Comparison of Contamination Effects in Silicon Oxide with that in Hafnium Oxide and Zirconium Oxide Gate Dielectrics

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The objective of this study was to study the effect of airborne molecular contamination in silicon dioxide and compare it with that of zirconium and hafnium dioxides considered as future gate dielectrics. The adsorption-desorption properties of moisture and organic contaminants on 50 Å thin films are grown or deposited by ALCVD are presented. Even a highly controlled ambient in modern processing environments contains parts-per-billion (ppb) levels of molecular contaminants, which can affect dielectric performance. Hence, most of the experiments were performed at ppb levels of contamination. Also presented is a direct comparison of the extent and energetics of contamination on HfO_2 with that of ZrO_2 and SiO_2 surfaces. Such a study can offer valuable insights into the relative levels of contamination of various gate dielectrics. It should also facilitate selection of the most appropriate dielectric film and design of process/equipment so that it can be more readily integrated into silicon technology.

Results and Discussion

Figure 1 shows the experimental set up for developed for this study. Figure 2 compares total amount of moisture adsorbed on HfO_2, ZrO_2 and SiO_2 surfaces at different temperatures for a 56 ppb challenge. For the same challenge concentration, the amount of moisture adsorbed was higher on HfO_2 and ZrO_2 than on SiO_2 at any given temperature. The greater rate of change in adsorption amount with respect to temperature for HfO_2 and ZrO_2 suggests that moisture contamination in HfO_2 and ZrO_2 is more problematic that that in SiO_2. Similar results for organic contamination shows that ZrO_2 had the highest adsorption loading, HfO_2 had the second highest loading, and SiO_2 was the lowest. Atmospheric molecular contamination can affect the quality of all three gate dielectric film studied. HfO_2 and ZrO_2 have similar moisture adsorption loading, but significantly higher than that of SiO_2. However, almost all the adsorbed moisture can be removed from SiO_2 and HfO_2 after a 300 °C bake under nitrogen purge, whereas ZrO_2 surfaces retain 20–30 % of the adsorbed moisture. Experiments with isopropanol show that the adsorption loading on the three surfaces has the following order: $ZrO_2 > HfO_2 > SiO_2$. A multi-layer model (Figure 3) for adsorption of water and IPA is developed to understand the mechanism of interactions of contaminants with the three surfaces. Results from the application of this multi-layer model to the experimental data indicate that ZrO_2 forms the strongest surface–hydroxyl (X–OH) bond.

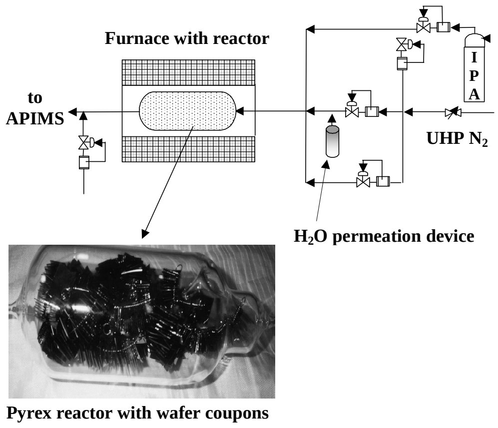

Figure 1. Schematic of the experimental set up

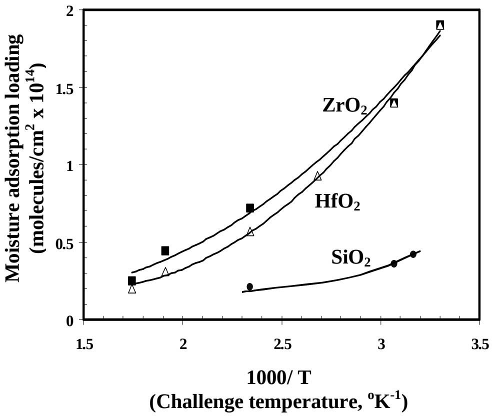

Figure 2. Comparison of contamination in three dielectric oxides

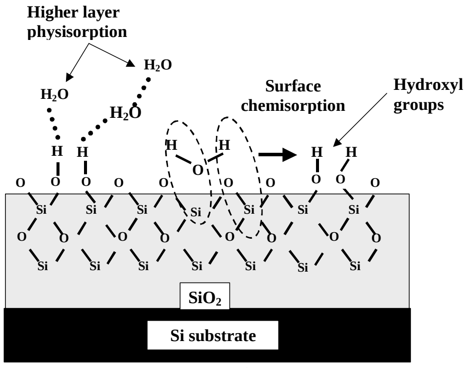

Figure 3. Chemical model for contamination adsorption and desorption