Thin Films
Room 329 - Session TF-MoA
Atomic Layer Deposition and Low-k

Moderator: S.M. George, University of Colorado

2:00pm **TF-MoA1 The Application of Plasma for Metal Atomic Layer Deposition for Cu Interconnect Technology**, *S.M. Rossnagel, **H. Kim**,* IBM T.J. Watson Research Center **INVITED**

As the semiconductor dimensions scale down to sub-65 nm regime with implementation of Cu interconnect technology, the need for introducing metal thin film deposition techniques with excellent conformality and thickness control at the nanometer scale has been increased. Atomic layer deposition (ALD) is expected to play an important role in depositing thin layers in nanoscale Si device manufacturing. Among the key materials used for modern semiconductor processing, thin films of inert, refractory or noble materials will continue to be used in interconnect applications as diffusion barriers, seed and adhesion layers as well as potential front end applications such as contacts or gate metallization. The plasma technologies that have been widely used for various aspects of the semiconductor device processing can be extended into ALD areas. Plasma enhanced ALD (PE-ALD) allows deposition at significantly lower temperatures with better film properties than both conventional thermal ALD and chemical vapor deposition. This low temperature process makes PE-ALD more attractive for emerging low-k interconnect materials. In addition, since ALD is surface-sensitive deposition technique, surface modification by plasma exposure can be used to alter nucleation and adhesion. In this presentation, we will present the PE-ALD of Ta-based thin films for Cu interconnect technology and the surface modification by plasma for metal and nitride ALD processes.

2:40pm **TF-MoA3 Copper Atomic Layer Deposition Using In Situ-Generated Cu@sub 3@Cl@sub 3@ and Hydrogen Radicals**, ***M.D. Groner**, S.M. George,* University of Colorado

Copper (Cu) atomic layer deposition (ALD) has been achieved using in situ-generated Cu@sub3@Cl@sub3@ and hydrogen radicals. The Cu ALD chemistry involves copper chloride adsorption on the substrate followed by copper chloride reduction to copper metal using hydrogen radicals. The copper chloride precursor, Cu@sub3@Cl@sub3@, is generated in situ when a small Cl@sub2@ or SnCl@sub4@ gas pulse transported by a carrier gas contacts a high surface area Cu braid at T> 200 °C. The in-situ generation of Cu@sub3@Cl@sub3@ overcomes the stability problems associated with using a heated CuCl source to generate the copper chloride. The Cu ALD is performed using a "moving sample" reactor in which a pneumatic transfer arm shuttles the sample between the Cu@sub3@Cl@sub3@ dosing region and the inductively coupled plasma (ICP) hydrogen radical source. This reactor design is important because close proximity to the hydrogen radical source is necessary to overcome efficient hydrogen radical recombination on the reactor walls. Cu ALD films have been grown on glass, sapphire, and silicon substrates. The Cu ALD films nucleate well on the various substrates after hydrogen radical exposures. Cu ALD growth rates of >1 Å/cycle have been achieved as determined by real-time in situ optical thickness measurements of the Cu film growth. The Cu films are very shiny and copper-colored and display a high reflectivity. X-ray diffraction (XRD) analysis of the Cu films show distinct (111), (200), (220) and (311) diffraction peaks with no additional XRD peaks. Preliminary studies have shown successful Cu ALD at substrate temperatures ranging from ~200-260 °C. Further results will be presented on the dependence of growth temperature, copper chloride precursor exposure and hydrogen radical exposure.

3:00pm **TF-MoA4 Dynamic Equipment and Process Simulation for Atomic Layer Deposition Technology**, ***W. Lei**, Y. Cai, L. Henn-Lecordier, G.W. Rubloff,* University of Maryland

While the self-limiting growth of atomic layer deposition (ALD) makes it a promising process for thin film deposition, the rapid precursor gas cycling required poses manufacturability challenges. We have developed dynamic simulation models for equipment and process behavior to explore the influence of detailed design on : (1) surface chemistry and resulting material quality; (2) manufacturing throughput; (3) materials utilization for environmental (ESH) and cost metrics; and (4) real-time sensor system design for integrated metrology and advanced process control. The dynamic simulators are flexible in accommodating a variety of process and surface chemistries as well as equipment designs. For a mini-chamber design motivated by manufacturing throughput requirements, we have compared operational modes based on static vs. dynamic gas flow, which shows ESH benefits for the former without sacrifice of throughput. The simulator reveals time-dependence analysis of ALD dynamics as a function of surface chemistry and equipment design, providing guidance for integrated metrology. Based on these results, we are developing a novel ALD reactor for process and metrology development which emulates the conditions found in emerging commercial reactors. @FootnoteText@ Supported by the National Institute of Science and Technology and by the NSF/SRC Center for Environmentally Benign Semiconductor Manufacturing.

3:20pm **TF-MoA5 Al@sub 2@O@sub 3@ Atomic Layer Deposition for the Enhancement of MEMS Performance and Reliability**, ***C.F. Herrmann**, N.D. Hoivik, F.W. DelRio, V.M. Bright, Y.C. Lee, S.M. George,* University of Colorado

Ultrathin and conformal films deposited using Atomic Layer Deposition (ALD) can enhance the reliability and performance of MEMS devices. Al@sub 2@O@sub 3@ ALD films are particularly useful because the Al@sub 2@O@sub 3@ ALD surface chemistry is very favorable and amenable to growth on a wide variety of substrates. Al@sub 2@O@sub 3@ ALD films on electrostatically-actuated polysilicon cantilever switches were found to prevent electrical shorting and increase the number of actuation cycles before device failure. In addition, the resonant frequencies of the cantilever beams were also increased by Al@sub 2@O@sub 3@ ALD films resulting from added stiffness. ALD can also be utilized to deposit robust and reliable hydrophobic coatings. The initial MEMS device is optimized for hydrophobic precursor attachment by: 1) covering the MEMS surface uniformly with a continuous adhesion layer; 2) providing a high surface coverage of hydroxyl groups for maximum precursor attachment; and 3) smoothing and removing nanometer-sized capillaries that may otherwise lead to microcapillaries and stiction problems. Quartz crystal microbalance (QCM) studies have been used to monitor the attachment of various chlorosilane and dialkylaminosilane hydrophobic precursors on the Al@sub 2@O@sub 3@ ALD adhesion layer. The QCM results are consistent with the deposition of a dense hydrophobic film on the Al@sub 2@O@sub 3@ adhesion layer. The hydrophobic films on Al@sub 2@O@sub 3@ ALD adhesion layers on silicon wafers were observed to increase dramatically the contact angle. The film properties and adhesion energies were also measured for hydrophobic films on MEMS cantilever beams. After submersion in water, the hydrophobic-coated beams showed much less stiction than the uncoated beams.

3:40pm **TF-MoA6 Processes and Properties of Porous CVD Low-k Materials**, ***Y. Travaly**, M. Van Hove, G. Beyer,* IMEC / SPDT / ITSMI, Belgium*; K. Maex,* IMEC / SPDT, Belgium **INVITED**

The aggressive down scaling of device dimensions in integrated circuits requires the introduction of non-traditional materials such as porous CVD low-k dielectrics together with thinner copper diffusion barrier with improved step coverage and conformality along via and trench side walls. This results in a number of concerns with respect to both the low-k film and Cu diffusion barrier to be implemented. Regarding the low-k dielectric, it appeared over the last few years, that not only its electrical properties are of importance but also its compatibility with the process steps encountered in the course of its integration. We therefore identified a number of key properties such as porosity, bulk diffusion of wet chemicals, slurries and barrier precursors, etc. and studied them in relation with surface sealing by plasma treatments, liner deposition or metallic barrier. For the Cu barrier, a number of factors come into play and influence dramatically the interconnect delay (RC delay) especially for the most aggressive pitches. Among these factors, one can easily control the quality of the barrier interface with the low-k or the Cu as well as the minimum barrier thickness. The cross-sectional barrier profile in interconnect appears also to be of prime importance for both RC delay and barrier reliability. To improve the step coverage and minimize the barrier area, we have considered various approaches including a highly conformal atomic layer deposition (ALD) process. However, when used in combination with porous low-k dielectrics, an ALD process gives rise to other issues such as the diffusion and interaction of ALD precursors with the various layers (low-k, hard masks) present in the dielectric stack. We studied these interactions and identified suitable methods to prevent detrimental effects. Ultimately, we studied the reliability of the Cu/low-k system in relation to barrier integrity.

4:20pm **TF-MoA8 Deposition of Low k OSG Films Exhibiting Enhanced Mechanical Properties by PECVD**, *J.L. Vincent, R.N. Vrtis,* ***A.S. Lukas,*** *M.L. O'Neill, B.K. Peterson, M.D. Bitner, G.J. Karwacki,* Air Products and Chemicals, Inc.

Silica is the traditional insulating material used in interlayer dielectrics and has a k of 3.9-4.2. To achieve the lower k's required for the next generation of IC's, methyl (Me) groups may be added to the silicate structure by using organosilane precursors. The lower k in the resulting organosilicate glass (OSG) is attributed to the decreased density, increased hydrophobicity, and reduction of the polarizability of the material. We previously demonstrated the use of diethoxymethylsilane (DEMS) to deposit OSG films by PECVD with k's of 2.7-3.3 (dense) and 2.0-2.5 (porous). However, this decrease in k comes at the expense of the mechanical properties due to the disruption of the silicate network by terminal Si-Me. Our modeling studies show that the benefit of adding Me to lower the k diminishes after a Si/Me ratio of about 2/1 in the OSG material, yet the mechanical properties continue to decline as the Si/Me ratio approaches 1/1. Our dense DEMS OSG films (k = 3.0) are deposited at temperatures > 350 C. These films have excellent mechanical strength and a Si/Me ratio of 2/1. However, our process for porous DEMS OSG (k < 2.5) requires a deposition temperature below 280 C, resulting in a Si/Me ratio close to 1/1 and significantly decreased mechanical strength. We found that the Me incorporation can be reduced in by using a precursor mixture of DEMS and a second silica source without Me groups. This allows the control of the terminal Me content in the final film chemically, as opposed to using process conditions such as high temperature or plasma power. We were successful in depositing OSG films with Si/Me ratios of 2/1 from precursor mixtures at deposition temperatures as low as 200 C. For example, a porous OSG with a post-anneal k of 2.2 and a nanoindention hardness of about 0.6 GPa was deposited at 270 C. This is a nearly 2-fold increase in the mechanical strength as compared to films with identical k deposited without the second silica source.

4:40pm **TF-MoA9 Expanding Thermal Plasma for Low-k Dielectrics: Guiding the Film Chemistry by Means of Selected Dissociation Paths in the Plasma**, ***M. Creatore****, Y. Barrell, W.M.M. Kessels, M.C.M. van de Sanden,* Eindhoven University of Technology, The Netherlands

As the need for low-k dielectrics in the ULSI technology becomes urgent, the research primarily focuses on the deposition of novel materials with appropriate electrical properties and on the challenges concerning their integration with subsequent processing steps. Within this framework, plasma-enhanced chemical vapour deposition of organosilicate glass films is considered promising due their chemical structure similar to SiO@sub 2@, which leads to a simpler process integration. In this contribution we address the remote expanding thermal plasma (ETP) as a novel technique for the deposition of low-k carbon-doped SiO@sub 2@ films from Ar/hexamethyldisiloxane (HMDSO)/oxygen mixtures. We have obtained low-k films which exhibit k values (yet not optimised) in the range 2.9-3.4 (at 1 MHz) and still fairly good mechanical properties (hardness of 1 GPa, modulus of 10 GPa). These results were not expected because literature, in general, reports on low-k films deposited from precursors with 2 Si-O and 1 Si-C bonds per Si atom (e.g., dimethoxymethylsilane and diethoxymethylsilane), in order to reach a compromise between dielectric and mechanical film properties. Our approach, on the contrary, utilizes HMDSO (apparently not suitable due to the high Si-CH@sub 3@: Si-O bond ratio) because the ETP technique allows selecting different fragmentation paths for the precursor and this can eventually be turned to the progressive cleavage of Si-C bonds. The relatively easy control on the process kinetics can be monitored by means of gas phase diagnostics, such as Mass Spectrometry and Cavity Ring Down Spectroscopy. The information on the HMDSO dissociation paths allows tailoring the organic functionalities in the low-k films by means of IR absorption spectroscopy, XPS, and spectroscopic ellipsometry.

5:00pm **TF-MoA10 Photoresist Removal on Porous Low-k Materials Using an Energetic (100s of eV) Oxygen Neutral Beam**, *D.J. Economou,* ***Q. Wang,*** University of Houston*; B. White,* AMD and International SEMATECH*; P.J. Wolf,* Intel and International SEMATECH*; T. Jacobs,* Philips Semiconductors*; J. Fourcher,* International SEMATECH

Integration of porous low-k materials for interconnect technology present many challenges to the etch, ash and cleans processes. One challenge is the post etch removal of photoresist on open porous low-k films. Porous low-k films are very susceptible to damage by plasma processing, which can raise the overall keff of the film. Traditionally, a pure oxygen plasma ash is one method used for photoresist removal on CVD dielectrics. This method cannot be applied to exposed low-k films, because chemical and physical damage occurs. Successful photoresist removal on low-k films can be achieved by reducing chemistries or dilute O2 processes in RIE etch tools. This work shows how an energetic (100s of eV) oxygen neutral beam can be used to strip photoresist, without physical or electrical damage to the exposed low-k material. @FootnoteText@ Work at UH supported by International SEMATECH.

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