T. A. E. C.
ÇEKMECE NUCLEAR RESEARCH AND TRAINING CENTER
İSTANBUL - TURKEY

ÇNAEM - R - 135

METALLIC ALUMINUM PARTICLE CONCENTRATION IN ALUMINUM OXIDE THIN FILMS

By

H. Birey

P. K. 1, Hava Alanı, İstanbul, Turkey

1974

Metallic aluminum particle concentration in aluminum oxide thin films

Hülya Birey*

Physics Department Cekmece Nuclear Research and Training Center P.K.1 Havaalani, Istanbul, Turkey
(Received 19 February 1974; in final form 15 May 1974)

Two different methods based on (a) the tunneling junction model and (b) the optical model are used to determine the metallic aluminum particle concentration in aluminum oxide thin films prepared by thermal evaporation of pure aluminum under appropriate vacuum conditions. The concentration determined from these two models agree with each other at high concentrations and show considerable deviation at low concentrations.

I. INTRODUCTION

Electrical current-voltage characteristics of vacuum-evaporated aluminum oxide thin-film sandwiches show different non-Ohmic conduction behavior for various samples prepared by thermal evaporation of pure aluminum at different evaporation pressures.[1] Variation of this non-Ohmic conduction behavior for various samples is attributed to the concentration of the metallic aluminum particles embedded in the oxide during the evaporation process.

In this paper, two different methods are used to determine the metallic aluminum particle concentration in aluminum oxide thin films evaporated in vacuum. These are (a) the electrical resistivity based on the tunneling current produced between aluminum particles embedded in the oxide and (b) the equivalence of the optical properties of the aluminum-embedded aluminum oxide film to that of an effective pure metallic aluminum thin film.

II. TUNNELING JUNCTION MODEL (REF. 2)

It may be assumed that the evaporated film consists of a continuous amorphous aluminum oxide in which small crystallines of pure aluminum spheres are uniformly dispersed. A cube full of touching identical spheres will represent 74% of the total volume. For metallic concentration C higher than 74%, these spheres will be in contact with each other and the grain boundaries of the spheres are occupied by the oxide. For C less than 74%, the spheres will be separated by the insulating barrier of amorphous oxide. The spacing between the metallic particles will thus depend on the diameter as well as the concentration of these particles. In these calculations, the radius of the spheres and their spacing are assumed to be constant for a given sample.

Let L be the thickness of the film, S its cross section, a the radius of the spheres, D the spacing between the centers of the neighboring spheres, $d=D-2a$, the nearest distance between the spheres, and r_j the resistance of one tunneling junction.

The total resistance R_j of a given sample is assumed to be made up of L/D resistors in series and S/D^2 resistors in parallel multiplied by the unit resistor r_j between two neighboring particles and thus

$$R_j = r_j(L/D)(D^2/S) = r_j(L/S)D. \tag{1}$$

The resistance of a tunneling junction is proportional to $\exp[k(d\sqrt{\varphi})]$ and inversely proportional to the area of the junction. Hence, r_j included between two spherical grains can be written

$$r_j = (A/\pi a^2)\exp[k(d\sqrt{\varphi})], \tag{2}$$

where k is a constant, A is the proportionality constant taking into account the spherical shape of the electrodes, and φ is the barrier height of the metal-oxide junction.

The parameters d and D are simply related to the volume concentration of crystallized aluminum concentration C by the following equations:

$$d = 2a[(0.74/C)^{1/3} - 1], \tag{3}$$

$$D = 2a(0.74/C)^{1/3}. \tag{4}$$

Using Eqs. (2)–(4), Eq. (1) can be written

$$R_j = R_0(y+1)\exp[k(2a\sqrt{\varphi})y], \tag{5}$$

where R_0 is the normalized resistance independent of the concentration and the particle size and

$$y = [(0.74/C)^{1/3} - 1]. \tag{6}$$

If a is expressed in Å and φ in eV, then $k = 1.025$ $\text{Å}^{-1}\,\text{eV}^{-1/2}$ and is taken to be unity for practical purposes.[3]

The total resistance R_t of a granular film can be written as the sum of R_G, the total metallic grain resistance, and R_j, the total barrier resistance, i.e.,

$$R_t = R_G + R_j \tag{7}$$

Two limit cases can be considered:

(1) At high metal concentrations, the resistance of the film corresponds essentially to that of the continuous paths of the metallic filaments, and $R_t \approx R_G$.

(2) At low metal concentrations, R_j is several orders of magnitude higher than R_G; hence, $R_t \approx R_j$.

In case (2), the total film resistance is due only to the barriers and depends on the concentration, grain size, barrier height and normalized resistance R_0.

Keeping the evaporation rate constant and increasing the evaporation pressure, the radius of the metallic spheres a may decrease as the concentration decreases. The current-voltage characteristics of such sandwiches indicate that the aluminum particles act as trap centers in the oxide with the effective Fermi level moving up toward the conduction band and the barrier height φ decreases for increasing concentration. Thus, in the tunneling current calculations, the product $2a\sqrt{\varphi}$ may be assumed constant for a wide range of concentration values. Therefore, if $\text{Ln}R$ is plotted against the parameter y for $y \ll 1$, the slope and the $y=0$ intercept of this curve will be equal to $k(2a\sqrt{\varphi})$ and R_0, respectively.

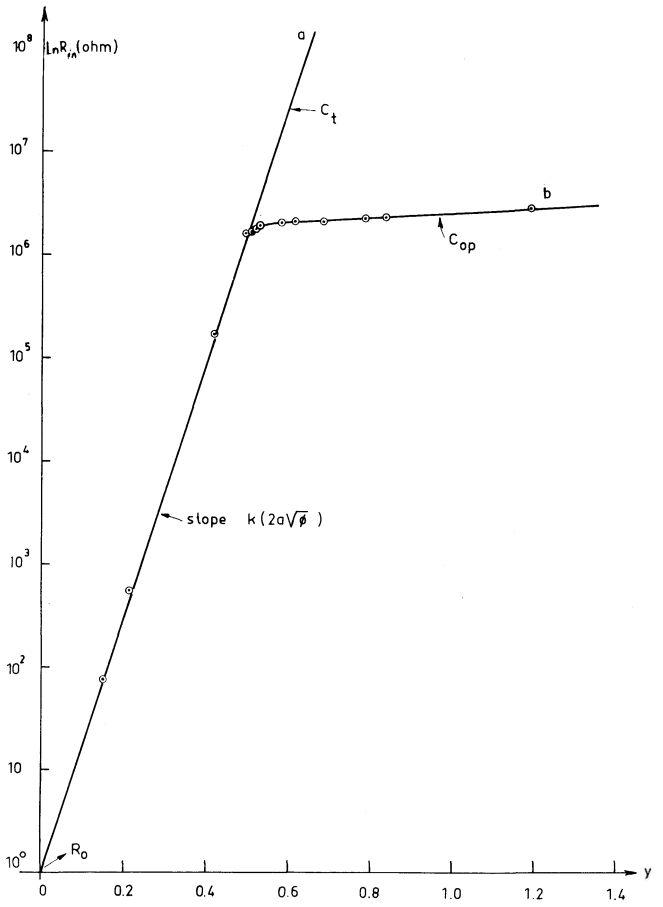

FIG. 1. LnR_{in}-vs-y plot, R_{in}, initial low field resistance of the sample; $y = 0.74^{1/3} - 1$. C_t and C_{op} are the concentrations based on the tunneling and optical model, respectively.

Equation (5) may now be used to calculate the aluminum concentration C_t within the oxide using the low field resistance values R_{in} of the samples determined from the slope of the corresponding initial current-voltage characteristics. C_t is the concentration which is determined according to the tunneling model. Figure 1(a) is drawn with a slope equal to $k(2a\sqrt{\varphi})$ using $2a = 20$ Å [2] and $\varphi = 2.0$ eV [4] with the $y = 0$ intercept of $R_0 = 1.2\ \Omega$ which is found experimentally for a pure metallic aluminum thin film having the regular sample geometry.[1] From this curve, the concentration C_t is determined using the corresponding electrically measured R_{in} values.

III. OPTICAL MODEL

The optical model for concentration determination of such films is based on the equivalence of an aluminum oxide thin film containing uniformly distributed metallic aluminum particles to that of a pure metallic aluminum thin film both having the same optical absorption characteristics.

The actual evaporated film is illustrated in Fig. 2(a). It consists of a substrate having an index of refraction of 1.5 coated with an amorphous aluminum oxide in which small crystallites of pure aluminum spheres are uniformly dispersed. The total reflectivity and transmissivity of such a sample are ρ and τ, respectively.

We now assume that the optically equivalent structure of this sample can be represented as shown in Fig. 2(b). It consists of the same substrate on which there is an equivalent pure metallic thin film with a reflectivity ρ_m and transmissivity τ_m. This metallic film is covered with a pure amorphous aluminum oxide which has an index of refraction of 1.5.

If the interferometrically measured thickness of the original sample is L_{in} and that of the equivalent metallic film, having the same optical absorption characteristics as the original sample, is L_m, the concentration of the metallic aluminum particles within the oxide can be calculated from the following relation:

$$C_{op}/0.74 = L_m/L_{in}. \tag{8}$$

Here, C_{op} is the concentration based on the optical model and the factor 0.74 is due to the difference between the pure metallic film and the volume occupied by the touching spheres.

The optical equivalence of the evaporated oxide film and the metallic aluminum film is based on the following assumptions:

(a) The total optical absorption A_t of the oxide is due only to the metallic absorption A_m by the embedded aluminum particles and it is calculated from

$$\rho + \tau + A_m = 1.$$

The scattering loss is neglected.[1]

(b) The reflectivity is also assumed to be due only to the metallic particles, since the index of refraction of a pure aluminum oxide film is experimentally found to be equal to that of the glass substrate ($n = 1.5$). This agrees with the other measured values found in the literature.[5]

Thus, the change in the reflectivity and transmissivity of the films having different concentrations is due only to different corresponding metallic thicknesses.

The reflectivity ρ, transmissivity τ and interferometric thickness L_{in} of an evaporated aluminum oxide film are measured. The reflectivity ρ_m and transmissivity τ_m are also measured as a function of the thickness L_m of vacuum-evaporated pure aluminum thin film for various metallic thicknesses. These data on metallic reflectivity and absorption of pure aluminum film as a func-

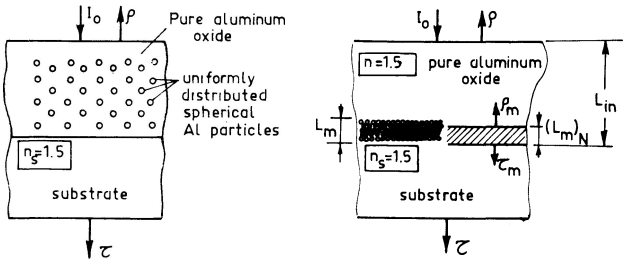

FIG. 2. Optical model. (a) Aluminum-embedded aluminum oxide film on a glass substrate with the reflectivity and transmissivity ρ and τ, respectively. (b) Optically equivalent film system. L_m, equivalent metallic film thickness; $(L_m)_N = 0.74L_m$, normalized thickness. ρ_m and τ_m are the reflectivity and transmissivity of the thin metallic aluminum film.

TABLE I. Electrical and optical data on typical samples. L_{in}, interferometrically measured thickness; R_{in}, initial resistance; ρ, reflectivity; τ, transmissivity; L_m, equivalent pure metallic thickness C_t and C_{op} are concentrations due to tunneling and the optical models, respectively; d, the nearest separation distance between the Al particles.

P (Torr)	L_{in} (Å)	R_{in} (Ω)	ρ (%)	τ (%)	L_m (Å)	C_t (%)	C_{op} (%)	d (Å)
4×10^{-3}	1400	12×10^6	8	92	0	19.1	0	1380
Decreasing pressure ↓	1345	7×10^6	19.3	78.5	73	19.8	4.0	349
	1330	4.5×10^6	46.5	42	126	20.4	7.0	190
	865	2.88×10^6	55.5	30.5	140	21.1	12	103.5
	770	2.5×10^6	64	20	162	21.3	15.6	74.8
	705	2.28×10^6	68.7	10.3	179	21.5	18.8	51.9
	700	2.1×10^6	71.7	8	197	21.5	20.8	50.4
	695	1.97×10^6	71.8	6.7	198	21.1	21.1	49.8
	685	1.5×10^6	72.5	4.8	206	22.3	22.2	46.3
	680	1.2×10^6	73	4.2	207	22.4	22.3	45.8
	670	0.167×10^6	76.5	2	236	25.8	25.8	31.3
	657	650	87.5	0.5	362	40.7	40.7	16.3
	653	82	90	0	428	48.4	48.4	10.5
10^{-5}	650	1.25	92	0	650	74	74	0

tion of thickness agrees with measurements found in the literature.[6] All the optical data are taken using $\lambda = 6328$ Å radiation of a He-Ne gas laser.

For a sample with a thickness L_{in}, the absorption value A_m is compared to that of a pure metallic thin film and the equivalent metal thickness L_m is found having this same optical absorption. The concentration C_{op}, which is calculated from Eq. (8) is then used to find the equivalent parameter y_{op} and these y_{op} values are plotted as a function of the corresponding initial resistance values R_{in}, as shown in Fig. 1(b).

As can be seen from Figs. 1(a), and 1(b), the two methods agree with each other at high concentrations up to $C = 21\%$ ($y = 0.5$) and the assumption of $2a\sqrt{\varphi}$ being a constant is thus verified for $y \leq 0.5$ by the optical model as well. The deviation of the two methods above $C = 21\%$ is attributed to the failure of the tunneling model which is effective up to metallic particle spacings of $d \approx 50$ Å [7] corresponding roughly to $y \approx 0.5$. The current-voltage characteristics of the samples having low concentration indicates that electrical transport properties besides tunneling phenomena should be considered above the particle spacing of ~50 Å.[8] In addition to these, Eq. (5) cannot simply be represented by a straight line on a logarithmic scale for $y > 0.5$. Therefore, the optically determined concentration values are considered to be the true concentration for further study on the oxide films.

Various parameters which are electrically and optically measured are listed in Table I. The reflectivity of a pure oxide sample verifies assumption (b) made for the optical model, since $\rho = 8\%$ and $\tau = 92\%$ for a pure oxide film is the same as the reflectivity of the glass substrate.

The optical thickness measurements have ±10 Å accuracy at 50 Å thickness.

ACKNOWLEDGMENT

The author wishes to acknowledge valuable discussions with Doc. Dr. Altan M. Ferendeci.

*Present address: General Physics Department, Istanbul University, Istanbul, Turkey.

[1] H. Birey, Appl. Phys. Lett. 23, 317 (1973).
[2] A. Fontain and F. Mennier, Phys. Kondens. Mater. 14, 119 (1972).
[3] J. G. Simmons, J. Appl. Phys. 34, 238 (1963); 34, 1793 (1963).
[4] A. I. Braunstein, M. Braunstein, and G. S. Picus, Phys. Rev. Lett. 15, 956 (1965).
[5] H. Birey and U. Tarim, Istanbul Univ. Fen Fak. Mecmuasi: Seri C 29, 161 (1964).
[6] A. Vasicek, *Optics of thin films* (North-Holland, Amsterdam, 1960).
[7] J. G. Simmons, J. Appl. Phys. 34, 1793 (1963).
[8] Detailed explanation of the electrical transport properties of these samples will be given in a forthcoming article.