

## Incorporating Principles of Industrial Ecology Room 304 - Session IE+PS+MS+SE-WeM

### Environmentally Friendly Process Development

**Moderator:** D.R. Baer, Pacific Northwest National Laboratory

8:20am **IE+PS+MS+SE-WeM1 CVD Films as Directly Patternable Low-k Dielectrics**, *K.K. Gleason, H.G. Pryce Lewis*, Massachusetts Institute of Technology; *G.L. Weibel, C.K. Ober*, Cornell University **INVITED**

As microelectronic feature sizes decrease to 100-nm and below, major advances in both interconnect and lithographic technologies are necessary. Novel low-k candidates being assessed include fluorine- and silicon-containing materials produced by chemical vapor deposition (CVD). Fluorine- and silicon-containing polymeric materials are also ideal resist candidates for 157-nm photolithography, as conventional photoresists are opaque at this wavelength. In this paper, we present a collaboration aimed at merging the role of sacrificial resist and low-k dielectric. Specifically, we are investigating a direct dielectric patterning process in which a low-k fluorocarbon or organosilicon material is deposited by CVD, exposed, and developed using no wet processing. In our scheme, a film is deposited using hot-filament CVD, a non-plasma technique which offers the ability to tailor film chemistries. The film is masked and exposed using e-beam or a 157-nm source, and developed using supercritical CO<sub>2</sub> as a dry developing medium. The patterned film then serves as a low-k material compatible with metallization schemes such as the damascene process. This technology would greatly simplify future device manufacture by reducing the number of steps involved in patterning. The CVD process and the use of dry development also offer environmental, safety and health advantages over solvent-based spin-on coating and aqueous development. Positive-tone contrast has been demonstrated in fluorocarbon CVD films and fully-developed images of 0.25-micron have been demonstrated from e-beam exposure. We are presently working to enhance sensitivity and optimize image resolution.

9:00am **IE+PS+MS+SE-WeM3 Characterization of Remote Plasma Clean Process for Plasma CVD Chamber**, *T. Tanaka, T. Nowak, M. Seamons, B.H. Kim, K. Lai, M. Cox, P. Loewenhardt, D. Silveti, S. Shamoulian*, Applied Materials Inc.

Remote plasma cleaning of CVD process chambers has proven to be more efficient than conventional in-situ plasma cleaning in terms of higher throughput and higher gas breakdown efficiency. It is still important, however, to maximize the efficiency of the remote plasma clean process because of the potential environmental impact and the cost of process gases. The remote clean process involves three steps: generation of reactive species (mostly fluorine atoms) in a remote plasma source, transport of the reactive gas, and the cleaning reaction in the CVD chamber. We studied the efficiency of the process in each step. Since accurate direct measurement of the atomic fluorine concentration in the various parts of the CVD reactor is difficult, we used etching of thermal oxide wafer coupons to estimate the relative distribution of atomic fluorine within the reactor. Source dissociation efficiency was studied using an indirect technique based on correlation of pressure to effluent composition. We found that it requires approximately 24eV to break down each NF<sub>3</sub> molecule. This translates to 1.7W/sccm of NF<sub>3</sub> flow. This was seen to be approximately the same for both a microwave discharge operating at 2.45GHz and an inductively coupled plasma at 13.56MHz. Results characterizing the transport step demonstrate the importance of system design on minimizing recombination losses of the reactive species which, for a parallel plate reactor, can be as high as 50% of the atomic fluorine generated in the remote plasma source. The experimental results are compared with a simple model, which describes the general behavior of the cleaning process.

9:20am **IE+PS+MS+SE-WeM4 Silicon Oxide Contact Hole Etching Process Employing Environmentally Harmonized Technique**, *K. Fujita, M. Hori, T. Goto*, Nagoya University, Japan; *M. Ito*, Wakayama University, Japan

Etching process of SiO<sub>2</sub> contact holes in ULSI has been developed by using high-density plasmas employing stable PFC gases. PFC gases, however, cause a serious environmental problem, namely global warming and hereby the uses of fluorocarbon gases would be restricted in the near future. Recently, we proposed environmentally harmonized technique replacing stable PFC gases for preventing global warming, where polytetrafluoroethylene (PTFE) is evaporated by a CO<sub>2</sub> laser and the generated fluorocarbon species (C<sub>x</sub>F<sub>y</sub>) are injected

into ECR plasma reactor from externally. This technique, therefore, enables us to achieve a novel plasma process with new gas chemistries. In this study, this system has been successfully applied to ECR plasma etching of SiO<sub>2</sub> contact hole and the behavior of CF<sub>x</sub> (x=1-3) radical densities in the plasma were evaluated by infrared diode laser absorption spectroscopy (IRLAS). The high SiO<sub>2</sub> etching rate of 780 nm/min was obtained at a microwave power of 400 W, a pressure of 2.7 Pa, a total flow rate of 80 sccm and a bias voltage of -450 V. Dependence of contact hole etching characteristics on Ar dilution and pressure has been investigated. Anisotropy of contact hole etching was improved with increasing the Ar dilution ratio and decreasing the pressure because the fluorocarbon polymer deposition was suppressed at the higher Ar dilution and the lower pressure. IRLAS measurements indicate CF<sub>2</sub> radicals and higher radicals (C<sub>x</sub>F<sub>y</sub>) have the good relation with the polymer deposition. The anisotropic contact hole etching was achieved at an Ar dilution ratio of 90 %, a pressure of 0.4 Pa and the etching rate of SiO<sub>2</sub>, selectivity of SiO<sub>2</sub> to Si and selectivity of SiO<sub>2</sub> to resist were 340 nm/min, 31 and 6.4, respectively. These results indicate that this environmentally harmonized technique will propose the alternative etching system replacing PFC gases.

9:40am **IE+PS+MS+SE-WeM5 Photocatalytic, Anti-fogging Mirror**, *K. Takagi*, ULVAC Japan, Ltd., Japan; *H. Hiraiwa, T. Makimoto, T. Negishi*, ULVAC Japan, Ltd.

Recently, environmental pollution is growing more serious everyday, and it is urgently required to develop resource-saving and non-chemical products, which may save and even purify the nature. In such circumstances, titanium dioxide (TiO<sub>2</sub>) thin coating film has come into the spotlight as a savior of the environmental problems. Because of its attractive photocatalytic natures, such as anti-bacterial, self-cleaning, decomposition of organic substances, and super-hydrophilic natures, TiO<sub>2</sub> has been studied and developed energetically in these days. Already, its super-hydrophilic and self-cleaning natures are applied to automobiles' anti-fogging side mirrors, which are now in practical use, and ULVAC Japan is one of the top makers for manufacturing vacuum deposition system for anti-fogging mirrors. The film architecture of this mirror is the double layer of SiO<sub>2</sub> / TiO<sub>2</sub> on the substrate coated by E/B evaporation or sputtering. The photocatalytic natures are as follows; 1. The contact angle of water on this surface is less than 10° after irradiation of Blacklight, on which the engine oil is spreaded and cleaned by washing. 2. The contact angle keeps less than 10° when this sample is preserved in the dark room. This report describes current developmental status of vacuum deposition system for TiO<sub>2</sub>/SiO<sub>2</sub> thin film coating that is applied to automobile-mounted photocatalytic mirrors and is useful for environment saving and purification.

10:00am **IE+PS+MS+SE-WeM6 Low-k Materials Etching in Magnetic Neutral Loop Discharge Plasma**, *Y. Morikawa, S. Yasunami*, ULVAC JAPAN Ltd.; *W. Chen, T. Hayashi*, ULVAC JAPAN Ltd., Japan; *H. Yamakawa, T. Uchida*, ULVAC JAPAN Ltd.

Many low-k materials, like Si containing inorganic / organic compounds, purely organic compounds and porous silicate glass, are proposed and examined as the interlayer dielectric one. The magnetic neutral loop discharge (NLD) plasma is very useful for very fine pattern etching process, because the NLD plasma has high density and low temperature characteristics and tends to form uniform density distribution on the substrate, at lower pressure region than 1 Pa under 13.56 MHz oscillating induction field. So we adopted the NLD plasma to etch organic low-k materials, with very high etch rate over 900 nm/min by using NH<sub>3</sub>. An etching issue for the purely organic low-k materials is bowing in the hole smaller than 200nm in diameter, probably caused by reaction of the hole-wall surface with hydrogen atoms. Based on this consideration, we carried out the etching by using nitrogen gas mixed with a low concentration of hydrogen gas in low pressures below 1 Pa. The etch rate increased abruptly at hydrogen addition of a few quantity and approached gradually to a constant value at 20%. But the bowing size became larger above hydrogen mixed ratio of 20%. So we measured mass spectra of ion species produced in the plasma to know the mechanism. It was found that intensity of N<sub>2</sub><sup>+</sup> also increased abruptly and then was close to a constant value at 20%. The other species did not show similar tendency. It is deduced from this result that N<sub>2</sub><sup>+</sup> ion may participate in main etching reaction to obtain the conformal etched profile. Etching characteristics for OSG, pure organic low-k materials and porous silicate glass will be shown. @FootnoteText@ @footnote 1@W.Chen, T.Hayashi, M.Itoh, Y.Morikawa, K.Sugita, H.Shindo and T.Uchida : Jpn. J. Appl. Phys.,

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38 (1999) 4296 @footnote 2@W.Chen, T.Hayashi, M.Itoh, Y.Morikawa, K.Sugita and T.Uchida : Vacuum, 53 (1999) 29 @footnote 3@W.Chen, T.Hayashi, M.Itoh, Y.Morikawa, K.Sugita, H.Shindo and T.Uchida : J. Vac. Sci. Technol. A17(5), (1999) 2546.

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