## Plasma Science and Technology

## Room: 606 - Session PS1-WeA

## Plasma-Wall Interactions

## Moderator: E.V. Barnat, Sandia National Laboratories

1:40pm **PS1-WeA1 Real-Time and Wafer-to-Wafer Control Strategies to Address Seasoning of Plasma Etching Reactors[1]**, *A. Agarwal,* University of Illinois at Urbana-Champaign, ***M.J. Kushner***, Iowa State University

Seasoning of plasma etching reactors refers to the deposition of materials on the wafer and non-wafer surfaces of the chamber that change the fluxes of reactants to the wafer. This influence results from changes in reactive sticking coefficients of radicals and ions on surfaces that change the density of gas phase reactants, the removal of materials that add to the reactive fluxes to the wafer and changes in electrical properties. The negative consequences include drift, either during a process or wafer-to-wafer, in etch rates or uniformity of the process. In this paper, we discuss results from a computational investigation of the seasoning of reactors and, in particular, the use of real-time and wafer-to-wafer control strategies to eliminate process drift. These results were obtained using the Virtual Plasma Equipment Model, an implementation of sensors, actuators and control algorithms in the Hybrid Plasma Equipment Model.[2] The demonstration system is $Ar/Cl_2$ of Si in inductively coupled and capacitively coupled plasmas in which redeposition of etch products on walls and the wafer change reactive sticking coefficients and produce etch blocks. Sputtering of dielectrics in contact with the plasma introduce additional etch-block capable species. The diagnostics include etch rate sensors, optical emission and bias power. Actuators include power supply voltage, gas flow rate and gas mixture. We found that use of real-time-control to stabilize processes during a single etch and wafer-to-wafer control are sometimes complicated by the changing state of the wafer compared to the walls. For example, the wall conditions at the end of the prior wafer and beginning of the next wafer do not necessarily change however the new wafer does not have redeposition products. As such, actuators must be reset for the new wafer. Multiple sensors-and-actuators may be needed to account for the transition between neutral limited to ion limited processes as wall and wafer conditions change.

[1]Work supported by the Semiconductor Research Corporation and National Science Foundation.

[2] S. Rauf and M. J. Kushner, "Virtual Plasma Equipment Model: A Tool for Investigating Feedback Control in Plasma Processing Equipment", IEEE Trans. Semiconductor Manufact. 11, 486 (1998).

2:00pm **PS1-WeA2 Chamber Walls Coatings during Hard Mask Patterning of Ultra Low-k Materials: Consequences on Cleaning Strategies**, ***T. Chevolleau***, LTM, France, *M. Darnon,* LTM-CNRS, France, *T. David, N. Posseme,* CEA-LETI-MINATEC, France, *J. Torres,* STM, France, *O. Joubert*, LTM-CNRS, France

Changes in chamber wall conditions (e.g., chemical surface composition) are identified as one of the main causes of process drifts leading to changes in the process performance (etch rates, etch profiles, selectivity, uniformity …). The impact of a metal hard mask on the coating formed on the chamber walls during dielectric etching processes and reactor dry cleaning procedure has been investigated. We have used a technique based on x-ray photoelectron spectroscopy (XPS) to monitor the chemical composition of the layer deposited on an electrically floating sample placed on the top of a patterned wafer exposed to typical plasma processing conditions. By using this simple technique, the $Al_2O_3$ sample surface (or other chamber walls materials) is, similarly than the chamber walls, bombarded by low energy ions. Since the wafer is simultaneously bombarded by high energy ions, the gas phase is fed by etch products which get redeposited on the electrically floating $Al_2O_3$ sample and on the chamber walls surfaces. We have patterned porous SiOCH damascene structures using a TiN hard mask. After hard mask opening in a silicon etcher using $Cl_2$ based plasmas, we have shown that the chamber walls are coated by a thin SiOCl layer containing small concentrations of Ti. After photoresist removal in the same etcher (with an $O_2$ plasma), the chamber walls coating is oxidized leading to the formation of a mixed SiOx-TiOx deposit. The cleaning strategy to remove this coating from the chamber walls consists in using a two step cleaning procedure: (1) a $Cl_2$ based plasma (Ti removal) followed by (2) a $SF_6/O_2$ plasma (SiOCl species removal). During low-k etch in an oxide etcher using fluorocarbon based chemistries, the chamber walls are coated by a fluorocarbon layer containing a significant Ti concentration. We have developed a two step cleaning procedure: (1) a $SF_6$ plasma to remove the fluorocarbon layer and Ti based species and (2) an $O_2$ flash plasma (for a short time) to clean up the remaining carbon from the chamber walls.

2:20pm **PS1-WeA3 How Electron Density and Collision Rate Reflect the Properties of Chamber Wall and Substrate in IC Manufacturing**, ***M. Klick***, *L. Eichhorn,* Plasmetrex GmbH, Germany, *R. Benson, D. Steckert*, Micron Technologies, Inc.

Chemically active plasmas as every process plasma interact with the driven electrode and chamber wall. The wall and the electrode is heated and material as byproducts and material from the substrate condense preferably at the chamber wall. Without any additional influence, the parameters of the plasma reach an equilibrium, depending on the external parameters of the discharge as RF power. On the other hand the often used assumption that neutrals in a plasma have room temperature is quite questionable. Hence the indirect heating of the gas by the RF power was really underestimated despite this is one of the major reason of the so-called first wafer effect. There are two reason for the gas heating; the collision with fast ions in the boundary sheathes and the heating of chamber wall without proper 'thermal grounding' and a subsequent heating of the gas by the now hot surface of these chamber parts. Some authors have shown a significant increase of the gas temperature up to 1000 K in a RF plasma. The heat transmission resistances depends on the material, surface roughness, cleanliness and contact pressure. We will start at the experimental example of an increase of the surface temperature of the driven electrode at a 300 mm semiconductor production chamber with dual frequency excitation and the characterization of varying the torque of screws used for mounting. The temperature increase is characterized by the decrease of the electron collision rate. The collision rate, provided by the Self Excited Electron Resonance Spectroscopy, depends via the ohmic heating on the density of the neutrals and so finally on the gas temperature. Furthermore we will provide a qualitative discussion of the temperature effects, in particular resulting in a higher weight of stochastic heating mechanisms. The second example is the interaction of of an substrate, here a 300 mm wafer covered by mainly a polymer mask, an the plasma, in particular the electron collision rate. The interaction of plasma physical mechanisms as electron heating the plasma chemistry is analysed in the same way as indicated above.

2:40pm **PS1-WeA4 Surface Reactions of Atomic and Molecular Chlorine on Anodized Aluminum Surface in Chlorine Plasmas**, ***J. Guha*****, *V.M. Donnelly*, University of Houston

Surface recombination reactions of Cl atoms on anodized aluminum have been investigated by the "spinning wall" technique in chlorine plasmas. Desorption of $Cl_2$ formed due to delayed (i.e. Langmuir-Hinshelwood) recombination of Cl atoms on the spinning surface was detected by mass spectrometry, and surface concentrations were measured in-situ by Auger electron spectrometry. Cl recombination probabilities were measured over a wide range of Cl atom flux by varying the plasma pressure and power. $Cl_2$ desorption was monitored over a time scale of 0.8 to 38 ms after the surface was exposed to the plasma (corresponding to the rotation frequencies of 35,000 and 800 rpm, respectively). The decay of $Cl_2$ desorption flux is highly non exponential within this time scale. Langmuir-Hinshelwood Cl recombination coefficients ($\gamma_{Cl}$) were measured by extrapolating the desorption flux to t = 0. For a typical condition of 5mTorr, 600W $Cl_2$ plasma the desorption flux was $2.8 \times 10^{15} cm^{-2} s^{-1}$ at t = 0. Absolute Cl atom densities close to the surface were measured by optical emission spectroscopy and Xe actinometry. $\gamma_{Cl}$ values ranged from 0.01 to 0.1 and were found to increase with increasing power and decrease with increasing total pressure. From the lowest pressure, highest power condition (1.25 mTorr, 600 W) to the highest pressure, lowest power case (20 mTorr, 100 W), the percent $Cl_2$ dissociation varied from 28% to 6%. With plasma off, $Cl_2$ also adsorbs on the surface, and desorbs over the same 0.8 - 38 ms time scale. Consequently $Cl_2$ adsorption competes with Cl adsorption with the plasma on, particularly at high pressure and low power. Physisorbed $Cl_2$ appears to block adsorption sites on the surface, thereby reducing the recombination probability, as observed. From Auger analysis of the surface during exposure to a 5mTorr, 600W $Cl_2$ plasma, the surface stoichiometry was found to be $Al_{3.2}Si_{3.3}O_{7.6}Cl$. Auger analysis of the surface at different plasma conditions suggests that less than 10% of adsorbed Cl atoms actually participates in surface recombination.

* PSTD Coburn-Winters Student Award Finalist

3:00pm **PS1-WeA5 Impact of Cu Contamination on Chamber Walls on Via-Hole CD Shift in Cu Dual Damascene Etching**, ***H. Hayashi***, *K. Sato, K. Yamamoto, T. Kaminatsui, A. Kojima, I. Sakai, M. Hasegawa, T. Ohiwa*, Toshiba Corporation, Japan

With shrinkage of ULSI design rule, Cu wiring and low-k materials such as SiOC and poly arylene ether film (PAE) have been introduced to reduce RC delay in the metal interconnects. Furthermore, wafer-to-wafer repeatability of etching processes becomes a major concern. Therefore, controlling the chamber wall condition has been widely studied. In the SiOC etching process, fluorocarbon based plasma is used, which forms fluorocarbon film on the chamber walls. Typically, chamber cleaning is performed using oxygen based plasma, which removes the fluorocarbon film. Cu, which is sputtered from the Cu wiring exposed to the plasma during etching, deposits on the chamber walls and possibly remains, even after chamber cleaning. In this report, the influence of this Cu contamination on etch performance is studied. The stacked films of the PAE/SiOC hybrid dual damascene (DD) structure[1] for 45nm- node logic device were sequentially etched in the same chamber (all-in-one process). Wafers with Cu surface which becomes exposed during DD etching were etched, and it was found that the via-hole critical dimension (CD) of the second wafer of a lot decreased by 20 nm compared to the first wafer. However, $SiO_2$ and resist etch rates did not show any significant change. Then, plasma analyses using optical emission spectrometry with a high resolution of 0.1 nm were carried out to investigate the cause of the via-hole CD shift. It was found that the Cu emission intensity in the plasma of the second wafer was higher compared with the first wafer. This Cu emission intensity increase originated from the Cu deposited on the chamber walls during etching of the first wafer. Then, a wafer was etched after a chamber cleaning process to remove Cu was carried out, and it was found that the via-hole CD was the same as the first wafer. The Cu emission intensity became equivalent to that of the first wafer, also. The Cu emission intensity had a correlation with via-hole CD shift. Thus, Cu optical emission is sensitive to Cu contamination on the chamber walls, and the monitoring of Cu emission is an effective method of controlling the via-hole CD shift.

[1] A. Kajita et. al., Proc. of IITC (2003) p.9.

4:00pm **PS1-WeA8 Plasma-Wall Interactions in Inductively Coupled Plasma Reactor and a Novel Method for Wall Condition Control**, ***H. Singh***, Lam Research Corporation **INVITED**

Semiconductor technology has been aggressively scaled from micron sized features to 45 nm features over the last three decades . For the upcoming 32 nm technology node, total variation from all sources for a typical gate etch process is expected to be less than 2 nm. In addition, many new materials are being introduced in recent etch stacks, adding to the productivity challenges due to increased likelihood on non-volatile etch by-products on chamber walls. Plasma-wall interactions have significant impact on the chemistry of low pressure (<100 mTorr) plasmas. Therefore, control of chamber wall condition is crucial for achieving the desired process capability. Waferless Auto Cleans (WAC) have been demonstrated as essential in controlling wafer to wafer process repeatability in volume manufacturing above 65nm node. WAC removes etch by-products deposited during the wafer etch, minimizing drifts in chamber condition. However, ensuring no buildup of etch by-products on reactor walls is not sufficient to meet the productivity requirements of sub-65 nm node in many cases. Advanced Chamber Condition Control technology (AC3$^{TM}$) is a novel method to significantly enhance the productivity of etch systems in volume production. AC3 involves deposition of a thin film on the reactor walls prior to wafer processing, thereby eliminating drift in the wall condition during production. Impact of changes in the wall conditions due to chamber wet cleans, parts aging and variability are significantly reduced, allowing CD control at the nanometer level.

4:40pm **PS1-WeA10 Recombination of Oxygen Atoms on Dynamic Stainless Steel Surfaces**, ***L. Stafford***, *J. Guha, V.M. Donnelly*, University of Houston

We investigated the desorption of $O_2$ molecules from electropolished stainless steel surfaces following Langmuir-Hinshelwood (L-H) (i.e. delayed) heterogeneous recombination of oxygen atoms, using the spinning-wall technique. In this experimental set-up, a cylindrical section of the wall of an inductively coupled plasma reactor is rotated and the surface is periodically exposed to the plasma, a mass spectrometer, and an Auger electron spectrometer in separate differentially pumped chambers. Measurements can be performed over a wide range of O flux by varying the absorbed power (50-600 W) and total gas pressure before plasma ignition (1.25-20 mTorr). When the substrate is spun with the plasma on, a large increase in the mass spectrometry signals and Auger chamber pressure is observed with increasing rotation frequency. This increase results from O atoms that adsorb on the stainless steel surface when it is in the plasma and then recombine over the ~1-15 ms period probed by changing the rotation frequency. L-H recombination probabilities of O atoms were determined by extrapolating the $O_2$ signals to t = 0 (i.e. infinite rotation frequency). For example, at an O atom flux of $10^{17}$ $cm^{-2}s^{-1}$ obtained at 5 mTorr pressure and 600 W plasma source power, we have found a recombination probability of 0.035. This value is lower than those previously reported for O on stainless steel (e.g. 0.07 by Mozetic and Zalar, Appl. Surf. Sci. 158, 263 (2000), and 0.14 by Kiehlbauch and Graves, J. Vac. Sci. Technol. A 21, 660 (2003)). It is, however, similar to those previously obtained for O on anodized aluminum under comparable plasma conditions, where a Si-oxide layer was observed to form on the surface, due to the slow erosion of the quartz discharge tube. In the present study, analysis by Auger electron spectrometry during the recombination measurement also showed that the stainless steel surface became rapidly coated with a Si-oxide layer (Fe:Si:O atomic concentration ratios of ~1:2:5). This suggests that the recombination kinetics of oxygen atoms in this plasma reactor is determined by the coating on the walls, and not as much by the wall materials.

5:00pm **PS1-WeA11 The Effect of Wall Conditions on the Self-Limiting Deposition of Metal Oxides by Pulsed Plasma-Enhanced Chemical Vapor Deposition**, *M.T. Seman, S.F. Szymanski*, ***C.A. Wolden***, Colorado School of Mines

Pulsed plasma-enhanced chemical vapor deposition (PECVD) has been engineered to deliver self-limiting growth (i.e. 1 Å/pulse) of metal oxides such as $Ta_2O_5$ and $Al_2O_3$. Pulsed PECVD may serve as a bridge between conventional ALD and PECVD, retaining monolayer control but with potentially much higher throughput. In this process the reactor walls are alternately exposed to atomic oxygen and metal precursors. The degree of adsorption in the latter step can dramatically influence both deposition rates and film quality. The impact of precursor adsorption on the plasma and gas-phase composition in these systems was measured using optical emission spectroscopy and quadrupole mass spectrometry, respectively. It is shown that the time scale for adsorption is much greater than gas-phase residence times. Adsorbed compounds significantly alter the reactor composition, particularly at the initiation of each pulse. As a consequence careful attention must be paid to reactor design and operation in order to control deposition rates and maintain quality.

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