Energy Frontiers Topical Conference
Room: Mesilla - Session EN+PS-MoM

Plasmas for Photovoltaics & Energy Applications
Moderator: B. Lane, TEL Technology Center America

8:20am **EN+PS-MoM1 Combinatorial Plasma CVD of Si Thin Films with a Multihollow Discharge Plasma CVD Reactor**, ***M. Shiratani***, *K. Koga, T. Matsunaga, Y. Kawashima, W. Nakamura, G. Uchida, N. Itagaki*, Kyushu University, Japan

A-Si and micro-crystalline thin films for solar cells are widely deposited by plasma CVD in industry. To realize combinatorial plasma CVD of such Si thin films, we have developed a multi-hollow discharge plasma CVD method, by which fluxes of H and SiH_3 as well as their flux ratio on the substrate placed perpendicular to the electrodes depend on the distance from the discharges [1-4]. Thus, we can simultaneously deposit Si thin films with various structures and properties. For 60 MHz discharges of H_2+SiH_4 (0.3%), no films were deposited just near the discharge regions due to Si etching by H, micro-crystalline films were deposited in a rather narrow area around the no film regions, and a-Si:H films were obtained in the rest wide area far from the discharges. The spatial distribution of film structures indicate that the density ratio of H to SiH_3 decreases sharply with increasing the distance from the discharges and the surface reaction probability of H is much higher than that of SiH_3, being consistent with the reported surface reaction probabilities [5, 6]. For 2-6 Torr, the micro-crystalline film structure such as crystalline volume fraction and grain size varies sharply not only along the direction perpendicular to the electrodes but also along the direction parallel to the electrodes. These results suggest that the micro-crystalline film structure is highly sensitive to spatial and temporal uniformity of fluxes of H and SiH_3 as well as their flux ratio.

[1] K. Koga, et al., Jpn. J. Appl. Phys. **44,** L1430 (2005).

[2] W. M. Nakamura, et al., IEEE Trans. Plasma Sci. **36**, 888 (2008).

[3] W. M. Nakamura, et al., J. Phys.: Conf. Series **100**, 082018 (2008).

[4] H. Sato, et al., J. Plasma Fusion Res. SERIES, **8**, 1435 (2009).

[5] A. Matsuda, et al., Surface Sci. **227**, 50 (1990).

[6] J. Perrin, et al., J. Vac. Sci. Technol. A, **16**, 278 (1998).

8:40am **EN+PS-MoM2 Infrared Solar Cells Using Plasma-Processed Carbon Nanotubes**, ***T. Kaneko***, *S. Kodama, Y. Li, R. Hatakeyama*, Tohoku University, Japan

Since the conventional silicon solar-cell conversion is limited to a certain window of solar cell photon energies over 1 eV, a full use of the solar spectrum is one of the crucial issues in order to greatly increase the solar cell efficiency. In this sense, carbon nanotubes (CNTs) are attracting much interest for photovoltaic energy conversion because of their broad absorption bands including the infrared range (0.2 ~ 1.3 eV) as well as other advantages such as large surface areas, high mobility of charge carrier, high mechanical strength, chemical stability, and so on. In this connection, we have developed a plasma-ion irradiation method, which enables pristine single-walled carbon nanotubes (SWNTs) to selectively encapsulate various kinds of atoms and molecules, such as metals and fullerenes, serving as electrons donors or acceptors inside their cavities. Then these enhanced p-type, n-type, and pn-junction housed semiconductor-SWNTs are applied toward the realization of high-efficient photovoltaic devices, which is composed of thin films of p- and n-types semiconductor SWNTs or an individual SWNT with p-n junction inside. Here, as a first step, electrical properties of p-n junctions fabricated using a combination of the thin films of pristine (empty) SWNT or C_{60}-encapsulated SWNT (C_{60}@SWNT), and n-doped Si (n-Si) are investigated.

The electrical properties of these SWNT film/n-Si devices show an obvious rectifying characteristic, and a short-circuit current I_{SC} and an open-circuit voltage V_{OC} through a downward shift of *I-V* curves are observed under illumination of light with wavelength of 1550 nm which corresponds to the photon energy of 0.8 eV. Moreover, it is found that the device fabricated with the C_{60}@SWNT film has a larger V_{OC} caused possibly by a large diffusion voltage in the interface of p-n junction compared with the device fabricated with the pristine SWNT film, due to the enhanced p-type behavior of SWNTs after C_{60} encapsulation. To investigate undesirable photovoltaic effects of n-Si, we fabricate a schottky barrier solar cell consisting of silver (Ag) and n-Si in the absence of SWNTs. It is confirmed that the Ag/n-Si schottky barrier solar cell generates photo currents in the visible range (1.5 ~ 3 eV), while there is almost no difference between with and without light in the infrared range (0.8 eV) because the light with photon energy less than 1 eV cannot be absorbed by Si.

Based on these results, high performance solar cells which work in the infrared region are for the first time demonstrated to be formed using SWNTs, especially p-type enhanced C_{60}@SWNT.

9:00am **EN+PS-MoM3 A Novel Method of Controlling Plasma Uniformity in a Large Area VHF Plasma Source for Solar Applications**, ***T. Tanaka***, *J. Kudela, E. Hammond, C. Boitnott, Z. Chen, J.A. Kenney, S. Rauf*, Applied Materials Inc. **INVITED**

Processing a large area substrate in a capacitively coupled plasma (CCP) reactor is becoming increasingly more difficult as the driving frequency required by the process is becoming higher and the size of the substrates is becoming larger. At the VHF (very high frequency) range the wave length of the driving signal is approaching the size of the substrate, and the resulting standing wave causes a severely non-uniform process. In this presentation, we will present a novel approach using magnetic boundary conditions in conjunction with phase modulation between multiple power feed points to improve process uniformity for a CCP reactor operating in the VHF range. The substrate size we consider is Gen 8.5 (2.2 m × 2.6 m substrate) and the VHF power applied to generate the plasma is 40 and 60 MHz. At 60 MHz, with the vacuum wavelength of 5 m, the size of the substrate is approximately ½ of the vacuum wavelength. An electromagnetic simulation with a pseudo plasma showed that, when 60 MHz is applied in a conventional manner, i.e. it is fed from the center of the back of one of the electrodes, it generates a dome shape electromagnetic field profile, which falls off sharply to almost zero at the voltage node before rising again towards the edges. A similar field pattern was also generated even when the VHF was fed from two feed points located at the opposing edges. The plasma distribution pattern measured with a 4 × 8 grid of optical emission spectroscopic (OES) probes revealed that the plasma was localized in the center when VHF the signal applied to the feed points were in phase. To modify the wave propagation pattern to change the shape of the standing wave in the central area, we placed ferrite material along two of the edges (edges that are away from the feed points) of the powered electrode. In this case, the peak in the central area was significantly stretched towards the ferrite-lined edges. We also found that the stretched “bar” of plasma could be moved over the substrate area by dynamically modifying the relative phase between the feed points in a manner similar to the technique employed by Yamakoshi *etal*. [1], and effectively distribute the processing plasma to much larger area.

[1] H.Yamakoshi *etal*. Appl. Phys. Lett. 88, 081502 (2006)

9:40am **EN+PS-MoM5 Novel Plasma Processing Routes of Si Nanocrystals for Photovoltaic Applications**, ***İ. Doğan***, *N.J. Kramer, MA. Verheijen,* Eindhoven University of Technology, Netherlands, *T.H. van der Loop,* University of Amsterdam, Netherlands, *A.H.M. Smets,* Eindhoven University of Technology, Netherlands, *T. Gregorkiewicz,* University of Amsterdam, Netherlands, *M.C.M. van de Sanden*, Eindhoven University of Technology, Netherlands

Photovoltaic applications have been developed mostly on silicon technology in order to generate electricity from solar energy by efficient conversion of solar spectrum. In this work, we have focused on the novel processing routes of Si nanocrystals (Si-NCs) in a remote expanding thermal plasma (ETP). Si-NCs were formed inside a SiH_4-Ar plasma by excessive heating of SiH_x clusters via electron and ion collisions. Formation routes of nanoparticles were investigated under different conditions by changing SiH_4 and Ar flow rates, deposition pressures and arc currents. The morphologies of the deposits were powder-like, consisting of densely packed crystalline particles and inter-space of amorphous Si. Due to the variations in plasma regions from center to side walls, the powder color and properties were different on the different parts of the deposited samples. The formation of nanoparticles on these parts was investigated by a number of diagnostic techniques. As a first exploration, transmission electron microscopy (TEM) and Raman spectroscopy (RS) measurements have been carried out. It was confirmed by both TEM and RS that the particle size and morphology was varying throughout the film. For most of the samples, nanoparticles seemed to be mixed in size but the general tendency is to have smaller size distributions from central part to the outer part of the films. Formation of crystalline structures was confirmed by X-Ray diffraction (XRD) with Si(111) peaks. It was also shown by photoluminescence spectroscopy (PL) that the optical emission was in the visible range and shifts with respect to size difference of Si-NCs. Size distribution as a function of PL emission energy has been demonstrated for particles less than 8nm. TEM was employed to investigate the size distribution of the larger particles which was around 50nm. The responsible mechanism in the plasma leading to a systematic change on the particle size was discussed by means of electron and ion density, and particle residence time. Getting a good control on the plasma conditions and particle size makes it possible for manipulating Si-NCs to higher packing densities in thin films which makes them suitable for photovoltaic devices such as down converters based on multi-exciton-generation (MEG).

10:00am **EN+PS-MoM6 Characterisation of Thin Film CdTe Multilayer Photovoltaic Devices Deposited by Closed Field Magnetron Sputtering**, *J.K. Bowers, S. Moh, A. Abbas, P.N. Rowley, H.M. Upadhyaya, **J.M. Walls***, Loughborough University, UK

A new magnetron sputtering strategy is introduced that utilises high plasma densities (~5mA.cm^{-2}) to avoid or reduce high temperature processing. The technique uses magnetrons of opposing magnetic polarity to create a “closed field” in which the plasma density is enhanced without the need for high applied voltages. A batch system has been used which employs a rotating vertical drum as the substrate carrier and a symmetrical array of four linear magnetrons. The magnetrons are fitted with target materials for each of the thin films required in the photovoltaic (PV) stack viz. CdTe absorber layer, CdS buffer layer, metal contact and the back transparent conducting oxide (TCO) contact using the superstrate configuration. The “closed field” sputtering technology allows scale up not only for larger batch system designs but it is also configurable for “in-line” or “roll to roll” formats for large scale production. The morphology of each of the layers is characterised together with the overall device performance.

10:40am **EN+PS-MoM8 Material Properties of Hydrogenated Nanocrystalline Silicon Thin Films by RF-PECVD using He-SiH_4 Mixture**, ***I.K. Kim**, J.H. Lim, K.N. Kim, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

Hydrogenated nanocrystalline silicon (nc-Si:H) and amorphous silicon thin film are expected to be promising

materials for solar cell and thin film transistor. Especially, nc-Si:H thin films have been reported to have

an enhanced stability due to its more rigid structure. These thin films are usually grown with

plasma enhanced chemical vapor deposition (PECVD) using silicon-containing gas mixtures such as SiH_4 and H_2.

To increase the photovoltaic efficiency and to improve the mobility of TFT devices, it is necessary to produce

nanocrystalline silicon films with higher crystallization percentages. But it is reported that high H_2. dilution leads to

a significantly lower deposition rate.

In this study, we investigated the influence of He mixture with SiH_4 gas instead of H_2 to improve the crystallization

percentage of the deposited silicon without significantly decreasing the deposition rate.

To find out properties of the thin film deposited with He/SiH_4 such as structural properties, crystalline volume fraction (Xc), active radicals in plasma, Si-H bonding characteristics, and conductivity, Scanning Electron Microscopy

(SEM), Raman spectroscopy, Optical Emission Spectroscopy (OES), Fourier-Transform-Infra-Red (FT-IR), and Keithley

measurement kit, were used respectively. The results showed the increase of crystallization percentage by using

He instead of H_2 as the additive gas and, with the increase of the applied RF power up to 140W, crystalline volume

fraction of about 80% could be observed.

11:00am **EN+PS-MoM9 Surface Composition and Gas-Phase Passivation of Plasma-Synthesized Si Nanoparticles**, ***B.N. Jariwala****, Colorado School of Mines, *N.J. Kramer*, Eindhoven University of Technology, Netherlands, *B.G. Lee, P. Stradins*, National Renewable Energy Laboratory, *M.C.M. van de Sanden*, Eindhoven University of Technology, Netherlands, *C.V. Ciobanu, S. Agarwal*, Colorado School of Mines

Tunable band gap of c-Si nanoparticles (NPs) (<5 nm) along with the possibility of multiple exciton generation has led to an increased interest in this form of Si as a material for 3rd generation photovoltaic (PV) devices. In addition to a high degree of control over the particle size, surface passivation of the NPs is key to their utilization in PV applications. In this presentation, we will primarily focus on understanding the growth of Si NPs in a dusty plasma, determining the surface composition of the NPs, and demonstrating novel techniques for passivation and encapsulation through the gas-phase. The particles are grown in a SiH_4/Ar plasma generated in a tubular flow rf discharge. The plasma source is attached to an in-house-built vacuum chamber equipped with *in situ* attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy and a quadrupole mass spectrometer. Using this technique, we have synthesized Si NPs in the size range of 3-7 nm, which transition from amorphous to crystalline over the rf power range of 5 to 40 W. The *in situ* IR data show that the surface hydride composition of the NPs is related to their crystallinity, which in turn depends on particle heating during synthesis. The as-synthesized NPs surfaces are terminated with Si mono-, di- and tri-hydrides. The higher hydride concentration decreases with increasing particle crystallinity, similar to previous observations on the amorphous Si surfaces, where higher Si hydrides are known to decompose with increasing deposition temperatures. These results also are consistent with the particle heating models proposed for dusty plasmas. In the first surface passivation approach, the as-synthesized H-terminated Si NPs, which oxidize even under high-vacuum conditions, are passivated *in situ* through hydrosilylation using 1-alkenes of different chain lengths. We have used density functional theory calculations to investigate the detailed reaction mechanism for various alkene chain lengths, and to understand the effects of alkene coverage on the oxidation of the surface. The surface reaction kinetics for hydrosilylation is observed *in situ* by monitoring the C-H and Si-H stretching vibrations. The ligand coverage is determined to be roughly 50% of the surface sites, which is sufficient to prevent oxidation for several hours. The quality of surface passivation is further determined through the photoluminescence quantum yield measurements, which show a higher yield for surface passivated NPs. In the second approach, the NPs are passivated with metal oxides using atomic layer deposition that involves the two different oxidation steps with O_3 and H_2O to achieve deposition at <200 °C.

11:20am **EN+PS-MoM10 Effects of Hole-Array-Electrode on the Characteristics of Radio Frequency Capacitively Coupled Plasma Sources for uc-Si Thin Film PECVD**, ***H.-J. Lee**, S.-S. Wi*, Pusan National University, Republic of Korea, *D. Kim, D. Hwang, W.S. Chang*, LG Electronics, Republic of Korea

In order to improve the productivity of thin film growth in rf capacitively coupled plasma based chemical vapor deposition system, modifications of electrode surface geometry has frequently been used. Array of holes in the shower head electrode is probably the most popular one. In this paper, using self-consistent fluid approximation with collisional sheath model, we have analyzed the effects of the hole array on the plasma characteristics in terms of plasma density, electron temperature, ion current density, sheath voltage and electron heating efficiency. It is shown that electron heating efficiency of the hole array electrode increases more than 10 % compared with that of flat electrodes. DC bias voltage at the substrate side increases with hole depth and pitch due to increase in surface area ratio between powered and substrate electrode. Peak electron density near throat region of the hole structure becomes more than 2 time higher than that of flat parallel electrode at the same voltage driving condition. It was experimentally verified that these variations of plasma properties is beneficial for high rate of Si thin film deposition

11:40am **EN+PS-MoM11 Arc Energy in Large Scale Magnetron Sputtering**, ***D. Carter**, H. Walde*, Advanced Energy Industries, Inc.

A detailed analysis of sputtering arcs on a large scale (3400 cm^2) magnetron source reveals some common trends related to energy absorbed in these events and the progression of current and voltage through their duration. Examination of these trends provides insight into the rapid release of arc energy and some of the practical limitations of the techniques used to minimize their impact on deposition processes. Two very different but equally important materials were studied, metallic aluminum and ceramic, aluminum-doped, zinc oxide. While the characteristics and behaviors of arcs from these two materials are generally similar, subtle distinctions in the evolution of current and voltage explain a significant difference in measured arc energies. These observations present factors for consideration regarding arc suppression and also raise the question of what is the minimum achievable arc energy. In an attempt to answer this fundamental question a stored energy model for a large scale magnetron system is proposed. Using practical assumptions for sheath capacitance and source inductance, minimum arc energy is calculated to serve as the ultimate goal for a next generation arc detection and suppression system.

***** Coburn & Winters Student Award Finalist

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