Thin Films
Room 303C - Session TF-MoM
ALD and Applications

Moderator: S.M. George, University of Colorado

8:20am **TF-MoM1 Atomic Layer Deposited Barriers for Copper Interconnects*, J. Schuhmacher*,** *A. Martin, D. Ernur, Zs. Tőkei, Y. Travaly, C. Bruynseraede, A. Satta, C.M. Whelan, D. Shamiryan, G. Beyer,* IMEC, Belgium*; T. Abell,* Intel affiliate at IMEC, Belgium*; V. Sutcliffe,* Texas Instruments affiliate at IMEC, Belgium*; M. Schaekers, K. Maex,* IMEC, Belgium **INVITED**

Development and properties of a WNC atomic layer deposited (ALD) barrier film in terms of requirements and performance for damascene BEOL process flows are discussed. Damascene type substrates comprise various surfaces. The interaction of a surface with the ALD precursors controls the growth of ALD films. The effects of the substrate are reflected by the characteristics of the transient, non-linear growth period. Examples show the importance of characterizing the nature of the substrate / ALD interaction. Surface preparation before or during the ALD process is a useful tool for improving ALD film quality. An example for the challenges set by the introduction of a new material in an existing process flow is given with the interaction of ALD WNC to the chemical mechanical planarization (CMP) process. Film reliability will be discussed on damascene test structures with ALD WNC in the range of 2 to 10 nm.

9:00am **TF-MoM3 Effects of Surface Chemistry on ALD Ta(N) Barrier Formation on Low k Dielectrics*, J. Liu*,** *J. Bao,* University of Texas at Austin*; M. Scharnberg,* Technische Fakultat der Christian-Albrechts-Universitat, Germany*; P.S. Ho,* University of Texas at Austin

For atomic layer deposition (ALD) of ultra-thin Cu barrier layers, the initial chemisorption at the substrate surface is important in controlling the barrier uniformity and morphology. It is particularly important for organosilicate (OSG) low k dielectrics generally characterized by inactive surface bonds which have to be properly activated for sufficient ALD nucleation. In-situ x-ray photoelectron spectroscopy (XPS) was employed to study the effects of the surface chemistry on ALD Ta(N) barrier formation on two main types of low k surfaces, OSG and SiLK. The initial chemisorption was confirmed to be through formation of Ta-O bonding on OSG films and charge transfer complexes on the aromatic SiLK films. The evolution of the low k surface chemistry revealed an initial transient growth region controlled mainly by the substrate surface chemistry. Pre-treatment of the OSG low k surfaces with nitrogen and hydrogen radical beams, particularly with nitrogen radicals, was observed to enhance significantly the chemisorption of the TaCl@sub 5@ precursor on the OSG surfaces. The enhancement was attributed to the dissociation of the weakly bonded methyl groups from the low k surface followed by surface nitrogen enrichment. The improvement of the growth rate observed in this study illustrates the criticality of the surface coverage at saturation for a successful ALD process. In the subsequent linear growth region, atomic hydrogen species was able to reduce the chlorine content under appropriate temperature and with sufficient purge. The role of the atomic hydrogen in this process enhancement is discussed. In addition, precursor penetration was observed to be suppressed as a result of surface activation on the mesoporous OSG, suggesting a possible approach to pore sealing of porous OSG with halide ALD chemistry.

9:20am **TF-MoM4 Evaluation of Plasma Enhanced Atomic Layer Deposition TaN for Metal Gate Electrode Application*, H. Kim,*** IBM Thomas J. Watson Research Center*; D.-G. Park, P. Ronsheim,* IBM Semiconductor Research and Development Center*; S.M. Rossnagel,* IBM Thomas J. Watson Research Center

TaN has been one of the most attractive materials as a diffusion barrier for Cu interconnect technology due to its good diffusion barrier properties, good adhesion to dielectrics, and high thermal stability. More recently, TaN has been considered as a strong candidate for a direct metal gate material due to its proper work function (~4.3eV) as n-type conductivity. As for the deposition technique of metal gate electrode, previous study on TiN metal gate demonstrated that atomic layer deposition (ALD) has benefits including negligible defect generation and improved device reliability compared to other deposition method. Previously, we have reported that PE-ALD from TaCl@sub 5@ and N@sub 2@/H@sub 2@ plasma produced low resistivity cubic TaN films with various N/Ta ratios with excellent barrier properties for Cu metallization. In this study, PE-ALD TaN was evaluated as a gate electrode for metal-oxide-semiconductor (MOS) capacitors composed of TaN/SiO@sub 2@/p-Si with nanoscale thick (1.8-5.5 nm) SiO@sub 2@ dielectric. For as-patterned MOS structure, the leakage current characteristics were strong functions of N/Ta ratio and plasma power. A dramatic decrease of leakage current with two orders of magnitude was observed with decrease of the plasma power from 500W to 200W. For PE-ALD TaN electrode with stoichiometric N/Ta ratio, we observed a severe damage at SiO@sub 2@/Si interface as observed by a distorted capacitance-voltage (C-V) curve shape near the valence band edge of Si band gap. While the interface damages were partially disappeared after forming gas anneal, the gate leakage current level was remained high. However, the reduction of leakage current was more prominent for TaN@sub x@ films deposited with N@sub 2@ only plasma at both high and low plasma power condition with improved C-V characteristics. Additionally, a comparative study with PVD TaN electrode will be presented focusing on the impurity effect of TaN metal gate.

9:40am **TF-MoM5 Nucleation and Electrical Characterization of Ruthenium formed by Selective Area Atomic Layer Deposition*, K.J. Park*,** *J.M. Doub, G.N. Parsons,* North Carolina State University

Ruthenium is a promising candidate for advanced metal gate electrodes in complementary metal-oxide-semiconductor (CMOS) transistors because of its thermal stability and low resistivity. Ru metal films were deposited by Atomic Layer Deposition (ALD) in a flow tube reactor system using Ruthenocene with oxygen as a reducing reactant on hydrogen terminated silicon, silicon oxide, HfO@sub 2@, as well as patterned organic monolayer surfaces at temperatures ranging from 300 to 375°C. Films were characterized by Auger electron spectroscopy, atomic force microscopy, and capacitance voltage analysis. Self limiting ALD behavior with ~1Å/deposition cycle was observed between ~315 and 350°C at 1.2 Torr operating pressure. At higher temperatures, growth rate per cycle increased indicating the onset of CVD growth conditions. No growth was observed at 300°C on any surface indicating no precursor adsorption, consistent with previous studies of the ruthenocene/oxygen ALD process. The incubation time for deposition was strongly dependent on the substrate. Growth initiated quickly on chemical oxide whereas >100 cycles were required for growth on Si-H surfaces and methyl terminated organic monolayers. The difference in nucleation allowed for selective area deposition of Ru on micron-scale pre-patterned surfaces, where >300Å of growth proceeded on oxide, with no visible deposition on the organic monolayer. Capacitor structures were formed by selective Ru deposition and characterized electrically using various thicknesses of dielectric films. Fitting the flatband voltage vs thickness results in an effective workfunction of 4.8eV on SiO@sub 2@, indicating that selective area deposition may be useful for integration of multiple metals into dual-metal gate CMOS structures. Possible mechanisms associated with nucleation and substrate dependence will be discussed.

10:00am **TF-MoM6 Atomic Layer Deposition for Metal Gate and Capacitor Electrodes*, D.-G. Park,*** IBM Microelectronics **INVITED**

An employment of atomic layer deposition (ALD) method into the semiconductor devices is becoming pivotal because of the excellent attributes offered by ALD process such as good coverage and low impurity level. The ALD technique provides thin film depositions of nanoscale high-permittivity (k) gate dielectrics, metal electrodes, deep metal contact fill, and liners and/or barrier layers of Cu. This paper will review and discuss about the properties of thin ALD films for direct metal gate and capacitor electrodes. As a direct metal gate electrode application, various ALD metal electrodes such as TiN, TaN, and WN films were evaluated on thin SiO2 and high-k gate dielectric films for metal-oxide-semiconductor (MOS) capacitors and transistors. The effects of impurities and process conditions on the MOS devices will be discussed. MOS devices gated with ALD thin films demonstrated much lower defect densities than those with sputtered films by means of lower interface trap density and orders of magnitude lower leakage current. This is most likely a result of the relatively damage-free ALD deposition process. Equivalent oxide thickness of sub-nanometer (< 1nm) was attained with ALD-metal/high-k stack against the thermal budget of complementary MOS device fabrication. Additionally, an application of ALD-TiN film into a capacitor electrode for extremely high aspect ratio (~ 70:1) trench capacitors for sub-100nm trench DRAM devices will be presented. It is necessary to keep focusing on the development of various ALD materials systems to meet device requirements such as relevant work function and stability across the required thermal cycle.

10:40am **TF-MoM8 Infrared Analysis of HfO@sub2@ ALD from Hafnium Diethyl-Amide on SiO@sub2@ and Si-H surfaces*, M.J. Kelly*,** *G.N. Parsons,* North Carolina State University*; J.G. Han, C.B. Musgrave,* Stanford University

An important advantage of atomic layer deposition is the potential to control bond structure at the initial growth interface. Deposition of high dielectric constant metal oxides on silicon typically leads to substrate oxidation and uncontrolled interface structure. To explore mechanisms in interface layer growth, we have used attenuated total internal reflection infrared spectroscopy to study of HfO@sub2@ formation on Si-OH and Si-H terminated surfaces from a tetrakis (diethylamido)hafnium metal organic precursor. Precursor exposure at 200°C on the Si-OH surface results show self-limiting chemisorption consistent with formation of Hf-O-Si bonds with substantial Hf-ethylamine ligands remaining. Exposing the surface to H@sub2@O results in removal of C-H modes, consistent with surface oxidation and formation of Hf-OH surface units. Precursor chemisorption is also observed on the Si-H starting surface, likely due to reaction with some surface OH. Distinct changes in the surface Si-H stretching modes are observed upon precursor adsorption, possibly due to interactions between the amine ligands and the surface hydrogen. Exposing this surface to H@sub2@O does not completely oxidize the surface products, consistent with alternate stable surface bonding configurations, likely involving formation of Si-C or Si-N bonds. Ab-initio results describing potential mechanisms of precursor dissociation and Si-H/ligand interactions will be discussed.

11:00am **TF-MoM9 Area-selective Atomic Layer Deposition for high-@kappa@ Dielectric Materials*, R. Chen*,** *D.W. Porter, S.F. Bent, H.S. Kim, R. Sreenivasan, P.C. McIntyre, H. Jagannathan, Y. Nishi,* Stanford University

Atomic layer deposition (ALD) is a technique that can be used to deposit a variety of materials. While ALD inherently provides nano-scale control of materials in the vertical direction, we are investigating an area-selective ALD technique that enables micro- and nano-scale definition of the lateral structure. Our research emphasizes controlling the substrate surface chemistry in order to impart spatial selectivity to ALD. Using a variety of analytical techniques, we show that functionalizing the surface with self-assembled monolayers (SAMs) can block the ALD chemistry in the growth of HfO@sub 2@ and ZrO@sub 2@, which are both high-@kappa@ materials for potential gate dielectrics. Specifically, we have investigated the surface chemistry needed to block ALD under the more extreme conditions used to deposit these metal oxide dielectrics from metal chloride and water precursors at temperature as high as 300 °C. The efficiency of blocking depends strongly on the quality of the SAMs and the chain length of the attached layer. The potential of the area-selective process for defining lateral structure has been examined using different patterning methods, including selective functionalization of patterned SiO@sub 2@/Si and soft lithography. Using a combination of image analysis by SEM and elemental analysis by scanning Auger microscopy, we demonstrate that the HfO@sub 2@ can be deposited with spatial selectivity. Other types of SAMs have also been investigated as monolayer resists against the HfO@sub 2@ ALD process on Si and Ge substrates. These monolayer films also exhibit good deactivation and selectivity.

11:20am **TF-MoM10 SiO@sub 2@ Atomic Layer Deposition Using HSi[N(CH@sub 3@)@sub 2@]@sub 3@ and H@sub 2@O@sub 2@*, B.B. Burton,*** University of Colorado*; S.W. Kang,* Pohang University of Science and Technology, Korea*; S.M. George,* University of Colorado

The atomic layer deposition (ALD) of SiO@sub 2@ has proven to be challenging. SiO@sub 2@ ALD can be accomplished using SiCl@sub 4@ and H@sub 2@O reactants at 600-800 K with large exposures of ~10@super 9@ L. Catalytic SiO@sub 2@ ALD is also achieved at room temperature with the same reactants but requires the presence of a Lewis base catalyst. Recently, we have observed efficient SiO@sub 2@ ALD with HSi[N(CH@sub 3@)@sub 2@]@sub 3@ and H@sub 2@O@sub 2@ reactant exposures. HSi[N(CH@sub 3@)@sub 2@]@sub 3@ is tris-dimethylaminosilane (Tris-DMAS). SiO@sub 2@ ALD was monitored on high surface area ZrO@sub 2@ particles that allowed the use of Fourier transform infrared (FTIR) spectroscopy to monitor the surface chemistry. Following the H@sub 2@O@sub 2@ exposures, the surface displayed vibrational modes consistent with SiOH* species. Tris-DMAS exposure at 825 K converted these species to Si-N(CH@sub 3@)@sub 2@* species and SiH* species. The subsequent H@sub 2@O@sub 2@ exposure converted these species back to SiOH* species. The exposures required for Tris-DMAS and H@sub 2@O@sub 2@ were ~10@super 6@L and ~10@super 7@L, respectively. These exposures are much more favorable than the ~10@super 9@ L exposures required to grow SiO@sub 2@ ALD films with SiCl@sub 4@ and H@sub 2@O at 600-800 K. Other advantages of using Tris-DMAS are the avoidance of HCl as a byproduct and the elimination of possible chlorine contamination in the SiO@sub 2@ film. The SiO@sub 2@ thin films were deposited at temperatures ranging from 525-825 K. The maximum growth rate of 1.9 Å/cycle at 825 K was determined by measuring the SiO@sub 2@ film thickness on ZrO@sub 2@ particles by transmission electron microscopy (TEM). When the temperature was decreased below 825 K, residual SiH* species were observed in the film and led to a decrease in the SiO@sub 2@ ALD growth rate. SiO@sub 2@ growth was also confirmed by the increase in absorbance from the Si-O-Si asymmetric stretch measured by FTIR spectroscopy.

11:40am **TF-MoM11 Radical-Enhanced Atomic Layer Deposition of Pure and Erbium-Doped Y@sub 2@O@sub 3@ Thin Films***, T.T. Van, **J.P. Chang,*** University of California, Los Angeles

The deposition of pure and Er-doped yttrium oxide thin films, using radical-enhanced ALD (RE-ALD), was investigated in this work. Yttrium oxide can be used as a high dielectric constant material, or as a waveguide material due to its high refractive index and compatibility with high concentration doping of optically active Er@super 3+@ ions. The Y@sub 2@O@sub 3@ films were deposited on Si using alternating pulses of Tris(2,2,6,6-tetramethyl-3,5-heptanedionato)yttrium(III) precursor, or Y(TMHD)@sub 3@, and O radicals. Erbium dopants were incorporated by introducing Er(TMHD)@sub 3@ after every ten ALD cycles of Y@sub 2@O@sub 3@. To assess the feasibility of RE-ALD, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM) were used to determine the chemical composition and distribution, crystallinity, surface morphology, and step coverage of the deposited films. Well-controlled RE-ALD of pure Y@sub 2@O@sub 3@ and Er@sub 2@O@sub 3@ were achieved with both precursors and O radicals. With reactant pulse time ratio of 1:1, stoichiometric films were deposited with minimal carbon incorporation. The ALD window for both materials ranged from 200 to 300°C. Above 300°C, the precursors decomposed, causing significant carbon incorporation into the films. AFM analysis yields a root mean square roughness of less than 5Å for films below 110Å. Conformal deposition of Y@sub 2@O@sub 3@ was achieved over 0.5-µm features with an aspect ratio of 4, determined by cross-sectional SEM. The Er@super 3+@ doping concentration was effectively controlled by varying the ratio of Y@sub 2@O@sub 3@:Er@sub 2@O@sub 3@ cycles. For example, up to 8 at.% of Er@super 3+@ concentration was achieved at 300°C with alternating 10 cycles of Y@sub 2@O@sub 3@ and 5 cycles of Er@sub 2@O@sub 3@. These results indicate that RE-ALD is a viable technique for doping and depositing metal oxide thin films.

Author Index

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