

SIMULATION OF MBI REFLECTION OF Al THIN-FILMS OXIDIZED NONISOTHERMALLY AT $T \geq T_{2D}$

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Received 12 July 1991

UDC 538.975

Original scientific paper

Oxidation of thin Al films in a linearly increasing temperature field, passing the temperature of 2-D melting [$T_{2D}(\text{Al}) = 639 \text{ K}$], produces inhomogeneous oxide films with the gradient of composition mixture of Al_2O_3 , unstoichiometric Al-oxides, and of unoxidized Al. Composition gradient of the mixture generates the gradient of the refraction index $\hat{n} = n(1 + ik)$, which changes with oxidation time. This gradient causes a strong exponential damping of interference reflection. The model for simulation of damped interference effects was developed from the model for homogeneous dielectric films by inserting the logarithmic oxidation kinetics $z(t) = A \cdot \ln(t - \tau)$, and by inserting the expression $k = k_0(e^{\gamma z(t)} - 1)$ for the gradient of imaginary part of refraction index. [$\gamma = \text{const.}$, $z = \text{film thickness}$, $t = \text{time}$; $n_{\text{Al}} \sim n_{\text{Al}_2\text{O}_3}$, $k_{\text{Al}} = 10^4 k_{\text{Al}_2\text{O}_3}$]. Excellent fitting of «in situ» He-Ne laser beam interference reflection measurements was obtained in all the cases considered.

1. Introduction

The previous study of nonisothermal Al oxidation (in the linearly increasing temperature field) has shown a strong influence of 2D-melting on the oxidation process¹⁾. The oxidation starts abruptly when T_{2D} is reached, because the oxide monolayer on the surface starts to crack enabling the oxygen to freely penetrate into the Al interior. Thus, the point T_{2D} is clearly distinguished in MBI (multiple-beam interference) curves.

The experimental data for T_{2D} of Al cover a broad interval between 500 K and 800 K, indicating a great dispersion of the measured values^{2,3}. The average value of the mentioned interval of T_{2D} values is 650 K. Theoretical expression derived by Zitto gives $T_{2D} = 0.59 T_{3D}$. Since $T_{3D}(\text{Al}) = 933 \text{ K}$, one finds from the Zitto's relation: $T_{2D}(\text{Al}) = 639 \text{ K} \approx 640 \text{ K}$ ^{2,3}. Our measurements of reflectance described in Ref. 1, indicated $T_{2D}(\text{Al}) \approx 640 \text{ K}$, which seems to be the most acceptable value for $T_{2D}(\text{Al})$. The experimental procedure is given in the above mentioned reference. The oxidation temperature has been increasing with the heating rate $\beta = \frac{\Delta T}{\Delta t} \approx \frac{6 \text{ K}}{\text{min}}$ starting from T_i (initial), chosen to be:

- (i) $T_i > T_{2D}$, (ii) $T_i < T_{2D}$ and (iii) $T_i \ll T_{2D}$.

The experiments have shown that the above three cases fall into two categories of the MBI curve's behaviour, whose mean reflection value can be described as follows:¹

- a) $T_i > T_{2D}$. The mean reflection value (reflectance), R , decreases with oxidation time, t , according to: $R = R_0 e^{-\alpha t}$, (t in minutes) where R_0 is reflection at $t = 0$ and α is parameter.
- b) $T_i < T_{2D}$ and $T_i \ll T_{2D}$. The reflectance, R , is constant: $R = R_0$, until temperature increasing with a given rate β reaches T_{2D} . From that moment on, R decreases according to: $R = R_0 e^{-\alpha(t-t_0)}$, where t_0 is the time lag from the beginning of oxidation to the moment when T_{2D} is reached: $t_0 = \frac{T_{2D} - T_i}{\beta}$.

The general characteristic is that the reflectance decreases with time following a simple exponential curve. This differs significantly from the usual case in which reflectance approaches to the bulk reflection value of the metal oxide. The exponential curve is altered by the superimposed interference effects. The origin of such behaviour lies in the nonuniform oxidation process, which generates a compositional gradient of the mixture of Al_2O_3 and of (still unoxidized) Al. This compositional gradient then generates the gradient of the refraction index. In the continuation of this work we have numerically simulated the exponentially damped interference effects taking into account the gradient nature of the optical parameters of the oxidized aluminium. The model developed describes the interference effects in compositionally and structurally inhomogeneous metal-oxide films, and involves the three step procedure:

- A. First, the model for MBI reflection, giving $R = R(z)$, ($z =$ film thickness), for homogenous films was chosen⁴.
- B. Second, the oxidation kinetics which gives $z = z(t)$ was substituted into the equations of the Browell-Anderson model, thus transforming the space-dependence of R into time-dependence of R , i. e. $R = R[z(t), \hat{n}]$, where \hat{n} is the complex form of the refraction index: $\hat{n} = n(1 + ik)$.
- C. Third, the effects of compositional gradient were introduced by taking into account that optical parameter \hat{n} changes with time, i.e. $\hat{n} = \hat{n}(t)$, resulting thus in time-dependent real and imaginary part of the refraction index. Inserting the exponential time dependence of the imaginary part of the refraction index k of the oxidized film into the model equations of the step B, one actually gets:

$$R = R[z(t), n(t)].$$

A. Interference model for homogenous films

From the optical point of view, homogenous Al_2O_3 structure was supposed to be a slightly absorbing film on absorbing substrate (quartz), so that monochromatic specular reflectance for perpendicularly polarized radiant energy illuminating the film is given according to Ruiz-Urbieta⁵⁾ and Browell-Anderson⁴⁾ by:

$$R = \frac{\rho_{12}^2 + \rho_{23}^2 e^{4v_2\eta} + 2\rho_{12}\rho_{23} e^{-2v_2\eta} \cos(\varphi_{23} + 2u_2\eta)}{1 + \rho_{12}^2 \rho_{23}^2 e^{-4v_2\eta} + 2\rho_{12}\rho_{23} e^{-2v_2\eta} \cos(\varphi_{23} + 2u_0\eta)} \quad (1)$$

where the indices 1, 2, 3, 12 and 23 are related to air above the film, the substrate, the air/oxide interface and the oxide/substrate interface, respectively. Quantities ρ_{12} and ρ_{23} in (1) are reflection coefficients of interfaces, and φ_{12} and φ_{23} are the corresponding phase changes at the interfaces. The films thickness, z , is substituted by a nondimensional thickness η , defined as:

$$\eta = \frac{2\pi z}{\lambda_0} \quad (2)$$

where λ_0 is the light wavelength in vacuum. Quantities ρ_{12} , ρ_{23} , φ_{12} and φ_{23} can be defined in terms of the incidence angle Θ , the index of refraction of the air n_1 , of the film $\hat{n}_2 = n_2(1 + ik_2)$ and of the substrate $\hat{n}_3 = n_3(1 + ik_3)$, respectively:

$$\rho_{12}^2 = \frac{(n_1 \cos \Theta_1 - u_2)^2 + v_2^2}{(n_1 \cos \Theta_1 + u_2)^2 + v_2^2} \quad (3)$$

$$\rho_{23}^2 = \frac{(u_2 - u_3)^2 + (v_2 - v_3)^2}{(u_2 + u_3)^2 + (v_2 + v_3)^2}$$

$$\varphi_{12} = \text{tg}^{-1} \left[\frac{2v_2 n_1 \cos \Theta_1}{u_2^2 + v_2^2 - n_1 \cos \Theta_1} \right] \quad (4)$$

$$\varphi_{23} = \text{tg}^{-1} \left[\frac{2(u_3 v_2 - u_2 v_3)}{u_2^2 - u_3^2 + v_2^2 - v_3^2} \right] \quad (5)$$

The constants are defined as follows:

$$2u_2^2 = c + (c^2 + d)^{1/2}, \quad 2v_2^2 = -c + (c^2 + d)^{1/2}, \quad (6)$$

$$c = n(1 - k_2^2) - n_1^2 \sin^2 \Theta_1, \quad d = 4n_1^4 k_2^2,$$

$$2u_3^2 = a + (a^2 + b)^{1/2}, \quad 2v_3^2 = -a + (a^2 + b)^{1/2}, \quad (7)$$

with

$$a = n_3^2(1 - k_3^2) - n_1^2 \sin^2 \Theta_1 \quad \text{and} \quad b = 4n_3^4 k_3^2.$$

The assumption of Brewell and Anderson was that the imaginary part of the complex refractive index, $n_2 k_2$, is less than 0.06. In this case, one finds:

$$3n_2 k_2 \ll 1, \quad 3k_2^2 \ll 1, \quad k_2^4 \approx 1. \quad (8)$$

With these approximations, it follows from (6):

$$v_2^2 = \frac{n_2^4 k_2^2}{n_2^2 - n_1^2 \sin^2 \theta_1}, \quad (9a)$$

$$u_2^2 = n_2^2 - n_1^2 \sin^2 \theta_1. \quad (9b)$$

Condition (8) in the Brewell-Anderson model assures that the error introduced by transition from Eq. (6) to Eq. (9a) and Eq. (9b) is less than 1%⁵⁾.

B. Oxidation kinetics

The model of space-dependent reflection, $R = R(z)$, for homogenous films, was transformed into the time-dependent one, which can be directly compared to the *in situ* measured reflection. For this purpose, the oxidation kinetics $z = z(t)$, was inserted into Eq. (2) of the reflection model, by using the logarithmic oxidation kinetics⁶⁾:

$$z(t) = A \ln(t - \tau) + C; \quad (10)$$

where A , τ and C , are the adjustable constants. This expression is valid for the case $T_t > T_{2D}$. For the cases $T_t < T_{2D}$ and $T_t \ll T_{2D}$ one has to distinguish the time t , running from the beginning of experiment, from the time t' (called the oxidation time) running from the moment when T_{2D} is reached in the lineary increasing temperature field.

One has:

$$t' = t - t_0,$$

where

$$t_0 = \frac{T_{2D} - T_t}{\beta}. \quad (11)$$

The equation (10) becomes:

$$z(t) = A \ln \left(\left| t - \frac{T_{2D} - T_t}{\beta} \right| - \tau \right) + C. \quad (12)$$

Since the oxidation starts in the moment when T_{2D} is reached (which happens in different times in every experiment, depending on the choice of T_t and β), constants A , τ and C should be determined for every particular case. The condi-

tion to be satisfied is: for $t = 0$, $z = z_0 \approx 1 \text{ nm}$ ($\approx 3-4$ atomic layers), corresponding to the thickness of the protective layer of Al_2O_3 , which appears spontaneously on the surface. As mentioned previously, this protective layer breaks at T_{2D} , enabling easy penetration of the oxygen.

C. Inhomogenous films

Linearly increasing temperature field and the viscous flow on the metal surface associated with T_{2D} represent a strongly variable oxidation conditions.

It is well known that variable growth conditions lead to the oxides with different surface stoichiometry. Depending on growth conditions the oxide films exhibit a surface stoichiometry similar to that of alumina or display an important deficiency of oxygen⁷⁾. Linearly increasing temperature field means permanently changing conditions. As the consequence, the film composition changes from the fully oxidized metal (Al_2O_3) on the surface, to the composition containing less and less oxygen with increasing depth, thus establishing the compositional gradient of the mixture $C \left[\frac{\text{Al}_2\text{O}_3}{\text{Al}} \right]$ ¹⁾. The equivalent expression in the time-picture would be that $C \left[\frac{\text{Al}_2\text{O}_3}{\text{Al}} \right]$ changes with $z(t)$:

$$C \left[\frac{\text{Al}_2\text{O}_3}{\text{Al}} \right] = C [z(t)]. \quad (13)$$

At this point we come to the question, how the optical properties are affected by this process. The direct influence on the optical properties can be expected through: $\hat{n} = \hat{n}[c(z(t))]$, where \hat{n} is the complex form of the refraction index: $\hat{n} = n(1 + ik)$.

To find the n_0 value of the composition gradient of mixture of $[\text{Al}_2\text{O}_3/\text{Al}]$, is not quite simple. Namely, for the homogeneously grown Al_2O_3 film (at room temperature), the $n_0 = 1.55$, while for the homogeneously grown film above 550 K the $n_0 = 1.63$. For the nonoxidized Al, the $n_0 = 1.50$. Since we have the gradient of the composition mixture, the n_0 lies between 1.50 and 1.63. Therefore, we take for n_0 the value: $n_0 = 1.55$, which is the room temperature value for Al_2O_3 , and in the same time the mean value of the composition mixture.

From the comparison of $\hat{n}_{\text{Al}_2\text{O}_3}$ and \hat{n}_{Al} ¹⁾:

$$\begin{aligned} n_{\text{Al}_2\text{O}_3} &= 1.55 & \text{and} & & k_{\text{Al}_2\text{O}_3} &= 0.00036,^{8,9)} \\ n_{\text{Al}} &= 1.50 & \text{and} & & k_{\text{Al}} &= 7^{8,9)}, \end{aligned} \quad (14)$$

it follows that increasing the Al content and decreasing the Al_2O_3 content in the oxidized film with time, will cause the significant change in the imaginary part k , of the refraction index. Thus, the question, how the optical properties of $\left[\frac{\text{Al}_2\text{O}_3}{\text{Al}} \right]$

mixture change with $z(t)$, is transformed into the question, how the imaginary part k , of the refraction index changes with $z(t)$. The change of k with $z(t)$ expressing the influence of the compositional gradient on the gradient of refraction index, can be expressed as: (see Appendix)

$$k[z(t)] \approx k_0 (e^{\nu \cdot z(t)} - 1), \quad (15)$$

with $z(t)$ given by Eq. (12).

This expression was inserted into Eq. (9) for k_2 ($k = k_2$ of the oxide film), the equation of the reflection model. By this final step, the model was modified to describe the time-dependence of the interference reflection for the compositionally inhomogeneous film.

This model was used to simulate the interference reflection in the three cases which were investigated experimentally: (The experimental procedure is described in Ref. 1)

$$(i) T_1 \ll T_{2D}, \quad (ii) T_1 < T_{2D} \quad \text{and} \quad (iii) T_1 > T_{2D}.$$

The results of simulation are shown in Figs. 1., 2. and 3. These figures show, both, the family of k_2 curves ($k_2^1, k_2^2, k_2^3, \dots$), and the corresponding $R(k_i)$ curves.

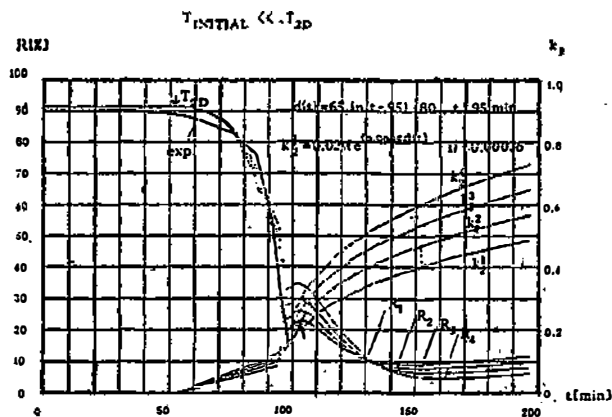


Fig. 1. Simulation of MBI reflection for nonisothermal oxidation of Al; $T_1 \ll T_{2D}$. With the linear heating rate $\beta = 6$ K/min, T_{2D} was reached for $t_0 \approx 50$ min. The scale on the right side of the graph, relates to the k_2 values, calculated from the expression given in the frame.

R_{exp} is the experimental curve.

$$[\lambda = 632.8 \text{ nm}; n_1 = 1.500; k_1 = -7.00; n_2 = 1.570; k_{Al_2O_3} = 0.00036].$$

Almost perfect simulation was obtained for the cases shown in Fig. 2 and Fig. 3, while the less perfect was obtained in the case of Fig. 1. The ranges of parameter variation are given in every figure.

One can conclude that the starting assumption about the logarithmic oxidation kinetics is fairly good for the observed time interval. In the case of Fig. 1. ($T_i \ll T_{2D}$), it is evident that the simulation fails after passing the first interference minimum. Theoretical curves in the Fig. 1. (for $t > 100$ min) are not damped strongly enough as the experimental one. The reason can be twofold: first, the oxidation kinetics probably changes into the linear one (at $t > 100$ min), and the second (and possibly more important) are the microstructural defects. In addition, the scattering effects on the surface (which may become important) are not included in the theoretical model.

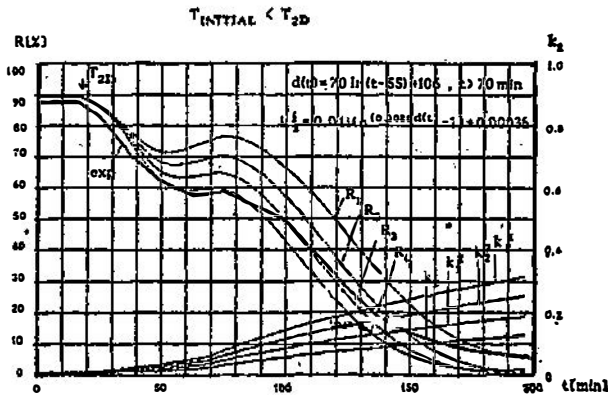


Fig. 2. Simulation of MBI reflection for nonisothermal oxidation of Al; $T_i < T_{2D}$. Temperature of 2-D melting, T_{2D} , was reached after $t_0 \approx 17$ min.

$[\lambda = 632.8 \text{ nm}; n_1 = 1.500; k_1 = -7.000; n_2 = 1.570; k_{Al_2O_3} = 0.0036].$

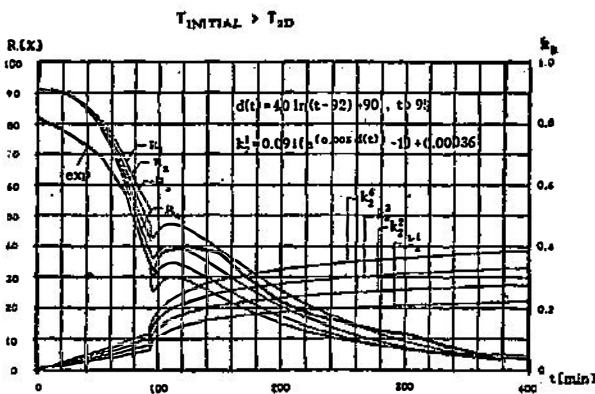


Fig. 3. Simulation of MBI reflection for nonisothermal oxidation of Al; $T_i > T_{2D}$. Oxidation starts immediately.

$[\lambda = 632.8 \text{ nm}; n_1 = 1.500; k_1 = -7.000; n_2 = 1.570; k_{Al_2O_3} = 0.0036].$

This indicates, that not only compositional inhomogeneity but also microstructural should be taken into account.

In short, the model we adapted for simulation of the reflection interference of compositionally inhomogenous films, gives excellent results in the characteristic cases considered.

APPENDIX

Dependence of k on the change of concentration C $\left[\frac{\text{Al}_2\text{O}_3}{\text{Al}} \right]$

Concentration C depends on the oxidation time t' :

$$C(t') = C_0 e^{-\alpha t'} \quad (1)$$

Taking into account the expression for the oxidation kinetics:

$$z = A \ln(t' - \tau) + C \quad (2)$$

$$t' \sim e^{\alpha' z} \quad (3)$$

Inserting expression (3) into (1), one finds

$$C(z) = C_0 e^{-\alpha} \cdot e^{\alpha' z}$$

Developing $e^{\alpha' z}$ into series: $e^{\alpha' z} = 1 + \alpha' z + \dots$, one finds

$$C = C_0 e^{-\alpha} e^{-\alpha \alpha' z}$$

Denoting $C_0 e^{-\alpha} = \varphi_0$, and $\alpha \alpha' = \gamma$, we have

$$C = \varphi_0 e^{-\gamma z} \quad (4)$$

Now we can go a step further. The change of k with the change of concentration can be expressed:

$$\Delta k \sim \Delta \left(\frac{1}{C} \right), \text{ which gives: } \frac{\partial k}{\partial z} \sim \frac{\partial}{\partial z} \left(\frac{1}{C} \right) \quad (5)$$

Derivation of the expression (4) gives:

$$\frac{\partial}{\partial z} \left(\frac{1}{C} \right) = \frac{\gamma}{\varphi_0} e^{\gamma z} \quad (6)$$

which for Eq. (5) gives

$$\frac{\partial k}{\partial z} = \frac{\gamma}{\varphi_0} e^{\gamma z},$$

and

$$dk = \frac{\gamma}{\varphi_0} e^{\gamma z} dz. \quad (7)$$

Integrating Eq. (7), one has:

$$\int_{k_0}^k dk = \frac{\gamma}{\varphi_0} \int_0^{z(t)} e^{\gamma z} dz, \quad (8)$$

$$k - k_0 = \frac{1}{\varphi_0} (e^{\gamma z(t)} - 1),$$

or simply:

$$k [z(t)] \approx k_0 (e^{\gamma z(t)} - 1), \quad (9)$$

where we denoted by $k_0, k_0 = \frac{1}{\varphi_0}$; k_0 is the adjustable constant in the simulation.

References

- 1) S. Lugomer and M. Stipančić, *Thin Solid Films* **131** (1985) 313;
- 2) R. Zitto, *Thin Solid Films* **60** (1979) 27;
- 3) R. Zitto, *The High Temperature Behaviour of Thin Metal Films*, Ph. D. Thesis, Univ. of Arizona, 1980;
- 4) E. V. Browell and R. C. Anderson, *J. Opt. Soc. Am.* **65** (1975) 919;
- 5) M. Ruiz-Urbieto, E. M. Sparrow and E. R. G. Eckert, *J. Opt. Soc. Am.* **61** (1970) 351;
- 6) P. Kofstad, *High Temperature Oxidation of Metal*, J. Wiley and Sons, Inc., N. York, 1963;
- 7) V. T. Binh and P. Melion, *Surface Science* **161** (1985) 234;
- 8) I. G. Schulz, *J. Opt. Soc. Am.* **44** (1953) 357;
- 9) I. G. Schulz and F. R. Tangerlini, *J. Opt. Soc. Am.* **44** (1953) 362.

SIMULACIJA MBI REFLEKSIJE TANKIH FILMOVA Al NEIZOTERMNO
OKSIDIRANIH NA $T \geq T_{2D}$

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Originalni znanstveni rad

Oksidacija tankih filmova Al u linearno rastućem termičkom polju koje prelazi temperaturu dvodimenzionalnog topljenja (T_{2D}), generira nehomogene filmove oksida s kompozicijskim gradijentom smjese Al_2O_3 , nestehiometrijskih Al-oksida i neoksidiranog Al. Kompozicijski gradijent smjese generira gradijent indeksa loma $\hat{n} = n(1 + ik)$, koji se mijenja s vremenom oksidacije. Taj gradijent izaziva jako eksponencijalno gušenje refleksijske interferencije. Razvijen je model za simulaciju gušene interferencije polazeći od modela za homogene dielektrične filmove, uvođenjem logaritamske oksidacijske kinetike $x(t) = A \ln(t - \tau)$, kao i uvođenjem izraza $k = k_0(e^{x(t)} - 1)$, za gradijent imaginarnog dijela indeksa loma. Vrlo dobro fitovanje «in situ» He-Ne laser MBI refleksionih krivulja, dobiveno je u svim razmatranim slučajevima.