Understanding the Surface Electrical Properties of Si(111) in Contact with Aqueous Fluoride Etching Solutions

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Silicon in contact with various aqueous fluoride etching solutions has been shown to display excellent surface electrical properties as evidenced by extremely low surface charge-carrier recombination velocities (SRVs). The low SRVs of silicon observed in these solutions could be achieved either through complete chemical passivation of surface electrical trap states or by the presence of a strong surface electric field that prevents either electrons or holes from getting to the surface to recombine across any electrical defects.

It has been proposed that weakly basic defects sites on silicon surfaces are chemically passivated through protonation in acidic solutions, such as aqueous HF or 18M H_2SO_4. Experiments in our lab have shown that surfaces having high electrical defect densities can nevertheless display good surface electrical properties (such as low SRVs) simply by contacting them with redox solutions having either relatively positive or very negative Nernstain cell potentials vs. SCE. Mott Schottky analysis of such semiconductor liquid contacts confirms the presence of strong surface electric fields that are formed as a consequence of electrochemical charge transfer equilibria.

Mott Schottky analysis is however ill-suited for the measurement of silicon in aqueous fluoride etching solutions since the severe reverse-bias conditions necessary for the analysis can lead to anodic oxidation and other surface reactions. Clearly another method is desired to probe the amount of surface band bending for silicon in contact with aqueous fluoride solutions.

In this study, the amount of band bending and the SRVs of Si(111) in aqueous fluoride solutions were determined for the first time at open circuit conditions. Near-surface-channel conductance measurements of n^+-p-Si(111)-n^+ devices and contactless photoconductivity decay measurements show that an accumulation of electrons is responsible for the low effective SRV in NH_4F and buffered HF solutions. These techniques were also used to study Si/$CoCp_2^{+/0}$ (strong accumulation for n-type) and corroborate this interpretation. Measurements in HF and H_2SO_4 indicate the absence of strong electric fields at the surface and that the good surface electrical properties may in fact be due to a chemical reduction of surface electrical trap states.