Monday Morning, November 3, 2003

Thin Films
Room 329 - Session TF-MoM

Atomic Layer Deposition
Moderator: S.M. Rossnagel, IBM T.J. Watson Research Center

8:40am **TF-MoM2 Advancements in ALD Chemistry*, M. Ritala,*** University of Helsinki, Finland **INVITED**

The atomic layer deposition (ALD) method has gained continuously increasing interest as a future manufacturing technology for microelectronics, and also several other potential application areas have been pointed out. This interest arises from the excellent conformality and large area uniformity and the atomic level composition and thickness control offered by ALD through its self-limiting film growth mechanism. While the ALD method is currently widely examined worldwide, a majority of the research is still largely focused on rather limited number of processes. A wider application of ALD in microelectronics and elsewhere is directly dependent on the availability of appropriate processes. There is thus a continuous need for developing cost-effective ALD processes for materials of an interest, like metals, metal nitrides, and high-k and ferroelectric oxides. In this presentation, recent advancements in ALD process development will be presented, mostly focusing on metals. Challenges for the future research will be discussed too.

9:20am **TF-MoM4 Incorporation and Control of Silica in Hafnium Silicates using Atomic Layer Deposition Techniques*, M.N. Rocklein,*** *F.H. Fabreguette, S.M. George,* University of Colorado

HfO@sub 2@ and hafnium silicates are leading high-k candidates for replacing SiO@sub 2@ as the gate dielectric in MOSFETs. Advantages of incorporating silica in HfO@sub 2@ are to reduce the interfacial oxide and to prevent crystallization. Very few studies have reported incorporation of silica in HfO@sub 2@ by atomic layer deposition (ALD). We have investigated a new silicon precursor for hafnium silicate ALD. Although sequential exposures of this Si-precursor and H@sub 2@O will not lead to continuous SiO@sub 2@ ALD, growth of hafnium silicates is possible by mixing this Si-precursor and H@sub 2@O exposures together with HfO@sub 2@ ALD from 200 - 260 °C. HfO@sub 2@ ALD is conducted using tetrakis-diethylamidohafnium (TDEAH). Compositional control of the hafnium silicate Hf@sub x@Si@sub (1-x)@O@sub 2@ is achieved by controlling the relative number of Si-precursor/H@sub 2@O and TDEAH/H@sub 2@O reaction cycles. Silica incorporation and control is demonstrated using quartz crystal microbalance (QCM), transmission Fourier tranform infrared (FTIR) spectroscopy and x-ray photoelectron spectroscopy (XPS) investigations. Various reactant exposure sequences yield SiO@sub 2@ content ranging from 0 - 70 %. Hafnium silicate growth rates are also measured and confirmed using a variety of techniques including QCM, spectroscopic ellipsometry, and x-ray reflectance (XRR). Growth rates decrease with increasing SiO@sub 2@ content and vary from 0.65 Å/cycle at 21% SiO@sub 2@ to 0.18 Å/cycle at 67% SiO@sub 2@.

9:40am **TF-MoM5 In-situ Infrared Analysis of Atomic Layer Deposition Half-Reactions: Hafnium Diethyl- Amide Adsorption and Dissociation on SiO@sub2@ and HfO@sub2@*, M.J. Kelly,*** *T.D. Abatemarco, G.N. Parsons,* North Carolina State University

A critical challenge in ALD is to control bond structure at the initial heterostructure interface. For example, the deposition of metal oxide dielectric materials on silicon results in unwanted substrate oxidation and uncontrolled interface structure. To better understand elementary ALD half reactions, we have built an in-situ attenuated total internal reflection infrared spectrometry system, and used it to observe adsorption, desorption and decomposition of Hf diethlyamide [Hf(N(CH@sub 2@CH@sub 3@)@sub 2@)@sub 4@] (HDA) on oxidized silicon and on deposited HfO@sub 2@ at substrate temperatures from 50 to 300°C. The effect of water exposure on adsorbed HDA was also characterized under some conditions. We find that for adsorption on thin HfO@sub 2@ at 50 and 175°C, the C-H stretching modes indicate adsorption and saturation of the molecular precursor at typical dosing pressures (10-40mTorr), followed by desorption upon pumping, consistent with molecular physisorption at low temperature. At 300°C, minimal CH stretching mode adsorption is observed, consistent with rapid decomposition of the precursor upon adsorption. At intermediate temperatures (250°C), non-self-limiting adsorption and decomposition are observed, and Si-O-H bond formation indicates silicon oxidation. Analyzing the precursor uptake curves as a function of temperature, we find that the rate of adsorption on HfO@sub 2@ is thermally activated with an effective barrier of ~0.1eV, consistent with a reduction in entropy upon adsorption. Results will be discussed in terms of the inter-relation of precursor structure and surface pretreatment on the energetics and kinetics of precursor reaction and substrate oxidation.

10:00am **TF-MoM6 Characteristics of Hafnium Aluminate Films for Gate Dielectric Applications Deposited by Atomic Layer Deposition Method*, J. Lee,*** *J. Koo,* Hanyang University, Korea*; Y. Kim,* Pusan National University, Korea*; H. Jeon,* Hanyang University, Korea

The decrease of SiO@sub 2@ gate oxide thickness in sub-100nm metal-oxide-semiconductor (MOS) technology causes high leakage current and serious device reliability problems. To avoid these problems, high-k materials such as HfO@sub 2@ and Al@sub 2@O@sub 3@ have been mainly investigated as a potential candidate to substitute SiO@sub 2@ gate dielectric. However, these high-k materials have some supplement to be solved for applying to MOS device. Hafnium aluminate films would solve relatively high leakage current and low dielectric constant problems of HfO@sub 2@ and Al@sub 2@O@sub 3@, respectively. Hafnium aluminate films were expected to have amorphous structure of Al@sub 2@O@sub 3@ while maintaining high dielectric constant of HfO@sub 2@. Hafnium aluminate films were deposited on p-type Si substrates by atomic layer deposition (ALD) method using HfCl@sub 4@ and trimethylaluminium (TMA) as Hf and Al precursors, respectively, with H@sub 2@O as reaction gas. All samples were rapid thermal annealed at 800°C for 10 seconds in N@sub 2@ ambient. Forming gas anneal was performed in an H@sub 2@+N@sub 2@ atmosphere at 450°C for 30 minutes after Pt gate electrode deposition. The physical and chemical properties were analyzed by cross sectional transmission electron microscope (XTEM), Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS). The electrical and reliability characteristics including equivalent oxide thickness (EOT), hysteresis, leakage current and interface defects were analyzed by I-V and C-V measurements. In this study, the characteristics of hafnium aluminate films for gate dielectric applications deposited by atomic layer deposition method were investigated. The chemical compositions and heat-treatments effects on the electrical and reliability characteristics of hafnium aluminate films for gate dielectric applications will be mainly presented. @FootnoteText@ @footnote 1@M. Leskela, M. Ritala, Thin Solid Films, 409(2002), 138, 146.

10:20am **TF-MoM7 Atomic Layer Deposition of Transition Metal Films*, R.G. Gordon,*** Harvard University **INVITED**

Effective reactions have been discovered for ALD of many metal compounds, including oxides, nitrides, sulfides and fluorides. However, ALD of pure metals has proven to be more difficult. Tungsten and ruthenium are the only metals previously deposited from molecular precursors by self-limiting, complementary ALD reactions. ALD of titanium, tantalum, copper and aluminum used atomic hydrogen as a reactant, which limits the step coverage attainable in deep trenches because of the rapid recombination of hydrogen atoms. It is also difficult to design ALD apparatus to distribute hydrogen atoms over large areas, and to avoid plasma damage to substrates. We synthesized many new metal acetamidinates, a class of metal precursors that we designed to have the properties needed for ALD of metals. These compounds have the required high thermal stability because two metal-nitrogen bonds hold each ligand onto the metal (chelate stabilization). Nevertheless, each metal-nitrogen bond is individually weak (formally a bond order of only one half) and highly reactive. The high volatility of these metal compounds (vaporization temperatures less than 100 C) arises from the outer surfaces of the molecules being entirely saturated hydrocarbons. For example, homoleptic N,N'-diisopropylacetamidinato metal compounds and molecular hydrogen gas were used as ALD reactants to form highly uniform and conformal thin films of transition metals including iron, cobalt, nickel and copper. We propose that these ALD layers grow by a catalytic hydrogenation mechanism that should also operate during the ALD of many other metals. The process should allow improved production of many devices, such as copper interconnections in microelectronics, magnetic information storage, micro-electromechanical structures and catalysts. Use of water vapor in place of hydrogen gives highly uniform, conformal films of metal oxides, while ammonia gives metal nitrides.

11:00am **TF-MoM9 Demonstration of AlN ALD Using Hydrazine as the Nitrogen Precursor*, F.H. Fabreguette,*** University of Colorado*; T.E. Seidel,* Genus, Inc.*; S.M. George,* University of Colorado

Aluminum nitride (AlN) has attracted widespread attention due to its remarkable thermal, electronic and mechanical properties leading to

numerous applications. AlN growth by chemical vapor deposition (CVD) is accomplished using trimethylaluminum (TMA) and ammonia (NH@sub 3@) precursors. AlN atomic layer deposition (ALD) has also been attempted using TMA and NH@sub 3@. Unfortunately, high ALD temperatures are required where TMA pyrolysis is a problem. Lower ALD reaction temperatures where TMA will not decompose can be obtained using hydrazine, N@sub 2@H@sub 4@ , as the nitrogen precursor. This study presents the use of hydrazine as a new route for AlN ALD at temperatures as low as 177°C. AlN ALD using both ammonia and hydrazine was monitored and compared using an in-situ quartz crystal microbalance (QCM). ALD uptake curves showed 'soft' saturation behavior for the TMA half-reaction and 'hard' saturation for the hydrazine half-reaction. The AlN growth rate using hydrazine was found to be about 1.0 Å/cycle at 177°C. The ammonia reactant produced a growth rate < 0.1 Å/cycle. Different characterizations were performed on the AlN ALD films grown at 177°C. Ellipsometry and x-ray reflectivity confirmed a growth rate of about 1 Å/cycle. The AlN ALD films were determined to be amorphous by x-ray diffraction and smooth when measured by atomic force microscopy. X-ray photoelectron spectroscopy showed aluminum and nitrogen in the films and an oxide surface layer. Electrical measurements for the dielectric constant and the leakage current density were in good agreement with results from AlN CVD films. This study demonstrates the potential of hydrazine as a suitable nitrogen precursor for low temperature AlN ALD.

11:20am **TF-MoM10 Low Temperature Deposition of SiN using Sequential Exposures of Si@sub 2@Cl@sub 6@ and NH@sub 3@***, J.Y. Ahn, J.G. Kim,* ***J.W. Lim****, H.S. Kim, U. Chung, J.T. Moon,* Samsung Electronics, Korea

Low temperature deposition of SiN is required in many applications for fabrication of high performance MOSFET devices. SiN films were deposited by atomic layer deposition (ALD) and cyclic chemical vapor deposition (CVD) using sequential exposures of Si@sub 2@Cl@sub 6@ and NH@sub 3@ at temperatures ranging from 400 to 600°C. The films were deposited in a mini-batch reactor employing cross-wafer gas flow scheme for rapid delivery of precursors and rapid evacuation of reactants. The saturated growth rate of ALD-SiN was 2.2Å/cycle. The films were characterized by AES, AFM, FTIR, RBS, SIMS, SEM, spectroscopic ellipsometry and TEM. The wet etch and reactive ion etch (RIE) characteristics were also investigated. ALD-SiN films are smooth, highly conformal and stoichiometric. In addition, they contain less hydrogen than the conventional LPCVD-SiN films deposited at equivalent temperatures, and exhibit high etch selectivity to SiO@sub 2@. The RIE selectivity to SiO@sub 2@ was determined to be nearly constant within the temperature range of 400-600°C. The properties of the films deposited by cyclic CVD method, in which self-limited surface saturation is not obtained, were comparable to ALD-SiN, and the Si:N ratio of cyclic CVD-SiN is controllable in the range of 0.7 - 1.0 by varying the Si source exposure and dilution. The electrical properties of the ALD and cyclic CVD films were evaluated by performing I-V and C-V measurements with MIS (Metal Insulator Silicon) capacitor structures. The physical and electrical properties of cyclic CVD films deposited at 590°C were as good as the conventional LPCVD films deposited at 700°C using DCS/NH@sub 3@ chemistry, and therefore the thermal budget for device fabrication can be reduced using cyclic CVD-SiN. The suitability of ALD-SiN films deposited at 450°C was reviewed for fabrication of high performance CMOS devices employing NiSi module process.

11:40am **TF-MoM11 Atomic Layer Deposition on Fine Particles***, J.D. Ferguson, A.W. Weimer,* ***S.M. George****,* University of Colorado

Because of the self-limiting nature of the sequential surface reactions in atomic layer deposition (ALD), atomic layer controlled and conformal films can be deposited on fine particles. Our recent work has investigated coatings on BaTiO@sub 3@ particles that are used to fabricate multilayer capacitors. SiO@sub 2@ has been coated on BaTiO@sub 3@ particles using NH@sub 3@-catalyzed SiO@sub 2@ ALD with tetraethoxysilane (TEOS) and H@sub 2@O as the reactants. ZnO has been coated on BaTiO@sub 3@ particles using ZnO ALD with diethylzinc (DEZ) and H@sub 2@O as the reactants. The ALD surface chemistry has been investigated using Fourier transform infrared (FTIR) spectroscopy. The FTIR studies observe the exchange of surface species as expected from the surface chemistry. In addition, the growth of the bulk SiO@sub 2@ and ZnO films versus number of reactant cycles is also observed in the FTIR spectra. Further confirmation of the SiO@sub 2@ ALD and ZnO ALD is obtained from transmission electron microscopy (TEM) analysis of the BaTiO@sub 3@ particles. The TEM analysis reveals conformal SiO@sub 2@ films with a SiO@sub 2@ growth rate of 0.7 Å per TEOS/H@sub 2@O reaction cycle at 300 K. TEM measurements also observe conformal ZnO films with a ZnO growth rate of 2.2 Å per DEZ/H@sub 2@O reaction cycle at 450 K. Additional FTIR and TEM studies have explored Al@sub 2@O@sub 3@ ALD on polyethylene (PE) particles at 350 K using trimethylaluminum (TMA) and H@sub 2@O as the reactants. The deposition of inorganic oxides on polymers may be important as gas diffusion barriers for packaging applications. The FTIR investigations observe the exchange of surface species during Al@sub 2@O@sub 3@ ALD and the growth of Al@sub 2@O@sub 3@ bulk features. The TEM measurements reveal a conformal Al@sub 2@O@sub 3@ film on the surface of the PE particles. ALD on large quantities of fine particles will be demonstrated using fluidized particle bed ALD reactors.

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