Plasma Science and Technology Division
Room 318/319/320 - Session PS-FrM

Plasma-Surface Interactions - II

Moderator: J.E. Johannes, Sandia National Laboratories

8:20am **PS-FrM1 Large Enhancement of Silicon Etch Rate by Metal Contamination***, **P.G.M. Sebel**[1], L.J.F. Hermans, H.C.W. Beijerinck,* Eindhoven University of Technology, The Netherlands

Given the ever decreasing dimensions of I.C.'s, it is essential to understand the various influences which affect the etching behaviour. We found a remarkably large enhancement of silicon etch rates by even small contamination with Ni and W. Our experiments indicate that the contamination migrates into the silicon due to vacancy production by ions. The experiments were performed in a molecular beam setup, where silicon is etched by XeF@sub 2@ and Ar@super +@ ions. The etch behaviour is monitored by a mass spectrometer using the SiF@sub 4@ signal. The effect of contamination appears very pronounced when the ion beam is switched off. With contamination, a temporary enhancement of the spontaneous etch rate is measured. With traces of contamination in the order of 0.01 ML the etch rate may be enhanced by a factor of 2 for W and somewhat less for Ni. It is concluded that the contamination moves into the silicon by diffusion to vacancies created by the Ar@super +@ ions, as proposed by Hart et. al. for Cu contamination.@footnote 1@ For 1 keV Ar@super +@ ions the contamination moves to a depth of 30 Å, equal to the penetration depth of the ions. As the effect of contamination disappears after etching of 170 Å, it is concluded that contamination has a catalytic effect on the silicon etch rate. Simulations, which describe the measured effect of contamination very well, indicate that only 3% of the contamination is removed after etching a monolayer silicon. Besides this catalytic effect, there are indications that the etch rate can be lowered under certain conditions, because of the formation of silicides. @FootnoteText@ @footnote 1@R.R. Hart, H.L. Dunlap and O.J. Marsh, J. Appl. Phys. 46, 1947 (1975).

8:40am **PS-FrM2 Laser Detection of Chlorinated Neutral Etch Products During Cl@sub 2@ / Ar@super +@ Etching of Si(100)***, **N. Materer**, R.S. Goodman, S.R. Leone,* JILA, NIST, and University of Colorado, Boulder

Pulsed laser single-photon ionization time-of-flight mass spectrometry is used to investigate neutral etch products formed during ion enhanced etching of Si(100). Single-photon ionization is accomplished using the ninth harmonic of a Nd:YAG laser at 118 nm to ionize neutral species. This approach eliminates dissociative ionization difficulties found in conventional electron impact ionization. Ions are first ejected from the region in frunt of the wafer by pulse field extraction prior to the laser pulse. The Ar@super +@ ion bombardment energy is varied from 275 to 1000 eV, and the flux of molecular chlorine is varied from 10@super 1@@super 4@ to 10@super 1@@super 5@ molecules per cm@super 2@. Under all conditions examined, SiCl is the major product. Neutral Si atoms are also detected during etching and there is some evidence for SiCl@sub 2@. The Si and SiCl products decay within 20µsec after a 500µsec ion pulse. This fast decay supports a mechanism in which these etch products are formed in a direct collisional process. In addition, the influence of the molecular chlorine flux is examined in detail. The introduction of molecular chlorine is found to first rapidly increase the yield of neutral Si and, at higher fluxes, to slowly decrease the yield. This subsequent decrease is attributed to the generation of an increasingly chlorinated surface. As in the case of Si, the yield of SiCl as a function of molecular chlorine flux increase rapidly at first. However unlike the Si yield, this fast increase is followed by a gradual increase at fluxes higher than 10@super 1@@super 5@ molecules per cm@super 2@. The direct detection of etch products results mechanistic details that can be compared to recent molecular dynamic simulations.

9:00am **PS-FrM3 Recombination of Halogen Atoms on Surfaces***, **J.W. Coburn**, G.P. Kota, D.B. Graves,* University of California, Berkeley **INVITED**

The recombination of halogen atoms [F, Cl, Br] has been measured as a function of temperature on a variety of surfaces [Si(111), poly-Si, WSi, W, quartz, photoresist, stainless steel, anodized Al]. Beams of halogen atoms were directed onto the surface under study in an ultrahigh vacuum system and the species evolved and reflected from the surface were detected with a differentially pumped modulated beam mass spectrometer. Since the halogen atoms undergo only a single collision with the surface, low recombination coefficients [less than a few percent] cannot be measured. In all cases studied, the recombination coefficient decreased with increasing surface temperature. The magnitude of the recombination coefficient for the various gas-surface combinations studied varied from as large as 0.8 to below the limit of our measurement [a few percent]. The recombination of Cl atoms on poly-Si was substantially larger than on Si(111). In general, the recombination coefficient for F atoms was much less than for Cl and Br atoms. The data is interpreted in terms of an incident atom or a moving physisorbed atom recombining with an immobile weakly chemisorbed atom.

9:40am **PS-FrM5 Removal of Si-O, Si-C and Si-F by Hydrogen Bake after Reactive Ion Etching on the Silicon Surface***, **Y.-B. Kim**, M. Caymax, H. Bender, S. Vanhaelemeersch,* IMEC, Belgium

In order to remove the damage/contamination left by Reactive Ion Etching (RIE) in a fluorocarbon chemistry on Si surface, a cleaning process consisting of an oxygen plasma/HF/H@SUB 2@ bake has been developed. ARXPS found Si-F, Si-C, Si-O and C-C/H bonds under the CF@sub x@ residues after RIE. Oxygen plasma formed a 2 nm thick film of fluorinated oxide on the RIE samples, removing the CF@sub x@ and C-C/H. A 2 % diluted HF dip for times between 10 and 200 s of the samples treated in RIE/oxygen plasma could not remove the Si-C, Si-F and Si-O. Next, the samples processed in RIE/O-plasma/HF were baked for 10 min at different temperatures (500 - 900 °C) in 1 bar of molecular hydrogen followed by quantitative XPS measurements. Up to 600 °C, no significant change in Si-C and Si-F was detected. Si-F and Si-C bonds decreased from 700 °C on and disappeared completely at 800 °C (Si-F) resp. 900 °C (Si-C). Si-O, which is abundantly present, is stable up to 800 °C, and abruptly decreases at 900 °C. AFM and MIR spectra respectively showed that the surface roughness decreases abruptly and the surface was reconstructed to a (2x1) dimer structure after a 900 °C anneal. A possible mechanism explaining these observations will be presented. Si-F and Si-C are formed by dissociation of the fluorocarbon radicals on the top surface and by insertion of the F and C into the upper atomic layers of the Si lattice by reactive ion mixing during the RIE. The observation that Si-O is removed very slowly by HF dipping indicates that O probably also gets buried into the Si matrix during the RIE. F is removed during hydrogen annealing by formation of the volatile HF at rather low temperature. The oxygen bonds are removed at 900 °C due to the consumption of the silicon surface atom on the Si-O sites by the well known reaction between Si and SiO@sub x@ resulting in volatile SiO. C is also removed at this temperature by its reaction with O into the volatile CO or CO@sub 2@.

10:00am **PS-FrM6 Characterisation of Self-aligned Contact Etch Processes using X-ray Photoelectron Spectroscopy, Time-Of-Flight SIMS, and Optical Emission Spectroscopy***, **F.H. Bell**,* Siemens AG, Germany*; T. Lill,* Applied Materials*; A. Cuthbertson,* Siemens Microelectronics Ltd, England*; U. Scheithauer, R. Treichler,* Siemens AG, Germany

The self-aligned contact process (SAC) is one of the key technologies for 64M DRAM fabrication and beyond. The oxide etch process relies on C@sub 4@F@sub 8@/CO/O@sub 2@ gas mixtures to provide high selectivity between oxide and the nitride barrier layer. Critical manufacturing issues are etch stop caused by fluorocarbon polymer deposition and shorts between bitline conatcts and gate due to insufficient oxide to nitride selectivity. The robustness of the process is strongly influenced by the ratio of the C@sub 4@F@sub 8@, CO, and O@sub 2@ gases. In order to understand the mechanism of the selective oxide to nitride etch, we analysed the oxide and nitride surfaces after etching using x-ray photoelectron spectroscopy (XPS) and time-of-flight SIMS. XPS results show that the composition of the fluorocarbon polymer film on nitride is only slightly influenced by the CO and O@sub 2@ gas flows whereas the thickness of the polymer film strongly decreases with oxygen addition. TOF SIMS analyses show that the higher the CO flow the more carbon is implanted into the nitride barrier layer. Since the nitride etch rates decrease as a function of CO flow and increase with oxygen addition, the selectivity between oxide and nitride is found to depend on two mechanisms: the passivation of the nitride barrier layer by formation of a fluorocarbon polymer film and the implantation of carbon in the nitride caused by the CO gas in the SAC etch chemistry. Due to the small open area of the SAC process, optical emission spectroscopy studies were performed to improve end point detection and thus establish a robust production process.

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[1] **PSTD Coburn-Winters Student Award Finalist**

10:20am **PS-FrM7 Experimental Investigation of the Respective Roles of Oxygen Atoms and Electrons in the PECVD Deposition of SiO@sub 2@ in O@sub 2@/TEOS Helicon Plasmas***, **A. Granier**, C. Vallée, A. Goullet, K. Aumaille, G. Turban,* Institut des Materiaux de Nantes, France

The respective roles of electrons and oxygen atoms in the plasma enhanced chemical vapor deposition of SiO@sub 2@-like films are investigated in a rf helicon oxygen/tetraethoxysilane (TEOS) plasma. The O atom density (a few 10@super 13@ cm@super -3@) and flux are monitored by actinometry and the electron density (a few 10@super 10@ cm@super -3@) by combination of optical emission spectroscopy (OES) and Langmuir probe analyses. The variations of the electron and atomic oxygen densities are studied as a function of the rf power (up to 500 W), the pressure (1-25 mTorr) and the organosilicon fraction in the O@sub 2@/TEOS plasma, simultaneously to the measurement of the deposition rate (using in situ ellipsometry) and analysis of the deposited films. The incorporation of ethoxy and silanol groups is determined from infrared spectroscopy. The refractive index and density of the films are deduced from UV-visible spectroscopic ellipsometry and gravimetric measurements respectively. It is shown that the TEOS fragmentation and the deposition rate are strongly related to the electron density while the main role of oxygen atoms is the etching of the organic part of the growing film, and not to dissociate the organosilicon molecules. In order to gain insight into the etching of the growing film by oxygen atoms, organosilicon films freshly deposited in a TEOS rich plasma are exposed to a pure oxygen plasma. During this post-exposure to an oxygen plasma, the film and the plasma are analyzed by ellipsometry and OES respectively : the film etching is clearly evidenced by the significant decrease in film thickness and the emission from CO, OH and H excited species which are related to the CO, CO@sub 2@ and H@sub 2@O etching products. It is furthermore shown that the film undergoes structural modifications over several ten nanometers.

10:40am **PS-FrM8 Surface Chemistry Mechanism of Oxide Etching by High Density C@sub 2@F@sub 6@ Plasma***, J. Feldsien, T. Panagopoulos, **D.J. Economou**,* University of Houston

Fluorocarbon plasmas have been studied extensively because of their use in selectively etching oxide over silicon. It is widely known that these plasmas produce unsaturated fluorocarbon radicals that may polymerize on surfaces in contact with the plasma. Oxide surfaces exposed to intense ion bombardment, on the other hand, are etching. More work remains to be done to understand the mechanisms that produce the observed behavior. In this work, a comprehensive surface chemistry model was developed to understand the mechanism of etching or deposition on oxide surfaces exposed to a high density C@sub 2@F@sub 6@ plasma. The surface chemistry model in combination with a gas phase plasma chemistry model developed by E. Meeks and J. Johannes of Sandia National Labs was implemented in the Modular Plasma Reactor Simulator (MPRES) to study oxide etching and uniformity under typical processing conditions. Simulation results on etch rate and uniformity as a function of source power, bias power, and pressure were consistent with experimental data. The transition from polymerization to etching as the ion bombardment energy (bias power) was increased was also captured by the simulation. Under low pressure conditions (several mtorr) the ion flux peaked at the wafer center while the neutral flux peaked at the wafer edge. Under such conditions, the oxide etch rate was edge fast. This supports the important conclusion that oxide etching is ion driven but neutral dominated. Surface coverages by important species and their interrelation to etch or deposition rate will also be discussed. This work was supported by Sandia National Laboratories/SEMATECH.

11:00am **PS-FrM9 Large Positive Silicon Ion Clusters in a Remote Silane Plasma***, **W.M.M. Kessels**, C.M. Leewis, M.C.M. van de Sanden, D.C. Schram,* Eindhoven University of Technology, The Netherlands

We report on the production of hydrogen poor cationic silicon clusters Si@sub n@H@sub m@@super +@ with up to ten silicon atoms in an expanding argon-hydrogen-silane plasma having implications for hydrogenated amorphous silicon films deposited by remote deposition techniques. It is shown that these cationic clusters are inevitably created by silane ions initiating chain reactions with silane when the product of silane density and geometrical path length is large. The initial silane ions are, in the plasma under consideration, produced by dissociative charge exchange between argon and hydrogen ions, emanating from the thermal plasma source, and silane. The deposition itself is dominated by SiH@sub 3@-radicals created by hydrogen abstraction from silane by atomic hydrogen emanating from the source and this has been determined by appearance potential mass spectrometry. The small hydrogen content (the clusters contain dominantly one hydrogen atom) in comparison with, e.g., ions in conventional rf silane plasmas is attributed to the high gas temperature due to the thermal plasma source used. The observation proves furthermore that the often quoted rates for the chain reactions of Mandich and Reents@footnote 1@ are not appropriate in this type of plasmas as even ions with more than six silicon atoms have been observed to a large extent. Moreover, a simple computer code showed that the rates for the chain reactions are not heavily depending on the number of silicon and hydrogen atoms present in the ion in contrast to their results. The contribution of the ions to film growth as determined from a combination of mass spectrometry and Langmuir probe measurements will be presented for various conditions and the influence of the ion clusters on the hydrogenated amorphous silicon film quality will be discussed. @FootnoteText@ @footnote 1@ See, e.g., W.D. Reents, Jr. and M.L. Mandich, Plasma Sources Sci. Technol. 3, 373 (1994).

11:20am **PS-FrM10 Surface Chemistry of NF@sub 3@ Plasma and Si Surface Interaction***, **T.W. Little**,* University of Washington*; A. Endou, A. Miyamoto,* Tohoku University, Japan*; M. Kitajima,* National Research Institute for Metals, Japan*; F.S. Ohuchi,* University of Washington

As an etchant gas, nitrogen trifluoride (NF@sub 3@) has become a viable contender to such mainstays in the semiconductor industry as carbon tetrafluoride (CF@sub 4@) and other perfluorocarbon compounds (PFCs) for certain plasma etching applications involving silicon (Si). Despite the technological importance of NF@sub 3@, there have been almost no studies on the interaction of NF@sub 3@ with Si from a surface science point of view. We have used x-ray photoelectron spectroscopy (XPS) and other diagnostics to determine the chemistry of interaction of NF@sub 3@ and Si surfaces. Although XPS results for the Si 2p core level are similar to those found for other etchants, we have seen unusual behavior in the F 1s core level and F 2s quasi-core level spectra. In addition to a F peak resulting from Si-F bonds, there are significant high-binding energy components which indicate that F is assuming a more positive or even neutral charge. The appearance of these peaks is closely related to both the type and amount of diluent gas. Upon heating, the high binding energy components are seen to disappear. These results lead to the supposition that F may be incorporated into the Si lattice as a result of an ion bombardment damage mechanism. While XPS is sensitive to changes in local chemistry, we have also applied a novel, in-situ Raman scattering technique which is sensitive to plasma surface interactions before they have progressed to the state in which chemical changes can be measured by XPS. The results of these measurements are described and compared with results obtained from XPS and other analytical techniques. In an effort to understand the energetics of F interaction with the Si lattice, we have also used cluster calculations to determine the most likely F sites.

11:40am **PS-FrM11 Operating High Density Plasmas in a Low Density Range : Applications to Metal Etch Processes***, **P. Czuprynski**,* France Telecom CNET/DTM/TFM, France*; O. Joubert, L. Vallier,* France Telecom CNET, France*; M. Heitzmann,* CEA LETI, France*; N. Sadeghi, J.P. Booth,* CNRS, France

In metal etching where complicated and thick metal stacks have to be etched on severe topography, selectivity between metal and resist is a critical problem. In practice, using standard Cl@sub 2@/BCl@sub 3@ etching chemistries and inductively coupled plasma sources (ICP) dedicated to metal processes, metal/resist selectivity higher than 3 are difficult to obtain. In this paper, we present a new way of operating high density plasma sources which greatly improve the selectivity issue of metal etch processes. The principal of the technique is to operate a high density plasma source in a low density mode (by strongly decreasing the RF power injected in the source, typically by a factor of 4) while keeping unchanged the RF power injected in the chuck to bias the wafer. Different techniques are used to compare the low density and high density modes. First, optical emission techniques are used to compare the dissociation efficiency of both modes and therefore get some information on the relative fluxes of Cl@sub 2@ and Cl species in the discharge. The ion current density (J@sub i@) and ion energy are also measured when the plasma source is operated in the low and high density modes (using identical chuck power conditions). The ion current density is measured using a new type of electrostatic probe whereas ion energy is simply estimated by measuring the self-bias voltage in the matching network of the chuck. The influence of low and high density modes on metal etch processes are evaluated using Cl@sub 2@/HCl chemistries. A strong increase in resist/metal selectivity is measured when the source is operated in the low density mode while perfectly anisotropic etching profiles of the metal stacks are still obtained. Finally, a simple model taking into account the chlorine coverage on the resist surface (as measured by in situ XPS), the ion density and ion energy is proposed to describe the resist etching rate. This simple model is useful to explain why operating ICP sources in a low density mode allows the resist consumption to be strongly decrease during etching processes. @FootnoteText@ This work has been carried out within the GRESSI consortium between CEA-LETI and France Telecom-CNET.

Author Index

Bold page numbers indicate presenter