

# Tuesday Afternoon, October 16, 2007

## Thin Film

Room: 613/614 - Session TF-TuA

## Surface Chemistry for Atomic Layer Deposition

Moderator: S. Rossnagel, IBM

1:40pm **TF-TuA1 Infrared Characterization of Atomic Layer Deposition and Post Annealing of Lanthanum Oxide Films**, *J. Kwon, M. Dai*, Rutgers University, *E. Langereis*, Eindhoven University of Technology, The Netherlands, *Y.J. Chabal*, Rutgers University, *K. Kim, R. Gordon*, Harvard University

$\text{La}_2\text{O}_3$  is a potential material for high-k gate dielectrics in microelectronics due to its relatively large permittivity, thermal stability in contact with Si, suitable band gap and conduction band offset. Uniform and conformal thin layers of metal oxides can be realized by a self-limiting atomic layer deposition (ALD) process. Surface nucleation and overall interface formation mechanisms are unfortunately not well understood since most of film characterization has been performed with ex-situ measurements. We report on in-situ Fourier transmission infrared (FTIR) studies of ALD growth and post-deposition annealing of La-oxide thin films on Si substrates using a metal-amidinate precursor<sup>1</sup> and  $\text{D}_2\text{O}$ . Film growth rates were determined from ex-situ RBS measurements. Atomically flat hydrogen-terminated Si(111) surfaces were used as substrates for La-oxide film growth. IR spectra were obtained at every half-cycle of the initial stages and post-deposition annealing was studied up to 800°C by performing IR measurements after 20 cycles of ALD process at 100°C increments. Between 200 and 300°C substrate temperatures, the first La-precursor exposure consumes approximately 30% of surface hydrogen, as measured by the intensity loss of the monohydride Si-H stretching mode (2083  $\text{cm}^{-1}$ ). A  $\text{D}_2\text{O}$  exposure is used each time to complete the cycle. More than 90 % hydrogen is consumed after the third metal-precursor dosing (2.5 cycle) at 300°C deposition temperature.  $\text{La}_2\text{O}_3$  grown at 200°C shows higher concentration of carbonate species (modes in the 1390 ~ 1470  $\text{cm}^{-1}$  region) incorporated into the film compared to 300°C grown films, probably due to incomplete elimination of the metal precursor by  $\text{D}_2\text{O}$ . The intensity of these modes decreases with increasing annealing temperature and almost completely disappears at 400 ~ 500°C annealing. Carbonate groups in the films grown at 300°C are lower, but profound ligand decomposition is observed around 2000  $\text{cm}^{-1}$ . Si-O-Si modes (900 ~ 1200  $\text{cm}^{-1}$ ) are observed to increase from the very initial ALD cycle, consistent with interfacial  $\text{SiO}_x$  formation at 300°C. Films grown at 200°C show much slower interface oxide formation, but even a mild (400°C) post-deposition anneal triggers substantial interfacial  $\text{SiO}_x$  formation.

<sup>1</sup> B. S. Lim et al., Appl. Phys. Lett. 84, 3957 (2004).

2:00pm **TF-TuA2 Understanding the Long Nucleation Period for Pd ALD on Alumina Substrates**, *D.N. Goldstein, S.M. George*, University of Colorado

Palladium (Pd) atomic layer deposition (ALD) can be performed on alumina substrates using  $\text{Pd}(\text{hfac})_2$  ( $\text{hfac}$ = hexafluoroacetylacetonate) and formalin. However, this system requires a nucleation period of 50-100 cycles before Pd grows steadily at 0.2 Å/cycle. To understand the long nucleation period, this study explored the details of the surface reactions occurring during Pd ALD nucleation. This research utilizes in situ Fourier Transform Infrared (FTIR) spectroscopy on nanopowder substrates to observe the surface species.  $\text{Pd}(\text{hfac})_2$  dissociatively adsorbs on the  $\text{Al}_2\text{O}_3$  substrate to yield surface  $\text{Pd}(\text{hfac})$  and  $\text{Al}(\text{hfac})$  during the initial  $\text{Pd}(\text{hfac})_2$  exposure. During the first formalin exposure, only the  $\text{hfac}$  ligands attached to Pd are removed and the  $\text{Al}(\text{hfac})$  species remain on the substrate. In addition, the formalin exposure adds formate species to the available Lewis acid sites on  $\text{Al}_2\text{O}_3$ . After the first cycle, no more surface  $\text{Pd}(\text{hfac})$  is observed and formalin exposures remove some of the  $\text{Al}(\text{hfac})$  species. These  $\text{Al}(\text{hfac})$  species are believed to be the cause for the long nucleation period. Surface  $\text{Al}(\text{hfac})$  is continually produced from  $\text{Pd}(\text{hfac})_2$  exposures and competes with Pd metal for the same surface sites. The fate of  $\text{Al}(\text{hfac})$  is either thermal decomposition to trifluoroacetate groups or removal from the surface as a volatile enol isomer. Formalin provides hydrogen to release the enol of  $\text{hfac}$  but cannot remove the trifluoroacetate groups. Trifluoroacetate groups may be a source of fluorine contamination in the films. The nucleation period ends when the volatile  $\text{hfac}$  products desorb and Pd can cover the original  $\text{Al}_2\text{O}_3$  surface. At this point, only  $\text{Pd}(\text{hfac})$  species are observed in the FTIR spectra. Transmission electron microscopy studies reveal Pd nanocrystallites that increase in number with increasing

number of ALD cycles. These crystallites eventually coalesce to a conformal Pd film.

2:40pm **TF-TuA4 Simulations of the Surface Chemistry of HfO<sub>2</sub> Atomic Layer Deposition**, *C.B. Musgrave, A. Mukhopadhyay*, Stanford University, *J.F. Sanz*, Universidad de Sevilla, Spain **INVITED**

We have used a combination of theoretical techniques to explore the surface chemistry of atomic layer deposition of metal oxides and nitrides, including HfO<sub>2</sub>, HfN, HfO<sub>x</sub>N<sub>y</sub> and WN. Our main focus has been on the chemical mechanisms involved in the ALD of HfO<sub>2</sub>. Density functional theory has been employed using both the cluster and periodic supercell models of the reacting surface to determine detailed mechanisms of the surface chemistry of ALD. In addition to locating transition states and applying transition state theory to predict reaction rates, we also simulate ALD surface reactions using Born-Oppenheimer quantum molecular dynamics. These simulations provide a rich and complex picture of the atomistic detail of the ALD process which shows that the chemistry of ALD is much more complicated than initial descriptions suggested. In addition to finding various reaction pathways and predicting their relative rates, we also investigate processes such as dissociation of adsorbed precursors via microsolvation and the effect of surface hydration on the ALD mechanism.

4:00pm **TF-TuA8 Passivation and Atomic Layer Deposition on Halide-Terminated Ge Surfaces**, *P. Ardalan, C.B. Musgrave, S.F. Bent*, Stanford University

Because of the poor oxide of germanium, alternative passivation methods are required for practical use of Ge in devices. We have studied the passivation of germanium surfaces by alkanethiolate self-assembled monolayers (SAMs) and by ALD-deposited titanium dioxide ( $\text{TiO}_2$ ). We have also investigated the ability of the SAMs to block  $\text{TiO}_2$  deposition for application to area selective ALD. Our studies started with halide-terminated (Cl- or Br-) Ge(100) and (111) surfaces, which have been shown to exhibit good stability and resistance to oxidation. The initial functionalization of Ge surfaces by HCl and HBr was investigated by various experimental and theoretical methods, including x-ray photoelectron spectroscopy and density functional theory. Next, these surfaces were exposed to 1-alkanethiols to form alkanethiolate self-assembled monolayers (SAMs), where the formation and bonding of such SAMs were studied by the same methods. We also investigated the ALD of  $\text{TiO}_2$  on halide-terminated Ge surfaces, with the results showing a strong temperature dependence of the growth process. Finally, we have explored the area selective ALD of  $\text{TiO}_2$  at the Ge surfaces. We observe that the 1-alkanethiolate SAMs protect the Ge surfaces from ALD, leaving  $\text{TiO}_2$  to deposit only at regions of the Ge surfaces which are functionalized by halides but not protected by the SAMs. The results demonstrate a new route to Ge surface functionalization and passivation.

4:20pm **TF-TuA9 Step by step in-situ X-ray Photoelectron Spectroscopy Investigation on ALD  $\text{Al}_2\text{O}_3$  Films using TMA and Water**, *K.J. Choi*, University of Texas at Dallas, *S.J. McDonnell*, Dublin City University, Ireland, *R.M. Wallace, J. Kim*, University of Texas at Dallas

In atomic layer deposition (ALD) of  $\text{Al}_2\text{O}_3$  on H-terminated silicon substrates, it is often observed that the initial growth rate of  $\text{Al}_2\text{O}_3$  films is much slower than that in the steady-state condition after several cycles. This phenomenon is frequently called an incubation period, which has been extensively investigated by using various in-situ surface characterization methods, such as quartz crystal microbalance, quadrupole mass spectroscopy, FT-IR etc. Although X-ray photoelectron spectroscopy (XPS) provides useful chemical binding information at the surface, a relatively few papers have been published regarding in-situ XPS investigations possibly due to a ultra-high vacuum (UHV) requirement which is not easily compatible to ALD system. In this study, in-situ XPS is used to investigate on chemical binding status during formation of  $\text{Al}_2\text{O}_3$  thin films on an HF-last Si wafer. All experiments were carried out in a UHV system consisting of various deposition tools, including atomic layer deposition, sputter deposition, molecular beam epitaxy/deposition, and e-beam evaporation, as well as surface characterization methods including XPS, UPS, STM and AFM. The  $\text{Al}_2\text{O}_3$  film was grown at 300°C on HF-last Si substrate using trimethylaluminum [ $\text{Al}(\text{CH}_3)_3$ , TMA] as the aluminum precursor and  $\text{H}_2\text{O}$  as the oxidizing agent. A cycle of the deposition process consisted of 0.1 s of TMA pulse, 10 s of  $\text{N}_2$  purge, 0.1 s of  $\text{H}_2\text{O}$  pulse and 10 s of  $\text{N}_2$  purge. The growth rate is about 0.11 nm/cycle. XPS analysis was conducted on  $\text{Al}_2\text{O}_3$  thin films resulting from a 3-cycle deposition. The  $\text{Al}_2\text{O}_3$  thin films were grown in half cycle steps (TMA pulse+ $\text{N}_2$  purge or  $\text{H}_2\text{O}$  pulse +  $\text{N}_2$  purge) and analyzed in-situ so that the initial growth of  $\text{Al}_2\text{O}_3$  could be observed. The  $\text{Al}_{2p_{3/2}}$  photoelectron emission peak appears

after the 1 cycle + TMA pulse + N<sub>2</sub> purge. As the number of cycles is increased, the peak intensity of Al<sub>2p<sub>3/2</sub></sub> increases in TMA pulse + N<sub>2</sub> purge step, and does not increase in H<sub>2</sub>O pulse + N<sub>2</sub> purge step. In addition, we will also present in-situ vs. ex-situ XPS analysis of ALD Al<sub>2</sub>O<sub>3</sub> in this presentation.

**4:40pm TF-TuA10 Multi-Scale Simulation of High-κ Gate Dielectrics Deposited by Atomic Layer Deposition, Z. Hu, C.H. Turner, The University of Alabama**

Two of the most critical issues currently facing the semiconductor industry are the discovery of high-κ gate dielectric replacement materials for SiO<sub>2</sub> and the development of deposition processes that will afford high surface uniformity and controlled growth at the atomic scale. Atomic layer deposition (ALD) is an ideal candidate for meeting these challenges, enabling the deposition of a material through highly uniform and conformal growth, with thickness control at the atomic layer level. Our current work involves the use of a multi-scale modeling strategy to gain theoretical insights into the structure, properties and deposition process of high-κ dielectrics materials, which can provide a better understanding of experimental results and accurate predictions of specific properties of the thin films deposited by atomic layer deposition (ALD). In this work, we present results obtained from ab-initio quantum mechanical cluster calculations and periodic density functional theory (DFT) calculations based on tight-binding techniques. A series of calculations were carried out to study the initial ALD surface reactions. We present detailed chemical mechanisms and kinetic data at typical ALD temperatures range from 150°C to 450°C. This information can be used to understand experimental results and optimize operating conditions. The effects of surface functionalities and precursors on the thin film deposition process are discussed. Our DFT calculations show the complexity of the growth mechanisms during ALD processing. In addition, we predicted a new oxygen incorporation mechanism, which is relevant to the formation of the SiO<sub>2</sub> interfacial oxide layer during the ALD of Al<sub>2</sub>O<sub>3</sub>. As a replacement material for SiO<sub>2</sub>, the potential high-κ oxide should form a high-quality interface with Si. We used molecular dynamics (MD) simulation to study the TiO<sub>2</sub>/Si interface. A variable-charge inter-atomic potential was developed to describe the TiO<sub>2</sub>/Si interface where the coordination environment may change. The TiO<sub>2</sub>/Si interface structure was investigated by using MD with simulated annealing technique. The post-annealing oxidation process of the Si substrate was simulated by introducing external O atoms into the system to create concentration gradient. The atomic-scale mechanisms that govern the oxidation process can provide fundamental insight into the formation of the SiO<sub>2</sub> interfacial oxide and a better understanding of the TiO<sub>2</sub>/Si interface structure.

**5:00pm TF-TuA11 Branched Interfacial Organic Layers: Controlling Nucleation and Growth of Thin Films, M. Sharma, A. Dube, K.J. Hughes, J.R. Engstrom, Cornell University**

Organic layers hold great potential for use in modern electronic and optoelectronic devices, owing to both their unique material properties, and their processing properties, such as their tendency towards self-assembly. In the work we describe here we have investigated the use of self-assembled monolayers (SAMs), or more accurately interfacial organic layers (IOLs), that possess a branched backbone for use as nucleation site multipliers and amplifiers. Here we describe the synthesis and characterization of two branched IOLs, their reactivity with precursors for atomic layer deposition (ALD), and the subsequent nucleation and growth of ALD thin films of TiN on these layers. The first IOL we consider is a layer that possesses a regular branched backbone with terminal -NH<sub>2</sub> groups, based on a sequential chemical reactions and application of polyamidoamine (dendrimer) chemistry. Here, an appropriately chosen -NH<sub>2</sub> terminated SAM serves as the anchor, from which additional growth is seeded, forming an IOL with a "Y" backbone and -NH<sub>2</sub> termination. A second IOL we consider is a randomly branched organic film, possessing -OH groups both at terminal points and along the backbone, which have been grown using anionic ring-opening polymerization of glycidol. In both cases the IOLs themselves have been characterized using X-ray photoelectron spectroscopy (XPS), ellipsometry and contact angle measurements. Furthermore, the layers have been characterized concerning their reactivity with two precursors for ALD, Ti[N(CH<sub>3</sub>)<sub>2</sub>]<sub>4</sub> and Ta[N(CH<sub>3</sub>)<sub>2</sub>]<sub>5</sub>, using XPS. For the dendrimer we find that the adsorptive capacity of the surface scales with the generation of the dendrimer, i.e., the branching step effectively doubles the reactivity of the surface. For the poly-G layer, however, we find that sufficiently thick layers can virtually strip the Ta complex of all of its ligands, forming a TaO<sub>x</sub> core. These observations are borne out in the subsequent growth of ALD thin films of TiN on these layers. Nucleation on the dense -NH<sub>2</sub> terminated dendrimer is relatively facile, and STEM shows a highly conformal layer. Growth on poly-G depends sensitively on its thickness-thin layers behave in a manner similar to the dendrimer IOL, whereas thicker poly-G layers

behave more akin to unreactive long-chain -CH<sub>3</sub> layers. We will conclude with a discussion of our results on porous low-κ materials.

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