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USE OF FILM-FORMATION MODELS FOR THE INTERPRETATION OF
ELLIPSOMETER OBSERVATIONS

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ABSTRACT

Mathematical film-formation models have been used for the interpretation of ellipsometer measurements of anodic films on metals. The models consider the simultaneous or sequential formation of several surface layers with time-varying properties. Mass transport between layers is modeled to take place by diffusion, migration and convection. In experiments, mass transport is controlled and current and potential are measured simultaneously with the ellipsometer measurements. The application of continuous mass and charge balances in the models makes it possible to derive values of up to seven film parameters by fitting time-dependent ellipsometer measurements in multi-dimensional space.

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I. INTRODUCTION

A recurring dilemma in the use of ellipsometry for the characterization of surface layers is that often the number of unknown quantities that need to be determined is larger than the number of measured optical parameters, even if reflectance is considered in addition to changes in state of polarization. For this reason, an isolated ellipsometer measurement considered by itself normally permits multiple, sometimes an infinity of interpretations.¹ It has long been recognized that the freedom of interpretation is greatly reduced if series of measurements with continuous changes in one film parameter, are evaluated. The changing parameter is often chosen to be film thickness,² with other properties assumed constant. A common experience with this approach is that reasonable film properties can be deduced over a certain range of film thickness, but different assumptions, which often cannot be uniquely determined and may lead to conflicting interpretations, have to be made outside this range.

It has not been sufficiently recognized that the time-factor inherent in the continuous transient ellipsometer measurements which can now be obtained with automatic instruments can be used to greatly restrict the interpretation of measurements. For the case of electrochemical film formation considered here, the simultaneous measurement of current and potential provides additional input on the rates of surface reactions and the nature of products formed and can be used to further constrain interpretations. In addition, the use of controlled

mass-transport conditions permits one to predict the transport of material in the liquid phase. The simultaneous consideration of these factors requires the use of a mathematical model in which the movement of reactants and products is followed in time and restricted by use of continuous mass and charge balances.

The models considered are consistent with published results of other investigators. The chemical composition of surface layers for the systems considered here is known on the basis of potential measurements. Optical constants of these materials have been determined separately by use of compressed powders. Their porosity has been determined and taken into account in the derivation of the optical constants of nonporous material. The optical constants of anodic surface layers depend on degrees of porosity and hydration and are obtained by use of mixing rules. Linear and Lorentz-Lorenz equations have been used as mixing rules. The properties of surface layers are therefore characterized by porosity, hydration and film structure rather than by refractive index.

II. MODELS INVESTIGATED

In the course of developing refined ellipsometer interpretations,³ eight models of anodic film formation have been investigated. They attempt in different ways to accommodate observations reported in the literature for dissolution-precipitation mechanisms and are illustrated in Fig. 1. The first model represents the classical single, homogeneous film of increasing thickness. In most cases of anodic film growth, this model is not satisfactory. In the second and all subsequent models a mass-transport boundary layer (MTBL, indicated by the dot pattern) is also taken into account. The optical effect of

this optically inhomogeneous layer is significant where highly soluble products are formed. Even with low solubilities, however, the layer is important for mass-balance considerations.

A second homogeneous film is added in model 3 and changes in the roughness of the substrate (modeled as another homogeneous or inhomogeneous layer) are introduced in model 4.

Model 5 has been investigated in great detail. Here, the anodic current is assumed to result in an equivalent flux of dissolved primary reaction products. A fraction of this flux enters a homogeneous solid film of time-varying porosity, growing on a smooth substrate, the remainder forms an inhomogeneous polymer (or colloid) overlayer and a mass-transport boundary layer which is also inhomogeneous. In model 6 roughness of the substrate is also considered and model 7 includes a dual solid film.

Model 8 has been found to best reproduce experimental observations for different materials over large ranges of film thickness and film formation conditions. Interpretations result in optical constants of product layers that are consistent with the nature of products expected on the basis of potential measurements. The model includes the formation of secondary crystals and is further described below. The improvement in interpretation achieved by use of the more sophisticated models is illustrated in Table 1.

The physical meaning of the parameters used in the film model places limits on the range of acceptable values; they are therefore not simple adjustable parameters for curve-fitting in the usual sense. For this reason predictions from even the most complex model usually disagree with measurements by more than the experimental error.

III. DESCRIPTION OF MODEL 8

Features of model 8 are illustrated in Fig. 2. The six layers represent a composite of observations described in the literature. The outermost layer is a mass-transport boundary layer (MTBL) composed of ionic or polymeric material. This layer controls the flux of dissolved products away from the electrode by convective diffusion. Significant supersaturations typically occur near the electrode surface. The hydrate layer represents colloidal or polymeric forms of oxides, hydroxides or anion complexes.

The nomenclature for type I and II films has been introduced by Breiter and Powers⁴ for film formation on zinc. Similar observations have been reported for silver by Fleischmann and Thirsk.⁵ The type II primary layer is located next to the metal substrate. It forms by crystallization onto heterogeneous nucleation sites before the onset of secondary crystal growth. The secondary crystals also involve heterogeneous nucleation. They can be observed with the scanning electron microscope; in agreement with the literature, their number density and size depend strongly on transport conditions (current density, electrolyte flow and composition) which determine the degree of supersaturation of reaction products, as illustrated in Fig. 3. The type I film is also a primary layer. It results from homogeneous nucleation and subsequent precipitation and forms only after the onset of secondary crystal growth. The transport of reactants and products through type I and II layers results in resistance polarization and may lead to passivation.

Surface roughness of the substrate is described by a roughness layer and optically treated by the McCrackin square-ridge model,⁶

using two structure parameters and one rate parameter. Models using three structural parameters would require independent characterization of the topography. The use of a more sophisticated roughness model would only result in some minor changes in the predicted behavior at the initial stages of film growth because roughness values are small and at later stages the optical behavior of the systems studied is dominated by the formation of oxidic layers. Single crystals of close-packed orientation have been used as substrates in the experiments in order to minimize roughening rates.

The time-sequence of events involved in anodic film formation according to model 8 is illustrated in Fig. 4. Starting with an initially film-free surface (1), the substrate is roughened and a boundary layer is formed by the accumulation of dissolved reaction products (2). For sufficiently large current densities, the electrolyte becomes supersaturated and nucleation of type II film occurs (3). Following its growth to a limiting thickness, secondary crystals are nucleated (4). After an induction period, during which hydrated species are accumulated, precipitation of type I film begins (5). Secondary crystals and type I film then continue to grow (6).

The complete description of processes according to model 8 requires some 28 parameters listed in table IIa. Many of these parameters can be determined independently, some have been found to be of minor importance and are identified in the table. Up to seven parameters are considered unknown and are derived by a fitting routine in seven-dimensional space. For the interpretation of the present experiments the seven parameters are: the crystallization rate of type II film; time of onset, crystallization rate

and degree of hydration (or porosity) of secondary crystals; porosity and dehydration rate of the hydrate film; porosity of the type I film. Values of physical property parameters used in the interpretations are given in table IIb. Mathematical details of the model are described in the appendix.

Limits of uncertainty for the unknown parameters thus derived have been determined by fitting a parabola through the partial derivative of the deviation between measured and predicted ellipsometer data with respect to one of the unknown film parameters (with the others held constant). The parabolic error estimate is given by the change in the parameter value necessary to increase the deviation between predicted and measured ellipsometer data by a value comparable to the estimated experimental error.

A Monte Carlo Routine⁷ has been used to search the multi-dimensional space for multiple roots. In this procedure, new initial values for the minimization process are chosen at random.

A linear regression analysis was also performed to determine which parameters in the model are independent variables (depending on the electrochemical system of interest). The matrix of correlation coefficients provides a convenient means of preventing over-specification of the system by eliminating from the minimization procedure parameters which give large cross-correlation coefficients. For the

results presented in this paper, the diagonal elements of the matrix were all greater than 0.98, while the off-diagonal elements (cross-correlation coefficients) were less than 0.02.

IV. EQUIPMENT

An automatic ellipsometer of the self-compensating type previously described^{8,9} has been used for obtaining the experimental data (Fig. 5). Faraday cells provide for the fast and precise rotation of polarizer and analyzer azimuths to achieve a minimum response of the photodetector. A 1 ms response (slew rate 1600°/s) with 0.001° resolution in azimuth is obtained with a dynamic range of 55° (110° with new power supplies). One-zone measurements with the quarter wave compensator in the +45° orientation have been corrected for imperfections of optical components and cell windows.¹⁰ A mercury short-arc with narrow-band interference filters has provided monochromatic light ($\lambda = 546.1$ nm).

Constant current or constant potential power supplies have been used for the electrochemical experiments. Controlled convection has been obtained by use of an electrolyte flow loop and a flow channel cell. Film-formation in the absence of convection was conducted in an electrolytic cell with stagnant electrolyte and horizontal anodes facing upward. In all cases cell windows were oriented normal to the light beam.

Electrodes were formed from high-purity (99.999%) metals in polycrystalline or single crystal form. They were embedded in epoxy resin and usually showed an exposed surface of 1.2 x 3 cm. After

rough polishing through 0000 silicon carbide paper 10 μm of damaged surface layer was anodically removed in acid. Final polish was achieved with 1 μm diamond paste. Cathodic hydrogen evolution in alkali served for de-greasing.

V. RESULTS

Results on the anodic oxidation of silver in alkaline solutions are illustrated in Figs. 6-8. In each case the model predictions are in reasonable agreement with measurements, particularly if one considers that no ad-hoc assumptions on mechanisms and film properties have been made and film growth covers a large range of thicknesses. A moderate disagreement for small film thicknesses under constant current, apparent in Fig. 6, could have been reduced by considering the adsorption of hydroxide or the depletion of the hydrate layer. Constant potential film growth results in a rather different response of the ellipsometer parameters, as illustrated in Fig. 7. The model is found to be sufficiently flexible to produce good agreement with experiment for this mode of operation also. With flowing electrolyte, film growth is often observed to stop after a certain thickness has been reached. This situation is illustrated in Fig. 8. The interpretation indicates that only type II film and secondary crystals are formed. When the limiting thickness is reached (700Å for the type II film after 31s) all reaction products are transported into solution under the influence of a 15-fold supersaturation at the interface.

A typical set of film growth parameters, that resulted from the interpretation of ellipsometer data is shown in Table III. A surprising conclusion of this interpretation is that initial (Type II) film

formation occurs with only about 1% current efficiency. The limits of uncertainty derived are reasonable, supporting the assumptions of the model. The large uncertainty for the onset of secondary crystal growth is due to their insufficient optical effect at the beginning of growth. The degree of hydration of the secondary crystals corresponds to the composition $\text{Ag}_2\text{O} \cdot \text{H}_2\text{O}$.

Anodic film formation with several metal-electrolyte combinations has been interpreted by use of the same model. Modifications of the model have been found necessary where patchwise film formation or growth of large secondary crystals occurred.

VI. CONCLUSIONS

The automated computer interpretation of time-dependent ellipsometer measurements of anodic film growth, under controlled mass-transport, based on film formation models, has been shown to yield considerably more information than is conventionally obtained. Different parameters of the model can be determined from the measurements, including kinetic and transport parameters not directly accessible by optical techniques in addition to optical and geometrical quantities. In the experiments, electrochemical current and potential, which determine the rate of product formation and its chemical nature, were measured in addition to the ellipsometer data. By considering the time-dependence of all the measured parameters, it appears that information inherent in the measurements can be used more fully.

A large number of models were investigated to determine the effect of alternate reaction mechanisms or film structures. The validity of models which result in equivalent residual errors between experimental

and predicted ellipsometer values cannot be distinguished. None of the models resulted in residual errors smaller than the estimated experimental error. This observation indicates that the interpretations are not meaningless parametric curve fits and that refinements in the model could be made.

It must be recognized that results may depend on the model chosen. Independent experimental evidence for some features of the model used is being obtained by the combination of ellipsometry with ion etching and Auger spectroscopy. New optical developments in progress to refine interpretations concern the properties of patchwise and particulate films.

VII. ACKNOWLEDGEMENT

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XIII. APPENDIX

1. Flux Densities Between Layers

Simplified equations have been used to describe the flux densities between layers because insufficient detail is known about the kinetics of electrode processes. The major assumption made in the expressions given in Table IV is that the concentrations of the reactants and products reach a constant, steady state value after transient increases. The flux densities are defined as current densities entering each layer.

For the type II Film, the formulation for the flux density i_{IIF} assumes a constant interfacial concentration and neglects changes in surface area. The flux density i_{sc} to the secondary crystals is shown by two limiting expressions: In the first case (Eq. (2a)), it is proportional to the surface area A_c of the crystals relative to the superficial electrode area A_b . This flux corresponds to crystallization via a constant concentration of surface adatoms with rate control by crystallization kinetics. The second expression (Eq. (2b)) describes crystal growth limited by transport of reactants to the crystal surface. The formulation for the flux density for the Type I Film (Eq. (3)) assumes zero order kinetics for the dehydration

of the Type I hydrate and would also be valid for constant concentration of the hydrate. In the flux density for the boundary layer (Eq. (4)), transient effects are modeled by the time-dependence of the boundary layer thickness $\delta(t)$ (see below). The flux density into the hydrate layer is found by a linear combination of the total electrode current density and the five previously defined flux densities. This measure prevents overspecification of the system. Formalization of the hydrate layer flux density would require describing the kinetics for the formation of polymers or anion complexes, and the corresponding unsteady-state mass-transport within an electric field.

The flux densities are expressed as current densities (mA/cm^2). Electrode areas have been normalized to a radius of influence of the secondary crystals defined by

$$R_i = \frac{10^8 \lambda}{2 N_0} \quad (6)$$

where N_0 is the number of crystals per sq cm. The radius R_i is the half distance between adjacent crystal centers.

2. Unsteady State Effects

a. Mass-Transport Boundary Layers (MTBL)

For constant-current experiments, the boundary layer thickness initially increases with time. Approximate solutions of the convective diffusion equation, which assume constant transport properties, have been used. For stagnant electrolytes, the Sand equation¹² gives

$$\delta = 1.129 \sqrt{Dt} \quad (7)$$

For forced convection in a flow channel, a series solution by Rosebrugh and Miller¹¹ for a finite boundary layer was used. A characteristic time constant α is defined as

$$\alpha = \pi D / 4 \delta_{bl}^2 \quad (8)$$

where δ_{bl} is the limiting, steady state boundary layer thickness given by Sherwood number correlations,

$$\delta_{bl} = d_h / Sh \quad (9)$$

where d_h is the hydraulic diameter. For $\alpha < 0.5$, the series solution is approximated by the Sand equation, and the growth of the boundary layer is described by Eq. (7).

It is assumed that the electrolyte must be supersaturated before film formation begins. The time to reach an ionic supersaturation C_{ss} is t_{ss} .

For $0 < t < t_{ss}$ the increase in interfacial ion concentration for stagnant electrolyte¹² and for forced convection¹¹ are given by Eqs. (10) and (11), respectively,

$$C_i = C_b + \frac{1.129 \sqrt{Dt}}{2FD} (1 - t_+) i \quad (10)$$

$$C_i = C_b + i \frac{\delta_{bl}}{zFD} \left[1 - \frac{8}{\pi^2} e^{-\alpha t} \right] \quad (11)$$

The time t_{ss} to reach the steady-state interfacial ion concentration C_{ss} for stagnant electrolyte and for forced convection is given by Eqs. (12) and (13), respectively,

$$t_{ss} = \left[\frac{zFD(C_{ss} - C_b)}{1.129i(1 - t_+) D^{1/2}} \right]^2 \quad (12)$$

$$t_{ss} = \frac{-1}{\alpha} \ln \left[\frac{\pi^2}{8} \left(1 - (C_{ss} - C_b) \frac{zFD}{i(1 - t_+) \delta_{bl}} \right) \right] \quad (13)$$

Before t_{ss} no film is formed, and after t_{ss} , the interfacial ion concentration is assumed constant.

The Sherwood Number correlations used for the limiting forced convection boundary layer thicknesses are:¹³

$$Sh = 1.40(ReSc d_h/X)^{1/3} \quad Re < 3000 \quad (14)$$

$$Sh = 1.40(3000 Sc d_h/X)^{1/3} \quad 3000 \leq Re < 5000 \quad (15)$$

$$Sh = 0.042 Re^{0.743} Sc^{1/3} \quad 5000 \leq Re \quad (16)$$

For the constant potential experiments, the time dependence of the boundary layer thickness was approximated by the Cottrell-Stefan solution¹⁴ to the diffusion equation

$$\delta = \sqrt{\pi D t} \quad (17)$$

This expression was used for both stagnant and forced convection transport conditions. For forced convection, the limiting thickness given by Eqs. (14) through (16) is used for large times. The interfacial ion concentration C_i as a function of time is computed from the concentration overpotential η_c :

$$\eta_c = \frac{0.0257}{z} \ln \frac{C_i}{C_s} \quad (18)$$

To obtain η_c , the experimental value of the total overpotential η is corrected for surface overpotential (charge transfer, reaction, crystallization) and resistance polarization. The surface overpotential is computed from a Tafel equation

$$i = i_0 \exp(\alpha z \eta_s / kT) \quad (19)$$

with the exchange current density i_0 evaluated by the computational procedure. The resistance polarization for surface films is computed under the assumption that Ohm's law applies. For both the Type I and Type II films, effective conductivities are calculated by assuming parallel resistances to transfer through pores and through the solid film. The total resistance is a series resistance across the Type II and Type I layers:

$$\eta_r = i \left[\sigma_{II} e^{T_{FII}} + \sigma_{Ie} T_{FI} (1 - f_{sc})^{-1} \right] \quad (20)$$

Blockage effects due to secondary crystal growth are included in the fractional surface coverage f_{sc} . Using experimental values of the electrode current density in Eq. (20), use of Eqs. (21), (20), and (19) gives

$$\eta_c = \eta - \eta_s - \eta_r \quad (21)$$

b. Type II Film

The Type II film is assumed to be the only surface layer forming during the time period $t_{ss} < t < t_{NUC}$. The time t_{ss} to reach supersaturation is calculated as outlined above from the steady state degree of supersaturation of the ionic species D_{ss} , for the experimental transport conditions. The time at which secondary crystal growth begins, t_{NUC} and D_{ss} , are determined by the interpretation procedure.

c. Type I Film

Growth of the Type I film begins at t_{NUC} . The growth rate is characterized by dehydration of the Type I hydrate. Because the flux density into the hydrate layer (Eq. (3)) depends on the flux density into the secondary crystals, the growth rate of the Type I film is inversely proportional to the growth rate of the secondary crystals. The Type I film can reach a limiting thickness for $i_{sc} = i$.

d. Type I Hydrate

Although the hydrate layer accounts for the homogeneous formation of polymers and anions, the growth rate of this layer is determined by the residual charge remaining after ionic transport and heterogeneous nucleation and crystallization have been accounted for. For the optical treatment of this layer, a characteristic time T_{diff} is evaluated by the computational procedure. T_{diff} is the time to reach the minimum porosity of the hydrate layer.

e. Secondary Crystals

Nucleation of the secondary crystals begins at time t_{NUC} . Three kinetic treatments of the crystal growth may be chosen for the computational procedure: (1) growth rate increases with surface area (crystallization control), (2) growth rate constant (transport control), (3) mixed kinetics where initially crystallization control applies until a characteristic time t_{KIN} (evaluated by the computation procedure) after which transport control applies.

f. Surface Roughness

Measurements of film-free surfaces can be interpreted by use of independently determined optical constants and the effect of a finite surface roughness. A square-ridge model⁶ has been used for roughness of the metal substrate. Three empirical parameters are required to describe the growth of the layer representing the roughness: (1) the initial peak to peak roughness, (2) an initial porosity or area fraction of the "valleys," and (3) the fraction of the current density which creates void volume (product of area fraction of valleys

and peak to peak roughness) during the dissolution process. Two treatments of the growth process may be chosen for the computational procedure; the thickness of the layer remains constant and the increase in voids results in an increase in porosity, or the porosity of the layer remains constant and the increase in void and volume is used to compute an increase in the thickness of the layer. The computer program allows changes in this layer to stop at the onset of secondary crystal growth t_{NUC} or the layer may continue to grow indefinitely.

3. Mass and Charge Balances

a. Volume Changes

The flux densities defined above describe the current densities into each type of layer. Changes in volumes for the layers are computed by the use of Faraday's law, bulk densities, molecular weights, valence, and the number density of secondary crystals. The general proportionality factor P_i is

$$P_i = \frac{M_i \times 10^8}{z \rho (0.965) N_0} \quad (22)$$

This factor gives volume changes in cubic angstroms per radius of influence of secondary crystal for current densities in mA cm^{-2} , density ρ in g cm^{-3} , and number density N_0 in crystals μm^{-2} .

The incremental changes in volumes are then as listed in Table V.

b. Dimensions of the Layers

The thicknesses of the Type II Film, Type I Film and Hydrate, and the size of the secondary crystals are computed from the volumes of the solids as defined above and the volume fractions of solution (porosities or hydration degree). For the Type I Film and Hydrate, a correction is included for inhomogeneous effects by assuming the porosity ϵ to increase parabolically in the direction normal to the surface from ϵ_b at the bottom of ϵ_i at the top.

$$\epsilon - \epsilon_i = (\epsilon_b - \epsilon_i)(1 - y/T)^2 \quad (27)$$

The time increments used to compute V_i are taken from the experimental values used as input to the program. The areas involved are:

$$A_B = 10^8 / N_0 \quad (32)$$

$$A_{BC} = (1 - f_{sc}) A_B \quad (33)$$

$$A_C = (4P + 2P^2) T_{sc} \quad (34)$$

For N_0 measured in secondary crystals cm^{-2} , A_B is measured in square angstroms. A_{BC} is the surface area not covered by the secondary crystals, and A_C is the surface area of crystals having height T_{sc} and width PT_{sc} . For $P = 1$, the crystals are cubes.

4. Optical Treatment of the Layers

a. Mass Transport Boundary Layer

Computationally, the continuously varying concentration in the (optically inhomogeneous) boundary layer can be represented by a series of (optically homogeneous) layers of uniform refractive index, with refraction and reflection of the light beam taking place at each interface between layers. An investigation of 3 refractive index profiles with parabolic or linear decrease away from the surface (Eqs. (35) and (36), respectively) as well as a homogeneous film with the same interfacial refractive index n_i has been conducted.

$$n = (n_i - n_b)(1 - y/\delta)^2 + n_b \quad (35)$$

$$n = (n_i - n_b)(1 - y/\delta) + n_b \quad (36)$$

This study showed that for thick boundary layers, the values of Δ and ψ can be determined from the change in the angle of incidence ϕ_i on the substrate. This effect depends on the refractive indices n_b in the bulk fluid and n_i at the interface and can be derived from the angle of incidence ϕ_0 outside the boundary layer by use of Snell's law.

$$\sin \phi_i = \frac{n_b}{n_i} \sin \phi_0 \quad (37)$$

For very thin boundary layers, the homogeneous film was found to approximate the effect of inhomogeneous films described by Eqs. (35) and (36) below a boundary layer thickness¹⁵ given by Eq. (38).

$$\delta = \frac{\lambda_0}{2(n_i^2 - n_b^2 \sin^2 \phi_0)^{1/2}} \quad (38)$$

The optical effect of the mass transport boundary layer was therefore determined by using two limiting approximations. For boundary layers thinner than the thickness given by Eq. (38), it was treated as a homogeneous film having the refractive index n_i . Thicker boundary layers were treated by modifying the angle of incidence according to Eq. (37). For short times, prior to the formation of the hydrate layer, the refractive index n_i corresponds to the concentration of ionic species at the interface. When the hydrate layer is present, the value of n_i depends on the theoretical treatment of the hydrate layer (see below).

b. Hydrate Layer

Either of three descriptions of the optical effect of the hydrate layer may be chosen for the computational procedure:

(1) The hydrate layer is viewed as a homogeneous film with refractive index n_H and the thickness given by Eq. (30). The refractive index is a linear average of the solid refractive index of

the hydrated species n_{ppt} (specified as input to the computer program) and the refractive index of the electrolyte n_{soln} , as given by Eq. (39).

$$n_H = (1 - \epsilon_H) n_{\text{ppt}} + \epsilon_H n_{\text{soln}} \quad (39)$$

For this treatment, the refractive index n_i of the MTBL is given by the concentration of ionic species at the MTBL-hydrate layer interface.

(2) The hydrate layer is viewed as an extension of the MTBL. The MTBL-hydrate interface represents a gradual change in refractive index between the two layers. The refractive index n_H (calculated as specified above) becomes n_i for the MTBL.

(3) The hydrate layer is viewed as an inhomogeneous film with a parabolic distribution of porosity (Eq. (27)). The multiple-film method is used¹⁶ with five equivalent homogeneous films. The refractive index of each homogeneous film is determined by the use of Eqs. (27) and (39). The refractive index n_i of the MTBL is the same as described in case (1).

c. Type I Film and Type II Film

The type I film is treated as a homogeneous film of thickness T_{IF} as given by Eq. (29). The refractive index of the film is computed by a linear average (Eq. (39)) of the solid film refractive index n_{IFS} and the electrolyte refractive index n_{soln} . The constant porosity of the film ϵ_{IF} used in the linear average is determined by the computations.

The type II film is also treated as a homogeneous film. The thickness T_{IIF} is given by Eq. (28) and the refractive index again is the linear average of the solid film refractive index n_{IIFS} and the electrolyte refractive index n_{soln} . For the computational procedure, the porosity of this layer can be set at the constant value of 0.21 (corresponding to close-packed spheres), or allowed to decrease to 0.21 linearly with time until the time t_{nuc} . The decrease with time is an approximate treatment of patchwise film formation on the scale of the lateral coherence of the light beam.

d. Secondary Crystals

The optical treatment of the secondary crystals is determined by the number density of crystals, or equivalently, their size. Two regimes of crystal sizes T_{sc} have been distinguished:¹⁷

$$T_{\text{sc}} \ll \lambda_i = \lambda/n_i \text{ and} \quad (40)$$

$$T_{\text{sc}} > \lambda_i, \quad (41)$$

where λ_i is the wavelength of light in the material i . For very small crystals or large number densities ($N_0 = 0(10^{10} \text{ cm}^{-2})$), the crystals are not individually distinguishable, and are treated as a homogeneous film. Crystals having sizes larger than the wavelength of light act as scattering centers and do not significantly affect the state of polarization in the specular direction; only the primary layers are visible to the ellipsometer.

e. Small Crystals

In this regime of secondary crystal sizes, homogeneous films are used to present the optical effect of the layer of crystals. The thickness of the layer T_{sc} is given by Eq. (31). Because the electrode surface between the crystals is covered by the Type I film and the hydrate layer, the layer of secondary crystals is divided into two sublayers having thicknesses T_{IF} (Eq. (29)), and $T_{sc} - T_{IF}$. The refractive indices of the films are linear functions of the optical surface coverage of the crystals as given by Eq. (42).

$$n_{sce} = C_c n_c + (1 - C_c) n_{uc} \quad (42)$$

For the bottom layer n_{uc} is the Type I film, while for the top sublayer, n_{uc} is the hydrate material. (If $T_{IH} < T_{sc} - T_{IF}$ a third sublayer is included).

To calculate the optical effect of the six-layer structure shown in Fig. 2, the multiple-film method was used for the 4 or 5 (depending on the treatment at the hydrate layer) homogeneous layers covered by the inhomogeneous mass-transport boundary layer.

f. Depletion of the Hydrate Layer

The formation of secondary crystals diminishes the amount of dissolved material which accumulates in the hydrate layer prior to the nucleation of the crystals. To account for the optical effect of the depletion of the hydrate layer, the porosity of the hydrate layer may

be increased from the minimum value at T_{DIFF} up to 0.999 at a characteristic time T_{PAC} . The increase is a linear function of time, and T_{PACK} is evaluated by the computational procedure.

5. Computational Procedure

Interpretation of the experimental data is accomplished by finding values of characteristic parameters in the model which will best reproduce the experimental values of Δ and ψ . The computer program calculates an error term (for fixed values of the characteristic parameters) defined as the average distance per point between experiment and theory, as given by Eq. (43)

$$\epsilon_{\ell} = \frac{1}{(n - i)} \sqrt{\sum_{j=1}^n (\Delta_e - \Delta_t)_j^2 + (\psi_e - \psi_t)_j^2} \quad (43)$$

The characteristic parameters are evaluated by minimizing the error term. Simplex¹⁸ and Davidon variable matrix¹⁹ algorithms are used to evaluate all (or specifically chosen) parameters. Parabolic error estimates in which a parabola is fitted through the partial derivative of each parameter near the minimum are used to provide limits of uncertainty for the parameters. A measure of uncertainty is given by the change in parameter value necessary to change ϵ_{ℓ} (the distance between experimental and calculated points) by a specified value. In addition, a Monte Carlo routine²⁰ may be used to search the multi-dimensional space for multiple roots. In the routine, new initial values for the iteration process for the parameters being evaluated are chosen at random, and a new minimization is conducted.

The characteristic parameters in the model which may be evaluated by the computational procedure are given in Table II. In practice, only a few of these parameters are simultaneously evaluated, with the remaining parameters becoming input variables.

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Table I. Models for Anode Film formation. Deviation between experiment and theory for Ag(100), 6 M KOH stagnant, 1MA/Cm², 52s.

<u>Model No.</u>	<u>Ave Deviation (deg.)</u>
1	56.2
2	56.2
3	62.0
4	9.1
6	6.0
7	7.7
8	4.9

Table 11a. Parameters for film formation model.

*Of minor importance for present experiments.

+Derived from data interpretation.

+Crystallization Rate of the Type II Film

Porosity of the Type II Film

+Dehydration Rate of Hydrate Layer

+Porosity of Hydrate Layer

+Porosity of Type I Film (Initial)

Number Density of Secondary Crystals

+Crystallization Rate of Secondary Crystals

+Hydration of Secondary Crystals

*Rate of Void Formation in Roughness Layer

*Porosity of Roughness Layer

*Initial Thickness of Roughness Layer

*Initial Thickness of Type II Film

*Width to Height Ratio of Secondary Crystals

Degree of Supersaturation of Metal Cations

*Charge-Transfer Exchange Current Density

+Time, Onset of Secondary Crystal Growth

*Time, Minimum Porosity of Hydrate Layer

*Final Porosity of Type I Film

*Time for Compaction of Type II Film

*Limiting Coverage of Secondary Crystals

Refractive Index of Substrate

Refractive Index of Electrolyte

Refractive Index of Film Material

Solubility of Reaction Product

Diffusion Coefficient of Reaction Product

Bulk Densities for Substrate, Electrolyte and Film

Table IIb. Values of physical property parameters used for the interpretation of experiments presented.

<u>Properties</u>	<u>Materials</u>	<u>Values</u>
Optical Constants	Ag	0.18-3.61i
	Ag ₂ O	2.17-0.28i
	AgOH	1.87
	1 M KOH	1.343
	6 M KOH	1.387
Bulk Densities	Ag	10.49
	Ag ₂ O	7.14
	AgOH	5.7
	6 M KOH	1.238
Diffusion Coefficients	Ag(OH) ₂ ⁻	$1.14 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$
Solubilities of Ag(OH) ₂ ⁻ in	1 M KOH	$1.5 \times 10^{-4} \text{ M}$
	6 M KOH	$4.7 \times 10^{-4} \text{ M}$

Table III. Parameters Derived from Ellipsometer Interpretation. Anodic Oxidation of Silver 6 M KOH stagnant, 1 mA/cm², Ag(100)

<u>Parameter</u>	<u>Value</u>	<u>Measure of Uncertainty*</u>	
		<u>Positive</u>	<u>Negative</u>
Crystallization Rate of Type II Film	0.012 mA/cm ²	0.013	0.003
Crystallization Rate of Secondary Crystals	0.158 mA/Cm ²	0.008	0.019
Porosity of Type I Film	0.260	0.046	0.073
Porosity of Hydrate Layer	0.999	0.001	0.013
Dehydration of Hydrate Layer	1.00 mA/cm ²	0.001	0.043
Onset of Secondary Crystal Growth	6.13 s	4.23	3.25
Hydration of Secondary Crystals	0.40	0.053	0.012
Time to reach steady state hydrate concentration	13.05 s	-	-
*Change in Parameter Value resulting in 0.5 deg. deviation.			

Table IV. Formulation of flux densities between layers.

Layer	Flux Density	
Type II Film	$i_{IIF} = C_{IIF}$	(1)
Secondary Crystals	$i_{sc} = C_{sc}(A_c/A_b)$	(2a)
	or $i_{sc} = C'_{sc}$	(2b)
Type I film	$i_{IF} = f_R i_{IH}$	(3)
Boundary Layer	$i_D = \frac{zFD(C_{ss} - C)}{(1 - t_+) \delta(t)}$	(4)
Type I Hydrate	$i_{IH} = i - i_D - i_{sc}$ (or i_{IIF})	(5)

Table V. Incremental volume changes during film growth.

Layer	Volume growth rate ($\text{\AA}^3$ Per Secondary Crystal Site)		
Type II Film	$dV_{\text{IFF}} = P_{\text{IFF}} i_{\text{IFF}} dt,$ $= 0$	$t \leq t_{\text{nuc}}$ $t > t_{\text{nuc}}$	(23)
Type I Film	$dF_{\text{IV}} = 0,$ $= P_{\text{IF}} f_{\text{R}} (I - i_{\text{d}} - i_{\text{sc}}) dt,$	$t \leq t_{\text{nuc}}$ $t > t_{\text{nuc}}$	(24)
Type I Hydrate	$dV_{\text{IH}} = P_{\text{IH}} (i - i_{\text{d}} - i_{\text{IFF}}) dt,$ $= (1 - f_{\text{R}}) P_{\text{IH}} (I - i_{\text{d}} - i_{\text{sc}}) dt,$	$t \leq t_{\text{nuc}}$ $t > t_{\text{nuc}}$	(25)
Secondary Crystals	$dV_{\text{sc}} = 0$ $dV_{\text{sc}} = P_{\text{sc}} i_{\text{sc}} dt,$	$t \leq t_{\text{nuc}}$ $t > t_{\text{nuc}}$	(26)

Table VI. Thickness changes during film growth.

Layer	Thickness	
Type II Film	$T_{IIF} = V_{IIF}(1 - \epsilon_{IIF})^{-1}A^{-1}B$	(28)
Type I Film	$I_{IF} = V_{IF}[1 - (2/3 \epsilon_{IF} + 1/3 \epsilon_{IH})]^{-1}A^{-1}BC$	(29)
Type I Hydrate	$T_{IH} = 1.5 V_{IH}(1 - \epsilon_{IH})^{-1}(ABC + A_C)^{-1}$	(30)
Secondary Crystals	$T_{SC} = [V_{SC}P^{-2}(1 - \epsilon_{SC})^{-1}]^{1/3}$	(31)

Table VII. Nomenclature

<u>Symbol</u>	<u>Description</u>	<u>Equations</u>
A_B	Electrode area covered by secondary crystals.	32, 33
A_b	Superficial surface area of electrode.	2a
A_{BC}	Surface area not covered by secondary crystals.	33, 29, 30
A_C	Surface area of secondary crystals.	2a, 30, 34
$\text{\AA}$	Angstrom units.	6
C	Concentration of ionic species.	4
C_b	Concentration in bulk solution.	10 - 13
C_c	Surface coverage of secondary crystals.	42
C_i	Interfacial concentration.	10, 11, 18
C_s	Solubility of ionic species	18
C_{sc} , C'_{sc}	Crystallization rate of secondary crystals.	2a
C_{ss}	Steady-state interfacial concentration.	4, 12, 13
C_{IIF}	Crystallization rate of type II film.	1
D	Diffusion Coefficient.	4, 7, 8, 10, 11, 12, 13, 17
D_{ss}	Degree of supersaturation.	
d_h	Hydraulic diameter of flow channel cell	9, 14, 15
dt	Increment in time	23 - 26
dV_{sc}	Increase in volume of secondary crystals.	26

dV_{IF}	Increase in volume of Type I film.	24
DV_{IH}	Increase in volume of Type I hydrate.	25
dV_{IIF}	Increase in volume of Type II film.	23
e	Basis of natural logarithms.	11
F	Faraday's constant, 9.65×10^4 coul./g-eq.	4, 10 - 13
f_R	Fraction of hydrate layer flux forming Type I film.	3, 24, 25
f_{sc}	Fraction of surface covered by secondary crystals.	20, 33
i	Total anodic current density.	5, 10 - 13
i_{Di} , i_d	Flux density of ions entering mass-transport boundary layer.	4, 5, 24, 25
i_o	Exchange current density.	19
i_{sc}	Mass-flux density to secondary crystals.	2a, 2b, 5, 24 - 26
i_{IF}	Flux density to Type I film.	3
i_{IH}	Flux density to Type I hydrate layer.	3, 5
i_{IIF}	Mass flux density to Type II film.	1, 5, 23, 25
k	Boltzmann's constant.	19
M_i	Molecular weight of species i .	22
N_o	Number density of secondary crystals.	6, 22, 32
n	Refractive index of electrolyte.	35, 36, 43
n_b	Refractive index in bulk fluid.	35 - 38
n_c	Refractive index of secondary crystal layer.	42
n_H	Refractive index of hydrate layer.	39

n_i	Refractive index of fluid at interface, or n.i. of medium i.	35 - 38, 40
n_{ppt}	Refractive index of colloidal material, e.g., AgOH	39
n_{sce}	Refractive index of secondary crystal material.	42
n_{soln}	Refractive index of electrolyte.	39
n_{uc}	Refractive index of region between secondary crystals.	42
n_{IFS}	Refractive index of solid (compact) Type I film.	
n_{IIFS}	Refractive index of solid Type II film.	
P	Height-to-width ratio for secondary crystals.	31, 34
P_i	Proportionality factor for film volume, with subscripts for.	22
P_{sc}	-secondary crystals.	26
P_{IF}	-Type I film.	24
P_{IIF}	-Type II film.	23
P_{IH}	-Type I hydrate.	25
PT_{sc}	Width of secondary crystals.	
R_i	Radius of influence for secondary crystal growth.	6
Re	Reynolds number, DV/ν .	14, 15, 16
Sh	Sherwood number.	9, 14 - 16
Sc	Schmidt number, ν/D .	14 - 16
T	Temperature, deg. Kelvin.	19, 27
T_{DIFF}	Time to reach minimum porosity of hydrate layer.	

T_{FI}	Thickness of Type I film.	20
T_{FII}	Thickness of Type II film.	20
T_{PACK}	Time constant for depletion of hydrate layer.	
T_{sc}	Height of secondary crystals; thickness of equivalent layer.	31, 34, 40, 41
T_{IF}	Thickness of Type I film.	29
T_{IH}	Thickness of Type I hydrate film.	30
T_{IIF}	Thickness of Type II film.	28
t	Time	6, 10, 11, 17
t_{KIN}	Time for change in crystal growth rate expression.	
t_{NUC}	Time for start of sec. crystal and Type I film growth.	
t_{ss}	Time to reach steady-state interfacial concentration.	12, 13
t_+	Transference number.	4, 10, 12, 13
V_{IH}	Volume of Type I hydrate.	30
V_{IIF}	Volume of Type II film.	28
V_{sc}	Volume of secondary crystals.	31
y	Distance normal to surface.	27, 35, 36
z	Valence of species.	4, 10 - 13, 18, 19, 22
α	Tafel slope constant.	19
α	Time constant for forced-convection mass-transport.	8, 11
Δ	Relative phase difference between s and p components of electric field.	
Δ_e , Δ_t	Experimental and theoretical value of Δ .	43

δ	Boundary layer thickness.	4, 7, 17, 35, 36, 38
δ_{bl}	Steady-state boundary layer thickness for forced-convection mass transport.	8, 9, 11
ϵ	Film porosity.	27
ϵ_b	Porosity at bottom of film.	27
ϵ_c	Porosity at colloial	
ϵ_H	Porosity of hydrate.	39
ϵ_i	Porosity at top of film.	27
ϵ_{IF}	Porosity of Type I film.	29
ϵ_{IIF}	Porosity of Type II film.	28
ϵ_{IH}	Porosity of Type I hydrate.	29, 30
ϵ_{sc}	Porosity of secondary crystals.	31
ϵ_l	Average difference between theoretical and experimental ellipsometry data.	43
η	Total overpotential.	21
η_c	Concentration overpotential.	18, 21
η_r	resistence polarization.	20, 21
η_s	Surface overpotential.	19, 21
λ_i	Wavelength of light in material i.	38
λ_0	Wavelength of light in vacuum.	38
ϕ_i	Angle of incidence on the substrate.	37
ϕ_0	Angle of incidence outside boundary layer.	37, 38
ψ	Relative amplitude change between s and p components of electric field.	
ψ_e	Experimental value of ψ .	43

ψ_t	Theoretical value of ψ .	43
ρ	Density (bulk value)	22
σ_{Ie}	Conductivity of Type I film.	20
σ_{IIe}	Conductivity of Type II film.	20

FIGURE CAPTIONS

Fig. 1. Models of anodic films investigated for the interpretation of ellipsometer measurements.

Fig. 2. Anodic film model Number 8 used for the automated interpretation of ellipsometer measurements.

Fig. 3. Electron micrographs showing higher number density of secondary crystals with higher current density. Anodic oxidation of silver, 6 M KOH Stagnant, Ag(100).

Fig. 4. Time sequence of events in anodic film formation according to Model 8.

Fig. 5. Arrangement of components for the automatic self-compensating ellipsometer.

Fig. 6. Interpretation of ellipsometer measurements, constant current. Comparison of experiment (+) and model prediction (x). Anodic oxidation of silver, 0.1 M KOH stagnant, 0.2 mA/cm² Ag(100). Primary layer thickness indicated along the curve, small secondary crystals.

Fig. 7. Interpretation of ellipsometer measurements. Constant potential, high initial current density. Comparison of experiment (+) and model prediction (x). Anodic oxidation of silver, 1 M KOH, +0.55V vs Hg/HgO, Ag(100). Primary layer thickness indicated along the curve.

Fig. 8. Interpretation of ellipsometer observations, forced convection. Comparison of experiment (+) and model prediction (x). Anodic oxidation of silver, 6 M KOH, $Re = 1000$, 1 mA/cm^2 , Ag(100). Primary layer thickness indicated along the curve.

XBL 785-871

FIGURE 1

Ion and polymer
boundary layer

Hydrate film
Secondary crystals
Type I film

Type II film
Surface roughness

Substrate

XBL 785-872

FIGURE 2

0.2 mA/cm², 120 s
 7.4×10^7 crystals/cm²

1.0 mA/cm², 25 s
 4.7×10^8 crystals/cm²

Figure 3

XBB 785-6826

FIGURE 4

1. Bare Metal

2. Rough Metal,
Mass Transport
Boundary Layer

3. Growth of
Type II Film

4. Nucleation of
Secondary Crystals

5. Type I Hydrate
and Film Begin

6. Growth of Secondary
Crystals, Type I Film

Light Source
Condenser
Interference Filter
Collimator
Polarizer
Iris Diaphragm

Polarizer
Faraday Cell
Quarter Wave
Compensation
Iris Diaphragm

Cell with reflecting
Surface

Iris Diaphragm
Analyzer
Faraday Cell
Iris Diaphragm
Analyzer

Telescope

Photomultiplier

XBL 787-9518

FIGURE 5

XBL 786-9084

FIGURE 6

XBL 786-9083

FIGURE 7

XBL 786-9086

FIGURE 8

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