temperatures from 350 to 450°C.

While samples treated without an external voltage are not crystalline, those annealed in the presence of applied voltage become crystalline as confirmed using SEM, XRD and TEM analyses and conductivity measurement. Growth starts from the negative electrode with a high rate of 60µm/hr at 450°C, extending up to 1.5mm. Also a low rate of 4µm/hr is observed for the growth from the positive electrode. The value of applied voltage plays a crucial role in crystalline quality of Si films. Samples annealed with 10V, show a sheet resistance of 10<sup>9</sup>Ω/□ whereas those treated with 100V show a value 10 times higher, indicating a lower conductivity and inferior carrier mobility.

Polysilicon grains vary between 0.1 and 0.2µm, as exhibited by SEM. It also shows that grains are distributed in a wavy fashion extending outward from the cathode side. Samples treated with 10V during annealing show sharp and well-identified rings in TEM analysis, but in those annealed with 100V the rings are hazy. For the former samples, crystallization has been further confirmed using XRD analysis, where Si < 220 > peak is quite discernible. We speculate that a combination of lateral growth in the Ge film as a distributed seed for crystallization of Si and external electric field is responsible for such a fast and metal-free growth. Also attempts are being made to fabricate Si-TFTs using an inverted-staggered structure.

**4:00 PM A16.4**

PREDICTION OF THE INTERFACE RESPONSE FUNCTIONS FOR AMORPHOUS AND CRYSTALLINE Si AND Ge AND THE IMPLICATIONS REGARDING EXPLOSIVE CRYSTALLIZATION. Erik Albenze and Paulette Clancy, School of Chemical and Biomolecular Engineering, Cornell University, Ithaca, NY.

Interface response functions for amorphous and crystalline forms of Si and Ge were studied for several empirical atomic-scale models and compared to results from continuum modeling as well as experiments. The empirical potential models of interest include the Stillinger-Weber (SW), Environment-Dependent Intermolecular Potential (EDIP), and the Modified Embedded Atom Method (MEAM) models for Si and the SW for Ge. All of these models were found to produce unacceptable representations of the interface response functions of both solid phases due either to their poor prediction of the amorphous melting point and/or significant error in the prediction of the maximum solidification velocity. Given that the best of these models was the SW potential, which produces a very accurate interface response function (IRF) for crystalline silicon, this potential was modified to concurrently improve the prediction of the melting of the amorphous phase crystal. Increasing the three-body SW term by about 15% produced a significant improvement in the melting line for a-Si and a-Ge with little impairment of the prediction of the crystalline IRF. The implications of these results to explain the kinetics of explosive crystallization processes are discussed. However, these simulations also expose the inadequacy of an IRF representation of the amorphous phase in the light of significant evidence for homogenous melting in the bulk amorphous material as well as heterogeneous melting at the amorphous/liquid interface. A new two-mode model for amorphous group IV melting is proposed which helps explain recent new experimental data on the explosive crystallization of a-Ge. [A. Chojnacka and M.O. Thompson, PhD thesis, Cornell University, 2001].

**4:15 PM A16.5**

ADVANCED LATERAL CRYSTAL GROWTH OF a-Si THIN FILMS BY DOUBLE-PULSED IRRADIATION OF ALL SOLID-STATE LASERS. Toshio Kudo, Koji Seike, and Kazunori Yamazaki, Research and Development Center, Sumitomo Heavy Industries Ltd., Kanagawa, JAPAN; Cheng-Guo Jin, ACT Center, TIC Corporation, Tokyo, JAPAN.

A compact annealing machine with all solid-state green lasers has been developed, which has the advantage of widely adjustable solidification rate through the delay time control of long pulses (pulse width 100ns). And advanced lateral crystal growth (ALCG) process has been first proved by the double-pulsed all solid-state laser annealing (DASLA). The laser beam has a line shape 0.1mm wide and 17mm long, and the beam profile on the short axis is quasi gaussian

(FWHM 0.1mm). Scanning the line beam along the short axis at the 86% overlapping ratio, the lateral crystal growth area of pitch 14µm parallel to the long axis is extended towards the scanning direction. The advanced lateral growth mechanism is easily explained with a crystal growth model of an a-Si thin film 50nm thick: (1) At the first irradiation, each seed of width 1µm and length 4µm generates near the maximum energy density gradient of the quasi gaussian profile parallel to the long axis. (2) At the second irradiation of scanning length 14µm, each seed melts and grows laterally to 8µm outward. (3) At the third irradiation of scanning length 2x14µm, each of regrowth area melts and regrows to 14µm in the same way till the lateral growth areas from each seed bump each other. The ALCG process proved by the DASLA is on the technical extension of excimer laser annealing (ELA) without a high precision mask, a high performance stage and a complex optical system, and is suitable for the next generation of low temperature crystallization process in the field of LCD and OLED.

**4:30 PM A16.6**

INFLUENCE OF LASER ANNEALING ON HYDROGEN BONDING IN DISORDERED SILICON THIN FILMS. N.H. Nickel, Hahn-Meitner-Institut Berlin, Berlin, GERMANY.

Excimer laser annealing is a well established method to produce large-grained polycrystalline silicon (poly-Si) through the crystallization of hydrogenated amorphous silicon (a-Si:H). Since the amorphous starting material can contain a hydrogen concentration of up to 40 at.% depending on the deposition temperature, a dehydrogenation and crystallization procedure is employed. In this paper we investigate hydrogen bonding in a-Si:H, partially and completely crystallized poly-Si. Hydrogenated amorphous silicon films were prepared by rf glow discharge decomposition of silane. The initial H concentration in the a-Si:H films was modified by varying the deposition temperature between 80°C and 350°C. Then the samples were crystallized at room temperature with a shot density of 100 per unit area. Information on H bonding in the starting material (a-Si:H) and the resulting poly-Si films was obtained from hydrogen effusion measurements. The H effusion spectra of the starting material show two peaks. The peak close to 700°C is commonly assigned to thermal crystallization of a-Si:H while the low temperature peak is characteristic for amorphous silicon. In partially crystallized samples this peak is not observed. From the effusion spectra the H density-of-states distribution is derived. In fully crystallized poly-Si four peaks are observed in the H density-of-states at  $\approx -2.15, -2.4, -2.7$ , and  $-3.25$  eV; zero in energy corresponds to a free H atom.

Interestingly, the deposition temperature of the initial amorphous silicon influences H bonding in the laser crystallized poly-Si films. With increasing deposition temperature the peaks in the H density-of-states become more pronounced and considerably more H is accommodated in complexes with larger binding energies. The data will be discussed in terms of models developed to describe H complex formation.

**4:45 PM A16.7**

METAL CONTAINING LINK FORMED IN AMORPHOUS SILICON METAL-TO-METAL ANTIFUSE. Frank Hawley, Farid Issaq, Jeeewika Ranaweera, Roy Lambertson, John McCollum, ACTEL Corporation, Technology Development, Sunnyvale, CA.

A Metal-to-Metal (M2M) antifuse is formed using an amorphous silicon film (<1000Å) as a dielectric material between two metal electrodes (i.e. Titanium Nitride (TiN) or Tungsten (W)). The M2M antifuse is used as a programmable device in an FPGA (Field Programmable Gate Array), where it is placed between two metal layers of a Logic CMOS process and then programmed by the end users to interconnect their required logic circuits. The Unprogrammed M2M antifuse has low leakage (<1E-10Amps at Vcc) and small capacitance (<1E-15Farad). The Programmed M2M antifuse has low resistance (20 to 200 ohms) depending on the applied programming current. The amorphous silicon is deposited at 350°C in a PECVD system compatible with aluminum process. The Silicon source is Silane (SiH<sub>4</sub>) with Argon dilution. The Programmed M2M antifuse link contains a metal /silicide formed between the antifuse top and bottom barrier metals. Structural analysis from SEM, TEM, EDS and electrical measurements of the TiN antifuse link confirm the following conclusions: The link contains both metal and silicon. EDS measured concentration of metal in a horizontal cross section of the link varies; the center of the link has the highest metal to silicon ratio (Ti : Si = 1.8:1) and the edges of the link have the lowest (Ti : Si = 0.2:1). The link in the vertical direction, based on SEM and TEM analysis, show that the link source metal is from the cathode (electron source) side of the antifuse. The link resistance and size are dependent on both the programming current and the cathode material properties such as metal and silicide resistivity, thermal conductivity, melting temperature and silicon diffusivity (i.e. TiN vs. W). The link resistance is generally described by ( $R_{link} \propto I_{pp}^{-n}$ ) where  $R_{link}$  is the programmed link resistance (ohms),  $I_{pp}$  is the programming current (amperes) and  $n=1.2$ .

#### **A17.1**

**CHARACTERIZATION OF ULTRATHIN AMORPHOUS SILICON AND CORRELATION WITH CRYSTALLINE EVOLUTION AFTER THERMAL ANNEALING.** Jin-Won Park, C.A. Richter, N.V. Nguyen, John E. Bonevich, and Eric M. Vogel, National Institute of Standards and Technology, Semiconductor Electronics Division, Gaithersburg, MD; Jin Yong Kim, National Institute of Standards and Technology, Ceramics Division, Gaithersburg, MD.

Ultrathin amorphous silicon (especially less than 10 nm thick) has tremendous potential for use in single electron memory devices, optoelectronic devices, and tunneling nanoelectronic devices. In this ultrathin regime, physical metrology issues such as thickness, morphology, structural density, and interfaces become important factors for the control of zero-dimensional or one-dimensional confined structures. We will present results of precise physical characterization of ultrathin amorphous silicon and discuss how crystalline evolution is affected by these physical properties during thermal annealing. Ultrathin amorphous silicon layers were deposited by low pressure chemical vapor deposition at 550°C. The thickness of these layers is controlled between 2 nm and 20 nm. The thickness of amorphous silicon was measured by both vacuum ultraviolet spectroscopic ellipsometry (VUV-SE) and cross section transmission electron microscopy (TEM). Atomic force microscopy (AFM) and TEM were used to characterize the microstructural changes. RMS surface roughness of amorphous silicon, as measured by AFM, is shown to be independent of film thickness. The band-gap energy measured by VUV-SE appears to increase with decreasing film thickness in the studied thickness range. Simultaneous oxidation and annealing techniques were used to crystallize the ultrathin amorphous silicon. We experimentally observe that the crystalline evolution depends upon the thickness and microstructure of the initial amorphous silicon layer. Above 10 nm thickness of amorphous silicon, only polycrystalline silicon is observed to evolve. We will also show the various crystalline characteristics that evolve for films below that thickness.

#### **A17.2**

**STUDY BY SPREADING RESISTANCE MEASUREMENTS OF 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, Hong Kong Univ of Science and Technology, Dept. of Elec, HONG KONG.

The process of TFT fabrication, in which amorphous silicon (a-Si) layers after metal induced lateral crystallization (MILC) are used, generates a need for rapid and accurate method of quality control. Optical measurements of MILC regions has potential for information about size only. A new application of spreading resistance probe (SRP) measurements for this aims was proposed. A layer of 3000 Å a-Si was deposited on silicon substrate oxidized up to 7000 Å. Silicon film was ion implanted at a dose  $10^{15} \text{ cm}^{-2}$  and an energy 100 keV with  $\text{B}^+$ ,  $\text{BF}_2^+$ ,  $\text{P}^+$ ,  $\text{As}^+$  ions. 50 Å thickness nickel island seeds were used with different pattern. Temperature and time of recrystallization was varied from 550°C to 1100°C and from 10 seconds to 20 hours. The sizes of MILC regions were in the range from some microns to 200 μm. Then MILC regions were measured by spreading resistance profiler with the distance between probes 100 μm. The length and the steps of SRP measurement on surface were changed in dependence on the MILC size and carried out perpendicular nickel/MILC regions. We have been found, that SRP method can use for characterization of MILC process of a-Si. It was shown, that dynamic range of SRP data has about 5 orders that makes possible to measure with high accuracy of the samples having MILC regions differ greatly in conduction, crystallinity, and doping. On a basis of SRP data there is possibility to reveal the degree of recrystallization of a-Si in comparison with single crystal and poly-Si, to find the electrical size of MILC regions for different recrystallization, doping, and impurities, to define the nickel effect and the homogeneity of continuous MILC region from different nickel seeds, to obtain the depth and surface distributions of carrier concentration and mobility.

#### **A17.3**

**EFFECT OF SiO<sub>2</sub> CAPPING LAYER ON A LASER CRYSTALLIZATION OF a-Si THIN FILM.** Myung-Koo Kang, Hyun Jae Kim, Sook Young Kang, Su Gyeong Lee, Chi Woo Kim, Kyuha Chung, Samsung Electronics Co., Research Team, Kyunggi-Do, KOREA.

The effect of SiO<sub>2</sub> capping layer on a laser crystallization of a-Si thin

film has been extensively investigated. For optimum thickness, capping layer remained on a p-Si film after laser crystallization and large grained poly-Si could be obtained with relatively lower energy density and less number of shots. With this p-Si films protected by capping layer, low-cost LTPS TFT fabrication process without HF cleaning steps was successfully developed.

#### **A17.4**

**LASER INTERFERENCE STRUCTURING OF a-GeN FOR THE PRODUCTION OF OPTICAL DIFFRACTION GRATINGS.**

M. Mulato, Departamento de Física e Matemática, Faculdade de Filosofia Ciências e Letras de Ribeirão Preto, Universidade de São Paulo, Ribeirão Preto, SP, BRAZIL; A.R. Zanatta, Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, SP, BRAZIL; D. Toet FlexICs Inc., Milpitas, CA; I.E. Chambouleyron, Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas - Unicamp, Campinas, SP, BRAZIL.

Laser processing is a technology of growing interest in the semiconductor industry. Short pulse laser crystallization of amorphous semiconductors, in particular, has attracted a lot of attention since it enables the fabrication of high performance polycrystalline devices on low temperature substrates, e.g. for flat panel display applications. Bringing two laser beams to interference on the surface of an amorphous film results in a sinusoidal modulation of the light intensity and leads to a pattern consisting of alternating amorphous and polycrystalline lines. In this work, we study the pulsed laser crystallization of hydrogen-free amorphous germanium-nitrogen alloys (a-GeN). We discuss the role of nitrogen during phase transitions and the possible application of the resulting structure as an optical diffraction grating. The samples of the present work were produced by the rf sputtering technique, using a germanium target in an Ar+N<sub>2</sub> atmosphere. Corning 7059 glass and c-Si bar substrates were used, and held at 230°C during deposition. Typical samples are 0.5 μm thick. The nitrogen concentration in the alloy is about 30%. The samples were treated by a single shot of either one or two simultaneous 10ns laser pulses ( $150 \text{ mJ/cm}^2$ ) of the third harmonic (355nm) of a Nd-YAG laser. The crystallized region results of pure microcrystalline germanium ( $\mu\text{-Ge}$ ). An indication that Ge-N bonds have broken and nitrogen outdiffused of the film is obtained from infrared spectroscopy and confirmed by Raman spectra. A pattern of alternating a-GeN and  $\mu\text{-Ge}$  lines with a period of about 4 μm acts as an optical diffraction grating due to the difference in optical properties between the two materials, and the three dimensional surface profile, caused by N<sub>2</sub> effusion, that is formed on the sample.

#### **A17.5**

**EXCIMER LASER CRYSTALLIZED PHOSPHORUS-DOPED AMORPHOUS SILICON.** Rosari Saleh and Jurusan Fisika, Fakultas MIPA, Universitas Indonesia, Depok, INDONESIA; Norbert H. Nickel, Hahn-Meitner-Institut Berlin, Berlin, GERMANY.

P-doped amorphous silicon thin films were grown on a quartz substrate by rf-glow discharge method using a mixture of hydrogen diluted silane and phosphine. The substrate temperature was fixed at 230°C while phosphine was varied from 1 to 1000 ppm. The films were crystallized in a step by step process using XeCl excimer laser at room temperature starting at a laser fluence of  $100 \text{ mJ/cm}^2$  and ending at  $480 \text{ mJ/cm}^2$  using steps of  $40 \text{ mJ/cm}^2$ . After each crystallization step the films were characterized by Raman spectroscopy and hydrogen effusion measurements. Results of Raman measurements showed that a structural transformation takes place during the initial sequence of crystallization process. The films exhibit a two-layer system with polysilicon on the top of amorphous silicon. From spectral analysis the crystalline volume fraction was 45 % and nearly independent of phosphine concentrations. Raman spectra of as-deposited films also show the Si-H stretching band that can be deconvoluted into two peaks at 2000 and  $2100 \text{ cm}^{-1}$ . The intensity of the lower frequency peak is dominant for all films deposited at various phosphine concentrations. However, the integrated intensity ratio of these two peaks  $I_{2100}/I_{2000}$  increases with rising phosphine concentrations. During laser crystallization the intensity of lower frequency peak decreases faster than the one at higher frequency. Hydrogen concentrations  $C_H$  were obtained from hydrogen effusion measurements. In the as deposited samples  $C_H$  amounts to approximately 17 at. %. The hydrogen effusion spectra show two peaks at low ( $450^\circ\text{C}$ ) and high ( $700^\circ\text{C}$ ) temperature. The peak positions are very weak influenced by phosphine concentrations. During laser crystallization the two hydrogen effusion peaks are no longer pronounced and hydrogen concentrations decreased and reached the value of 6 at. % for completely crystallized sample. The results of Raman spectroscopy and hydrogen effusion will be correlated and discussed.

#### **A17.6**

**INFLUENCE OF LOW TEMPERATURE CRYSTALLIZATION OF Si:H ON TANDEM SOLAR CELL STRUCTURE EFFICIENCY.**

The large improvements obtained in performance and stability of hydrogenated amorphous silicon (a-Si:H) has been due to the protocrystalline nature of these Si:H materials. From the other side, an alternative approach has also achieved considerable progress both in terms of cells efficiency and understanding of the material properties. We will illustrate the relation of microstructure and the properties of microcrystalline silicon and efficiency of tandem solar cells. We will show our first results on field depended crystallization. We will present also decrease of temperature necessary for crystallization of a-Si:H and possibility of deposition of silicon at low temperatures (25°-100°C) on flexible substrates. Deposition was performed at high pressure and high plasma power resulting in high (up to 5Å/s) deposition rates on ZnO covered glass substrates. The structure of p-i-n-p-i-n Si:H was studied by Cross Sectional Transmission Electron Microscopy and Grazing Incidence X-Ray Analyzing. It was carried out analyzes of FF,  $V_{oc}$  and  $I_{sc}$  of the structures with respect to the low temperature crystallization.

**A17.7**  
APPLICATION OF ALTERNATING MAGNETIC FIELD TO LOW TEMPERATURE CRYSTALLIZATION OF AMORPHOUS-Si THIN FILMS. Ku-Hyun Kang, Jin-Ha Hwang, Seung-Eui Nam, and Hyung-June Kim, Hongik Univ., Dept. of Mat. Sci. and Eng., Seoul, KOREA.

Polycrystalline Si (polysilicon) TFTs have opened a way for the next generation of displays, due to higher mobility of charge carriers, relative to amorphous Si (a-Si) TFTs. The applications of polysilicon extend from the current liquid crystal displays (LCD) to the next-generation organic light-emitting diode (OLED) displays. In particular, the OLED devices require a strict control of properties of polysilicon layer, gate oxide, and their interface. The polysilicon layer is generally obtained by annealing thin film a-Si layer using solid phase crystallization, metal-induced lateral crystallization, excimer laser annealing, etc. A new approach has been studied using polysilicon crystallization using alternating magnetic field. In combination with the conventional metal induced lateral crystallization (MILC), the alternating magnetic field enhanced the Si crystallization kinetics in terms of growth rate, operating temperature, and activation energy. The effect of alternating magnetic field was investigated systematically according to processing conditions. Comparative approach has been made on i) solid phase crystallization using diffusion furnace, ii) metal-induced lateral crystallization, iii) alternating magnetic field crystallization, and iv) crystallization through excimer laser annealing. The microstructural features were investigated from microscale to nanoscale range using a variety of microscopy techniques (optical, SEM, FESEM) along with the surface characteristics using AFM. The crystallinity was evaluated using Raman spectroscopy which incorporates both amorphous and polycrystalline portions. The influence of undesired impurities on the electrical properties in polysilicon was investigated using the electrodes designed specially for polysilicon. The ramifications will be discussed in conjunction with active-matrix TFT for OLED.

**A17.8**  
OBSERVATION AND ANNEALING OF INCOMPLETE RECRYSTALLIZED JUNCTION DEFECTS DUE TO THE EXCIMER LASER BEAM DIFFRACTION AT THE GATE EDGE IN POLY-Si TFT. Woo-Jin Nam, Kee-Chan Park, Sang-Hoon Jung, Soo-Jeong Park and Min-Koo Han, Seoul National University, School of Electrical Engineering, Seoul, KOREA.

Polycrystalline silicon thin film transistors (Poly-Si TFT) recrystallized by excimer laser have attracted considerable attention for various device application. Recently crystalline defects in the poly-Si channel layer at source/drain junction have been reported to degrade the TFT characteristics such as stability and on-current. It is well known that the source/drain region of TFT is amorphized during the ion implantation for source/drain doping and then recrystallized by excimer laser annealing. We have observed that considerable lattice disorder of amorphized silicon film at the gate edge, which results in junction defects, still exists even after laser beam annealing. It is noted that the junction defects maybe originated from residual amorphized silicon generated due to insufficient laser activation energy at the source/drain junctions of the poly-Si film. The purpose of our work is to observe the junction defects near the source/drain junction are resulted from insufficient activation energy due to the laser beam diffraction at the gate edge. We also propose a new method of eliminating the junction defects by simple excimer laser annealing. Thickness of Al gate has been varied from 1,000 Å to 10,000 Å in order to evaluate laser beam diffraction effect on the junction defects. The laser beam is rather diffracted when the gate thickness is higher, which agrees with our simulated result. By high-resolution TEM investigation we observed that distribution range of the junction

defect is wider as the gate thickness increases. We propose a simple method of oblique incident laser beam annealing which successfully eliminates the residual junction defects. The laser beam is irradiated with oblique incident angle and undesirable laser beam diffraction effect at the gate edge is fairly reduced. The ion implantation damages of source/drain junction are cured by the proposed annealing technique so that TFT performance has been improved.

**A17.9**  
2-DIMENSIONAL CONTROLLED LARGE LATERAL GRAIN GROWTH ON THE FLOATING AMORPHOUS SILICON FILM BY EXCIMER LASER RECRYSTALLIZATION. In-Hyuk Song, Su-Hyuk Kang, Woo-Jin Nam, Min-Koo Han, School of Electrical Engineering, Seoul National University, Seoul, KOREA.

A polycrystalline silicon (poly-Si) thin film transistor (TFT) employing excimer laser annealing (ELA) is a promising device for high-resolution flat panel display such as active matrix liquid crystal display (AMLCD) and active matrix organic light emitting diode (AMOLED). XeCl ELA of amorphous silicon (a-Si) results in poly-Si film with relatively low defect density. However, the grain size of poly-Si is not large enough (typically less than 1µm) for high performance poly-Si TFTs. The field-effect mobility and driving current of TFTs are critically dependent on the grain size and the potential barrier of grain boundary. It is noted that high quality poly-Si films with controlled grain size and grain boundary location are required in order to improve the performance. We have already reported ELA method with floating active structure which produces the large lateral grain and controls the location of grain boundary. However, grain boundaries parallel to the current flow may disturb the carrier drift motion during operation of poly-Si TFT. The purpose of our work is to report a new ELA method which can produce large lateral grains and control the grain boundary parallel to current path. A new ELA process also decreases the number of grain boundaries parallel to current flow by employing pre-patterned multi-channel on floating amorphous silicon layer. We have successfully obtained large lateral grains exceeding 8µm. The proposed ELA method produces 2-dimensional grain growth because the temperature gradient is induced in two directions. Along the channel direction, the floating active structure produces thermal gradient. Along the perpendicular direction to channel, the surface tension effect produces thermal gradient. The proposed ELA method can control the grain boundary perpendicular and parallel to current path.

**A17.10**  
POLYCRYSTALLINE Si<sub>1-x</sub>Ge<sub>x</sub> FILMS PREPARED BY SOLID PHASE CRYSTALLIZATION METHOD. Yoichiro Aya, Kouichi Nakahata, Masao Isomura, Kenichiro Wakisaka and Koji Nishio, Sanyo Electric Co., Ltd., Osaka, JAPAN.

Solid phase crystallization (SPC) is a candidate process for realizing low-cost, large-area electronic devices. However, the required temperature for SPC of Si is usually above 700°C, therefore, low-cost substrates cannot be used. To solve this problem, we investigated the possibility of reducing the crystallization temperature by employing Si<sub>1-x</sub>Ge<sub>x</sub> films, because they are expected to enable a lower crystallization temperature and high electrical performance. We also investigated a hydrogen plasma treatment to achieve passivation of the defects in the Si<sub>1-x</sub>Ge<sub>x</sub> films. Amorphous Si<sub>1-x</sub>Ge<sub>x</sub> films (a-Si<sub>1-x</sub>Ge<sub>x</sub>) were deposited onto glass substrates using the plasma enhanced chemical vapor deposition (PE-CVD) method from SiH<sub>4</sub> and GeH<sub>4</sub> gases. SPC was performed in a vacuum chamber for 24 hours. Hydrogen treatment was performed under helicon-wave plasma. The crystallization temperature of a-Si<sub>1-x</sub>Ge<sub>x</sub> decreased from 700°C to 600°C when the Ge content of x was increased from 0 to 0.7, and then reached 400°C in the case of pure a-Ge. In order to achieve a further reduction of the SPC temperature, we employed an a-Ge/a-Si<sub>1-x</sub>Ge<sub>x</sub> bi-layer structure in which the a-Ge is expected to act as a seed-layer. *The SPC temperature of a-Si<sub>0.3</sub>Ge<sub>0.7</sub> successfully decreased from 600°C to 500°C by using the bi-layer structure, suggesting the ability to use low-cost substrates.* On the other hand, the SPC Si<sub>1-x</sub>Ge<sub>x</sub> films strongly show p-type conduction. To obtain intrinsic properties, we applied the hydrogen plasma treatment. *After the treatment, the electrical conductivity effectively decreased, and intrinsic Si<sub>1-x</sub>Ge<sub>x</sub> films were achieved.* This helicon-wave hydrogen plasma treatment is an effective method for obtaining practical properties in SPC-Si<sub>1-x</sub>Ge<sub>x</sub> for device application. These results suggest that the combination of the bi-layer structure and the hydrogen plasma treatment makes it possible to realize high-quality SPC-Si<sub>1-x</sub>Ge<sub>x</sub> for the low-cost, large-area electronic devices of the next generation.

**A17.11**  
IMPROVED ELECTRICAL PROPERTIES IN NANO-CRYSTALLINE Si FORMED BY METAL-INDUCED GROWTH. Chunhai Jiand Wayne A. Anderson, University at Buffalo, The State University of New York, Dept of Electrical Engineering, Buffalo, NY.



Nanocrystalline silicon (nc-Si) films were formed by using a metal induced growth (MIG) method, in which Si is sputtered onto a substrate covered by a thin metal catalyst. nc-Si films epitaxially grow via the formation of metal disilicide due to an extremely small lattice mismatch between the Si and silicide. In order to apply the MIG nc-Si for photovoltaics or flat panel displays, the nc-Si must have good electrical properties. Low temperature deposition (as low as 475°C for Ni induced growth) and crystallinity control using different metal prelayers (Ni and Co) has been reported. Recent studies reveal that controlling the doping level of the films and annealing in forming gas (15% H<sub>2</sub> and 85% N<sub>2</sub>) can improve the quality of the nc-Si films. From SIMS analysis on the nc-Si film deposited from a highly doped target, the nc-Si can duplicate the doping level of the sputtering target. Study of p-type doped nc-Si films shows that the fabrication of Schottky diodes on nc-Si films made from an extremely high-doped target ( $\sim 10^{20}$  cm<sup>-3</sup>) or low-doped target ( $\sim 10^{15}$  cm<sup>-3</sup>) was not successful. For highly doped p-type films, tunneling causes Ohmic conduction instead of rectifying conduction. For the nc-Si film deposited from a low-doped p-type target, the film shows conversion to n-type characteristics when measured by a hot probe. This might be due to defects or oxygen in the film. N-type films at the middle doping level ( $\sim 10^{17}$  cm<sup>-3</sup>) show good Schottky diodes after annealing the film in forming gas at 700°C. The Schottky diodes fabricated by high work-function metal (Au and Pd) show the rectifying ratio of  $\sim 10^3$ . Current-voltage-temperature (I-V-T) measurement, used to understand the conduction mechanisms, show the combined effects of thermionic emission and thermionic field emission. As a preliminary study, an n-type Schottky photodiode (0.36 cm<sup>2</sup>) was fabricated. Under 100 mW/cm<sup>2</sup> illumination the open-circuit voltage ( $V_{oc}$ ) and short-circuit current ( $I_{sc}$ ) were 0.1 V and 0.3 mA/cm<sup>2</sup>, respectively, for a Si film thickness of 0.5  $\mu$ m.

#### **A17.12**

**A SIMPLE LATERAL GRAIN GROWTH OF POLY-Si BY SINGLE EXCIMER LASER CRYSTALLIZATION OF AMORPHOUS SILICON FILM DEPOSITED ON POLYGON SHAPED TRENCH.** Sang-Hoon Jung, Su-Hyuk Kang and Min-Koo Han, School of Electrical Engineering, Seoul National University, Seoul, KOREA.

Polycrystalline silicon thin film transistors (poly-Si TFTs) employing excimer laser annealing (ELA) of amorphous silicon (a-Si) film are promising devices in various applications. The characteristics of poly-Si TFT are dependent on the size of poly-Si grain and the grain boundaries in the channel. Various efforts, such as sequential lateral solidification (SLS) or  $\mu$ -czoehrski (grain-filter) process, have been reported to increase the grain size and to control the location of grain boundaries. However SLS requires a rather sophisticated beam scan process and grain-filter process requires extremely narrow hole (about a diameter of around 100 nm) with rather deep trench (about 1  $\mu$ m). The purpose of our work is to report a simple lateral grain growth method employing single excimer laser irradiation. Rather shallow about 300 nm oxide trench, of which the shape is a polygon with an acute angle, was patterned by widely used RIE. a-Si film was deposited by PECVD and crystallized by single excimer laser irradiation. In the angular point of the polygon trench, the circular grains having a diameter of 3  $\mu$ m is observed while about 1.5  $\mu$ m grains is observed near the side of the polygon trench. The thickness difference of a-Si film in the boundary of the trench results in the different full melting condition of the a-Si film, which induces lateral growth of poly-Si grain. The location of large grain is easily controlled by the angular point of the polygon because the seed for crystallization is located near the angular point. We will also report the detail mechanism of the lateral grain growth and the characteristics of the TFT fabricated by the proposed method.

#### **A17.13**

**FORMATION OF LARGE, ORIENTATION-CONTROLLED, NEARLY SINGLE CRYSTALLINE Si THIN FILMS ON SiO<sub>2</sub> USING CONTACT PRINTING OF ROLLED AND ANNEALED NICKEL TAPES.** Hwang Huh, Jung H. Shin, Department of Physics, Korea Advanced Institute of Science and Technology (KAIST), Taejeon, KOREA.

Fabrication of large-grained polycrystalline (poly-Si) silicon thin films is an essential step for fabrication of many important devices such as flat panel displays. Yet while there exist several methods for producing large-grained poly-Si thin films, the grains themselves are randomly oriented, leading to non-uniformities and formation of high-angle grain boundaries that compromise the device performance. However, since a poly-Si with controlled grain orientation is tantamount to an single crystalline Si film, developing such orientation-controlled poly-Si films will not only improve the performances of poly-Si based devices, but also expand their uses to high-performance devices that so far have been limited to single crystalline Si wafers. In this paper, we report on forming large-grained poly-Si film with controlled location and orientation of grains using contact printing of rolled and annealed nickel tapes. Crystallization was achieved by first annealing

the a-Si film in contact with patterned Ni tape at 600°C for 20 min in a flowing forming gas (90% N<sub>2</sub>, 10% H<sub>2</sub>) environment, then removing the Ni tape and further annealing the a-Si film in vacuum for 2 hrs at 600°C. An array of crystalline regions with diameters of up to 20  $\mu$ m could be formed. Electron microscopy indicates that the regions are essentially single-crystalline except for the presence of twins and/or type A-B formations, and that all regions have the same orientation in all 3 directions even when separated by more than hundreds of microns. High resolution TEM analysis shows that formation of such orientation-controlled, nearly single crystalline regions is due to formation of nearly single crystalline NiSi<sub>2</sub> under the point of contact, which then acts as the template for silicide-induced lateral crystallization. Detailed crystallographic analysis between the silicide phase and crystalline Si as well as the performance of thin film transistor based on such films will be discussed.

#### **A17.14**

**FORMATION OF NANOCRYSTALLINE SILICON DOTS BY THE THERMAL ANNEALING OF AMORPHOUS SILICON FILMS.** Sukti Hazra, University of Delaware, Dept of Material Science and Engineering, Newark, DE; Isao Sakata, Mitsuyuki Yamanaka, Eiichi Suzuki, National Institute of Advanced Industrial Science and Technology, Tsukuba, JAPAN.

We have fabricated nanocrystalline silicon dots by thermal annealing (TA) of thermal chemical-vapor-deposited (CVD) amorphous silicon (a-Si:H) films with thickness in the range of 4 to 247 nm. In ref. 1, we established that the ultrathin amorphous films with thickness (less than 10 nm) are stressed by the presence of paracrystallites, Paracrystallites are deformed crystallites. Since the deposition temperature is low (less than 500°C), growth of amorphous silicon films starts with dense deformed crystalline nuclei (paracrystallites) and lot of grain boundaries. So, at the initial stage films become heavily stressed with high free energy. With the advance of deposition process, surface reactions supply energy to paracrystallites and these come gradually to its relaxed state with the continuous change of the imperfect crystallinity of paracrystallites towards a completely disordered state. Increasing thickness decreases the stress in the films. The initial stress in the amorphous films plays the governing role to control the dimension and density distribution of nanocrystalline dots in the annealed films. Stress in the films inversely controls the crystallization by TA. For instance, highly stressed films (4.1 nm) cannot be crystallized by TA even at 1100°C and the TA of a-Si:H films of 6.2 nm and 9.8 nm thick yields Si nanocrystallites with the dimensions of less than 5 nm and 10 nm, respectively. Completely relaxed amorphous networks lead to the formation of polycrystalline films by TA. [1] S. Hazra, I. Sakata, M. Yamanaka, and E. Suzuki, Appl. Phys. Lett. 80, 1159 (2002).

#### **A17.15**

**LIFETIME MEASUREMENTS OF POROUS SILICON STAIN ETCHED AND HYDROGEN PASSIVATED.**

Ricardo Guerrero-Lemus and Cecilio Hernandez-Rodríguez, Dept Física Basica, Universidad de La Laguna, SPAIN; Fathi Ben-Hander, José Martínez-Duart, Dept Física Aplicada C-XII, Universidad Autonoma de Madrid, SPAIN; Christoffer Ballif, Dietmar Borchert, Laboratory and Service Centre, Institut fuer Solare Energiesysteme, Fraunhofer Institut, Gelsenkirchen, GERMANY.

Porous silicon layers stain etched in low nitric acid concentrations, and formed only in some tens of seconds, exhibits surprising low reflectance values (< 4%) in the whole 300 - 1100 nm spectral range. This property can be useful to apply this kind of layers on top of silicon-based photodetectors and solar cells. Consequently, the quantum efficiencies of these devices can be increased with respect to conventional antireflection layers on top of silicon. However, the surface states induced by this porous layer on the silicon wafer act as high velocity recombination centres. Then, it is necessary to efficiently passivate the porous layers to reduce this detrimental effect. In this work we present the first micro-wave photo-conduction decay measurements for porous silicon stain etched and hydrogen-passivated. These technique measures the lifetime of the charge carriers photogenerated, and it is extremely useful to characterise the surface recombination properties of silicon wafers. We also study the time evolution of the carriers lifetime for samples exposed to ambient conditions. We observe a decrease of the carrier lifetime for porous silicon with respect to the silicon substrate before stain etching. However, when the samples are hydrogen-passivated, the lifetime for porous silicon increases to larger values than the silicon substrate before stain etching.

#### **A17.16**

**ANOMALOUS BEHAVIOUR OF STAIN ETCHED POROUS SILICON PHOTOLUMINESCENCE.** Ricardo Guerrero-Lemus and Cecilio Hernandez-Rodríguez, Dept Física Basica, Universidad de La Laguna, SPAIN; Fathi Ben-Hander, José Martínez-Duart, Dept Física Aplicada C-XII, Universidad Autonoma de Madrid, SPAIN.

The photoluminescent properties of porous silicon electrochemically etched are commonly attributed to excitonic transitions of carriers in silicon nanostructures embedded in the porous matrix. The evolution of these properties are mainly influenced by quantum confinement effects, but also depends on the surface composition of the radiation centres (M.V. Volkin, J. Jorne, P.M. Fauchet, G. Allan and C. Delerue, Phys. Rev. Lett. 82, 197 (1999)). This model explains the experimental observation of a low increase of the emission energy of the porous silicon photoluminescence when the excitation energy is increased at higher rates. On the contrary, for porous silicon stain etched in low nitric acid concentrations, the increase of the excitation energy implies a low decrease of the emission energy. This anomalous experimental result can be explained in terms of the oxidation degree of this kind of porous structure and its particular hydrophobic characteristics.

#### A17.17

SCATTERING RINGS IN OPTICALLY ANISOTROPIC POROUS SILICON. Claudio J. Oton, Zeno Gaburro, Mher Ghulinyan, Nicola Daldosso, Lucio Pancheri, Paolo Bettotti, Luca Dal Negro and Lorenzo Pavesi, INFN and Department of Physics, University of Trento, ITALY.

We report the observation of strongly anisotropic scattering of visible light at oblique incidence on a (100)-oriented porous silicon layer.

Pores in heavily-doped p<sup>+</sup>-type porous silicon have columnar shape with vertical walls. The verticality of the pores produces anisotropic cone-shaped scattering of light, which is observed as a bright ring on a screen situated in front of the sample. We report the observation of this phenomenon for the first time. The same ring pattern is observed in transmission through free-standing samples. Two additional bright rings concentric to the main one (one internal and one external), are also observed. We propose a model which explains this phenomenon as a consequence of optical anisotropy of the porous silicon layer. After the scattering event, polarization of light can change. This leads to a change in the refractive index, because the medium is optically anisotropic. Therefore, a refraction event deviates the light, leading to an internal ring for one input polarization and an external ring for the opposite polarization. Measurements of the radii of the scattered rings directly give a quantitative value of optical anisotropy. We have characterized anisotropy of different types of porous silicon samples. We also report changes in the scattered pattern when pores are filled with liquids and when the sample is in presence of different humidity conditions. Possible applications of the phenomenon are finally discussed.

#### A17.18

LIGHT AND THERMALLY INDUCED METASTABILITIES IN NANOCRYSTALLINE SILICON. N.P. Mandal and S.C. Agarwal.

Porous silicon (PS) in the form of nanocrystalline silicon made by the electrochemical anodization of boron doped Si wafers shows photoluminescence (PL) is at  $\approx 797\text{nm}$  (FWHM  $\approx 132\text{nm}$ ) when excited by a He-Ne Laser (632 nm). PS shows an asymmetric ESR signal which can be resolved into three signals having  $g_{\perp} \approx 2.0081 \pm 0.0006$  (width  $\approx 1.5\text{G} \pm 0.5\text{G}$ ),  $g_{\parallel} \approx 2.0028 \pm 0.0006$  (width  $\approx 1.8\text{G} \pm 0.5\text{G}$ ) and  $g \approx 2.0055 \pm 0.0006$  (width  $\approx 6.4\text{G} \pm 0.5\text{G}$ ) [1]. We have studied the change in PL, dark current (DC), photocurrent (PC) and ESR upon light soaking (LS) and thermal quenching (FQ). PL intensity increases by more than a factor of two, after a brief exposure ( $t_x \approx 900\text{s}$ ) to white light. This is accompanied by a decrease in ESR signal by about 70%. Further, the DC and PC increase with increasing  $t_x$  ( $t_x \leq 2700\text{s}$ ) and remain high for several hours even at 300K. This is similar to the persistent photoconductivity observed in doping modulated and compensated a-Si:H. For  $t_x \geq 3000\text{s}$  the changes in PL, DC, PC and ESR are in opposite direction. Fast cooling ( $\approx 400\text{K}/\text{min}$ ) from about  $150^{\circ}\text{C}$  to room temperature brings PS to a metastable state (FQ) which is similar to that produced by short exposure to light. The LS and FQ states can be erased by annealing ( $150^{\circ}\text{C}$ , 1h) but not by exposure to IR light. Micro Raman study shows the presence of a-Si:H phase (peak  $\approx 480\text{cm}^{-1}$ ) along with the nanocrystalline silicon (peak  $\approx 512\text{cm}^{-1}$ ) in our PS. In LS as well as FQ state the increase (decrease) in PL, DC and PC is accompanied by a decrease (increase) in the number of dangling bonds (ESR). These results will be explained in terms of structural changes. [1] H.J. Von Bardeleben et al, J. Lumin. 57, 39 (1993).

#### A17.19

PHYSICO-CHEMICAL CHARACTERIZATION OF POROUS SILICON SURFACES ETCHED IN SALT SOLUTIONS OF VARYING COMPOSITIONS AND pH. Mariem Rosario-Canales, Ana R. Guadalupe, Univ of Puerto Rico, Rio Piedras Campus, Dept of Chemistry, San Juan, PR; Luis F. Fonseca, Oscar Resto, Univ of Puerto Rico, Rio Piedras Campus, Dept of Physics, San Juan, PR.

In this research we are interested in seeking alternatives to

hydrofluoric acid and other highly acidic or basic etchants to grow porous silicon (PSi). We prepared PSi structures by standard electrochemical processes using salt solutions under mild conditions. The samples grown by this approach showed high porous densities, structural uniformity and can be kept in aqueous environments for extended periods of time without any mechanical damage. In addition, they do not need to be submitted to any special drying procedure to preserve the porous integrity. All the above conditions are needed when immediate use in biological applications is desired as is our objective. Crystalline silicon wafers used in this study were p-type, Boron doped and had the  $\langle 100 \rangle$  orientation with an Al contact on the back side. The wafers had the following range of resistivities: 1-2 and 20-30  $\Omega\cdot\text{cm}$ . We report the dependence of the porous structure on the variation of the pH values and salt concentration as well as current density of the electrochemical etching process. Characterization has been done by Scanning Electron Microscopy (SEM) and X-Ray Photoelectron Spectroscopy (XPS) to study pore size and distribution and surface chemical composition respectively. Results show that the PSi grown has two different structures depending on the applied current density. Low current densities produce a uniform, high-density arrangement of pores while high current densities yield a porous structure resembling an aerogel network with an average pore size of one micron in both cases. XPS revealed that the porous framework appears to be covered with a silicon dioxide layer that allows the direct immobilization of biological material without the need for any further treatment.

#### A17.20

IN-SITU TEM STUDIES OF Ni-MEDIATED SILICON CRYSTALLISATION. M.A. Verheijen, Philips CFT, Eindhoven, THE NETHERLANDS; P.J. van der Zaag, S.-Y. Yoon and N.D. Young, Philips Research Redhill, Surrey, UNITED KINGDOM.

Poly-Si is a promising material for thin film transistors (TFT's) used in active matrix displays because it enables the integration of functionality on glass. One way of obtaining poly-Si on glass is by means of Ni-based metal induced crystallisation (MIC) of amorphous Si. In this process NiSi<sub>2</sub> precipitates are formed that subsequently migrate through the amorphous Si thin film, thereby crystallising the Si. So far, however, the leakage current of MIC-based poly-Si TFT's was found to be too high for display applications. The high leakage current was thought to be caused by the Ni present in the channel region. In this work the Ni-mediated Si crystallisation process was studied in-situ in the Transmission Electron Microscope (TEM) at  $550^{\circ}\text{C}$  and recorded on digital videotape. These in-situ TEM movies show that the crystallisation process is a two-step process: a relatively fast MIC step, followed by a very slow (10-60 hours, depending on Ni-dose) solid phase crystallisation process (SPC) which does not involve NiSi<sub>2</sub>-mediated growth. The source of the high leakage current was found to be related to incomplete crystallisation after the SPC stage. By crystallising the remaining amorphous fraction acceptably low leakage currents could be obtained ( $<1\text{ pA}/\mu\text{m}$  at VDS = 5V). Additionally, it was shown that the leakage current is independent on the Ni concentration. The crystallisation itself did appear to be dependent on the Ni-dose. At a Ni-concentration of  $7.5\text{E}18/\text{cm}^{-3}$  crystallisation proceeded by the well known one-dimensional growth along  $\langle 111 \rangle$  directions of the NiSi<sub>2</sub> precipitates. At higher concentrations (e.g. at  $5\text{E}19/\text{cm}^{-3}$ ) the overall crystallisation process is speeded up significantly due to repetitive splitting of the NiSi<sub>2</sub> precipitates, resulting in a significantly larger amount of Si grains and, as a result of this, a smaller average grain size.

SESSION A18: POSTER SESSION  
IMAGERS AND DEVICES

Thursday Evening, April 24, 2003  
8:00 PM

Salon 1-7 (Marriott)

#### A18.1

PERFORMANCE OF THIN-FILM SILICON MEMS RESONATORS IN VACUUM. J. Gaspar<sup>a,b</sup>, V. Chu<sup>a</sup>, J.P. Conde<sup>a,b</sup>, <sup>a</sup>INESC

Microsistemas e Nanotecnologias, Lisbon, PORTUGAL; <sup>b</sup>Department of Materials Engineering, Instituto Superior Tecnico, Lisbon, PORTUGAL.

Thin-film microelectromechanical systems (MEMS) extend the applications of MEMS to large-area substrates such as glass and plastic. The microbridge structures are bilayers consisting of aluminum as the top layer and amorphous silicon (a-Si:H) or nanocrystalline silicon (nc-Si:H) as the bottom layer. The structure is suspended over a gate electrode that can be used to provide an electrostatic force for actuation of the microstructures. The resulting movement is detected optically. These structures exhibit resonance frequencies in the MHz range.

Quality factors (Q) up to 100 are obtained in air. Air damping and squeeze-film damping effects due to media viscosity and air pumping

action from the gap region limit the Q's. This paper reports on the resonance behavior of thin-film bridges in vacuum. So far, an increase in Q and a reduction of the actuation voltage (V) by factors greater than 10 are observed. The resonator response is studied between atmospheric pressure and  $10^{-6}$  Torr for  $10\ \mu\text{m}$  wide devices with lengths varying from  $10\ \mu\text{m}$  to  $50\ \mu\text{m}$ . Below the 10 - 100 mTorr range, the resonators no longer interact with the ambient molecules and the intrinsic dissipative behavior of the structures can be observed.

A detailed study of the resonance frequency and the dependence of Q on the dimensions of the bridge, on the structure of the bridge (bilayer or a single thin-silicon layer) and on the material used as structural layer (a-Si:H or nc-Si:H, intrinsic or doped) is presented. These results are analyzed with an electromechanical model. The possibility of obtaining thin-film Si-based high-frequency, low-V, high-Q resonators allows the application of thin-film Si MEMS to sensor arrays and RF filters, as well providing a means to study elementary energy dissipation processes in thin-film Si.

#### **A18.2**

**CHARACTERIZATION OF AMORPHOUS SILICON THIN FILMS FABRICATED BY RF MAGNETRON SPUTTERING FOR MICROBATTERY.** Ki Lyung Lee, Hee-Soo Moon, Seung Won Lee, Jong-Wan Park, Division of Materials Science and Engineering, Hanyang University, Seoul, KOREA.

Numerous studies currently aim at the improvement of the specific capacity of the anode material in Li-ion cells. Despite interesting performances of Sn based oxides, the irreversible capacity loss systematically observed on the first cycle for these compounds is a main drawback for their use as anode materials in lithium ion cells. Not only tin is efficient in forming alloys with lithium, Silicon can also react with lithium to form alloys with a high Li/Si ratio, like  $\text{Li}_{22}\text{Si}_5$ . Despite the high theoretical capacity of silicon (4000 mAh/g), the alloying of lithium with well crystallized silicon can hardly occur at room temperature by deposition processing. To determine the active role of amorphous silicon in anodes, thin films have been prepared on Pt-coated p-type Si wafer by rf magnetron sputtering and their electrochemical performance has been characterized. The deposited film are characterized by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), atomic force microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS), ellipsometry. Constant-current galvanostatic charge-discharge tests of half cells are performed. In order to avoid mechanical disintegration of the silicon based electrodes, Also, the silicon material was deposited on porous copper substrates. It was believed that porous structure and roughness of the substrate can help the active silicon material to accommodate a volume change without pulverizing. Furthermore, the high specific area of the copper foils can help to keep a good electrical contact between the current collector and the silicon layer during the electrochemical tests. It showed the good retention of discharge capacity.

#### **A18.3**

**AREA DEPENDENT SWITCHING IN THIN FILM SILICON DEVICES.** Jian Hu, Warren Jackson<sup>†</sup>, Scott Ward, Pauls Stradins, Howard M. Branz, and Qi Wang, National Renewable Energy Laboratory, Golden, CO; <sup>†</sup>Hewlett-Packard Laboratories, Palo Alto, CA.

We report the area dependence of switching in both  $\text{Cr/p}^+\text{a-Si:H/Ag}$  and  $\text{Cr/p}^+\mu\text{-Si:H/Ag}$  filament switches. The doped amorphous (a-Si:H) or microcrystalline ( $\mu\text{-Si}$ ) thin Si layers are made by hot-wire chemical vapor deposition. We vary device active region area (A) over 4 orders of magnitude, from  $10\ \mu\text{m}^2$  to  $0.01\ \text{cm}^2$  using photolithographically-defined Ag and Al top contacts. Switching is stimulated with either a slow current-ramp from 0 to 50 mA ( $\sim 20$  sec), or a short current pulse lasting 500  $\mu\text{sec}$ . Before switching the resistance of  $100\text{-}\mu\text{m}^2$  devices is normally about 100 k $\Omega$  for  $\mu\text{-Si}$  and 10 G $\Omega$  for a-Si:H. During switching, the resistance decreases to a few hundreds ohms in all devices. Optical microscopy reveals morphology changes at the device surface that are a result of rising temperature before switching. We observe that, in a-Si:H devices, the switching voltage ( $V_{\text{sw}}$ ) decreases with increasing device area according to  $V_{\text{sw}} \propto V_0 - \text{alog}(A/A_0 + 1)$  with  $a=2V$ ,  $V_0 \geq 14V$ , and  $A_0 = 10^{-7}\ \text{cm}^2$ , while the switching current density obeys the power law  $J_{\text{sw}} \propto A^{-\beta}$  with  $\beta \sim 1$  in the a-Si:H devices. In contrast, in a-Si devices, the switching current density varies significantly with device area, following  $J_{\text{sw}} \propto A^{-\beta}$  with  $\beta \sim 0.5$ , while switching voltage is roughly independent of area, with  $V_{\text{sw}} = 2$  to 3V. We explain the dependence of  $V_{\text{sw}}$  and  $J_{\text{sw}}$  on device area by assuming that each device consists of a many small elements that function as statistically independent devices. The total device characteristics represent an aggregation of the elements' statistically distributed switch characteristics, with the easiest-to-switch elements dominating the observed behaviour. Differences between  $\mu\text{-Si:H}$  and a-Si:H switching characteristics and area scaling are discussed in the framework of this statistical model.

#### **A18.4**

**HOT-WIRE CHEMICAL VAPOR DEPOSITION OF HIGH HYDROGEN CONTENT SILICON NITRIDE FOR SOLAR CELL PASSIVATION AND ANTI-REFLECTION COATING APPLICATIONS.** J.K. Holt, D.G. Goodwin, Harry A. Atwater, California Institute of Technology, Dept of Applied Physics, Pasadena, CA; A.M. Gabor, Evergreen Solar, Inc., Marlboro, MA; F. Jiang and M. Stavola, Lehigh University, Bethlehem, PA.

Silicon nitride films have been grown by hot-wire chemical vapor deposition and film properties have been characterized as a function of silane-to-ammonia flow ratio. Quadrupole mass spectrometry measurements revealed that the flow rate of silane should be small relative to ammonia ( $< 0.1$ ), due to the lower decomposition probability of ammonia on the wire. Silicon nitride films were produced with refractive indices ranging from 1.8-2.5 and H-content from 9-18 atomic % as the flow ratio increased from 0.01 to 0.08. Fourier Transform Infrared Spectroscopy (FTIR) revealed a change from predominantly N-H to Si-H bonding as the flow ratio increased beyond 0.06. Subsequent annealing studies showed different kinetics for H release from Si versus N. Films grown with a low silane-to-ammonia ratio were found to oxidize readily (23 atomic %) after exposure to air, while larger ratios yielded no oxygen incorporation. Defect hydrogenation was studied using FTIR spectroscopy on platinum-diffused silicon substrates, with a measured Pt-H concentration of up to  $10^{14}\ \text{cm}^{-3}$ . Hot-wire nitride layers were deposited onto diffused-emitter String Ribbon silicon substrates, producing solar cells with comparable electrical properties to those fabricated using plasma CVD nitride layers.

#### **A18.5**

**PROPERTIES OF SILICON NITRIDE FILMS PREPARED BY COMBINATION OF CATALYTIC-NITRIDATION AND CATALYTIC-CVD.** A. Izumi, A. Kikkawa, K. Higashimine and H. Matsumura, JAIST, Tatsunokuchi, JAPAN.

Silicon nitride ( $\text{SiN}_x$ ) 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,  $\text{SiN}_x$  films are formed by combination of direct nitridation (catalytic-nitridation) and catalytic-CVD at low temperature around  $250^\circ\text{C}$ . In this method, catalytic-nitridation is performed by irradiation to the Si substrate of activated nitrogen-related species, which are generated by  $\text{NH}_3$  catalytic cracking reactions with a heated tungsten catalyst placed near substrates, and so that ultra-thin  $\text{SiN}_x$  films below 2 nm are formed. Thicker  $\text{SiN}_x$  films are deposited on them by catalytic-CVD succeedingly.

#### **A18.6**

**HIGH-RATE ( $>1\ \text{nm/s}$ ) AND LOW-TEMPERATURE ( $<400^\circ\text{C}$ ) DEPOSITION OF SILICON NITRIDE USING AN  $\text{N}_2/\text{SiH}_4$  AND  $\text{NH}_3/\text{SiH}_4$  EXPANDING THERMAL PLASMA.** J. Hong, W.M.M. Kessels, M.C.M. van de Sanden, Dept of Applied Physics, Center for Plasma Physics and Radiation Technology, Eindhoven University of Technology, THE NETHERLANDS.

For decades, PECVD of silicon nitride (a-Si $_x$ :H) films has been crucial technology for micro-optoelectronics. More recently, the a-Si $_x$ :H films have been also applied as functional coatings (antireflection and passivation layer) for Si-based photovoltaics. In our previous studies, high-rate deposited a-Si $_x$ :H films using an expanding thermal plasma (ETP) technique showed a bulk defect passivation effect for multicrystalline Si solar cells, which demonstrated that these materials are very promising for high throughput production of solar cells because the deposition rates can be attained higher than 1 nm/s. This paper deals with the influence of the substrate temperature on the growth of the ETP deposited a-Si $_x$ :H films from a  $\text{N}_2/\text{SiH}_4$  and  $\text{NH}_3/\text{SiH}_4$  gas mixture in the low-temperature range  $50\text{-}400^\circ\text{C}$ . Structural and optical properties of the films have been investigated by elastic recoil detection, spectroscopic ellipsometry, and infrared spectroscopy. Several observations have been found: i) Deposition rate decreases and film mass density increases when the temperature increases in this range. ii) The a-Si $_x$ :H films deposited from  $\text{N}_2/\text{SiH}_4$  are more vulnerable to post-deposition oxidation than the films deposited from  $\text{NH}_3/\text{SiH}_4$ . iii) Porous and fractal-like columnar structure starts to develop at the temperature below  $200^\circ\text{C}$  for the films deposited from  $\text{NH}_3/\text{SiH}_4$ . iv) Application of an extended valence model for hydrogenated silicon oxynitride showed a good prediction for the composition of the films. Furthermore, deposition mechanisms at this low-temperature range will be extensively discussed in terms of evolution of deposition rate, composition, optical band gap, and microstructure of the films. Especially, combined study of in situ real-time spectroscopic ellipsometry and ex situ atomic force microscopy gave an insight on the surface roughness evolution of the films during the film growth.

#### **A18.7**

SWITCH ON TRANSIENTS AND STATIC CHARACTERISTICS OF POLYMORPHOUS AND AMORPHOUS SILICON THIN-FILM TRANSISTORS. V. Tripathi and Y.N. Mohapatra, Department of Physics, IIT, Kanpur, INDIA; P. Roca i Cabarrocas, Laboratoire de Physique des Interfaces et des Couches Minces, Ecole Polytechnique, Palaiseau, FRANCE.

Polymorphous Silicon (Pm-Si) being an admixture of amorphous and ordered phase silicon shows improved optical and electrical properties due to the presence of nanocrystallites. In order to compare the dynamic and steady state electrical properties in a-Si:H and pm-Si, bottom gate Thin Film Transistors (TFT) of these materials were fabricated with SiO<sub>2</sub> as the insulating layer. The active materials were deposited using plasma-enhanced chemical vapor deposition (PECVD) by varying pressure, temperature and hydrogen dilution. Transfer characteristics of TFTs made using pm-Si show lower leakage current, higher on-current and sharper volt per decade change than similar TFTs made from a-Si:H. Density of states in pm-Si as calculated from field effect conductance using incremental method is observed to be an order of magnitude lower than in a-Si:H based devices. To compare dynamic characteristics, we studied the switch-on transient characteristics of polymorphous and amorphous silicon TFTs by pulsing the gate to different voltages in the temperature range of 150-300K. We observe a richer variety of switch-on transients in pm-Si based devices. A slow rising transient reveals two distinct regions. The initial rising part of the transient is observed to be exponential which is eventually overtaken by a second slower mechanism. This rise is shown to be activated with an activation energy of 0.3 eV. In similar devices fabricated using a-Si:H, following onset of conduction we observe only decaying non-exponential current transients with weak temperature dependence. In both cases, the switch-on transients are trap limited. However, the initial rising transient appears to originate from metastable states associated with nanocrystals or their interfaces acting as giant traps with effective energy of 0.3 eV. The origins of transients are interpreted in terms of trap limited carrier dynamics and charge redistribution within the distribution of localized states.

#### **A18.8**

DEPENDENCES OF STRUCTURAL PARAMETERS ON THE CHARACTERISTICS OF POLY-Si THIN-FILM TRANSISTORS AFTER PLASMA PASSIVATION. Cheng-Ming Yu, Tiao-Yuan Huang, Tan-Fu Lei, Horng-Chih Lin, Natl Chiao-Tung Univ, Hsin-Chu, TAIWAN.

The effects of plasma treatment and device's structural parameters on the characteristics of poly-Si thin-film transistors (TFTs) with source/drain extensions induced electrically by a bottom sub-gate were explored. The plasma treatment was performed in either hydrogen or ammonia ambient for 3 hours. It was found that an anomalous hump appears in the subthreshold region for devices with short channel length (e.g.,  $L < 1.5$  micron) and large channel width (e.g.,  $W > 5$  micron). Such phenomenon also leads to an anomalous current increase in the output characteristics of short-channel devices. Some defects near the bottom interface of the channel generated during processings are believed to be responsible for such leakage. This is supported by the observation that the hump becomes invisible as channel width is scaled below 5 micron, owing to the shorter path for the passivating species to diffuse. Moreover, ammonia plasma was found to be more effective than hydrogen plasma for passivating defects.

#### **A18.9**

MICROCRYSTALLINE SILICON THIN FILM TRANSISTORS DEPOSITED BY DC REACTIVE MAGNETRON SPUTTERING. Sreenivas Jayaraman and John R. Abelson, University of Illinois, Department of Materials Science and Engineering, Urbana, IL; Steven D. Theiss, 3M Company, St. Paul, MN.

Microcrystalline silicon is of great commercial interest as the active layer in thin film transistors (TFTs) used as switching elements and drivers in flat panel displays. It offers advantages in terms of higher electron mobility and greater threshold voltage stability compared to amorphous silicon. We fabricate TFTs using microcrystalline silicon ( $\mu\text{c-Si:H}$ ) as the channel layer and amorphous silicon nitride ( $\text{a-Si}_x\text{N}_y\text{:H}$ ) as the gate dielectric. The microcrystalline film is deposited by DC reactive magnetron sputtering (RMS) at high hydrogen partial pressures ( $\geq 5$  mTorr) while the nitride is deposited by pulsed DC RMS in an atmosphere of Ar, H<sub>2</sub> and N<sub>2</sub>. The substrate temperature during the entire process is kept below 300°C and there is no post treatment of the films. We obtain a high degree of crystallinity ( $\sim 90\%$ ) as measured by Raman spectra for deposition rates between 0.2-1.0 Å/s. The TFTs are fabricated in both bottom gate and top gate staggered configurations. Although process optimization is still in the early stages, we consistently observe lower TFT threshold voltages in microcrystalline silicon ( $\sim 3\text{V}$ ) as opposed to amorphous silicon ( $\sim 15\text{V}$ ). It should be noted that the channel

mobility in these early devices remains similar for both the amorphous and microcrystalline TFTs ( $\sim 0.5\text{cm}^2/\text{Vs}$ ). We anticipate that further process refinements will result in enhanced mobility for the microcrystalline devices. Based on our previous work using RMS deposition, we also expect to essentially eliminate any incubation layer, reduce the growth temperature, and optimize the device performance. Our goal is to develop a growth process which is suitable for flexible plastic substrates and a roll to roll industrial coating technology.

#### **A18.10**

ABOVE-THRESHOLD PARAMETER EXTRACTION INCLUDING CONTACT RESISTANCE EFFECTS FOR a-Si:H TFTS ON GLASS AND PLASTIC. Peyman Servati, Denis Striakhilev, and Arokia Nathan, Department of Electrical and Computer Engineering, University of Waterloo, Waterloo, Ontario, CANADA.

This paper presents a fast and accurate method for extraction of the above-threshold physical parameters (such as threshold voltage, mobility, conduction band tail slope, and contact resistance) from measurement data in the linear and saturation regions for a-Si:H TFTs fabricated on glass and plastic substrates. Although the principles of parameter extraction for a-Si:H TFTs are similar to those of MOSFETs, the method of extraction is different by virtue of the departure from the square law dependence of the current-voltage characteristics, with a power parameter ( $\alpha$ ) greater than 2. In addition, there is a broader range of process-induced variation in material properties. The method presented here takes into account the non-ideal parameters such as contact resistance, which may vary by orders of magnitude due to process variations, thus strongly influencing the extracted values of TFT parameters. In fact, the presence of a high contact resistance ( $> 1 \Omega\text{-cm}^2$ ) stemming from the  $n^+$ -a-Si:H contact layers can be detrimental to the accuracy of extracted threshold voltage, mobility, and the power parameter. In this paper, the effect of contact resistance on the extracted values is systematically investigated and identified using TFTs with different channel length. The extracted values for TFTs on glass and plastic substrates highlights very clearly the differences in material and interface properties stemming from the different process conditions, and provide insight that is invaluable for subsequent device/process optimization.

#### **A18.11**

THIN FILMS TRANSISTORS BASED ON STOICHIOMETRIC a-SiC:H OBTAINED BY PECVD. Alessandro Ricardo de Oliveira, Marcelo Nelson Paez Carreño, Department of Engineering of Electronic Systems, Polytechnic School, Universidade de Sao Paulo, Sao Paulo, SP, BRAZIL.

In the last 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 by Plasma Enhanced CVD (PECVD) a-Si<sub>1-x</sub>C<sub>x</sub>:H films close to stoichiometry ( $x \sim 0.5$ ) and with a chemical and structural order similar to c-SiC. We have also studied the n-type and p-type electrical doping of these a-SiC:H films through the ion implantation of impurities and have obtained promising doping levels. Here, we describe a thin films transistor completely based on stoichiometric a-SiC:H obtained by PECVD. The a-SiC:H films are grown by PECVD at 300°C from appropriated gas mixtures of methane and silane diluted in H<sub>2</sub>. The substrates are of glass plates (Corning 7059) and silicon wafers previously oxidized (3000 Angstroms). The doping of the source and drain areas was accomplished through ion implantation of phosphorus with concentration of  $10^{21}$  at/cm<sup>3</sup> and the thermal annealing for the electrical activation of the impurities and restructuring of the material was done in the 550-1000°C temperature range. As gate insulator we utilized high quality SiO<sub>2</sub> also obtained by the PECVD technique at low temperature (300°C). The devices operate in accumulation regime and preliminary results show a clear transistor effect and the possibility of operation at temperatures higher than 200°C. We also compare the performance of devices fabricated with as deposited a-SiC:H and thermally induced polycrystalline PECVD SiC.

#### **A18.12**

MECHANICAL STRESS AND PROCESS INTEGRATION FOR DIRECT X-RAY DETECTOR AND TFT IN a-Si:H TECHNOLOGY. Czung-Ho Lee, Isaac Chan, and Arokia Nathan, Electrical and Computer Engineering, University of Waterloo, Waterloo, ON, CANADA.

We recently reported a direct X-ray detection scheme based on

Mo/a-Si:H Schottky diode structure for imaging low-energy X-rays. Here, a 500 nm thick Mo layer acts not only as a Schottky barrier but also as a direct converter, which transforms X-rays into energetic electrons. One critical issue with the Mo/a-Si:H Schottky diode is the mechanical stress, both intrinsic and extrinsic, which constrains the process integration of the detector and TFT for an active matrix array. Extensive characterization of the intrinsic stress in single- and multi-layer structures has been reported, in an attempt to reduce the stress through appropriate process conditions. However, it is achievable only over very narrow process latitude, which limits the process flexibility for improving electrical performance. Therefore, an alternate process integration strategy is considered to avoid the stress issues. In the conventional Schottky diode process, the bottom (Cr) electrode, intermediate a-Si:H absorption layer, and the top Mo Schottky layer are patterned in a bottom-up sequence. The corners of the patterned layer from the prior process step exert an extrinsic stress on the subsequently deposited films. This issue is observed in the deposited Mo film, which shows cracks or even peels off from the corners of the bottom electrode patterns. Reversing the patterning sequence into a top-down manner can reduce this extrinsic stress effectively. In this case, the Mo film does not encounter the high extrinsic stress due to the sharp corners of the bottom electrode patterns, as in the original process, thus we do not observe any damage on the Mo film. This improves the structural integrity of the photodiode without altering any process conditions. Further details on the mechanical stress issues pertinent to the Mo/a-Si:H Schottky diode process, along with the leakage current and X-ray sensitivity characterization will be discussed in the paper.

#### A18.13

STACKED PIN-PIN HETEROJUNCTIONS FOR IMAGE RECOGNITION AND COLOUR SEPARATION. M. Vieira, P. Louro, A. Fantoni, M. Fernandes, D. Brida, Electronics Telecommunications and Computer Dept, ISEL, Lisbon, PORTUGAL; Yu. Vygranenko, Univ. Waterloo, CANADA.

A new design based on a stacked pinpin structure is proposed for the Colour Laser Scanned Photodiode sensor, CLSP. The CLSP is a two terminal wavelength-optimised sensor based on one single large area (4x4 cm<sup>2</sup>) p-i-n sensing element and a scanning reader. In short circuit mode, it can detect a black and white image with a spatial resolution of 20  $\mu\text{m}$ . Under forward bias, colour separation is also possible, with a reasonable rejection rate. No optical filters are used during the image acquisition process. To tune the spectral sensitivity of the device we propose a stacked sensing element deposited by PE-CVD on a glass substrate (ZnO:Al/p(SiC:H)/i(Si:H)/n(SiC:H)/p(SiC:H)/i(SiC:H)/n(SiC:H)/ZnO:Al). 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. The first p-i-n photodiode confines the carriers at the illuminated regions while the second one, driven by the scanner, gives information on their location (image shape) density (image intensity) and absorbed wavelength (image colour). In this work the efforts are focused mainly on the design of the structure and composition of the layers and its role on sensor performance. We use different doped and intrinsic layers with different thickness and composition. The structural and optoelectronic characterisation of the single layers is presented. Junction properties, carrier transport and photogeneration are investigated from dark and illuminated current-voltage characteristics and bias dependent spectral response. The role of the design of the sensing element, doped layer composition and thickness, read-out parameters (applied voltage, scanner modulation, and wavelength) on the image acquisition and colour detection process are analysed. A physical model is presented and supported by a numerical simulation of the output characteristics of the sensor. Preliminary results show the possibility to tailor an a-SiC:H stacked heterostructure in order to optimise the CLSP as an image and colour recognition sensor.

#### A18.14

DEVELOPMENT OF VERTICALLY INTEGRATED IMAGING AND PARTICLES SENSORS. Nicolas Wyrsh, Clément Miazza, Sylvain Dunand, Arvind Shah, Université de Neuchâtel, Institut de Microtechnique, Neuchâtel, SWITZERLAND; Nicolas Blanc, Rolf Kaufmann, CSEM SA, Photonic Division, Zurich, SWITZERLAND; Pierre Jarron, CERN, EP Division, Meyrin, SWITZERLAND.

Active pixel sensors (APS) in CMOS technology have recently gained a lot of interest. However, the fact that the pixel readout-electronics shares the dye area with the photodiode array is a limiting factor for the imager light sensitivity. A vertical integration of the light sensor by depositing an amorphous silicon (a-Si:H) layer on the CMOS readout chip may greatly improve the sensitivity [1]. This so-called thin-film on ASIC (TFA) technology has therefore an interesting potential for high-sensitivity, low-level or high-dynamics imaging [2]. In particle physics, the increasing accelerator energies and fluences used in experiments call for radiation-hard particle detectors. In this

context, the same TFA technology may be applied by depositing radiation-hard a-Si:H detectors directly on the CMOS readout chip. For both application fields, very low dark current a-Si:H detectors are required. For this purpose, a-Si:H detectors have been developed and first deposited on glass substrates, thereby attaining (for 1  $\mu\text{m}$  thick detectors) dark currents as low as of  $3.3 \times 10^{-12}$  A/cm<sup>2</sup> at 3 V inverse polarisation. The same type of detectors have then be deposited on CMOS readout chips. Thereby, a significant increase in the dark current values have been observed. In this paper, the causes and remedies relating to this effect will be discussed in detail. The overall performances of the TFA sensors realized in our laboratory for vision and for particle detection will also be presented. For the latter, a direct detection of particles has been achieved by the use of very thick (up to 30  $\mu\text{m}$  thick) a-Si:H diodes deposited directly on CMOS chips. [1] S. Benthien et al., IEEE Journal of Solid State Circuits, vol. 35, No. 7, pp. 939-945, 2000. [2] B. Schneider et al., in B. Jähne, H. Hauecker, P. Geiler, Handbook on Computer Vision an Applications, Academic Press, Boston, pp. 237-270, 1999.

#### A18.15

AN AMORPHOUS SILICON PHOTOCONDUCTOR FOR UV DETECTION. Matthias Hillebrand, F. Blecher, J. Sterzel, M. Böhm, Institut fuer Mikrosystemtechnik (IMT), Universität-GH Siegen, Siegen, GERMANY.

An amorphous silicon photoconductor to detect wavelengths between 180nm and 380nm without scintillator is presented. The design of the new UV detector in TFA technology (Thin Film on ASIC) is discussed. UV imagers are widely used in chemical industry, in medical-biological technology for fluorescence measurement, and in security technology. The photoconductor 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 through a thin transparent passivation layer, the incident radiation is directly absorbed in the intrinsic a-Si:H material. The carrier collecting electrical field is applied vertically to the incoming light. The contact configuration can be varied, both on top or below the photoactive layer or in a mixed arrangement, according to the requirements, e.g. for one-dimensional or two-dimensional sensor arrays. The crucial parameters for the quantum efficiency are the surface dangling bond density of the back and front side, as well as the active layer thickness. The surface defect density highly depends on the production process and the passivation material. Test structures have been fabricated with sputtered chromium contacts on top of a 0.3  $\mu\text{m}$  thick carbonized hydrogenated i-layer. The spacing between the Schottky contacts is varied between 3  $\mu\text{m}$  and 100  $\mu\text{m}$ . They are deposited on top of or below the a-SiC:H layer. With this simple coplanar design a quantum efficiency of 10% was obtained at 230 nm wavelength. To verify the results calculations are performed to simulate the behavior of the photoconductor. The influence of parameters like dangling bonds at the surface, spacing between the contacts or thickness of the i-layer is investigated. With these results an optimization of the photodetector for different applications is possible, e.g. for flamedetectors with suppression of the visible light.

#### A18.16

CORRELATION BETWEEN THE TUNNELLING OXIDE AND I-V CURVE OF MIS PHOTODIODES. H. Aguas, L. Perreira, E. Fortunato, R. Martins, Depart de Materiais, Fac de Ciencias e Tecnologia, Univ Nova de Lisboa, Caparica, PORTUGAL; A.Goulet, Lab des plasmas et Couches Minces, Institut des Matériaux Jean Rouxel, Nantes, FRANCE.

It is known that metal-insulator-semiconductor (MIS) photodiodes present some advantages over the p-i-n structures when high response speed and high breakdown voltages are required. In this work we present results of a studied performed on: substrate (glass) / Cr (2000Å) / a-Si:H n+ (400Å) / a-Si:H i (5000Å) / oxide (20-40Å) / Au (100Å) structures where the main objective was to determine the influence of the oxide layer grown by different techniques on the performance of the MIS devices. The results achieved show that the oxides grown chemically by anodic oxidation in an ethylene-glycol solution and by hydrogen peroxide present characteristics as good as the ones obtained by the evaporation of SiO<sub>2</sub>, using an electron gun system, or by the chemical deposition of SiO<sub>2</sub> by plasma of HMDSO (hexamethyldisiloxane). The experimental data also show that the thickness of the oxide is easily controlled with the hydrogen peroxide oxidation technique, which is also the easiest and cheapest technique. By proper control of the oxide thickness it was possible to achieve photodiodes exhibiting an open circuit voltage of 0.7V and short circuit current density under AM1.5 illumination above 11 mA/cm<sup>2</sup>, with a response times less than 1 ms, a diode quality factor of about 1 and a ratio of 10<sup>7</sup> between forward and reverse currents. The ideal oxide thickness, determined by spectroscopic ellipsometry was estimated to be on the range of 25 to 30 Å, depending on the oxidation technique used, which determines the degree of films

compactness achieved. In this work it is also presented a method for reducing the saturation current of the diodes, by burning small pinhole short-circuits by applying to the device a controlled reverse voltage.

#### **A18.17**

**a-Si:H PROPERTIES RELEVANT TO MICROBOLMETER INFRARED DETECTORS.** A.J. Syllaos, J.H. Tregilgas, T.R. Schimert, W.L. McCardel, Raytheon Commercial Infrared, Dallas, TX.

An emerging application of a-Si:H thin films is in infrared detection and imaging microbolometer array technologies [1,2]. Among the a-Si:H material properties affecting the design and performance of microbolometer detectors are electrical resistivity and its temperature coefficient, surface morphology, and thermal and mechanical properties. For a-Si:H films grown by PECVD the effects of material growth parameters such as growth temperature, dopant concentration and thickness on device relevant material properties will be reviewed with emphasis on electrical resistivity and temperature coefficient of resistance (TCR). [1] A. J. Syllaos, et al., MRS Symp. Proc. 609, A14.4.1-6(2001). [2] E. Mottin, et al., SPIE Proc. 4369, 250-6(2001).

#### **A18.18**

**NUMERICAL SIMULATION OF THE INFLUENCE OF THE GAP STATE ON THE CHARACTERISTICS OF a-Si PIN/OLED.** Chunyu Wu, Yousu Chen, Guanghua Yang, Juan Li, Zhenhua Zhou, Ying Zhao, Xinhua Geng and Shaozheng Xiong, Inst. of Photo-electronic Thin Film Devices and Technology, Nankai University, Tianjin, P.R. CHINA; Huidong Yang, Inst. Of Thin Film & Nano-material, Wuyi Univ., Jiangmen, Guangdong, P.R. CHINA; Lizhu Zhang, Tianjin Mechanical and Electronic Vocational Technical School, Tianjin, P.R. CHINA.

Large area a-Si PIN/OLED image/sensor devices were proposed in our previous papers. The structure of one pixel is an a-Si PIN connecting in series but in opposite polarity with OLED. The a-Si PIN photodiode is used as a light sensor and converts the input light into a photocurrent. The photocurrent will be directly coupled to OLED, which is biased in forward and used as a display device. In this paper, the influence of the gap state density and the gap band width of the intrinsic a-Si:H active layer on the characteristics of a-Si PIN/OLED coupling pair was analyzed by a-Si:H PIN/OLED CAD simulation model. The CAD simulation model was carried out based on a-Si PIN Hack & Shur model and OLED TCL transport model. At the same gap band width, for the intrinsic a-Si:H active layer with the larger gap state density, the reverse current of a-Si PIN tended to be saturated at the higher reverse bias. As a result, I-V curve of a-Si PIN/OLED around the turn point  $V_t$  become smoother with the increase of the gap state density. At the same gap state density, the light induced current of a-Si PIN increased with the decrease of the band gap width as shown in Fig1, assuming the input light has the same spectrum as AM1.5 solar light. Thus the luminance emitted from OLED increased with the decrease of the band gap width because OLED belongs to the light-emitting device controlled by current. The simulation results showed that the influence of the gap state density intensified with the increase of the gap band width of a-Si:H. In the other words, the impact of the gap state density on I-V curve of a-Si PIN/OLED in the saturated region at the lower gap band width was less than that at the higher gap band width.

SESSION A19: POSTER SESSION  
DEFECTS AND LUMINESCENCE  
Thursday Evening, April 24, 2003  
8:00 PM

Salon 1-7 (Marriott)

#### **A19.1**

Abstract Withdrawn.

#### **A19.2**

**SILICON NANOSTRUCTURED FILMS FORMED BY PULSED-LASER DEPOSITION IN INERT GAS AND REACTIVE GAS.** Xiaoyu Chen, Yongfeng Lu, Yihong Wu, Byung-Jin Cho, Laser Microprocessing Laboratory and Silicon Nano Device Laboratory, Department of Electrical and Computer Engineering, National University of Singapore, SINGAPORE.

We report silicon (Si) nanostructured films formed by pulsed-laser deposition (PLD) in both inert gas argon (Ar) and reactive gas oxygen (O<sub>2</sub>). The as-deposited nanostructured films with visible photoluminescence (PL) peaked  $\sim 1.9$  eV show a transition from film structure to nanocrystal ( $\sim 7$  nm), as the ambient gas pressure is increased from 1 mTorr to 1 Torr. By varying the substrate-to-target distance, the transition is explained by the increased collisions between the ejected species as gas pressure increases. The oxygen

composition of SiO<sub>x</sub> is found to rise with increasing O<sub>2</sub> gas pressure by x-ray photoemission spectroscopy (XPS), while Si 2p peak of the SiO<sub>x</sub> oxide also becomes dominate. At 100 mTorr O<sub>2</sub> gas, XPS reveals almost complete SiO<sub>2</sub> structure. Dry oxidation and annealing were applied to the as-deposited nanostructured films. Intensity changes and blue shifts of the PL spectra at 1.9 eV are observed after oxidation, while the PL intensities are increased by about two to four times of magnitude after annealing. The 1.9 eV PL is attributed to the light emission from Si core by quantum confinement. An addition peak at 2.55 eV with no peak shift appears with increased oxidation treatment, which is attributed to the light emission from SiO<sub>x</sub>. Raman shifts are found for all samples before and after oxidation and annealing. The nanocrystal size distribution in the nanostructured films is observed by transmission electron microscopy (TEM). X-ray diffraction (XRD) reveals that the as-deposited nanostructured films have a polysilicon structure. Subsequent anneal is necessary for a more stable structure and better crystallinity.

#### **A19.3**

**ORIGIN OF LOW-ENERGY PHOTOLUMINESCENCE IN MICROCRYSTALLINE SILICON FILMS.** In-Taek Jang, Kwang-Wook Jeon, Dong-Hyun Park, Jong-Hwan Yoon, Kangwon National University, Department of Physics, Chunchon, Kangwon-Do, KOREA.

It is well known that hydrogenated microcrystalline silicon films ( $\mu$ c-Si:H) reveal a photoluminescence (PL) band with a peak located within 0.8 - 1.0 eV. It has been suggested that this low-energy PL is attributed to either to defects in an amorphous phase or in the crystalline phase or to radiative transition between band-tail states in the crystalline or grain-boundary region. However, the origin of low-energy PL band still remains unclear. In this work we have investigated the low-energy PL in  $\mu$ c-Si:H using various experiments: the effects of hydrogen and argon dilution, temperature and excitation-intensity dependences, the effects of annealing, dilution ratio, and deposition power.  $\mu$ c-Si:H films were grown from either hydrogen or argon diluted SiH<sub>4</sub> gas using a conventional plasma-enhanced chemical vapor deposition (PECVD) excited at 13.56 MHz. It is shown that the PL peak energy appears at different position, 0.87 eV and 0.97 eV for hydrogen and argon diluted samples with high volume fraction of crystallites, respectively. Both samples show that the peak intensity monotonically decreases with increasing temperature, but no energy shift is observed. The excitation-intensity dependence of the PL peak shows that the increasing rate of the PL peak is higher for low intensity than for high one. It is also found that rf power, annealing, and dilution ratio significantly affect the position of the PL peak energy. Annealing results in the red-shift, while the blue-shift is observed with increasing amorphous phase, which are obtained by growing  $\mu$ c-Si:H films using low rf power and dilution ratio. From these results, a possible origin for the low-energy PL will be presented.

#### **A19.4**

**EFFECT OF Tb, Er-DOPING ON THE STRUCTURAL AND OPTICAL CHARACTERISTICS OF NANO-CRYSTALLINE Si THIN FILMS.** K.-H. Han, M.-B. Park, N.-H. Cho, Inha Univ., Dept. of Materials Sci. and Engineering, Incheon, KOREA.

The nano-structural and optical characteristics of Tb, Er-doped Si thin films, which were prepared by RF magnetron sputter techniques, were investigated as a function of Tb, Er-contents and post-deposition heat-treatment conditions. The nano-structural and chemical features are related with the photoluminescence(PL) phenomena of the films. The PL intensity increased with the amount of Tb(or Er) as well as Si nano-crystallites in the films. A strong PL peak was observed at about 545 nm owing to the electronic structure of Tb<sup>3+</sup>. Post-deposition heat-treatment increased the fraction of nano-crystallites of less than 10 nm in size; this resulted in enhancing the PL generated by the intra-4f Tb<sup>3+</sup> transition.

#### **A19.5**

**EXCIMER-LASER ENHANCED FORMATION OF LUMINESCENT NANOCRYSTAL-Si/SiO<sub>2</sub> SUPERLATTICES.** Daigil Cha, Yohan Sun and Jung H. Shin, Department of Physics, Korea Advanced Institute of Science and Technology (KAIST), Taejeon, KOREA.

Great interest lies in formation of high density of small (<4nm in diameter) nanocrystal Si (nc-Si) for applications in photonics and novel electronic devices. A proven method for fabrication of such films is crystallization of amorphous Si/SiO<sub>2</sub> superlattices with nm-thin layers. Unfortunately, such films required are highly resistant to crystallization, necessitating prolonged anneals at temperatures in the excess of 1200°C that can lead to break up and agglomeration of nc-Si, and may represent an unacceptably high thermal budget. In this paper, we report on use of excimer laser irradiation to enhance formation of luminescent nc-Si/SiO<sub>2</sub> superlattices. a-Si/SiO<sub>2</sub> superlattices with nominal thickness of 3nm and 4nm, respectively,

were deposited by electron-cyclotron resonance plasma enhanced chemical vapor deposition of SiH<sub>4</sub> and O<sub>2</sub>. 3 sets of samples, one with thermal anneal at 1100°C only, one with excimer laser irradiation only, and one with thermal anneal at 1100°C followed by excimer laser irradiation were prepared. We find that excimer laser irradiation alone does not lead to a significant formation of luminescent nc-Si. Thermal anneal alone results in a weak nc-Si luminescence. However, the nc-Si photoluminescence intensity can be increased by more than 3 fold by a subsequent excimer laser irradiation. Excimer laser irradiation also results in a slight redshift of the nc-Si luminescence peak position and a reduction in the luminescence lifetime. The nc-Si luminescence is consistent with excitonic luminescence with singlet-triplet splitting of ~7meV, with a long lifetime (~70μsec at room temperature. Based on the results, we argue that the main role of excimer laser irradiation is removal of defects and amorphous regions remaining after thermal anneal, and that such a combination of thermal anneal followed by excimer laser irradiation may provide a way to form a dense array of small, highly luminescent small nc-Si at a much reduced thermal budget.

**A19.6**  
**POST-TRANSIT ANALYSIS OF TRANSIENT PHOTOCURRENTS FROM HIGH-DEPOSITION-RATE a-Si:H SAMPLES.** Monica Brinza and Guy J. Adriaenssens, Halbleiterphysik Dept., University of Leuven, BELGIUM; W.M.M. Kessels, A.H.M. Smets, M.C.M. van de Sanden, Department of Applied Physics, Eindhoven University of Technology, THE NETHERLANDS.

The analysis of transient photocurrents in the post-transit-time regime of a time-of-flight experiment allows a determination of the distribution and density of localized gap states in a-Si:H. Since electron and hole transients can be measured separately in a sandwich-cell geometry with blocking contacts, independent determinations of the density-of-states (DOS) from the conduction and valence band sides of the gap can be obtained. In order to investigate the effect on those DOS distributions of high deposition rates, and the high temperatures they require, we have determined gap-state densities for a series of a-Si:H samples prepared by means of the expanding thermal plasma (ETP) technique, at a deposition rate of 7nm/s and with substrate temperatures varying from 250 to 500°C. Fairly featureless distributions are resolved with, for samples with room-temperature electron mobilities near 1 cm<sup>2</sup>/Vs, a gap state density on the order of 4×10<sup>16</sup> cm<sup>-3</sup> eV<sup>-1</sup> on the conduction band side and about 10<sup>16</sup> cm<sup>-3</sup> eV<sup>-1</sup> on the valence band side. Corresponding values for the gap-state density were obtained, using the same experimental techniques and sample geometry, for a-Si:H layers prepared by other techniques. In an earlier publication [1], and in contrast to the featureless distribution mentioned above, we reported considerable structure in the electron post-transit currents from some of the ETP samples. However, a more detailed examination of the temperature dependence of the current transients, and specifically of the position on the transient where the observed structure manifests itself, leads to the conclusion that this part of the transient is not related to carrier emission from deep traps, and, therefore, does not contain information on the DOS of the material. In fact, the extra feature can be understood as a photo-induced leakage current due to a modification of the sample's Cr/a-Si:H Schottky barrier by the exciting light pulse. In support of this interpretation, measurements have been carried out on ETP a-Si:H time-of-flight samples with different barrier structures, including the replacement of Cr by Mo and the use of an n-i-p cell.  
 [1] M. Brinza *et al.*, J. Non-Cryst. Solids 299 (2002) 420.

**A19.7**  
**SIZE DISTRIBUTION OF EMBEDDED NANO-CRYSTALLITES IN POLYMORPHOUS SILICON STUDIED BY RAMAN SPECTROSCOPY AND PHOTOLUMINESCENCE.** V. Tripathi, M.N. Islam, S. Gupta and Y.N. Mohapatra, Department of Physics, IIT, Kanpur, INDIA; P. Roca i Cabarrocas, Laboratoire de Physique des Interfaces et des Couches Minces, Ecole Polytechnique, Palaiseau, FRANCE.

Polymorphous Silicon (pm-Si:H), deposited by Plasma Enhanced Chemical Vapour Deposition (PECVD) is a recent alternative material to amorphous silicon (a-Si:H). Deposition parameters of pm-Si are such that small crystallites get embedded in a relaxed amorphous silicon matrix, thus improving the optical and electrical properties. We study the size of crystallites and degree of order in pm-Si using Raman and photoluminescence (PL) spectra of pm-Si and a-Si:H. Raman Spectra of a variety of hydrogenated nanostructured silicon (pm-Si:H) and amorphous Silicon (a-Si:H) samples grown at different pressures were analyzed. A comparison of TO peak in Raman spectra between a-Si:H and pm-Si:H samples reveals asymmetry and red shift in pm-Si:H samples. In spite of many attempts to fit Raman spectra using Quantum Confinement Models, there exists a discrepancy between the experimental data and theoretical predictions. Specifically, experiments indicate comparatively smaller

red shift than predicted. We show that a quantum confinement model that incorporates gaussian size distribution can accurately predict particle size of nanocrystallites embedded in the amorphous matrix. A comparison of TA-TO region of Raman Spectra from a-Si:H and pm-Si:H material also implies pm-Si:H as material having higher degree of order. Photoluminescence (PL) emission and excitation spectra of various polymorphous Silicon samples were recorded in the range of 200nm to 700nm. We observed strong PL in ultra-violet blue range. Deconvolution of the spectra reveals two distinct peaks at 412 and 438nm with excitation wavelength (λ<sub>ex</sub>=325 to 380nm) and a separate broad band with lesser intensity in 500-600nm range (λ<sub>ex</sub>=425nm). Assuming that PL peaks between 500-600 nm can be attributed to nano-crystals, deconvolution of the spectra and fitting to gaussian size distribution show the particle size to be in the range of 2-3.5 nm, in agreement with Transmission Electron Microscopy (TEM) and Raman results.

**A19.8**  
**HIGHLY-SENSITIVE DETERMINATION OF THE DEFECT DENSITY IN a-Si:H FILMS BY CAVITY RINGDOWN SPECTROSCOPY AT SUB-GAP ENERGIES.** I.M.P. Aarts, A.H.M. Smets, B. Hoex, R. Engeln, W.M.M. Kessels, M.C.M. van de Sanden, Eindhoven University of Technology, Dept of Applied Physics, Center for Plasma Physics and Radiation Technology, Eindhoven, THE NETHERLANDS.

The highly-sensitive cavity ring down technique has been applied to probe the density of states of hydrogenated amorphous silicon (a-Si:H) films at a range of sub gap energies (0.8 - 1.25 eV). It is shown that this straightforward and absolute absorption technique is easily capable of detecting absorptions in thin films as small as 10<sup>-7</sup> (single shot) without the need for calibration procedures. Results for the absorption coefficient, which is directly associated with the a-Si:H defect states, show very good agreement with photothermal deflection spectroscopy. The high sensitivity of the technique enables accurate measurements of the defect density for ultra-thin films. For thin plasma deposited a-Si:H films at 250°C the existence of a defect-rich surface layer with a surface defect concentration of 5.6 × 10<sup>11</sup> cm<sup>-2</sup> has been extracted. The density of states for both the bulk film and the surface layer will be further investigated at a broader sub gap energy range of 0.7 - 1.4 eV using an optical parametric oscillator laser system. Furthermore, the detection of defect states by an evanescent wave that probes the film from a total internal reflection element will be presented. This enables the use of the technique *in situ* during plasma deposition and will reveal more information about the role of defects in the growth mechanism of thin silicon films.

**A19.9**  
**HIGH FREQUENCY ELECTRON SPIN RESONANCE STUDY OF HYDROGENATED MICROCRYSTALLINE SILICON.** Takashi Ehara, Ishinomaki Senshu Univ, School of Science and Engineering, Miyagi, JAPAN.

Paramagnetic species in hydrogenated microcrystalline silicon (μc-Si:H) have been studied by Q-band electron spin resonance (ESR) spectroscopy. In the present work, the μc-Si:H samples were prepared at various substrate temperature from 70°C to 370°C. In X-band ESR spectra, all the samples showed asymmetric dangling bond defect (DB) signal at g = 2.005 - 2.006 with spin density of 10<sup>18</sup> cm<sup>-3</sup>. The DB signal shows little dependence on substrate temperature in the X-band ESR spectra. In the Q-band ESR spectra, existence of at least two centers in DB signals is clearly indicated by the shape of the spectra. The fitting reveals that one center is at g = 2.005 - 2.006 and the other is around at g = 2.004. The g-values of two centers observed are consistent with the attributions reported in the previous works. In addition, the DB signal showed dependence on substrate temperature. The dependence of the spectra is due to change of intensity ratio of signals by these two centers. The relative intensity of signal by the center at g = 2.004 to the one at g = 2.005 - 2.006 in the sample prepared at 70°C is larger than that in other samples. As a result, the existence of two centers are observed more clearer in this sample than in the other samples. The substrate temperature dependence of Q-band ESR spectra observed here is thought to be due to the change in the structure of samples.

**A19.10**  
**IMPURITY-INDUCED DEFECT CREATION AT P/I INTERFACE IN MICROCRYSTALLINE SILICON P-I-N SOLAR CELLS.** Takuya Matsui, Takashi Fujibayashi, Yoshiyuki Nasuno, Michio Kondo, Akihisa Matsuda, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, JAPAN; Hitoshi Fukuhori, Yoshihiko Kanemitsu, Nara Institute of Science and Technology, Ikoma, Nara, JAPAN.

Intrinsic microcrystalline silicon (μc-Si:H) thin films grown by 100 MHz plasma-enhanced chemical vapor deposition at different growth temperatures have been applied to superstrate-type p-i-n junction

solar cells in order to investigate effects of i-layer growth temperature ( $T_s$ ) on p/i interface properties. Although high quality  $\mu$ c-Si:H films (low defect density and large (220) grain size) are obtained at  $T_s \sim 250^\circ\text{C}$ , such high temperature growth of i-layer in the superstrate solar cells results in poor blue response and shows a strong bias-voltage dependent carrier collection behavior in the quantum efficiency spectra. Since blue response of p-i-n solar cells is dominated by p/i interface properties, high temperature growth of i-layer is likely to deteriorate p/i interface. From the secondary ion mass spectroscopy (SIMS) impurity depth profiles, appreciable boron diffusion from p-layer into i-layer is found to occur during i-layer growth when  $T_s \sim 250^\circ\text{C}$  [1]. In addition, we studied photoluminescence (PL) from i-layers in the vicinity of p/i interface. As a result, the integrated intensity of PL peak at 1.4 eV decreases by three orders of magnitude when  $T_s$  is increased from 150 to 250 $^\circ\text{C}$ . SIMS and PL results provide strong evidence that diffused boron creates non-radiative recombination center at p/i interface. We propose that such anomalous low-temperature boron diffusion is occurred by the interaction with atomic hydrogen during i-layer growth. [1] Y. Nasuno et al. Appl. Phys. Lett. 81, 3155 (2002).

**A19.11**  
GAP STATE DENSITY OF THIN a-Si:H LAYERS ANALYSED BY UV-PHOTOELECTRON SPECTROSCOPY. Manfred Schmidt, Oliver Milch, Andreas Schoepke Hahn-Meitner-Institut, Berlin, GERMANY.

We report on a detailed study on gap-state distribution in thin amorphous silicon emitter layers (a-Si:H) on c-Si wafers performed by UV excited photoelectron spectroscopy (UV-PES). The excitation with photon energies below 10 eV is of advantage because the information depth increases up to 7nm. This enabled us to detect the energetic distribution of gap- and upper valence band states in 5-10 nm thick a-Si:H emitter layers as a function of the phosphorus doping level and in-situ treatment as hydrogen effusion. The comparison between the total-yield excitation spectra and the constant final state yield spectroscopy (CFSYS) reveals that the measured density of states distribution is not distinctly affected by scattering processes in the a-Si:H itself. Basing on this result we determined the position of the Fermi level with respect to the valence band, the slope of the valence band tail states (Urbach energy) and the gap state distribution. It was found, that that for phosphorous doping the position of the Fermi level saturates at  $E_F - E_V = 1.47\text{eV}$ . This corresponds to a gas phase concentration of 20000ppm  $\text{PH}_3$  in  $\text{SiH}_4/\text{H}_2$  mixture which was used in the PECVD deposition process. The variation of the doping level from 0 to 20000 ppm  $\text{PH}_3$  addition results in an increase of the Urbach energy from 51meV to 101meV and in an increase of the gap state density at midgap ( $E_V - E_i = 0.86\text{eV}$ ) from  $3 \times 10^{18}\text{cm}^{-3}\text{eV}^{-1}$  to  $2 \times 10^{19}\text{cm}^{-3}\text{eV}^{-1}$ . The UV-PES method is the only way to determine all these quantities in such thin layers including the first stages of film growth. We will discuss the results in particular comparing with results obtained with classical methods (photoconductivity, thermally activated currents) for thick a-Si:H layers.

**A19.12**  
DETERMINATION OF DEFECT DENSITIES BY CONSTANT PHOTOCURRENT METHOD - COMPARISON OF AC AND DC METHODS. C. Main, S. Reynolds and I. Zrinscak, Univ Abertay Dundee, School of Computing and Advanced Technologies, Dundee, UNITED KINGDOM.

Discrepancies have been observed by a number of groups [1-4] in the absorption spectrum of a-Si:H measured by DC and AC constant photocurrent methods (CPM). Our own measurements, reveal discrepancies in the absorption coefficient  $\alpha$ , of up to an order of magnitude. DC measurement gives the higher value for  $\alpha$  at photon energies below the Urbach tail. In this paper we examine free carrier generation paths in AC CPM, and the influence of these paths on the photocurrent frequency response to modulated sub-gap illumination. A simple kinetic model is used to attempt to explain quantitatively the differences in the photocurrent frequency response for sub- and super-gap excitation. At first sight the basic AC technique is of doubtful validity, even at exciting frequencies as low as 1 Hz, since maintaining a constant AC photocurrent does not guarantee a constant carrier lifetime. On the other hand, the DC method involves several parallel excitation paths, obfuscating attempts to extract a density of states from the absorption spectrum. We demonstrate that a simple variation of AC CPM can provide a more accurate means of determining the density of states than DC CPM. [1] P. Sladek, P. Stahel and M-L. Theye, Philos. Mag. B71, 871, 1995 [2] A. Eray, G. Nobile and F. Palma, in Thin Film Materials and Devices - Developments in Science and Technology, ed. J.M. Marshall, N. Kirov, A. Vavrek and J.M. Maud (World Scientific, Singapore, 1999) 341. [3] G. Conte, F. Irrera, G. Nobile and F. Palma, J. Non-Cryst. Solids 164-166, 419, 1993. [4] P. Sladek and M.L. Theye, Solid State Commun. 89, 199, 1994.

**A19.13**  
DEPTH PROFILING OF LIGHT-INDUCED DEFECTS IN HYDROGENATED AMORPHOUS SILICON BY TRANSIENT PHOTOCURRENT SPECTROSCOPY. Steve Reynolds and Charlie Main, Univ of Abertay Dundee, Sch of Computing and Advanced Technologies, Dundee, UNITED KINGDOM; Rudi Brueggemann, Fachbereich Physik, Universitaet Oldenburg, GERMANY.

Transient photoconductivity (TPC) is an established probe of the energetic distribution of localised states in amorphous semiconductors. The technique reveals the creation of light-induced metastable defects in hydrogenated amorphous silicon (a-Si:H) and is therefore useful in the optimisation of these materials for device applications. It has recently been demonstrated that TPC is also sensitive to the spatial location of defects within a film. This is manifested in small but reproducible differences in the photocurrent decay that depend on the wavelength of the laser flash used to generate excess carriers. Analysis of the decays suggests an increased presence of deep-level defects when more strongly absorbed (green) laser light is used, compared with more uniformly absorbed (red) light, consistent with a higher defect density in the surface layer of the film. Here, we extend this work to study the effects of light-soaking with different wavelengths, with a view to controlling to some extent the spatial profile of metastable defects. We find that light-soaking of PECVD a-Si:H from either the free surface or through the glass substrate using an AM1 source increases the overall defect density (bulk and surface), but the increase in the surface density, as revealed by the TPC technique, is greater at the surface on which the soaking light is incident. This is attributed to the increased absorption of the shorter-wavelength portion of the white light, and hence an increased rate of defect creation, in this region. Further, we have soaked with blue-green filtered white light, and as expected the defect density at the incident surface is increased while the bulk density is largely unaffected. Our results are discussed in the light of previous studies of spectrally-resolved steady-state photoconductivity, and prospects for a quantitative interpretation are considered.

**A19.14**  
A STUDY OF ELECTRONIC DEFECTS IN HYDROGENATED AMORPHOUS SILICON PREPARED BY THE EXPANDING THERMAL PLASMA TECHNIQUE. Steve Reynolds, Charlie Main, Univ of Abertay Dundee, Sch of Computing and Advanced Technologies, Dundee, UNITED KINGDOM; Zdravka Aneva, Diana Nesheva, Inst of Solid State Physics, Bulgarian Academy of Sciences, Sofia, BULGARIA.

The expanding thermal plasma (ETP) deposition of hydrogenated amorphous silicon (a-Si:H) permits high growth rates to be achieved whilst retaining acceptable electronic quality. ETP a-Si:H films have previously been studied using time-of-flight spectroscopy [1], and the results suggest hole mobilities some ten times higher than in PECVD material. However, electron mobilities are found to be similar. The post-transit photocurrent decay (following the electron transit) has also been analysed, and interpreted in terms of a steeply-rising deep defect density, although more recently it has been suggested that this feature may be an artefact associated with the sample contacts [2]. Here, we have applied transient photocurrent spectroscopy (TPC) in the study of ETP a-Si:H. As TPC measures the secondary photoconductivity and the gap cell structures used here show a linear current-voltage characteristic, such difficulties with contacts cannot arise. Analysis of TPC decays obtained between 125 K and 380 K suggest a two-segment conduction band tail, of some 20 meV slope at energies shallower than 0.15 eV and 40 meV slope between 0.15 eV and 0.3 eV, followed by a defect plateau of estimated density  $10^{17}\text{cm}^{-3}\text{eV}^{-1}$  at energies deeper than 0.4 eV. The deep defect region was also investigated by analysis of the steady-state lux-ampere versus temperature characteristics, and the results obtained are in good qualitative agreement with the TPC data. Finally we measured thermally stimulated currents, which show a pronounced peak between 250 K and 300 K. The origins of this feature are discussed in terms of the density of states proposed above. [1] M. Brinza et al, J. Non-Cryst. Sol. 299-302, 420 (2002). [2] M. Brinza and G.J. Adriaenssens, 12th ISCMP, Varna, Bulgaria, September 2002 (to be published in Journal of Materials Science - Materials in Electronics).

SESSION A20: THIN FILM TRANSISTORS  
Friday Morning, April 25, 2003  
Salon 5/6 (Marriott)

**8:30 AM \*A20.1**  
LOW-TEMPERATURE GROWTH OF POLY-Si AND SiGe THIN FILMS BY REACTIVE THERMAL CVD AND FABRICATION OF HIGH MOBILITY TFTs OVER  $50\text{cm}^2/\text{Vs}$ . Jun-ichi Hanna and Kousaku Shimizu, Imaging Science and Engineering Laboratory, Nagatsuta Midori-ku, Yokohama, JAPAN.



We have investigated a new CVD process that makes it possible to grow device-grade polycrystalline Si (poly-Si) for large-area electronic devices directly onto the glass substrate. This process has to satisfy several requirements, i.e., film growth at the temperatures lower than 500°C, high and uniform crystallinity of the films in area and depth profiles, and suppressed powder formation and wall deposition. In order to realize a clean process for large-area application in which powder formation and wall deposition are suppressed, we feature a cold-wall type of thermal CVD, in which the reaction zone responsible for the film deposition is limited in the vicinity of the substrate surface. Furthermore, in order to reduce the growth temperature of 600°C required for poly-Si, we utilized a small amount of reactive gases such as germanium tetrafluoride (GeF<sub>4</sub>) and fluorine (F<sub>2</sub>) to promote structural relaxation of Si-network into the crystal, in addition to decomposition of Si source gas of disilane (Si<sub>2</sub>H<sub>6</sub>) in the vicinity of the heated substrate. Thus, this new CVD process provides us with quality poly-Si<sub>1-x</sub>Ge<sub>x</sub> (x < 0.05) and poly-Si thin films at 450°C. 200nm bottom-gate TFTs fabricated on SiO<sub>2</sub>/Si substrates exhibited high mobility over 50cm<sup>2</sup>/Vs, which has not been ever achieved with low-temperature CVD poly-Si. In this talk, we will describe the structural and electrical properties of the films deposited by this technique and discuss the TFT performance with respect to those.

#### 9:00 AM A20.2

USING LETTERPRESS PRINTED POLYMER MASKS TO FABRICATE AMORPHOUS SILICON THIN FILM TRANSISTORS. Scott M. Miller and Sandra M. Troian, Department of Chemical Engineering, Princeton University, Princeton, NJ; Sigurd Wagner, Department of Electrical Engineering, Princeton University, Princeton, NJ.

Flexible electronics, and in particular those fabricated on ultra-large scales and in high volumes, will require novel approaches to pattern formation. We have developed a fabrication scheme that utilizes letterpress printing instead of photolithography to directly print masks for the fabrication of amorphous silicon thin film transistors. A stamp with raised features picks up a thin polymer melt film and transfers it to a workpiece where it can serve as a mask for wet etching or reactive ion etching. Using this printed polymer ink as an etch mask, we are able to eliminate many process steps without changing the overall fabrication scheme and without changing the structure of our finished devices. The changeover from photolithography to printing comes without changing the transistor on/off ratio or mobility. In addition to describing the specific printing technology and transistor performance, we will show how theoretical process modeling can be used to predict the fidelity of printed patterns, and suggest ways in which pattern distortion can be used to advantage.

#### 9:15 AM A20.3

IMPROVEMENT OF GATE OXIDE INTEGRITY IN LOW TEMPERATURE POLY SILICON TFT. Seok-Woo Lee, Dae Hyun Nam, Jin Mo Yoon, Hyun Sik Seo, Kyoung Moon Lim, Chang-Dong Kim, LCD R&D Center, L.G. Philips LCD, Anyang, KOREA.

The characteristics of Silane-based gate oxide deposited by plasma enhanced chemical vapor deposition (PECVD) have been investigated with respect to gate oxide integrity (GOI) and its reliability. For the experiment, metal oxide semiconductor (MOS) capacitors with 100 nm-thick gate oxide were fabricated on p-type silicon wafers. It was found that the GOI strongly depended on the charge trapping and deep level interface states generation under FN stress. By applying elevated temperature post anneal without vacuum break after the gate oxide deposition, highly reliable gate oxide was obtained, i.e., increased charge to breakdown and reduced flat band voltage shift by FN stress, which could be explained by the reduction of charge trapping and deep level interface states generation compared with as-deposited gate oxide. Detailed FN stress experiments demonstrated that the early stage of degradation process was dominated by hole trapping and following stress duration was dominated by electron trapping led to gate oxide breakdown. The device characteristics of CMOS poly silicon TFT fabricated on glass substrate were also examined. By applying post anneal after gate oxide deposition, improved hot carrier stress immunity of less field effect mobility degradation and of less threshold voltage shift as well as increased initial field effect mobility was obtained. Under FN stress, Id-Vg transfer curve showed negative shift and degradation of subthreshold swing, which were reduced by adopting post annealed gate oxide mainly because of the lowered charge trapping and reduced deep level interface states generation. Besides, the TFT with post annealed gate oxide showed around 10 times higher charge to breakdown under constant current gate injected FN stress with commonly biased source and drain. These improvements of GOI reliability and CMOS performances will give a solution for system integration on panel of LCDs in the near future.

#### 9:30 AM A20.4

GATE AND DRAIN-BIAS INDUCED V<sub>T</sub> METASTABILITY IN a-Si:H TFTS FOR ANALOG APPLICATIONS. Karim S. Karim, Arokia Nathan, University of Waterloo, Electrical and Computer Engineering, Waterloo, ON, CANADA.

The bias-induced threshold voltage (V<sub>T</sub>) metastability in a-Si:H TFTs can have adverse effects on circuit performance if the circuit is improperly designed or operated. Metastability concerns become particularly important when the TFT is used as an analog device. In contrast to traditional applications (e.g. in LCDs) where the TFT is used as a switch, analog applications require the device to withstand prolonged voltages on both, drain and gate terminals. This work attempts to develop an understanding of V<sub>T</sub> shift ( $\Delta V_T$ ) on TFT circuit performance at low bias voltages (e.g. < 25 V), where the  $\Delta V_T$  for a TFT operating in linear mode is found to be considerably larger than for a TFT operating in saturation mode. Defect state creation and charge trapping are the widely accepted mechanisms for V<sub>T</sub> instability in a-Si:H TFTs. Defect creation dominates at lower bias voltages while charge trapping in the gate insulator is dominant at higher biases. The point at which charge trapping overtakes defect state creation has been shown to be a function of the gate nitride stoichiometry. However, power requirements in emerging analog applications of a-Si:H technology (e.g. active pixel sensor (APS) imagers and organic light emitting diode (OLED) displays) underscore the need to move towards low power and reduced supply voltages, where defect state creation dominates. Experiments at constant drain and gate voltage stresses on in-house fabricated a-Si:H TFTs indicate that defect state creation is the dominant  $\Delta V_T$  mechanism in our TFTs at small bias voltages (< 25 V). The developed  $\Delta V_T$  model is employed in an APS imaging pixel for gain degradation estimation and was found to be in good agreement with experimental data. The  $\Delta V_T$  model presented here can predict the performance of a-Si:H analog circuits for a variety of emerging a-Si:H TFT applications.

#### 9:45 AM A20.5

CHARACTERISTICS OF BOTTOM GATE THIN FILM TRANSISTORS WITH SILICON RICH POLY-Si<sub>1-x</sub>Ge<sub>x</sub> AND POLY-Si FABRICATED BY REACTIVE THERMAL CHEMICAL VAPOR DEPOSITION. Kousaku Shimizu, JianJun Zhang, Jeong-Woo Lee and Jun-ichi Hanna, Imaging Science and Engineering Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN.

In the fabrication of thin film transistors (TFTs), little attention has been paid to the polycrystalline silicon (poly-Si) thin films prepared at low temperatures where the glass substrates are adopted so far. This is because the film quality is not good enough to achieve high mobility, e.g., over 50 cm<sup>2</sup>/Vs in spite of high benefit in their industrial fabrication. We have fabricated bottom gate TFTs with poly-Si and poly-SiGe thin films deposited at 450°C by newly developed low-temperature LPCVD technique and characterized electrical characteristics of the TFTs: disilane (Si<sub>2</sub>H<sub>6</sub>) and a small amount of either germanium tetrafluoride (GeF<sub>4</sub>) or fluorine (F<sub>2</sub>) were used as material gases and helium (He) as carrier gas; 200nm-thick of poly-SiGe or poly-Si was deposited onto n-type (100) Si wafer with 75nm-thick silicon dioxide on the surface: after the photo-resist patterned, 2-5x10<sup>15</sup> (ions/cm<sup>2</sup>) of phosphorus or boron ion was implanted under the conditions of 30 keV; through the TFT fabricating process, thermal annealing for dopant activation and atomic hydrogen treatment for defect passivation were carried out. We found that the hydrogen passivation process is important for improving TFT performance effectively, and furthermore that the thermal treatment at 450°C for 1 hr is also quite effective to the improvement. Finally the mobility of p-channel and n-channel TFTs have attained 36.3-54.4 cm<sup>2</sup>/Vs and 57 cm<sup>2</sup>/Vs, respectively. The present results are quite encouraging for low cost fabrication of poly-Si TFTs in the future.

SESSION A21: IMAGERS  
Friday Morning, April 25, 2003  
Salon 5/6 (Marriott)

#### 10:30 AM A21.1

DIGITAL LITHOGRAPHIC PROCESSING FOR a-Si:H THIN-FILM TRANSISTOR ARRAYS. William S. Wong, Steven E. Ready, Jeng-Ping Lu, Jackson Ho, and Robert A. Street, Palo Alto Research Center, Palo Alto, CA.

The cost and complexity of fabricating large-area electronics by conventional device processing is an impediment to the availability of inexpensive ubiquitous displays, large-area image sensors, and evolving technologies such as electric paper. In many large-area electronics applications, the minimum feature size for a TFT device is approximately 10-50 μm. For this dimension, many less expensive and simpler techniques are available as a substitute for photolithography. Digital lithography, in which a digitally imaged etch mask is

jet-printed onto a process wafer to define features for semiconductor processing, is one method to reduce the cost and complexity of semiconductor device fabrication. The spatial control of jet-printing makes it an ideal technology for implementing the direct writing of etch masks. Digitally processed, jet-printed etch masks were used to fabricate hydrogenated amorphous silicon thin-film transistor (TFT) matrix-addressing arrays. Wax-mask features with a minimum feature size of  $\sim 40 \mu\text{m}$  were used to pattern device structures using a multi-ejector piezoelectric printhead in place of conventional photolithography. Bottom-gate TFTs with source-drain contacts overlapping the channel were created using a four-mask process. The TFTs in a  $64 \times 64$  matrix-addressing array of  $300 \mu\text{m}$  square pixels had I-V characteristics comparable to photolithographically patterned devices. The average mobility was  $0.8\text{--}9 \text{ cm}^2/\text{V}\cdot\text{s}$  with a threshold voltage of  $3\text{--}4 \text{ V}$ , and on/off ratios exceeding  $10^8$ . The implementation of these arrays for backplanes in image sensor applications will also be discussed.

#### 10:45 AM **A21.2**

**OPTOELECTRONIC DETECTION OF DNA MOLECULES ON THIN-FILM DNA CHIPS USING AN AMORPHOUS SILICON PHOTOCONDUCTOR.** E. Fixe<sup>a,b</sup>, D.M.F. Prazeres<sup>b</sup>, V. Chu<sup>a</sup> and J.P. Conde<sup>a,c</sup>; <sup>a</sup>INESC Microsistemas e Nanotecnologias, Lisbon, PORTUGAL; <sup>b</sup>Biological Engineering Research Group, Instituto Superior Tecnico, Lisbon, PORTUGAL; <sup>c</sup>Department of Materials Engineering, Instituto Superior Tecnico, Lisbon, PORTUGAL.

The objective of this work is to demonstrate the use of an amorphous silicon (a-Si:H) photodetector to sense the presence of a DNA molecule tagged with a fluorescent marker. An array of such detectors can be used for optoelectronic data acquisition in DNA chip or microarray applications. The device is based on the photoconductivity of a-Si:H in a coplanar electrode configuration. The spectral response of such a device has a peak in absorption between  $550\text{--}600 \text{ nm}$ . A fluorescent molecule, 1-(3-(succinimidyl)oxycarbonyl)benzyl)-4-(5-(4-methoxyphenyl)oxazol-2-yl) pyridinium bromide (PyMPO, SE) was chosen due to its large Stoke's shift ( $\lambda_{\text{excitation}} = 400 \text{ nm}$ ;  $\lambda_{\text{emission}} = 560 \text{ nm}$ ) and because it can be chemically attached to the amine termination of the DNA molecule. The presence of a tagged DNA molecule is detected by exciting the PyMPO molecule using UV light producing an emission of visible light which is converted to a photoconductive signal in the detector. Measurement of the spectral response curve of the detector with and without the presence of PyMPO shows an increase in signal in the  $400\text{--}450 \text{ nm}$  range when PyMPO is present. To optimize the sensitivity of the device, thin film UV filters were deposited over the a-Si:H photoconductor to lower its absorption of light at the excitation energy. Different concentrations of DNA marked with PyMPO were detected and the detection limit of the present device structure was of the order of  $100 \text{ pmol}/\text{cm}^2$ . From literature, the typical density of DNA immobilized and hybridized on a functionalized surface is in the range of  $1\text{--}200 \text{ pmol}/\text{cm}^2$ . In this paper we describe in detail the design, fabrication and characterization of this integrated a-Si:H bio-detector.

#### 11:00 AM **A21.3**

**FABRICATION OF NOVEL TFT-LCD PANELS WITH A HIGH APERTURE RATIO USING a-SiCO:H FILMS AS A PASSIVATION LAYER.** W.S. Hong, Sejong University, Dept of Electronics Engineering, Seoul, KOREA; B.K. Hwang and G. Cerny, Dow Corning, Electronic Industry and Advanced Materials Business, Midland, MI; K.W. Jung, S.H. Yang, J.H. Choi, K.Chung, Samsung Electronics Co, AMLCD Division, Yongin-city, KOREA.

Fabrication of a novel TFT-LCD panel, using amorphous silicon oxycarbide (a-SiCO:H) films as a passivation layer, was successfully demonstrated for the first time. The a-SiCO:H low-k films having a dielectric constant between 2.7 and 3.5 and high transmittance in the range of visible light were successfully deposited using a standard PECVD (plasma-enhanced chemical vapor deposition) reactor from a gas mixture of trimethylsilane ( $\text{Si}(\text{CH}_3)_3\text{H}$ ) and  $\text{N}_2\text{O}$ . Structural analysis showed that the amount of  $(\text{CH}_3)$  radicals in the film had a direct influence on the dielectric constant, deposition rate, and hardness. Source gas mixing ratio ( $[\text{Si}(\text{CH}_3)_3\text{H}]/[\text{N}_2\text{O}]$ ) and other deposition parameters, such as plasma power and chamber pressure, were successfully controlled to obtain simultaneously a dielectric constant as low as 2.7 and a deposition rate as high as  $1.2 \mu\text{m}/\text{min}$ . The transfer characteristics of the TFT's having a-SiCO:H as a passivation layer was comparable with that of a conventional TFT with PECVD-grown  $\text{SiN}_x$  passivation layer. Stability of the resulting TFT was performed under prolonged bias conditions, and the source-drain current was fairly constant over the test period. Equivalent line capacitance ( $C_{eq}$ ), the cumulative capacitance contributed from all parasitic capacitance formed around the data (column) electrode, decreased with the passivation thickness of low-k a-SiCO:H film, as predicted by the capacitor equation ( $C \propto 1/d$ ). A thick ( $>2 \mu\text{m}$ ), low-k films were shown to be suitable for reducing the parasitic capacitance formed between vertically-spaced electrodes in

the pixel array structure, and thus making it possible to increase the aperture ratio. The cross-talk values were inversely proportional to the passivation thickness, implementing the coupling through the passivation layer to be the major cause. The LCD panel with the a-SiCO:H passivation layer showed 30% higher brightness than that of the standard panel.

#### 11:15 AM **A21.4**

**DIODE EDGE EFFECTS IN COMMON I-LAYER P-I-N a-Si:H PHOTODIODE ARRAYS.** Jeremy A. Theil, Semiconductor Product Group, Agilent Technologies, Santa Clara, CA.

Hydrogenated amorphous silicon photodiode arrays form the basis of monolithic three-dimensional integrated circuit sensor technology. In these arrays, the intrinsic a-Si:H layer covers the entire area to maximize light collection. One technique by which the pixel diode is defined, is to pattern the bottom contact layer independently of the intrinsic layer. One of the most important characteristics of any diode array, however, is that the dark-state leakage currents must be as low as possible to minimize diode noise. This study examines the leakage currents associated with the pixel edges in the array. These structures are unique in that the edge of the diode is defined by the local electric field between diodes, rather than the physical surface of an a-Si:H film. The effect of the diode edge has been found to induce a field-dependent component to the reverse bias leakage current. For  $5500 \text{ \AA}$  i-layer diodes, the junction leakage is  $45 \text{ pA}/\text{cm}^2$ , while the edge-dependent current component can be as high as  $0.045 \text{ pA}/\text{cm}$ , and may significantly contribute to overall diode leakage. In addition, it will be shown that the i-layer thickness plays a key role in the effect of the edge component. The effect of the field-induced component will be discussed in term of its ramifications for controlling reverse bias leakage current.

#### 11:30 AM **A21.5**

**IMPROVING NOISE PERFORMANCE OF FLAT PANEL IMAGERS USING PIXEL LEVEL AMPLIFIERS.** J.P. Lu, J. Ho, Y. Wang, K. Van Schuylenbergh, C.W. Shih, and R.A. Street, Palo Alto Research Center, Palo Alto, CA.

Flat panel imagers (FPIs) have become an important application in the arena of large area, thin film electronics aside flat panel displays. Conventional flat panel imagers, similar to most flat panel displays, are simple arrays of photo sensors connected to active matrix switching networks of amorphous Si Thin Film Transistors (TFTs). The recent development of high performance, excimer-laser annealed (ELA) poly-Si TFTs enables us to develop next generation FPIs that integrate more sophisticated circuits like gate line drivers, data line multiplexers, and pixel level pre-amplifiers. Pixel level pre-amplifiers are particularly interesting because they potentially enable a sensitivity that is fundamentally impossible with conventional FPIs. We previously reported on the successful implementation of imager prototypes with  $384 \times 256, 90 \times 90 \mu\text{m}^2$  square pixels in our ELA poly-Si TFT process. The prototypes included a source-follower pre-amplifier in every pixel. Adequate uniformity, linearity, and image quality was demonstrated. We also reported a measured noise level of  $1300 \text{ eRMS}$ , which is already comparable to some of the best commercially available, conventional FPIs. This paper reports on further improvements in the noise performance of these source-follower imagers. An improved read out process, based on the application of double correlated sampling at the level of the photo sensor, not only enables us to reduce the detrimental effect of the  $1/f$  noise found in the previous report, but also to subtract the noise related to the reset process, which is not possible with conventional FPIs. The reset-related noise is understood as the fundamental imager noise limit. We measure noise levels of around  $800 \text{ eRMS}$ , well below the typical levels of conventional large FPIs. The noise spectrum, source, and physical process of the individual noise components will also be discussed in detail.

#### 11:45 AM **A21.6**

**ENHANCED BLUE SENSITIVITY IN ITO/a-Si<sub>x</sub>:H/a-Si:H MIS PHOTODIODES.** S. Tao, Y. Vygranenko, A. Nathan, University of Waterloo, Dept of Electrical and Computer Engineering, Waterloo, CANADA.

We report an ITO/a-Si<sub>x</sub>:H/a-Si:H MIS photodiode with improved performance in terms of the dark current and its stability, and spectral response in the blue region. The a-Si:H and a-Si<sub>x</sub>:H thin film layers were deposited by PECVD on a glass substrate with patterned Mo back contact. The deposition of the polycrystalline ITO with a wide band gap ( $> 3.75 \text{ eV}$ ) was performed at room temperature by magnetron sputtering. SIMS (Secondary Ion Mass Spectrometer) measurements show that the ultra thin a-Si<sub>x</sub>:H film (a few nm) can effectively block the diffusion of oxygen from the ITO to the a-Si:H. In addition, the insulator layer provides a barrier for electrons, which serves to reduce the dark current. This is in contrast to the ITO/a-Si:H Schottky photodiode whose electrical and optical

performance is impaired by the large defect density at the interface due to oxygen diffusion from the ITO. At a reverse bias of 1 V, the dark current density of the MIS photodiode is as low as 4 nA/cm<sup>2</sup>. Spectral photoresponse measurements show a dramatically enhanced sensitivity in the UV/blue spectral region. A maximum quantum efficiency of 80% is achieved at a wavelength of 440 nm. The high quantum efficiency of the MIS photodiode can be attributed to reduction of both optical and recombination losses by virtue of the highly transparent polycrystalline ITO and the low defect density a-SiN<sub>x</sub>:H/a-Si:H interface.