

Dynamic method of measuring optical and diffusion constants of oxide films

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A dynamic method is proposed for determining the real and imaginary parts of the dielectric constant in the far infrared region and the thermodiffusion constants of metal oxides; the method is based on measuring the temperature of the metal in the course of its heating by radiation in an oxidizing atmosphere.

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In a number of problems involving the physics of thin-layer coatings it is important to measure exactly the optical and thermodiffusion constants of oxide films. The traditional method of determining the real and imaginary parts of the dielectric constant are based on measuring the intensities of the reflected and transmitted electromagnetic radiation,^[1,2] are laborious, and are in many cases not sufficiently accurate (for example, in the far infrared region). In addition, the optical constants of thin films on the surfaces of metals can differ somewhat from the optical constants of the oxides themselves. The reason is that the lattice of compact thin oxide films aligns itself with the metal lattice.^[3] A sufficiently accurate measurement of thermodiffusion constants of the oxides also encounters considerable difficulties.^[3,4]

The idea of the method proposed in the present paper consists in the following: When a metal is heated in an oxidizing atmosphere, an oxide film grows on its surface. It is then possible to observe in the developing layered "oxide + metal" system interference phenomena whose dynamics are quite sensitive to the values of the optical constants of the components. This makes it possible, as will be shown below, to determine the optical constants themselves by measuring the temperature of the metal while it is heated. From the values of the temperature at the interference minima, in turn, it is easy to calculate also the thermodiffusion constants of the oxide. If for a thermodynamically thin plate, the rate of change of the temperature T under the influence of radiation of constant power P is

$$\frac{dT}{dt} = \frac{P}{mc_0} A, \quad (1)$$

where A is the absorptivity of the layered "metal + oxide film" system, m is the mass, and c_0 is the specific heat of the metallic target. In formula (1) we have neglected the influence of heat losses, which can be readily accounted for in the experimental determination of the true $A(T)$ dependence.^[5]

The absorptivity A is expressed in terms of the optical characteristics of the metal oxide. For the case of normal incidence of the radiation we have^[1,6]

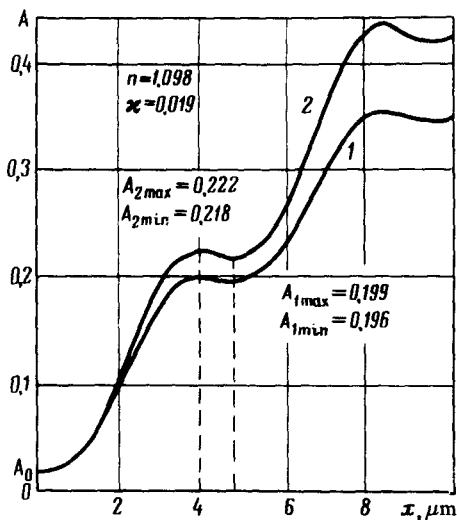


FIG. 1. Theoretical plot of $A(x)$. Curves 1 and 2 are based on formulas (2) and (4), respectively.

$$A(x) = 1 - |R|^2, \quad R = \frac{r_{12} e^{-2i\psi} + r_{23}}{e^{-2i\psi} + r_{12} r_{23}}, \quad (2)$$

where

$$\psi = \frac{\omega}{c} x \sqrt{\epsilon} = \frac{1}{2}(\beta + i\alpha)x, \quad r_{12} = \frac{1 - \sqrt{\epsilon}}{1 + \sqrt{\epsilon}}, \quad r_{23} = \frac{r_{12} - r_{13}}{r_{12} r_{13} - 1}$$

$$1 - |r_{13}|^2 = A_0$$

ω is the radiation frequency, c is the speed of light, x is the thickness of the oxide film, r_{12} and r_{13} are the amplitude reflection coefficients from the oxide and from the metal, respectively, A_0 is the absorptivity of the metal without the oxide film (for good conductors we have^[6] $r_{13} = -1 + 0.5A_0(1-i)$, $A_0 \ll 1$), ϵ is the dielectric constant of the oxide, $\sqrt{\epsilon} = n + i\kappa$, $\alpha = 2\kappa\omega/c$ is the absorption coefficient of the oxide, and $\beta = 2n\omega/c$.

The growth of the thickness x of the oxide film is described by the equation^[3,4]

$$\frac{dx}{dt} = \frac{d}{x} e^{-T_d/T}, \quad (3)$$

where T_d is the activation energy of the oxygen (or metal) ion in the oxide layer, and d is connected with coefficients of the ion diffusion through the oxide layer.^[3]

The absorptivity $A(x)$ of a layered system is characterized by the presence of oscillations (Fig. 1) due to interference phenomena in the oxide layer. These oscillations

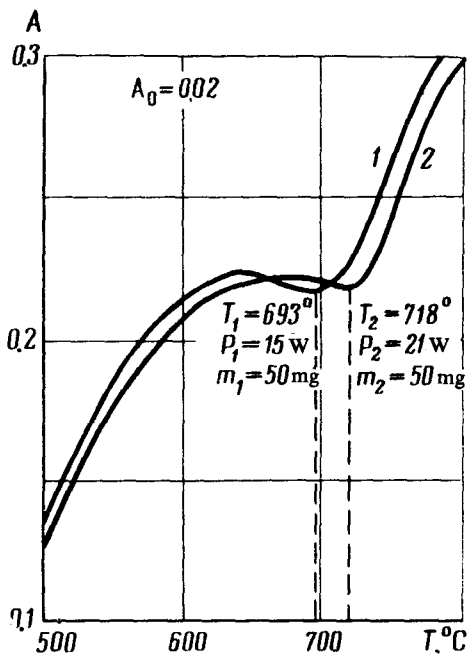


FIG. 2. Experimental plots of $A(T)$ obtained at different incident-radiation powers.

tions manifest themselves in the $A(T)$ dependence and were observed experimentally in the measurement of dT/dt .^[5] An example of the experimental $A(T)$ dependence for oxidation of copper under the influence of CO_2 -laser radiation is shown in Fig. 2.

Most metal oxides satisfy in the far infrared the condition $\kappa \ll n$. Therefore the first oscillations are characterized by small values of the optical thickness ($\alpha x \ll 1$). In this approximation we easily obtain for the function $A(x)$ the expression

$$A(x) = \frac{n^2 A_0 + 2\kappa(\beta x - \sin \beta x)}{n^2 + (1 - n^2) \sin^2 \frac{\beta x}{2}} \quad (4)$$

It follows from (4) that the values of the function $A(x)$ at the point of the first minimum A_1 and first maximum A_2 are

$$A_1 = A_0 + \frac{4\pi\kappa}{n}, \quad A_2 = n^2 A_0 + 2n\alpha x_1,$$

where x_1 is the first root of the equation

$$\text{tg} \frac{\beta x}{2} = \frac{1 - n^2}{2} \left(\beta x + \frac{n^2 A_0}{2\kappa} \right).$$

We see therefore that from the values of A_1 and A_2 we can easily determine the quantities n and κ :

$$n = \sqrt{\frac{A_2}{A_0 + (A_1 - A_0)z/\pi}}, \quad \kappa = \frac{n^2}{4\pi} (A_1 - A_0), \quad (5)$$

where z is the first positive root of the equation

$$\pi \frac{A_2 - A_0}{A_1 - A_0} = z - \operatorname{tg} z.$$

To determine the thermodiffusion constants d and T_d we must use an expression that follows from (1) and (3)

$$\int_{T_{in}}^T dT \exp\left(-\frac{T_d}{T}\right) = \frac{P}{m c_0 d} \int_0^x x A(x) dx, \quad (6)$$

where T_{in} is the initial temperature.

By determining the temperatures T_1 and T_2 corresponding to the same minimum point of the absorptivity $A(T)$ at different powers P_1 and P_2 and different target masses m_1 and m_2 , we can obtain the diffusion activation energy T_d . As a rule, the conditions $T \ll T_d$, $T - T_{in} \gg T_{in} T / T_d$ are satisfied for the first extremal points, so that (6) yields the relation

$$T_d = \frac{T_1 T_2}{T_2 - T_1} \ln \left[\frac{P_2 m_1}{P_1 m_2} \left(\frac{T_1}{T_2} \right)^2 \right]. \quad (7)$$

Knowing T_d , we easily determine also the quantity d from formula (6). At the minimum point of $A(T)$, the integral in the right-hand side of (6) is an easily evaluated constant. Then

$$d = \frac{P \mu}{m c_0 T_d} \left(\frac{T_d}{T_{min}} \right)^2 \exp\left(\frac{T_d}{T_{min}}\right), \quad \mu = \int_0^{x_{min}} x A(x) dx. \quad (8)$$

Finally, we note that the $A(T)$ dependence allows us also to determine the thickness of the oxide film (cf. Figs. 1 and 2).

The described procedure was used for an experimental determination of the optical and thermodiffusion constants of the oxide Cu_2O . A polished copper plate with dimensions $\approx 3 \times 1 \times 1$ mm was exposed to a cw CO_2 laser of ~ 20 W power. $T(t)$ was determined with a chromel-alumel thermocouple imbedded in the plastic on the rear side. The $y(t) = dT/dt$ signal was registered with a differentiating RC network having a time constant $\approx 10^{-2}$ sec. Both signals were simultaneously recorded on an N-115 loop oscilloscope, both in the course of heating of the target and in the course of its cooling; this made it possible to take the thermal losses into account.^[5] The value of $A(T)$ was determined by summing the amplitudes of the signals $y(t)$ on the heating and cooling curves at the same temperature T . Characteristic $A(T)$ curves are shown in Fig. 2.

From them, using formulas (5) we obtain for Cu_2O the values $n=1.1$, $\kappa=0.019$, which agree well with the published data.^[2] A series of experiments for different samples yielded values $n=1.09-1.21$, $\kappa=0.019-0.023$. The scatter was governed mainly by the degree of purity of the plate surface. The value $T_d \approx 10\,000$ K, determined from formula (7), corresponds to the low temperature ($T \lesssim 550^\circ\text{C}$) behavior of the copper oxidation.^[4] In our experiment, d cannot be determined from formula (8), inasmuch as the copper oxidation begins to go over to its high-temperature behavior in the region $T \approx 550-600^\circ\text{C}$, and this changes greatly the value of the pre-exponential factor in (3).

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