

## Thin Films

### Room 329 - 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 Mechanisms and Energetics of H Insertion into Si-Si Bonds in Hydrogenated Amorphous Silicon Films**, *S. Sriraman, M.S. Valipa<sup>1</sup>, E.S. Aydil*, University of California, Santa Barbara; *D. Maroudas*, University of Massachusetts

Understanding the mechanism of chemically-induced disorder-to-order structural transitions is relevant to the synthesis of various technologically important materials, including nanocrystalline silicon thin films used in the fabrication of solar cells and flat panel displays. Thin hydrogenated amorphous silicon (a-Si:H) films crystallize at low temperatures when exposed to H atoms from an H@sub 2@ plasma, or when the SiH@sub 4@ feed gas is heavily diluted with H@sub 2@. Recently, we showed that H-induced crystallization is mediated by insertion of H atoms into strained Si-Si bonds as the H atoms diffuse through the a-Si:H film. This presentation focuses on analyses of the mechanisms and energetics of various pathways for H insertion into Si-Si bonds in a-Si:H. These pathways are generated through molecular-dynamics simulations of repeated H atom impingement on a-Si:H films, grown computationally on crystalline Si (c-Si) substrates. Prior to insertion, the diffusing H atom bonds to one of the Si atoms that form the original Si-Si bond; upon insertion, an intermediate bridging configuration forms where the H atom is bonded to both Si atoms. After the H atom leaves the bridging configuration, the Si-Si bond may be further strained or broken, or it may relax to restore the Si-Si bond closer to the equilibrium c-Si bond length. A diffusing H atom can also occupy the bond-centered (BC) location between two Si atoms that are not bonded together. However, after the H atom diffuses away from this BC location, the two Si atoms form a Si-Si bond. The activation energy barriers are calculated for the H insertion reactions; the resulting distribution of activation energies is correlated with the Si-Si bond strain. The role of these H-insertion reactions in the structural relaxation of the a-Si:H network that results in disorder-to-order transitions is discussed. FootnoteText@ footnote 1@ S. Sriraman, S. Agarwal, E. S. Aydil, and D. Maroudas, Nature 418, 62-65 (2002).

8:40am **TF-ThM2 Effect of Crosshatch Formation on the Kinetics of Si@sub 1-x@Ge@sub x@ Growth on Si(001) from Hydride Precursors**, *T. Spila*, University of Illinois; *P. Desjardins*, École Polytechnique de Montréal, Canada; *J. D'Arcy-Gall, R.D. Twisten, J.E. Greene*, University of Illinois

Compressively-strained Si@sub 0.7@Ge@sub 0.3@ layers were grown on Si(001) by gas-source molecular beam epitaxy from Ge@sub 2@H@sub 6@/Si@sub 2@H@sub 6@ mixtures at 450 °C. The combination of the relatively low growth temperature and high steady-state hydrogen surface coverage, @theta@@sub H@ = 0.52 ML, suppresses strain-induced roughening and provides extremely flat surfaces with root mean square widths  $w < 1.5 \text{ \AA}$  for fully-coherent layers. These samples were used to probe mechanisms controlling misfit-dislocation-induced surface roughening (i.e., crosshatch) along 90°-rotated directions. For film thicknesses  $t$  just larger than the critical value for misfit dislocation formation,  $t@sub c@ = 1000 \text{ \AA}$ , the surface roughness ( $w = 3.1 \text{ \AA}$  at  $t = 1350 \text{ \AA}$ ) is dominated by single- and multiple-atomic-height steps generated by the motion of threading dislocations associated with the interfacial misfits. The surface steps are preferential H desorption sites and the increased total step length results in a decrease in @theta@@sub H@ on terraces as well as at step edges. The latter effect allows higher adatom crossing probabilities at ascending steps leading to the formation of periodic ridges ( $w = 27 \text{ \AA}$  at  $t = 4400 \text{ \AA}$ ) in response to local strain fields associated with the misfit dislocation clusters. Simultaneously, the decrease in @theta@@sub H@ on terraces strongly affects film growth kinetics as deposition rates increase from  $10 \text{ \AA min@super -1@}$  with  $t < t@sub c@$  to  $60 \text{ \AA min@super -1@}$  with  $t = 1400\text{-}4400 \text{ \AA}$ . Overall, for films with strain relaxation  $R < 5\%$ , crosshatch is due to surface steps that result from multiple misfit dislocations on single glide planes, but for  $R = 22\text{-}78\%$ , crosshatch becomes dominated by local strain-induced roughening and leads to periodic ridge formation.

9:00am **TF-ThM3 Initial Growth of High Rate Deposited Silicon Thin Films Studied by In-situ Spectroscopic Ellipsometry and Attenuated Total Reflection Infrared Spectroscopy**, *P.J. Van den Oever, I.J. Houston, J. Hong, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

The trend towards high rate deposition in thin film research - driven by industrial demands - raises several issues in order to maintain good film properties. One particular issue in this respect is the control of the nucleation and initial growth in terms of film density and surface roughness. Therefore, we have investigated the growth of silicon-based films at growth rates up to 10 nm/s as deposited by the expanding thermal plasma technique. The time evolution of the dielectric functions, bulk thickness and surface roughness has been obtained from real time spectroscopic ellipsometry measurements and the surface roughness evolution has been compared to atomic force microscopy data. Attenuated total reflection infrared spectroscopy has been employed to obtain the hydrogen depth profile of the films. For hydrogenated amorphous silicon, the film growth is found to be homogeneous after nucleation. Hydrogenated microcrystalline silicon on the other hand shows a nucleation region of crystallites, which is followed by columnar film growth after the crystallites have reached coalescence. This is supported by the hydrogen depth profile where the nucleation and presence of the crystallites is accompanied by the emergence of surface-like bonded hydrogen that can be attributed to hydrogen passivating the grain boundaries of the crystallites. For silicon nitride films a clear difference has been observed in the surface roughness evolution between silicon-rich and nitrogen-rich films as deposited under different plasma conditions. This difference can be attributed to different growth modes that are determined by the surface free energy and the specific surface reactions taking place during film growth.

9:20am **TF-ThM4 Sn-mediated Ge/Ge(001) Growth by Low-temperature Molecular Beam Epitaxy: Effects on Surface Roughening and Epitaxial Thickness**, *K.A. Bratland, Y.L. Foo, T. Spila*, University of Illinois; *P. Desjardins*, École Polytechnique de Montréal, Canada; *J.E. Greene*, University of Illinois

Fully-strained single-crystal metastable Ge@sub 1-x@Sn@sub x@ layers were grown on Ge(001) in order to probe the role of dopant and dilute alloy concentrations ( $C@sub Sn@ = 1 \times 10^{18} \text{ cm@super -3@}$  to  $6 \text{ at}\%$ ) on surface roughening pathways leading to epitaxial breakdown during low-temperature molecular beam epitaxy (LT-MBE) of compressively strained films. The growth temperature was chosen to be 155 °C due to limited epitaxial thicknesses at lower temperatures and significant Sn surface segregation at higher temperatures. The addition of Sn during Ge(001) LT-MBE was found to give rise to two competing effects. At very low concentrations ( $x < 0.02$ ), the dominant effect is a Sn-induced enhancement in both the Ge adatom mobility and the rate of interlayer mass transport, thereby suppressing kinetic roughening and resulting in significant enhancements in the critical thickness  $h@sub 1@$  for the onset of epitaxial breakdown. With  $x = 0.010$ , for example, the surface width  $w$  normalized to  $h@sub 1@$ , which is  $2.6 \times 10^{10} \text{ super -3@}$  for pure Ge(001) layers, decreases to  $1.5 \times 10^{10} \text{ super -3@}$  while  $h@sub 1@$  increases from  $7700 \text{ \AA}$  to  $1.40 \text{ \mu m}$ . Furthermore, layers which are fully epitaxial to thicknesses  $h > 1.9 \text{ \mu m}$  are obtained with the incorporation of Sn in concentrations ranging from  $1 \times 10^{18} \text{ cm@super -3@}$  to  $1.0 \text{ at}\%$ . However, for  $x @>= 0.02$ , strain-induced roughening overcomes the Sn-induced surface smoothening effects and gives rise to a rapid decrease in  $h@sub 1@$ , which ranges from  $5700 \text{ \AA}$  with  $x = 0.029$  to  $2350 \text{ \AA}$  with  $x = 0.061$ .

9:40am **TF-ThM5 Understanding Radical-Surface Interactions in the Plasma-Assisted Deposition of Amorphous Hydrogenated Silicon**, *S. Agarwal, S. Sriraman*, Univ. of California, Santa Barbara; *A. Takano*, Fuji Electric Corp. R&D, Ltd., Japan; *M.C.M. van de Sanden*, Eindhoven Univ. of Tech., The Netherlands; *D. Maroudas*, Univ. of Massachusetts - Amherst; *E.S. Aydil*, Univ. of California, Santa Barbara

**INVITED**  
Hydrogenated amorphous silicon (a-Si:H) thin films grown by plasma-assisted deposition from silane-containing discharges are widely used in photovoltaic, imaging, and display devices. During plasma-assisted deposition, reactive radicals present in the discharge such as SiH@sub x@ ( $x = 1,2,3$ ) and H impinge onto the substrate surface leading to film growth and H incorporation. The properties of the deposited films depend on the various reactions of radicals present in the discharge with the growth surface and, therefore, a fundamental understanding of such interactions is required for improving a-Si:H deposition techniques. We have studied

<sup>1</sup> TFD Student Award Winner

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radical-surface interactions in the deposition of a-Si:H thin-films through synergic use of experimental diagnostics such as in situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy and molecular-dynamics (MD) simulations based on the Tersoff's potential for Si. We have identified the various reactions of H and SiH<sub>3</sub> with a-Si:H films and determined their mechanisms and energetics. Surface H is removed by abstraction through the Eley-Rideal mechanism. Silicon is incorporated into the growing film through radical attachment to surface dangling bonds, as well as radical insertion into Si-Si surface bonds including dissociative adsorption reactions. In addition, reactions that involve radical migration on the surface are identified and analyzed. Finally, the H-induced crystallization of a-Si:H films during their post-deposition treatment by an H<sub>2</sub> plasma is addressed. The MD simulations show that H atoms diffuse into the a-Si:H film and insert into strained Si-Si bonds to form intermediate bridging and bond-centered H (Si-H-Si) configurations mediating the structural relaxation of the amorphous Si matrix leading to the disorder-to-order transition. The existence of bond-centered H(D) in a-Si:H films exposed to H(D) atoms was verified experimentally through IR spectroscopy.

11:00am **TF-ThM9 From Ab-initio Modeling to Experimental Thin Film Synthesis of a Novel Boron-oxygen-yttrium Phase**, *D. Music, V. Chirita*, Linköping University, Sweden; *J.M. Schneider*, RWTH Aachen, Germany; *U. Helmersson*, Linköping University, Sweden

The B-O based material system is a promising candidate for a wide range of tribological applications. For example, crystalline boron suboxide has been reported to have the elastic modulus of 470 GPa. However, typical requirements to form crystalline boron suboxide include high pressure (5-7 GPa) and temperature (>2000 °C), and are very difficult to achieve with standard thin film synthesis techniques such as reactive sputtering. In this work, we use ab-initio calculations to theoretically design and then experimentally grow polycrystalline boron suboxide based films. A new crystalline boron-oxygen-yttrium (BOY) phase is obtained by alloying with Y. The essential element in the modeling is Y substituting for O in the boron suboxide structure with Y/B and O/B ratios of 0.07. The overall effect of electron doping, induced by the Y substitution, is to shorten the chemical bonds in boron suboxide. This renders the formation of the BOY phase characterized by a 45% volume reduction and consequently a 23% increase in bulk modulus (from 235 to 289 GPa). The calculations predict that the BOY phase is 0.36 eV/atom more stable than crystalline boron suboxide and experiments confirm the formation of crystalline thin films. The BOY phase was synthesized with reactive RF magnetron sputtering and identified with x-ray and selected area electron diffraction. Films with Y/B ratios ranging from 0.10 to 0.32, as determined via elastic recoil detection analysis, were grown over a wide range of temperatures (300-600 °C) and found to withstand 1000 °C. Details of the electronic structure of this new phase will also be presented.

11:20am **TF-ThM10 Low Temperature Nitride and Oxide Thin Film Growth using an Energetic Atom Source**, *A.H. Mueller, E.A. Akhadov, M.A. Hoffbauer*, Los Alamos National Laboratory

Depositing one or more metals on a substrate exposed to an energetic neutral atom beam allows for the growth of high quality oxide and nitride films at low temperatures. The unique surface chemistry afforded by the exposure of the substrate to oxygen or nitrogen atoms possessing kinetic energies between 1 and 5 eV allows the deposition of dielectric and semiconducting films on materials that would undergo thermal decomposition under the conditions necessary for conventional thin film growth (e.g. CVD, sputtering, laser ablation, etc.). This low temperature epitaxy technique, called Energetic Neutral Atom Beam Lithography/Epitaxy (ENABLE), permits the growth of semiconducting nitride and dielectric oxide films on substrate surfaces patterned by an organic polymer, as well as substrates consisting entirely of low melting point materials. The crystallinity, optical and electrical properties of ENABLE grown films have been examined using numerous techniques including XRD, TEM, photoluminescence spectroscopy, and four point probe resistance measurements. Results of film deposition on various substrate materials, including patterned film deposition, will be discussed.

11:40am **TF-ThM11 Physical Self-assembly and the Nucleation of 3D Nanostructures by Oblique Angle Deposition**<sup>1</sup>, *T. Karabacak, G.-C. Wang, T.-M. Lu*, Rensselaer Polytechnic Institute

Thin film growth front morphology formed by physical vapor deposition is controlled by many factors including surface diffusion and shadowing effects. Instabilities can occur if shadowing is more dominant compared to other surface effects and can lead to many diverse physically self-

assembled 3D nano-size structures<sup>2,3</sup> that are otherwise difficult to produce by lithographical techniques. The unique geometrical shapes from a large variety of materials suggest that shadowing effects can be used as an efficient tool to understand and control the growth morphologies by many traditional deposition techniques. In this paper, we explore the fundamental nucleation and growth mechanisms of these structures. Monte Carlo simulations were carried out to predict the island density, island size distribution, and island-island correlation during the initial stages of growth. The results are compared to that obtained by the oblique angle sputter deposited W films imaged by atomic force microscopy and scanning electron microscopy. Isolated islands with quasi-periodic distribution are formed as a natural consequence of the shadowing effect. Isolated columnar structures are shown to grow on these islands and the width  $w$  of the columns is predicted to grow as a function of time  $t$  in the form of a power law,  $w \sim t^p$ , where the exponent  $p$  is between 0.3 and 0.5. The predicted  $p$  is consistent with the experimentally determined exponent values for growth of column widths from a variety of materials such as W, Co, Cu, and Si. <sup>1</sup>FootnoteText<sup>1</sup> <sup>2</sup>Footnote 1<sup>2</sup> Work supported by NSF<sup>2</sup> <sup>3</sup>Y.-P. Zhao, D.-X. Ye, G.-C. Wang, and T.-M. Lu, "Novel nano-column and nano-flower arrays by glancing angle deposition", *Nano Letters* 2, 351-354 (2002). <sup>3</sup>Footnote 3<sup>3</sup> K. Robbie, M. J. Brett, and A. Lakhtakia, "Chiral sculptured thin films," *Nature* 384, 616-616 (1996).

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