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Conduction parameters in chemically deposited thin silver films

C. R. PICHARD, J. -P. DREXLER*, A. J. TOSSER, J. FLECHON*
*Laboratoire d'Electronique and *Laboratoire de Physique des Depots Metalliques, Universite de Nancy 1, B.P. 239, 54506 Vandoeuvre-les-Nancy Cedex, France*

Experimental data related to the resistivity of chemically deposited silver films, and the TCR are interpreted from linearized equations in the framework of the three-dimensional conduction model. The electronic transmission coefficient at the grain boundary, t, and the electronic specular reflection coefficient at the film surface, p, are calculated from both resistivity and TCR measurements; no marked departure is observed. The high value of t agrees with crystallographic data.

1. Introduction

As shown by the pioneering experiments of Freundlich and Steiner [1] thin silver films can be deposited chemically, by reducing silver dioxide (in ammonium solution) with hydroxylamine or hydrazine.

Hydrazine is used because no measurable oxidation of thin silver films is observed at room temperature for a week [2], nor any measurable alteration in the mass of the film [2].

At room temperature the reduction reaction is so fast that the reproducibility in the preparation of thin films is questionable; therefore a complexing salt is introduced in the solution; ethylene diamine tetraacetic (EDTA) is chosen since no reduction effect occurs at room temperature [3, 2].

The reported experimental data are related to thin films deposited at 30° C onto glass substrates and stabilized by ageing for 12 h at 350° C in a vacuum of 10^{-6} torr [2, 4]. The composition of the chemical solution is [2]:

250×10^{-6} m^3	$AgNO_3$	to	40 g ℓ^{-1}
250×10^{-6} m^3	NH_3, H_2O	to	20–21%
250×10^{-6} m^3	EDTA	to	40 g ℓ^{-1}
250×10^{-6} m^3	N_2H_4, H_2SO_4	to	5 g ℓ^{-1}

2. Experimental data and interpretation

Previous reports [2, 4] have shown that the conductivity of an infinitely thick film, σ_g, differs markedly from the bulk conductivity, σ_0, ($\sigma_g = 4.08 \times 10^7\ \Omega^{-1}\ m^{-1}$ [4], $\sigma_0 = 6.289 \times 10^7\ \Omega^{-1}\ m^{-1}$ [5]) and that the Hall mobility takes values very close to those of the conductivity at any temperature between − 100° C and 300° C [6]. It can be concluded then that the films exhibit a polycrystalline structure and do not contain impurities. Consequently the interpretation [4] of experimental data relating to film resistivity, ρ_f, and its temperature coefficient of resistivity (TCR), β_f, in terms of the Fuchs–Sondheimer conduction model, the F–S model, must be re-examined in the framework of a conduction model for polycrystalline films.

Linearized expressions for ρ_f/ρ_g and β_f/β_g (where the subscript g refers to an infinitely thick film) can be derived from several theoretical models, such as the effective F–S model [7] the three-dimensional model [8] and the isotropic grain-boundary scattering model [9]; these analytical linearized equations [9–12] have a form similar to the asymptotic equations empirically proposed by some authors [13–15].

For the sake of simplicity we use the following equations [9]:

$$d\rho_f \approx d\rho_g + \tfrac{3}{8}\rho_0\lambda_0 \ln\frac{1}{p};\ d > 80\,\text{nm} \quad (1)$$

and

$$d\beta_f^{-1} \approx d\beta_g^{-1} + \tfrac{3}{8}\beta_0^{-1}\lambda_0 \ln\frac{1}{p};\ d > 80\,\text{nm} \quad (2)$$

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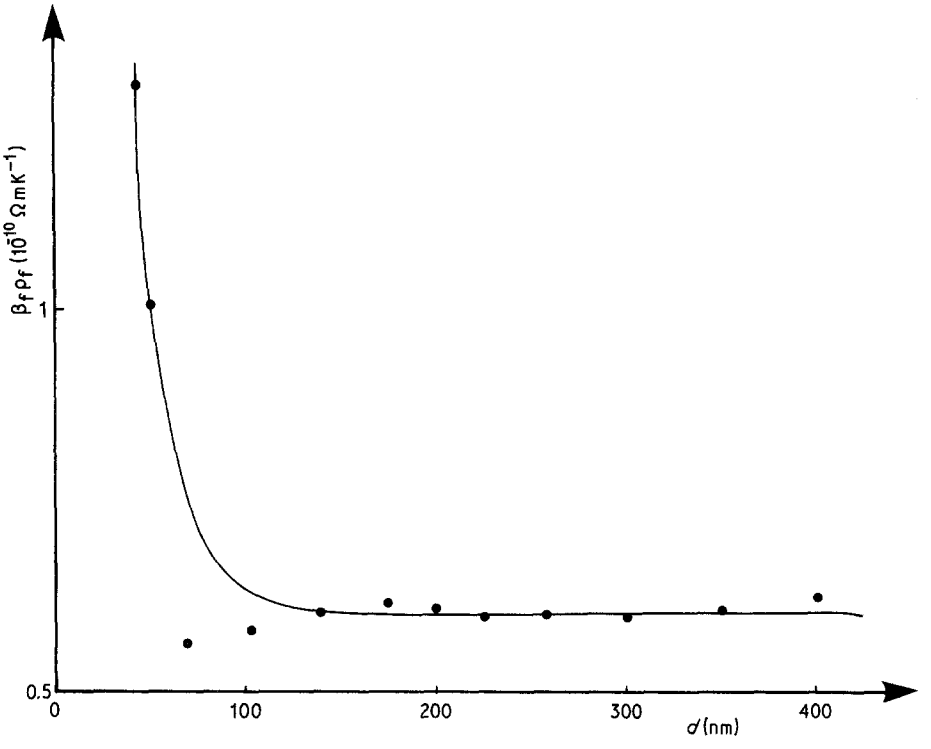

Figure 1 Plot of $\beta_f \rho_f$ against d, the film thickness.

where d is the film thickness, λ_0 is the electron mean free path in the bulk material and p is the electron specular reflection coefficient at film surface, as initially defined by Sondheimer [16].

The above equations clearly suggest that:

$$\rho_f \beta_f = \rho_g \beta_g; \quad d > 80\,\text{nm}$$

in good agreement with experimental data, as shown in Fig. 1.

The ratios ρ_g/ρ_0 and β_g/β_0 can be calculated in the framework of either the Mayadas–Shatzkes conduction model [17] (and derived models [10, 18–22]) or the three-dimensional model [11] and derived models [23, 24].

For the sake of consistency the isotropic grain boundary scattering model [9] is retained. Moreover, it has been previously shown [25, 26] that the roughness of grain boundaries in the multidimensional statistical models [25, 8, 9, 23] is defined in a more physical manner than in the Mayadas–Shatzkes model [17].

The reduced resistivity and TCR or infinitely thick polycrystalline film is then given by [9]:

$$\rho_g/\rho_0 = 1 + 1.45\, D_g^{-1}\, \lambda_0 \ln \frac{1}{t}, \qquad (3)$$

and

$$\beta_g/\beta_0 = (\rho_g/\rho_0)^{-1}, \qquad (4)$$

where D_g is the average grain size and t the electronic transmission coefficient at grain boundary.

It is clear that Equation 3 involves the existence of a grain of cubic shape. However it has been recently shown [37] that a marked departure from the cubic shape in a direction induces slight variations in the resistivity.

In the experimental conditions described above, it has been observed that the film becomes continuous when the thickness exceeds 50 nm [2, 27]; therefore it is assumed that $D_g = 50$ nm; it must not be forgotten that the film growth due to chemical deposition is markedly determined [2, 28] by the temperature and the composition of the chemical medium, so that the average grain size can vary markedly with the composition of chemical medium.

As shown in Figs. 2 and 3, linear laws are obtained by plotting $d\rho_f$ and $d\beta_f^{-1}$ against d.

We can then calculate:

$$\rho_g = 2.45 \times 10^{-8}\ \Omega\,\text{m}$$

$$\beta_g = 2.48 \times 10^{-3}\ \text{K}^{-1},$$

hence:

$$\beta_g \rho_g = 6.076 \times 10^{-11}\ \Omega\,\text{m}\,\text{K}^{-1},$$

and, from the values cited in the literature [5]:

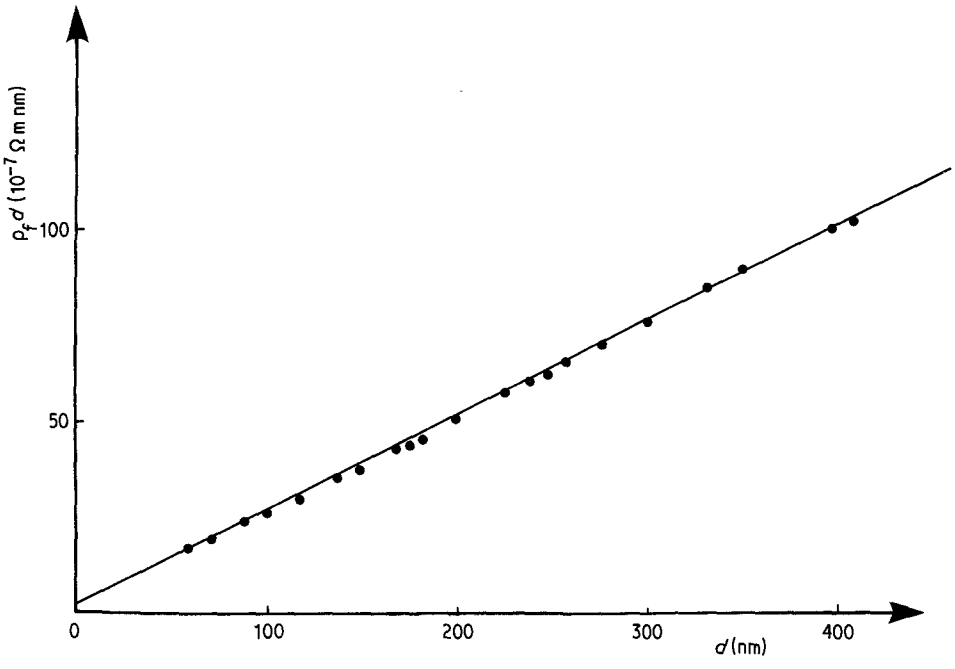

Figure 2 Plot of $d\,\rho_f$ against d, the film thickness.

$$\beta_0\rho_0 = 6.042\ 10^{-11}\ \Omega\,\mathrm{m\,K^{-1}}.$$

As attempted:

$$\beta_g\rho_g \approx \beta_0\rho_0$$

in good agreement with Equation 4.

From the slopes of the linear plots of ρ_f/ρ_g and β_g/β_f against d^{-1}, experimental values of p are obtained, assuming that ρ_0 and λ_0 take the values cited in the literature [5], i.e. $\rho_0 = 1.59\ 10^{-8}\ \Omega\,\mathrm{m}$ and $\lambda_0 = 59\,\mathrm{nm}$.

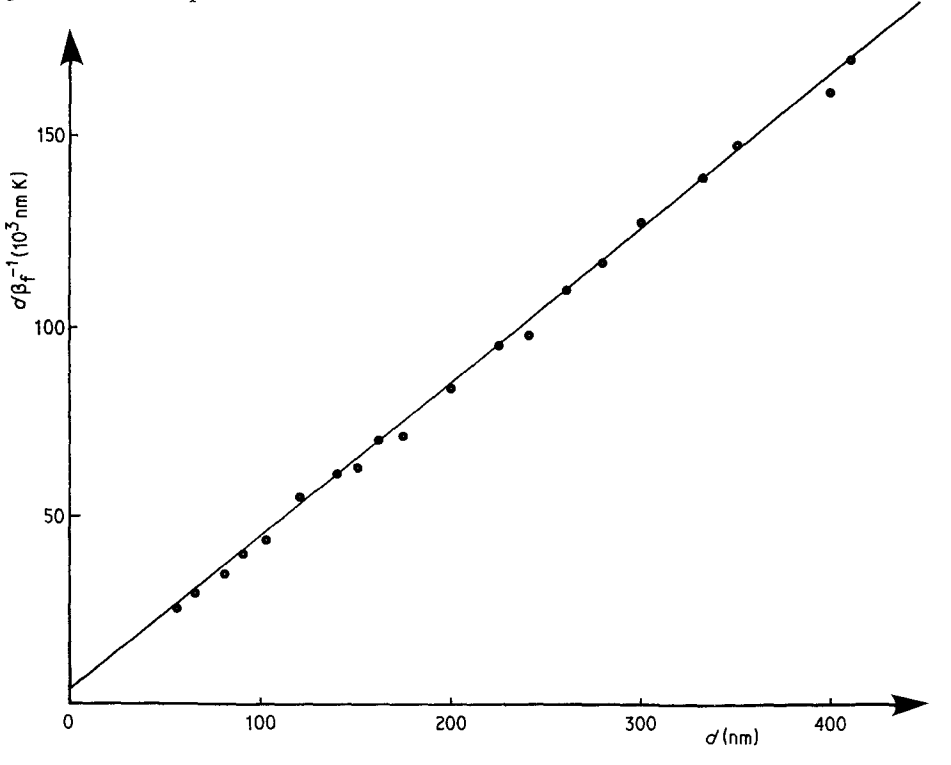

Figure 3 Plot of $d\,\beta_f^{-1}$ against d, the film thickness.

From

$$\rho_f/\rho_g,\ p_{exp} = 0.49$$

and from

$$\beta_g/\beta_f,\ p_{exp} = 0.52.$$

These values are in agreement with those calculated from F–S equations, as attempted since the effective F–S equations [7, 10] can give alternative expressions for three dimensional linearized equations when the grain boundary scattering is not too marked [11].

From equations 3 and 4, we then deduce:

$$t|_{exp} \approx 0.73$$

The high values of t is not surprising since a crystallographic study from electronic diffraction micrographs allows the accurate identification of the 111, 200, 220, 222, 400, 331, 420, 422 rays (deviation in the calculated intereticular distances d_{hkl} from the theocritical values is less than 1%) [2].

3. Discussion

In order to show that these chemically prepared polycrystalline films are not identical to those obtained by other procedures, some features must be emphasized.

1. Discontinuous films are obtained up to large thickness (not less than 30 nm for silver films [2]).

2. The deposition rate does not vary markedly with the nature of the substrate, glass slide or metallic layer, and no catalytic effect of the deposited grains is observed [2, 27]; moreover no measurable variations in the deposition rates are observed for a series of substrates simultaneously immersed in the chemical solution; these features suggest that the metal particles to be deposited appear in the volume of the chemical solution [2, 29].

This assumption is sustained by the fact that a limit to the film thickness exists, directly related to the p_H (see Table I) [2].

TABLE I Limit of the film thickness, d_{lim}, for various chemical conditions

p_H	volume NH_3, H_2O at 20–21% (cm^3)	d_{lim} (nm)
≈ 9.5	25	≈ 10
9.8	50	≈ 30
10.4	125	> 200
11.0	250	> 300

3. The fact that the Hall coefficient of these films takes a constant value ($-12 \times 10^{-11}\ m^3\ C^{-1}$) [6] which differs from that of the bulk material ($-10.4 \times 10^{-11}\ m^3\ C^{-1}$) cannot be attributed to the structure, since recent works [30, 31] have shown that size effects in Hall coefficient can be observed at very low thickness only. Since no impurity effect alters the validity of the relation "Hall mobility = electrical mobility" [6], we then assume that the number of either the atoms per unit volume, N_a, or the free electrons per atom, n, differs from that of the bulk material. The first prediction is in agreement with the fact that defects can be observed in the micrographs [2]. Moreover it seems more suitable to assume that n is altered since the observed unusual [32] large variations in the Hall coefficient with temperature [6] can be justified only by a marked unusual thermal dependence of n, as previously shown [33].

Finally, the fact that the polycrystalline silver films have been obtained by ageing amorphous layers deposited chemically must be connected directly with some unusual aspects of electrical properties. A crystallographic model for such films would be necessary for a complete interpretation of the properties. The models [34–36] used for metallic glasses could give some insight. However, in our opinion, the variety in the interpretations is too marked to actually suggest any modification suitable for interpreting the data related to chemically deposited silver films.

4. Conclusion

Experimental data related to the electrical conductivity of thin silver films, chemically deposited, can be conveniently interpreted from a three-dimensional statistical model for polycrystalline films; physically consistent values for the grain transmission coefficient and the electron specular reflection coefficient at film surface are thus obtained.

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