Plasma Science and Technology
Room 2009 - Session PS1-FrM

Plasma-Surface Interactions III

Moderator: W.M.M. Kessels, Eindhoven University of Technology, The Netherlands

8:00am **PS1-FrM1 Subplantation and Interface Modification during Ion Assisted Low-Pressure Plasma Deposition of Oxides at the RF-Biased Electrode**, *A. Amassian,* Cornell University*; P. Desjardins,* ***L. Martinu,*** Ecole Polytechnique de Montreal, Canada

Significant research effort has been devoted to linking plasma characteristics, ion-surface interactions, and film properties in PVD, PECVD, and hybrid PECVD/PVD processes, leading to a qualitative understanding of surface processes and thin film growth mechanisms. In this paper, we report on the sub-surface effects of subplantation in an O@sub 2@ RF discharge during plasma treatment and thin film deposition at the RF-biased electrode. Using in situ real-time spectroscopic ellipsometry (RTSE), we have obtained time-resolved quantitative information about depth-dependent modifications of c-Si(001) exposed to intense ion bombardment under conditions typically used for oxide deposition. RTSE analysis indicates almost immediate damage formation (1 to 2s); it forms near the surface of the target on top of an O deficient interfacial damage layer (DL). Both layers experience a self-limiting growth behavior, as oxide and DL thicknesses reach bias-dependent saturation values, determined by the maximum ion penetration depth. The results are independently confirmed by cross-sectional high resolution TEM analysis. The in situ experimental study was complemented by Monte-Carlo TRIDYN simulations based on the binary collision approximation, which were modified to calculate dynamic changes in the structure and composition of a target exposed to a broad-energy ion source (ion energy distribution at RF electrode) at high fluence. This novel approach has allowed us to obtain the first quantitatively accurate simulation results of ion bombardment-induced sub-surface oxygen incorporation on time-scales from <

8:20am **PS1-FrM2 Process Performance of H@sub 2@ Remote Plasma Based Photoresist Ashing Processes and Their Influence on ULK Materials Modifications**, ***M.S. Kuo,*** *G.S. Gottlieb,* University of Maryland at College Park*; P. Jiang,* Texas Instruments*; P. Lazzeri, M. Bersani, S. Pederzoli, M. Anderle,* ITC-irst, Center for Scientific and Technological Research, Italy

We have examined the damage introduced in a blanket ultralow-k (ULK) dielectric material (nanoporous silica - NPS) and compared it with that inflicted on a low-k (LK) material (chemical-vapor-deposited organosilicate glass - OSG) for remote plasma conditions used to ash 193 nm photoresist (PR). For different substrate temperatures and H@sub 2@-based ashing chemistries, we found little damage in ULK/LK materials for H@sub 2@-based ashing processes without N@sub 2@. The damage depth increased dramatically with N@sub 2@ addition to H@sub 2@, while the PR ashing rate did not increase with N@sub 2@ addition. For our remote plasma, elevated substrate temperature (200 to 275 °C) conditions, N@sub 2@ addition to H@sub 2@ is ineffective in reducing ULK damage relative to (PR) ashing rate. The higher activation energy of PR ashing (~0.4 eV) than that of ULK/LK damage introduction (~0.1 eV) for remote plasma processing favors a higher substrate temperature for ashing process optimization. In addition, to address issues connected with sequential plasma etching and ashing steps, we also investigated the effect of surface residues due to prior capacitively coupled plasma (CCP) etching on PR ashing process efficacy and ULK/LK damage. The application of these approaches to etching/ashing actual trench structures is also described. Finally, we used D@sub 2@ ashing processes to investigate the behavior of deuterium/hydrogen in ULK/LK materials.

8:40am **PS1-FrM3 Measurement of Etching Kinetics and Surface Roughening of SiO2 and Coral Films during Plasma Etching**, ***Y. Yin,*** *H.H. Sawin,* Massachusetts Institute of Technology

Plasma etching processes often roughen the feature sidewalls, leading to the formation of anisotropic striations. The primary cause of sidewall roughening is the templating of mask roughness into the underlying film. Specifically, the inherent roughening of photoresist provides the mask for templating effect. To fully understand the sidewall roughness evolution, it is critical to understand the mechanism of the inherent roughening of photoresist as well as other materials, such as low-k dielectric film. The etching kinetics and surface roughening of thermal SiO2 and low-k dielectric Coral in Ar, C2F6/Ar, and C4F8/Ar plasma beams have been measured as a function of ion energy, ion bombardment angle, etching time and plasma composition in an inductively coupled plasma beam system. For all plasma chemistries, the etching yield at normal impingement angle scales linearly with the square root of ion energy. The angular dependence of the etching yield of both films in Ar plasma followed the typical sputtering yield curve, with a maximum around 60-75 degree off-normal angle. By adjusting the plasma etching conditions, the etching yield in fluorocarbon plasmas can follow either the ion-enhanced-etching yield curve or a sputtering-like yield curve. The surface roughening of both films showed different trends in Ar and fluorocarbon plasmas. In Ar plasma, both films stayed smooth after etching at normal angle while became rougher at grazing angles. Specifically, the striation formed at grazing angles can be either parallel or transverse to the beam impingement direction. More interestingly, the sputtering caused roughening at different off-normal angles can be qualitatively explained combining the corresponding angular dependent etching yield curve. In fluorocarbon plasmas, the films kept smooth at normal angle; while at grazing angles, the surface can be either rougher when the etching is sputtering-like or remain smooth when ion-enhanced etching is dominant.

9:00am **PS1-FrM4 Spectroscopic Studies of Ammonia Plasmas**, ***S.J. Kang,*** *V.M. Donnelly,* University of Houston

Surprisingly, there is little understanding of the basic chemical mechanisms in PE-CVD of carbon-containing materials such as carbon nanotubes, including the role of added NH@sub 3@. In this study we investigate the plasma chemistry of NH@sub 3@ decomposition in NH@sub 3@/Ar-containing plasmas at 1 Torr. Absolute NH@sub 3@ number densities were measured as a function of inductively-coupled plasma power and substrate temperature (T@sub s@) by ultraviolet (UV) absorption spectroscopy. Plasma-induced optical emission was used to qualitatively identify species such as NH and H, formed from NH@sub 3@ electron impact dissociation and subsequent reactions. A new "self-actinometry" method was introduced to measure the absolute number density of N@sub 2@ that is formed following dissociation of NH@sub 3@ and secondary reactions. In this approach, small amounts of N@sub 2@ were added to the NH@sub 3@-containing plasma, leading to an increase in the N@sub 2@ C->B state emission intensity, above the level of intensity observed in the absence of added N@sub 2@. By extrapolating to zero added N@sub 2@, we obtain the calibration factor that allows us to convert relative N@sub 2@ C-> B emission intensities into absolute number densities. We assume that very little of the added N@sub 2@ is dissociated; given its strong bond energy and low T@sub e@ at 1 Torr, this assumption is valid. The number densities of NH@sub 3@ decreased with increasing power and T@sub s@, reaching >90% dissociated at 400W and 900K. Conversely N@sub 2@ densities increased with power and T@sub s@. It appears that the majority of dissociated NH@sub 3@ leads to the formation of N@sub 2@ (i.e. the total nitrogen content is conserved in the sum of these two species).

9:20am **PS1-FrM5 Study of Downstream NH@sub 3@ Plasma Damage to Low k Dielectrics**, ***J. Bao,*** *H. Shi, J. Liu, P.S. Ho,* The University of Texas at Austin

Carbon Doped Oxide (CDO) films were treated by downstream NH@sub 3@ plasma. The effects of film porosity, ion energy, process time, substrate temperature on carbon depletion and nitrogen incorporation were studied by In-situ angle resolved X-ray photoelectron spectroscopy. Transmission electron microscopy, Fourier transform infrared spectroscopy, Spectroscopic ellipsometry and Atomic force microscopy were employed to evaluate the extent of damage to the films. NH@sub x@ reacted with the surface weakly bonded groups to form a densification layer. It was observed that this structural modification concentrated mainly within 10 nm at the surface region with the underlying film being undamaged. Mechanism of this plasma damage was investigated by analyzing the residual gas during the process. Hybrid beams damaged low k dielectrics more severely due to the combination of ions and neutrals. Roles of ions and neutrals in the plasma to cause carbon depletion will be compared and discussed. Moisture uptake after the plasma treatment was found to be a major reason to induce dielectric constant increase.

9:40am **PS1-FrM6 Investigation of the Plasma-Activated Catalytic Formation of Ammonia in N@sub 2@ - H@sub 2@ Plasma**, *J.H. van Helden, P.J. van den Oever,* Eindhoven University of Technology, The Netherlands*; W.M.M. Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; M.C.M. Van De Sanden, D.C. Schram,* ***R. Engeln,*** Eindhoven University of Technology, The Netherlands

In this contribution we report on the investigation of the plasma-activated catalytic formation of ammonia in N@sub 2@-H@sub 2@ containing

plasmas. The formation of ammonia is generally ascribed to stepwise addition reactions from adsorbed nitrogen and hydrogen radicals at the surface, i.e. the ammonia is formed via subsequent hydrogenation of adsorbed nitrogen atoms and the intermediates NH and NH_2 at the surface. To obtain further insight in the ammonia formation mechanism, the plasma chemistry in a plasma expansion created from mixtures of nitrogen and hydrogen is studied in more detail. The ammonia density and the NH_x radical density were determined by means of cavity enhanced absorption and cavity ring-down spectroscopy, respectively. It will be shown that ammonia can be formed efficiently in plasmas generated from mixtures of hydrogen and nitrogen. At optimal conditions 11% of the total background pressure, typically in the order of 20 - 100 Pa, was measured to be ammonia. This result turned out to be independent of the position in the plasma reactor. The NH_x radical densities, however, show a decrease as function from the distance from the exit of the plasma source, i.e. along the expansion axis. The measured NH and NH_2 densities are at maximum only about 1% of the ammonia density. Also, the NH_x radicals show the temperature of the plasma expansion, i.e. about 1500 K, while the ammonia molecules show the temperature of the background gas, i.e. about 600 K. These results indicate that the NH_x radicals are produced in the plasma expansion, while the ammonia is formed at the wall of the reactor. First results of a model describing the trends of the NH_x radical densities, indicate that NH is mostly produced in reactions of hydrogen molecules with N atoms, while NH_2 is most probably formed out of NH_3.

10:00am **PS1-FrM7 Transient Differential Charging of High Aspect Ratio Dielectric Features*, J.A. Kenney*,** *G.S. Hwang,* University of Texas at Austin

Plasma processing of high aspect ratio dielectric structures is well-known to encounter complications due to differential charging of features, owing to the dissimilar natures of the ion and electron angular distributions. As device dimensions shrink to below 100 nm, however, the differential charging of the features is no longer an approximate steady-state. Rather, the charging behavior oscillates as individual ions and electrons have a larger impact on the local electric fields. We investigate this phenomenon and its impact on the ion energy and angular distributions exiting the high aspect ratio structure, using a range of values for the surface conduction and entering ion energy and angular distributions. In addition, we look at how this behavior influences feature profile evolution, also as a function of the incoming ion energy and angular distributions.

10:20am **PS1-FrM8 On-wafer Monitoring of Charge Accumulation during Plasma Etching Processes*, B. Jinnai,*** Tohoku University, Japan*; T. Orita, M. Konishi, J. Hashimoto,* STARC, Japan*; S. Samukawa,* Tohoku University, Japan

The high aspect-ratio (AR) contact hole etching of dielectrics, especially silicon dioxide, is a key process in the manufacture of ULSI devices. During the plasma etching process, a large amount of charge accumulates in the contact hole due to electron shading effect, and leads to many problems, such as charge-build-up damage, etching-stop, and microloading effects. For overcoming these problems, it is indispensable to monitor the amount of charge in the real patterns and control the charge accumulation. In this paper, we evaluated the amount of charging in the real contact holes using our developed on-wafer monitoring sensor. We fabricated more than 100 sensor chips on an 8 inch wafer in a mass production line. The sensor had Poly-Si/SiO_2/Poly-Si layered structure on silicon substrate and contact holes with two kinds of AR: 10 and 3.3. We measured the potential differences between the top and bottom Poly-Si electrodes during plasma etching processes. It is corresponding to the actual charge accumulation in the contact holes. By increasing AR of contact holes, the potential was drastically enlarged. This result clarified that electron-shading effects were enhanced in higher aspect contact holes and that our developed on-wafer monitoring sensor could achieve in situ monitoring of charge accumulation in the real contact holes.

10:40am **PS1-FrM9 An In-situ Diagnostic to Detect Charging During Plasma Etching*, E. Ritz*,** *D. Ruzic,* University of Illinois at Urbana-Champaign

In plasma etching processes, especially those with high aspect ratios, it is known that defects can occur such as trenching, bowing, and twisting. These defects are particularly noteworthy in the manufacture of DRAM deep-trench capacitors. In order to investigate the role of charging on these phenomena an in-situ diagnostic was fabricated using photolithographic and deposition techniques. The device consists of a base layer of tungsten with alternating layers of silica and tungsten. During the construction of the device, vias are integrated into the layout, extending all the way from the top surface to the substrate. The silica layers act as insulators to create discrete measurement layers, provided by the tungsten layers. The tungsten layers are attached to voltage measurement leads and can then be used to measure the build up of sidewall charging at different heights along the via when exposed to a plasma. To determine the effect of geometry, if any, on charging, several aspect ratios were used by maintaining the same device thickness but varying the diameter of the vias. The entire stack is 30 microns thick, with vias ranging in diameter from 30 microns to only 1 micron, thereby producing aspect ratios of 1:1 to 30:1. Results from the diagnostic will be shown for various etching recipes.

11:00am **PS1-FrM10 Reduction of UV Irradiation Damage in CCD Image Sensor using CF_3I Gas Plasma*, Y. Ichihashi,*** Tohoku University and Sanyo Electric Co., Ltd., Japan*; Y. Ishikawa,* Tohoku University, Japan*; R. Shimizu, H. Mizuhara, M. Okigawa,* Sanyo Electric Co., Ltd, Japan*; S. Samukawa,* Tohoku University, Japan

The generation of the SiO_2/Si interface states is one of the most serious problems for the metal-insulator silicon (MIS) devices such as charge-coupled devices (CCDs) or memories. For CCDs, the generation of the interface state causes the increase in dark current. We previously reported that the interface state in MIS devices were increased by the UV irradiation during the plasma process. Especially, the UV wavelength of 200 nm to 350 nm, which induced by C_xF_y high-molecular-weight radicals, generates the interface states. Namely, the elimination of UV wavelength of 200 nm to 350 nm could keep the low-density interface state even after the etching process. In this paper, we propose the CF_3I gas plasma for the reduction of interface state density during the dielectric film etching process. By using the CF_3I plasma, a large amount of CF_3^+ are effectively generated without C_xF_y radicals. As a result, no UV photon of 200 nm to 350 nm were observed in the plasma. Additionally, CF_3I is known as a gas for low global warming potential (GWP). For example, the GWP for CF_3I is about 1/1600 of C_4F_8 GWP. To solve the reduction of UV irradiation damage and the global warming improvement at the same time, we actually investigated the effect of the CF_3I plasma for the reduction in MIS devices. We used inductively coupled plasma with CF_3I and C_4F_8 gases. The plasma irradiation damages were evaluated by using MIS-FET as charge pumping current (Icp), and we measured UV spectra of plasma. The Icp was drastically reduced by using the CF_3I plasma comparing with C_4F_8 plasmas. In CF_3I plasma, no UV photon of 200 nm to 350 nm induced were observed.

11:20am **PS1-FrM11 Defect Generation due to UV Radiation in Plasma Etching Process*, Y. Ishikawa,*** Tohoku University, Japan*; A. Uedono,* Tsukuba University, Japan*; S. Yamasaki,* National Institute of Advanced Industrial Science and Technology, Japan*; S. Samukawa,* Tohoku University, Japan

During the plasma process, plasma-induced ultraviolet (UV) photon generates the crystal defects in the dielectric films or in the interfaces. Especially in the SiO2 film, the UV photon generates the E' centers (Si dangling bond in the SiO2 film) in near the surface of the SiO2 film within 10 nm in depth. We had already reported that the E' center could be drastically reduced by using the pulse-time-modulated (TM) plasma. In this paper, we discussed the generation and restoration of defects during the TM plasma irradiation by using positron annihilation technique. In solid materials, the positrons are trapped at defects such as vacancy or voids with producing two 511 keV γ-ray photons. To understand the situation of defects in detail, the Doppler Broadening of the γ-ray photo-peak was evaluated using the S-parameter and W-parameter. S-parameter corresponds to the amount of the defects in the films, whereas, W-parameter corresponds to the electron energy distribution in the film. 500 nm of thermal SiO2 film were used, and irradiated to the Ar plasma. After the plasma irradiation, S-parameter in the case of irradiating TM plasma was the same as that in the case of using continuous wave (CW) plasma. Conversely, W-parameter after the TM plasma irradiation was much higher than that in the case of using CW plasma. These results indicate that the electron energy distributions in the SiO2 films after TM plasma irradiation are much different from that after CW plasma irradiation. Namely, different kinds of crystal defect were generated in both plasma. This result also suggests that the defects generated by TM plasma irradiation might be unstable than that generated by CW plasma. Consequently, it is speculated that the defects generated by TM plasma irradiation are easily restored through the thermal annealing. As a result, the TM plasma is much effective to eliminate generating defects due to UV irradiation during the etching processes.

11:40am **PS1-FrM12 Evaluation of Sticking Probability of Ti Atoms in Sputtering Deposition*, N. Nafarizal,*** *K. Sasaki,* Nagoya University, Japan

Knowledge on sticking probability is essential in predicting the deposition profile of a thin film inside a fine trench and a fine hole. In numerical simulations of the deposition profile, the sticking probability of metal atoms is widely assumed to be unity, but to our knowledge, there is no reliable experimental evidence of that. In this work, we evaluated the sticking probability of Ti atoms in magnetron sputtering deposition experimentally. We measured the spatial distribution of the Ti atom density in the discharge region sandwiched by a Ti target and a substrate by laser-induced fluorescence imaging spectroscopy. It was found that the Ti atom density on the substrate was not zero, clearly indicating that the sticking probability of Ti is less than unity. The magnitude of the sticking probability was evaluated by comparing the spatial distribution of the Ti density with a diffusion model proposed by Chantry (P. J. Chantry, J. Appl. Phys. 62, 1141 (1987)). The Chantry's model includes the diffusion coefficient and the gas temperature. The diffusion coefficient was obtained from a literature (D. Obhesian, et al., Opt. Comm. 32, 81 (1980)), and the gas temperature was evaluated from the Doppler-broadened linewidth of an Ar metastable state. As a result, the sticking probability was evaluated to be 0.4-0.5. The sticking probability was almost independent of the discharge power and the gas pressure. In addition, similar sticking probabilities were observed when the substrate was heated up to 520 K and when an rf bias corresponding to a self bias voltage of 200 V was applied to the substrate.

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