Wednesday Afternoon, November 2, 2011

Plasma Science and Technology Division
Room: 202 - Session PS+EM-WeA

Low-K Materials & Integration
Moderator: S. King, Intel Corporation

2:00pm **PS+EM-WeA1 Electric and Optical Characterization of Leakage and Breakdown in Low-k Dielectric Materials**, *J.M. Atkin, R. Laibowitz,* Columbia University, *T.M. Shaw,* IBM T.J. Watson Research Center, ***T.F. Heinz***, Columbia University **INVITED**

Low-k dielectric thin films are finding increased use in integrated circuits for the faster signal speed that they permit. These materials, however, have higher leakage currents and shorter lifetimes than SiO_2–based dielectrics. With the continued push to lower values of k, these problems are becoming more acute.

In this paper, we present results of several complementary characterization techniques for determining key physical properties, such as trap densities and barrier heights, that influence leakage and time-dependent dielectric breakdown (TBBD) phenomena. Electrical characterization techniques include impedance spectroscopy and the measurements of transient currents. In addition, we make use of distinctive optical characterization techniques to obtain specific information about the underlying material properties. Internal photoemission (or photocurrent) spectroscopy yields information on interfacial barrier heights from the photon energies required to induce a current. Optical second-harmonic generation (SHG) provides a sensitive, non-contact method for measuring both photo-driven and spontaneous charge transport. From these methods, we show that the increase in current with long time biasing, which is in turn a precursor to electrical breakdown, can be directly correlated with increased trap densities. Conduction models accounting for the early failure mechanism will be discussed. Partial support for this work from the Semiconductor Research Corporation is gratefully acknowledged

2:40pm **PS+EM-WeA3 Electron Spin Resonance Study of Low-K Dielectrics and Etch Stop Layers**, ***B.C. Bittel***, *P.M. Lenahan, T.A. Pomorski,* Penn State University, *S. King*, Intel Corporation

The electronic properties of thin film low-κ interlayer dielectric (ILD) and etch stop layers (ESL) are important issues in ULSI development. However as the semiconductor industry looks to transition to 16 nm and beyond technology nodes, numerous concerns with low-κ materials need to be addressed. Leakage currents, time dependent dielectric breakdown and stress induced leakage currents are critical problems that are not yet well understood in ILD. A topic of current interest is ultraviolet light (UV curing) of low-κ materials.

We have made electron spin resonance (ESR) and current density versus voltage measurements on a moderately extensive set (over 50 films) of dielectric/silicon structures involving materials of importance to low-κ interconnect systems. Most of the dielectrics studied involve various compositions of SiOC:H. In addition we have also made measurements on other dielectrics including SiO_2, SiCN:H and SiN:H, some of which are utilized as ESLs. In our study we have made ESR and current density versus voltage measurements both before and after exposing the dielectrics to UV light ($hc/\lambda \leq 5$ eV), and films that have experienced an industrial UV curing process. We observe extremely gross differences in the ESR spectra and leakage current versus voltage response of these low-k films. We find that UV exposure consistently increases both the density of paramagnetic defects and the leakage current density at a given field. Paramagnetic point defects observed in these films include, E’ centers, silicon dangling bond defects in which the silicon is back bonded to oxygen, the 74 gauss doublet which is E’ center complexed to a hydrogen atom, the 10.4 gauss doublet which is a hydrogen coupled E’ center, the K-center which are silicon vacancies back bonded to three nitrogens, and possibly silicon and carbon dangling bond centers and likely organic radicals. We have also made electrically detected magnetic resonance (EDMR) spin dependent trap assisted tunneling measurements on some ILD films. The close correspondence between the ESR and SDT result establishes a direct link between the defects observed in ESR and the defects responsible for the increased tunneling currents. We have also observed a correspondence between ESR amplitudes and leakage currents. Our preliminary results suggest the UV curing process creates paramagnetic centers which take part in trap assisted tunneling. Our results indicate quite clearly that the processing parameters have extremely gross effects upon defect densities within these films.

4:00pm **PS+EM-WeA7 The Nature of Defects in Low-*k* Organosilicate Glass and their Response to Plasma Exposure**, ***H. Ren***, *M.T. Nichols,* University of Wisconsin-Madison, *G. Jiang, G.A. Antonelli,* Novellus Systems, *Y. Nishi,* Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

Defect concentrations in low-*k* organosilicate glass [SiCOH] films deposited on high-resistivity silicon were measured with electron-spin resonance. Both plasma exposure and ultraviolet exposure were used. During argon electron-cyclotron resonance plasma exposure, ion and photon bombardment increased the measured defect concentrations. Ultraviolet lamp exposure was also shown to increase the defect concentrations. SiCOH samples with several dielectric constants were examined showing that as the value of the dielectric constant was lowered, the defect concentrations were shown to increase significantly.[i] In addition, the nature of the defects in SiCOH was investigated using air and nitrogen plasma exposure. The defects were found to be silicon dangling bonds. Air-plasma exposure increases the defect concentrations by breaking silicon-hydrogen bonds, measured by Fourier-transform infrared spectroscopy. Nitrogen-plasma exposure as well as free-radical exposure have only a small influence on the bond breaking. It was also shown that UV curing improves the chemical-damage resistance of the dielectric.

Work Supported by the Semiconductor Research Corporation under contract 2008-KJ-1781 and the National Science Foundation under Grant CBET-1066231.

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[i] H. Ren, M. T. Nichols, G. Jiang, G. A. Antonelli, Y. Nishi, and J.L. Shohet, *Applied Physics Letters* **98**, 102903 (2011).

4:20pm **PS+EM-WeA8 The Effects of Plasma Exposure on the Time Dependent Dielectric Breakdown of Low-k Porous Organosilicate Glass**, ***M.T. Nichols***, *H. Sinha,* University of Wisconsin-Madison, *G.A. Antonelli,* Novellus Systems, Inc., *Y. Nishi,* Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

Time dependent dielectric breakdown (TDDB) is a major concern for newly emerging low-*k* organosilicate (SiCOH) dielectrics. TDDB degradation can be caused by changes in electrical, chemical, and mechanical properties of the dielectric materials.[i] [ii] [iii] [iv] In order to examine the effect of plasma exposure on TDDB degradation, time-to-breakdown measurements were made on porous SiCOH before and after exposure to a variety of plasma exposure conditions. Plasma parameters were changed between exposures such that each sample was subjected to different charged particle and vacuum ultraviolet photon fluxes in order to determine how TDDB degradation was affected by each of them during plasma exposure. By utilizing a capillary-array window to separate charged particle and photon bombardment, it is possible to show that each process is responsible for causing different types of TDDB degradation.

A constant voltage TDDB measurement technique was implemented to analyze unexposed, VUV-irradiated and plasma (charged-particle and photon bombardment) exposed samples to examine the degradation in TDDB. It was observed that the time to breakdown reduces as the electric field stress in increased, which is consistent with what has been previously predicted. It was also found that the unexposed samples exhibit longer time-to-breakdown, indicating highest reliability. Capillary-array-window covered samples exhibited marked degradation in leakage currents and time-to-breakdown relative to the unexposed samples. However, samples exposed to both charged particle and VUV photon bombardment exhibited the most significant degradation, resulting in substantially reduced breakdown times and increased leakage currents. Thus both charged particle and photon bombardment degrade TDDB.

This work has been supported by the Semiconductor Research Corporation under Contract 2008-KJ-1871 and by the National Science Foundation under Grant CBET-1066231.

[i] E. T. Ogawa, J. Kim, G. S. Haase, H. C. Mogul, and J. W. McPherson, *Proc. IEEE Int. Rel. Physics Symp*., p. 166. (2003)

[ii] Kok-Yong Yiang, H. W. Yao, A. Marathe, and O. Aubel, *Reliability Physics Symposium Proceedings, 44th Annual IEEE International* (2009).

[iii] F. Chen, O. Bravo, K. Chanda, P. McLaughlin, T. Sullivan, J. Gill, J. Lloyd, R. Kontra, J. Aitken, *Reliability Physics Symposium Proceedings, 44th Annual IEEE International* (2006)

[iv] C. Guedj, E. Martinez and G. Imbert, *Mater. Res. Soc. Symp. Proc.* **990** (2007)

4:40pm **PS+EM-WeA9 Modeling the Penetration of Vacuum Ultraviolet Photons in Porous-ULK Films**, ***J. Lee***, *D.B. Graves*, University of California, Berkeley

VUV radiation inherent in plasma discharges have been shown to be a concern during plasma processing of low-*k* materials [1, 2]. VUV photons are known to break Si-C bonds, thereby transforming the material into a SiOx-like material post-exposure. Damage to samples exposed to a Xe VUV lamp (λ = 147 nm) in a vacuum chamber compared to corresponding effects in an Ar/O2 plasmas (λ = 104, 106, and 130 nm) suggests that chemical modification is limited by the penetration depth of the VUV photons, which is in turn dependent on wavelength. The formation of a SiOx-like layer near the surface of the material, which deepens as more carbon is lost, introduces a dynamic change of integrated VUV absorption throughout the material over time. As a result, the rate of carbon loss is continuously changing during the exposure. We present a model that captures this dynamic behavior and compare the model to experimental data by fitting a parameter that represents the effective carbon photolysis using a procedure described previously [3]. For sample exposures to argon plasmas, the model shows good agreement with the experimentally obtained carbon loss profile, inferred from post-processing, ex-situ Fourier transform infrared spectroscopy (FTIR). For O2 plasma, there is evidence that an additional effect, perhaps oxygen radicals, plays a major role in chemical modification at short times near the surface of the material. By contrast, we conclude that VUV photons contribute more to damage in the bulk. By exposing samples to VUV radiation in He plasmas (λ = 58 nm), it may be possible to treat and modify the surface of low-*k* films with high energy, low penetrating VUV photons to limit damage to the near-surface.

[1] B. Jinnai, T. Nozawa, and S. Samukawa, J. Vac. Sci. Tech. B **26**, 1926 (2008).

[2] J. Lee and D. B. Graves, J. Phys. D: Appl. Phys. **43**, 425201 (2010).

[3] M. J. Titus, D. G. Nest, and D. B. Graves, J. Phys. D: Appl. Phys. **42**, 152001 (2009).

5:00pm **PS+EM-WeA10 Characterization of Plasma-Induced Damages on Low-k during Interconnection Integration by Scatterometric Porosimetry**, ***R. Hurand***, STMicroelectronics, France, *M. Darnon, T. Chevolleau, D. Fuard*, CNRS-LTM, France, *F. Bailly, R. Bouyssou*, STMicroelectronics, France, *T. David*, CEA Leti, France, *O. Joubert*, CNRS-LTM, France, *F. Leverd*, STMicroelectronics, France

With the continuous downscaling of devices, interconnects get narrower and narrower, and necessitate using porous low-k as insulator. Plasma processes required for the integration of low-k may cause damage at the sidewalls of the patterns, which degrades the dielectric properties of the material. The impact of the modified layer on the low-k sidewalls is becoming more critical when interconnects dimensions are scaled down. Developing low-damage plasma processes for porous low-k materials integration is compulsory, but requires a trustworthy characterization technique. Electron microscopy which leads to material shrinkage and does not precisely reveal the damaged layers is reaching its limitations. A new characterization technique, so-called Scatterometric Porosimetry has been recently proposed (Bouyssou et al. JVSTB, 2010). In this paper, we explain the principles of the method and demonstrate it can be used on complex industrial-relevant dielectric patterns (more than 9 dielectric layers, 140nm pitch). This technique can also be used to determine fundamental mechanisms of plasma induced modification to porous low-k dielectrics.

Scatterometric Porosimetry (SP) is a combination of scatterometry and porosimetric ellipsometry. Scatterometric measurements under vacuum give access to the pattern dimensions while measurements under controlled partial pressure of solvent give access to the material porosity or permeation (with low-polar solvent) or to the thickness of the hydrophilic damaged layer when water is used as a solvent.

Using this technique on an industrial stack, we determined the pattern profile and damaged layer thickness at the pattern sidewalls after each step of the etch process in a non destructive and high accuracy way. We identified that low-k main etch step is more damaging than barrier open or post etch plasma treatments: the damaged layer thickness representing 28% of the low-k width. On the contrary, the pattern profile is mostly controlled by the barrier opening step. A similar trend is measurable by SEM using decoration technique (measure before and after HF dip) but with less accuracy. We also investigated by SP the kinetic of sidewall modification during standard plasma processes including fluorocarbon-based processes or oxidizing or reducing plasma treatments.

5:20pm **PS+EM-WeA11 Photon Effects in Damage of Porous Low-k SiOCH During Plasma Cleaning**, ***J. Shoeb***, Iowa State University, *M.J. Kushner*, University of Michigan

Porous dielectric materials offer lower capacitances that reduce RC time delays in integrated circuits. Typical *low-k* materials include SiOCH – silicon dioxide with carbon groups, principally CH_3, lining the pores. Fluorocarbon plasmas are often used to etch *low-k* materials, a process that leaves a fluorocarbon polymer on the *low-k* surface that must be removed. With porosities as high as 0.5, pores which are internally connected provide pathways for reactive species to enter into the porous network. During cleaning using oxygen plasmas, reactions of O atoms with the CH_x groups, can remove carbon as CO/CO_2. After the process, H_2O from air can form hydrophilic Si-OH which can further adsorb H_2O through hydrogen bonding or physisorption.[1] As such, O_2 plasmas can degrade the low *k* value of the porous SiCOH. Plasma cleaning with He/H_2 mixtures causes less damage to SiCOH as reaction of H atoms with $–CH_3$ is endothermic. These damage scenarios are complicated by the UV/VUV photons produced by the plasma. Photons produced by the plasma can break Si-C bonds and separate $–CH_3$ radicals from SiO_2 to enhance the C removal rate.[2] 130 nm photons of Ar/O_2 plasmas can penetrate into SiCOH $\approx$100 nm but photons of He/H_2 plasmas (<100 nm) penetrate $\approx$20 nm. As a result, VUV photons from O_2 plasmas can produce Si-C bond scission approximately 5 times deeper in the low-*k* material compared to the VUV photons from He/H_2 mixtures. These penetration depths are sensitive functions of porosity and interconnectivity. For example, penetration depth increases nearly linearly with increases in interconnectivity due to the alignment of pores. In this talk, we discuss results from modeling of the plasma damage of porous SiOCH in He/H_2 and Ar/O_2 plasmas. The HPEM (Hybrid Plasma Equipment Module) was employed to obtain the ion energy and angle distributions of reactive fluxes from inductively coupled plasmas. These are used as input to the MCFPM (Monte Carlo Feature Profile Module) with which profiles of the low-*k* materials after the plasma exposure are predicted. The role of photons in porous SiCOH damage and validation of numerical results will be discussed in terms of treatment time, interconnectivity and photon flux. Overall, we found that due to its lower photon penetration depth and less reactivity, He/H_2 plasmas cause approximately 3 times less damage than Ar/O_2 plasmas, which is in agreement with experiments.

1. J. Proost, E. Kondoh, G. Vereecke, M. Heyns, and K. Maex, J. Vac. Sci. Technol. B **16**, 2091 (1998).

2. B. Jinnai, S. Fukuda, H. Ohtake, and S. Samukawa, J. Appl. Phys. **107**, 43302 (2010).

* Work supported by Semiconductor Research Corp.

5:40pm **PS+EM-WeA12 X-ray Photoelectron Spectroscopy Investigation of the Schottky Barrier at BN/Cu Interfaces**, ***M. French***, *M. Jaehnig, M. Kuhn, J. Bielefeld, S. King, B. French*, Intel Corporation

Due to a low dielectric constant (4-4.5) and high density (1.8-2.0 g/cm^3), Plasma Enhanced Chemically Vapor Deposited (PECVD) boron nitride (BN) is an intriguing material for use in low-k/Cu interconnect structures as a Cu diffusion barrier material. However, relatively little is known about the electrical leakage performance of BN in Cu interconnects or the Schottky barrier formed at the interface between these two materials. In this regard, x-ray photoelectron spectroscopy (XPS) was utilized to determine the Schottky barrier formed at the interface between polished Cu substrates and PECVD BN thin films. Our measurements indicate a barrier height of 3.0 ± 0.2 eV for the BN/Cu interface. This barrier height is nearly 2X that determined for a-SiCN:H and a-SiOC:H Cu capping layers and is attributed to the significantly larger band gap of BN (> 5 eV).

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