Wednesday Morning, November 6, 2002

Thin Films
Room: C-101 - Session TF+VT-WeM

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

8:20am **TF+VT-WeM1 The PE-ALD of Ta Based Metals/Nitrides: The Growth, Materials Properties, and Applications to Future Device Fabrications**, ***H. Kim***, *S.M. Rossnagel*, IBM T.J. Watson Research Center **INVITED**

Thin film deposition techniques producing high quality and highly conformal films with atomic level control are increasingly required as semiconductor device size shrinks into nanoscale regime. Atomic layer deposition (ALD) is expected to play an important role in depositing thin layers in nanoscale Si device manufacturing. Plasma enhancement of the process allows deposition at significantly lower temperatures than both conventional thermal ALD and chemical vapor deposition. Among the key materials used for today's semiconductor processing, thin films of inert, refractory 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. In this presentation, the Ta-based ALD systems have been explored at low temperature for a variety of semiconductor devices applications. Ta-based metals/nitrides films were grown by plasma-enhanced atomic layer deposition (PE-ALD) at temperatures from room temperature up to 400 °C using an inorganic halide source and RF plasma-produced atomic H as metal precursor and the reducing agent, respectively. The growth mechanism, microstructure, and chemical composition were studied using various ex situ analyses techniques. Good quality films with low contamination levels were obtained at low growth temperatures. Additionally, thermal stability, diffusion barrier property, resistivity, and other electrical properties, which are the essential materials properties for semiconductor device fabrication, were investigated. These results indicate that the PE-ALD process scales to manufacturing dimensions and applications and will facilitate the extension of interconnect technology beyond 100 nm dimensions.

9:00am **TF+VT-WeM3 Characteristics of TiN Films Deposited by rf Remote Plasma Enhanced Atomic Layer Deposition (ALD) Method using Metal Organic Precursor**, ***S. Seo***, *J. Kim, Y. Kim, Y.D. Kim, H. Jeon*, Hanyang University, Korea

Titanium nitride (TiN) has been most widely used as a diffusion barrier in ULSI devices because of its very low resistivity, good chemical and thermal stability, and impermeability to Si diffusion as well as the excellent adhesion to Si and SiO_2 films.[1-3] TiN barrier layer has been deposited predominantly by sputtering and chemical vapor deposition method.[4] However, as the device dimension has been shrinking down continuously, TiN films deposited by sputtering and CVD have faced the serious problems such as poor step coverage and conformality. Also, especially for the TiN films deposited by CVD using metal organic precursors, a relatively considerable amount of carbon impurity is still incorporated into the TiN films. For these reasons, we investigated TiN films deposited by rf remote plasma enhanced atomic layer deposition (ALD) technique which is expected to reduce or eliminate the problems related with sputtering and CVD.[5] TiN films were deposited using tetrakis-dimethyl-amido-titanium (TDMAT) as Ti precursor and ammonia (NH_3) and reactant gas at the optimized ALD processing windows. Rf remote plasma was used to reduce the carbon incorporation and to enhance chemical stability. The physical, chemical and electrical characteristics of TiN films were analyzed using Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), rutherford backscattering spectrometer (RBS), cross-sectional transmission electron microscope (XTEM) and four-point probe method.

[1]M. Ritala, M. Leskela, E. Rauhala and J. Jokinen, J. Electocem. Soc., Vol. 145, 8 (1998) 2914.
[2]M. T. Schulberg, M. D. Allendorf and D. A. Outka, J. Vac. Sci. Technol., A 14(6) (1996) 3228.
[3]M. Eizenberg, MRS Bull. 20 (1995) 38.
[4]A. Bouteville, L. lmhoff and J. C. Remy, Y. R. Yang and Y. F. Hsieh, J. Vac. Sci. Technol. B 16(4) (1998) 2013.
[5]H. Jeon, J. W. Lee, Y. D. Kim, D. S. Kim and K. S. Yi : Vac. Sci. Technol. 18 (2000) 1595.

9:20am **TF+VT-WeM4 Importance of Hydrogen Recombination on Flow Tube Walls During Hydrogen Radical-Assisted Metal Atomic Layer Deposition**, ***R.K. Grubbs***, *S.M. George*, University of Colorado, Boulder

Many metals can be deposited with atomic layer control using hydrogen radical-assisted metal atomic layer deposition (ALD). Designing the hydrogen plasma source and hydrogen radical delivery for efficient hydrogen radical-assisted metal ALD in a viscous flow reactor offers many challenges. In particular, hydrogen recombination on the flow tube walls to form H_2 is a serious loss to the hydrogen radical flux. To quantify the hydrogen radical flux and its loss caused by hydrogen recombination on the flow tube walls, a dual thermocouple probe was constructed based on exposed and covered Pt/Rh thermocouple junctions. This probe measured hydrogen radical concentration by determining the heat evolved from hydrogen radical recombination on the exposed thermocouple surface. The thermocouple probe was then employed to measure hydrogen radical concentration versus distance from the hydrogen radical source for four flow tube materials. The hydrogen radical concentration decreased dramatically versus distance and was different for stainless steel, aluminum, pyrex and quartz flow tube materials. By modeling the decrease in hydrogen radical concentration versus distance, a hydrogen radical recombination coefficient could be determined from the data. The recombination coefficient ranged from $\gamma = 1.5 \times 10^{-4}$ for stainless steel to $\gamma = 5.7 \times 10^{-5}$ for pyrex. Given the magnitude of the hydrogen radical recombination coefficients, the reaction chamber for hydrogen radical-assisted metal ALD must be positioned very close to the hydrogen radical source.

9:40am **TF+VT-WeM5 Improved Nucleation of TiN ALD Films on Low k Polymer Dielectrics Using Al_2O_3 ALD Adhesion Layers**, ***C.A. Wilson***, *J.W. Elam, M. Schuisky, Z.A. Sechrist, S.M. George*, University of Colorado

Diffusion layers are required to prevent copper from diffusing into low k polymer dielectrics in backend interconnects. The ability to deposit conformal diffusion layers, such as TiN, onto high aspect ratio low k polymer features requires atomic layer deposition (ALD) techniques. This study examined TiN ALD on low k polymer dielectrics using tetrakis-dimethylamino titanium (TDMAT) and NH_3. X-ray fluorescence spectroscopy (XRFS), optical microscopy and surface profiling of the TiN ALD films deposited on the low k polymer dielectrics revealed discontinuous films displaying distinct patchy regions of thinner TiN coating. To study TiN ALD nucleation, in situ quartz crystal microbalance (QCM) measurements were performed by spin-coating a low k polymer dielectric onto the QCM sensor. Subsequent QCM measurements during TiN ALD revealed very low initial TiN ALD growth rates indicating poor nucleation. Al_2O_3 ALD was then performed on the low k polymer dielectric using trimethyl aluminum and H_2O. Surface profiling, XRFS, QCM and transmission electron microscopy measurements revealed that the Al_2O_3 ALD films nucleate immediately on the low k polymer dielectric producing continuous Al_2O_3 films. In addition, QCM measurements showed that TiN ALD nucleates readily on the Al_2O_3 surface. Intermediate Al_2O_3 ALD adhesion layers may facilitate the growth of continuous TiN ALD films on low k polymer dielectrics. Examination of TiN ALD films prepared on low k polymer dielectrics with progressively thinner Al_2O_3 ALD adhesion layers revealed that 10 Al_2O_3 ALD cycles are sufficient to promote the nucleation of the TiN ALD films.

10:00am **TF+VT-WeM6 Alternating Layer Deposition of Dielectric Films**, ***A.P. Paranjpe***, *B. McDougall, K.Z. Zhang, W. Vereb*, TORREX **INVITED**

Interest in alternating layer deposition (ALD) for the deposition of thin films used in semiconductor devices has grown rapidly due to the numerous advantages offered by ALD. Often, relatively high exposure doses are required to achieve self-limited surface saturation that is necessary for good uniformity, conformal deposition in high aspect ratio features, low impurity incorporation, and superior electrical properties. The low deposition rates make ALD using conventional reactors impractical in a semiconductor manufacturing environment for film thickness values > 10 nm. We describe a Parallel Wafer Processing reactor architecture capable of processing 1 - 25 wafers simultaneously that provides a 3X - 4X throughput advantage over single wafer ALD processes for both standalone and clustered operation. This reactor architecture is well-suited for the deposition of SiN and SiO_2, since initial surface chemisorption rates are relatively high, but high exposures (> 10 Torr-s) are required to achieve self-limited surface saturation. Exceptionally smooth (Ra < 0.15 nm), stoichiometric SiN films with conformality of ~ 100% in high aspect ratio features can be deposited at 0.1 - 0.2 nm/cycle in the temperature range of 450 - 550°C. The hydrogen content and wet etch rates are significantly lower than CVD SiN films deposited at equivalent temperatures confirming that ALD provides superior film quality. Electrical leakage is lower compared to SiN deposited in a conventional furnace at 750°C. SiN films have also been deposited via cyclic CVD which is analogous to ALD except that the chemisorption of the Si source deviates from the ideal self-limited behavior. Cyclic CVD

offers deposition rates that are up to 50% higher than deposition rates achievable in ALD, but film properties including conformality are intermediate between ALD and CVD films. We will also discuss the deposition of other dielectric films using the Parallel Wafer Processing reactor.

10:40am **TF+VT-WeM8 Photochemically-Assisted ALD of BN Thin Films**, ***J. Olander***, *M. Ottosson, K.M.E. Larsson*, Uppsala University, Sweden

Boron nitride-based materials have properties like high thermal stability, oxidation resistance and interesting electronic properties and are thus suitable materials for electronic devices, heat resistant semiconductors and lubricants. Thin films of BN materials have only to limited extent been prepared and the film properties are not well known. A combined experimental and theoretical investigation of BN growth from NH3 and BBr3 has been performed. Thin films of Boron Nitride have been deposited on SiO2 by means of Laser-Assisted Atomic Layer Deposition (ALD) using an ArF excimer laser. The deposition temperatures were between 300 and 750 °C. In order to investigate the growth at an atomic level, theoretical calculations have been performed using the DFT method. Theoretically, the adsorption of the NH3 and BBr3 and their fragmented components were found to be favorable for continued growth of cubic BN. However, the films obtained in the present study are of turbostratic structure. Both NH3 and BBr3 were observed to strongly absorb light from the ArF excimer laser. As a result of the photofragmentation of the precursors, the growth rate of the BN films was increased. At lower temperatures, the densities of the grown BN films were also enhanced.

Authors Index

Bold page numbers indicate the presenter