Monday Morning, October 25, 1999

Thin Films Division
Room 615 - Session TF-MoM

Fundamentals of PECVD

Moderator: M.C.M. van de Sanden, Eindhoven University of Technology

8:20am **TF-MoM1 Investigation of the Plasma Properties and Fluxes in a Hydrogenated Amorphous Carbon Deposition Process***, B.K. Kim,* ***T.A. Grotjohn,*** Michigan State University

The deposition process and conditions used for hydrogenated amorphous carbon (a-C:H) film deposition from acetylene, acetylene-helium, and acetylene-argon gas mixtures in a microwave ECR plasma reactor are studied. This paper quantifies the plasma discharge fluxes to the substrate based on experimental measurements and plasma discharge modeling. The film properties are also correlated to the plasma discharge conditions. The films are deposited on glass and silicon substrates which are placed on an rf biased (13.6 MHz) substrate holder located just at the exit of a multipolar, permanent magnet ECR plasma source operating at 2.45 GHz. The deposition parameters varied during this investigation included rf induced dc substrate bias voltage (-50 to -300 V), pressure (0.1-1.0 mTorr) and argon/acetylene (or helium/acetylene) gas flow ratio. The properties of the plasma discharge measured include electron temperature, ion saturation current, and residual gas composition. The films deposited with different gas mixtures, pressures and rf biases have substantially different properties including deposition rate, mass density, optical absorption coefficient, optical bandgap and hydrogen content. The use of lower pressures to obtain an increased ion-flux/neutral-flux ratio to the substrate was found to be critical for obtaining dense, low hydrogen content films from acetylene. The addition of argon and helium were found to substantially change the plasma discharge deposition conditions, as well as, influence the deposited film properties.

8:40am **TF-MoM2 Time-resolved Study of C@sub x@N@sub y@ Growth by Means of Fourier Transform Infrared Reflection Spectroscopy***,* ***A. de Graaf****, B. Schreur, M.C.M. van de Sanden, D.C. Schram,* Eindhoven University of Technology, The Netherlands

Fourier transform infrared (FTIR) reflection spectroscopy is used to study the composition of carbon nitride (C@sub x@N@sub y@) films in situ during the early stages of growth and during etching. The C@sub x@N@sub y@ films are deposited from a thermal Ar/N@sub 2@ plasma expanding through a graphite nozzle. The graphite is chemically etched leading to strong CN emission both at the nozzle exit and at the substrate level 65 cm downstream. The observation of C@sub 2@N@sub 2@ in the mass spectrometer gives further support to the idea that CN radicals are formed during deposition. In order to measure small reflection changes on a (sub)monolayer level and on a short enough time scale, a special substrate has been developed which enhances the IR absorption considerably at a specific wavelength. With this substrate the evolution of the different bonds (sp@super 1@, sp@super 2@ and sp@super 3@ C-N) in the film can be followed. The results show a relative increased absorption of the sp@super 1@ C-N bond during initial growth as compared to the absorption in the bulk material. This strongly suggests that CN radicals are indeed involved in the deposition. After film growth the absorption of sp@super 1@ C-N bonds decreases while the absorption of sp@super 2@ C-N bonds increases. Etching of the C@sub x@N@sub y@ films by an expanding Ar/N@sub 2@ or Ar/O@sub 2@ plasma also shows a different response in the absorption signal of sp@super 1@ C-N as compared to sp@super 2@ C-N. The optical constants of the material and growth rate are derived from an optical model and are correlated to in situ ellipsometry measurements performed simultaneously. Based on these findings a tentative growth model is presented. In a next step this model will be extended to describe deposition at different substrate temperatures and bias voltages.

9:00am **TF-MoM3 Surface Reactions of CH@sub x@ and SiH@sub x@ Radicals during Plasma Deposition of a-C:H and a-Si:H Films***,* ***A. von Keudell,*** Max-Planck-Institut für Plasmaphysik, Germany **INVITED**

The surface reactions of CH@sub x@ and SiH@sub x@ radicals as the dominant growth precursor during plasma deposition of amorphous hydrogenated carbon and silicon films are investigated by exposing a-C:H and a-Si:H film surfaces to low temperature plasma discharges or to quantified radical beams. The surface reactions are monitored in real time by using in-situ ellipsometry and in-situ infrared spectroscopy. The measurement of the surface reaction probability of various hydrocarbon radicals indicates that the reactivity of larger C@sub x>1@H@sub y@ radicals at the a-C:H surface is much higher than that of CH@sub y@ radicals. This has several consequences for the understanding of a-C:H film growth, which will be described in detail. The deposition of a-Si:H from silane discharges is assumed to be similar to the growth of a-C:H films since in both cases the dominant growth precursor is CH@sub 3@ or SiH@sub 3@, respectively. However, the dominant interaction mechanism of silyl radicals with a-Si:H surfaces, as identified by isotope labeling experiments, is very different to that of CH@sub 3@ radicals on a-C:H surfaces. Whereas methyl radicals can only adsorb at open bonds at the a-C:H film surface, silyl radicals are able to insert into strained bonds at the a-Si:H surface. A comparison of microscopic growth processes during a-C:H growth and a-Si:H growth will summarize this presentation.

9:40am **TF-MoM5 Quantitative Characterization of a Particle Beam Source for Atomic Hydrogen and Hydrocarbon Radicals for Thin Film Growth Studies***,* ***Th. Schwarz-Selinger****, A. von Keudell, W. Jacob,* Max-Planck-Institut für Plasmaphysik, Germany

Hydrocarbon radicals are the dominant neutral growth precursors for the deposition of amorphous hydrogenated carbon films (a-C:H). For the investigation of the growth mechanisms a particle beam source was developed, which is able to produce thermal beams of neutral hydrocarbon radicals. The radicals are produced in a resistively heated tungsten capillary by thermal dissociation at the hot walls of the capillary. The maximum temperature of the capillary, achievable is around 2600 K, which is sufficient to also produce atomic hydrogen from H@sub 2@ with a high yield. A rotatable (@+-@ 20°) quadrupole mass spectrometer in line of sight to the capillary exit was employed to study the emanating particle beam. This setup allows to identify the emitted species and their angular distribution and permits to quantify the emitted fluxes. For hydrogen the degree of dissociation and the total flux of atomic hydrogen as a function of temperature and gas flow is presented. With the same source methyl radicals are produced. Results are presented for the total amount of methyl radicals using different hydrocarbon source gases. First results of surface reactions of these radicals, investigated by monitoring the interaction of the particle beam with a-C:H film surfaces in real time by in-situ ellipsometry and in-situ infrared spectroscopy, complete this presentation.

10:00am **TF-MoM6 High Rate a-Si:H Growth Studied by in situ Ellipsometry***,* ***A.H.M. Smets****, B.A. Korevaar, W.M.M. Kessels, M.C.M. van de Sanden, D.C. Schram,* Eindhoven University of Technology, The Netherlands

In this contribution the results of in-situ HeNe rotating compensator ellipsometry measurements performed on hydrogenated amorphous silicon (a-Si:H) growth using an expanding thermal plasma are presented. This remote thermal plasma technique is developed as a promising tool for high deposition rate (10 nm/s) of a-Si:H on a roll to roll production line of low cost thin film solar cells on a flexible foil. The measurements can be simulated using an optical growth model consisting of a substrate layer, SiO@sub 2@ layer, intermediate layer, a-Si:H bulk layer and a top layer, corresponding to the surface roughness. Using this model the roughness evolution during deposition can be monitored. At deposition conditions at which "device quality" a-Si:H is grown the surface roughness is the smallest, indicating that roughness and material quality are related. The correlation between incorporation of SiH@sub 2@ complexes and the surface structure will be discussed. From the roughness evolution in time at various substrate temperatures the length scales which dominate the high rate a-Si:H growth can be deduced. The activation energy of the diffusion processes is also determined and its significance for the Matsuda-Perrin-Gallagher growth model will be discussed.

10:20am **TF-MoM7 Ab-initio Study of H Abstraction from Amorphous Silicon Surface By Hydrogen and silyl(SiH@sub 3@) Radicals: Implications for Stability of 3-center Bond Formation***,* ***A. Gupta****, H. Yang, G.N. Parsons,* North Carolina State University

Plasma deposition of amorphous and micro-crystalline silicon from silane/hydrogen gas mixtures is widely utilized in the manufacture of solar cells and in thin film transistors (TFT) required in the active matrix liquid crystal displays (AMLCD). A fundamental understanding of the surface reactions that may result in the removal of bonded H will be useful to further optimize the deposition process. The surface H may be abstracted by H or SiH@sub 3@ radicals to form H@sub 2@ or SiH@sub 4@ respectively leaving behind a dangling bond which provides an active site for chemisorption of SiH@sub n@ radicals. It has been proposed that the first step in a-Si deposition is the formation of a stable 3-center (Si-H-Si) bond by the SiH@sub 3@ radicals and the surface hydrogen groups but the energetics of this elementary step are unknown. We have used configuration interaction (CI) and density functional (DFT-BLYP) calculations to compare the abstraction of surface hydrogen by H as well as SiH@sub 3@ radicals. Our results indicate that the H radicals are more likely to abstract the surface H compared to the SiH@sub 3@ radicals. The activation energy for the former reaction was determined to be ~5.5 kcal/mol and the heat of reaction was ~-11 kcal/mol while the latter reaction had an activation energy ~9.4 kcal/mol and an energy change ~-6 kcal/mol. Thus we can conclude that the H radicals are more likely to abstract the hydrogen from the Si(111) surface as compared to SiH@sub 3@ radicals. The potential energy surface for the reaction of SiH@sub 3@ radicals with the surface H generated using the DFT method does not indicate the presence of a stable 3-center bond within the accuracy of the method. The activation energy using this method was ~6 kcal/mol and the reaction energy was ~-7 kcal/mol. These results indicate that long-standing models for surface and bulk bond structure development need to be re-examined and support the possibility of other reaction schemes viz. SiH@sub 3@ insertion into Si-Si bonds on the surface.

10:40am **TF-MoM8 Impact of Helium Dilution on Low-Temperature Silicon Depositions Using Electron Cyclotron Resonance and RF Plasma Sources***, **S.H. Bae**, Y.C. Lee, R.T. McGrath,* Pennsylvania State University

Low temperature silicon films have been prepared at 110° C using electron cyclotron resonance (ECR) plasma, ECR plasma plus RF substrate bias, and RF plasma only. As dilution media, both pure hydrogen and hydrogen mixed helium gases have been employed for these low-temperature depositions. In order to relate the plasmas to the properties of these low temperature Si films, in-situ optical emission spectrum (250 ~ 800 nm) for each plasma condition has been examined. Regardless of the presence of RF substrate bias during ECR plasma depositions, intensity of optical emission of ECR plasma much higher than that conventional RF plasma. In the ECR plasmas, the emission intensities of H radicals much stronger than those in RF plasma mode by two order of magnitude. In both H @sub 2@ and H@sub 2@ +He diluted RF plasmas, H @gamma@ (434 nm) and H @beta@ (486 nm) emissions are not noticeable for 0.6 second integration of optical spectrum while H @alpha@ (656 nm) line is observable in the RF plasma. Addition of He gas in ECR plasma results in strong He radical emission lines (389 nm and 502 nm); i.e., this indicates highly excited hydrogen plasma can be produced by the metastably excited He radicals. X-ray diffraction (XRD) analysis shows that low-temperature pure RF mode Si films do not have any crystallinity regardless of addition of He gas while the Si films prepared with ECR plasmas have high crystallinity. However, these high-crystallnity low-temperature ECR films are very porous and columnar. In terms of micro-etching effect due to hydrogen radicals in high-density plasmas, H @sub 2@+He dilution is more efficient than the case of H@sub 2@ dilution.

11:00am **TF-MoM9 Hydrogenated Amorphous Silicon Surface Growth Mechanism Characterized by Fourier Analysis of the Surface Topography***, **K.R. Bray**, A. Gupta, L. Smith, G.N. Parsons,* North Carolina State University

Hydrogenated amorphous silicon (a-Si:H) is widely used for the manufacture of solar cells and for thin film transistors (TFT) in active matrix liquid crystal displays (AMLCD). There have been many studies of the gas-phase reactions occurring in the plasma, but less is known of what takes place on the growing silicon surface. An increased understanding of its growth mechanism is desirable to optimize the quality of the a-Si:H films. Atomic force microscopy (AFM) was used to image the surface topography of PECVD deposited a-Si:H. Surface topography was compared for samples deposited over a wide range of temperatures (25° C - 350° C) and film thicknesses (20 - 2000 Å). The rms surface roughness has been used to characterize surface growth. During the initial 30 seconds of nucleation using 100 sccm of 2% SiH@sub 4@/He, the rms is between 1 - 4 nm. As the deposition continues from 1 to 5 minutes, the rms increases to between 13 and 28 nm. After film coalescence, the rms roughness reduces to between 1 and 4 nm. A Fourier analysis of the surface topography produces an index (i), which has been correlated with different surface growth mechanisms. The Fourier indices for these samples range from i = 3.8 to 4.8, and increase with temperature. These results indicate that surface diffusion (i = 4) is the primary smoothing mechanism during growth. But the deviation from 4 suggests that the actual mechanism is more complex than simple surface diffusion. A shift in i suggests that there is a change in the growth mechanism as the film coalesces. We will discuss correlations between the Fourier index and film quality as deduced from structure and electrical characterizations.

11:20am **TF-MoM10 Deposition of Silicon Oxide Films using a Remote Thermal Plasma***, M.C.M. van de Sanden, **M.F.A.M. van Hest**, D.C. Schram,* Eindhoven University of Technology, The Netherlands

A cascaded arc (p=0.1 â€“ 0.2 bar) has been used to generate a remote thermal argon plasma, which expands into a vacuum vessel (p=0.1 mbar). In this expanding thermal argon plasma oxygen is injected at the arc nozzle. Downstream HMDSO (hexamethyldisiloxane) is injected as a precursor. The cascaded arc as a plasma source has some big advantages in comparison to the more conventional techniques (i.e. CVD). The first advantage is that the deposition rate obtained is much higher with the use of the cascade arc (>100 nm/s) than with the use of conventional techniques (couple of nm/s). The second advantage is that the deposition rate does decrease with increasing substrate temperature. Therefore it is not necessary to heat the substrate to very high temperatures (>500°C) before the film can be deposited. The deposited films have been analysed using in situ ellipsometry, elastic recoil detection (ERD), and in situ Fourier transform infrared reflection absorption spectroscopy. Ellipsometry shows that the deposited films have good optical properties. FTIR absorption spectrosopy measurements as well as ERD measurements show that the deposited films contain carbon. To get a better understanding of the film growth, in situ FTIR reflection absorption spectroscopy measurements are done. The effect of post deposition plasma exposure is discussed. The gas phase of the depositing plasma has been analysed by means of mass spectrometry and gas phase FTIR absorption spectroscopy. These measurements show that in the gas phase new stable species (i.e. C@sub 2@H@sub 2@) are created.

11:40am **TF-MoM11 Dielectric Properties of Silicon Nitride Deposited by High Density Plasma Enhanced Chemical Vapor Deposition@footnote 1@***, **J.B.O. Caughman**, D.B. Beach, G.E. Jellison, W.L. Gardner,* Oak Ridge National Laboratory

The dielectric properties of silicon nitride films have been investigated. The films were deposited on silicon substrates at temperatures <400 degrees C by using a high density inductively coupled plasma source. The plasma source is operated at 13.56 MHz using a flat spiral coil. A nitrogen plasma is formed in the ionization region of the source and 100% silane is injected downstream. Properties of the films are determined by using 2-modulator generalized ellipsometry and FTIR. Growth rates vary from 20-45 nm/min, depending on the processing parameters. For nitrogen/silane gas flow ratios of 0.25 to 10.0, the refractive index of the films (at 350 nm) vary little and are around 1.82. The band gap ranges from 4.5 to 6.2 eV. The addition of hydrogen in the ionization region results in an increase in the refractive index and a reduction in the band gap. For nitrogen/silane ratios of 0.25 to 2.0, the refractive index varies from 2.18 to 1.95 and the band gap varies from 3.1 to 4.4 eV. In addition, the hydrogen content in the film actually decreases with the addition of the hydrogen in the ionization region. A mass spectrometer imbedded in the substrate is used to correlate film properties with processing parameters. It is believed that the addition of the hydrogen increases the reactivity of silane in the gas phase, and that the flux of atomic hydrogen at the surface helps to abstract hydrogen from the growing film. @FootnoteText@ @footnote 1@ORNL is managed by Lockheed Martin Energy Research Corp. for the U.S. Department of Energy under contract no. DE-AC05-96OR22464.

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