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INTERPRETATION OF ELLIPSOMETER OBSERVATIONS OF ANODIC FILMS

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INTERPRETATION OF ELLIPSOMETER OBSERVATIONS OF ANODIC FILMS*Craig G. Smith**and**Rolf H. Muller*

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ABSTRACT

An automated interpretation of ellipsometer measurements of anodic film growth, which takes electrical charge passed and mass transport in the electrolyte into account, has been developed. The optical model assumes the existence of a homogeneous solid film, covered by two inhomogeneous layers in the liquid phase. A computer program finds a least-squares fit in seven-dimensional space.

INTRODUCTION

This work was undertaken to include mass-transport processes in the interpretation of ellipsometer measurements of anodic film formation and to more fully use electrochemical data collected simultaneously. The reaction rate at the electrode surface is derived from the current density, and the amount of reacted material accumulated at different distances from the substrate is obtained from a balance of mass fluxes. Electrode potential measurements are used to identify thermodynamically possible products and major changes in products with time. The formulation of an initial model for the use of this information is presented here. A search of the multi-dimensional space for all possible solutions that satisfy the constraints of the model is conducted in order to determine the values of seven adjustable parameters.

Previous investigations of anodic film formation¹ have shown that ellipsometer measurements often cannot be interpreted by assuming the presence of a single, homogeneous film. Anodic film formation is accompanied by the transport of reactants and products to and from the solid-liquid interface. For reactions proceeding at significant rates, the resulting mass-transport boundary layers can have a significant optical effect on ellipsometer observations.² Film properties have also been shown to depend on mass transport-conditions.^{3,4,5}

EXPERIMENTAL

Experiments on the anodic oxidation of silver were performed by use of a self-compensating ellipsometer.⁶ The values of Δ and ψ determined include corrections for azimuth errors and component imperfections.⁷ The 6 M KOH electrolyte was deoxygenated with a purified nitrogen stream. The electrode for the experiments discussed here was a (111) single crystal with dimensions 1.1 x 3.0 cm, cast in an epoxy holder and polished with 1 μ m diamond paste. The electrode pretreatment consisted of cathodic evolution of hydrogen to remove organic materials remaining from the polishing process. The horizontal electrode faced upward to avoid natural convection.

PRELIMINARY INTERPRETATION

The potential usefulness of several simple optical models was initially evaluated by conventional computation. Figure 1 illustrates that homogeneous films with different complex refractive indices cannot account for the measurements. According to the dissolution-precipitation mechanism of anodic film formation,⁵ the primary reaction products are soluble and film growth occurs by precipitation from a supersaturated solution. It is therefore possible, that precipitation also occurs some distance away from the solid surface, thus resulting in a colloidal suspension^{8,9} near the solid film. Assuming the existence of such a layer dramatically improves agreement with observation, as shown in Fig. 2.

(The refractive index of this region is too high to be due to ionically dissolved silver, which has a solubility of only 4.7×10^{-4} M in this solution.)

Calculations for uniaxial birefringence, with the optical axis normal to the surface,¹⁰ do not fit the data. Calculations for biaxial anisotropy have not been conducted, but the deviations from isotropic single film behavior are much greater than birefringence effects presented by other investigators.¹¹ The consideration of dual, or inhomogeneous, solid films and surface roughness will be investigated in the future as refinements of the present model.

OPTICAL MODEL

The optical film model used for the automated interpretation of ellipsometer measurements is illustrated in Fig. 3. It consists of a smooth substrate, a homogeneous solid film (which may be porous), a colloidal overlayer and a mass-transport boundary layer.

A constant anodic current density i (based on macroscopic surface area) is passed across the electrolyte-metal interface and results in the production of an equivalent flux of dissolved primary reaction product. A fraction of this flux, corresponding to the current density i_c , enters the colloidal layer, the remainder is precipitated as solid film. Part of the dissolved material is precipitated in colloidal

form, and the remainder (flux density j_D) enters the mass-transport boundary layer.

The parameters used in the computations are listed in Tables I and II. The values presented for the parameters determined by experimental conditions are specific for the experiment shown in Figs. 1, 2 and 5. The Sand equation,¹² valid for diffusion into a stagnant, semi-infinite medium, is used for determining the boundary layer thickness as a function of time:

$$\delta = 1.129 \sqrt{Dt} . \quad (1)$$

The computer search provides fixed values for the parameters $n_s - ik_s$, f , T_{cl} , n , ϵ_0 , and T_{fl} . The refractive index $n_s - ik_s$ represents the non-porous film material. A uniform film porosity is modeled to decrease from an initial value of ϵ_0 to zero at an adjustable film thickness of T_{fl} :

$$\epsilon = \epsilon_0 (1 - T/T_{fl})^2 . \quad (2)$$

To account for a possible restriction in the removal of primary dissolution product by the growing film, the dissolution current i_c is modeled to decrease to zero at an adjustable thickness T_{cl} :

$$i_c = i f(1 - T/T_{cl}) . \quad (3)$$

The refractive index n of the colloidal layer is assumed to remain constant, an approximation valid for a steady state process.

Parameter values which vary with time are the porous film and colloidal layer thicknesses T_f and T_c , the porous film refractive index $n_f - ik_f$, the film porosity ϵ , the ionic diffusion flux j_D , and the dissolution current i_c . Neglecting ionic migration effects¹⁴ (valid due to the large excess of KOH), the diffusion flux across the boundary layer of dissolved reaction products is given by -

$$j_D = \frac{-D\Delta C}{\delta} , \quad (4)$$

where ΔC is the concentration difference between the colloidal layer and the bulk solution. A value of 2.3 time the solubility of silver hydroxide¹⁸ has been used for the ionic concentration at the boundary between the colloidal layer and the diffusion layer. The refractive index of the porous film is calculated using the Lorenz-Lorenz mixing rule¹³ to average $n_s - ik_s$ with the colloidal suspension in the pores. The film thickness T_f at each moment is determined by using the valence, molar volume, porosity, and charge consumed in film formation to calculate the volume per cm^2 of solid reaction products. The thickness of the colloidal overlayer at each

moment is determined as follows: The integrated difference between the dissolution current and diffusion flux gives the charge used in film formation. Valence and molar volume then give the total volume of colloidal particles formed. The volume fraction of colloidal particles is calculated with the Lorenz-Lorenz mixing rule using the values of n , n_c , n_b , ρ_s and ρ_c (see Table I). The ratio of the volume per cm^2 and volume fraction gives the thickness.

To reduce computational time, the optical effects of the inhomogeneous boundary and colloidal layers are represented by two limiting models. For the thin-film regime, a homogeneous film with equal thickness and interfacial refractive index is used; above a critical thickness δ_1 , an asymptotic thick-film approximation² is used. The critical thickness has been chosen to be at 1/4 of the repetition cycle of the homogeneous film response (Fig. 4). It is

$$\delta_1 = \frac{\lambda}{2(n^2 - n_b^2 \sin^2 \phi)^{1/2}} \quad (5)$$

where λ is the wavelength of light and ϕ the macroscopic angle of incidence. For the colloidal layer with $n = 1.45$, $\lambda = 5461 \text{ \AA}$ and $\phi = 75^\circ$, δ_1 equals $4800 \text{ \AA}$.

The seven descriptive parameters are evaluated by a computer-implemented minimization of a point-by-point least-squares fit between calculated and experimental values of Δ

and ψ . The experimental values of time are used. Simplex¹⁵ and Davidon variable matrix¹⁶ algorithms are combined to evaluate all (or specifically chosen) parameters. Parabolic error estimates are used to provide limits of uncertainty for the parameters. A parabola is fitted through the partial derivative of each parameter near the minimum. A measure of uncertainty is given by the change in parameter value necessary to change d (the distance between experimental and calculated points) by a specified value.

In addition, a Monte Carlo routine¹⁷ has been used to randomly search the seven-dimensional space for multiple roots. In this routine, new values for the parameters are chosen at random and a new minimization is conducted.

RESULTS AND DISCUSSION

Shown in Table III and Fig. 5 are the results of the least-square fit for the first 8 experimental points of Fig. 2. The parameter values determined by experimental conditions are given in Table I. A CDC 7600 computer required 5 seconds to evaluate all seven parameters. The accuracy of the fit, an average distance of 0.5 deg between experimental and calculated points, agrees favorably with experimental uncertainties of ± 0.1 deg in Δ and ± 0.25 deg in ψ which were indicated by the error analysis for the automatic ellipsometer. However, the accuracy of the fit decreases if

later portions of the experimental curve are included, due possibly to changing composition of the film or the simplifications in the model which will be discussed later.

The refractive index found for the colloidal overlayer, 1.448, agrees with the previous estimate. The initial average porosity of 0.27 is reasonable, and additional techniques such as scanning electron microscopy will be used for verification. A value of 1770 for T_{f1} indicates a gradual decrease in average film porosity, but the large uncertainty limits assigned by the parabolic error indicates that refinements to the model are necessary.

The value of 0.018 for the initial fraction of current used in dissolution agrees with current efficiencies estimated by other investigators.⁵ However, the small value of T_{c1} (as well as the non-parabolic behavior of f and T_{c1} about the minimum in the fitting process) indicates that the modeling of the colloidal layer is inadequate. For instance, the increase in interfacial concentration which precedes the formation of the colloidal layer has been neglected.

A second discrepancy is the value found for the refractive index of the compact film material, $1.47 - 0.31i$. Calculations using atomic polarizabilities suggest a value of 2.1 for the real part of the refractive index of Ag_2O , the reaction product assigned to the electrode potential of + 0.34 V vs. Hg/HgO measured experimentally.⁵ The apparent refractive index of silver is $0.4 - 3.2i$. The value of

1.47 for the real part of the compact film material refractive index n_s could be the result of excess silver in the film, or may indicate that the substrate roughens during dissolution. Samples prepared from purified silver oxide will be used to experimentally determine the refractive index of the compact film material.

The minimum given by the parameter values is the best obtained after numerous Monte Carlo searches, supporting uniqueness of the solution. Although seven parameters are involved in fitting the $\Delta - \psi$ curve, various characteristics of the model provide additional constraints. Besides values of Δ and ψ , the shape of the curve and the charge passed as a function of time are 2 additional experimental quantities. The mass balances in the model also constrain the values.

CONCLUSIONS

Models which include electrode current density and mass transport considerations may be effectively used to interpret ellipsometer observations of anodic film formation. Simplifications that need to be refined in the model presented here appear to be the neglect of substrate roughening and the transient increase of the concentration of dissolved reaction products. A more sophisticated model is presently being developed which includes these effects. Electrode potential is also included in the model in order to account for changes in film composition by the use of experimental data or inhomogeneous solid film structures.¹⁸

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The accumulation of dissolution products during film formation appears to have a significant optical effect. Verification of the the existence of a colloidal overlayer will be sought by varying transport conditions. The projected combined use of ellipsometry, ion-bombardment, and Auger spectroscopy should provide information on possible dual or inhomogeneous solid film structures.

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TABLE I

Variables in the Anodic Film Formation Model Pre-determined by Experimental Conditions. (Values used are for the experiment shown in Figs. 1, 2 and 5.)

i	-	Anodic current density.	0.6 mA/cm^2
z	-	Valence of primary reaction products.	1
n_{cs}	-	Substrate refractive index.	$0.496 - 3.06i$
n_b	-	Bulk solution refractive index.	1.3858
ρ_f	-	Solid film bulk density.	7.14 g/cm^3
ρ_c	-	Colloid bulk density.	5.56 g/cm^3
ρ_s	-	Electrolyte bulk density.	1.300 g/cm^3
δ	-	Mass-transport boundary layer thickness.	$\delta = 1.129 \sqrt{Dt}$
D	-	Diffusion coefficient of AgOH.	$1.1 \times 10^{-5} \text{ cm}^2/\text{s}$
n_c	-	Refractive index of compact colloid material.	1.87

TABLE IIParameters of Anodic Film Formation Determined by the Automated Interpretation.

Time-invariant parameters:

$n_s - ik_s$	-	Solid film refractive index.
f	-	Initial current fraction used for dissolution, eq. (3).
T_{cl}	-	Film thickness for zero dissolution current, eq. (3).
n	-	Refractive index of colloidal overlayer.
ϵ_0	-	Initial film porosity, eq. (2).
T_{fl}	-	Film thickness for zero porosity, eq. (2).

Time-dependent variables (functions of the time-invariant parameters):

j_D	-	Ionic diffusion flux density, eq. (4).
i_c	-	Dissolution current density, eq. (3).
ϵ	-	Film porosity, eq. (2).
T_f	-	Thickness of porous film.
T_c	-	Thickness of colloidal overlayer.
$n_f - ik_f$	-	Refractive index of porous film.

TABLE III

Least-Square Fit of Anodic Film on Silver. Average Distance
Between Experimental and Calculated Points d: 0.50 deg.

Parameter	Value	Measure of Uncertainty†	
		Positive	Negative
n_s	1.474	+0.031	-0.156
k_s	0.306	+0.036	-0.027
f	0.018	*	*
T_{cl}	130 Å	*	*
n	1.448	+0.059	-0.038
ϵ_o	0.272	+0.223	-0.167
T_{fl}	1,770 Å	4,250	*

† Change in parameter value resulting in 0.83 deg change in d.

* Non-parabolic behavior about the minimum, resulting in excessive number of iterations.

FIGURE CAPTIONS

- Fig. 1 - Anodic film formation on silver in alkaline solution. The calculated curves represent different film porosities. Monovalent and divalent oxides are the products indicated by electrode potential measurements.
- Fig. 2 - The use of a Colloidal Overlay of constant refractive index $n = 1.45$ and constant thickness $T_c = 1200 \text{ \AA}$ in a preliminary interpretation. Same film refractive indices as in Fig. 1.
- Fig. 3 - Optical Model for automated interpretation of measurements with definitions of layer thicknesses and flux densities between layers.
- Fig. 4 - Effect of dissolution mass-transport boundary layer on ellipsometer parameter Δ . Computed for parabolic and linear concentration (refractive index) profiles and compared with homogeneous film model. Bulk solution 0.1 M CuSO_4 ($n=1.3372$), interface concentration 0.2 M CuSO_4 ($n=1.3401$); Cu substrate, $n = 0.94 - 2.33$; angle of incidence 75° .
- Fig. 5 - Least-squares fit of the ellipsometer measurements of anodic film formation on silver.

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Fig. 1

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Fig. 2

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Fig. 3

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Fig. 4

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Fig. 5

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