Plasma Science and Technology
Room: 308 - Session PS2-FrM

Plasma Surface Interactions II

Moderator: Ryan M. Martin, IBM T.J. Watson Research Center

8:20am **PS2-FrM1 Enhancement of Surface Migration by Photoemission-assisted Plasma for Atomic-Scale Surface Smoothing**, *A. Saijian, Y. Kotanikawa, Y. Ohtomo,* ***Shuichi Ogawa****, Y. Takakuwa*, Tohoku University, Japan

As a novel tool of plasma ion beam techniques for surface smoothing, we have developed a photoemission-assisted plasma ion source (PAP) [1]. It has been confirmed that the Ar^+-PAP treatment has an effect to smooth mechanically grinded Al and Cu surfaces with an initial surface roughness (Ra(0)) of a few hundred nanometers [1]. To clarify the surface morphology changes by PAP ion source and understand the PAP ion source-surface interaction, in this study, Cu deposited on Si rare surface (Cu(200 nm)/Si_R) with Ra(0) ~13 nm, has been used for surface smoothing treatments. Plasma parameters have been measured by a cylindrical single Langmuir probe to better understanding the characteristics of the PAP.

In the experimental apparatus of PAP, a Xe excimer lamp with UV light (λ = 172 nm) was employed, leading to the order of 10^{12} photoelectrons/cm^2/s, which enabled us to generate uniformly glow discharge over 2-inch Si wafer at bias voltage V_B of 200 V under Ar atmosphere with pressure of 300 Pa, and to increase a discharge current up to 10^{-6}-10^{-4} A at smaller V_B than 200 V, which is referred to as Townsend plasma. According to the plasma potential measured by Langmuir probe, taking the energy loss due to elastic collisions between Ar+ ion and Ar atom into account, we estimated the E_k of Ar ion upon the impingement with the substrate to be 10.7 and 0.79 eV for glow and Townsend discharge, respectively. Based on the estimated values of E_k, a surface flattening model of the dry planarization process is discussed.

When the Cu surfaces irradiated by the photoemission-assisted glow discharge plasma (E_k = ~10.7 eV), and the photoemission-assisted Townsend discharge (E_k = ~0.79 eV), the surface roughness was improved down to ~69.8% and ~54.5%, respectively. It indicated that the PAP has the ability to reduce the surface roughness down to atomic-scale under both discharge conditions. It has been reported that diffusion barrier of Cu atom via hopping or exchanging on Cu surface is 0.04 ~ 0.66 eV [2] and the threshold energy of Cu sputtering by Ar^+ is between 25~50 eV [3]. Therefore the enhancement of surface migration of Cu atoms is mainly responsible for the improvement of Ra in discharge conditions. Conclusively it is considered that the photoemission-assisted plasma works as an ion source with E_k in the order of eV, which sufficiently makes the surface morphology improved due to the enhancement of surface migration.

Reference

[1] Y. Ohtomo, S. Ogawa, and Y. Takakuwa, Surf. Interf. Anal. **44** (2012) 670.

[2] J. Wang et al., Modelling Simul. Mater. Sci. Eng. **12** (2004) 1209.

[3] J. D. Kress et al., J. Vac. Sci. Technol. A **17** (1999) 2819.

8:40am **PS2-FrM2 Silicon Etching using CW, Synchronized Pulsed and Bias Pulsed Cl_2 Plasma**, ***Odile Mourey****, G. Cunge, C. Petit-Etienne, M. Darnon, P.D. Brichon, E. Despiau-Pujo, E. Latu-Romain, O. Joubert*, LTM - MINATEC - CEA/LETI, France

The semiconductor industry is more and more challenged by the miniaturization of integrated circuits and the introduction of new devices architectures. Typical high density plasma show limitations in terms of anisotropy, selectivity and ion induced damages to etch stacks of ultrathin layers. New plasma technologies that provide an atomic level control of etching processes are now required and pulsed plasmas are promising candidates. In this work, we compare the performances of typical CW ICP plasma with synchronous pulsed plasma (ICP and bias power pulsed in phase) and bias pulsed plasma (ICP is CW and bias pulsed). In each case we use Cl_2 plasma to etch silicon and several parameters are monitored including etch rate, surface roughness, thickness of $SiCl_x$ reactive layer, ions flux and ions energy. We also investigate the importance of the surface preparation. Using atomic force microscopy, we show that (by contrast with CW plasmas) the surface roughness increases as a function of etching time in pulsed plasmas and that this worsens at small duty cycle. Preliminary results of molecular dynamic simulations suggest that this could be attributed to the modulation of the ion energy in pulsed plasma: in the OFF period radicals can attack the surface defect created by individual ions impacts during the previous ON period.

9:00am **PS2-FrM3 Utilizing Absorption, Emission, and Fluorescence Spectroscopies to Elucidate the Energetics of Plasma-Surface Interactions**, *J.M. Blechle, R.B. Davidson, E.J. Sutor,* ***Ellen Fisher***, Colorado State University

Plasma-enhanced chemical vapor deposition (PECVD), plasma etching, and plasma modification of surfaces are integral to a range of technologies including microelectronics, optical or protective coatings and biomaterials. Many mechanistic details for plasma processing of these materials, however, remain unknown. Understanding surface interactions of plasma species provides critical molecular level information about plasma processing, especially at interfaces. In addition, power dissipation and energetics are also important for elucidation of mechanistic details in plasma-surface interactions. The imaging of radicals interacting with surfaces (IRIS) technique measures interactions of radicals during plasma processing of a variety of materials. This technique combines molecular beam and plasma technologies with laser-induced fluorescence (LIF) to provide information on radical-surface interactions during plasma processing. Furthermore, IRIS provides direct information on the energetics of plasma-generated radicals as well as for species scattering off of surfaces. IRIS data for species in PECVD and etching environments will be presented. We have also employed both time-resolved optical emission spectroscopy (TR-OES) and broadband absorption spectroscopy (BAS) to our plasma systems to further explore the gas-phase chemistry and gas-surface interactions. In particular, IRIS, TR-OES and BAS data on oxygen-containing systems (O atoms, OH radicals), fluorocarbon radicals (CF and CF2), , and nitrogen-containing molecules (NO, NH, NH2, CN) will be presented by comparing and contrasting these groups of molecules. Correlation of gas-phase data, surface analysis information, and plasma-surface interface reactions will also be presented to provide more comprehensive mechanisms for overall plasma polymerization processes.

9:20am **PS2-FrM4 Transmission of Plasma-Generated Free Radicals through Dielectric Films**, ***Faraz Choudhury****, G. Sabat,* University of Wisconsin-Madison, *Y. Nishi,* Stanford University, *J.L. Shohet*, University of Wisconsin-Madison

During plasma processing, low-k dielectrics are exposed to free radicals from the plasma that may adversely affect the chemical, mechanical and electrical properties of the films. Modern low-k dielectrics have highly porous structures (up to 50%) and interconnected pores provide pathways for reactive species to enter into the material making them more susceptible to damage. Previous work utilized simulations[1] to determine the free-radical density and doses from the processing plasma. Several techniques have been developed and tested over the years for radical measurements[2], but the methods do not provide a direct measurement of the free radical concentrations at the location of the sample during processing. A new technique, using fluorophore dyes, can detect free radicals in a processing plasma and determine the their fluence at the surface of a sample during processing is investigated. The fluorophore used in this work is Alexa Fluor® 488. After reaction with reactive oxygen species (ROS), the bright green fluorescence (excitation/emission maxima ~490/515 nm) of the dye is significantly degraded. This degradation is measured using a fluorometer. The change in intensity of the fluorescence can be used to measure the free radical fluence from the plasma. This technique can also be used to determine the number of free radicals that can penetrate through a layer of low-k dielectric film as follows. Alexa 488 is placed under free-standing dielectric films such as SiO_2 and SiCOH of various thicknesses to determine the penetration depth of free radicals that are present in a typical processing plasma. Fluorescent dyes that selectively react with specific types of free radicals can also be used. In particular, we will use hydroxyphenyl fluorescein (HPF) that is a hydroxyl (OH) radical sensor. The change in fluorescence of this dye after plasma exposure can be used to determine the OH radical fluence from the plasma. I-V, C-V and TDDB measurements can also be made as a function of plasma exposure time to determine the extent of damage to the electrical properties of the films.

This work has been supported by the Semiconductor Research Corporation under Contract No. 2012-KJ-2359 and the National Science Foundation under Grant No. CBET-1066231.

[1] Shi, H. and Huang, H., Bao, J., Liu, J., Ho, P. S., Zhou, Y., Pender, J.T., Armacost, M. D. and Kyser, D., *Journal of Vacuum Science & TechnologyB*, **30**, 011206 (2012)

[2] Moon, C.S., Takeda, K., Takashima, S., Sekine, M., Setsuhara, Y., Shiratani, M., and Hori, M., *Journal of Applied Physics*, **107**, 103310 (2010)

9:40am **PS2-FrM5 Gas-Phase Chemistry and Plasma Surface Interactions**, ***Matthew Goeckner***, University of Texas at Dallas **INVITED**

Plasmas have been used extensively in the semiconductor industry for almost half a century. However as processing has reached the production of nano-scale devices, development of industrially viable processes have become more difficult. In part this is because of all of the free parameters that exist in such plasmas. To overcome this economic issue, tool vendors and semiconductor companies have turned to complex computational models of processing plasmas. The accuracy of those models requires a thorough understanding of the links between gas-phase chemistry and surface processes. In this talk, we will give a brief overview of what is known about the links between the gas-phase chemistry and surface processes and what still needs to be understood.

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10:40am **PS2-FrM8 Plasma Induced Roughness Formation on Photoresist Examined by HBr Plasma-Beam Etching**, *Y. Zhang*, ***Makoto Sekine***, *K. Ishikawa, K. Takeda, H. Kondo, M. Hori*, Nagoya University, Japan

For highly precise patterning technologies in device fabrication, it is required to suppress roughness formations on photoresist (PR) polymers during plasma etching processes. The HBr plasma treatment called 'plasma cure' was proposed to reduce the roughness formation [1]. In the previous studies, by using a beam irradiation system, we reported the PR roughness formation in fluorocarbon plasma [2], and the effect on roughness suppression by HBr plasma cure [3]. In this report, we have extensively investigated the roughness formation mechanism on the PR for ArF photolithography by some surface analyses and power spectral density (PSD) of the roughness.

The photoresist roughness observed by the atomic force microscope (AFM) is characterized by two dimensional (2D) PSDs and the frequency distribution for a digitized height profile [4]. Average slope and roll-off frequency of PSD are characterized by frequency components, the high-frequency roughness [5]. We treated the roughness data for six samples: (a) initial (pristine), (b) after Ar plasma beam irradiation (Ar), (c) after Ar plasma beam irradiation followed by HBr plasma cure (Ar→HBr), (d) after HBr plasma cure (HBr), (e) after HBr followed by Ar plasma beam irradiation (HBr→Ar), and (f) after HBr followed by H_2 plasma beam and Ar plasma beam irradiation (HBr→H_2→Ar).

The PSD slopes were changed by each process. The Ar plasma beam irradiation affected higher-frequency roughness, i.e. fine roughness induced on the PR surface. Thus the ion bombardments affected the local fine roughness. In particular for (e), Ar irradiation after HBr cure, the higher-frequency roughness could be reduced. This indicates that the HBr cure possibly hardened the PR surface by crosslinking polymeric chains, and the behavior was observed apparently on the decrease of roll-off frequency. On the other hand, the HBr cure after Ar irradiation, (c), increased lower frequency components of roughness compared with just Ar plasma beam irradiation, (b). We speculated that the Ar-plasma beam formed a crust layer on the PR surface with unrelieved stress and HBr cure may soften the bulk PR to relieve the stress and cause agglomeration of polymers at the size over 10 nm.

References

[1] A. Ando et al., Thin Solid Films 515, 4928 (2007).

[2] T. Takeuchi et al., J. Phys. D: Appl. Phys. 46, 102001 (2013).

[3] Y. Zhang et al., 74th Japan Society of Applied Physics Meeting, 17a-C2-7 (2013).

[4] diNanoScope Software 7.0 User Guide. Veeco Instruments Inc., pp. 163 (2006).

[5] B. N. J. Persson et al., J. Phys.: Condens. Matter, 17 R58 (2005).

11:00am **PS2-FrM9 Novel Gases for Obtaining High Etch Selectivity of Oxide to Nitride for Contact Etch**, ***Vijay Surla***, *L. Daniel, R. Gupta, V. Pallem*, Air Liquide

Contact oxide etch is a critical process in developing the next generation integrated device fabrication. With the gate feature size scaling down, the aspect ratio of the features increases and contact oxide etch process becomes more challenging. Very high etch selectivities of Oxide to Nitride are required for contact etch, and there is an increasing need for finding new etch gases that can perform better than the traditional gases like C_4F_8 and additive mixtures used by the semiconductor industry. To this end, Air Liquide is actively working on finding novel etch gas chemistries and in this work, we present the performance of some of the promising etch molecules that offer high etch selectivity of oxide to nitride and mask for contact etch application.

From a new etch molecule design standpoint, there are key etch performance indicators for contact etch, the most important of which are the etch selectivity of oxide to nitride and the oxide etch rate. In this study, several novel fluorocarbons have been first tested systematically using dual CCP etch tool to find a correlation between the etch molecule (structure, and function), and its affect on the etch performance. The use of mass spectrometry as a diagnostic to qualitatively understand the plasma species, with a simple matrix analysis, is presented. Molecules are initially screened based on etch rate and selectivity of different planar films. Sidewall protection is important when etching these features, and so the polymerizing nature of etch gases is also investigated. Specifically, the role of ion energy and oxygen addition on controlling the rate of polymerization is studied in order to find the operating process window that yields high etch selectivity. The perfomance of the etch gases is finally tested on an oxide pattern structure with amorphous carbon as mask material. SEM cross-sections are presented to show the effect of etch gas on etch profile, mask selectivity and mask preservation. The new gases have demonstrated significant selectivity improvement in comparison to traditional etch gases.

11:20am **PS2-FrM10 Dielectric Barrier Discharges: Statistical Analysis of Discrete Filaments and Multi-filament Dynamics**, ***Floran Peeters***, *R.F. Rumphorst*, Eindhoven University of Technology, Netherlands, *M.C.M. van de Sanden*, FOM institute DIFFER, Netherlands

Dielectric Barrier Discharges (DBD's) are used on a large industrial scale and have been studied for more than a century, with increasing interest in recent years in the areas of materials processing, plasma medicine and solar fuels. DBD's in filamentary mode consist of many small, transient microdischarges with diameters of ~ 0.1 mm and durations on the order of several 10's of nanoseconds, distributed over the dielectric surface. We study the collective behaviour of many such filaments in air by using a fast analog circuit capable of measuring the conductively transferred charge per filament. By using a miniature planar DBD with a 7 mm^2 electrode area, we determine charge/filament distributions without significant overlap between filaments in time, even at high filament number densities of up to 200 filaments/cm^2/period. Contrary to previous work, we find that the charge/filament distributions are log-normal in nature. Furthermore, the distributions are independent of filament number density for a given DBD geometry. With conventional charge-voltage (Q-V) measurements, Lissajous figures are obtained for the miniature DBD, where the slope during a discharge period has a clear 'staircase' shape. Analysis of these Lissajous figures, for 8 different DBD geometries, reveals that filaments do not occur randomly within a discharge period, as is often assumed, but affect each other's moment of ignition. Using both measurement techniques, we infer that multi-filament discharge dynamics are regulated by residual conductivity of the gas near the surface of the dielectric, resulting in step-wise ignition of filaments as a function of applied voltage. The log-normal charge/filament distributions, on the other hand, develop from the locally trapped charges on the dielectric. We suggest that both mobile charges from residual conductivity and immobile trapped charges need to be considered in models of DBD's, especially when converting data from the abundant single-filament models in DBD literature to real devices.

11:40am **PS2-FrM11 Single Step Conversion of Metal/Polymer Films to Flexible, Electrically Conductive Patterns by a Scanning Atmospheric-Pressure Microplasma Process**, ***Souvik Ghosh***, *R. Yang, A.C. Barnes, S. Rowan, C.A. Zorman, P.X.-L. Feng, R.M. Sankaran*, Case Western Reserve University

Atmospheric-pressure plasmas are often used to modify the surface of thin polymer films because of their ability to carry out reactions at low temperature and add unique functionality via radical chemistry. Recently, polymer films containing metal components have been exposed to plasmas to convert dispersed metal cations to supported metal nanoparticles. [1,2,3]

Such materials may be of interest for emerging applications in organic electronics, photovoltaics, and medical devices. However, few studies have assessed the electrical conductivity which is critical to these technologies.

Here, we show that polymer films loaded with metal cations can be converted to electrically conductive surfaces by an atmospheric-pressure plasma process. [4] Films of polyacrylic acid are loaded with Ag cations by solution processing and doctor's blade casting technique. The films are exposed to an atmospheric-pressure microplasma jet so that by scanning the plasma across the surface, microscale patterns with ~300 μm line width are produced. Reduction to crystalline metal is confirmed by X-ray diffraction. Characterization of the films by scanning electron microscopy and energy dispersive spectroscopy reveals that plasma exposure results in nucleation and growth of aggregated Ag nanoparticles. Additionally, cross sectional images show that the formation of Ag is limited to near the surface (~5 μm). Electrical characterization of the films shows that the patterns are highly

conductive with a bulk resistivity of ~1 mΩ-cm. To understand the mechanism for reduction, we compared our process with UV irradiation, heating, and laser treatment. None of these approaches produced similar reduction, crystallinity, or conductivity. We hypothesize an electrodiffusion model whereby Ag cations diffuse in the polymer film only in the presence of the plasma which creates an electric field through the film. This results in an enrichment of Ag cations at the surface. Reduction by the plasma then leads to a near-surface metallized layer. Thus, highly conductive surface patterns are generated from relatively low loadings of metal . References: [1] J. J. *et al.*, *Langmuir* **22**, 11388 (2006). [2] S. W. Lee *et al.*, *Adv. Func. Mater.***21**, 2155 (2011). [3] S. W. Lee *et al.*, *Macromolecules***45**, 8201 (2012). [4] S. Ghosh *et al.*, ACS Appl. Mater. Interfaces **6**, 3099 (2014).

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