Atomic Layer Etching
Room Grand Ballroom A-C - Session ALE-TuM

Modeling of ALE

Moderators: Prof. Dr. Michael Nolan, University College Cork, Dr. Thomas Tillocher, GREMI CNRS/Orleans University

11:15am **ALE-TuM-14 Plasma Oxidation of Copper: Molecular Dynamics Study with Neural Network Potentials***, **Yantao Xia,*** University of California at Los Angeles*; S. Philippe,* University of California, Los Angeles

The formation of thin oxide films is of significant scientific and practical interest. In particular, the semiconductor industry is interested in developing a plasma atomic layer etching process to pattern copper, replacing the dual Damascene process. Using a nonthermal oxygen plasma to convert the metallic copper into copper oxide, followed by a formic acid organometallic reaction to etch the copper oxide, this process has shown great promise. However, the current process is not optimal because the plasma oxidation step is not self-limiting, hampering the degree of thickness control. In the present study, a neural network potential for the binary interaction between copper and oxygen is developed and validated against first principles calculations. This potential covers the entire range of potential energy surfaces of metallic copper, copper oxides, atomic oxygen, and molecular oxygen. The usable kinetic energy ranges from 0 - 20 eV. Using this potential, the plasma oxidation of copper surfaces was studied with large-scale molecular dynamics at atomic resolution, with an accuracy approaching that of the first principle calculations. An amorphous layer of CuO is formed on Cu, with thicknesses reaching 2.5 nm. Plasma is found to create an intense local heating effect that rapidly dissipates across the thickness of the film. The range of this heating effect depends on the kinetic energy of the ions. A higher ion energy leads to a longer range, which sustains faster-than-thermal rates for longer periods of time for the oxide growth. Beyond the range of this agitation, the growth is expected to be limited to the thermally activated rate. High-frequency, repeated ion impacts result in a microannealing effect that leads to a quasicrystalline oxide beneath the amorphized layer. The crystalline layer slows down oxide growth. Growth rate is fitted to the temperature gradient due to ion-induced thermal agitations, to obtain an apparent activation energy of 1.0 eV. A strategy of lowering the substrate temperature and increasing plasma power is proposed as being favorable for more self-limited oxidation.

11:30am **ALE-TuM-15 Multi-scale Simulation Study for the Role of High C/F ratio Plasma on Etch Selectivity of SiO_2 and Si_3N_4 in q-ALE***, **Hojin Kim,** D. Zhang, T. Hisamatsu, A. Ko,* TEL Technology Center, America, LLC, USA

Using multi-scale simulation techniques, we studied how C/F ratio in plasma affected the etch selectivity between Si_3N_4 and SiO_2 with a formed thin FC film on each surface during a q-ALE process. In SAC etching for via or contact holes into oxide to make a contact, nitride also can be etched, resulting in the yield issue. Thus, we need to reduce the nitride loss effectively. However, as the device becomes smaller, it is hard to control to obtain enough selectivity.Previous experiments with various C_xF_y gases showed the enhancement of etch selectivity between Si_3N_4 and SiO_2 with high x/y ratio gas. However, the understanding of the underlying behavior has been not clear. First, we revealed the relationship between intrinsic C/F ratio neutral and species fluxes by using the plasma simulation, observing that high C/F ratio gas could create high C/F ratio radicals. With atomistic Molecular Dynamics (MD) simulation and DFT calculation, we also studied the possible role of C/F ratio on FC film formation on both substrates and following an ion bombardment. MD simulation results showed that with higher C/F ratio plasma, harder and denser FC film could be formed on Si_3N_4 by significantly increasing absorbed carbon (C), Si-C, and C-C bonds. In the SiO_2 case, we could observe many O-C bonds that cause to weaken the formed FC film by converting it to highly volatile materials (i.e., CO_2). The highest C/F ratio gas case showed that significant O-C bonds on SiO_2 were generated. Following the ion bombardment step with both modified substrates, we observed that the highest C/F ratio case exhibited less loss of total atoms and regenerated Si-C bonds, probably a dangling bond behavior. In Si_3N_4, N-C bonds were generated more to protect the substrate but not in SiO_2; O-C bonds were lost during the ion bombardment. We confirmed the surface reaction with DFT calculation. It showed that both Si and N removal was difficult without F, while O removal was possible even without F. Thus, we determined that Si_3N_4 etching was more F-limited than Ox, indicating that selectivity at high C/F ratio gas would be improved. Based on all findings, We concluded that using the plasma with high C/F ratio radical helped to increase selectivity by protecting Si_3N_4 more with denser and harder FC film but not on SiO_2 due to the O-C bonds in formed FC film. This study will help to understand the fundamental behavior of the dielectric selectivity with various C/F ratio plasmas during the q-ALE process and ultimately provide the guideline for the experiment.

11:45am **ALE-TuM-16 Selecting a Method for ALE Modeling***, Y. Barsukov, S. Jubin, S. Ethier,* ***Igor Kaganovich,*** Princeton University Plasma Physics Lab

Several methods can be used for modeling dry etch processes, such as transition state theory (TST), classical and ab-initio molecular dynamics (MD), and density functional based tight binding (DFTB) approaches. The combination of TST and quantum chemistry methods, usually DFT (density function theory), enables the calculation of rate constants for the elementary steps of gas-surface reactions during the etching process. This allows insight into the etching mechanism, and we can then perform chemical kinetics modeling to predict the etch rate as a function of gas phase species fluxes and surface temperature. One limitation of the TST approach is the evolution of the structure and composition of the surface during the etching process, which results in a change in the rate constants. The purpose of chemical kinetics modeling is to find the rate-limiting step in surface reactions that determines the overall rate of the whole etching process. Here we present simulation results explaining the orientation dependence of silicon surface etching by F2 molecules using the TST approach. Namely, we show that the Si etching in the (111) direction is much slower than in the (100) and (110) directions; therefore, F2 can be used for the anisotropic etching process to produce black silicon. Moreover, this approach allows us to propose a new reactant to etch silicon with higher anisotropy. Among the other methods, classical and ab-initio MD simulations enable the study of surface transformation during the etching process, as well as the dynamics predicting surface composition and structure. However, great care must be taken when choosing the interatomic potentials for classical MD and the semi-empirical parameters for DFTB in order to correctly represent the surface reactions and their rates. Our simulations showed that bond order MD potentials unrealistically described boron adsorption on a graphene sheet, and available DFTB parameters sets were unable to predict the existence of NH4F and NH5F2 salts, which are broadly used for SiO2 and Si3N4 etching. The ab-initio MD method completely avoids these issues but is so time-consuming that simulating surface reactions proceeding through significant barriers can become prohibitively long. Nevertheless, it can be successfully used for studying barrier-free reactions or reactions with low barriers, such as SiO2 and Si3N4 etching by NH4F and NH5F2 salts. Thus, the selection of suitable modeling methods allows our group to simulate etching and identify key processes. These methods can be used for optimization of process parameters in designing new etchants.

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