GAS-PHASE AND SURFACE REACTIONS IN PLASMA ENHANCED CHEMICAL ETCHING OF HIGH-K DIELECTRICS

Lin Sha and Jane P. Chang

Department of Chemical Engineering
University of California
Los Angeles, CA 90095

Patterning novel high-k dielectric materials is a critical step for fabricating the next generation complementary metal oxide semiconductor (CMOS) devices at feature dimensions below 100 nm. In the work, we investigated the gas-phase and surface reaction kinetics of etching ZrO_2 and HfO_2 in chlorine based chemistries in an Electron Cyclotron Resonance (ECR) high-density plasma reactor.

In etching ZrO_2, the plasma density and electron temperature were first determined by Langmuir probe measurements as a function of plasma operating conditions. The gas phase species, including the reactants (Cl_2, Cl_2^+, Cl, Cl^+, Cl^-) and the etching products (zirconium chlorides and chlorine oxides), were identified with optical emission spectroscopy (OES) and quadrupole mass spectroscopy (QMS). The etch rate was determined to scale linearly with the square root of ion energy in the higher ion energy regime ($E_{ion} > 60$ eV), indicating that it is limited by the momentum transfer to the etched film. At low ion energies, the etch rate was quite constant, likely due to reactive sputtering of the metal oxides. No Zr nor ZrCl were observed as the etching product, indicating that physical sputtering is not important during the etching process. The etching products were found to be predominantly $ZrCl_3$ (>70%) at low ion energies. However, $ZrCl_4$ became dominant at higher ion energies. This is likely due to the enhanced surface chlorination under higher-energy ion impact. This is in good agreement with the X-ray photoelectron spectroscopy (XPS) measurements, which revealed increased surface chlorine content in the film etched at higher ion energies. The concentrations of the gas phase species were quantified with OES based actinometry and QMS, as a function of the chlorine pressure, ion energy, and the microwave power. The etching selectivity with respect of silicon was greatly enhanced with the addition of BCl_3, while the main etching products became $ZrCl_x$ and $B_xO_yCl_z$. The root-mean-square surface roughness at the etching endpoint is about 3-4 Å, indicating the feasibility of these etching chemistries in patterning ZrO_2 on silicon.

In etching HfO_2, the observed chemical etching pathways were very similar to those observed in etching ZrO_2. The major difference is that $HfCl_2$ was not observed as the etching product, likely due to the stronger Hf-O bond and the lower volatility of $HfCl_x$, making the removal of $HfCl_2$ during the etching process less likely. Moreover, the observed etching rate is about 15-20% slower compared to the ZrO_2 etching rate.

Finally, the etching reaction mechanisms were formulated based on the gas-phase diagnosis and surface compositional analyses. The rate coefficients in the proposed etching reactions were determined based on a CSTR model and CHEMKIN was used to simulate the etching process and the results were compared with the experimental measurements for modeling validation.

Reference:

[1] G. D. Wilk, and R. M. Wallace, and J. M. Anthony, J. Appl. Phys. 87 (1), 484 (2000).

[2] J. P. Chang and Y. S. Lin, Appl. Phys. Lett., 79 (22), 3666 (2001).

[3] Y. S. Lin, R. Puthenkovilakam, and J. P. Chang, Appl. Phys. Lett., 81(11), 2041 (2002).

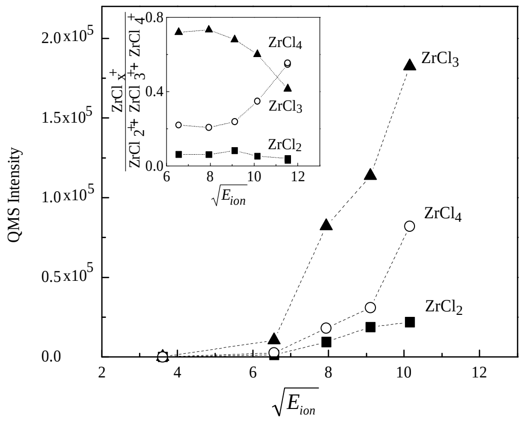

Figure 1: Primary ZrO_2 etching products were $ZrCl_2$, $ZrCl_3$, and $ZrCl_4$. No Zr nor ZrCl were identified, suggesting that physical sputtering is not important.

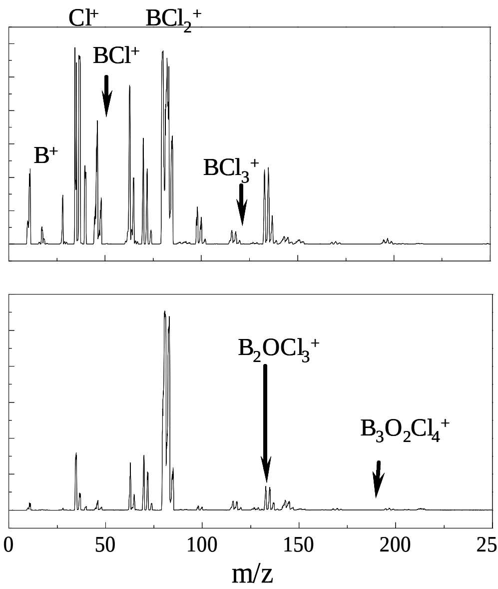

Figure 2: Etching selectivity between ZrO_2 and Si was greatly enhanced with the addition of BCl_3 (50%). The primary etching products were $ZrCl_x$ and $B_xO_yCl_z$.

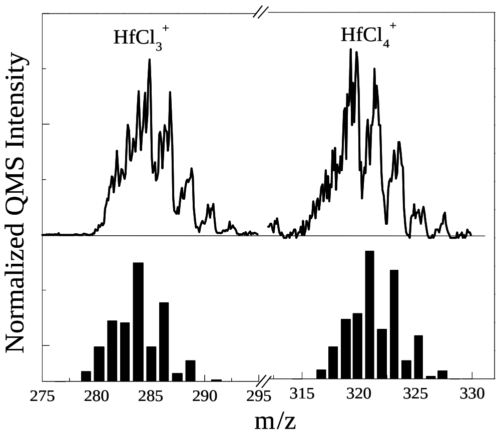

Figure 3: The primary HfO_2 etching products were $HfCl_3$ and $HfCl_4$. $HfCl_2$ and other less chlorinated species were not found during the etching process.