Plasma Science and Technology

Room: 606 - Session PS1-ThM

Plasma-Surface Interactions II

Moderator: C.A. Wolden, Colorado School of Mines

8:00am **PS1-ThM1 Plasma Modification of Surface Traps in Mesoporous TiO_2**, ***D.J.V. Pulsipher***, *E.R. Fisher*, Colorado State University

Plasma surface modification can be effective in permanently modifying inorganic nanosurfaces. Particularly, mesoporous films formed from TiO_2 nanoparticles are interesting candidates for modification due to their important surface states needed for photovoltaic and photocatalytic applications. Plasma processing offers the opportunity of selectively modifying surface states to facilitate their investigation. Electron trap states in TiO_2-based devices, which are predominately located on TiO_2 particle surfaces,[1] can be detrimental in photovoltaic devices or beneficial in photocatalytic devices; consequently, controlling the quantity of these surface states by learning what causes and affects them will lead to more efficient devices. Here, low temperature inductively coupled plasmas are used to modify the surfaces of mesoporous TiO_2 films. Precursor gases such as O_2, H_2O, and H_2 have been used. Film surface states were primarily monitored by X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL). The binding energy of a second O1s peak in the XPS spectra increases for increasing O_2 plasma powers in the range of 75-225 Watts, and the modified films have at least a 6% increase in surface altering oxygen sites which persisted for more than 6 months. PL results suggest[2] a decreased density of surface traps in oxygenated films.

[1] N. Kopidakis, N. R. Neale, K. Zhu, J. van de Lagemaat,A. J. Frank, J Appl. Phys. Lett. 87, 202106.1 (2005).

[2] D. Zhang, J. A. Downing, F. J. Knorr, J. L. McHale, J. Phys. Chem. B 110, 21890 (2006).

8:20am **PS1-ThM2 A Robust Passivation-Enhanced Cryogenic Process used for Silicon Deep Etching**, ***L.E. Pichon***, *E.H. Oubensaid, C. Duluard, R. Dussart, P. Lefaucheux,* GREMI/CNRS, Université d'Orléans, France, *M. Boufnichel,* STMicroelectronics Tours, France, *P. Ranson,* GREMI/CNRS, Université d'Orléans, France, *L.J. Overzet*, University of Texas at Dallas

The need to scale down integrated circuits can be achieved by reducing transistor dimensions and also by 3D-integration. The latter takes advantage of high aspect ratio features and uses the silicon wafer volume as well as its surface. As a consequence, deep silicon etching is of crucial importance for 3D-integration. At GREMI laboratory, the cryogenic process is investigated for etching high aspect ratio structures in silicon. Generally, an inductively coupled SF_6/O_2 plasma is used to simultaneously etch silicon and deposit a passivation layer on the sidewalls at low temperature. When the wafer is warmed up to ambient temperature, the passivation film desorbs. Thus, the sidewalls are clean and have a low roughness.[1] The standard cryogenic process allows high etch rates but the passivation layer is not robust. This reduces the use of the cryogenic process in industry. To overcome this problem, passivation mechanisms have been investigated. A previous work has shown that SiF_4 plays a significant role in passivation layer formation.[2] Hence, it is possible to deposit a SiO_xF_y passivation film in SiF_4/O_2 plasma when the silicon substrate is cooled down to cryogenic temperatures. Moreover, a study has shown that the robustness of the passivation film is enhanced when it is grown using a SiF_4/O_2 plasma rather than SF_6/O_2 plasma[2]. We will show the use SiF_4/O_2 plasmas to reinforce the passivation layer during a standard cryogenic process. In brief, the SF_6/O_2 anisotropic etching plasma is regularly stopped and the silicon substrate is exposed to a SiF_4/O_2 plasma to strengthen the SiO_xF_y passivation film. This passivation-enhanced cryogenic process allows to significantly reduce the undercut (e.g. by a factor of 6 for a 10 µmm wide trench). Besides, the undercut can be completely eliminated for submicron trenches with an aspect ratio of 15 while the etch rate dropped only by a factor 1.3. We will present the passivation-enhanced cryogenic process and its performances.

[1] R. Dussart et al, J. Micromech. Microeng., 14 (2004) 190-196

[2] X. Mellhaoui et al, J. Appl. Phys., 98 (2005) 104901 .

8:40am **PS1-ThM3 3-D Profile Simulation of Silicon Etching: The Effects of Redeposition on Surface Roughening**, ***H. Kawai***, *W. Guo, Y.P. Yin, H.H. Sawin*, Massachusetts Institute of Technology

Line edge roughness (LER) on the sidewalls of gate electrodes in metal oxide semiconductor transistors is one of the most challenging issues in the microfabrication process today. Since the roughness does not scale with the feature size, the problem becomes more significant as critical dimensions get smaller for the future technology nodes. To understand LER, we have developed a 3-dimensional feature scale profile simulator to model and simulate the surface and sidewall roughening during the etching process of polysilicon in chlorine, hydrogen bromide and argon plasmas. We simulated the etching process using a dynamic Monte Carlo model, where the simulation domain is discretized into an array of cubic cells. The local surface conformation is fitted with a polynomial, which is used to compute the surface normal, scattering angle, and flux on the 3-D surface. Our results show that the roughening in physical sputtering process is a strong function of ion incidence angle and redeposition of sputtered materials. At normal ion incidence, the surface remains smooth, but at very grazing ion incidence, the surface is roughened along the ion beam direction. At grazing angle, the roughness is enhanced by the redeposition of sputtered materials. The simulator is also capable of modeling the transfer of roughness from the photoresist layer to the underlying layer during the gate etching processes.

9:00am **PS1-ThM4 In Situ Measurement of the Ion Incidence Angle Dependence of the Ion-Enhanced Etching Yield in Plasma Reactors**, ***R.J. Belen***, *S. Gomez,* University of California Santa Barbara, *M. Kiehlbauch,* Lam Research Corporation, *E.S. Aydil*, University of Minnesota

In sputtering and ion-assisted etching processes, the material removal rate is quantified through the use of the sputtering yield, which depends on the energy and the incidence angle of the ions bombarding the surface. The sputtering or ion-assisted etching yield is defined as the number of surface atoms removed per ion impinging on the surface. The most widely used expression for the sputtering yield assumes that it is a product of separable functions of the ion energy and incidence angle and is proportional to the square root of the ion energy and f(φ), a function that attempts to capture the dependence of the yield on the ion incidence angle, φ, measured with respect to the surface normal. We demonstrate a technique to measure the dependence of the etching yield on the ion incidence angle by examining cross-sectional scanning electron micrographs (SEM) of features etched under realistic plasma conditions in an arbitrary plasma reactor. The idea for the technique described herein is based on the observation that ions bombarding the surface of a semi-circular shaped feature impinge on various points along the feature at different angles that span the range from normal incidence, , φ, = 0°, to grazing incidence, , φ, = 90°. Thus, the technique is based on measuring the etch rate as a function of position along the walls of features that initially have nearly semi-circular cross sections. These initial feature shapes can be easily obtained by wet or isotropic plasma etching of holes patterned through a mask. The etch rate as a function of distance along the feature profile provides the etching yield as a function of the ion incidence angle. The etch rates are measured by comparing digitized SEM cross-sections of the features before and after plasma etching in gas mixtures of interest. We have applied this technique to measure the ion incidence angle dependence of the Si etching yield in HBr, Cl_2, SF_6 and NF_3 plasmas and binary mixtures of SF_6 and NF_3 with O_2. Advantages and limitations of this method will be discussed.

9:20am **PS1-ThM5 Modeling of Angular Dependence in Plasma Etching Used for Profile Simulation**, ***W. Guo***, *Y.P. Yin, H.H. Sawin*, Massachusetts Institute of Technology

We have completely modeled the angular etching behavior for poly-silicon etching in chlorine chemistry as well as oxide in fluorocarbon chemistry at various operating conditions, including different neutral-to-ion flux ratios, ion energies and ion incidence angles. With this angular model incorporated into the 3-dimensional profile simulation, we can quantitatively predict the line-edge roughness on the sample sidewall. We developed the angular model within the framework of the translating mixed-layer kinetics model described previously. Unlike other kinetics models, we estimated the concentrations of chemical complexes based on the surface composition and assumptions of random atomic mixing and bonding within the top surface layer. Angular curves of various fundamental reactions including physical sputtering, ion-induced etching and dangling bond creation are analyzed using simulation tools such as TRIM. Based on those individual angular curves we predicted the apparent angular dependences at different neutral-to-ion flux ratios and ion energies for poly-silicon etching in chlorine plasmas as well as oxide etching in fluorocarbon chemistry. The simulated etching yields showed quantitative agreement with experimental data. At low neutral-to-ion flux ratio, the etching yield peaks around 60 degree off-normal angle then drops off, similar to physical sputtering. At high neutral-to-ion flux ratio, the etching yield monotonically decreases with ion incidence angle, which is indicative of ion-induced etching. Surface

fractions remain stable as a function of ion incidence angle for both poly-silicon and oxide etching, consistent with experimental observation.

9:40am **PS1-ThM6 Geometrical Effects on Etching Profile Evolution**, ***H. Fukumoto***, *K. Eriguchi, K. Ono*, Kyoto University, Japan

Two-dimensional etching profile evolution in two different geometries, an axisymmetric hole and an infinitely long trench, has been calculated to clear the effects of geometrically different structures on etching profile evolution. In the simulation, SiO_2 etching by CF_4 plasmas is assumed because of widely employed processes for the fabrication of contact and via holes, which have various and unique geometrical shapes. The model takes into account the transport of particles in microstructures, together with surface reactions therein through sputtering, ion-assisted etching, chemical etching, and deposition. The model includes ions and neutrals (CF_x^+, CF_x, F; x=1~3) coming from the plasma, under different conditions of particle temperature, density, and ion energy. The simulation domain is enclosed by the sheath-surface interfaces and the feature surfaces of SiO_2 with an inert etching mask. The neutral particles from the plasma onto substrate surfaces are assumed to travel in microstructures with diffusive reflections on feature surfaces, while the ions accelerated through the sheath on the substrate travel with specular reflections on feature surfaces. The cell removal method is employed to represent the feature profile evolution, where the SiO_2 is represented by two-dimensional discrete cells. Numerical results indicate that the etching profiles of hole and trench have the similar tendency under different plasma conditions. However, the two etching profiles have some differences each other; the profile evolution is narrower and slower in the hole than in the trench, where the incident neutral fluxes are more reduced in the hole. Moreover, the profile of the trench has lateral etches such as undercut and bowing on sidewalls. The lateral etches decrease with increasing the ratio of neutral fluorocarbon fluxes, where the neutral fluorocarbons contribute to deposition. The velocity distribution of neutral particles also contribute to the difference of the etching profile evolution in the two structures; in effect, the velocity distributions are the more anisotropic in the hole, because more neutral particles interact with mask sidewalls in the hole, so that more anisotropic particles are conducted onto bottom surfaces after passing the mask features. Thus, it follows that geometrical structures contribute significantly to the behavior of neutral particles therein, and characterize the resulting etched profiles.

10:00am **PS1-ThM7 Growth Precursor Measurements and Study of Plasma Chemistry by Means of Mass Spectrometry**, ***J. Benedikt***, *A. Consoli*, Ruhr-University Bochum, Germany, *M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands, *A. von Keudell*, Ruhr-University Bochum, Germany **INVITED**

The knowledge of absolute fluxes of reactive species such as radicals or energetic ions to the surface is crucial in understanding the growth or etching of thin films. These species have due to their high reactivity very low densities and their detection is therefore a challenging task. Mass spectrometry (MS) is an ultra sensitive technique and it will be demonstrated in this talk that it is an optimal choice for identification of growth precursors and for the study of plasma chemistry in general. MS measures the plasma composition directly at the surface, it is not limited by (non)existence of accessible optical transitions, as is for example laser spectroscopy, and when properly designed and carefully calibrated, it provides absolute densities of measured species. Two examples of application of MS will be presented. First, the composition of remote argon/acetylene expanding thermal plasma at the position of the substrate has been analyzed by means of molecular beam threshold ionization MS. More than twenty species have been detected including radicals with densities as low as 10^{10} cm^{-3}. Resonantly stabilized radicals, with C_3 being the most important one, have been identified as growth precursors of hard hydrogenated amorphous carbon films and the plasma chemistry pathway leading to their formation has been understood. In the second example, a temporal evolution of neutral species densities during initial stage of dust particle formation in a low pressure acetylene discharge has been measured. Mass spectra with time resolution of 100 ms have been obtained using a step-scan approach and they have been decomposed and quantitatively and qualitatively analyzed using Bayes statistics and calibration measurements. Based on a comparison of our results with in literature available positive and negative ion mass spectra measurements and plasma chemistry modeling of comparable plasma, the electron attachment to larger C_nH_2 species is proposed as an initial step in dust particle formation. Additionally, the analyses indicates the involvement of vinylidene, isomer of acetylene, or vinylidene anion in formation of first aromatic ring and it shows that surface reactions are a significant source of aromatic compounds.

10:40am **PS1-ThM9 Ground and Metastable Atom Densities in Rare-Gas Diluted O_2 and N_2 Plasmas and Silicon Oxynitride Growth**, ***T. Kitajima***, *T. Nakano*, National Defense Academy of Japan, *T. Makabe*, Keio University, Japan

The application of rare gas diluted O_2 plasmas for oxide growth have gained interests due to the improved growth rate and film property. Metastable O atoms produced by rare gas metastables may contribute to the enhanced diffusion or reaction of the oxygen atoms at the interface of the film and the substrate. We have shown the increase of the metastable $O(^1D)$ atoms produced in the rare gas diluted O_2 plasma by VUV absorption spectroscopy.[1] The kinetics of the increased $O(^1D)$ atoms and the film growth can be explained by the deduced atom flux using diffusion model. In the study, we extend the scheme to the nitridation of silicon and finally to the oxynitride growth. The ground state $N(^4S)$ density in the rare gas diluted N_2 CCP is measured by the VUV absorption spectroscopy using 120 nm emission from the discharge light source ($N(^4P) \rightarrow N(^4S)$). $N(^4S)$ density is 8×10^{10} cm^{-3} for 0.5 Torr and 30 W in pure N_2 CCP and stays 5×10^{10} cm^{-3} even for 1 % of N_2 fraction in Ar diluted N_2 plasma. The trend is also found for the case of He diluted N_2 plasma and should be due to the reduced energy loss of electrons by vibrational excitation. The grown nitrides are examined by the depth profiles of XPS and the growth rate corresponds to the trend of $N(^4S)$ density. Detailed results and the case of oxynitrides are shown in the presentation.

[1]T.Kitajima, T.Nakano, and T.Makabe, Appl. Phys. Lett. 88, 091501 (2006).

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