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SIZE AND GRAIN-BOUNDARY EFFECTS IN THE ELECTRICAL CONDUCTIVITY OF THIN MONOCRYSTALLINE FILMS

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By assuming that the scattering processes from other sources than grain-boundaries can be described by a single relaxation time τ^* and then by solving a Boltzmann equation in which grain-boundary scattering is accounted for, we have obtained an analytical expression for the thin monocrystalline film conductivity in terms of the reduced thickness k and the grain-boundary reflection coefficient r. Numerical tables are given to show the agreement of the above expression with the Mayadas-Shatzkes expression.

1. INTRODUCTION

Several investigators[1–8] have reported both experimental results[1–5] and theoretical expressions[6–8] for the thickness dependence of the electrical resistivity of polycrystalline and monocrystalline metallic films on the basis of the Mayadas–Shatzkes model (M–S model).[6,7] However this theory leads to a rather complicated expression which involves the use of a computer to obtain numerical solutions. The purpose of this paper is to derive an analytical expression of the thin monocrystalline film resistivity by assuming that in such films the transition probability of a carrier in state k being scattered to a state k′ by all types of scatterers other than the grain-boundaries, can be expressed in term of a relaxation time τ^*.

Let us recall that in monocrystalline metallic films, carriers suffer scattering from phonons and point defects (background scattering), external surfaces and grain-boundaries and that, in the M–S model the operative grain-boundaries can be represented by a series of randomly spaced partially reflecting planes, perpendicular to the electric field $\mathbf{E}_x$ whose normal lies in the substrate surface.

Mayadas and Shatzkes have solved the general problem by following the lines of the Fuchs-Sondheimer (F–S) calculation;[9,10] in particular they have introduced into the Boltzmann equation an effective relaxation time τ_{eff} which takes into account the background and grain-boundaries scattering processes occuring simultaneously within the film.

Then the total film conductivity σ_F is expressed as;

$$\sigma_F = \sigma_o\ [f(\alpha) - A^*] \tag{1}$$

where σ_o is the bulk conductivity (i.e. the conductivity of an infinitely thick monocrystalline film) and where A^* is given by

$$A^* = \frac{6(1-p)}{\pi\ \ k}\int_0^{\pi/2} d\phi \int_1^{\infty} dt\ \frac{\cos^2\phi}{H^2(t,\phi)}\left(\frac{1}{t^3} - \frac{1}{t^5}\right)\cdot \frac{1 - \exp\ -ktH(t,\phi)}{1 - p\exp\ -ktH(t,\phi)} \tag{2}$$

$$H(t,\phi) = 1 + \frac{\alpha}{\cos\phi}(1 - \frac{1}{t^2})^{-1/2} \tag{3}$$

and where $f(\alpha)$ is given by

$$f(\alpha) = \frac{\sigma_g}{\sigma_o} = 1 - \frac{3}{2}\alpha + 3\alpha^2 - 3\alpha^3\, ln(1 + \frac{1}{\alpha}) \tag{4}$$

k is the ratio between film thickness a and bulk mean free path ℓ_o (i.e. the reduced thickness) and σ_g is the conductivity as modified by grain-boundary scattering.

The parameter α is related to the bulk mean free path ℓ_o, average grain diameter a_g and "grain-boundary reflection coefficient" r by Eq. (5)

$$\alpha = \frac{\ell_o}{a_g} \frac{r}{1-r} \qquad (5)$$

In monocrystalline films the average grain diameter a_g is found to be equal to the film thickness a; from a simplistic point of view the contributions of grain-boundaries or external surfaces to the total film resistivity become comparable at this point. Consequently, in this paper we propose an analysis which consists of superimposing the grain boundaries effect and the F–S effect.

2. EXTERNAL SURFACES SCATTERING (F–S EFFECT)

The F–S theory is based upon the assumptions of a free electron, isotropic bulk relaxation time τ_o and a boundary condition for electronic distribution function which states that a fraction p of electrons is specularly reflected from both surfaces of the film,[10] the remainder being diffusely scattered. The film conductivity σ_F^* (without grain boundaries effect) is given by

$$\sigma_F^* = \sigma_o [1 - A(k)] \qquad (6)$$

where $A(k)$ is a function of the reduced thickness k which is generally expressed[11] as

$$A(k) = \frac{3}{2k}(1-p) \int_1^\infty \left(\frac{1}{t^3} - \frac{1}{t^5}\right) \frac{1 - e^{-kt}}{1 - p.e^{-kt}} dt \qquad (7)$$

The $1 - A(k)$ function has been tabulated for different values of the specularity parameter p by several authors.[10,12,13]

It is assumed that we may define a total relaxation time τ^* for the simultaneous background and external surface scattering effects so that the film conductivity σ_F can be rewritten in the form

$$\sigma_F^* = \frac{ne^2}{m} \tau^* \qquad (8)$$

Thus from Eq. (6) we derive

$$\tau^* = \tau_o [1 - A(k)] \qquad (9)$$

3. TOTAL FILM CONDUCTIVITY

To find the total film conductivity in the presence of grain boundaries we follow the lines of the M–S analysis[6,7] and we suppose that the grain-boundaries are represented by N planes whose positions x are distributed according to a Gaussian probability distribution with a standard deviation s.

With the assumption that the scattering from other sources (i.e. phonons, point defects and external surfaces) can be described by a relaxation time constant τ^*, the Boltzmann equation takes the form

$$eE_x v_x \frac{\partial f_o(\mathbf{k})}{\partial \epsilon} = \int p_{\mathbf{k}}^{\mathbf{k}'} [\Phi(\mathbf{k}) - \Phi(\mathbf{k}')]\, d\mathbf{k} + \frac{\Phi(\mathbf{k})}{\tau^*} \qquad (10)$$

where $p_{\mathbf{k}}^{\mathbf{k}'}$ is the transition probability for an electron in state $\mathbf{k}$ to be scattered into state $\mathbf{k}'$ by the grain-boundaries. The quantity $\Phi(\mathbf{k})$, given by $\Phi(\mathbf{k}) = f(\mathbf{k}) - f_o(\mathbf{k})$ measures the deviation of the distribution function $f(\mathbf{k})$ from its equilibrium value $f_o(\mathbf{k})$.

After a treatment identical to the M–S calculation which consists in considering the potential $V(x)$ lying at the position x_n of the *nth* plane as a perturbation on the free electron Hamiltonian, the transition probability $p_{\mathbf{k}}^{\mathbf{k}'}$ becomes:[7]

$$p_{\mathbf{k}}^{\mathbf{k}'} = F(|k_x|)\delta(k_t - k_{t'})\delta(k_x + k_{x'}) \qquad (11)$$

where k_t is the component of $\mathbf{k}$ in the y,z plane and

$$F(|k_x|) = \frac{\alpha}{2\tau_o} \frac{k_F}{|k_x|} \frac{1 - e^{-4k_x^2 s^2}}{1 + e^{-4k_x^2 s^2} - 2e^{-k_x^2 s^2} \cdot \cos 2k_x d} \qquad (12)$$

Note that the bulk relaxation time τ_o has been artificially introduced in Eq. (12) in a such way that the parameter α is related to the bulk mean free path (Eq. 5).

Under the assumptions that the interplanar spacing d can be identified with the average grain diameter a_g and that $k_F^2 s^2 \gg 1$, the function $F(|k_x|)$ reduces to

$$F(|k_x|) = \frac{\alpha}{2\tau_o} \frac{k_F}{|k_x|} = \frac{\alpha}{2\tau_o |\cos\theta|} \qquad (13)$$

where k_x is the x-component of the Fermi wave vector k_F.

The Boltzmann equation is now:[7]

$$\Phi(\mathrm{k}) = \tau_{\mathrm{eff}}\, eE_x v_x \frac{\partial f_o}{\partial \epsilon} \tag{14}$$

where

$$\frac{1}{\tau_{\mathrm{eff}}} = \frac{1}{\tau^*} + 2F(|k_x|) \tag{15}$$

and ϵ the electron energy.

And the total film conductivity σ_F is found to be

$$\sigma_F = \frac{e^2}{4\pi^3}\int \frac{\tau_{\mathrm{eff}}\, v_x^2}{|\mathrm{grad}_k \epsilon|} dS_{\mathrm{Fermi}} = \frac{3}{2}\frac{\sigma_o}{\tau_o}\int_0^{\pi} \tau_{\mathrm{eff}} \cos^2\theta \sin\theta d\theta \tag{16}$$

and can be rewritten in the form

$$\sigma_F = \frac{3}{2}\frac{\sigma_o}{\tau_o}\int_0^{\pi} \cos^2\theta \cdot \tau_o \cdot \frac{1}{\dfrac{1}{1-A(k)} + \dfrac{\alpha}{|\cos\theta|}} \sin\theta d\theta \tag{17}$$

that leads to

$$\sigma_F/\sigma_o = [1 - A(k)] \cdot f[B(k)] \tag{18}$$

where

$$f[B(k)] = 1 - \frac{3}{2}B(k) + 3B^2(k) - 3B^3(k)ln[1 + \frac{1}{B(k)}] \tag{19}$$

and

$$B(k) = \alpha\, [1 - A(k)] \tag{20}$$

In the case of monocrystalline films, the function $B(k)$ depends on the reduced thickness k and the grain-boundary reflection coefficient r. As the $1 - A(k)$ function has been intensively tabulated earlier, the total film conductivity σ_F from the analytical expression Eq. (18) can be evaluated without using a digital computer as previously reported by several authors.[7,14]

4. DISCUSSION

Let us note that the new formulation proposed (Eq. 18) satisfies essential qualitative physical requirements e.g.

1) When the surface scattering is entirely specular (i.e. $p = 1$) Eq. (18) can be rewritten in the form

$$\sigma_F/\sigma_o\Big]_{p=1} = 1 - \frac{3}{2}\alpha + 3\alpha^2 - 3\alpha^3 ln(1 + \frac{1}{\alpha})$$

and the conductivity σ_F coincides with the grain-boundary conductivity σ_g (Eq. 4).

2) When the grain-boundary reflection coefficient r approaches zero, Eq. (18) reduces to

$$\sigma_F/\sigma_o\Big]_{r \to o} = 1 - A(k)$$

and the value of the total film conductivity becomes identical to that of the F–S film conductivity σ_F^* as expected.

In the case of monocrystalline films, numerical values of the resistivity ratio ρ_F/ρ_o (Eq. 18) have been calculated for different values of the specularity parameter p and grain-boundary reflection coefficient r; the results of the relaxation time method (Eq. 18) are compared with those of the M-S theory (as tabulated by Mola and Heras,[14] Eq. 1).

Tables I and II show that, the greater the values of the parameters r and p, the larger the range of applicability of Eq. 18. For example, in the case of diffuse scattering on external surfaces ($p = 0$) we obtain a deviation less than 3% for k between 0.2 and 10 with $r = 0.1$ and for k between 0.06 and 10 with $r = 0.62$.

From examination of table II it follows that the percentage deviations from the M-S function decrease with increasing values of the specularity parameter p.

We have previously proposed an approximate expression of the resistivity ratio ρ_F/ρ_o that deviates by less than 6% in the 0.01 to 2 k-range, 0 to 0.5 p-range and 0.1 to 0.62 r-range;[21] this expression introduced a function $m(r)$ which has been tabulated for different values of the grain-boundary reflection coefficient r ($0.1 \leqslant r \leqslant 0.62$).

Recently, Chaudhuri and Pal[22] have analyzed their experimental data in the light of the M-S theory and have obtained a value of the grain-boundary reflection coefficient r equal to 0.005. When the reflection coefficient r approaches zero the function $m(r)$ is not easy to evaluate; on the contrary, in the present model, the analytical Eq. 19 allows the calculation of the thin monocrystalline film resistivity, even for very low values of r, without any tabulation.

Hence, we will attempt, in a future paper, to derive from Eq. 19 an analytical expression of the thin monocrystalline film t.c.r which is valid in a large r-range and reduces to the F–S equation when r becomes equal to zero.

5. CONCLUSION

It is now well established[4,15-20] that thin metal films thicker than 100 Å (i.e k generally greater than 0.5 at room temperature) may be regarded as continuous; furthermore in the range $0.5 \leq k \leq 10$ Eq. 18 deviates by only 3% in the case of diffuse scattering on external surfaces and by only 1% when a fraction p of electrons is specularly scattered from external surfaces ($p = 0.5$). It thus appears that the procedure

TABLE I
Thin monocrystalline films: comparison of the values of the resistivity ratio ρ_F/ρ_0 as given by the equations indicated for the case of diffuse scattering on external surfaces: $p = 0$.

k	$r = 0.1$ Equation 18	Equation 1	$r = 0.22$ Equation 18	Equation 1	$r = 0.42$ Equation 18	Equation 1	$r = 0.62$ Equation 18	Equation 1
0.01	41.9005	54.8700	64.8423	81.0040	124.0639	139.7323	245.1942	257.4954
0.02	23.1831	28.1572	34.7980	41.0842	64.4468	70.3962	125.5034	129.2758
0.04	13.0317	14.7706	18.8605	21.1111	33.7082	35.7139	64.0170	65.1412
0.06	9.4225	10.2924	13.3185	14.4523	23.2293	24.1581	43.4434	43.7736
0.08	7.5376	8.0442	10.4659	11.1224	17.9047	18.3841	33.0730	33.0978
0.1	6.3724	6.6870	8.7170	9.1207	14.6755	14.9164	26.8126	26.6870
0.2	4.0303	3.9367	5.2133	5.1055	8.2065	7.9802	14.2861	13.8682
0.4	2.5310	2.5127	3.1272	3.0775	4.6318	4.5070	7.6790	7.4578
0.6	2.0391	2.0186	2.4393	2.3917	3.4473	3.3459	5.4839	5.3194
0.8	1.7829	1.7652	2.0844	2.0451	2.8437	2.7638	4.3748	4.2492
1	1.4624	1.5107	1.8673	1.8356	2.4772	2.4137	3.7049	3.6064
2	1.3028	1.2972	1.4257	1.4134	1.7352	1.7108	2.3555	2.3174
4	1.1444	1.1430	1.2067	1.2034	1.3641	1.3574	1.6792	1.6679
6	1.0942	1.0936	1.1360	1.1347	1.2421	1.2391	1.4544	1.4492
8	1.0698	1.0696	1.1013	1.1006	1.1814	1.1798	1.3420	1.3390
10	1.0555	1.0554	1.0808	1.0803	1.1451	1.1441	1.2744	1.2725

TABLE II
Thin monocrystalline films: comparison of the values of the resistivity ratio ρ_F/ρ_0 as given by the equations indicated for the case of partially specular scattering on external surfaces: $p = 0.5$

k	$r = 0.1$ Equation 18	Equation 1	$r = 0.22$ Equation 18	Equation 1	$r = 0.42$ Equation 18	Equation 1	$r = 0.62$ Equation 18	Equation 1
0.01	27.1537	32.8003	50.0748	57.0046	109.0969	116.2411	230.1133	236.6560
0.02	14.8837	17.0153	26.3670	29.0588	59.3451	58.6566	115.7219	118.8614
0.04	8.4082	9.1070	14.1644	15.0774	28.9403	29.8525	58.8594	59.9413
0.06	6.1314	6.4629	9.9810	10.4166	19.7834	20.2553	40.0203	40.3109
0.08	4.9575	5.1364	7.8484	8.0863	15.2473	15.4599	30.3863	30.5030
0.1	4.2325	4.3361	6.5495	6.6857	12.4727	12.5799	24.5863	24.6133
0.2	2.7148	2.7176	3.8821	3.8778	6.8535	6.8190	12.5799	12.8364
0.4	1.8967	1.8846	2.4870	2.4619	3.9817	3.9338	6.9851	6.9463
0.6	1.6079	1.5978	2.0047	1.9840	3.0066	2.9687	5.0368	4.9810
0.8	1.4591	1.4513	1.7587	1.7427	2.5138	2.4844	4.0402	3.9971
1	1.3683	1.3622	1.6093	1.5967	2.2160	2.1928	3.4401	3.4060
2	1.1896	1.1811	1.3047	1.3011	1.6143	1.6053	2.2261	2.2194
4	1.0903	1.0898	1.1526	1.1513	1.3098	1.3071	1.6209	1.6199
6	1.0531	1.0596	1.1016	1.1010	1.2075	1.2063	1.4197	1.4175
8	1.0446	1.0446	1.0761	1.0759	1.1561	1.1555	1.3166	1.3154
10	1.0357	1.0356	1.0609	1.0607	1.1253	1.1243	1.2545	1.2536

proposed for analyzing the monocrystalline film resistivity is suitable and we obtain a simple expression which is easy to evaluate over large ranges of the r and p parameters and allows a direct comparison of the theoretical results with experimental data.

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