JOURNAL OF MATERIALS SCIENCE 26 (1991) 2007–2014

Electrical properties of thin oxidized aluminium films

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Thin aluminium films of thickness 40 to 200 nm were deposited on to glass substrates at 573 K in a high vacuum. The deposition was carried out layer by layer and the interfaces between these layers were exposed to oxygen. The electrical resistivity was studied as a function of the film thickness, annealing time, annealing temperature and oxygen pressure. The temperature coefficient of resistivity and the activation energy for the conduction electrons were studied as a function of the film thickness and oxygen pressure. Fuchs–Sondheimer theory for electrical conduction was applied to the experimental results. The mean free path of the conduction electrons was calculated as a function of temperature and agreed well with the theoretical relation.

1. Introduction

Aluminium has broad applications in industry and modern technology because it is very cheap, lightweight, easily deformed and manufactured, and forms a set of alloys of special characteristics. For all these reasons, aluminium has been studied in the bulk form as well as in thin film form. The electrical resistivity has been studied as a function of the film thickness for aluminium films deposited at room temperature on to glass substrates [1], on to fused quartz and oxidized silicon [2], and on to crystalline sodium chloride substrates [3]. When aluminium films is deposited on oxidized silicon substrates at room temperature in the presence of oxygen or water vapour, it has been found that the grain size of aluminium decreases and finally the film becomes granular [4]. The deposition of aluminium films on to sodium chloride and glass substrates at 573 K in the presence of oxygen results in the formation of aluminium films of smaller grain sizes with higher surface roughness, and as the pressure of oxygen increases, hillocks are produced [5]. The role of annealing temperature on the electrical resistivity of aluminium films has been studied in the temperature range 40 to 400 K [6–9] and from 400 K to the melting point [9–11].

The aim of this work is to study the effect of film thickness, annealing temperature, annealing time and oxygen pressure on the electrical resistivity of thin oxidized aluminium films. The effect of film thickness and oxygen pressure on the temperature coefficient of resistivity (TCR) and the activation energy for the conduction electrons, E, were studied too. Fuchs–Sondheimer theory for electrical conduction was applied to the experimental results, and the mean free path for the conduction electrons was calculated as a function of temperature.

2. Experimental procedure

Aluminium wires of purity 5N were thermally evaporated from tungsten spiral evaporation sources in a high vacuum. Aluminium films were deposited on to glass substrates at 573 K in a vacuum at a pressure 5×10^{-5} Pa. The film thickness and deposition rate were measured and monitored using a quartz crystal thickness monitor. The temperature of both the substrate and overgrowth were measured and controlled using Ni–CrNi thermocouples stuck to the substrates. Four platinum electrodes were attached to the substrates for the electrical measurements. The electrical resistivity was measured *in situ* during the film deposition as well as after deposition during both the oxidation and annealing processes.

A series of experiments was carried out by depositing aluminium films of thickness 40 to 200 nm with a deposition rate of 0.3 nm sec^{-1}. These films were deposited step by step at stages of 5 nm for films of thickness 40, 50, and 60 nm, and of 10 nm for films of thickness 70, 100 and 200 nm, and between these steps or layers of pure aluminium, oxygen of a pressure 5×10^{-4} Pa was introduced for a period of 10 min to oxidize the outer surfaces of these deposited layers, i.e. to form a series of pure and oxidized aluminium layers. The electrical resistivity was measured during all these events as a function of the film thickness d.

Another series of experiments was carried out to study the effect of oxygen pressure on the electrical resistivity by depositing aluminium films of thickness

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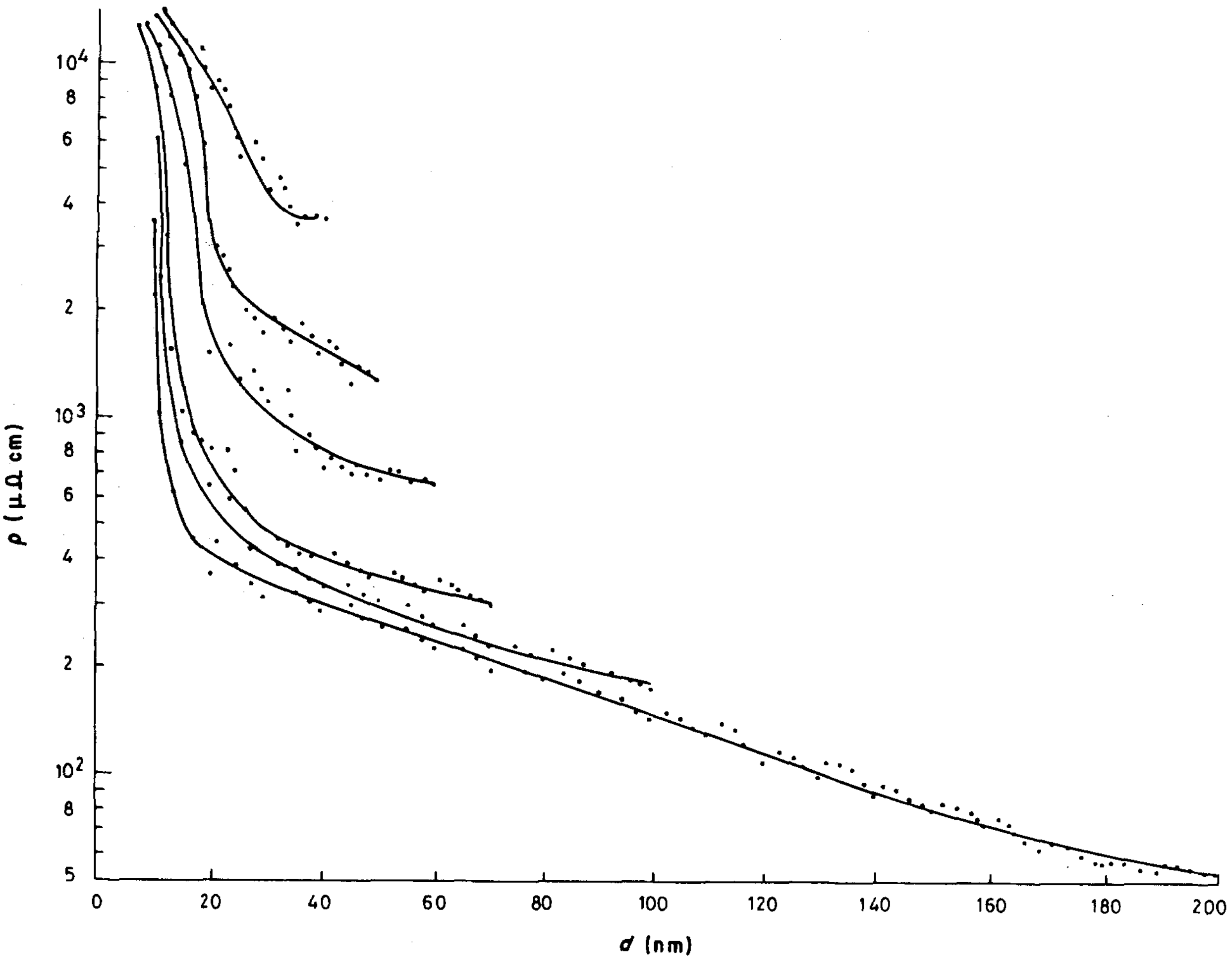

Figure 1 The dependence of the electrical resistivity ρ on the film thickness *d* for aluminium films deposited on to glass at 573 K in a high vacuum and oxidized step by step in the presence of oxygen of pressure 5 × 10^{-4} Pa.

60 and 70 nm. The introduced oxygen pressure ranged from 10^{-3} to 10^{-2} Pa. A third series of experiments was carried out to study the effect of annealing temperature on electrical resistivity for aluminium films of the first and second series. A fourth series of experiments was carried out to study the effect of annealing time on the electrical resistivity of aluminium films of thickness 50 and 60 nm deposited 573 K and annealed at 673 K, the oxygen pressure being 5 × 10^{-4} Pa.

3. Results and discussion

The dependence of the electrical resistivity ρ on the film thickness *d* is shown in Fig. 1 for thin oxidized aluminium films of various thicknesses deposited at 573 K on to glass substrates. It is clear that the electrical resistivity decreases as the film thickness increases. Aluminium films of small thickness contain a large number of small grains or islands and many empty channels in between; these grains are randomly oriented [5]. Aluminium films of small thickness have higher values of the electrical resistivity ρ, and this can be related to the scattering of the conduction electrons by the grain boundaries, inter-island distances, defects and the random orientational effect of these small grains. As the film thickness increases, the sizes of these grains become larger, the inter-island distances decrease and consequently their scattering effect will decrease. As a result, the electrical resistivity decreases as the film thickness increases.

Over these randomly oriented pure aluminium grains are the oxidized aluminium layers which are partially or completely covering the surface of the randomly oriented aluminium crystallites. This leads to the separation of aluminium grains during their growth [12, 13]. The formation of the foreign oxide layers can influence the growth mechanism as well as the physical and chemical properties. As a result, the electrical resistivity increases directly after oxidation, then decreases as the deposited film thickness increases, where the oxide layers are embedded and screened by the freshly deposited pure aluminium layers. The electrical resistivity of the oxidized aluminium films is higher than for pure aluminium films [14].

The relationship between the electrical resistivity and the annealing temperature *T* (which is lower than the deposition temperature) is illustrated in Fig. 2a for aluminium films of thickness 40 to 200 nm oxidized step by step at an oxygen pressure of 5 × 10^{-4} Pa, and Fig. 2b for aluminium films of thickness 60 and 70 nm oxidized step by step in the presence of oxygen of various pressures. The variation of the electrical resistivity with annealing temperature can be related mainly to one of two competing processes. The first is the rearrangement and reorientation (recrystallization) of the small crystallites of the film; this decreases

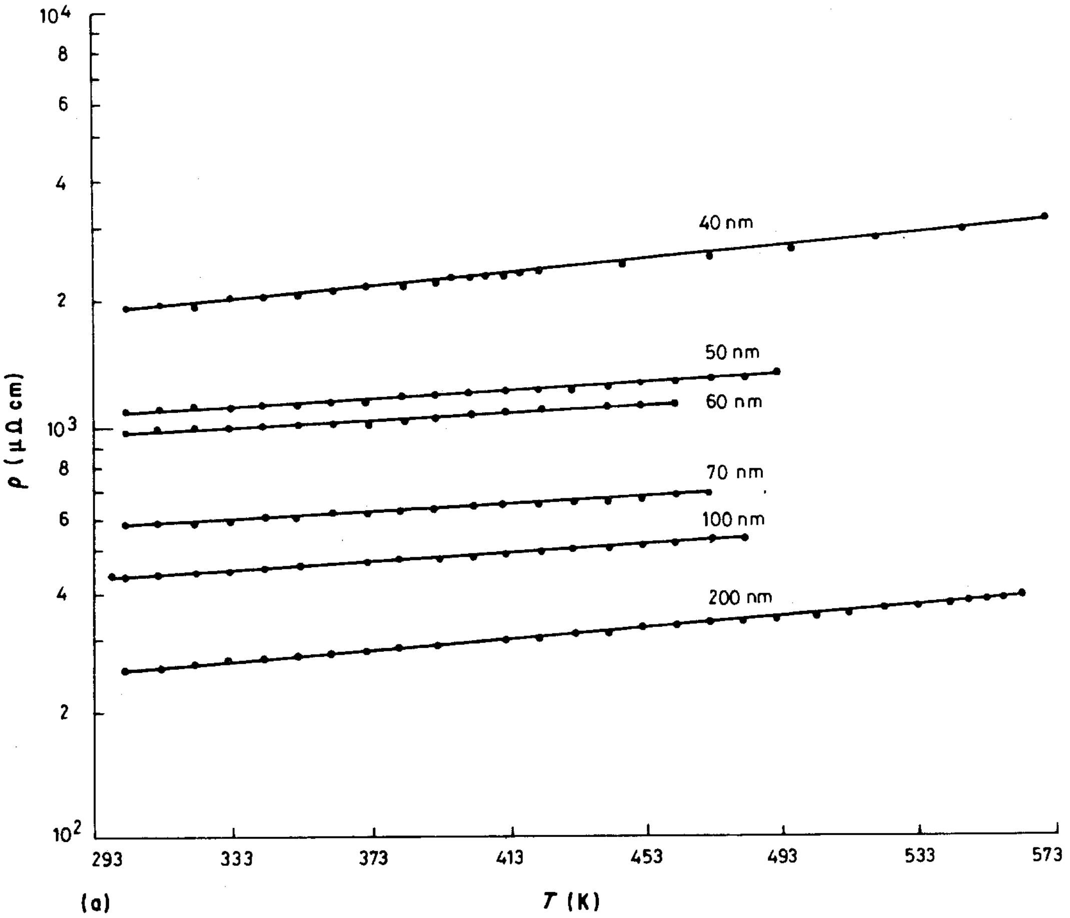

Figure 2 The relationship between the electrical resistivity and the annealing temperature T for (a) aluminium films of various thicknesses deposited in a vacuum and oxidized step by step in the presence of oxygen of pressure 5×10^{-4} Pa, and (b) aluminium films of thickness (●) 60 and (○) 70 nm deposited in a vacuum and oxidized step by step in the presence of oxygen at a pressure ranging from 10^{-3} to 10^{-2} Pa.

the electrical resistivity. The second process is the thermal generation of lattice defects, grain boundaries and the formation of the oxide layers; this process increases the values of the electrical resistivity. The electrical resistivity as shown in Fig. 2a increases with the annealing temperature, and this can be related to the second process, i.e. to the thermal generation of lattice defects, grain boundaries and the formation of the oxide layers.

However, according to Fig. 2b the electrical resistivity decreases as the annealing temperature and the film thickness increase and as the oxygen pressure decreases. The decrease of ρ with the annealing temperature in Fig. 2b can be related to the first process, i.e. to the rearrangement and recrystallization of the small crystallites in the film. As the oxygen pressure increases, the thickness of the oxide layers increases, and as a result, the resistivity increases. The study of the electrical resistivity with annealing temperature during the cooling, heating and cooling cycles proved that the dependence of the electrical resistivity on the annealing temperature is an irreversible process.

Fig. 3 shows the dependence of the electrical resistivity on the annealing time at 673 K for aluminium films of thickness 50 and 60 nm. It is clear that the electrical resistivity decreases as the annealing time increases. This decrease of ρ is related mainly to the rearrangement and recrystallization of aluminium grains or crystallites, which leads to a marked decrease of the number of defects and inter-island distances; therefore the electrical resistivity decreases.

The TCR, β, as a function of the film thickness d is presented in Fig. 4 for aluminium films. Fig. 4 indicates that β increases as d increases and as the temperature T decreases. Aluminium films of thickness 60 and 70 nm deposited in a vacuum and oxidized step by step at an oxygen pressure ranging from 5×10^{-3} to 10^{-2} Pa (films presented in Fig. 2b) have a negative β; these values are listed in Table I as a function of oxygen pressure. From Fig. 4 and Table I, it is clear that β as a function of d has positive values for pure films [14] or for lower values of oxygen pressure (lower contamination rate), while β has negative values for higher values of oxygen pressure (higher rate of contamination), but generally β increases as d increases. The occurrence of the negative TCR can be related to the existence of higher levels of the trapped impurities, inherent film defects and the variation of the coefficient of thermal expansion with the film material, i.e. to the existence of a periodic array of pure oxide and aluminium films [15, 16]. The Fuchs–Sondheimer (FS) theory for electrical conduction [17, 18] expresses the electrical resistivity ρ and the TCR β of the film in terms of the resistivity ρ_0, TCR β_0 and the mean free path of the conduction electrons λ_0 of the bulk material, the specularity parameter P and the film thickness d. According to FS theory, the electrical resistivity and TCR of the film

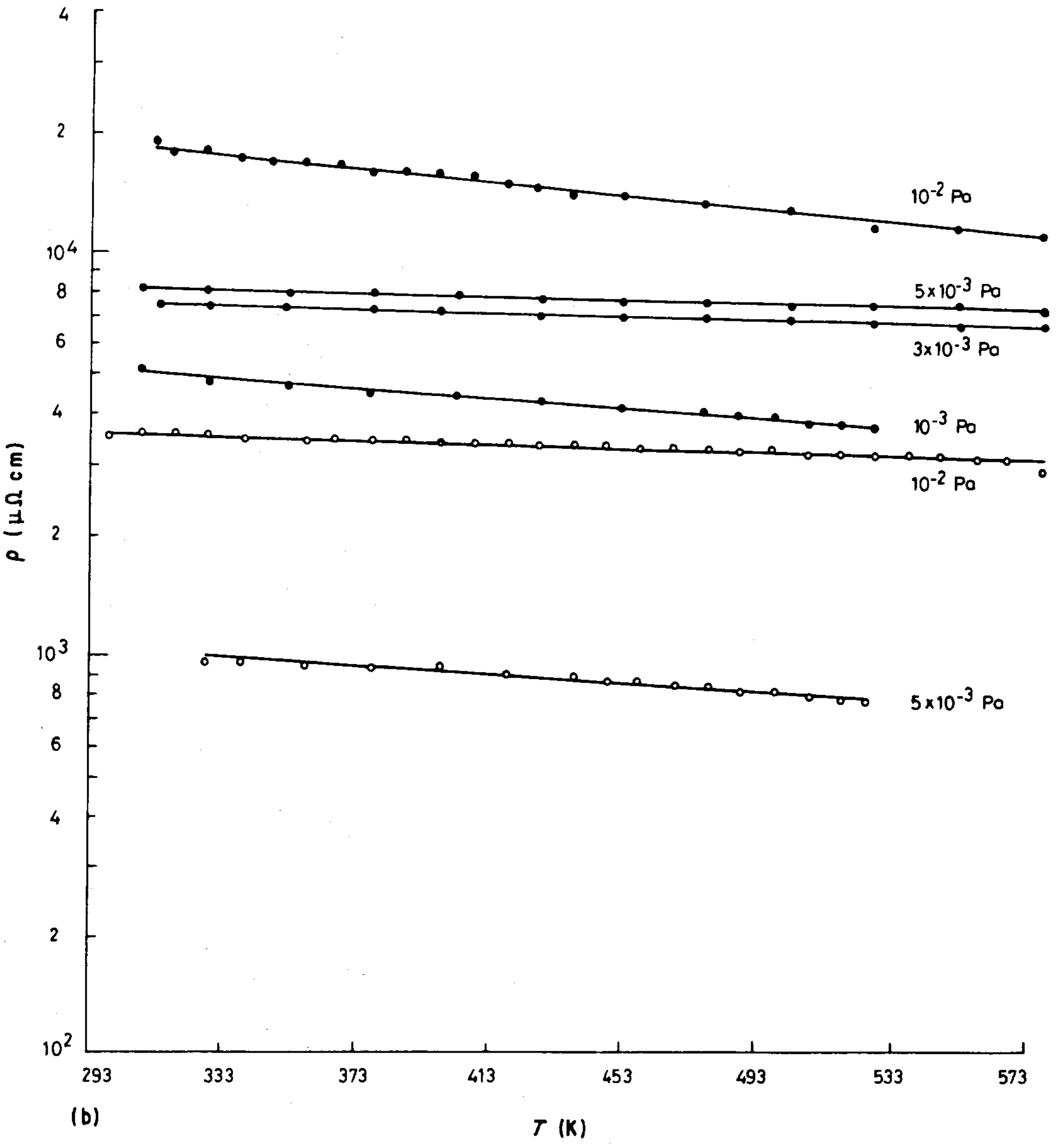

Figure 2 Continued.

can be written as

$$\frac{\rho}{\rho_0} = 1 + \frac{3}{8}\left(\frac{1-P}{d}\right)\lambda_0 \qquad (1)$$

$$\frac{\beta}{\beta_0} = 1 - \frac{3}{8}\left(\frac{1-P}{d}\right)\lambda_0 \qquad (2)$$

Using the experimental results in Equation 1, by drawing the relation between ρ and d^{-1}, straight lines will be obtained with slopes $3/8(1-P)\rho_0\lambda_0$ and intercepts ρ_0 on the vertical axis. Since each line

TABLE I Negative values of TCR as a function of oxygen pressure

Thickness, d (nm)	Oxygen pressure (10^{-3} Pa)	TCR, β (10^{-4} K)
60	10	1.68
	5	3.03
	3	3.61
	1	3.75
70	10	4.36
	5	4.95

TABLE II Activation energy for conduction electrons as a function of film thickness

Thickness, d (nm)	Activation energy (eV)
40	0.026
50	0.016
60	0.012
70	0.010
100	0.009
200	0.007

TABLE III Activation energy for conduction electrons as a function of oxygen pressure

Thickness d(nm)	Oxygen pressure (10^{-3} Pa)	Activation energy (eV)
60	10	0.029
	5	0.011
	3	0.008
	1	0.007
70	10	0.010
	5	0.009

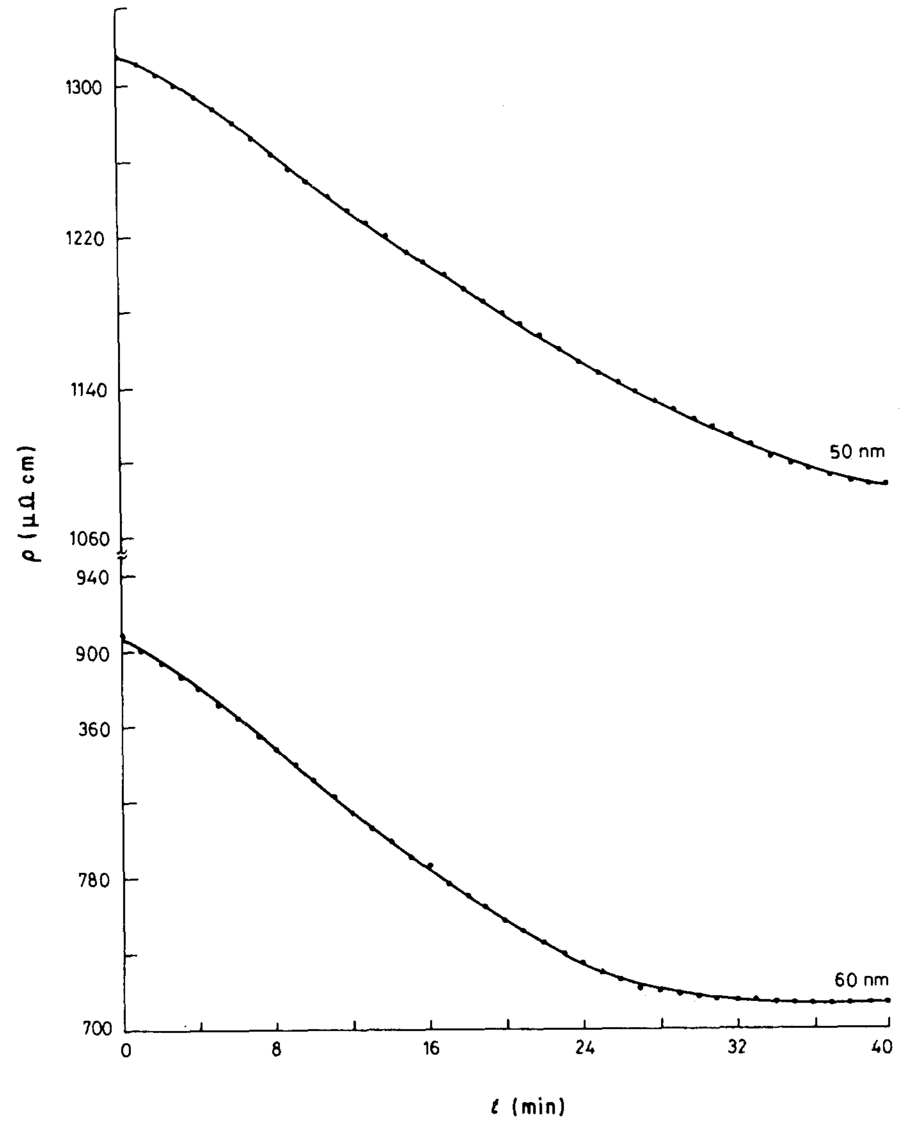

Figure 3 The effect of annealing time at 673 K on the electrical resistivity of thin aluminium films of thickness 50 and 60 nm.

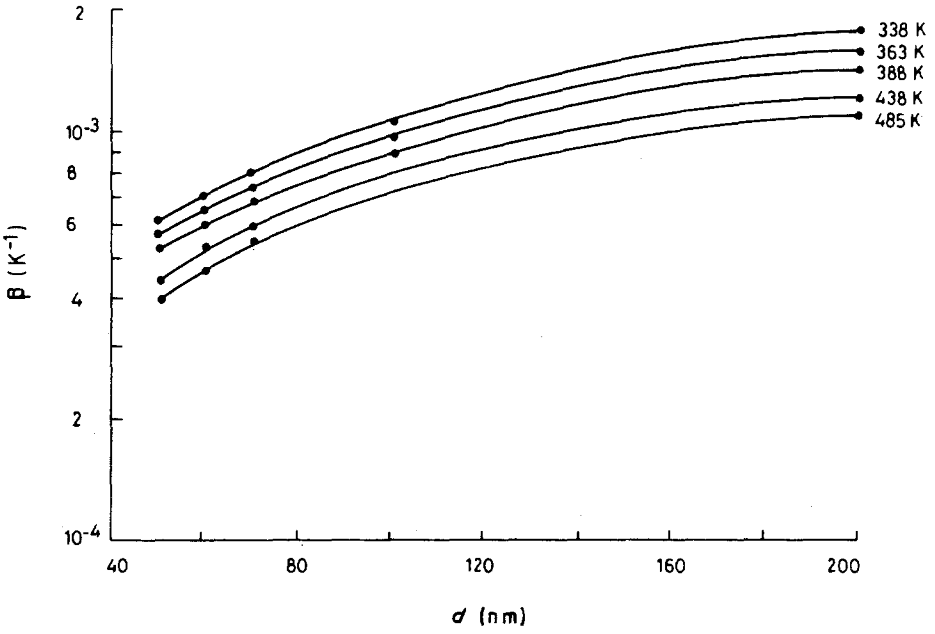

Figure 4 The variations of TCR, β, with the film thickness d for aluminium films deposited in a vacuum and oxidized step by step in the presence of oxygen of a pressure of 5×10^{-4} Pa.

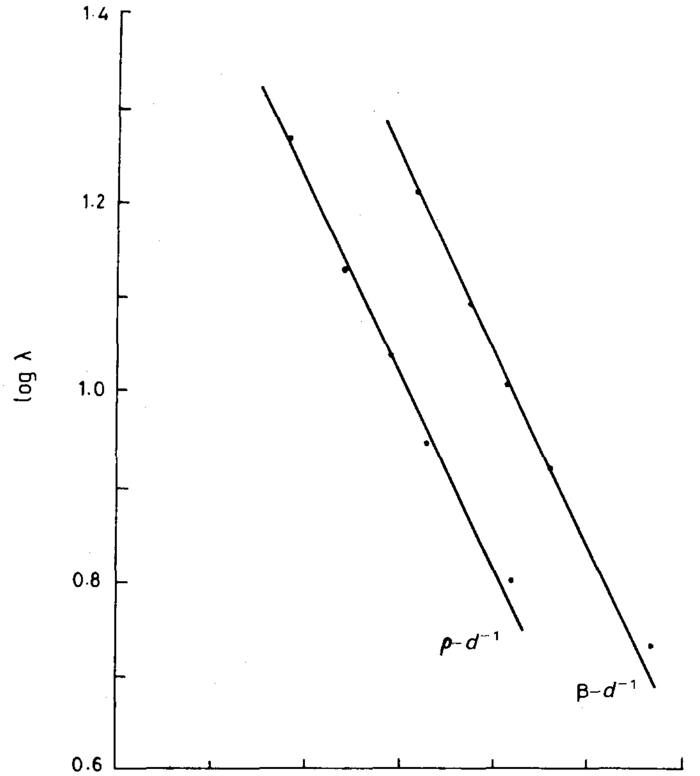

Figure 5 The logarithmic relation between the mean free path of the conduction electrons λ_0 and the temperature T.

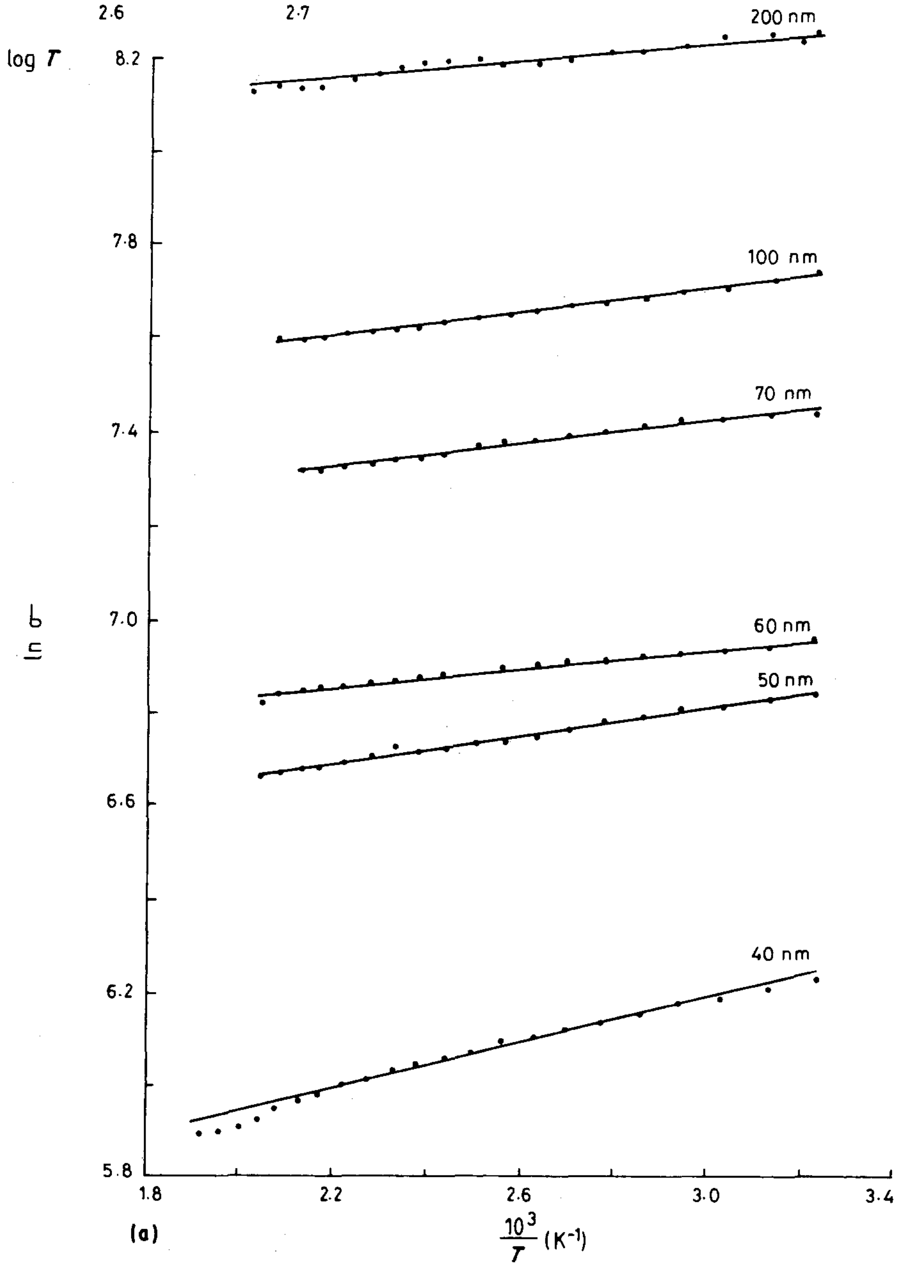

Figure 6 The relation between $\ln\sigma$ and $1/T$ for (a) aluminium films of various thickness deposited in a vacuum and oxidized step by step in presence of oxygen of pressure 5×10^{-4} Pa, and (b) aluminium films of thickness (●) 60 and (○) 70 nm deposited in a vacuum and oxidized step by step in the presence of oxygen of pressure ranging from 10^{-3} to 10^{-2} Pa.

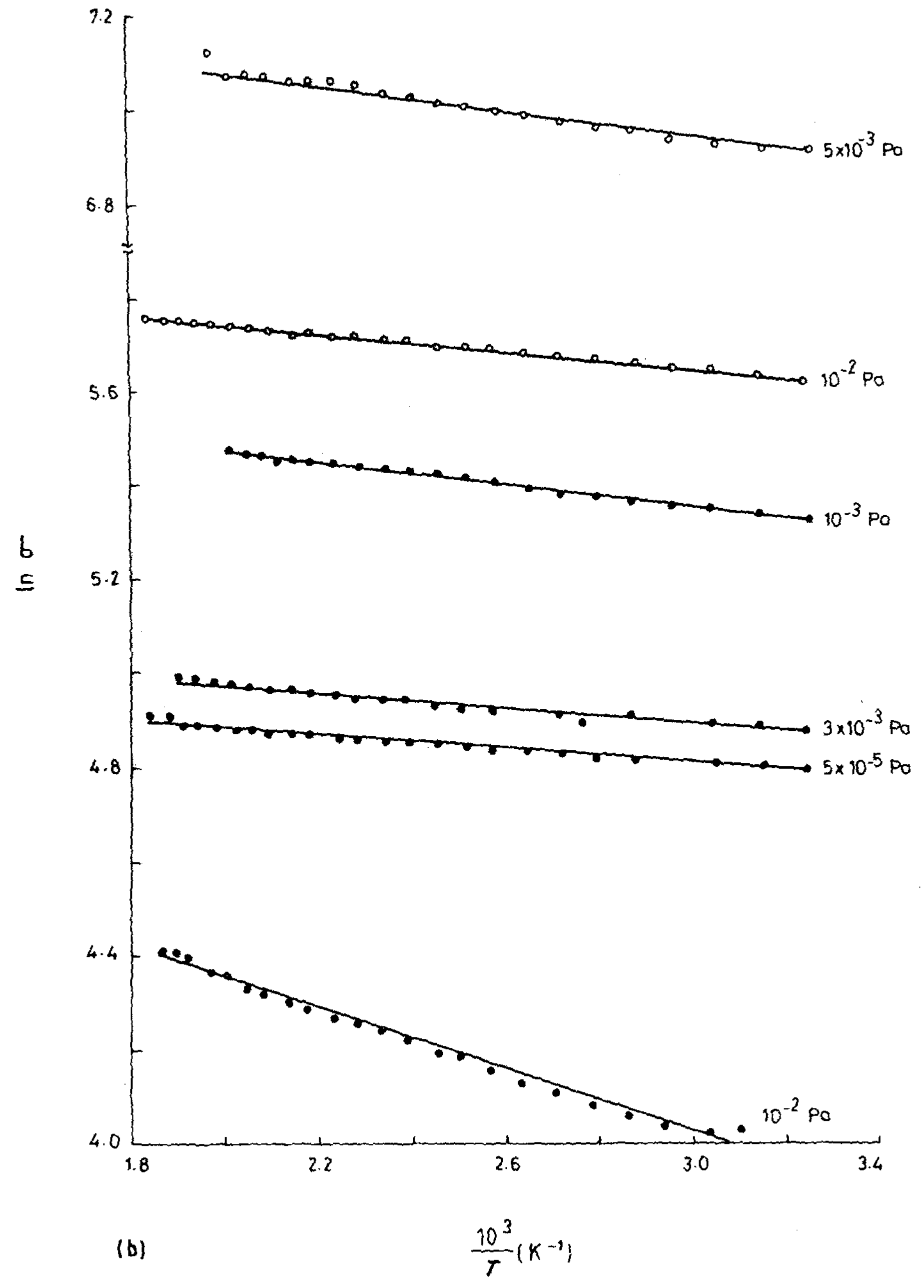

Figure 6 Continued.

representing Equation 1 is drawn at a given temperature, then the mean free path λ_0 can be calculated as a function of temperature T, when $P = 0$. In the same way, drawing the relation between β and d^{-1} according to Equation 2 and using the experimental results, from the slopes and the intercepts the values of the mean free path λ_0 as a function of temperature T can be calculated. Drawing the logarithmic relation between λ_0 and T, using the previously calculated data from both the relations ρ-d^{-1} and β-d^{-1}, two straight lines of slopes -4.6 are obtained as shown in Fig. 5. The theoretical relation between λ_0 and T [19, 20] can be written as

$$\lambda_0 = AT^{-5} \qquad (3)$$

where A is a constant. It is clear from Equation 3 that the slope of the logarithmic relation must be -5, which is in fairly good agreement with the experimental value of -4.6.

The electrical conductivity σ of the film can be written as

$$\sigma = \sigma_0 \exp(E/kT) \qquad (4)$$

where σ_0 is the bulk conductivity, T is the absolute temperature, k is the Boltzmann constant and E is the activation energy for the conduction electrons. The relationship between $\ln\sigma$ and $1/T$ according to Equation 4 is presented in Fig. 6a for aluminium films which were deposited in a vacuum and oxidized step by step in the presence of oxygen of pressure 5×10^{-4} Pa, while Fig. 6b is for films of thickness 60 and 70 nm deposited in a vacuum and oxidized step by step in the presence of oxygen at various pressures. From the slopes of these lines, the activation energies for the conduction electrons are calculated as a function of the film thickness d (from Fig. 6a) and listed in Table II, and as a function of oxygen pressure (from Fig. 6b) as listed in Table III.

Table II indicates that the activation energy E decreases as the film thickness increases. The conduction electrons face many scattering centres such as inter-island distances, defects and a large number of small grain boundaries; all these centres increases the film resistivity. As the film thickness increases, these scattering centres decrease in number, therefore the electrical resistivity decreases and the conductivity increases; as a result the activation energy for the conduction electrons decreases as the film thickness increases. Table III indicates that the activation energy increases as the oxygen pressure increases. This can be related to the formation of oxide layers which become thicker with higher scattering effect as the oxygen pressure increases, which therefore increases the values of the activation energy for the conduction electrons.

4. Conclusion

The analysis of the present results can be summarized as follows:

1. The electrical resistivity of thin oxidized aluminium films decreases as the film thickness and annealing time increase and as the oxygen pressure decreases.
2. The electrical resistivity increases as the annealing temperature increases for lower values of oxygen pressure (lower rate of contamination), while it decreases with increasing temperature for higher values of oxygen pressure (higher rate of contamination).
3. The variation of the electrical resistivity with temperature is an irreversible process.
4. The temperature coefficient of resistivity increases as the film thickness increases for lower values of the rate of contamination (oxidation). These values become negative for higher values of oxygen pressure.
5. The activation energy for the conduction electrons decreases as the film thickness increases and as the oxygen pressure decreases.
6. The experimental relationship between the mean free path of the conduction electrons and the temperature is in fairly good agreement with the theoretical relation.

Acknowledgements

The authors wish to express appreciation and gratitude to Dr A. Barna, Dr L. Toth and Mr G. Barcza, Research Institute for Technical Physics HAS, Budapest, for their help and fruitful cooperation during the course of this work.

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Received 14 June 1989
and accepted 14 August 1990