The Effect of Deposited Oxide Thickness and Implanted Cl on the Pitting Behavior of Aluminum

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Chlorine implantation (above a critical fluence) into pure aluminum has been shown to be sufficient to initiate pitting even in Cl^--free electrolytes (1). When an implanted sample is exposed to a chloride solution, the contributions of implanted Cl and aqueous Cl to destabilization of the oxide cannot be differentiated. To address this limitation, Cl implanted aluminum thin films were capped with a Cl-free deposited oxide and exposed to Cl^- -containing and Cl^- -free electrolytes to assess the resulting pitting behavior.

Samples were prepared using a series of steps. First, pure Al thin films (99.9999%, 2000 Å) were prepared using electron beam deposition of aluminum onto a thermal SiO_2 layer on a standard silicon wafer. The native oxide was formed by exposing the samples to laboratory air. Next, samples were implanted with 35 keV Cl^+ at room temperature. In the final step, an electron cyclotron resonance (ECR) plasma was used to deposit a Cl-free oxide layer over the implanted sample. The resulting distribution of Cl in the sample is shown schematically in Figure 1.

Cl-free oxides were deposited at various thicknesses to examine the effect of oxide thickness on pitting behavior. Initial samples were made with 70 and 140 Å deposited oxides. Test results from these samples indicate that the pitting potential is insensitive to oxide thickness for both Cl-implanted and non-implanted samples when exposed to aqueous chloride (Figure 2). Interestingly, when the samples were exposed to only one source of chloride (implanted or aqueous) high fields were required to initiate pitting, while samples with both sources of chloride (implanted and aqueous) exhibit a much lower barrier to pitting, despite the presence of a 70 Å deposited oxide (Figure 3). These results suggest that exposure of the oxide to aqueous chloride results in a modification of oxide properties that is relevant to pit nucleation, possibly oxide growth and/or vacancy migration mechanisms. To investigate this further, samples with thicker oxides (150, 200, 250 and 300 Å) have been prepared and are currently being evaluated. Exposure of thicker oxides to aqueous chloride should allow rate determining steps (e.g. Cl transport) to be determined.

Additional work is in progress to address the following outstanding issues: 1) critical implant fluence for pit initiation (believed to be between $2x10^{16}$ and $3x10^{16}/cm^2$), 2) mechanical damage due to implantation and 3) chlorine distribution in the metal. The distribution of chlorine in the metal can be modified (leaving the concentration in the oxide relatively unchanged) by changing the implant energy. For a given implant fluence, higher energies result in the peak concentration deeper into the substrate (Figure 4). Modifying the distribution in the metal should allow the role of chlorine in the oxide vs. in the metal to be better defined.

References:

1. F.D. Wall, C.M. Johnson. J.C. Barbour, M.A. Martinez, JES 151 (2) B77-B81 (2004).

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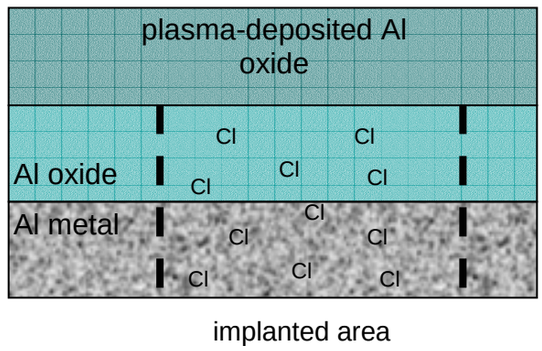

Figure 1. Schematic of thin film cross-section showing Cl implantation in Al oxide and metal and Cl-free deposited oxide.

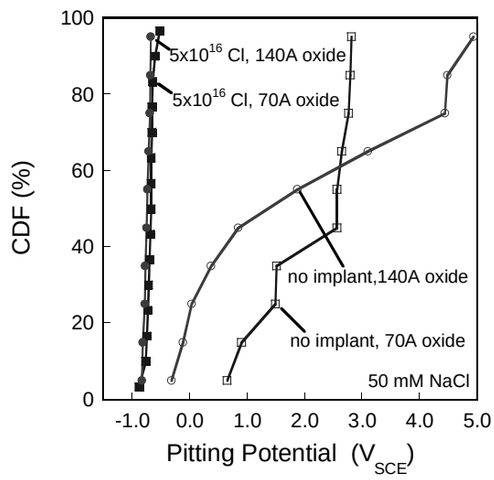

Figure 2. Cumulative distribution function plots showing pitting potential distributions for Cl-implanted and non-implanted samples with 70 and 140 Å deposited oxides in 50mM NaCl.

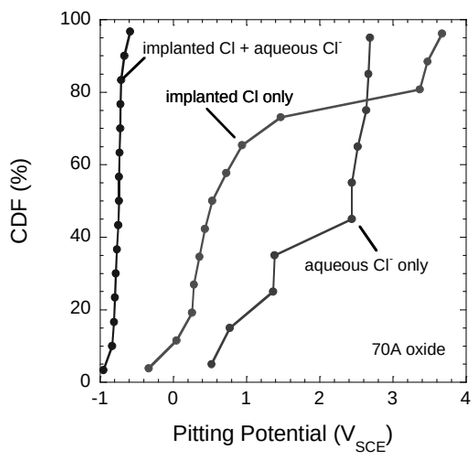

Figure 3. Cumulative distribution function plots showing pitting potential distributions for samples with a 70Å deposited oxide (implantation level $5x10^{16}$ Cl/cm^2 and 50mM NaCl when applicable).

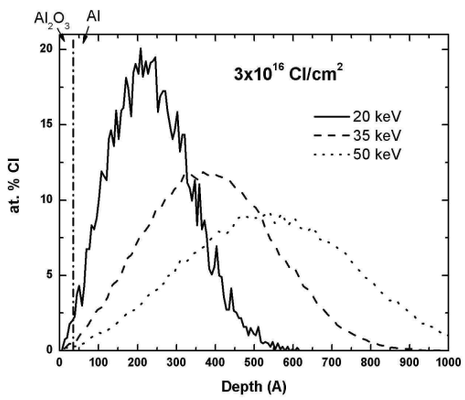

Figure 4. Calculated depth profiles for a chlorine fluence of $3x10^{16}$ $/cm^2$ implanted at energies of 20, 35 keV and 50 keV.