Friday Morning, November 8, 2002

Thin Films Room: C-101 - Session TF-FrM

Fundamentals of Thin Flm Growth

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

8:20am TF-FrM1 Supersonic Molecular Beam Studies of Thin Film Nucleation and Growth, J.R. Engstrom, Cornell University INVITED For over three decades supersonic molecular beams have been used as tools in fields such as rarefied gas dynamics, spectroscopy and chemical reaction dynamics. Over the past several years we have been employing supersonic molecular beam techniques to investigate the fundamental aspects of Si and Si_{1-x}Ge_x thin film growth from gaseous precursors, and more recently to study the nucleation of Cu on $\check{SiO}_2,\, Ti\dot{N}$ and TaN surfaces. These beams prove useful in our case due primarily to two factors- their (kinetic) energy tunability, and their high spatial and temporal resolution. This work using molecular beams has been combined with in situ surface sensitive analytical techniques, such as x-ray photoelectron spectroscopy, low-energy ion scattering and low-energy electron diffraction. We have also made use of independent sources of energetic species, in particular atomic sources, to examine cooperative and synergistic effects in thin film growth. The overall emphasis has been on both developing a better fundamental understanding of existing processes, and potentially developing new processes. We will present a brief overview of our work, focusing on investigations of the effects of strain on gas-surface reactivity in $Si_{1-x}Ge_x$ epitaxial alloys; the growth of thin films at grazing angles of incidence; the exploration of scaleup strategies (experiment and computer simulation) for deposition over large areas, the use of atomic hydrogen to promote the selective area growth of epitaxial Si (and Si_{1-x}Ge_x) on patterned Si-SiO₂ substrates, and the nucleation and growth of Cu on TiN and TaN barrier layers, and poly-Si on three-component (Ca-Al-Si)-oxide glasses.

9:00am **TF-FrM3 Mechanism for Epitaxial Breakdown during Lowtemperature Ge(001) Molecular Beam Epitaxy**, *K.A. Bratland*, *Y.L. Foo*, *J.A.N.T. Soares*, *T. Spila*, *J. D'Arcy-Gall*, University of Illinois, *P. Desjardins*, École Polytechnique de Montréal, Canada, *J.E. Greene*, University of Illinois

Experiments utilizing in-situ RHEED and post-deposition AFM, XTEM, and high-resolution XTEM, together with kinetic Monte Carlo models were designed to probe surface roughening pathways leading to epitaxial breakdown during low-temperature MBE of group-IV semiconductors. We conclusively demonstrate that epitaxial breakdown is not controlled by background hydrogen adsorption or gradual defect accumulation as previously suggested, but is a fundamental phase transition driven by kinetic surface roughening. Ge(001) layers grown at T_s > 170 °C remain fully epitaxial to thicknesses $h > 1.6 \mu m$, while deposition at $T_s < 170 \text{ °C}$ leads to a locally abrupt transition from epitaxial to amorphous growth at critical film thicknesses h_a(T_s). Surface morphology during low-temperature Ge(001) MBE evolves via the formation of a periodic array of selforganized round growth mounds which, for deposition at $T_s > 115$ °C, transform to a pyramidal shape with square bases having edges aligned along <100> directions. Surface widths w and in-plane coherence lengths d increase monotonically with film thickness h. As h approaches $h_d(T_s)$, deep cusps bounded by {111} facets form at the base of interisland trenches and we show that epitaxial breakdown is initiated on these facets as the surface roughness reaches a critical T-independent aspect ratio, w/d = 0.02. $h_d(T_s)$ and $h_a(T_s)$ follow relationships $h_{d(a)} = exp(-E_{d(a)}/kT_s)$, where E_d is 0.61 eV and $E_a = 0.48$ eV. E_t is approximately equal to the Ge adatom diffusion barrier on Ge(001) while $(\dot{E}_d-E_a) = 0.13$ eV is the free energy difference between crystalline and amorphous Ge. We summarize our results in a microstructural phase map vs T_s and h, and propose an atomistic growth model to explain the epitaxial to amorphous phase transition.

9:20am **TF-FrM4 Si**_{1,y}**C**_y**/Si(001) Gas-source Molecular Beam Epitaxy** from Si₂H₆ and CH₃SiH₃: Surface Reaction Paths and Growth Kinetics, *Y.L. Foo*, K.A. Bratland, B. Cho, University of Illinois, P. Desjardins, École Polytechnique de Montréal, Canada, J.E. Greene, University of Illinois

Si_{1-y}C_y(001) alloy layers were grown by gas source molecular-beam epitaxy (GS-MBE) from Si₂H₆/CH₃SiH₃ mixtures as a function of C concentration y (0 to 2.6 at%) and deposition temperature T_s (500-600 °C). High-resolution x-ray diffraction reciprocal lattice maps show that all layers are in tension and fully coherent with their substrates. Film growth rates R decrease with

both y and $T_{\!\scriptscriptstyle S}\!\!$, and the rate of decrease in R as a function of y increases rapidly with T. In-situ isotopically-tagged D temperature-programmed desorption (TPD) measurements reveal that C segregates to the secondlayer during steady-state Si_{1-y}C_y(001) growth. This, in turn, results in charge-transfer from Si surface dangling bonds to second-layer C atoms, which have a higher electronegativity than Si. From the TPD results, we obtain the Coveragesi*(y,Ts) of Si* surface sites with C backbonds as well as H₂ desorption energies E_d from both Si and Si* surface sites. Coverage_{Si*} increases with increasing y and Ts in the kinetically-limited segregation regime while E₁ decreases from 2.52 eV for H₂ desorption from Si surface sites with Si backbonds to 2.22 eV from Si* surface sites. This leads to an increase in the H₂ desorption rate, and hence higher film deposition rates, with increasing y and/or T_s during $Si_{1-y}C_y(001)$ growth. This effect, however, is more than offset by the decrease in Si₂H₆ reactive sticking probabilities at Si* surface sites. Film growth rates R(T_s,J_{Si} 2H6,J_{CH3SiH3}) calculated using a simple transition-state kinetic model, together with measured kinetic parameters, were found to be in good agreement with the experimental data.

9:40am **TF-FrM5** In-Situ Infrared Chemometrics During BPSG Dielectric Thin Him Growth, *L.D. Flores, J.E. Crowell*, University of California, San Diego

Dielectric thin film growth of boron and phosphorus doped silicate glass (BPSG) has been studied using the atmospheric pressure reaction between trimethylborate (TMB), trimethylphosphite (TMPi), tetraethoxysilane (TEOS) and ozone (O₃). In-situ gas-phase transmission FTIR spectroscopy was performed between 400-600°C by probing the variable region between the injector, heated Si wafer and the exhaust zones. Experimental methods for reliable quantitative infrared measurement of gaseous species in the CVD environment will be demonstrated. These studies involve low temperature ozone initiated deposition of dielectric thin films using a new atmospheric-pressure chemical vapor deposition (APCVD) reactor utilizing a commercial monoblok vent assembly. We quantify $N_2 / O_2 / O_3$ reaction products from BPSG precursors while varying the reactant ratios and probing as a function of infrared beam position within the reactor. The products produced during the reaction of TEOS and ozone are compared to those products measured during dopant reaction and incorporation from TMB and/or TMPi addition. Absorbances due to isolated silanol groups (3738 cm⁻¹) are treated using PCA (principle component analysis) techniques as a function of temperature and input reagent concentration to determine formation kinetics. The silanol groups and their reactions with boron and phosphorus dopant sources have been investigated in order to clarify their role in the oxidation process and to determine the reaction mechanism. Pathways involved in the hydrolysis and polycondensation process leading to siloxane formation and network film growth will be presented.

10:00am TF-FrM6 Surface Chemistry of TaCl₅ on Polycrystalline Ta and Cu, A.M. Lemonds, J.M. White, J.G. Ekerdt, The University of Texas at Austin

The surface chemistry of TaCl5 on polycrystalline Ta and Cu was studied by X-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) following adsorption at 130 K. XPS determined that no surface reactions occurred during adsorption at 130 K on Ta, and binding energy shifts in the Ta 4f and Cl 2p XP spectra suggested interactions between TaCl₅ molecules in contact with the Ta substrate. TPD analysis from 130 to 900 K showed the desorption of two molecular states between 200 and 300 K from Ta, and the higher temperature state is more structurally ordered than the low temperature state. Chemical reaction between the TaCl₅ interfacial layer and O absorbed in the Ta lattice was observed for the 250 K annealing of multilayers adsorbed at 130 K. Surface coverages estimated by XPS were less than coverages estimated by TPD for adsorption on Ta, and the discrepancy is explained by the forward scattering of the substrate Ta 4f metallic photoelectrons through ordered TaCl₅ adlayers. A multilayer formed for TaCl5 adsorption on Cu at 130 K, and a single multilayer desorption peak was observed at 275 K. At 300 K, TaCl₅ dissociatively adsorbed on Cu, and uptake saturated at less than one monolayer, limited by adsorbed Cl ligands. TPD for this adsorption showed Ta^+ (m/z 181) and Cu⁺ (m/z 63) desorption features at 355 and 495 K. respectively. No detectable Ta or Cl was observed by XPS on the Cu surface following TPD, in which the surface temperature reached 900 K.

10:20am TF-FrM7 Theoretical Design of Thin Film Growth with Functional Properties, K.M.E. Larsson, Uppsala University, Sweden INVITED

Advanced surface engineering based on thin films technology is of growing importance in materials sciences today. Techniques to produce materials with tailor-made properties are being developed. Vapor growth processes like CVD (Chemical Vapor Deposition) are especially suited for this purpose. Vapor growth of materials is a very complex and dynamic process. It involves the generation of surface vacancies and adsorption of different gaseous species to various radical surface sites. Other important processes include surface abstraction and migration, as well as nucleation and a continued growth. Quantum mechanical calculations are useful for us to be able to get the atomic-level understanding that is necessary to reach for an understanding of these processes, as well as for making predictions about materials properties. Materials properties can generally be changed in two different ways. Firstly, it is possible to change it by changing the chemical and/or structural composition of the material. Secondly, a change may be obtained by varying the size of nanoparticles, or by varying the film thicknesses. Currently there is a great scientific and technological interest in these types of quantum confinement effects. The underlying reason is that various materials properties can be manipulated in fascinating ways by controlling dimension, rather that by controlling composition alone. Various inorganic compounds, with interatomic bonds that range from covalent to ionic types, will be focused in this presentation. One of the major goals is then to investigate and compare the growth processes for these different materials. Another main goal is to investigate the effect of various parameters (e.g., surface termination, amount and types of defects and dopants, sizes) on materials properties like electrical, optical and mechanical. All of these knowledges are very useful in the development of new experimental designs, as well as in the deposition of more artificial structures.

11:00am TF-FrM9 Chemical Bonding Requirements for Forming Passive Semiconductor Oxide Interfaces, J.Z. Sexton, A.C. Kummel, University of California, San Diego

The formation of passive, electronically unpinned metal oxide semiconductor interfaces is a critical part in the development of III / V MOSFET technology. A high quality gate oxide will unpin the Fermi level and will form an interface with low interfacial defect densities. We have done first-principles density functional theory calculations to investigate the chemical bonding requirements for forming a passive gate-oxide semiconductor interface. Upon MBE deposition onto the GaAs(001)β2(2x4) surface, Ga 2O inserts into a pair of surface As-dimers. This layer unpins the Fermi level and allows for growth of bulk amorphous oxide. This is in contrast to O2 chemisorption which displaces surface arsenic atoms and pins the Fermi level. First principles calculations were done to elucidate the mechanism for Fermi level unpinning on this surface. Calculations comparing Ga2O and O2 chemisorption on GaAs(001)- B2(2x4) indicate that the requirements for the formation of a passive interface are: 1) charge balance restoration of surface As atoms to near-bulk values, 2) restoration of surface geometry to a bulk-like bonding environment, and 3) sequestering of oxygen atoms near the interface into sites ionically bonded to gallium atoms. These three bonding requirements act synergistically to passivate the interface. The effects are observed in DFT calculations of the local charge densities per atom, interfacial geometry of gallium and arsenic atoms, and local density of states in the band-gap region of the GaAs(001)- $\beta 2(2x4)$ - Ga₂O interface. These calculations provide a roadmap for identifying passivation oxides for other semiconductor surfaces.

11:20am TF-FrM10 In-situ Observation of the Electron-Current Effect on Mass-Flow in Thin Ag Films on an Insulating Substrate¹, O. Bondarchuk, M. Degawa, E.D. Williams, University of Maryland

As electronic device dimensions become smaller, we can expect surfaceinduced changes in the electrical properties, including transport phenomena² and electromigration phenomena.³⁻⁵ The fluctuations and motion of singlelayer steps under the electromigration driving force are the key connection between the atomic scale mechanism and the continuum scale response. This connection can be quantified by using the predictions of Pierre-Louis and Einstein⁵ concerning the motion of single-layer deep pits and singlelayer height islands under an electromigration force. We have designed an experimental configuration to directly test the theoretically predicted shape distortion and net migration of voids and islands, on thin crystalline Ag films using STM. The Ag films of ~100-200 nm thickness with large (0.5-1 mm in size) features were deposited on mica and studied in-situ under UHV conditions. Growth parameters were tuned to create films with large grains, large atomically flat surface areas, and continuous electrical conductivity while minimizing film thickness. STM imaging was performed with sample carrying up to ~ 1 A, corresponding to a current density of ~ 2.5x105 A/cm2. Voids and islands were created by removing ~0.5

monolayer by 1 keV Ar-ion sputtering at room temperature. Evolution of morphology occurring via thermal activation of metastable structure decay is a competing process with structural evolution via electron current effects. ¹Work supported by the NSF NIRT and MRSEC programs.

² O. Pfennigstorf, A. Petkova, H.L. Guenter, and M. Henzler, Phys. Rev. B 65, 045412(2002).

³P.J. Rous, Phys. Rev. B61, 1 (2000).

⁴A.V. Latyshev, A.L. Aseev, A.B. Krasilnikov, S.I. Stenin, Surf. Sci. 213, 157 (1989) ⁵O.Pierrre-Louis and T.L. Enstein, Phys.Rev.B62, 13697 (2000).

11:40am TF-FrM11 Effect of Metal Underlayers on Low Temperature Silicon Growth, K. Xu, A. Pradhan, S.I. Shah, University of Delaware

Previously, we have reported the effect of Kr on the crystallinity of Si films grown at low temperatures on temperature sensitive substrates. An additional contribution to the Si film crystallinity comes from metal underlayers. Silicon films were deposited on glass, metal-coated glass and metal-coated polymer substrates at temperatures between 130-200°C. X-ray diffraction showed that the films deposited on substrates with gold underlayers were polycrystalline while those deposited on bare glass or polymer substrates were x-ray amorphous. Atomic force microscopy (AFM) was used to study the topography and ad-atom diffusion on the surface. AFM micrographs showed that the polycrystalline silicon films had an average grain size of 95nm. The surface diffusion length was calculated from the AFM micrographs. The results showed films deposited on substrates with gold underlayers had larger diffusion lengths which help to increase the grain size. In order to understand the effect of the underlayer grain size, gold films were annealed to temperatures up to 400°C. Silicon films deposited on these annealed substrates showed even higher crystallinity and larger grain size. The results of XRD, AFM and Raman characterizations will be presented. We will correlate the grain size to the diffusion length and present a model for grain growth in silicon films on temperature sensitive substrates.

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