

Tuesday Afternoon, October 19, 2010

Plasma Science and Technology
Room: Aztec - Session PS1-TuA

Advanced BEOL/Interconnect Etching II

Moderator: Y. Zhou, Applied Materials Inc.

2:00pm **PS1-TuA1 Reaction Mechanism and Profile Evolution for Cleaning and Sealing Porous Low- k Dielectrics using He/H₂ and Ar/NH₃ Plasmas.** *J. Shoeb*, Iowa State University, *M.J. Kushner*, University of Michigan, Ann Arbor

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 CH₃, lining the pores. Fluorocarbon plasmas are often used to etch low- k materials. These processes leave a fluorocarbon polymer on the low- k surface that must be removed. This is often done with oxygen containing plasmas. With porosities as high as 0.5, pores open to the surface and which are internally connected provide pathways for reactive species to enter into the porous network. Reactions during plasma cleaning of, for example, O atoms with the CH_x groups, can increase the k value of the material by removing C atoms. To maintain the low- k value, cleaning the CF_x polymer and sealing of the surface must be performed without significantly altering the SiOCH material properties, and not removing the CH_x groups. Plasma cleaning with He/H₂ mixtures is capable of removing these CF_x residues without harming the underlying low- k surface and can also strip off the hydrocarbon photoresist (PR) mask.

In this talk, we discuss results from modeling of the plasma cleaning and sealing of porous SiOCH in sequentially applied He/H₂ and Ar/NH₃ 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 exposures are predicted.

We found that hot hydrogen atoms can remove the CF_x polymer, generating mainly HF and fluorohydrocarbons such as CHF₂. These hot H-atoms can simultaneously remove H from the surface resident CH₃ groups thereby activating the SiOCH surface by creating C dangling bonds. He ions are also effective at breaking Si-O bonds creating dangling while also removing H-atoms from CH₃ group, both of which activate the SiOCH surface. Unlike O₂ plasma cleaning, the He/H₂ clean creates more reactive CH_x ($x = 1,2$) sites without significantly damaging the substrate. Following the He/H₂ plasma cleaning, NH₃ plasma treatment seals the pores by NH_x ($x=1,2$ and 3) species passivating previously produced dangling bonds, forming Si-N and C-N bonds.[1] Initial results indicate that combined He/H₂ and Ar/NH₃ plasma treatment of SiOCH with pores having radii of 0.8 nm can seal nearly 100% of the surface pores.

* Work supported by Semiconductor Research Corp.

[1] A. M. Urbanowicz, M. R. Baklanov, J. Heijlen, Y. Travaly, and A. Cockburn, *Electrochem. Solid-State Lett.* **10**, G76 (2007).

2:20pm **PS1-TuA2 Mechanism of Modification in Si-O-Si Structure in Porous SiOCH Low- k Films by H₂/N₂ Plasmas.** *H. Yamamoto*, *K. Takeda*, *K. Ishikawa*, *H. Kondo*, *M. Sekine*, *M. Hori*, Nagoya University, Japan, *T. Imamura*, *H. Hayashi*, *I. Sakai*, *T. Ohiwa*, Toshiba Corporation, Japan

Introduction of porous low-dielectric-constant (low- k) materials such as porous (p-) SiOCH film, to the interlayer dielectric is important for improving performances of ULSI devices. The trench sidewall in the p-SiOCH film is known to suffer serious damage during the plasma processes. The *in-situ* evaluation is crucial for the clarification of damage generation mechanism because the damaged films are easily modified during air exposure. In this work, we have investigated the impact of ions, radicals and light from H₂/N₂ plasma and subsequent air exposure on Si-O-Si bond structure in the film using *in-situ* Fourier transform infrared reflection absorption spectroscopy. A 75-nm-thick p-SiOCH film was coated on 150-nm-thick Tungsten film deposited on Si substrate. A Si plate or an MgF₂ window which transmits light (greater than 115 nm in wavelength) was set 1 mm above or just on the film during the plasma exposure. Samples were placed on the lower electrode in a VHF-CCP etcher with (a) no plate for evaluating the interaction of ions, radicals, and light, (b) Si plate for evaluating the impact of radicals, (c) MgF₂ window for evaluating the effect of light and radicals, and (d) MgF₂ window with no space for evaluating the light effect. To investigate the Si-O-Si bond modification in the films, IR absorption signal in 985-1250 cm⁻¹ were decomposed to three bands with

peaks at 1035, 1065, and 1149 cm⁻¹, which correspond to the linear, network and cage structures, respectively. The change in the three peak area ratios were investigated after H₂/N₂ plasma and air exposures. The peak area ratio of the linear structure decreased and the ratio of network and cage structure increased after the H₂/N₂ plasma exposure in all samples. The ratio of linear structure decreased and the ratio of cage structure increased after the air exposure in all samples. In the case of sample (a), that was exposed to ions, radicals, and radiation, the amount of change in Si-O-Si structure was relatively smaller than the amount of decrease in Si-CH₃ bond. It was confirmed that a portion of Si-O-Si linear structure in the SiOCH film changed to network and cage structure with decrease in Si-CH₃ bond during the H₂/N₂ plasma exposure. Si-NH₂ bonds and dangling bonds formed by the plasma exposure reacted with water in the atmosphere and the Si-O-Si structure was modified with Si-OH bonds formation. Ion bombardment made the top surface shrink and the densified layer inhibited moisture uptake into the film during air exposure. This work was supported by Grant-in-Aid for Scientific Research (21 • 10187).

2:40pm **PS1-TuA3 Effect of UV-wavelength on Hardening Process of Porogen-containing and Porogen-free Ultra-low- k PECVD Glasses.** *A.M. Urbanowicz*, *K. Vanstreels*, *P. Verdonck*, *E. Van Besten*, *Ch. Trompoukis*, *D. Shamiryan*, *S. De Gendt*, *M.R. Baklanov*, IMEC, Belgium

The ITRS scaling of ultra-large-scale integrated circuits requires mechanically robust materials with low k -value. Low- k materials recently used in the Cu/low- k integration scheme have k -values between 2.5 and 3.0. One of the limiting factors in further reduction of k -value is mechanical robustness, since major way to decrease k -value is increasing the material porosity. The PECVD low- k deposition of ultra low- k films uses a porogen-based approach. The matrix material is deposited by oxidation of alkylsilanes in a plasma-enhanced chemical vapor deposition (PECVD) process. The porogen molecules, usually cyclic hydrocarbons, are introduced into a SiOCH film by co-deposition with the matrix material. To create porosity, the porogen is removed from the films using UV-assisted thermal curing. The porogen molecules are photo-dissociated by UV-light with the formation of volatile hydrocarbons and non-volatile carbon-rich residues (porogen residue) [1]. We have shown recently that SiOCH glasses with improved mechanical properties and ultra-low- k value could be obtained by controlled decomposition of the porogen molecules prior to the UV-hardening step [2]. The controlled removal of porogen can be performed by H₂-based afterglow plasma treatment of PECVD film [1,2].

In this work we study the effect of narrow band 172 nm and broadband >200 nm UV-sources in the new curing scheme of the PECVD dielectrics. The data are compared with the PECVD films fabricated in the conventional UV-curing scheme. The effect of both 172 nm and >200 nm UV-sources is comparable for porogen-containing conventional PECVD films. However, the porogen-free films cured with 172 nm UV-source shows approximately twice as higher Young's modulus (YM) of 6.64 GPa (k 100kHz ~ 2.2, 44% open porosity) than those cured with >200 nm UV with YM of 3.38 GPa (k 100kHz ~ 2.0, 48% open porosity). The mechanical properties, optical properties 150 nm - 800 nm, dielectric constants at 100 kHz and 4 GHz, porosities and pore size distributions, bonding structure are presented. The impact of porogen on optical characteristic and therefore on photochemical UV-hardening mechanism is discussed. The achieved mechanical properties are explained on a basis of the percolation of rigidity theory and random network concepts.

References

[1] A. M. Urbanowicz, K. Vanstreels, D. Shamiryan, S. De Gendt and M. Baklanov, *Electrochem. Solid State Lett.*, **12**, H292 (2009).

[2] A. M. Urbanowicz, K. Vanstreels, P. Verdonck, D. Shamiryan, S. De Gendt and M. R. Baklanov, accepted at *J. Appl. Phys.* 107,xxx, (2010).

3:00pm **PS1-TuA4 CF₃I for Low- k Etching: Overcoming Current Technology Limitations.** *V. Omarjee*, American Air Liquide – Delaware Research and Technology Center, *A.G. Gildea*, *E. Eisenbraun*, The University at Albany-SUNY, *N. Stafford*, *F. Doniat*, *C. Dussarrat*, American Air Liquide – Delaware Research and Technology Center

Every technology node brings new processing challenges. The etching of low- k and ultra-low- k ($k=2.4$ and below) materials that are currently used in leading edge interconnects is very demanding. With a porosity varying from ~15 to 30%, the films are easily damaged during the various processing steps and it is easy to have undesired film modifications (physical defects,

collapse, impurity penetration, roughening of the surfaces, moisture uptake...) that degrade interconnect reliability and performance.

In this talk we will present recent work done on optimization of dielectric etching using CF₃I, a promising replacement gas for CF₄ in interconnect etch applications. Using a Design of Experiment (DOE) approach through a Taguchi-like Method combined with the capabilities of a State-of-the-Art Unaxis 200mm wafer etch system, the influences of the key parameters on the etching mechanism and performance will be presented. The DOE approach is introduced here to minimize the number of experiments while maximizing the process understanding. For instance, one of the results of the experimental matrix suggests an etching rate contribution of CF₃I that is non-linear. In addition to characterization of etch rate, the samples are characterized using RBS, AES and SEM to fully understand the impact of the process parameters on overall film quality. Baseline data as well as structure patterning will be presented after the optimization process using CF₃I alone and also using CF₃I mixed with well established fluorocarbons.

4:00pm PS1-TuA7 Challenges in sub-100nm Dual Damascene Etch of Porous Oxycarbosilane Ultra Low-k Dielectrics for BEOL Integration, R.L. Bruce, S.U. Engelmann, S. Purushothaman, IBM T.J. Watson Research Center, T.J. Frot, IBM Almaden Research Center, M. Darnon, M. Lofaro, S. Cohen, IBM T.J. Watson Research Center, W. Volkens, T.P. Magbitang, L. Krupp, G. Dubois, IBM Almaden Research Center

There has been much interest recently in porous oxycarbosilane (POCS)-based materials as the interconnect layer dielectric (ILD) in back-end-of-line (BEOL) manufacturing due to their superior mechanical properties compared to conventional porous SiCOH at equivalent porosity and dielectric constant. [1-4] While it is well known that plasma etching and ashing processes can cause significant damage to porous ultra-low k dielectric materials in general, little has been reported about the effect of plasma damage to POCS as the ILD material. In this work, we discuss the effect of plasma etching and ashing processes on POCS during the fabrication of single and dual damascene structures for BEOL integration. We used TEM-EELS to quantify chemical composition changes at the top, bottom, and sidewalls of POCS trenches after each plasma etching and ashing step. After plasma processing, POCS structures undergo extensive plasma damage such as pitting, microtrenching, and the generation of trench bottom roughness. Opening of the cap layer exacerbates these etch damage features. Damage is reduced by increasing the neutral-to-ion ratio of the gas discharge in the ULK trench etch and eliminating O₂ from the ashing process. The use of vapor phase silylation between etch process steps is also shown to repair plasma-damaged POCS. However, we show that the most significant improvement to post-plasma damage occurred by reducing the pore size of the starting POCS material while maintaining comparable porosity, i.e. dielectric constant.

[1] W. Volkens, *et al.*, Chem. Rev. 110, 56 (2010).

[2] G. Dubois, *et al.*, J. Of Sol-Gel Science and Technology 48, 187 (2008).

[3] G. Dubois, *et al.*, in *Dielectric Films for Advanced Microelectronics*, edited by M. Baklanov, *et al.*, (Wiley, New York, 2007), p. 33.

[4] G. Dubois, *et al.*, Adv. Materials 19, 3989 (2007).

4:20pm PS1-TuA8 Mechanism of Highly Selective SiO₂ Etching over Photoresist Using New Alternative Gas, C₅HF₇, Y. Miyawaki, Y. Kondo, K. Takeda, K. Ishikawa, M. Sekine, H. Kondo, Nagoya University, Japan, A. Ito, M. Nakamura, Zeon Corporation, Japan, M. Hori, Nagoya University, Japan

With the continuous demand for increasing the storage capacity of semiconductor memory devices, a much precise etching process for high aspect ratio contact holes in SiO₂ film is indispensable. The aspect ratio of more than 20 will be required for 45-nm node in 2010. Furthermore, deterioration of the SiO₂ selectivity over a fragile, thin photoresist would cause the sidewall roughness and poor pattern-width definition. In this study, we utilized a newly designed environmentally-friendly (low global warming potential) gas, C₅HF₇, and compared the etch performances with conventional C₅F₈ gas. A very-high-frequency (VHF) capacitively coupled plasma (CCP) etcher was used with 1800 W VHF power and 2 MHz bias of 1200 W. C₅F₈ or C₅HF₇ gas was introduced with O₂ and Ar (C₅F₈ or C₅HF₇/O₂/Ar = 15 / 10-35 / 300 sccm). We evaluated the dependence of O₂ flow rate on the etching rates of SiO₂ and KrF photoresist and SiO₂ selectivity to the resist. The gas phase species, O radical (O*) and CF₃⁺, were measured using Vacuum Ultraviolet Laser absorption spectroscopy (VUVLAS) and a

quadruple mass spectroscopy (QMS). The C₅F₈ gas chemistry showed the maximum selectivity of 3.7 with the etching rate of 416 nm/min at 20 sccm O₂ flow rate. In contrast, C₅HF₇ chemistry realized much higher selectivity (more than 13.5) with the etching rate of 356 nm/min at 25 sccm O₂ flow rate. It was confirmed that almost four times higher selectivity than that of the conventional C₅F₈ gas was obtained by using the new C₅HF₇ gas. In the both gas chemistry, the density of CF₃⁺ ion, that could be one of the dominant etch species for SiO₂, showed the maximum value at the maximum etch rate conditions. The variation trends for O* densities were similar to the resist etch rate in C₅HF₇/O₂/Ar plasma. It was also speculated that the H atoms from C₅HF₇ reduced the density of F radical that would enhance the resist etch rate. The reason for the high selectivity would be examined by measuring the surface chemical compositions and the gas phase species, such as CF_x and F.

4:40pm PS1-TuA9 Etch Characteristics of SiO₂ in the C₅F₇ Dual-Frequency Capacitive Coupled Plasma, M.H. Jeon, S.K. Kang, J.Y. Park, G.Y. Yeom, Sungkyunkwan University, Republic of Korea

5:00pm PS1-TuA10 Ultra-high Selectivity Silicon Nitride Liner Etch: Mitigating Substrate Damage in Logic-based Contact Level Interconnects, A. Metz, H. Cottle, Y. Chiba, P. Biolsi, TEL Technology Center America, M. Luo, E. Geiss, Global Foundries, S.H. Sung, Samsung Electronics, M. Aminpur, R. Wise, IBM Microelectronics

Reactive Ion Etch [RIE] of Silicon Nitride films, utilized primarily as spacers, hard masks or etch stop layers [ESLs], is pervasive throughout logic and flash microelectronics fabrication processes. While the most critical RIE-related specifications vary widely depending on the specific application and photolayer, contact level liner/ESL removal is among the most challenging. This application ideally requires high etch selectivities to multiple material types [including NiSi, SiO₂, Si, and Si_xGe_y] at the bottom of a high aspect ratio feature where etch stop marginality in a polymer rich regime can impact opens yield. Furthermore, relying on high radical density, low ion energy, primarily chemical etch processes utilized for Si_xN_y type spacer applications often lack profile control where sidewall bowing can result in metallization related yield fallout.

This work characterizes a new contact RIE process developed for 28nm and beyond technology nodes. Reported is the successful integration of an ultra high selectivity Si_xN_y liner removal process [$> 40:1$ in hole selectivity for Si_xN_y : Si]. Cross-sectional characterization of contact profile and in hole selectivity data will be provided. High Opens/Shorts yield [equal or better than baseline] as determined by voltage contrast metrology and inline E-Test will be shown. In addition, a 10x reduction in gate leakage will be shown based in-line E-Test attributable to reduced active area Si loss/recess.

5:20pm PS1-TuA11 Achieving Lithographically Independent sub-35nm Vias for Phase Change Memory Applications, E.A. Joseph, R. Dasaka, M. Breitwisch, A.G. Schrott, C.H. Lam, IBM T.J. Watson Research Center

Non-volatile phase change based memory has recently garnered significant interest due to its potential for scalability beyond that of conventional DRAM and Flash memory technologies.[1] However, multiple etch challenges exist in the fabrication of robust PCM devices and not all have been thoroughly discussed and/or researched. For instance, patterning of the novel phase change material without causing material modification and performance degradation is a well known issue and has been reviewed in the past.[2,3,4] On the other hand, the ability to fabricate robust and uniform sublithographic contacts (to the phase change material) is rarely discussed from an etch perspective. In this presentation, this latter issue is explored in detail and a lithographically independent etch process scheme with the capability of yielding sub-35nm vias is presented. Critical factors such as oxide and nitride etch selectivity, taper angle and etch stop phenomenon are all reviewed. Lastly, the application of this method for logic applications such as gate contacts and BEOL via patterning will also be discussed with a focus on the ultimate scaling limitations of this process.

[1] Y.C. Chen, C.T. Rettner, S. Raoux *et al.*, IEDM Tech. Dig., p. S30P3, 2006.

[2] P. Petruzza, Paper PS-MoA4, AVS 54th International Symposium, 2007

[3] E. A. Joseph, T. D. Happ, S.-H. Chen, S. Raoux, *et al.*, Symp. VLSI-Technology Systems and Applications, 2008. pg 142-143, 2008

[4] E. A. Joseph, S. Raoux, J. L. Jordan-Sweet, D. Miller, H-Yu Cheng, A. Schrott, C-F. Chen, R. Dasaka, B. Shelby, Y. Zhang, C. Lam, J. Washington, G. Lucovsky and M. Paesler, Paper PS1-ThM11, AVS 56th International Symposium, 2009

5:40pm **PS1-TuA12 The Evaluation of Sidewall Polymerization during Platinum Dry Etching Process using Inductively Coupled Cl₂/O₂/Ar and CH₃OH Plasmas**, *J.Y. Moon, J.W. Park, M.S. Lee, B.G. Jyun, W.J. Choi, S.H. Cho, J.S. Roh, S.-K. Park*, HYNIX Semiconductor Inc., Republic of Korea

It has been reported that platinum is the most appropriate resistive switching RAM (ReRAM) electrode material due to its good oxidation-resistance, high electrical conductivity and low leakage current characteristics. However, platinum does not easily form the volatile products, and the unwanted sidewall polymer which is produced during plasma etch process gives a large shift in the pattern size of the etched pattern and also makes it difficult to remove. In this study, experimental studies of platinum etching process have been performed to understand the characteristics of sidewall polymerization using inductively coupled Cl₂/O₂/Ar and CH₃OH plasmas etching process. The effects of etch parameters such as gas combination and substrate temperature on the characteristics of etch properties of platinum were also investigated to minimize sidewall polymer re-deposition in the point of re-deposited sidewall polymers. The thickness of re-deposited polymers related to platinum were measured and studied by high resolution transmission electron microscopy (HR-TEM). The chemical reactions on the etched surface also have been studied by X-ray photoelectron spectroscopy (XPS).

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