Thursday Morning, October 5, 2000

Plasma Science and Technology Room 310 - Session PS1+TF+SE-ThM

Fundamentals of Plasma Enhanced Chemical Vapor Deposition

Moderator: A. von Keudell, Max-Planck-Institut für Plasmaphysik

8:20am PS1+TF+SE-ThM1 Analysis of Pulsed O@sub 2@/TEOS Helicon Plasmas by Time-resolved Optical Spectroscopy, *A. Granier*, Institut des Materiaux de Nantes, France; *A. Rousseau*, Laboratoire de Physique des Gaz et des Plasmas, France; *L. Le Brizoual*, Institut des Materiaux de Nantes, France

The use of pulsed plasmas instead of continuous plasmas in Plasma Enhanced Chemical Vapor Deposition is known to improve film quality and adherence, due to the reduction of stress. Here, pulsed low pressure (2 mTorr) helicon oxygen/tetraethoxysilane (TEOS) plasmas are investigated by time-resolved optical emission spectroscopy in order to monitor the kinetics and lifetime of radical species in the plasma-off and plasma-on periods. The 300W rf power is 100% modulated and the duty cycle is varied from 1 to 500 Hz. The time behavior of Ar (750 nm), O (844 nm), H (486 nm), OH (306 nm) and CO (296 nm) emissions in the diffusion chamber are studied. The Ar line takes less than 100 microseconds to reach its equilibrium. The H. OH. O and CO intensities take significantly greater times to equilibrate due to the relatively long lifetime of their ground states, and it was necessary to go to a duty cycle of 1 Hz, including a 130 ms plasma-on time and a 860 ms plasma-off time to reach the stationary state. Under the plasma conditions investigated (a 2 mTorr pressure including a TEOS partial pressure of 0.2 mTorr) the OH, O, H intensities take about 1ms, 40ms and 80 ms, respectively to reach their equilibrium. In addition, their intensities normalized to the Argon line intensity increase from a value close to zero at the ignition time, which indicates that the excited states of OH, O, H radicals are created by electron impact excitation on their ground-states and that these radicals have completely disappeared after 860 ms. In contrast, the normalized CO intensity increases from almost zero but has not yet reached its equilibrium after 130 ms, which is consistent with the fact that CO is a stable molecule which is lost by convection to the pump. Additional results obtained in pure oxygen plasmas are also presented and compared to those obtained in O@sub 2@/TEOS plasma.

8:40am PS1+TF+SE-ThM2 Aluminum Oxide Deposition in an Ionized PVD System, N. L¹, D.N. Ruzic, University of Illinios, Urbana-Champaign; A. Paranjpe, CVC Inc.; J.E. Norman, J.P. Allain, University of Illinios, Urbana-Champaign

An Aluminum target of a planar magnetron system is powered by a pulsed DC plasma generator to deposit AlOx film using a mixture of Ar and O2. Compared with the conventional sputtering magnetron system, the pulsed directed current (DC) bias is able to discharge the accumulated ions on the insulating AlOx film surface effectively during the positive duty cycle. The chamber also contains a secondary radio-frequency (RF) plasma source to ionize the sputtered metal neutral flux, and generate oxygen atoms and radicals. The directionality of the ion flux can be important for high aspect ratio features. The deposition rates of AI and AIOx films as a function of O2 partial pressure vs. Ar are examined with and without the RF plasma. The deposition rate of AlOx with 400 Watts RF is actually much higher than the deposition rate of Al without the RF at the same total pressure of 25mTorr. Hysterisis curves showing the transition point from metallic mode to poison mode at a certain partial pressure are presented. The presence of a secondary plasma producing ionization makes the metallic sputtering mode possible at a higher O2 partial pressure. A gridded energy analyzer and a guartz crystal microbalance (QCM) are embedded in the substrate plane to allow the ion and neutral deposition rates to be determined. Electron density and electron temperature changes caused by the RF power are measured by a Langmuir Probe. SEM photos of deposited films show differences in film quality as a function of RF power.

9:00am PS1+TF+SE-ThM3 Surface Transport Kinetics in Plasma Deposition of Hydrogenated Amorphous Silicon, K.R. Bray, A. Gupta, G.N. Parsons, North Carolina State University

The concept of dynamic scaling was developed to help understand the role of kinetic phenomena that occur on surfaces during non-equilibrium processes (such as film deposition). Plasma deposition of a-Si:H is particularly intriguing because it is well known that over a wide

temperature range, kinetic growth process results in very smooth (nonrandom) surface texture indicating significant surface species transport, but the growth rate is not thermally activated. We have used rf plasma deposition to form a-Si:H films with both helium and argon diluted silane, and used dimensional and frequency analyses to analyze surface topography obtained from AFM images. Surface fractal scaling parameters, including static (a) and dynamic (b) scaling coefficients, Fourier index, saturation roughness, and lateral correlation length (Lc), were determined as a function of film thickness and temperature. After film coalescence (15-20 s) the scaling coefficients are consistent with the surface topology being described as a self-similar structure; a is constant with growth time and is ~1.0, b is ~4.0, and the saturation roughness value increases exponentially with time as tb/a. Based on Herring's models of surface transport, the scaling coefficient values are consistent with surface smoothening being driven by diffusion. In this picture, the lateral correlation length can be equated with the surface diffusion length. We find that Lc ranges from ~50 to 200nm, and is thermally activated, corresponding to a diffusion activation energy of ~0.2eV. This result has important implications for current growth models, where diffusion length is proposed to decrease with increasing temperature because of increasing density of diffusionterminating dangling bond sites. Possible modifications to current models, consistent with our observed data, will be discussed and presented.

9:20am **PS1+TF+SE-ThM4 Hydrogenated Amorphous Silicon Fractal Growth and its Relation to the Growth Mechanism**, *A.H.M. Smets*, Eindhoven University of Technology, The Netherlands; *D.C. Schram*, Eindhoven University of Technology, The Netherlands, Netherlands; *M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

The roughness evolution of the anorphous hydrogenated amorphous silicon (a-Si:H) growth has been studied using in situ HeNe ellipsometry. The a-Si:H depositions are performed using expanding thermal plasma (ETP) deposition technique. With the ETP technique it is possible to grow a-Si:H under dominantly SiH@sub 3@ flux conditions with growth rates ranging over two orders magnitude (1-100 Å/s). The roughness evolution can be divided in an initial growth phase corresponding to a nucleation phase followed by a post initial phase in which the a-Si: H bulk is grown. The post initial growth phase can be described following the universal scaling law, i.e. the roughness scales as t@super beta@ where t is the time and @beta@ the dynamic scaling exponent which depends on the surface relaxation mechanism. The measured scaling exponent @beta@ for growth rates equal or smaller than 22 Å/s is temperature dependent and drops from 0.5 at 100 Celsius down to 0.06 at 500 Celsius. A simple solid on solid (SOS) model is introduced, based upon an activated site at which growth can occur and which can diffuse with a site dependent surface diffusion. With this model the temperature dependent @beta@ can be simulated and the activation energy of the diffusion mechanism can be deduced without the knowledge which process is really responsible for the surface relaxation. The obtained activation energy is equal to ~ 1.0 eV on a terrace site, much higher then what would be expected from physisorbed SiH@sub 3@ dominated a-Si:H growth. At higher growth rates (70 Å/s) the @beta@ shows a maximum around 300 C Celsius. The obtained @beta@ at low temperatures and high deposition rates corresponds to a phase in which the roughness evolution tends more to ballistic fractal growth. Possible relaxation mechanism to explain the high diffusion activation energy will be discussed.

9:40am PS1+TF+SE-ThM5 Interactions of Chemically Reactive Radicals with Si Growth Surfaces during Plasma Deposition of Si Thin Films, S. Sriraman, University of California, Santa Barbara, U.S.A; S. Ramalingam, E.S. Aydil, D. Maroudas, University of California, Santa Barbara

Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasma deposition from SiH@sub 4@ containing discharges are widely used in photovoltaic and flat-panel display technologies. The structural quality and electronic properties of the deposited films depend on the identities and fluxes of chemically reactive species that originate in the plasma and impinge on the growth surface. Atomic-scale simulations of radical-surface interactions are of utmost importance in understanding the fundamental mechanisms of the deposition process. In this presentation, moleculardynamics (MD) simulations of radical-surface interactions during deposition of a-Si:H from chemically reactive radicals, SiH and SiH@sub 2@, are analyzed. The simulations reveal a broad class of reaction mechanisms and predict surface reaction probabilities that are in good agreement with experimental measurements. The growth of a-Si:H films starting from an initial H-terminated dimerized Si(001) surface is studied through MD simulations of repeated impingement of the individual radical precursors. Special emphasis is placed on the identification of the

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elementary surface chemical reactions that govern the deposition process. Effects of the reactions on the growth surface are examined by analyzing local structural configurations and surface chemical reactivity in the vicinity of the surface reaction sites. Evolution of the films' structure, surface morphology and roughness, surface reactivity, and surface composition are analyzed in detail and comparisons made with similar films deposited from individual SiH@sub 3@ precursor. The resulting surface hydride compositions in the deposited films are compared with experimental data. The comparisons are used to discuss our current understanding of the deposition process and implications for plasma deposition of a-Si:H.

10:00am PS1+TF+SE-ThM6 SiH@sub x@ Radical Densities in a Remote SiH@sub 4@ Plasma for High Rate Deposition of a-Si:H, W.M.M. Kessels,

J.P.M. Hoefnagels, M.G.H. Boogaarts, Eindhoven University of Technology, The Netherlands; D.C. Schram, Eindhoven University of Technology, The Netherlands, Netherlands; M.C.M. van de Sanden, Eindhoven University of Technology, The Netherlands

The ground state densities of SiH@sub x@ radicals in a remote Ar-H@sub 2@-SiH@sub 4@ plasma used for high rate deposition of device quality a-Si:H (up to 100 Å/s) have been investigated in detail by cavity ring down absorption spectroscopy (CDRS) and threshold ionization mass spectrometry (TIMS). SiH@sub 3@ has been measured by CRDS using the broadband à @super 2@A@sub 1@ <- @td X@ @super 2@A@sub 1@ absorption peak at 200 - 260 nm and revealed very good agreement with the TIMS measurements on SiH@sub 3@. SiH@sub 2@ has been measured by TIMS and SiH and Si by CRDS on the transitions A @super 2@@DELTA@ <- X @super 2@@PI@ (~414 nm) and 3p4s <- 3p@super 2@ (~251 nm), respectively. The generation and loss processes for the silane radicals have been investigated thoroughly for different plasma conditions and the contribution of the radicals to film growth has been determined. It is shown that for optimum a-Si:H film properties, the contribution of SiH@sub 3@ is approximately 90%, of SiH@sub 2@ is smaller than 5%, of SiH is ~2%, and of Si is 0.2%. For these conditions, the spatially resolved axial and radial SiH@sub 3@ densities in the plasma are compared with 2-D axisymmetric fluid dynamics model calculations using Phoenics CVD, in which the basic gas phase and surface reactions are taken into account. Furthermore, the first time-resolved silane radical measurements in a modulated rf biased plasma for the determination of the radicals' surface reaction probability will be presented.

10:20am PS1+TF+SE-ThM7 Fundamentals of Plasma Enhanced Chemical Vapor Deposition, J. Meichsner, Ernst-Moritz-Arndt-University Greifswald, Germany INVITED

Applications of non-isothermal plasmas for chemical vapor deposition and plasma surface modification imply the understanding of the fundamental problem: the plasma-surface interaction. From the plasma physics point of view the transition between the gas plasma and the solid state is characterized by the plasma sheath in front of the surface which controls the flux and kinetic energy of the charged particles. Additionally, in a reactive molecular plasma the complex chemical reactions must be taken into account in the gas phase and at surfaces. Depending on nature of molecular gases, surface material and plasma properties the modification of a thin surface layer, etching or thin film deposition may be found simultaneously on electrodes, immersed samples or surrounding walls. Insitu diagnostic tools are preferably qualified to provide detailed information about processes in the gas plasma and at surfaces. The experimental investigations involved plasma diagnostics by means of optical spectroscopy (OES, LIF) and mass spectrometry (energy selective ion analysis, electron attachment mass spectrometry) as well as surface and thin film characterization using special methods of FTIR-spectroscopy (IRRAS, ATR, fiber based), ellipsometry and microgravimetry. In a low pressure rf-discharge of Hexamethyldisiloxane the chemical conversion of the monomer gas into new stable gas molecules and deposition of a thin organic film were investigated in dependence on characteristic process parameters. The changed atomic composition and molecular structure of the organic films were connected with varied film properties interesting for semipermeable membranes, photo-conducting films, optical or protective coatings. In fluorocarbon plasmas the investigation of the Polyethylene and Polystyrene surface modification as well as thin film deposition revealed the dynamics between incorporation of atoms/molecules and etching of surface material.

11:00am PS1+TF+SE-ThM9 Thin Film Growth via Surface Reactions of CH@sub 3@, C@sub 2@H@sub 2@ and H as Investigated by Radical Beam Experiments, *M. Meier*¹, *A. von Keudell*, Max-Planck-Institut für Plasmaphysik, Germany

The knowledge about surface reactions of hydrocarbon radicals is a key element for the understanding of thin film growth in low temperature plasmas using hydrocarbons as precursor gas. Besides the formation of hard coatings by using an additional ion bombardment during growth, it is possible to deposit polycrystalline diamond at elevated substrate temperature from a methane discharge diluted in 99 % hydrogen. The dominant species which are believed to be responsible for diamond formation are atomic hydrogen together with either CH@sub 3@ or C@sub 2@H@sub 2@. In our experiment, we employ particle sources for the production of quantified beams of the radicals CH@sub 3@ and H and for C@sub 2@H@sub 2@ molecules to study the interaction of these species with a hydrocarbon film surface. The emitted fluxes of these beam sources are quantified by using angular resolved ionization threshold mass spectrometry. Recently it has been shown that the sticking coefficient of CH@sub 3@ increases from 10@super -4@ to 10@super -2@ if atomic hydrogen reacts simultaneously with the growing film surface at a low substrate temperature of 320 K. A similar experiment using C@sub 2@H@sub 2@ and H revealed no significant growth via C@sub 2@H@sub 2@ adsorption at the film surface. The variation in the film composition during the synergistic growth is monitored via in situ real time infrared spectroscopy. From the interpretation of these spectra a growth synergism for the simultaneous interaction of CH@sub 3@ and C@sub 2@H radicals with the film surface is observed. This demonstrates that the various synergisms between the growth precursors have to be taken into account for a consistent description of thin film growth via radical adsorption.

11:20am PS1+TF+SE-ThM10 Deposition Kinetics in Methane rf Glow Discharges: A Combined Experimental and Modeling Study, J.R. Doyle, D. Cole, B. Magocsi, Macalester College

Methane rf glow discharges are commonly used for diamond-like carbon deposition, but in spite of many experimental and theoretical studies, the details of the plasma chemistry, and in particular the identity of the dominant film precursors, are still debated. In this work we present a comprehensive model of the film deposition using a "semi-empirical" approach. Optical emission measurements and measured electrical properties of the discharge are combined with a Particle-in-Cell/Monte Carlo (PICMC) simulation, which is then used to calculate ion and neutral radical production rates and profiles. Diffusion-reaction-drift (fluid) equations are then solved for stable gas production and ion and radical transport to the electrode surfaces. The model is corroborated by mass spectrometry measurements of the stable gas partial pressures. Film growth rates are calculated from the model and are compared to measured growth rates as a function of pressure and power on both the grounded and powered electrode. The results suggest that C@sub n@H@sub m@ radicals and ions with n > 1 are the dominant sources of mass deposition under conditions used to produce diamond-like films.

11:40am PS1+TF+SE-ThM11 Using Plasma Energetics to Influence Silicon Nitride Step Coverage, K.L. Seaward, Agilent Technologies; M.L. Jezl, University of Wisconsin, Madison

PECVD silicon nitride is widely used in the fabrication of electronic and optical devices, integrated circuits, and display devices. An important characteristic of PECVD silicon nitride is step coverage, which describes how well the deposition conforms to features that are being coated. Both high and low step coverage are technologically important. In the present work, we investigate altering the plasma energetics to change the amount of PECVD silicon nitride deposited on the underside of structures. Models that predict such step coverage suggest that the precursor sticking coefficient is the dominant factor. Accordingly, different inert gases were added to the deposition plasma to either increase or decrease sticking coefficients by way of increasing or decreasing the plasma electron energy. Depositions were run with 4% ammonia, 1% silane, and 95% He, Ar, Xe, or N@sub 2@. Deposited films were characterized by etch rate, stress, FTIR, Auger, and SEM. Deposition plasmas were characterized by optical emission and rf tuning parameters. The only characteristic related to step coverage was the ratio of N-H bonds to Si-H bonds in the films. Since PECVD silicon nitride films have between 10% and 30% hydrogen content, it is expected that hydrogen plays a large role in film properties. What appears to happen for step coverage is a change in bonding configuration from nitrogen being primarily three-fold coordinated to silicon (high step

¹ PSTD Coburn-Winters Student Award Finalist

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coverage) to nitrogen being primarily two-fold coordinated to silicon with the third bond being to hydrogen (low step coverage). This latter material, called silicon diimide, is a chemical analog of SiO@sub2@ which, when plasma-deposited with silane, also has low step coverage. This analogy with SiO@sub2@ deposition suggests that precursor sticking coefficients are high during formation of silicon diimide, and this occurred most prominently with mixtures of He and N@sub2@ present in the plasma.

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