## Thin Films
## Room 203 - Session TF-MoA

### Atomic Layer Chemical Vapor Deposition II

**Moderator:** S.M. Rossnagel, IBM T.J. Watson Research Center

2:00pm **TF-MoA1 The Effect of Atomic Layer CVD Flow Parameters on the Growth Orientation of AlN Thin Films**, ***J.N. Kidder***, *J.W. Rogers, T.P. Pearsall,* University of Washington

We have observed a strong dependence of growth orientation on reactant pulse length in an atomic layer CVD of AlN. The AlN thin films were deposited on Al@sub2@O@sub3@ and Si substrates at 523-723 K and 25 Torr using an amine-alane Al source. The Al precursor, dimethylethylamine alane (DMEAA) and ammonia were delivered to the growth surface in separate steps. Strict self-limited adsorption did not occur for the DMEAA at these process conditions but a kinetic barrier to rapid decomposition of DMEAA coupled with process flow control provided a means to generate film formation through a sequence of adsorption/reaction steps. We observed that film microstructure was strongly dependent on ALCVD pulse lengths and substrate temperature. By this process, crystalline AlN films were deposited at temperatures as low as 573 K. AlN films deposited on Si(100), Si(111), Al@sub2@O@sub3@(00.1) tended to show a preferred orientation with the AlN{00.1} planes aligned parallel to the substrate surface. AlN{11.0}oriented growth was observed on Al@sub2@O@sub3@(01.2)substrates. The growth orientation was strongly dependent on the pulse length and substrate temperature. Both random and well-oriented films were deposited on Al@sub2@O@sub3@(00.1). By varying the reactant flow sequence the growth orientation on Al@sub2@O@sub3@(01.2) could be controlled to be either AlN{00.1} or AlN{11.0}oriented. X-ray four circle diffractometry scans showed in-plane orientations associated with epitaxial alignment for films deposited at temperatures as low as 673 K. These results illustrate the potential for using sequential reactant delivery in CVD to tailor the microstructure of thin film materials.

2:20pm **TF-MoA2 Atomic Layer Deposition (ALD) Films for Advanced Capacitors**, ***O. Sneh***, *R.C. Phelps, T. Seidel,* Genus, Inc.

We will present new data on Atomic Layer Deposition (ALD) films. Films were deposited on our recently announced dielectric ALD processing module. Our ALD process equipment, now at beta phase, is a single wafer 200 mm process module that operates and fully integrates with Genus Lynx2 cluster tool. Data pertain for as deposited, fully stoichiometric Al@sub 2@O@sub 3@ and Ta@sub 2@O@sub 5@ films that are continuous and amorphous in the useful range of 15-200 Å, will be presented. CV and IV measurements indicate leakage current in the 10@super -8@ A/cm@super 2@ range for these films in the useful thickness range and dielectric constants of ~7.5 (Al@sub 2@O@sub 3@) and ~25 (Ta@sub 2@O@sub 5@). Step coverage over >15:1 aspect ratio structures with 100 nm width is 100 %. Supporting data will be presented and discussed. We will review data for dielectric films on silicon as well as over CVD and ALD deposited metal nitride thin films. Some aspects and applications of MIM and SIS capacitor technology development will be reviewed.

2:40pm **TF-MoA3 Tungsten Atomic Layer Deposition: Nucleation and Growth on Oxide Surfaces**, ***S.M. George***, *J.W. Klaus, J.W. Elam, C.E. Nelson, R.K. Grubbs, S.J. Ferro,* University of Colorado **INVITED**

Tungsten atomic layer deposition (ALD) can be accomplished by separating the binary reaction WF@sub6@ + Si@sub2@H@sub6@ --> W + 2SiHF@sub3@ + 2H@sub2@ into two self-limiting half-reactions.@footnote 1@ The two self-limiting half-reactions are: (A) W-SiHF@sub2@* + WF@sub6@(g) --> W-WF@sub5@*+ SiHF@sub3@(g); and (B) WF@sub5@* + Si@sub2@H@sub6@(g) --> W-SiHF@sub2@* + 2H@sub2@(g) + SiHF@sub3@(g). In situ FTIR spectroscopy studies have determined the temperatures and pressures required for these two half-reactions to reach completion. In situ spectroscopic ellipsometry studies have examined the growth of W ALD films. Successive exposure to WF@sub6@ and Si@sub2@H@sub6@ in an ABAB... reaction sequence produced W ALD at a rate of 2.5 Å per AB cycle at 425 K. The nucleation and growth during W ALD on SiO@sub2@ and Al@sub2@O@sub3@ surfaces have also been studied using Auger electron spectroscopy (AES). The AES results displayed an initial nucleation period of several AB cycles. After the deposition of one tungsten monolayer, the AES signals for W and Si oscillated dramatically versus WF@sub6@ and Si@sub2@H@sub6@ exposures. These studies indicated that W ALD displays nearly ideal layer-by-layer (Frank van der Merwe) growth after the initial nucleation period. W ALD can be used together with Al@sub2@O@sub3@ ALD@footnote 2@ to fabricate W/Al@sub2@O@sub3@/W/Al@sub2@O@sub3@ nanolaminates. Cross-sectional transmission electron microscopy (TEM) studies have examined the W/Al@sub2@O@sub3@/W/Al@sub2@O@sub3@ nanolaminates deposited on Si(100). The growth of the nanolaminates is dependent on the details of the surface chemistry during the nucleation of W ALD on Al@sub2@O@sub3@. @FootnoteText@ @footnote 1@ J.W. Klaus, S.J. Ferro and S.M. George, Thin Solid Films 360, 145 (2000). @footnote 2@ A.W. Ott, J.W. Klaus, J.M. Johnson and S.M. George, Thin Solid Films 292, 135 (1997).

3:20pm **TF-MoA5 Radical Enhanced Atomic Layer Deposition (ALD) of Diffusion Barrier Films at Low Temperatures**, ***A. Sherman***, *F. Turner,* Sherman & Associates*; C. Pan,* ASM America*; S.M. Rossnagel,* IBM T.J. Watson Research Center **INVITED**

Atomic Layer Deposition (ALD) processes can be extended to low deposition temperatures by the use of an appropriate free radical in place of a conventional molecular reactant. Typically, the ALD process has been carried out using stable gaseous reactants, and the surface reaction was thermally driven in the temperature range of 300-400°C. Radical enhanced ALD has been carried out for the deposition of Ti, TiN, Ta, TaN, and Al@sub 2@O@sub 3@ at temperatures from room temperature to 400°C. Remote inductive plasma sources, operating at frequencies from 400 KHz to 13.56 MHz were used to generate free radicals from O@sub 2@, N@sub 2@, H@sub 2@ and NH@sub 3@ gas sources. Residual gases in the reactor chamber were removed after each dosing step by evacuating the chamber with a vacuum pump, rather than purging with an inert gas. Titanium films were deposited from 25-250°C using titanium tetrachloride and hydrogen. The conformality in high aspect ratio vias and the thickness uniformity across 200 mm wafers was excellent. Tantalum films were deposited using tantalum pentachloride and hydrogen at temperatures from 25-400°C. Additional experiments have been carried out using TDMAT (tetrakis(dimethylamido)titanium) at room temperature to deposit titanium bearing films. Aluminum oxide films were deposited at room temperature from TMA (trimethyl aluminum) and oxygen. Experimental results, including SEM observations in high aspect ratio features, as well as chemical analysis (RBS, XPS, AES) and structural (XRD) measurements will be reported.

4:00pm **TF-MoA7 Vacuum Beam Studies of Radical Enhanced Atomic Layer Chemical Vapor Deposition**, ***F. Greer***, *D. Fraser, J.W. Coburn, D.B. Graves,* University of California, Berkeley

As device dimensions continue to shrink and aspect ratios continue to increase, it will become increasingly difficult to deposit highly conformal thin films for applications such as Cu diffusion barrier layers. Atomic Layer Chemical Vapor Deposition (ALCVD) has been proposed as one way to achieve these highly conformal thin films due to the layer-by-layer growth that is possible when a precursor and a stable reactive specie are introduced sequentially into a deposition chamber. One problem with conventional ALCVD is that the deposition temperatures that are required to achieve reasonable growth rates can be relatively high, and may be incompatible with the integration of these barrier films with temperature-sensitive films such as organic low-k materials.@footnote 1@ It has been recently proposed that by using a more reactive specie like a radical as the second reactant, atomic layer film deposition at lower temperatures may be possible.@footnote 2@ It may also be possible to find radical surface treatments that either promote or hinder adsorption of the precursor specie on different surfaces, allowing even more control over the deposition process. This work focuses on the tetrakisdiethylamide class of precursors for the deposition of nitrides and other films. By directing independent beams of these precursors and hydrogen radicals at different surfaces (inc. Si, SiO@sub 2@, and Au), deposition parameters of interest such as the sticking and reaction probabilities of these compounds have been measured as a function of temperature and surface preparation. The products evolved from the surface during each step of the deposition process, including the precursor ligands and surface reaction products, have also been measured using modulated beam mass spectrometry as a function of these same parameters. XPS analysis of the deposited films will also be presented. @FootnoteText@ @footnote 1@A. Satta et al. Spring MRS Meeting 2000 D6.5 @footnote 2@A. Sherman US Patent 5916365.

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