Thin Films
Room 303C - Session TF-ThM
Modeling & Fundamentals in Thin Film Deposition

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

8:20am **TF-ThM1 Evolution of Surface Morphology during Thin Film Growth by Hot-Wire CVD: Short-Range Smoothening and Long-Range Roughening**, ***B.A. Sperling***, *J.R. Abelson,* University of Illinois at Urbana-Champaign

During thin film growth by low-pressure chemical vapor deposition, the surface morphology evolves due to a kinetic competition between roughening, driven by self-shadowing or stochastic processes, and smoothening due to surface diffusion. When a very smooth substrate is used, the surface roughness increases only very slowly. A more powerful way to study the surface dynamics is to prepare a substrate with an intentional roughness of ~ 5 nm, then deposit film under "high quality" conditions that favor smoothness, and measure the rapid decrease in surface roughness with increasing film thickness. We use this procedure to study the growth of hydrogenated amorphous silicon by hot-wire chemical vapor deposition. Using in situ spectroscopic ellipsometry, we observe that the surface roughness of the film decreases as it grows. However, post-deposition atomic force microscopy reveals a linear increase in the roughness. We resolve this apparent discrepancy by analyzing the power spectrum densities of the atomic force images, which indicate that the growth surface is experiencing both short-range smoothening and long-range (global) roughening. The ellipsometry data agree semi-quantitatively with the short-range atomic force microscopy data, but due to light scattering they exclude information about the long-range components of roughness. The slope of the power spectrum density (short-range scaling) indicates that surface diffusion is the dominant smoothening mechanism, while the linear increase in roughness is consistent with columnar growth caused by self-shadowing. We also discuss possible means to interpret the rate of smoothening data in terms of the adspecies surface diffusivity during hot-wire chemical vapor deposition.

8:40am **TF-ThM2 Atomic-Scale Analysis of SiH@sub 3@ and H Surface Diffusion on Plasma-Deposited Amorphous Silicon Thin Films**, *M.S. Valipa,* University of California, Santa Barbara*; T. Bakos,* University of Massachusetts, Amherst, usa*; E.S. Aydil,* University of California Santa Barbara*;* ***D. Maroudas***, University of Massachusetts, Amherst

Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasma-assisted deposition from silane-containing discharges are used widely in the fabrication of solar cells and flat panel displays. Film properties, such as surface roughness and film crystallinity, depend on the mobility of reactive species that impinge on the film surface during deposition. Surface transport of SiH@sub 3@ radicals and H atoms is particularly important in determining film smoothness and affecting film crystallinity, respectively. This presentation focuses on detailed atomic-scale analysis of diffusion of SiH@sub 3@ and H on the a-Si:H surface. Using molecular-dynamics (MD) simulations of repeated impingement of SiH@sub 3@ radicals on the growth surface, we modeled the deposition of a-Si:H films on crystalline Si (c-Si) substrates. MD-grown a-Si:H film surfaces were found to be remarkably smooth due to valley-filling mechanisms mediated by diffusion of SiH@sub 3@, the mobile precursor, and resulting in passivation of dangling bonds present in surface valleys or at valley edges. Surface migration of SiH@sub 3@ is driven by the Si-Si bond strain distribution on the surface, which is strongly coupled with the surface morphology and reactivity. In addition, exposure of MD-grown a-Si:H films to H atoms from an H@sub 2@ plasma leads to formation of nanocrystalline regions in the films. Analysis of MD trajectories revealed that H atoms diffuse on the a-Si:H surface and into the bulk film and insert into strained Si-Si bonds; this leads to local structural relaxation and triggers disorder-to-order transitions. We also report results of first-principles density functional theory (DFT) calculations performed using c-Si surfaces as representative models of atomic bonding at film growth surfaces. The DFT results are consistent with the mechanisms of SiH@sub 3@ and H transport identified by the MD simulations and provide quantitative predictions of the migration energetics.

9:00am **TF-ThM3 Substrate Temperature Dependence of the Roughness Evolution of Hot-wire Deposited a-Si:H Studied by Real-Time Spectroscopic Ellipsometry and Atomic Force Microscopy**, ***W.M.M. Kessels***, *J.P.M. Hoefnagels, E. Langereis, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

The growth process of hydrogenated amorphous silicon (a-Si:H) by hot-wire CVD is studied by analyzing the surface roughness evolution during film growth for different substrate temperatures. This analysis gives information on aspects such as nucleation and initial film growth, surface roughening and smoothening, and surface diffusion mechanisms. Purely amorphous films have therefore been deposited at low deposition rates while monitoring the growth by real time spectroscopic ellipsometry for temperatures between 70 and 450 @degree@C. The thickness of the surface roughness is deduced from a two-layer optical model and analyzed as a function of the film thickness. Furthermore, the surface roughness of the as-deposited films has also been analyzed by atomic force microscopy (AFM) yielding information about the lateral scaling of the roughness. The initial film roughness is identical for all substrate temperatures indicating a similar nucleation behavior at the different temperatures. The position of the amorphous-to-amorphous roughening transition is observed within the film thickness range of 10-20 nm while an optimum is found for 250 @degree@C. The final surface roughness at a film thickness of 200 nm decreases up to substrate temperatures of 250 @degree@C after which the surface roughness remains fairly constant. The growth exponent @beta@ deduced from the roughness evolution as a function of deposition time, however, decreases for increasing temperature from ~0.20 at 70 @degree@C to ~0.05 at 450 @degree@C in agreement with the temperature dependence of the roughness exponent @alpha@ deduced from the AFM measurements. This suggests a thermally activated surface diffusion mechanism which will be discussed in detail and the relation between the surface roughness evolution and the a-Si:H film properties will be addressed.

9:20am **TF-ThM4 A Self-Consistent Prediction of a Deposition of Cu Sputtered in a rf Magnetron Plasma**, ***T.Y. Yagisawa***, *T.M. Mine, S.K. Kuroiwa, T.M. Makabe,* Keio University, Japan

Magnetron sputtering has been widely used for thin film deposition in material processing. Radio frequency magnetron is practically employed in the field of dielectric material sputtering in addition to metal targets. In the rf magnetron sputtering system, neutral transport sputtered from a target is of first importance to deposit uniform film. In this paper, we have performed a self-consistent prediction of an rf magnetron plasma structure, velocity of ions impinging a target surface and its erosion profile, ejection neutral atom from the target, and neutral transport to the substrate by using a hybrid model consisting of PIC/MC model of electrons, RCT model of ions and MCS of sputtered neutrals. Typical example is shown in an rf sputtering of Cu target at 13.56 MHz in Ar at 5 mTorr. It is found that rf magnetron at low power supply is maintained mainly by the electron multiplication at the region where ExB is maximum, and auxiliary by the secondary electrons from the target in the region with ExB=0. The latter mechanism which is completely different from the dc magnetron sputtering will become dominant with increasing the dissipated power. Ion velocity distribution at the target surface shows a strong anisotropy due to low pressure and radial dependence. Flux and velocity distribution of sputtered neutrals incident on the substrate surface will be shown and discussed.

9:40am **TF-ThM5 Effects of Steering and Shadowing in Epitaxial Growth**, ***J.G. Amar,*** University of Toledo **INVITED**

While shadowing has been known to play a role in some thin-film deposition processes, until recently it has been assumed that in epitaxial growth the effects of steering and shadowing are negligible. Here we present theoretical and molecular dynamics results describing the effects of steering due to both the short-range and the long-range van der Waals attraction on metal (100) and (111) epitaxial growth. Our results lead to a general picture of the process of deposition near step-edges@footnote 1,@@footnote 2@ which is quite different from the standard downward funneling picture. In particular, we find that short-range attraction plays an important role both after as well as before collision with the step. As a result, it can significantly enhance the uphill current, selected mound angle, and surface roughness for typical energies used in epitaxial growth. For the case of deposition on metal (111) surfaces we also find a significant asymmetry between the interaction at A and B steps which may be explained by differences in the step geometry. We have also calculated the van der Waals constant describing the long-range interaction between a Cu

atom and a Cu(100) surface. Our result is large enough to explain recent observations@footnote 3@ of a significant increase in mound angle in Cu/Cu(100) growth for large angles of incidence (@theta@ > 50 °) and also indicates that for smaller angles of incidence the dominant effects are due to the short-range rather than to the long-range interaction. Finally, we discuss the effects of shadowing in oblique incidence epitaxial growth and its implications for the formation and control of nanoscale patterning during growth. @FootnoteText@ @footnote 1@ J. Yu and J.G. Amar, Phys. Rev. Lett. 89, 286103 (2002).@footnote 2@ J. Yu and J.G. Amar, Phys. Rev. B 69, 045426 (2004)@footnote 3@ S. van Dijken et al, Phys. Rev. B 61, 14047 (2000).

10:20am **TF-ThM7 Inhomogeneous Transport of Energetic and Thermalized Neutrals in a Magnetron Sputter System***, **F.J. Jimenez,*** University of Alberta, Canada*; S. Leonard,* Matrikon, Canada*; P. Beatty, S. Dew,* University of Alberta, Canada

Thermalization of energetic neutrals in a typical magnetron sputter deposition system occurs as energetic particles collide with background gas atoms. Most of these energetic neutrals are created at the cathode as a result of positive ions striking the target and causing sputter ejection/reflection. After a few collisions these energetic neutrals are greatly slowed until they reach thermal energies and their transport is believed to be governed by diffusion phenomena. This effect is responsible for reducing the energy of incoming particles to the substrate which in turn affects the characteristics of the film being deposited. It is known that island formation and coalescence stages of film growth strongly depend on temperature, angle of incidence and energy of neutrals. A coupled model that approximates transport of the thermalized particles in a typical magnetron sputter chamber is presented. The thermalized model follows a fluid approach to predict steady state spatial distributions of thermalized particles as a function of space. Transport equations are solved in a three dimensional space with a nonuniform grid and anisotropic transport coefficients. Particle diffusion is coupled with a temperature solver to consider the impact of gas heating. Shadowing effects due to the rather complex geometry of a common magnetron chamber are also taken into consideration in the model. Transport of energetic reflected neutrals and sputtered atoms from the target is simulated with a MonteCarlo approach which includes the gas rarefaction and heating effects. A study of the effect that power has on the steady state temperature of the gas is included. The simulation is performed assuming a typical aluminum deposition in an argon environment at constant voltage and pressure. Steady state temperature profiles and particle distributions in the whole chamber are presented indicating a clear temperature dependence on power as previous works have reported.

10:40am **TF-ThM8 A Target Material Pathways Model for High Power Pulsed Magnetron Sputtering***, **D.J. Christie,*** Advanced Energy Industries, Inc.

The potential of high power pulsed magnetron sputtering (HPPMS) has created growing interest, because it can generate a dense plasma with high target material ion content. However, deposition rates are significantly lower than for DC sputtering at the same average power.@footnote 1@@super ,@@footnote 2@ The HPPMS rates are typically only 25% to 35% of the DC rates at the same average power when the process parameters are equal. The fraction of target material arriving at the workpiece which is ionized ranges from 5% to 70%@footnote 3@@super ,@@footnote 4@@super ,@@footnote 5@ as reported so far by workers in the field. Optical emission spectroscopy suggests a highly metallic plasma, but even so, the fraction of ionized target material arriving at the workpiece can be low. A simple pathways model has been developed to explain these experimental results. In addition, parametric evaluation of the model suggests target material characteristics which are desirable in order to achieve higher deposition rates and a greater ionized fraction of target material reaching the substrate. The model will be presented, with representative characteristic results and implications on HPPMS processes. In addition, insights from approximate model equations and their significance will be presented. @FootnoteText@ @footnote 1@J. A. Davis et al., to be published in Proc. 47th Annual SVC Tech. Conf., (2004).@footnote 2@W. D. Sproul et al., to be published in Proc. 47th Annual SVC Tech. Conf., (2004).@footnote 3@V. Kouznetsov et al., Surface and Coatings Technology 122, 290 (1999).@footnote 4@A. P. Ehiasarian et al., Surface and Coatings Technology 163-164, 267 (2003).@footnote 5@B. M. DeKoven et al., Soc. of Vac. Coaters 46th Annual Tech. Conf. Proc., 158 (2003).

11:00am **TF-ThM9 Complex Target Poisoning Effects in Reactive Sputtering***, **D. Rosen**, O. Kappertz, T. Nyberg, I. Katardjiev, S. Berg,* Uppsala University, Sweden

Target poisoning is the major factor limiting the deposition rate in reactive sputtering processes. Chemisorption of the reactive gas at the target surface is the main poisoning mechanism which has been studied in detail and is realatively well understood. However, there are both experimental and theoretical indications that there exists an additional target poisoning process taking place simultaneously with chemisorption. This is implantation of ionized reactive gas molecules into the subsurface of the target. These ions will penetrate some 40-80 Angstrom beneath the surface depending on target voltage. At this position these molecules will also undergo chemical reactions with the target metal atoms and form compound molecules. The target is continously etched by the mixture of energetic argon ions and ionized reactive gas molecules. Thus, the compound molecules formed by ion implantation will be brought to the surface as the target is etched. In this way additional compound molecules will be brought to the surface as compared to the case when only chemisorption at the surface would have taken place. We present a simple treatment for how these two target poisoning mechanisms will affect the processing behaviour of the reactive sputtering process. Our results indicate that the chemical reactivity between the target metal atoms and reactive gas molecules will determine if chemisorption or ion implantation is the dominating mechanism for taget poisoning. The most surprising result, however, is that we found that due to recoil implantation with the energetic argon ions the depth of the partly formed compound sub-layer will be almost identical irrespective whether chemisorption or ion implantation is the dominating target poisoning mechanism.

11:20am **TF-ThM10 Process Parameter - Film Structure/Optical Property Study of Reactive Sputter Deposited Hafnium Dioxide***, **E. Hoppe**, C.R. Aita,* University of Wisconsin-Milwaukee

HfO@sub 2@ is a refractory material that has gained importance in thin films for high k, high n, wide band gap applications. Here, we deposited HfO@sub 2@ films by sputtering a Hf target in rf-excited Ar/O@sub 2@ discharges. 150-nm thick films were grown at room temperature on Si and fused SiO@sub 2@ substrates. Nine combinations of cathode voltage (500 to 1000 V) and O@sub 2@ gas content (10 to 40%) were used. Our goal was to determine the relationship between deposition process parameters and the films atomic structure (long and short range order) and near ultraviolet-visible-infrared absorption and reflection behavior. X-ray diffraction showed the following results: (1) All films were nanocrystalline with monoclinic (m) HfO@sub 2@, the STP phase, predominant. (2) For a fixed cathode voltage, m-HfO@sub 2@ orientation with respect to the substrate was strongly dependent upon the gas O@sub 2@ content. Specifically at high gas O@sub 2@ content, a preferred m(11-1) orientation, the lowest energy growth orientation, was observed. Other orientations of m-HfO@sub 2@ became strong at low gas O@sub 2@ content and low cathode voltage, including a preferred m(111) orientation. (3) A trace amount of tetragonal (t) HfO@sub 2@, a high temperature phase, was observed in some films. This phase was possibly stabilized by a finite crystal size effect, analogous t-ZrO@sub 2@. However, the tetragonal phase occurs in significant amounts in ZrO@sub 2@ but in trace amounts in HfO@sub 2@ films grown under similar conditions, suggesting that the critical radius above which t transforms to m is smaller in HfO@sub 2@ than in ZrO@sub 2@ films, consistent with a lower t-to-m transformation temperature in bulk ZrO@sub 2@. All films are highly transparent. Transmission v. wavelength curves yielded an optical band gap of ~6.4 eV. Optical absorption edge characteristics were independent of film nanocrystal orientation, consistent with this property depending chiefly upon short-range order in wide band gap oxides.

11:40am **TF-ThM11 Integrated Modeling of Al@sub 2@O@sub 3@ Atomic Layer Deposition***, **H. Simka**, D. Thakurta, S. Shankar,* Intel Corp.

Atomic Layer Deposition (ALD) has become an increasingly attractive option for deposition of various crucial semiconductor material layers, including high-K dielectrics and barrier metal applications. ALD advantages, which include excellent film coverage, uniformity, composition and thickness targeting, can be realized by optimizing precursor reactivity and process conditions. Fundamental understanding of these factors is often limited, especially for surface reaction pathways involving new materials. One possible approach, based on first-principles quantum chemistry investigations of precursor reactions, is described in this work. The goal of this general approach is to reduce the amount of process characterizations needed, and to complement available surface science and growth data. As an example, Density-Functional Theory was used to determine molecular

properties and reaction energy barriers for Al@sub 2@O@sub 3@ ALD with Trimethylaluminum (TMA) and H@sub 2@O precursors, building on results from a previous quantum chemical study (1). A reaction mechanism containing important surface reactions controlling ALD behavior was developed, and integrated with a reactor model. The approach was validated against Al@sub 2@O@sub 3@ ALD data in a well-characterized flow-tube reactor (2). Model predicted growth rates in excellent agreement with data, and explained effects of process conditions (temperature, pressure, precursor cycle-times) on ALD growth. Differences in species reactivity on both alumina (important for growth) and silica substrates (important for nucleation) will be discussed. Acknowledgements: Prof. Steven George (U. Colorado-Boulder), Prof. Charles Musgrave (Stanford U.). References: (1) Y. Widjaja and C.B. Musgrave, Applied Physics Letters, 80(18), 3304 (2002) (2) J.W. Elam, M.D. Groner, and S.M. George, Review of Scientific Instruments, 73(8), 2981 (2002).

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