Simultaneous Ellipsometric and Potentiostatic Study of Aluminum Oxide Growth and Dissolution in Acetate Buffer

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It is well known[1] that the growth of the barrier oxide layer on aluminum during low-current anodic polarization in nearly neutral buffered aqueous solution occurs in accordance with the high-field Cabrera-Mott growth law.[2] Information about the dissolution kinetics is scarce, indicating an apparently chemical[3] and mass-transfer controlled[4] process. Most studies of oxide growth on aluminum are based on electrochemical polarization and gravimetric methods, which may introduce complications in terms of correction for the leakage current and the contribution from the growth of a porous hydrated layer, respectively. This work intends to combine electrochemical and *in situ* multi-wavelength visual spectroscopic ellipsometry (VISSE) for investigating barrier oxide growth and dissolution on pure aluminum in response to step changes in the applied potential in acetate buffer solution.

Experiments were conducted in a conventional three electrode electrochemical cell equipped with optical windows for shining visual incident light on the aluminum specimen and collecting the light reflected from the sample surface for ellipsometric analysis. The electrochemical method consisted of stabilizing the specimen at a preselected potential, at which the thickness of the barrier film developed was measured by electrochemical impedance spectroscopy (EIS). A predetermined potential step was then applied in the positive or negative direction and the resulting optical and electrochemical transient response of the surface were recorded. The procedure was repeated for several potential steps on the same sample. The EIS measurements were performed for the purpose of calibrating the barrier film thickness at steady state attained after each potential step.

The ellipsometric data were analyzed by use of a two layer model for a composite barrier and hydrated film, as discussed in Ref. 5. In this model, the thickness of the hydrated oxide layer, measured at steady-state corresponding to the previous potential step, was assumed to remain constant during the variation of the barrier oxide thickness in response to the new potential step, since the time constant for barrier oxide response is much smaller than that of the hydrated oxide. The refractive indexes of the oxide layers, metal and solution were assumed constant. For oxide growth, calculation of the film thickness was attempted also from the current-time data by use of the relationship

$$\Delta\delta(t) = \frac{M}{nF\rho} \int_0^t (i(t) - i_{ss})dt \qquad (1)$$

where $\Delta\delta(t)$ is the variation in film thickness, $i(t)$ is the measured current density, i_{ss} is the steady-state current density, F is faraday's constant, n is the number of electrons transferred per mole of Al_2O_3 formed, and M

and ρ are the molecular weight and density of the barrier oxide, respectively.

The growth data were analyzed by use of the integrated form of the Cabrera-Mott law, according to Ghez,[6] giving the well-known inverse logarithmic growth law, as shown in Fig. 1. Barrier layer thickness calculated both from the ellipsometry and current density data fitted the Ghez equation well for oxide growth.
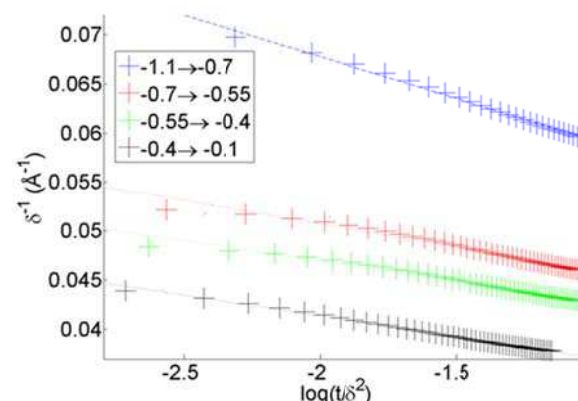

Figure 1. Inverse thickness, calculated from current transients according to Eq. 1, correlated according to the Ghez equation for inverse-logarithmic growth law, corresponding to successive potential steps (V_{Hg/Hg_2SO_4}), specified in the legend, in 13 mM acetate buffer at pH = 6.

The current density data were not useful for studying oxide dissolution because of the complexity of the current response to a negative potential step, as discussed by Greef and Norman.[3] The short-time ellipsometry data indicated Cabrera-Mott type of high-field controlled dissolution. However, this behavior shifted quickly, after a few seconds, to a mass-transfer controlled dissolution rate, which could be analyzed by use of Fick's 2nd law. The boundary condition at the surface, assumed to be constant and equal to the solubility of the barrier oxide, was determined by the applied potential, as would be expected from thermodynamic considerations. The diffusion coefficient calculated from this type of analysis resulted in values within the correct order of magnitude, about $5 \cdot 10^{-6}$ cm^2/s for Al^{3+}.[7]

References

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