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Influence of grain boundary scattering on the electrical properties of platinum nanofilms

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The electrical conductivity and temperature coefficient of resistance of polycrystalline platinum nanofilms have been investigated experimentally and theoretically. The results show that these electrical properties have been greatly reduced mainly by grain boundary scattering. By applying the theory of Mayadas and co-workers [Appl. Phys. Lett. **14**, 345 (1969); Phys. Rev. B **1**, 1382 (1970)] to predict the electrical conductivity and temperature coefficient of resistance with the same reflection coefficient, however, obvious discrepancies have been found. These discrepancies indicate that Drude's relation for bulk metals cannot be applied directly in the nanosized grain interior of polycrystalline metallic films. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2338885]

Metallic thin films have been widely used in modern integrated circuits. Studies on the electrical conductivity of these films have attracted much attention for the significant reduction from the bulk values. Such a decrease was mainly attributed to surface scattering, which was first studied by Thomson,[1] followed by Fuchs[2] and Sondheimer,[3] and grain boundary scattering, which was initially researched by Mayadas and co-workers.[4,5] Since the above two mechanisms usually exist in polycrystalline thin films simultaneously, it seems to be very difficult to estimate the relative magnitudes.

Sambles[6] pointed out that the temperature-dependent resistivity needs to be analyzed in order to distinguish grain boundary scattering from surface scattering. If grain boundary scattering is the dominating factor, the temperature-dependent part of the thin film resistivity is almost identical to that of bulk material, while a deviation will be expected if surface scattering becomes more important. Such a criterion can be substantiated by recent studies on the electrical conductivity of monocrystalline gold films,[7] as well as polycrystalline copper wires.[8] Devries[9] gave an interpretation about this criterion that only electrons within a distance of less than the mean free path (MFP) from the surface can be scattered at the surface. Since the MFP depends on the temperature, surface scattering tends to affect the temperature-dependent part of the thin film resistivity. For grain boundary scattering, however, such an argument is not valid since the electrons will have to pass through the grain boundaries independent of temperature in order to produce electrical conduction. Therefore, the temperature-dependent part of the thin film resistivity is considered to be identical to that of the bulk material. It should be noted that the mean grain size in the polycrystalline copper wires[8] tends to be much larger than the corresponding electron MFP at room temperature. It is still an open question, however, whether the above criterion is valid for those metallic films with the mean grain size comparable to or much less than the MFP.

Studies on the electrical properties of platinum nanofilms have been carried out in the present work to find out the main mechanism leading to the greatly reduced electrical conductivity and temperature coefficient of resistance (TCR) and to check whether the above criterion is still valid for those very fine grained metallic nanofilms. Our platinum nanofilms are fabricated by electron beam physical vapor deposition and the corresponding fabrication processes can be referred in Refs. 10 and 11. The electrical conductivity of the nanofilms is measured by a direct electrical heating method[10,11] at a temperature ranging from 80 to 300 K, from which the corresponding TCR can be readily calculated. The advantage of the present method is that the effect of the substrate as well as that of the temperature rise caused by the Joule heating on the measured conductivity can be eliminated.

The measured electrical conductivity and TCR of the nanofilms as well as the corresponding bulk values at 300 K are shown in Fig. 1. It is found that these electrical properties of the nanofilms have been greatly reduced. In consideration that the nanofilm thickness is comparable to the electron MFP of about 23 nm for platinum at 300 K, the Fuchs and Sondheimer (FS) theory is applied to predict the thickness-dependent electrical conductivity[2,3] as well as the thickness-dependent TCR (Ref. 12) to estimate the effects of the surface scattering as expressed by

$$\frac{\sigma}{\sigma_0} = 1 - \frac{3(1-p)}{2k}\int_1^{\infty}\left(\frac{1}{t^3} - \frac{1}{t^5}\right)\frac{1-\exp(-kt)}{1-p\exp(-kt)}dt, \qquad (1)$$

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$$\frac{\beta}{\beta_0}=\frac{1-(3/4k)(1-e^{-k})+(k^3/8)E_1(k)-(1/4-k/8+k^2/4)e^{-k}}{1-(3/8k)(1-e^{-k})+(3/4)(k-k^3/12)E_1(k)-(5/8+k/16-k^2/16)e^{-k}}, \tag{2}$$

where σ and σ_0 represent the thin film and bulk electrical conductivities, respectively; β and β_0 represent the thin film and bulk TCRs, respectively; k is the ratio between the film thickness δ and the bulk electron MFP l_0; p is the probability for an electron to be specularly reflected from the film surface, which ranges from 0 to 1; and $E_1(k)=\int_k^\infty (e^{-t}/t)dt$. In the present calculations, p was taken to be zero, which means a completely diffusive scattering at the surface and hence represents the lowest values that the FS theory can predict. The calculated σ and β are also plotted in Fig. 1, from which we can find that the predicted results obviously overestimate the nanofilm electrical properties. It is considered, therefore, that there must be other mechanisms that dominate the great reduction of the electrical conductivity and TCR of the present nanofilms.

X-ray diffraction (XRD) studies show that the mean grain size d, as shown in Fig. 2, tends to increase with increasing the thickness. The unexpected low mean grain size of the 62.0–63.0 nm thick nanofilms is considered to be caused by the increased deposition rate from 0.08 to 0.10–0.11 nm/s. It is found that the mean grain size is much smaller than the corresponding thickness δ, as well as the electron MFP of platinum at 300 K. Under such a condition, grain boundary is supposed to have important influence on the electrical properties. By assuming that the electron scattering on the surface is completely specular ($p=1$), the Mayadas and Shatzkes (MS) theory is applied to study the effects of grain boundaries, which is expressed as

$$\frac{\sigma_g}{\sigma_0}=1-\frac{3}{2}\alpha+3\alpha^2-3\alpha^3\ln\left(1+\frac{1}{\alpha}\right)=F(\alpha), \tag{3}$$

where σ_g represents the electrical conductivity of the polycrystalline films, $\alpha=l_0R/d(1-R)$, and R is the reflection coefficient, which means the probability for a conduction electron to be elastically reflected when striking the grain boundaries. The measured grain-size-dependent electrical conductivity and TCR at 300 K, as well as the predicted values made by the MS theory, are plotted in Fig. 3. It is found that the calculated electrical conductivity agrees well with the measured results if an average reflection coefficient is taken to be 0.80. Such a high electron reflection at the grain boundaries is considered to greatly reduce the electrical conductivity. The individual reflection coefficient for every nanofilm is found to be within the range of 0.67–0.83. It should be noted that the out-of-plane mean grain sizes obtained from XRD studies in the present work are used in the MS theory, while the in-plane values are actually needed. From the inserted micrograph as shown in Fig. 2, which is obtained by the transmission electron microscope (TEM), we can see that the in-plane mean grain size is somewhat less than the corresponding out-of-plane value. Therefore, the reflection coefficient may be overestimated to some extent in consideration that α is the only one combined variable in the MS theory. Fortunately, this does not affect the forthcoming analyses and conclusions.

After some deduction, Tellier and Tosser[13] obtained an expression to calculated the TCR of polycrystalline films as

$$\frac{\beta_g}{\beta_0}=1+\frac{G(\alpha)}{F(\alpha)}, \tag{4}$$

where β_g represents the TCR of the polycrystalline films. $G(\alpha)$ is expressed as

$$G(\alpha)=-\frac{3}{2}\alpha+6\alpha^2+\frac{3\alpha^3}{1+\alpha}-9\alpha^3\ln\left(1+\frac{1}{\alpha}\right). \tag{5}$$

The above formula has ignored the effect of surface scattering, i.e., $p=1$. By applying the same average reflection coefficient as that obtained from the electrical conductivity, i.e., $R=0.80$, to predict the TCR, however, the calculated results are found to be much underestimated compared with those experimental data, as shown in Fig. 3. With a smaller value, i.e., $R=0.57$, the calculated results agree well with the measured ones. When the individual reflection coefficients, e.g.,

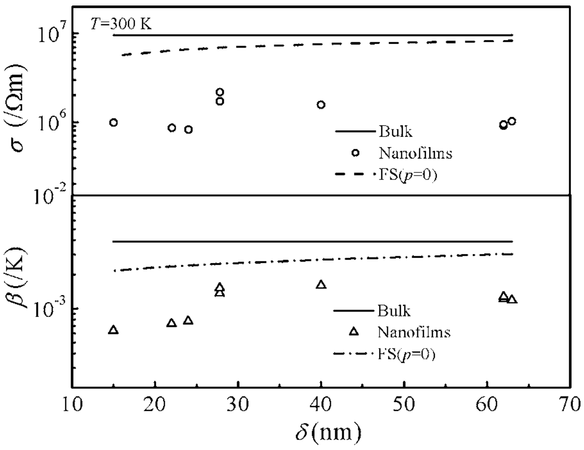

FIG. 1. Variations of the electrical conductivity and TCR along the nanofilm thickness at 300 K.

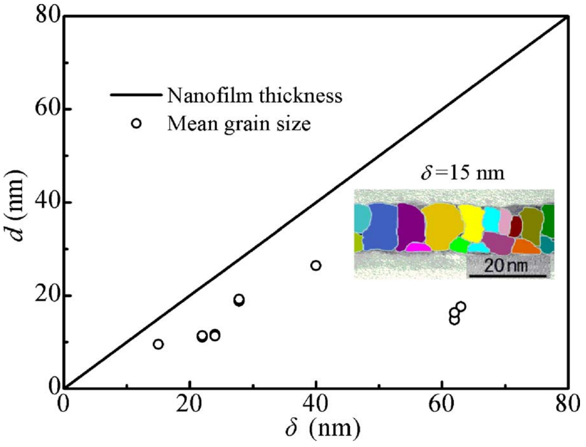

FIG. 2. (Color online) Variations of the out-of-plane mean grain size obtained from XRD along the nanofilm thickness. The inset shows a TEM micrograph of the nanofilm with the thickness of 15 nm.

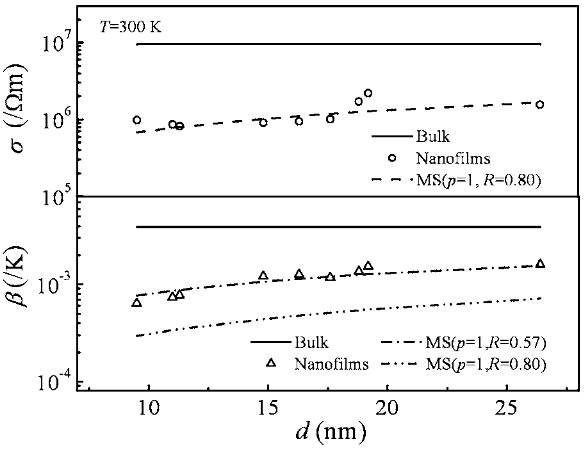

FIG. 3. Variations of the electrical conductivity and TCR along the mean grain size at 300 K.

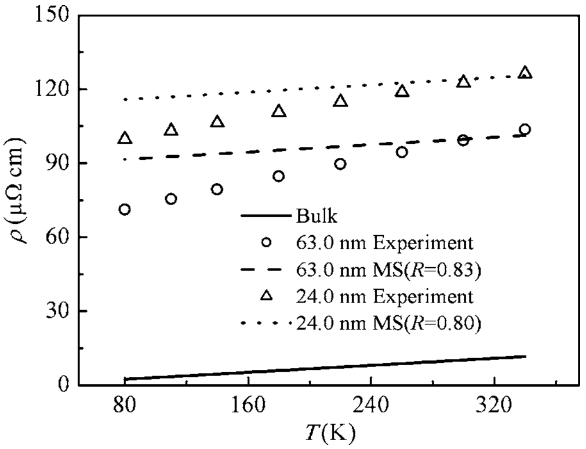

FIG. 4. Variations of the resistivity along the temperature ranging from 80 to 340 K.

$R=0.80$ for the 24 nm film and $R=0.83$ for the 63 nm film, are applied to predict the temperature-dependent resistivity, another discrepancy is also found. The calculated curves of the temperature-dependent resistivity are parallel to that of the bulk value as expected,[8] but rather flatter compared with those of the experimental results, as shown in Fig. 4. These results cannot be understood at the beginning, since the formula to calculate the TCR as expressed by Eq. (4) is derived from the expression to predict the electrical conductivity as shown in Eq. (3), and the formula to predict temperature-dependent resistivity is just the same one to calculate the grain-size-dependent conductivity. However, several assumptions[13] should be considered in the above derivation and calculation: (1) the reflection coefficient R is temperature independent, (2) the grain size is unaltered, and (3) Drude's relation $\rho_0 l_0=\text{const}$ is still valid, among which ρ_0 represents the background resistivity in the grain interiors and has the same value as that of the bulk material in the MS theory. Since the reflection coefficient and the grain size variations along with the temperature can be ignored,[13] the third assumption has to be reestimated.

In the MS theory, it is assumed that a grain boundary can be represented by a δ-function potential and that the electron states of the pure single crystal can be described well by free-electron states. When solving the linearized Boltzmann equation, an additional assumption was made that background scattering can be described by a relaxation time τ_0 and operates independently from grain boundary scattering. With these assumptions, the MS theory holds that Drude's relation for bulk metallic materials $\rho_0 l_0=\text{const}$ is also applicable in the grain interior of the polycrystalline metallic films. When the grain size is much larger than the MFP,[8] the above assumptions are rather reasonable. When the grain size becomes much smaller than the MFP, however, the electrons' behavior inside the grains is considered to be affected by the grain boundaries, and hence the above assumptions may not be valid anymore. Studies about the effects of the nanoparticle size on the electrical conductivity show a lowering of the effective Debye temperature as the particle size is reduced.[14,15] This was mainly attributed to a phonon softening effect due to the small size of the metal particles. According to the famous Bloch-Grüneisen law, the decrease of the Debye temperature will lead to an increased temperature-dependent resistivity. Therefore, discrepancies will be found if Drude's relation for bulk metallic materials is applied directly for the grain interior of the polycrystalline films.

In summary, the reduced electrical conductivity and TCR for the present polycrystalline platinum nanofilms are mainly dominated by grain boundary scattering. The reflection coefficient of electrons striking the grain boundaries was approximated to be 0.80 for the measured grain-size-dependent electrical conductivity at 300 K. By applying the same reflection coefficient, however, the grain-size-dependent TCR and the variation of the resistivity along the temperature predicted by the MS theory deviate from the measured results. These discrepancies show that Drude's relation for bulk metallic materials may be invalid in the very fine grained metallic films. We attribute the invalidity to the increase of the background resistivity due to the decrease of the effective Debye temperature.

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