Friday Morning, November 8, 2002

Plasma Science
Room: C-103 - Session PS-FrM

Plasma Surface Interactions II
Moderator: W.M.M. Kessels, Eindhoven University of Technology

8:20am **PS-FrM1 Study of SiO_2 Etching with Plasma-beam Irradiation**, ***K. Kurihara***, *A. Egami, M. Nakamura*, Association of Super-Advanced Electronics Technologies (ASET), Japan

Fluorocarbon gases are widely used for Si/SiO_2/SiN etching to achieve high etching performance. A study of the SiO_2 etching mechanism has been still needed to construct a process simulator without experiments of trial and error. A plasma-beam irradiation apparatus, which can control plasma parameters, such as ion energy and radical/ion composition, is very useful to examine the plasma-surface interactions under a real etching environment. We measured Si containing desorbed products from the SiO_2 substrate by quadrupole mass spectrometer during $^{13}CF_4$/Ar gas mixture plasma beam irradiation. Furthermore we analyzed a surface reaction layer by a quasi-in situ X-ray photoelectron spectroscopy analysis after the plasma-beam irradiation. Composition of the desorbed products was almost independent on the ion energy under the condition that the ratio of the radical flux to the ion flux was small (1~2:1). Major desorbed products were SiF_2 and SiF_4. The thickness of the surface reaction layer including Si-F bond increased with increase in the ion energy, but bonding state in the reaction layer did not change. At the relatively high ion energy above 500 eV and ion rich condition, ions play an important role in etching. On the other hand, under the condition that the ion energy was low (~300eV) and the ratio of the radical flux to the ion flux was about 10:1, the relative ratio of highly fluorinated species (SiF_4) increased slightly. Radical species may affect the production of desorbed products at the low ion energy. We will discuss mechanisms of selective etching of SiO_2 to Si or SiN under these conditions, which leads the achievement of the high selectivity for sub-100nm LSI circuit production. This work was funded by NEDO.

8:40am **PS-FrM2 Measurements of Desorbed Products and Etching Yield by CFx+(x=1,2,3) Ion Irradiation**, ***K. Karahashi***, *K. Ishikawa, H. Tuboi, K. Yanai, K. Kurihara, M. Nakamura*, Association of Super-Advanced Electronics Technologies (ASET), Japan

Fluorocarbon plasma has been widely used to etch silicon dioxide in the fabrication of semiconductor devices. For further development of integrated semiconductor devices, more precise control of the etching process is required. Thus, we have developed a mass-analyzed ion beam apparatus; Energy controlled single species ions are irradiated to SiO2 surface under ultra-high vacuum condition, and we can study the roles of individual fluorocarbon ion irradiation without gas phase reactions or neutral radicals irradiation. In the present work, we have investigated desorption products and etching yields for silicon or silicon dioxide by CFx+ (x = 1-3) ion bombardments. Desorbed products could detected with a quadrupole mass spectrometer by pulse ion beam method, and estimate the kinetic energy of desorbed products from the time delay of waveform from incident ion pulse. In SiO2 etching by CFx+ ion irradiation, the major desorbed product, which contains silicon, was SiF2. The kinetic energy of SiF2 was less than 0.1 eV. Therefore, products were different from physical sputtering particles such Si and SiF as desorbed from silicon surfaces by CFx+ (x = 1-3) ion bombardments. Etching yields for SiO2 were measured as a function of incident ion energy. The etching yield by F+ ion was smaller than that of Ar+ ion. The effect of chemical reaction of F+ ion did not clearly appeared. Etching yields of CFx+ (x = 1-3) increased with increasing the ion energy and with increasing number of fluorine atom in the ions. Above 1000 eV, etching yields is gradually saturated. Below 500 eV, etching yields abruptly dropped with decreasing ion energy, and fluorocarbon films grew on surfaces. These results suggest that the etching reaction is affected by chemical reactivity of the incident ions, and that the etching reactions are controlled by the incident ion energy and species. This work was supported by NEDO.

9:00am **PS-FrM3 Etch Mechanisms of SiOC and Selectivity to SiO_2 and SiC in Fluorocarbon Based Plasmas**, ***N. Posseme***, *T. Chevolleau, L. Vallier, O. Joubert*, CNRS/LTM, France, *P. Mangiagalli*, Applied Materials, France

In CMOS technology, the traditional SiO_2 is being replaced by the so called low k materials in order to reduce the total resistance capacitance (RC) delay in the interconnect levels. Many inorganic materials such as doped oxide and organic materials are being investigated as potential candidates. In this work, the study is focused on the etching of two carbon doped oxide materials: SiOC (k = 2.9) and porous SiOC (k=2.2 with a porosity of 40%). With these new inorganic materials, fluorocarbon-based etch processes have to be revisited to obtain adequate profile control in high aspect ratio structures, high etch rate and good selectivities to etch stop or hard mask such as SiO_2 (k = 3.9) and SiC (k = 4). This study is dedicated to an analysis of the etch mechanisms of SiOC, SiO_2 and SiC in fluorocarbon plasmas. The etching of these materials is carried out on blanket wafers in a MERIE reactor (Magnetically Enhanced Reactive Ion Etcher) using different fluorocarbon gas (CF_4, C_4F_6, CH_2F_2) mixed with Ar, O_2 and N_2. X-ray Photoelectron Spectroscopy (XPS) analysis of the surface after partial etching shows that the fluorocarbon layer thickness formed at the surface plays a key role in controlling the etch rate and selectivity of SiOC, SiO_2 and SiC. The XPS results indicate that the fluorocarbon layer thickness depends on the plasma chemistry and also on the oxygen and carbon concentration in the etched materials The polymerising gas addition such as CH_2F_2 to CF_4/N_2/Ar gas mixture induces an increase in thickness of the fluorocarbon layer which generates a decrease in etch rate. Similar XPS analysis are also conducted on the SiOC sidewalls using the chemical topography analysis technique.

9:20am **PS-FrM4 Hydrophilic Plasma Surface Modification of Membranes: Surface Analysis, Gas-Phase Diagnostics, and Mechanisms of Energy Transfer**, ***K.R. Kull***, *J. Zhang, E.R. Fisher*, Colorado State University

Treatments with nitrogen containing plasma that render asymmetric polyethersulfone (PES) membranes permanently hydrophilic are reported. The modification strategy entails treating these membranes downstream from an inductively coupled rf plasma source. Contact angle measurements confirm that the membranes are wettable as a result of treatment with plasmas containing nitrogen species (Ar/NH_3, O_2/NH_3, N_2). More importantly, the hydrophilic modification is permanent as plasma-treated membranes remain wettable for more than eight months after plasma treatment. The change in wettability is a result of chemical changes in the membrane induced by plasma treatment. FTIR and XPS analysis of treated membranes reveals the incorporation of nitrogen functionalities into the treated membranes. Moreover, there is a concomitant increase in the oxygen to carbon ratio compared to the untreated PES membrane. Mass spectral data reveals gas-phase species are created from plasma-membrane interactions and SEM investigations reveal no visually observable structural damage as a result of the treatment parameters employed. We have also investigated the role of NH and NH_2 radicals in the modification process using laser-induced fluorescence measurements. The velocity of NH radicals in the nitrogen-containing plasmas has been measured and appears to be rf power dependent. Additional data on the surface interactions of NH with PES membranes as well as velocity measurements for scattered NH radicals will be presented and compared to earlier results for NH_2 radicals.[1] Implications for plasma modification mechanisms will also be discussed.

[1]C. I. Butoi, M. L. Steen, J. R. D. Peers, E. R. Fisher, J. Phys. Chem. B 105, 2001, 5957.

9:40am **PS-FrM5 Radical Reactions with Organic/Polymeric Surfaces**, ***J. Torres***, *C.C. Perry, S. Bransfield, D.H. Fairbrother*, Johns Hopkins University

Plasmas play an important role in polymer surface modification based on their ability to introduce new functionalities at the interface. Atomic or molecular radicals are often cited as the key species responsible for initiating surface reactions during plasma processing. Due to the wide range of reactive species within a plasma, however, surface reactions of individual species are hard to determine. In our work we report the results of the reactions of O and Cl radicals generated by thermal dissociation of O_2 and Cl_2 respectively, with organic thin films and polymers. The present study focuses on the interaction of atomic and molecular oxygen and chlorine with an X-ray modified hexadecane thiols adsorbed on gold using in situ XPS. Oxygen reaction with these hydrocarbon films proceeds in three stages. Initially the reaction dynamics are dominated by the incorporation of new oxygen containing functionalities at the vacuum/film interface. At intermediate O/O_2 exposures, when a steady state concentration of C-O, C=O and O-C=O groups has been established, the production of volatile carbon containing species, including CO_2 is responsible for etching the hydrocarbon film. Upon prolonged O/O_2 exposures, O atoms penetrate to the film/substrate interface, producing Au_2O_3 and sulfonate (RSO_3) species. In contrast, chlorine radicals do not etch the hydrocarbon surface and produce a uniform distribution of CCl and CCl_2 species in the near surface region. The advantages of employing self-assembled monolayers as models for polymeric interfaces as well as the interaction of oxygen and chlorine radicals with polyethylene characterized by XPS, ATR-IR and AFM will also be presented.

10:00am **PS-FrM6 The Interaction Dynamics of Ar/H Plasmas with Silicon Surfaces**, *J. Villette, F. Gou,* ***M.A. Gleeson****, A.W. Kleyn*, Leiden University, The Netherlands

Despite its technological importance the basic reaction dynamics of plasma deposition and etching processes are not known, even though in this case the process takes place almost under vacuum and should be easily accessible to studies at the molecular level. We have developed a new machine for such studies. Samples are placed in the centre of a 70 cm diameter reaction chamber, which can be evacuated up to ultra high vacuum. A cascaded arc plasma source produces an atmospheric plasma, which is collimated and differentially pumped. With a quadrupole mass spectrometer (QMS) we can monitor the particles emitted. An ion beam is produced in an independent source and can be scattered from the crystal that is being modified by the plasma. A time and position sensitive detector (PSD) records the scattered ions and neutrals individually. From their energy and scattering pattern we reconstruct the actual state of the surface. In order to prepare and characterize samples we can remove them from the reaction chamber into the preparation chamber under vacuum. Scattering of protons from clean and hydrogen covered silicon has been studied extensively by Souda et al.[1] The protons reflection is very sensitive to the state of the surface. In our machine we apply this to hydrogen treatment of Si(110). We note that the reflected yield goes up dramatically when switching on the hydrogen discharge. Switching to an Ar discharge we observe the disappearance of the strong hydrogen signal, indicating that even hyperthermal Ar from a cascaded arc recombining plasma is capable of removing hydrogen from silicon.

[1] R. Souda, E. Asari, T. Suzuki, and K. Yamamoto, Surf. Sci. 431, 26 (1999).

10:20am **PS-FrM7 Electron-Stimulated Atomic Scale Recovery of Ion-Induced Damage on Si(100)**, ***T. Narushima***, NRI-AIST, Japan, *M. Kitajima*, NIMS, Japan, *K. Miki*, NRI-AIST and NIMS, Japan

Recently, an importance of process under plasma irradiation is getting higher, because of its high reactivity and reducing process temperature. Surface damages induced by the plasma can be troubles for subsequent processes. But, effects of the plasma irradiation on the damage with atomic level have not been well studied. Previously, we reported that low energy (<40eV) electrons may be used to athermally release the compressive stress in the Si(001) surface layer induced by Ar^+ ions (<100eV) with using the ion and electron accelerated from Ar plasma [Narushima et al., Appl. Phys. Lett. 79, 605 (2001)]. In particular, we have strong evidence that the stress relaxation was found to depend only on the number of irradiated electrons and was independent of the total energy deposition. This indicates that complete relaxation is not promoted by a thermal activation mechanism, but by a non-thermal mechanism. In this paper, we show using scanning tunneling microscope (STM) that the underlying cause of the surface stress relaxation is athermal recrystallization of the surface atoms. Our finding is opposite to the previous report by Nakayama et al. [Phys. Rev. Lett. 82, 980 (1999)] that energetic electrons (>90eV) induce atomic scale damage. This discrepancy may be explained if we delineate 40-90 eV (in the case of Si) as the threshold between thermal and athermal processes for electron-surface atoms interactions. Our STM observation shows chracteristic features to support our hypothesis. The ion-bombarded surface does not have the thermally-generated 2x1 surface reconstruction, but instead a 1x1 reconstruction, which is slightly closer to positions of a 'bulk terminated' surface.

11:00am **PS-FrM9 Reduction of Hole Currents and E' centers in SiO_2 Induced by Vacuum-Ultraviolet-Light Using Pulse-Time-Modulated Plasma**, ***Y. Ishikawa****, M. Okigawa, S. Kumagai, S. Samukawa*, Tohoku University, Japan

Plasma processes have been widely used in the fabrication of MOS-LSIs. Some vacuum-ultraviolet lights (VUV) in the plasma generates electron-hole pairs in SiO_2 because of its higher energy than the SiO_2-band-gap. The holes are trapped in SiO_2 and interface states are often formed at the SiO_2-Si boundary.[1] We have reported that pulse-time-modulated (TM) plasma reduce the VUV in the plasma and the hole current in SiO_2.[2] In this study, to understand the relationship between the hole current and damages in SiO_2, the hole current and E' centers (trapped electron at oxygen vacancy in SiO_2) are measured by on-wafer-monitoring and electron-spin-resonance technique (ESR). An aluminum film was deposited on SiO_2 of the on-wafer-monitoring device to eliminate charged particles from the plasma. The more the hole current, the more E' centers were observed in the on-wafer-monitoring device when the TM-He-plasma condition were varied. We also evaluated the time-resolved measurement of the electron density and the VUV intensity in the TM plasma. The VUV light intensity and the hole current decayed just after the plasma-off in TM plasma, whereas the electron density declined with four times longer decay constant. These results indicate that the TM plasma reduce an increase in E' centers as damages due to decrease in the hole current resulting from suppression of the VUV. Additionally, we appraised a depth profile of E' center, resulting in gradually decline and reaching nearly zero at a depth of 15 nm. The relationship between a VUV penetration depth and the E' center profile will be discussed in the meeting.

[1] D. V. McCughan and V. T. Murphy: J. Appl. Phys. 44 (1973) 2008, T. Yunogami, T. Mizutani, K. Suzuki and S. Nishimatsu: Jpn. J. Appl. Phys., 28 (1989) 2172

[2] S. Samukawa, Y. Ishikawa, S. Kumagai and M. Okigawa: Jpn. J. Appl. Phys., 40 (2001) L1346.

11:20am **PS-FrM10 Evolution of Line Edge Roughness During Poly-Si Gate Stack Etching**, ***S. Rauf****, P.J. Stout, J. Cobb*, Motorola Semiconductor Products Sector

As the transistor dimensions in integrated circuits continue to shrink, the influence of gate surface roughness on transistor electrical characteristics is expected to grow. As a consequence, there is considerable need for gate fabrication processes that minimize or mitigate photoresist and poly-Si gate surface roughness. An integrated 2-dimensional (2D) plasma equipment - feature evolution model has been used to study roughness evolution on photoresist and poly-Si gate surfaces during gate stack etching. The model considers a sequence of typical gate etch processes including resist trimming, anti-reflective coating etching, and poly-Si etching. The plasma equipment simulations of the low-pressure inductively coupled plasmas are based on the Hybrid Plasma Equipment Model (developed at the University of Illinois) and include validated plasma chemical mechanisms for the relevant gas mixtures. The 2D string based feature evolution model (BabyBean) has been developed at Motorola, and it considers reactive ion etching, ion assisted physical sputtering, polymer deposition and sputtering, and isotropic etching by neutral radicals. The feature evolution model has been validated by comparing with process experiments. Simulations show that ions are able to remove "rough" protrusions on the photoresist surface through physical sputtering. This is accompanied by changes in etching or polymer deposition within "rough" cavities due to reduction in local neutral flux. Roughness evolution is sensitive to roughness amplitude and frequency.

11:40am **PS-FrM11 Ar^+/XeF_2 Beam Etching of Si: What about Doping?**, ***A.A.E. Stevens****, E. Te Sligte, H.C.W. Beijerinck*, Eindhoven University of Technology, The Netherlands

To circumvent the complexity of plasma etching, well-defined beams of Ar^+ ions and XeF_2 etch precursor gas are used to study the fundamentals of the etch process of silicon. Ellipsometry has been applied in the beam etching experiment in an attempt to bridge the gap between beam etching and plasma etching. The ellipsometric properties of Si(100) (n-type (P), resistivity = ~ 10 Ω cm) during physical sputtering by Ar^+ ions, spontaneous etching by XeF_2 and ion-assisted etching have revealed basic information regarding the reaction layer dynamics and composition. Sputtering by Ar^+ ions results in an ion damage layer that consists of amorphous silicon (a-Si) with a surface roughness of less than 0.3 nm. The thickness of the a-Si layer can be described well with TRIM simulations. Spontaneous etching by XeF2 is found to cause a rough reaction layer up to 13 nm thick that can be thought of as a rough and (partially) fluorinated silicon (SiF_x) surface. Ion-assisted etching is a combination of sputtering by Ar^+ions and etching by XeF_2, which resembles the actual etch process in plasmas. The reaction layer in this case is a mixture of rough a-Si and SiF_x layer on top of an a-Si layer. In order to obtain a reliable comparison between ellipsometry measurements and simulations the surface roughness has to be known. Atomic force microscopy has been applied to study the surface roughness evolution of Si for various etching conditions, which has been used as input in the ellipsometry simulations. This more detailed description of the reaction layer dynamics and composition has enabled the study of n- and p-doped Si(100) samples with various types of dopants (As, Sb, P, B) and doping concentration (resistivity = 0.001-10 Ω cm). New information regarding the still unanswered question of the effect of doping on the etch mechanism will be presented.

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