

Wednesday Morning, November 11, 2009

Plasma Science and Technology

Room: B2 - Session PS2+TF-WeM

Plasma Deposition and Plasma-assisted ALD

Moderator: E.R. Fisher, Colorado State University

8:00am **PS2+TF-WeM1 Plasma Polymerization of bis-1, 2-(triethoxysilyl) Ethane (BTSE): Interfacial Characterization by ToF-SIMS and XPS.** *A. Batan*, Univ. Libre de Bruxelles, Facultés Univ. Notre-Dame de la Paix, Belgium, *N. Mine, B. Douhard*, Facultés Univ. Notre-Dame de la Paix, Belgium, *F. Brusciotti, I. De Graeve, J. Vereecken*, Vrije Univ. Brussel, Belgium, *M. Wenkin, M. Piens*, Coating Research Inst., Belgium, *H. Terryn*, Vrije Univ. Brussel, Belgium, *J.J. Pireaux*, Facultés Univ. Notre-Dame de la Paix, Belgium, *F. Reniers*, Univ. Libre de Bruxelles, Belgium

Plasma polymerized BTSE films were deposited by vacuum and atmospheric plasma on aluminum (99.99%) substrate. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been used for probing the metal/film interface. Ion etching by Xe⁺ 500 eV and 250 eV, depending on the plasma polymer BTSE film thickness, exposed the interfacial region, while Ga⁺ (15 keV) ions analysed the material composition.

An AlOSi⁺ fragment was identified at nominal mass m/z = 70.9539 amu in high mass resolution spectra. The presence of this aluminium-oxygen-silicon ion fragment is a strong indication of an existing chemical interaction between the plasma polymer BTSE film and the aluminum substrate: the nature of this interaction implies the formation of a covalent bond between the silane and the aluminum substrate. Until now, this strong interaction silane-aluminum has never been observed in plasma polymer BTSE films.

Ageing tests combined with X-ray photoelectron spectroscopy measurements allowed the evaluation of the adhesion performance of plasma polymerized BTSE films on aluminum. The Si2p signal intensity was measured before and after dipping the coated sample in an ultrasonic water bath for 30 min, at room temperature. The Si2p peak intensity remained constant after the sonication test, showing a strong adhesion between the deposited layer and the aluminum substrate.

Acknowledgements

The project partners VUB, ULB, FUNDP and CoRI gratefully acknowledge the Belgian Science Policy for funding the FOMOS project (P2/00/04) in the "Programme to stimulate knowledge transfer in areas of strategic importance". www.belspo.be

8:20am **PS2+TF-WeM2 Self-limiting Deposition of Nanolaminates by Pulsed PECVD.** *P.C. Rowlette, C.A. Wolden*, Colorado School of Mines

Self-limiting synthesis of alumina-titania nanolaminates (ATO, Al₂O₃/TiO₂) was accomplished via pulsed plasma-enhanced chemical vapor deposition. At the synthesis temperature of 150 °C the alumina layers were amorphous, while TiO₂ layers displayed a polycrystalline anatase structure. Digital control over nanolaminate structure was demonstrated through elemental analysis and TEM imaging. The optoelectronic properties of the ATO structures were examined as a function of composition and bilayer thickness. C-V measurements showed that the effective dielectric constant (κ) of the nanolaminates was consistent with treating the structure as individual capacitors in series. I-V measurements showed that leakage current deteriorated with TiO₂ content, though low leakage was restored through interfacial engineering. With respect to dielectrics these results suggest that the best nanolaminate would employ Al₂O₃ interface layers deposited by PE-ALD to minimize leakage current, and that these two layers would sandwich a single TiO₂ layers whose thickness would set the effective dielectric constant. We will also present work in SiO₂-TiO₂ nanolaminates formed by the same technique at room temperature with applications as optical components. Finally, we will present recent findings in the area of inorganic/organic hybrid nanolaminates formed by alternating oxide and polymer layers.

8:40am **PS2+TF-WeM3 Tailoring PECVD Ultra-Low-k Films for Nanoscale Interconnects.** *E.T. Ryan*, GLOBALFOUNDRIES, *S.M. Gates, S. Cohen, Y. Ostrovski, V. Patel, E. Simonyi, C. Dimitrakopoulos*, IBM T.J. Watson Research Center, *A. Madan*, IBM Microelectronics, *G. Dubois*, IBM Almaden Research Center, *A. Grill*, IBM T.J. Watson Research Center

INVITED

Ultra-low-k (ULK) insulating films are critical to reduce the resistance-capacitance (RC) delay in interconnect wires. This talk will briefly review the history of low-k materials that culminated with ULK nanoporous organosilicate glass (also called pSiCOH) films deposited by plasma-enhanced chemical vapor deposition (PECVD).

Nanoporous ULK pSiCOH films pose many interconnect fabrication challenges, and the needs of integration impose limits on the material properties of the films. For example, the pSiCOH film can be damaged by exposure to other plasma processes, and the degree of damage is related to material properties such as porosity, pore size, pore interconnection, carbon content, and bonding arrangement.

The stress and mechanical strength (modulus) of the pSiCOH film is critical for the structural stability of the interconnect wires. Spontaneous cracking is directly related to both modulus and stress. Packaging imposes additional stresses on the interconnect lines. Furthermore, if the modulus of the ULK film becomes too low, capillary forces during post-etch wet cleaning can cause the patterns in the pSiCOH film to collapse.

These integration needs require balancing various trade offs in material properties, and this constrains the process space for pSiCOH film deposition. The talk will review our work to design pSiCOH films with different properties to meet different integration needs. Examples of PECVD films with properties tailored to meet these interconnect needs illustrate the trade offs we face.

First we review our efforts to design films that are resistant to damage by the plasmas used for etch and ash and cap deposition. Mechanical properties were also maintained at favorable values. We modified a conventional pSiCOH film (V1) prepared from DEMS and BCDH porogen by adding a carbosilane skeleton precursor to incorporate new carbon structures. The modified films (V2, V3) can be adjusted by the choice of the carbosilane precursor. The films were characterized for electrical and mechanical properties, pore characteristics, and FTIR. The plasma damage of the films was characterized by thickness loss after HF etch of the damaged layer and depth profiling by ToF-SIMS. The new pSiCOH V2 and V3 films show reduced plasma damage. Our effort to optimize the pSiCOH modulus will be discussed, with the overall goals of reducing plasma induced damage and maintaining favorable stress and modulus.

9:20am **PS2+TF-WeM5 Amplitude Modulated Pulse RF Discharges for Producing and Driving Nano-Blocks.** *S. Iwashita**, *H. Miyata, H. Matsuzaki, K. Koga, M. Shiratani*, Kyushu University, Japan

We have proposed a bottom-up nanosystem-fabrication method, which consists of production of nano-blocks and radicals (adhesives) in reactive plasmas, transport of nano-blocks towards a substrate, their arrangement on the substrate using pulse RF discharges with the amplitude modulation (AM) of the discharge voltage. For the method, control of the size of nano-blocks and their manipulation without their agglomeration are important. Up to now, we have succeeded in controlling the size of nano-blocks by pulse RF discharges,¹ and have realized their rapid transport from their generation region towards a substrate with suppressing agglomeration by pulse RF discharges combined with AM.^{2,3} Here we report a criterion for driving nano-blocks rapidly and discuss their transport mechanisms.

Experiments were carried out using a capacitively coupled RF discharge reactor described elsewhere.¹⁻³ Nano-blocks were formed in 13.56 MHz RF discharges of Si(CH₃)₂(OCH₃)₂ diluted with Ar. Nano-block transport in AM discharges is classified into two kinds: one is the rapid transport at a velocity more than 60 cm/s during the modulation period and the other is the slow transport at a velocity of 3-5 cm/s after turning off discharges due to temperature gradient. The key parameters to the rapid transport are the period Δt and voltage V_{AM} of the modulation and asymmetry of the discharges, which is characterized by the dc self-bias voltage V_{dc} . The larger nano-blocks need longer Δt , higher V_{AM} , and higher V_{dc} , for their rapid transport because of their large inertia. All nano-blocks of 26 nm in size, for instance, are transported rapidly during the modulation period for $V_{dc} = -412$ V, $\Delta t = 100$ ms and $V_{AM} = 1076$ V, while 54 % of them are transported rapidly during the modulation period and 46 % of them are transported after turning off discharges for $V_{dc} = -350$ V, $\Delta t = 100$ ms and

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$V_{AM} = 883$ V. Just after the initiation of the modulation, electrostatic force drives nano-blocks, and then ion drag force drives them towards a substrate. It should be noted that although most nano-blocks are neutral, some of them turn into ones charged negatively due to charge fluctuation and such nano-blocks charged negatively are driven by electrostatic and ion drag forces. The method was applied to deposition of nano-block composite porous low- k films and dielectric films of $k = 1.4$ and Young's modulus above 10 GPa were realized.

¹S. Nunomura, M. Kita, K. Koga, M. Shiratani, and Y. Watanabe, *J. Appl. Phys.*, **99**, 083302 (2006).

²K. Koga, S. Iwashita, and M. Shiratani, *J. Phys. D: Appl. Phys.*, **40**, 2267 (2007).

³M. Shiratani, K. Koga, S. Iwashita, and S. Nunomura, *Faraday Discuss.*, **137**, 127 (2008).

9:40am **PS2+TF-WeM6 Plasma Deposition of Platinum-Based Nanocomposite Films as Fuel Cell Electrocatalysts**, *A. Milella, E. Dilonardo*, University of Bari, Italy, *F. Palumbo*, Institute for Inorganic Methodologies and Plasmas (IMIP)- CNR, Italy, *S. Martin*, CEA-G/ Leti, France, *R. d'Agostino, F. Fracassi*, University of Bari, Italy

In Proton Exchange Membrane Fuel Cells (PEMFC) the electrode reactions rely heavily on the use of platinum catalysts. Since cost of this precious metal is one of the main barriers for commercialization of fuel cells, many research efforts are addressed to obtaining higher catalytic activity than the standard carbon-supported platinum particle catalysts used in current PEM fuel cells, with a reduced amount of metal. In this framework, plasma processes are particularly appealing since they allow the dispersion of catalyst in form of nanoparticles and the control of the film thickness to the nanometer scale. Few examples are present in literature concerning the use of low pressure plasma for platinum-containing films as catalytic electrodes.

In this contribution we report our latest results on the one-step deposition of nanocomposite thin films containing platinum nanoclusters (high specific area), with definite concentration and uniform in size. Thin films are obtained from a simultaneous plasma-enhanced chemical vapour deposition of ethylene (C_2H_4) / argon gas mixtures and RF sputtering of a platinum target. The main advantages of this approach consist in the reduced thickness (less than 1 micron), the possibility to coat complex shapes, and the easy scale up in a continuous process. A comprehensive study on the effect of different parameters (RF power, deposition time, gas flow rates) on the film chemical composition and structure will be presented. In particular, it will be shown that the platinum content in the film, determined by X-ray Photoelectron Spectroscopy (XPS), can be continuously varied by properly controlling the RF power and the monomer flow rate. Field Emission Gun-Scanning Electron Microscopy (FEG-SEM) shows that films are porous with a cross-section characterized by columnar structures of different size and orientation, depending on the deposition parameters. Transmission Electron Microscopy (TEM) confirms that platinum aggregates in crystalline nanoclusters of diameters in the range 3-7 nm, uniformly distributed in the film. The electrochemical active area of the films, as determined from *ex-situ* Cyclic Voltammetry (CV) analyses, reaches a maximum correspondingly to a platinum load of about 60%. Preliminary results on device testing will be also presented.

Acknowledgments

This work was founded by the European Project *NAPOLYDE* (NMP2-CT-2005-515846).

10:40am **PS2+TF-WeM9 Contribution of CN Radicals to the Nitrogen Content of Plasma-Deposited a-CN_x Materials**, *J.M. Stillahn**, *E.R. Fisher*, Colorado State University

This work details our efforts to explore the plasma-enhanced chemical vapor deposition of amorphous carbon nitride (a-CN_x) materials, which exhibit a variety of interesting physical and chemical properties. These properties depend critically on the manner and extent to which nitrogen is substituted into the amorphous film network, but the mechanisms responsible for nitrogen incorporation are often obscured by the complexities of mixed-precursor systems (e.g., CH_4/NH_3) that are frequently used to study a-CN_x deposition. Single-source precursors (e.g., CH_3CN , $BrCN$) help to simplify the gas phase chemistry, and in this work we have employed such precursors to learn about nitrogen incorporation mechanisms in more complex systems. The CN radical is examined with particular interest as it exhibits near-unity surface reaction probabilities under all conditions, providing a stark contrast with other N-containing plasma species such as the less-reactive NH radical. Interestingly, this difference in surface reactivity is echoed by disparities in the molecules'

internal energies, which are characterized in this work by the rotational temperature. The contributions of the CN radical become especially evident with the use of $BrCN$ plasmas, yielding films that delaminate and buckle upon exposure to atmosphere. This behavior may reflect a high concentration of terminating groups in the film, leading to a porous material that is compressively stressed as it absorbs water. Data such as these can be used to form a more complete understanding of the chemical mechanisms that lead to a-CN_x deposition.

11:00am **PS2+TF-WeM10 Comparison between a DC Reactive Magnetron Sputtering Discharge in an Ar/NH₃ and Ar/H₂/N₂ Gas Mixture**, *F. Henry, A. Batan, F. Reniers*, Université Libre de Bruxelles, Belgium

The reactive magnetron sputtering technique is widely used for thin films deposition. This one offers many advantages like: a large choice of composition of the deposited films, a low temperature of deposition that allows to use a large scale of substrates and a high speed of deposition. Other techniques used for thin films deposition like CVD often required the use of hazardous gases and required a high temperature of deposition.

In this study, two different gas mixtures (Ar/NH_3 and $Ar/H_2/N_2$) used for the deposition of silicon nitride thin films were compared. Optical Emission spectroscopy spectrum (OES) were recorded to characterize the plasma gas phase. X-ray Photon-electron Spectroscopy (XPS) was used to determine the stoichiometry of the deposited thin films and used to perform a depth profiling of the silicon target after exposure to the reactive magnetron sputtering discharge. Optical interferometry was used to measure the film thickness and current-voltage curves were plotted to determine the electric characteristics of the discharge.

The influence of the plasma parameters such as the molar fraction of reactive gas and the total pressure was studied. The same parameters were investigated for both kind of gas mixture and a detailed comparison was performed.

The experiments were performed in a stainless steel chamber equipped with a home-made magnetron cathode. The total pressure was set between 5×10^{-3} Torr and 2×10^{-2} Torr and the molar fraction varied between 0 and 0.6 in reactive gas. During all experiments the discharge current was set to 300 mA.

The excited species detected into the Ar/NH_3 and $Ar/H_2/N_2$ plasma were the same, except for the NH radical that was not detected in the $Ar/H_2/N_2$ plasma.

The stoichiometry of the thin films deposited with the two kind of gas mixtures was investigated by XPS, a N/Si ratio of 1.33 was determined for the $Ar/H_2/N_2$ plasma and 1.22 for the Ar/NH_3 plasma.

The current voltage curves were plotted at different molar fractions of reactive gas and at different total pressures. A typical drop of the tension due to a poisoning of the target was observed for the Ar/NH_3 plasma and for the $Ar/H_2/N_2$.

11:20am **PS2+TF-WeM11 The Application of AC Diode Sputtering for Aluminum Thin Films in Small Apertures**, *D.R. Walters*, Argonne National Laboratory

A thin conductive film was applied on the inner surface of a small-aperture vessel using the AC Diode Sputtering process. This paper describes the process and the technical equipment used in this thin-film method. The process configuration presented here employs a dual-electrode arrangement, which creates a glow discharge field around both electrodes, thereby spreading out the affected area. An example of coating performed in a 5 mm by 12.5 mm rectangular channel by 3.4 m in length is present along with examples of circular cross-sectional channels. A significant challenge of this configuration is how to get a homogeneous pressure throughout a long constricted channel; results show that the dual inlet-output gas flow circuit was able to achieve the constancy needed for a satisfactory film. Analyses of the sample films confirm acceptable uniformity even in the pressure region of 600 mTorr. Further work has shown that the glow discharge can be maintained into a pressure regime of greater than 10 Torr.

11:40am **PS2+TF-WeM12 3D Plasma Simulations of a High Density Plasma CVD Reactor using VIZGLOW**, *P. Kothnur, R. Kinder*, Novellus Systems, Inc., *X. Yuan*, Esgee Technologies, Inc., *L. Raja*, The University of Texas at Austin

High-density plasma CVD (HDP-CVD) reactors are used to provide void-free gap fill of high-quality dielectric films in high aspect ratio device structures. The ability to accurately model a prototype or development design is a necessary capability of any equipment manufacturer in order to lower cost and shorten design cycle times. However, the ability to model an HDP-CVD tool accurately remains a difficult challenge due to the complex coupling of power deposition and plasma transport in a CVD chamber. To investigate issues related to power deposition and electron transport, we

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have used the VIZGLOW simulation software developed at Esgee Technologies to simulate 3D geometries. The simulation software enables the solution of the energy equation for electron temperature, while solving for the electron density and electrostatic fields through a quasi-neutrality condition. Electron heating is produced by electromagnetic fields, while the energy equation is solved for all heavy species. The HDP-CVD tool considered is a hemispherical inductively coupled plasma (ICP) source. The simulation results are compared to previously published experimental measurements with Langmuir probes, voltage and current monitors, optical emission spectroscopy, ion mass spectrometry, and gas quadrupole mass spectrometry. Furthermore, results from VIZGLOW are benchmarked against simulation results obtained from the Hybrid Plasma Equipment Model (HPEM). Results for experimentally measured process gases (Ar, Ar/O₂, Ar/O₂/H₂) at low pressures (< 15 mTorr), operating at 3-6 kW's of input power, and varying rf frequency (400 kHz –13 MHz) are discussed.

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