## Plasma Science and Technology
## Room: A8 - Session PS2+PV-MoM

### Plasma Processing for Photovoltaics
**Moderator:** T.A. Gessert, National Renewable Energy Laboratory

8:40am **PS2+PV-MoM2 Plasma Etching and Texturing of Multi-Crystalline for Silicon Solar Cells using Remote-Type Pin-To-Plate Dielectric Barrier Discharge**, ***J.B. Park***, *J.S. Oh, E.L. Gil, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

During the preparation of the wafers for the multi-crystalline silicon (mc-Si) solar cells, the mechanical saw damage induced during the slicing of mc-Si ingots into wafers needs to be removed by etching in addition to the texturing of the silicon surface for the increased light scattering. For the etching and texturing of the mc-Si substrates, isotropic wet processing by using alkaline or acid solution is generally applied, however, wet treatments are environmentally undesirable due to the large amount of chemicals used.

In this study, an atmospheric pressure plasma called “remote-type pin-to-plate DBD” was used for the application to the etching of the saw damage removal and texturing process of mc-Si to increase the processing rate by increasing the plasma density without damaging the substrate surface. Especially, the effect of additive gases such as $NF_3$ and $O_2$ to the $N_2$-based atmospheric pressure plasma on the etching and texturing characteristics of mc-Si was investigated.

The results showed that the addition of $NF_3$ up to 1 slm increased the mc-Si etch rate continuously by increasing the F radicals in the gas mixture. Furthermore, the addition of a certain amount of $O_2$ (400sccm) to the mixture of $N_2$(40 slm) /$NF_3$(1slm) increased the mc-Si etch rate further by showing the two times higher etch rate of mc-Si (749.6 nm/scan, 1meter/scan). Especially, the addition of $O_2$ to the $N_2$/$NF_3$ improved the surface morphology by increasing surface texturing and, by the addition of 600sccm $O_2$, the reflectance less than 20% could be obtained.

9:00am **PS2+PV-MoM3 Production of Crystalline Si Nanoparticles for Third Generation Photovoltaics using a Multi-Hollow Discharge Plasma CVD Method**, ***Y. Kawashima***, *H. Sato, K. Koga, M. Shiratani*, Kyushu University, Japan, *M. Kondo*, AIST, Japan

Novel solar cells employing multiple exciton generation (MEG) are attracting much attention as third generation solar cells of high efficiency above 20%. For the MEG, an energetic exciton is generated in a semiconductor nano-crystal by a high energy photon more than twice as large as the band gap of the nano-crystal. Subsequently, the energetic one produces another in the nano-crystal by the inverse Auger process [1]. An issue for realizing the MEG solar cells is production of size-controlled crystalline Si nanoparticles. We have produced crystalline Si nanoparticles of 1 nm in size using a multi-hollow discharge plasma CVD method [2]. For the multi-hollow discharge plasma CVD method, discharges are sustained in small hollows of 5 mm in diameter. Crystalline nanoparticles are nucleated and grow in the discharges of $SiH_4$+$H_2$ (>99.5%) and then they are transported to the downstream region by gas flow. Their size is limited up to a few nm in size due to a short gas residence time in hollows. Nanoparticles are collected by stainless mesh grids located at the downstream region. They are dispersed in methanol to measure their photoluminescence. The excitation laser wavelength is 244nm or 405nm. For 405nm light irradiation,the photoluminescence spectrum has a peak at 490nm (2.53eV), corresponding to the bandgap of the Si nanoparticles of 1 nm in size. For 244nm light irradiation, the spectrum has a 380nm (3.27eV) peak corresponding to recombination centers at their surface as well as a 484nm (2.56eV) peak corresponding to their bandgap. These experimental results demonstrate generation of excitons in the Si nanoparicles. Si nanoparticles produced may be applicable as a material for MEG solar cells. We also have measured absorption spectrum of Si nanoparticles dispersed in methanol. Si nanoparticles show stronger light absorption at the shorter wavelength (<250 nm). To realize MEG solar cells, fabricating nanoparticles of an optimaized size for MEG in large quantity is important.


[1] A.J.Nozik, Physica E **14**, (2002)115.

[2] T. Kakeya, Kazunori Koga, Masaharu Shiratani, Yukio Watanabe, Michio Kondo, The Solid Films, **506-507**, (2006)288.


9:20am **PS2+PV-MoM4 Novel Model-Based Sensor for Thin Film Deposition on Large Area Substrates**, *M. Klick*, Plasmetrex, Germany, ***L. Eichhorn***, *R. Rothe*, Plasmetrex

Large area plasma coating becomes more important with increasing diameter of semiconductor wafers and thin film Si solar cells. The layer characteristics as uniformity of films produced by capacitive RF plasmas depends on effects as the standing wave and skin effect.

A reduced plasma physical model in the novel sensor is used to describe special features of large area and capacitive RF plasmas. It involved dynamic electron effects by a fluid model for the plasma bulk and nonlinear mechanisms by a nonlinear sheath model - called it Nonlinear Extended Electron Dynamics (NEED).

It involves also the nonuniformity and nonlinearity of the plasma sheath in the front of the substrate electrode, large electrode area, and medium pressure. The model provides also the dependence of the Fourier spectrum of the local RF current on the plasma density and the electron collision rate. Only lower harmonics of the RF current can be observed at medium pressure (100 Pa – 1000 Pa). Depending on the amount of harmonics of the local RF current used, it can be utilized also to estimate important plasma parameters as the electron collision rate and the ratio of the excitation frequency to the resonance frequencies of the spatial modes is found to determine the nonuniformity caused by the standing wave. The skin depth can be estimated as well to show the influence on spatial distribution of the RF current.

The major advantage is the real time, robust, and non-intrusive characterization of large area plasmas. An additional feature is the easy calculation of the plasma sheath voltage distribution at the grounded counter electrode. Both is mandatory to understand and to control the deposition rate distribution in particular for large area RF plasmas. So cost-efficient virtual metrology can substitute partially the expensive and time intensive real metrology.

9:40am **PS2+PV-MoM5 Plasma Processing of Thin Silicon Films for Photovoltaic Applications**, ***A.H.M. Smets***, National Institute of Advanced Industrial Science and Technology, Japan and Eindhoven University of Technology, Netherlands, *M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands, *T. Matsui, M. Kondo*, National Institute of Advanced Industrial Science and Technology, Japan **INVITED**

Hydrogenated amorphous silicon (a-Si:H) and hydrogenated microcrystalline silicon (μc-Si:H) are thin film silicon phases which are generally deposited at low processing temperatures by means of plasma enhanced chemical vapour deposition (PECVD) using hydrogen diluted silane gas mixtures. The lattice of dense a-Si:H is best described by a vacancy rich network (1-2 %) which lacks any medium and long range order, whereas the lattice of μc-Si:H consists of crystalline silicon grains (few nm’s up to microns) imbedded in to an amorphous network or tissue. One hot application of these films is the integration in to thin silicon film photovoltaic devices. In comparison to a-Si:H phase, the μc-Si:H phase has the advantage of an enhanced spectral response in the red part of the solar spectrum and a better opto-electronic stability under illumination.

Since the deposition of the μc-Si:H phase under low processing temperatures (~160-250 $^oC$ ) is obtained by increasing the hydrogen dilution in a silane plasma, it is believed that additional flux of atomic hydrogen at the surface enhances crystalline relaxation of the silicon atoms in the lattice during growth.

With respect to photovoltaic applications of μc-Si:H, high quality material is classified as dense material without any significant post-deposition oxidation, as oxidation is linked to a reduction in the red response of the *p-i-n* solar device. This specific μc-Si:H phase has the following properties: 1) crystalline grains with a preferentially [220] oriented growth, 2) has no crystalline grain boundaries, as these internal surfaces have been identified as the location at which the unwelcome post-deposition oxidation occurs and 3) is deposited close to conditions in which the growth transfers from amorphous to microcrystalline.

In this contribution we will address in detail the material properties of μc-Si:H and its relation to its performance in solar cells, the growth mechanism of the μc-Si:H phase under plasma deposition conditions and the crucial role of the control of plasma processing in obtaining device grade material. Finally, we will discuss the upscaling of the deposition technology (high deposition rates over large areas), which is an important issue in substantially reducing the cost-price of thin silicon photovoltaic products. We will present the recently explored deposition regime at higher processing pressures (~5-25 Torr), which has a high potential to bring about this important breakthrough in the thin silicon film photovoltaic technology.

10:40am **PS2+PV-MoM8 Atomic Hydrogen Induced Defect Kinetics in Hydrogenated Amorphous Silicon: An In Situ Real Time Study**, ***M.C.M. van de Sanden**, F.J.J. Peeters,* Eindhoven University of Technology, The Netherlands, *J. Zheng,* Peking University, China, *I.M.P. Aarts,* ASML, The Netherlands, *A.C.R. Pipino,* Tanner Research, *W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

Near-IR Evanescent-Wave Cavity Ring-Down Spectroscopy (EW-CRDS) is applied to an a-Si:H thin film subjected to quantified H fluxes from an atomic H source in the range of $(0.4\text{-}2)\text{x}10^{14}$ $cm^{-2}s^{-1}$. To this end 20-80 nm a-Si:H films were grown on the Total Internal Reflection (TIR) surface of a folded miniature optical resonator by thermal decomposition of silane on a hot filament. Measurements are performed over a temperature range of 80 – 200 ºC. The observed changes in the optical loss during H dosing of a-Si:H are attributed to the creation and healing of sub-gap Dangling Bond (DB) defect states and were measured with a sensitivity of ~ $10^{-6}$ and a time resolution of 33 ms. The DB density is shown to increase during H dosing cycles and the DBs reversibly 'heal' when the H flux is terminated. The effect increases in magnitude with H flux and decreases with temperature. Through the use of polarizing optics the CRDS signal was split into s- and p-polarized components, which, combined with field calculations, revealed that H-induced DB formation is not limited to the surface of the film but progresses into the bulk with a penetration depth of ~10 nm. Due to their limited lifetime the created DB defects are identified as the result of H insertion into strained Si-Si bonds in the bulk material. Extensive kinetic modeling of this process is used to determine activation energies for the hydrogen-material interactions and DB formation in a-Si, which are of key importance in a-Si:H thin film solar cells. Moreover the implications of this study for Eley-Rideal type reactions on the surface and hydrogen exchange reactions in the bulk will be addressed.

11:00am **PS2+PV-MoM9 Hydrogen-dominated Plasma, Due to Silane Depletion, for Microcrystalline Silicon Deposition**, ***A.A. Howling**, R. Sobbia, Ch. Hollenstein*, EPFL Lausanne, Switzerland **INVITED**

Plasma conditions for microcrystalline silicon deposition generally require a high flux of atomic hydrogen, relative to $SiH_x$ radicals, on the growing film. The necessary dominant partial pressure of hydrogen in the plasma is conventionally obtained by hydrogen dilution of silane in the flow inlet. However, a hydrogen-dominated plasma environment can also be obtained due to plasma depletion of the silane in the gas mixture, even up to the limit of pure silane inlet flow, provided that the silane depletion is strong enough. At first sight, it may seem surprising that the composition of a strongly-depleted pure-silane plasma consists principally of molecular hydrogen, without significant contribution from the partial pressure of silane radicals. The aim here is to bring some physical understanding by means of a zero-dimensional, analytical plasma chemistry model. The model is appropriate for uniform, large-area showerhead reactors as shown by comparison with results of three-dimensional numerical simulations. The $SiH_x$ densities remain very low because of their rapid diffusion and surface reactivity, contributing to film growth which is the desired scenario for efficient silane utilization. Significant $SiH_x$ densities due to poor design of reactor and gas flow, on the other hand, would result in powder formation wasting silane. Conversely, hydrogen atoms are not deposited, but associate on the film surface and re-appear as molecular hydrogen in the plasma. Therefore, in the limit of extremely high silane depletion fraction (>99%), the silane density falls below the low $SiH_x$ densities, but only the H radical can eventually reach significant concentrations in the hydrogen-dominated plasma.

11:40am **PS2+PV-MoM11 Plasma Uniformity Measurements in a Scalable, Multi-Electrode, VHF/UHF Plasma Source**, ***D. O'Farrell**, A.R. Ellingboe, S. Linnane, C. Gaman*, Dublin City University, Ireland

The ability to deposit large area thin film amorphous silicon films using PECVD is of significant interest in a number of fields including photovoltaics and flat panel display. The desire to deposit larger area films faster has lead to a recent push towards the use of VHF/UHF frequencies which result in faster deposition rates but also result in significant film non-uniformities due to wavelength effects even over relatively small areas. Several methods have been employed in an attempt to overcome these non-uniformity issues but many barriers still exist when it comes to wide scale application. In this work a scalable, multi-electrode, VHF/UHF plasma source is described which aims to resolve these issues. Data is presented demonstrating plasma uniformity over the source for a series of powers, pressures and operating frequencies. Different operating regimes are discussed.

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