

Thursday Morning, October 21, 2010

Plasma Science and Technology

Room: Galisteo - Session PS+TF-ThM

Plasma Deposition and Plasma Enhanced ALD

Moderator: M. Shiratani, Kyushu University, Japan

8:00am **PS+TF-ThM1 High Rate Synthesis of Crystalline Si Film by Control of High Density Radicals with Dual Frequency PECVD**, *J.G. Han, Y.S. Choi, Y.J. Kim, I.S. Choi*, Sungkyunkwan University, Republic of Korea **INVITED**

8:40am **PS+TF-ThM3 Room Temperature PECVD Synthesis of Hybrid Organic-Inorganic Nanolaminates**, *R. Patel, C.A. Wolden*, Colorado School of Mines

Nanolaminates enable a new class of optoelectronic structures that are ultra lightweight, dimensionally stable, and have low cost with increased durability and flexibility. They are integral components in various applications serving as advanced dielectrics, flexible barrier coatings, and as optical components. In this work plasma enhanced chemical vapor deposition (PECVD) is employed to deposit functional polymer thin films on flexible substrates in order to make hybrid organic-inorganic nanolaminates for the applications described above.

Silicone-like coatings were deposited using hexamethyldisiloxane (HMDSO) and oxygen as precursors at room temperature. Film composition was assessed by spectroscopic ellipsometry and FTIR. A wide range of coatings, from inorganic SiO₂-like films to flexible polymeric films could be deposited by appropriate control of parameters including the O₂/HMDSO ratio, rf power, and working pressure. In this work we report on how these variables impact deposition rate, film composition, and nanolaminate performance. Growth rates as high as 100 nm/min were obtained, and crack free silica and polymeric films have been deposited on polyethylene.

For the production of organic-inorganic nanolaminates, two approaches were used for the formation of the inorganic layer. In one case HMDSO was used for deposition of both the silicone- and silica-like layers. In this case, the flowrate of HMDSO was held constant while other variables (power/O₂ flowrate) were adjusted. In the second case, the inorganic layer was aluminum oxide that was formed using tri-methyl aluminum (TMA) and oxygen at room temperature. Self-limiting growth of alumina (~Å/pulse) was achieved by both plasma-enhanced ALD and pulsed PECVD. No impurities were detected in Al₂O₃ by FTIR by either technique under optimum conditions. Nanolaminates were constructed as a function of dyad composition and total number of dyads. In this paper we compare the performance of these various nanolaminates with respect to metrics such as adhesion and barrier properties.

9:00am **PS+TF-ThM4 Role of PEALD System Plasma Source Operation on Substrate Ion Bombardment and the Impact on HfO₂ and TiN Film Properties**, *M.J. Sowa, G.M. Sundaram, E.W. Deguns, R. Bhatia, M.J. Dalberth, A. Bertuch, G. Liu, J.S. Becker*, Cambridge NanoTech, Inc.

Plasma enhanced atomic layer deposition (PEALD) has seen increased interest in recent years. Replacing one of the half cycles of the ALD process with a plasma generated radical dose has been successfully demonstrated to improve film electrical properties, improve deposition rates, enable lower temperature processing, and enable the use of precursors unsuitable for thermal processes. It is typically advantageous to operate the plasma source of PEALD systems in a "remote" mode, such that the substrate being processed does not have any exposure to energetic charged species. Rather, the longer-lived radicals generated in the remote plasma source react with the chemisorbed precursor from the previous half-cycle to form the desired film. Exposure of the substrate to energetic ion bombardment during the plasma half cycle has been demonstrated to lead to decomposition of the chemisorbed precursor which gives thick, non-uniform films with poor electrical properties. We have observed that, depending on the processing conditions utilized for generating the plasma, the plasma may be confined to the remote plasma source or may extend into the ALD processing reactor to varying degrees. The remote plasma source on our system is an inductively coupled plasma design consisting of a cylindrical quartz tube surrounded by a water-cooled copper inductor. We have investigated the quality of HfO₂ and TiN films grown in our PEALD system with various, controlled levels of substrate ion bombardment. Up to 300W of 13.56MHz

rf is coupled to the copper inductor through an L-type matching network. Plasma gas mixtures of Ar with commonly used PEALD gases, O₂ or N₂, over a wide range of flow rates and pressures were investigated. We have quantified the encroachment of the plasma into the ALD reactor through the placement of Langmuir probes on the surface of a 200mm substrate which is placed onto the heated substrate holder of our PEALD system. We then deposited films of HfO₂ with tetrakis(dimethylamino)hafnium and Ar/O₂ plasmas and TiN with tetrakis(dimethylamino)titanium and Ar/N₂ plasmas at various levels of substrate surface bombardment. Resulting films were evaluated for stoichiometry, impurities, crystallinity, and relevant electrical properties including dielectric constant and leakage current for the HfO₂ and resistivity for the TiN.

9:20am **PS+TF-ThM5 HfTiSiON Film Growth by N₂ Plasma Exposure to Hf-Ti Liquid Nano Particles on SiO₂/Si**, *T. Kitajima, T. Nakano*, National Defense Academy, Japan, *T.M. Makabe*, Keio University, Japan

1. Introduction

HfSiON is the most applicable chemistry for the high-k gate dielectrics with proper energy band alignment, large area uniformity, and thermal stability. The direct formation of HfSiO film from the Hf overlayer and underlying SiO₂ utilizing the thermal interfacial reaction was previously proposed [1]. The process enables remarkably low leak current of the film due to the lack of carbon impurity. We applied N₂ plasma for the interfacial reaction and nitridation and realized plasma-based nanoparticle involved non-thermal chemistry for HfSiON.

2. Experiment

The system consists of a UHV-SPM chamber with an e-beam metal evaporation source, a separate VHF (50MHz) low pressure ICP plasma source [2], and ex-situ XPS. Commercial Si(100) wafer with native oxide is introduced to the chamber and Hf and Ti metal beam is exposed to the surface at room temperature. The morphological development of the surface is analyzed with the in-situ non-contact AFM. The N₂ ICP is exposed to the sample without any temperature control. The grown film surface is again evaluated on its surface flatness with nc-AFM. The change of the chemistry of the sample surface is analyzed with the XPS.

3. Results and discussion

The AFM image of self-assembled Hf nanoparticles on SiO₂ surface after the deposition reveals dome shaped particles with 3-6 nm width are close-packed on the surface with high density of 8.5×10¹² cm⁻². The N₂ ICP exposure induces the interfacial reaction of the Hf nanoparticle/SiO₂/Si structure and forms Hf(Ti)SiON(film)/SiON/Si. The angle-resolved Si2p XPS spectrum at 101.5 eV in 30deg. shows the Si included in the film is nitrided. Hf silicate formation is found in the component around 100 eV. The total amount of nitrogen atoms in the film well corresponds to the total supply from the N₂ ICP due to the absorption spectroscopy of N(⁴S) and N(²D) [2].

The AFM image shows the film has superior flatness of RMS roughness of 0.3 nm except the dips of 0.8 nm depth which disappear with Ti addition to the film.

5. Conclusions

The novel film growth process with plasma induced reaction of metal nanoparticles and the substrate is demonstrated for Hf(Ti)SiON. The process scheme is widely applicable to the nano-scale feature modification and chemistry with non-thermal reactions of non-equilibrium plasma.

References

- [1] H. Watanabe, M. Saitoh, N. Ikarashi, and T. Tatsumi, Appl. Phys. Lett. 85, 449 (2004).
- [2] T. Kitajima, T. Nakano, S. Samukawa, and T. Makabe, Plasma Sources Sci. Technol., 17(2), 024018 (2008).

9:40am **PS+TF-ThM6 Platinum and Platinum Oxide Films Prepared by Using Low Temperature Plasma Enhanced ALD**, *B.H. Liu, C.C. Kei, C.C. Yu, D.R. Liu, C.N. Hsiao*, National Applied Research Laboratories, Taiwan, Republic of China

In this study, smooth and pinhole-free platinum films were deposited on Si substrates by plasma enhanced atomic layer deposition (PEALD). Ar/O₂ inductively coupled plasma was applied to decompose the ligands of Pt precursor, MeCpPtMe₃. Partial pressures of Ar and O₂ were held at 0.3 and 0.1 Torr during the PEALD process, respectively. The substrate temperatures were varied between 100 and 200 °C to obtain Pt films. Crystal structure of deposited films was studied using an X-ray diffraction (XRD). Film morphology was obtained by using a field-emission scanning electron microscope (SEM). Electric properties of deposited films were measured by using a Hall effect measurement system. XRD pattern shows

that the film prepared at 200 °C has the fcc structure of platinum. Only a broad (102) peak of hexagonal alpha-PtO₂ was appeared for the films deposited at 100 and 150 °C, implying that oxidized Pt can not be reduced at a temperature less than 200 °C. The growth rate of Pt films is about 0.04 nm/cycle based on the SEM observation. The sheet resistances of Pt and PtO₂ film prepared by using 200 cycles are 30.57 and 85.19 Ω/sq, respectively.

Keywords: inductively coupled plasma, PEALD, sheet resistance

10:40am **PS+TF-ThM9 Dielectric Performance of Al₂O₃ Films Prepared by Direct Plasma PEALD**, C.C. Yu, Instrument Technology Research Center, Taiwan, Republic of China, Z.Y. Han, National Chiao Tung University, Taiwan, Republic of China, C.C. Kei, M.Y. Tsai, W.H. Cho, C.N. Hsiao, Instrument Technology Research Center, Taiwan, Republic of China, C.H. Chien, National Chiao Tung University, Taiwan, Republic of China, C.Y. Su, N.N. Chu, Instrument Technology Research Center, Taiwan, Republic of China

In this study, plasma enhanced atomic layer deposition system (PEALD) was used to deposit Al₂O₃ films at room temperature. Trimethylaluminum (TMA) and O₂ plasma were used as metal precursor and oxidant, respectively. A DC power supplier was applied to generate O₂ plasma with a parallel-plate electrode configuration. Nitrogen purge was applied between the exposures of TMA and O₂ plasma to prevent vapor phase reaction. Cycle numbers of PEALD were varied from 100 to 500 nm. The thicknesses of Al₂O₃ films were obtained from x-ray reflectivity measurement. Surface morphology and roughness was given by using scanning electron microscopy (SEM) and atomic force microscopy (AFM), respectively. C-V measurement was performed by using a HP4194 impedance analyzer to obtain the capacitance and dielectric constants. I-V curves were characterized by measuring with a Keithley 4832 multimeter. The growth rate of Al₂O₃ film increases with the increasing plasma power and reaches a saturation value of 1.7 Å/cycle when the plasma power exceeds 50 W. SEM images imply PEALD prepared Al₂O₃ films have a pin-hole free structure, and AFM result shows that Al₂O₃ film deposited for 100 PEALD cycles has a smooth surface roughness as 0.211 nm. The dielectric constant for Al₂O₃ films prepared by using 100 PEALD cycles is 4.53. A leakage current density of 3 × 10⁻⁹ A/cm² can be achieved for the 100 PEALD cycles prepared Al₂O₃ film. The interface charge trap density given by the C-V measurement increases with an increasing plasma power. This implies that high energy oxygen ion bombardment would lead to damage at interface and formation of the charge traps.

Key : PEALD, Parallel-plate electrode, Direct plasma, High-k material, C-V, I-V, D_{it}

11:00am **PS+TF-ThM10 Improving the Quality of PVD Cu Seed Layer for Interconnect Metallization**, A. Dulkan, E. Ko, L. Wu, I. Karim, K. Leiser, K.J. Park, Novellus Systems, Inc., L. Meng, D.N. Ruzic, University of Illinois at Urbana-Champaign

Physical Vapor Deposition (PVD) of Ta(N) barrier and Cu seed layers has been traditionally used in interconnect metallization process flow in VLSI manufacturing. Reliability of the manufactured devices greatly depends on the quality of different interfaces, particularly the barrier/seed one. Failure to ensure continuous seed coverage with good adhesion to the barrier may result in voided electrofill, post-CMP defects, and stress/electro-migration failures. Quality of the barrier/seed interface was greatly improved by enhancing Cu nucleation on the Ta surface through filtering of non-energetic species from the deposition flux, increasing the fraction of Cu ions, improving flux uniformity, and minimizing gas ion bombardment. The self-sputtering ability of Cu was combined with magnetically confined high density plasma in the Novellus HCMTM PVD source. Spatial profiles of plasma density and temperature, as well as ion flux, ion metal fraction, and ion energy, were measured by planar Langmuir probes, quartz crystal microbalance, and gridded energy analyzer, all located at the wafer level. Multiple criteria, such as seed step coverage and roughness, its resistance to agglomeration, and its stability in the plating bath, have been used to evaluate interface quality. As a result new and improved Cu PVD process which demonstrated superior stability during subsequent process steps and ensured successful electrofill performance with more than 50% reduction in minimal sidewall thickness requirement has been developed.

11:20am **PS+TF-ThM11 Pulsed Plasma Polymerization of 2-Chloro-p-xylene**, I.C. Estrada-Raygoza, P.L.S. Thamban, G. Padron-Wells, L.J. Overzet, M.J. Goeckner, University of Texas at Dallas

Parylene C is a high-quality protective layer used in a wide array of areas that includes dielectric applications, biomedicine and micro-electromechanical systems (MEMS). Using traditional deposition, poor adhesion to a broad range of substrates remains a main concern. Adhesion is greatly improved to almost any type of substrate if the deposition is via plasma polymerization. In the work reported here we use a wide set of data

to predict the film growth mechanisms during pulsed plasma polymerization of parylene C. Specifically, we examine plasma gas phase chemistry in a 2-Chloro-p-xylene pulsed discharge using of a novel e-beam probe as well as more traditional Fourier-Transform Infrared Spectroscopy and WISE[®] probe measurements. We contrast the gas phase chemistry with the bulk properties of the films deposited. Work supported in part by CONACYT Scholarship number 170201 and NSF (Grant CBET- 0922962).

11:40am **PS+TF-ThM12 Morphological Variation of Plasma Polymerized TiO_xC_y Films as a Function of Oxygen Concentration during PECVD**, L. Sun, H. Jiang, General Dynamics Information Technology, J. Grant, University of Dayton Research Institute, P. Lloyd, UES, Inc., T. Bunning, R. Jakubiak, Air Force Research Laboratory

Amorphous titanium oxide derivative films have relatively high index of refraction compared to purely organic thin films, retain much of the functionality of their crystalline counterparts and can be deposited at low temperature. Using PECVD operated at room temperature and in a remote configuration, plasma-polymerized (PP-) TiO_xC_yN_z films were derived from titanium (IV) isopropoxide using a mixture of argon and nitrogen as carrier gases. Upon exposure to ambient, the PP-TiO_xC_yN_z films undergo a continual decrease in film thickness and increased index of refraction that does not stabilize for several days after deposition. After one hour in air, the thickness of the films rapidly decreased by 14% and after three weeks the thickness decreased 30% (128 - 90 nm). This was accompanied by an increase of the refractive index from n₅₈₉ = 1.72 to 1.84. Broadly, the densification results from oxidation of low valence titanium moieties prevalent in films formed in an oxygen-poor environment. From AFM and SEM studies we know that the thin films possess a featureless, smooth (RMS - 0.5 nm) one phase 3-D crosslinking amorphous structure. When oxygen was substituted for nitrogen as a carrier gas, most of the titanium atoms retained the Ti⁴⁺ state of the monomer and little, if any densification was noted; however, the film morphology was strongly dependent on the argon to oxygen ratio in the carrier gas mixture. In oxygen rich conditions, the films contained granular columns (approximately 10 to 50 nm in diameter) composed of amorphous TiO₂, with void and crack defects between 10-20 nm in width. Films deposited in oxygen poor conditions exhibited a uniform, amorphous structure as seen in the nitrogen/argon case.

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