Surface Energies of Thin Oxides of Si(100) as a Function of Thickness, Composition, and Surface Processing

This project aims to correlate Surface Energy measurements of thin oxides of Si(100) with oxide thickness, composition, and surface processing methods. Various thin oxides of Si(100) are characterized: as-received native oxides on p-, and p+ doped wafers, RCA amorphous oxides, Rapid Thermal Annealed (RTA) oxides, ordered Herbots-Atluri (H-A) β-cristobalite silicon dioxide (β-cSiO2) oxides, and Rapid Thermal Oxidation oxides grown on β-cSiO$_2$. Preliminary results for correlation of Surface Energy as measured by Three Liquid Contact Angle Analysis (3LCAA) with oxide thickness and composition as measured through Ion Beam Analysis (IBA) are shown below. 3LCAA results are shown in Figure 1.

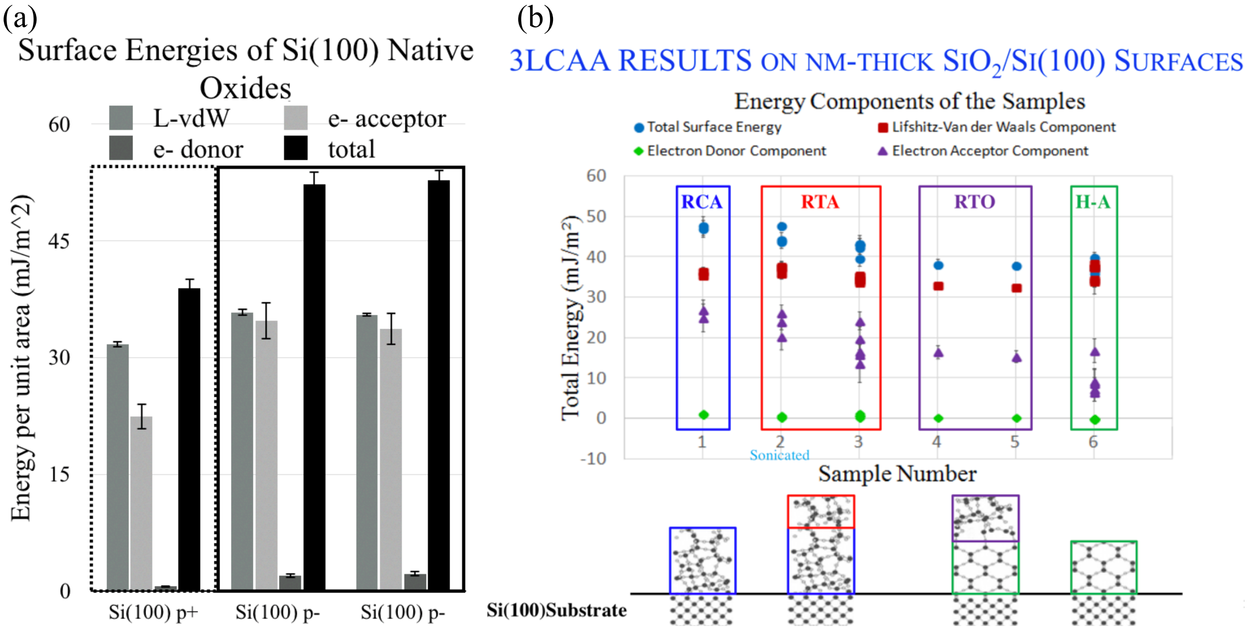

Figure 1. 3LCAA is performed on various of Si(100) wafers. (a) The surface energies of p+ doped Si(100) and p- doped Si(100) are shown. (b) The surface energies of RCA cleaned Si(100), RTA oxides on Si(100), H-A passivated Si(100), and RTO oxides after H-A passivation are shown.

Native oxides on Si(100) p- doped with 5×10^{13} B/cm^3 are found to be hydrophilic, with a total surface energy, γ^T, of 52.5 ± 1.5 mJ/m^2. RCA cleaned wafers have a lower surface energy of 47.3 ± 0.5 mJ/m^2, showing that RCA removes surface impurities, and results in a lower surface energy than native oxides. Yet an RCA oxide is still relatively hydrophilic. Subsequently annealed RTA oxides exhibit a lower surface energy than the RCA oxides, showing that these thicker oxides result in a more hydrophobic surface, a relation corroborated by correlation with oxide coverage measured by IBA. H-A passivated wafers have a lower oxygen coverage but a lower, more hydrophobic surface energy of 37.3 ± 1.5 mJ/m^2 because the surface is terminated by ordered $Si_2O_4H_4$. RTO on ordered H-A passivated wafers result in the most hydrophobic surfaces with a surface energy of 34.5 ± 0.5 mJ/m^2 as the underlying ordered $Si_2O_4H_4$ is capped by a thicker oxide.

3LCAA measurements are correlated with preliminary IBA data. IBA included rotating random spectra (RR) and channeling spectra done at 3.039 ± 0.01 MeV $^{16}O(\alpha, \alpha)^{16}O$ resonance in order to determine oxygen coverage in conjunction with the IBA simulation program SIMNRA. IBA results are shown in Figures 2 and 3. IBA analysis of native Si(100) wafers shows that a thicker oxide results in a more hydrophobic surface. The p+ doped wafer has an oxygen coverage of 13.3 ± 0.4 oxygen monolayers, compared to 11.3 ± 0.6 oxygen monolayers on p- doped Si(100), for which IBA spectra are shown in Figure 3. This difference is responsible for the lower, more hydrophobic surface energy of the amorphous SiO_2 of the p+ wafer and the higher, more hydrophilic surface energy of the amorphous SiO_2 of the p- wafer, as thinner oxides result in a greater exposure to surface defects, shown in Figure 1(a).

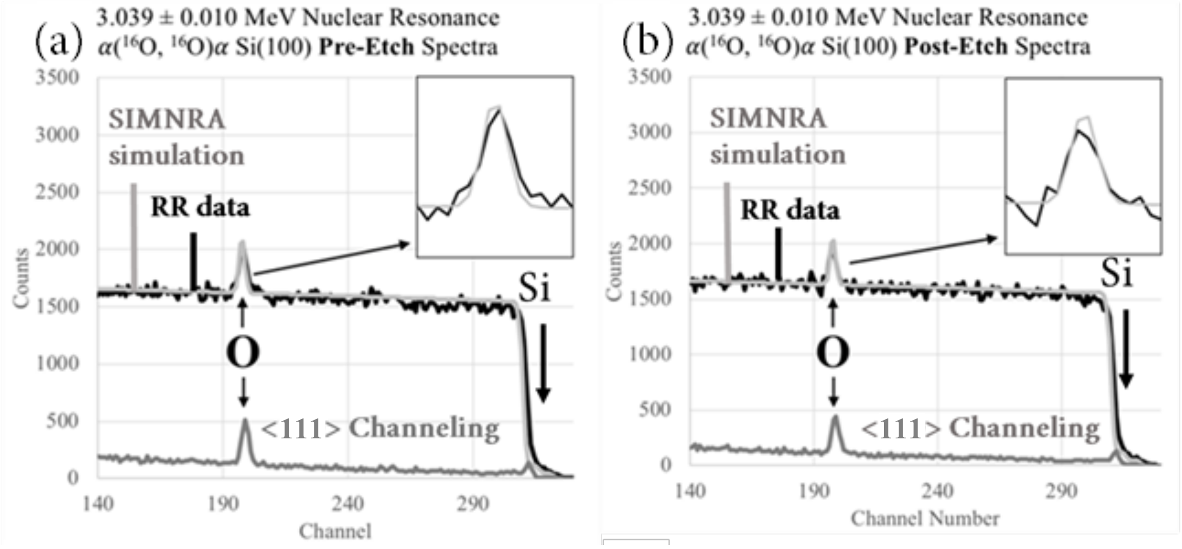

Figure 2. Simulated RR spectra are in light grey, experimental RR spectra are in black, and channeling spectra are in dark grey. Inserts give an expanded view of the oxygen peaks. (a) IBA spectra on Si(100) before etching. (b) IBA spectra on Si(100) after HF:H_2O (1:20) etch (H_2O re-oxidizes surface).

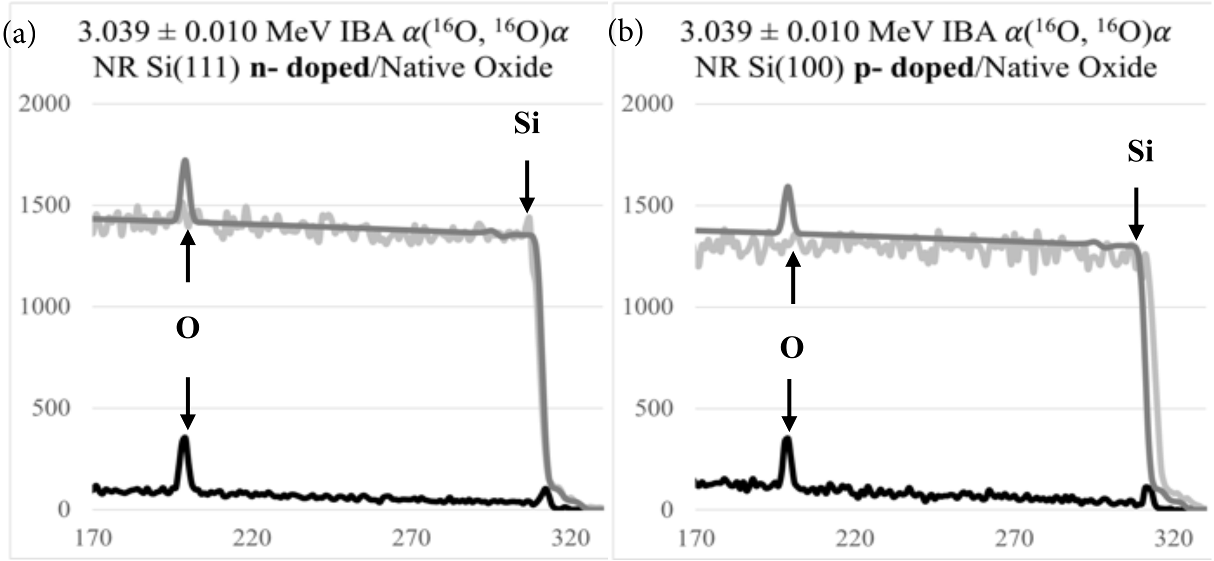

Figure 3. IBA spectra for the three wafer types, with channeling spectra in black, SIMNRA RR simulation in grey, and rotating random (RR) spectra in light gray, showing the location and magnitude of the oxygen and silicon signals at the 3.039 MeV oxygen resonance. (a) IBA spectra on Si(111) n- doped native oxide. (b) IBA spectra on Si(100) p- doped native oxide.

IBA analysis can further correlate surface preparation methods and oxide structure with 3LCAA surface energy measurements. Due to HF-H_2O etching seen in Figure 2, the oxide becomes thinner, with an pre-etch oxygen coverage of 13.3 ± 0.3 oxygen monolayers, compared to a post-etch coverage of 11.8 ± 0.4 oxygen monolayers. Despite a thinner oxide, the more ordered oxide that regrew after HF-H_2O etching resulted in a more hydrophobic surface energy.

Correlating quantitative oxygen coverage with accurate surface energy measurements provides new insights into surface reactivity, and into surface engineering for Nano-Bonding^{TM}. Even in these preliminary results, quantitative data has resulted in new and meaningful relationships between surface energies of thin oxides of Si(100) and oxide thickness, composition, and surface processing methods.