Selective Deposition as an Enabler of Self-Alignment Focus Topic
Room: 318 - Session SD-WeM

Fundamentals of Selective Deposition
Moderator: James Engstrom, Cornell University, Florian Gstrein, Intel Corporation

8:00am **SD-WeM1 Utilizing Inhibitor Molecules in Low Temperature CVD to Control Thin Film Nucleation, Surface Morphology and Conformality in Deep Features**, ***John R. Abelson***, University of Illinois at Urbana-Champaign **INVITED**

When performed at low substrate temperature, the growth of thin films by chemical vapor deposition can be strongly *inhibited* by the reversible adsorption of precursor, byproduct, or neutral molecule species on the active surface. The microscopic mechanism is typically that of site blocking: as the surface coverage of inhibitor species increases, the reaction probability of arriving precursor molecules drops, and can reach values as low as 10^{-6} under realistic growth conditions. In specific cases, the mechanisms of associative precursor desorption or coverage-dependent film growth rate also occur.

We will show that site blocking by the precursor itself can afford extremely conformal film growth in structures with aspect ratio > 100:1, and that the addition of a neutral molecule inhibitor to a 'non-conformal' precursor can provide good step coverage in features with aspect ratio ~ 10:1. We also solve the diffusion-reaction equation to predict the regimes of precursor pressure and substrate temperature that afford conformal growth, and map the boundaries onto a *conformal zone diagram*. Under conformal conditions the surface roughness is exceptionally low due to the smoothing effect of precursor re-emission, which mitigates the 'shadowing' of the incident flux by peaks in the surface morphology.

We then show that an inhibitor molecule can be used to control the film nucleation step. The inhibitor molecule must have a greater adsorption energy on the deposited material than on the bare substrate surface, or vice versa, such that the equilibrium coverage of inhibitor is large only on the strongly binding surface. For strong binding to the film, the deposit consists of a high density of nm-scale nuclei that coalesce into an ultra-smooth film; we give the example of HfB_2 growth on SiO_2 using NH_3 as the inhibitor. Conversely, when the inhibitor slows the nucleation rate, the deposit consists the sparse distribution of islands in a narrow size distribution that may be useful in photonic or catalytic applications; we give the example of Cu growth using VTMS as the inhibitor.

The use of inhibitors may provide a pathway towards selective deposition if film growth can be completely shut off on the surface that is intended to remain bare. Systems in which the inhibitor can drive associative desorption of the precursor are predicted to be especially useful, in that they remove unwanted precursor molecules. Another possibility is the use of activated species such as atomic H, generated by a remote plasma, that fully passivate covalently bonded surfaces but recombine rapidly (and therefore have no effect) on metallic surfaces.

8:40am **SD-WeM3 Metrology of Selective Functionalization of Semiconductor, Oxide and Nitride Surfaces**, *L. Liu, W.J.I. DeBenedetti, S. Karakaya, T. Peixoto,* University of Texas at Dallas*, R. Hourani, D.J. Michalak,* Intel Corporation*,* ***Yves Chabal***, University of Texas at Dallas **INVITED**

There is an increasing need to develop selective functionalization of surfaces. This goal requires careful control over surface cleaning, intermediate passivation, and chemistry (either vapor phase or wet) on oxide, semiconductor, and/or metal surfaces, many of which have not have been well-studied in the past. It is therefore critical to bring to bear a number of characterization techniques that can provide sufficient information to fully understand each of these three steps (cleaning, passivation, functionalization).

This talk will illustrate the role of characterization in examining surfaces such as silicon nitride, silicon oxide, and metallic surfaces with a unique cluster tool equipped with *in-situ* infrared (IR), X-ray photoelectron spectroscopy (XPS) and low-energy ion scattering (LEIS) for bonding, elemental, chemical and spatial characterization. These techniques are coupled with *ex-situ* AFM, spectroscopic ellipsometry, and SEM for full characterization of interesting surface species and products. Following a goal to achieving chemical selectivity between Si_3N_4 and SiO_2 surfaces, we first focus on the surface chemistry after cleaning and etching with aqueous HF. While H or NHx is typically believed to be the chemical termination of HF-etched silicon nitride surfaces, we find that such surfaces not only require careful preparation to remove salt byproducts, but are also essentially fluorine terminated. Despite the clear difference in surface termination between nitrides and oxides, both surfaces display surprisingly similar reactivity and bonding upon exposure to chloro- and ethoxysilane molecules: both surfaces display the formation of Si-O-Si bonds but the nitride surfaces show little removal of fluorine. We propose a novel concept for surface reaction involving the activation of surface atoms back-bonds, such as Si-N/Si-O in the case of F-terminated Si_3N_4. While such a process does not lead to selective chemistry of silicon oxide and nitride surfaces, its understanding opens the way for the selection of appropriate molecules for selectivity.

9:20am **SD-WeM5 First Principles Calculations of Substrate-Specific Reactions in ALD**, ***Simon Elliott****, M. Shirazi, S. Klejna*, Tyndall National Institute, Ireland

Selective-area atomic layer deposition (ALD) requires a new level of understanding of how to activate and deactivate substrates towards precursors and film growth, beyond the rather brute-force approach taken to date towards nucleation of ALD films. We present a review of substrate-specific interactions in ALD as determined by first principles calculations (mostly density functional theory). The substantial body of calculations in the literature of ALD onto oxide and H-terminated semiconductor substrates is introduced briefly as a baseline [S. D. Elliott, Semicond. Surf. Techn. 27, 074008 (2012)]. Our new results reveal at an atomic level why ALD reactions can be self-limiting on oxides [M. Shirazi et al., Chem. Mater. 25, 878 (2013)]. This is contrasted with computed mechanisms for reactions that do not self-limit and indeed where substrate oxides are consumed by precursors [Klejna et al., Chem. Mater. 26, 2427 (2014)]. Differences have also been computed for precursor adsorption and ligand reactions on metallic substrates (Cu, Ru) and these are discussed.

9:40am **SD-WeM6 Surface Chemistry during ALD of SiN_x from BTBAS and N_2 Plasma**, *C.K. Ande, K. de Peuter,* Eindhoven University of Technology, Netherlands*, H.C.M. Knoops,* Eindhoven University of Technology*, S.D. Elliott,* Tyndall National Institute, Ireland*,* ***Erwin Kessels***, Eindhoven University of Technology, Netherlands

There is an urgent need for a scalable, low-temperature ALD process for the deposition of high-quality silicon nitride (SiN_x). However the development of such process by thermal ALD has been challenging, particularly when the use of halide-free precursors is required. Plasma-enhanced ALD processes can provide a solution as we have recently demonstrated by the development of an ALD process based on $SiH_2(NH^tBu)_2$ (BTBAS) precursor and N_2 plasma. This process yields high-quality SiN_x with a low wet etch rate and a good conformality on surface features with an aspect ratio of <5. In this contribution the surface chemistry during the SiN_x ALD process will be addressed. On the basis of mass spectrometry and optical emission spectroscopy, the surface reactions during precursor adsorption will be discussed as well as the interaction of the N_2 plasma species with the growth surface. In particular, the question will be addressed why the ALD process is feasible when using a pure N_2 plasma but not when using a H_2-N_2 plasma or a NH_3 plasma. On the basis of carefully-designed experiments involving multiple plasma and gas exposures of the surface during an ALD cycle, it will be shown that the presence of under-coordinated N atoms at the surface is key for precursor adsorption. This will be supported by first-principles simulations in which the interaction of a Si_3N_4(0001) surface with precursor molecules and various co-reactants (atomic H, atomic N and NH_3) was probed. These atomic scale simulations reveal that atomic H and NH_3 passivate the under-coordinated N and Si atoms on the surface rendering it unreactive towards the BTBAS precursor. N atoms on the other hand bind to under-coordinated surface N and Si atoms, but still leave behind under-coordinated N atoms on the surface. This understanding is vital to advance the precursor design for SiN_x ALD as well as for further development and improvement of the SiN_x ALD processes and material properties.

11:00am **SD-WeM10 Enhanced Area-Selective Atomic Layer Deposition of TiN on HfO_2**, ***Sonali Chopra****, A.P. Lane, C.G. Willson, J.G. Ekerdt*, The University of Texas at Austin

This research targets the selective deposition of TiN onto HfO_2 for use as the word line in an STT-RAM (spin-transfer torque random access memory) device. It focuses on scalable technologies that are compatible with all steps in STT-RAM fabrication. Previous work has shown that chlorosilane and methoxysilane molecules can effectively block the HfO_2 surface from TiN deposition by area selective atomic layer deposition (AS-ALD). Other research has demonstrated the blocking efficiency of these organic layers declines with increasing number of cycles of atomic layer deposition. This deficiency has been attributed to imperfectly formed self-

assembled monolayers during deposition or degradation of the organic layer due to the high temperatures of the ALD process. The decline in performance of the organic blocking layer limits the thickness of the material that can be deposited in unblocked regions without loss of selectivity. In this presentation, we will reveal methods to improve the blocking characteristics of these organic layers. We will demonstrate how specially functionalized macromolecules such as dendrimers and sequential chemical vapor deposition reactions using bifunctional molecules can be used to achieve enhanced blocking characteristics. Using x-ray photoelectron spectroscopy, water contact angle measurements, atomic force microscopy, and x-ray reflectivity, we examine the nucleation of TiN on the organic blocking layer and the limits (temperature, number of ALD cycles) of these passivants. Finally, we report the effectiveness of these organic layers to block TiN deposition on substrates with pre-formed features and explore their potential for device applications.

11:20am **SD-WeM11 Selective Area Deposition of Short Cycle-Time ALD for Patterned-by-Printing Electronics**, ***CarolynR. Ellinger***, *S.F. Nelson*, Eastman Kodak Company

In this talk we will review our current understanding of the process space of spatial ALD and selective area deposition – including ALD cycle time, process temperature, precursors and choice of inhibitor. Data will be presented on inhibition of the precursors useful for making all of the layers necessary for thin film transistors over a temperature range of 100°C to 250°C, namely DEZ, DMAI, and H_2O. Our devices are composed of conductive aluminum-doped ZnO (AZO), semiconducting ZnO, and electrically insulating aluminum oxide.

We use selective area deposition as an alternative approach to printed electronics. We print an inhibiting polymer ink, and deposit active materials via spatial atomic layer deposition (ALD), thereby separating the ink requirements from the active materials requirements. We have previously shown a process flow using this methodology to make simple bottom gate ZnO thin film transistors (TFTs) that have the same device performance as TFTs using the same materials but patterned by more conventional photolithographic means. Here, we will present new data highlighting the advantages of the additive patterning allowed by selective area deposition. We demonstrate devices having architectures that are easily achievable with this approach, that are correspondingly difficult to achieve through subtractive processing methods.

In addition to providing design freedom, the patterned-by-printing process flow allows for high throughput and fast process speeds. The atmospheric spatial ALD system enables the use of very short cycle times, with single gas exposure times between 25 and 200 ms (cycle times of 100 to 800 ms). In addition, since there is no time penalty for pumping down a reaction chamber to vacuum levels, the process time is approximately the number of cycles required times the cycle time. Additional gains in process speed are to be had by using selective area deposition and printing, because there are no inorganic etch steps and no need for exposure or development of a photoresist. The process time is simply determined by the print rate and the time necessary to remove the inhibitor at the end of spatial ALD deposition. For our typical conditions, we complete a full pattern process cycle in less than 20 minutes, and can build functional circuits only hours after completing the layout of a new design. These studies show that the patterned-by-printing method offers a rapid cycle time approach to high quality electronics on a variety of supports.

11:40am **SD-WeM12 Self-limiting CVD of a Silicon Monolayer for Preparation of Subsequent Silicon or Gate Oxide ALD on InGaAs(001)-(2x4)**, ***Mary Edmonds***, *T. Kent,* University of California, San Diego*, R. Droopad,* Texas State University*, E.A. Chagarov, A.C. Kummel*, University of California, San Diego

A broader range of channel materials allowing better carrier confinement and mobility could be employed if a universal control monolayer (UCM) could be ALD or self-limiting CVD deposited on multiple materials and crystallographic faces. Si-OH is a leading candidate for use as the UCM, as silicon uniquely bonds strongly to all crystallographic faces of $InGa_{1-x}As$, $In_xGa_{1-x}Sb$, $In_xGa_{1-x}N$, SiGe, and Ge enabling transfer of substrate dangling bonds to silicon, which is then passivated by atomic hydrogen. The surface may subsequently be functionalized with an oxidant such as HOOH(g) in order to create the UCM terminating Si-OH layer. This study focuses on depositing a saturated Si-H seed layer via two separate self-limiting and saturating CVD processes on InGaAs(001)-(2x4) at substrate temperatures of 250°C and 400°C. XPS in combination with STS/STM were employed to characterize the electrical and surface properties of the saturated silicon seed layers on InGaAs(001)-(2x4).

The 250°C self-limiting CVD procedure includes a decapped $In_{0.53}Ga_{0.47}As$(001)-(2x4) surface dosed with 300 MegaLangmuir of Si_3H_8 at sample temperature of 250°C. The 400°C self-limiting CVD procedure includes a decapped surface dosed with 21 MegaLangmuir of Si_2Cl_6, followed by a 500 Langmuir dose of atomic hydrogen at sample temperature of 400°C, leaving the silicon surface hydrogen terminated. The XPS spectra following the saturated Si_3H_8 and Si_2Cl_6 doses shows the increase of the silicon 2p3/2 peak and decrease in the gallium 3p3/2 substrate peak, indicative of saturating coverage. Complete saturation is determined to occur once further dosing with Si_3H_8 or Si_2Cl_6 leads to no further increase in the silicon 2p peak or further decrease in the gallium 3p peak areas. STM images of the decapped surface following Si_3H_8 CVD at 250°C and post annealing shows high surface order. STM images of the saturated Si_2Cl_6 surface followed by 500 Langmuir atomic hydrogen at 400°C show silicon absorbs in a commensurate structure with average row spacing nearly identical to the (2x4) surface at 1.5 nm, consistent with III-V dangling bond elimination. Both CVD processes employ high pressure CVD pulses, which protect from unwanted carbon and oxygen contamination. The hydrogen terminated silicon surface achieved by both CVD procedures show identical STS results with the surface Fermi level remaining at the same location as the n-type clean (2x4) surface and conduction and valance band edges lining up, indicating both processes do not pin the Fermi level nor degrade the surface density of states.

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