Point Defect Generation in Tailored Passive Oxides on Aluminum in the Study of Localized Corrosion

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The point defect model has been successful at describing a range of behavior for both field-assisted growth of oxides and corrosion characteristics of passive oxides on active metals (1). This model invokes the formation of a cation vacancy condensate at the metal/oxide interface as the site where localized corrosion or pitting is initiated (2). Condensate nucleation sites are viewed at regions of high cation mobility where structural and/or compositional variations at the metal surface produce heterogeneity in the passive oxide defect structure. Establishing a quantitative correlation between eventual pit sites and high defect concentration zones in the oxide is difficult and has not been accomplished. One approach to accomplishing this goal is to externally introduce point defects into the oxide, independent of the metal substrate, and to explore their impact on pitting. This approach represents a first step toward introducing a defective zone in an oxide and testing the ability to predict the location of the most probable pitting site. In this paper, we describe a method for introducing oxygen vacancies in tailored oxides on Al and describe their subsequent electrochemical activity.

Our approach involves defect introduction into a controlled oxide on Al followed by short term electrochemical measurements to ensure the role of the defects is dominant. Plasma formed passive oxides (4.5 nm thick) are generated on 200 nm thick Al films deposited on Si wafers. These films are then irradiated using a 300 eV electron beam to generate O vacancies through an electron stimulated desorption mechanism. We have evidence that this vacancy population is stable with both air and short term solution exposure. The irradiated sample is then electrochemically interrogated (50 mM $NaCl_{aq}$, 25ºC) using a combination of electrochemical impedance spectroscopy and scanning potential techniques in a small area format to provide statistical information (i.e. pitting potential distribution). Small area electrochemical measurements are followed by small area surface spectroscopy (SIMS and XPS) to understand the correlation between oxide defects, electrochemical activity, and induced compositional changes in the film.

Moderate increases in O vacancy concentration above intrinsic levels significantly change the properties of the oxide. SIMS measurements, coupled with a fluoride maker in the oxide, show that the initial oxide is an Al cation conductor. These films maintain their basic structure (fixed thickness, no discernable film dissolution and reformation) as evidenced by a constant F^- distribution in SIMS depth profiles independent of immersion or applied potential. An increased O vacancy concentration produced by 100 mC cm^{-2} of electron fluence results in both a measurable decrease in the passive film resistivity as measured by EIS and an increase in passive current density in scanned potential experiments.

Large increases in oxide defect concentration produce localized compositional changes in these oxides. Electron fluences of 200 and 500 mC cm^{-2} result in further decreases in oxide film resistivity and increases in passive current density. These changes, along with cumulative polarization time, correlate with a local thickening of the oxide and incorporation of Cl^- as measured with a 0.5 µm diameter Ga beam in the SIMS analysis. Use of a fluoride marker, shows that this thickening is produced by OH^- incorporation indicating that increased O vacancy concentration is responsible for the onset of anion mobility in the film. We estimate the film thickness increase to be on the order of 10 to 20% (0.4 to 0.9 nm). This thickening is a general phenomenon which is distributed over a significant fraction of the analyzed area and can be distinguished from a lower density of spatially larger sites that show thickening and higher Cl^- concentrations. These latter sites appear to be regions of metastable pitting.

The mean value of pitting potential (E_{pit}) appears to be dependent on a combination of point defect concentration and polarization induced modification of the film. Figure 1 shows the pitting potential distribution, in the form of a cumulative distribution function, for identical oxides as a function of electron fluence. Moderate levels of introduced O vacancies shift the mean E_{pit} +60 mV, resulting in a film more stable toward pitting. The onset of anion incorporation at 200 and 500 mC cm^{-2} returns the mean E_{pit} to a nearly equivalent value as the intrinsic oxide.

These results suggest that a principal contribution to pitting in Al are dynamic changes produced by ion transport in the passive oxide, as opposed to latent defect structure.

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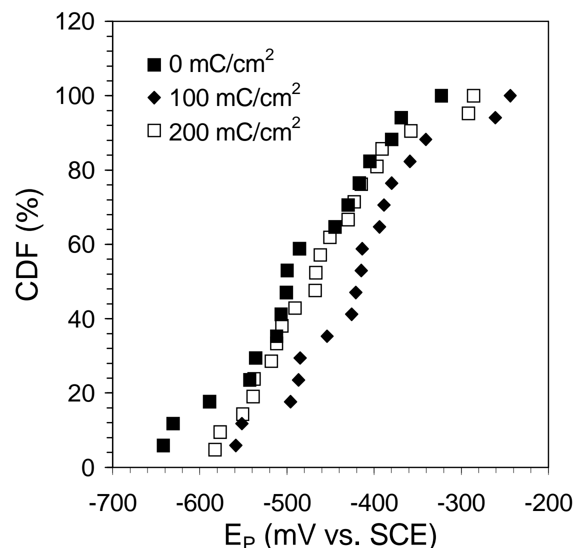

Figure 1: Cumulative distribution function for the pitting potential as a function of electron fluence.