Thin Films
Room 306 - Session TF-TuA
Atomic Layer Deposition - Metals

Moderator: S. Rossnagel, IBM

2:00pm **TF-TuA1 Materials Available by ALD*, R.G. Gordon,*** Harvard University **INVITED**

Atomic later deposition (ALD) can deposit pure thin films with precisely-controlled, uniform thickness and composition over large areas and on aggressive topologies. ALD is a vapor deposition process based on sequential self terminating surface reactions where the precursor vapors are injected separately in pulses added to a flowing carrier gas, separated by a purge of excess precursor vapor. Each pulse and purge sequence constitutes an ALD half-cycle. Ideally, each half-cycle adds a uniform new layer of material and then the reaction stops even if more precursor vapor arrives at the surface. This self-terminating character results in ALD's uniformity, conformality and precise thickness control. To achieve ALD's unique characteristics, ALD precursors must have very specific properties: high reactivity with surfaces (but not with themselves), high thermal stability, along with adequate volatility. In addition, their reaction byproducts must not react with the deposited films. Precursors with metal-nitrogen bonds have been found to be particularly effective for ALD of metal oxides, nitrides, silicates, phosphates and pure metals: dialkylamides of Al, Sn, Ti, Zr, Hf, Nb and Ta; dialkylamide-alkylimide mixed ligand compounds of Nb, Ta, Mo and W; dialkylacetamidinates of Mg, Ca, Sc, Ti, V, Cr, Mn, Fe, Ru, Co, Ni, Cu, Bi, Y, La and the other lanthanide metals. Examples of the materials made from these precursors include high-k dielectric insulators HfO@sub 2@, HfON, HfSiON and LaAlO@sub 3@; electrical conductors of Cu; conducting Cu diffusion barriers of WN and TaN@sub x@; metals Co and Ru that promote strong adhesion between Cu and nitride diffusion barriers; magnetic metals Fe, Co and Ni and their magnetoresistive combinations with Al@sub 2@O@sub 3@ or MgO; photonic crystals of high-dielectric constant material Ta@sub 3@N@sub 5@; insulating AlN for passivating Ge surfaces; conformal silica layers for insulation in microelectronics, and for optical interference filters and nano-optical devices.

2:40pm **TF-TuA3 Ru ALD and Applications for Advanced Devices*, H. Lee,*** *S.J. Lim, W.J. Maeng, H. Kim,* POSTECH, South Korea

Ru has good properties such as low resistivity, high thermal stability, and nobility. Thus, the atomic layer deposition (ALD) of Ru has been required for many applications in nanoscale device fabrication including memory capacitor electrode, Cu electroplating seed layer, and CMOS gate electrode with the scaling of devices. Although ALD of Ru has been reported by several groups previously, there are still crucial problems to be solved including the poor nucleation and practical limitation caused by the use of oxidant as a reactant. To address these problems, we have performed comparative studies using different Ru precursors including cyclopentadiel, pentadienyl, and carbonyl based precursors on various practically important substrates including Si, SiO@sub 2@, Ta@sub 2@O@sub 5@, TaN, and TiN. Also, plasma enhanced ALD using hydrogen and nitrogen plasma has been performed. Very low resistivity (as low as 10µ@ohm@cm) Ru with excellent conformality was obtained and the in situ plasma treatment produced promising results to enhance nucleation behavior. The microstructure of Ru layer as well as interface between Ru and substrates and chemical and electrical properties have been characterized. The results will be discussed focusing on the future semiconductor device applications including electrode and Cu electroplating seed layer.

3:00pm **TF-TuA4 Atomic Layer Deposition of Ruthenium on Organic Self Assembled Monolayers for Work Function Tuning*, K.J. Park,*** *D.B. Terry, G.N. Parsons,* North Carolina State University

Ruthenium is of interest for advanced metal/oxide/ semiconductor (MOS) transistor gate electrodes to reduce poly-silicon depletion and as a nucleation layer for copper interconnects. Patterned self assembled monolayers have previously been used to impede nucleation during ALD processing. In this work, metal atomic layer deposition was achieved on self-assembled monolayers, where the tail groups were chosen to promote, rather than impede nucleation, and the effect of the monolayer on the work function of the metal in an MOS capacitor is characterized. Specifically, Ru was deposited using bis-(cyclopetandienyl) ruthenium and oxygen onto HfSiO@sub x@, SiO@sub 2@, and onto 3-aminopropyltriethoxysilane (APTES) and undecenyl tricholosilane (UDS) monolayers formed on HfSiO@sub x@. Self-limiting atomic layer deposition was achieved at temperatures between ~310° and 350°C, corresponding to ~1 Å per deposition cycle. Capacitance vs. voltage (CV) with various thicknesses of dielectric was measured at 1MHz using p-type silicon substrates with doping levels of 1.5x10@super 18@ cm@super -3@, to determine the effective workfunction (@PHI@@sub m,eff@) of the ALD metal. The organic monolayer undergoes some reaction and modification during the metal ALD step, however CV measurements show relatively stable behavior at room temperature, with large changes observed after a 400°C forming gas anneal, suggesting stability of the monolayer during deposition. Ru on untreated HfSiO@sub x@ gives @PHI@@sub m,eff@ = 4.7 eV, whereas the APTES treated surface shows an increase in @PHI@@sub m,eff@ to about 4.8 eV, and a decrease to about 4.2 eV for the UDS surface. The shifts are consistent with dipoles in the monolayers at the organic/dielectric interface. The ability to deposit metal by ALD onto organic surfaces will likely be useful for a variety of advanced organic device structures.

3:20pm **TF-TuA5 Quartz Crystal Microbalance Measurements of W ALD Nucleation on Al@sub 2@O@sub 3@*, R.A. Wind*,** *F.H. Fabreguette, S.M. George,* University of Colorado

Nucleation phenomena can critically affect the growth of nanolaminates using atomic layer deposition (ALD). A good example is W/Al@sub 2@O@sub 3@ nanolaminates where the nucleation of W ALD on Al@sub 2@O@sub 3@ limits the minimum thickness of a continuous and ultrasmooth W nanolayer to ~25 Å. Quartz crystal microbalance (QCM) studies can measure the mass gain per cycle (MGPC) during ALD with a precision of ~0.4 ng/cm@super 2@. QCM investigations of W ALD nucleation on Al@sub 2@O@sub 3@ reveal complex behavior. During optimum nucleation conditions, WF@sub 6@ exposures lead to mass gain but Si@sub 2@H@sub 6@ exposures produce no measurable mass gain for the first 2 cycles. After 3 cycles, the MGPC for both reactants increases and reaches a maximum after 8 cycles for WF@sub 6@ and after 12 cycles for Si@sub 2@H@sub 6@. The total MGPC exhibits a "ringing" behavior and a second maximum is observed before reaching the steady state growth rate. For different reactant exposures, the positions of the first and second maxima in the MGPC shift to a longer number of cycles. Modeling of these QCM results is in agreement with three-dimensional W island growth that produces a maximum in the MGPC. This maximum corresponds to the largest W surface area prior to the coalescence of the W islands. The existence of these W islands is confirmed by atomic force microscope (AFM) measurements. The changing ratio of the WF@sub 6@ and Si@sub 2@H@sub 6@ MGPCs is consistent with distinct growth regimes. These different ratios suggest that the relative density of reactive surface sites evolves as W islands are created, grow, and coalesce prior to forming a continuous W film.

3:40pm **TF-TuA6 Novel ALD Reactor Design and Metrology Study for Tungsten ALD Process*, W. Lei,*** *L. Henn-Lecordier, G.W. Rubloff,* University of Maryland

We have developed a novel wafer-scale atomic layer deposition (ALD) reactor which incorporates small reaction volume for short cycle time, multi-mode operation for process flexibility, and in-situ chemical sensing for rapid process learning and control. A movable cap within the UHV chamber enables transfer and enclosure of the wafer within a 0.2 L mini-reactor. Operation is possible using steady-state flow with alternating gas species or using fill-and-pumpout cycling of each gas with pumpout acceleration by lifting the cap to employ the larger reactor volume as ballast. Downstream in-situ mass spectrometry (MS) provides direct process sensing. By integrating reaction product MS signal over each exposure, we are able to observe nucleation and linear film growth stages of ALD film growth and study nucleation kinetics under different process and initial surface conditions, which indicated the application of in-situ MS for advanced process control in ALD process. First wafer effects in in-situ MS sensing are apparent when a sequence of wafers are processed, particularly when time delays are introduced between wafers; this is attributed to concurrent reaction on mini-reactor walls, where different gas exposure history is encountered. Advanced process control can be improved by proper pre-process reactor treatment to reduce first wafer effect.

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