Influence of grain boundary scattering on the electrical and thermal conductivities of polycrystalline gold nanofilms

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The electrical and thermal conductivities of polycrystalline gold nanofilms have been measured simultaneously by a direct current heating method, and the measured results are compared with the Mayadas and Shatzkes theory. It is found that the reduced electrical and thermal conductivities of gold nanofilms are strongly dominated by grain boundary scattering. The reflection coefficient of electrons striking the grain boundaries for charge transport is 0.7, which agrees well with a previous scanning tunneling potentiometry study. The reflection coefficient for thermal transport, however, is only 0.25. The Lorenz numbers for the polycrystalline gold nanofilms, which are calculated from the measured electrical and thermal conductivities, are much greater than the value predicted by the Wiedemann-Franz law for the bulk material. The results indicate that the electron scatterings on the grain boundaries impose different influences on the charge and heat transport in the polycrystalline gold nanofilms. A model of effective density of conduction electrons has been utilized to interpret the violation of the Wiedemann-Franz law in polycrystalline gold nanofilms.

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I. INTRODUCTION

Metallic thin films are widely used as interconnects in the semiconductor industry. As the dimensions of these films become comparable to the electron mean free path (MFP), the electrical and thermal conductivities are found to be greatly reduced from the corresponding bulk values. The reduction can usually be attributed to the electron scatterings on the surface,[1,2] as well as on the grain boundaries.[3,4] Gold thin films are usually used to investigate the mechanisms leading to the decrease of the electrical and thermal conductivities. The earlier studies[5–7] show that the decreased electrical conductivity is mainly caused by grain boundary scattering and the reflection coefficient R of electrons striking the grain boundaries ranges from 0.10 to 0.35. The contribution of surface scattering is rather less important and the specular reflection parameter p is usually taken to be 0.5 for gold thin films. Some recent researches, however, have obtained a much higher reflection coefficient R of 0.7–0.9.[8,9] The discrepancies are then found in the above literatures.

The studies on the thermal conductivity of gold thin films are rather scarce compared with those on the electrical conductivity in view of the difficulties in measuring the thermal properties of metallic thin films. By applying the electrical-thermal analogy introduced by the Wiedemann-Franz (WF) law,[10] the researchers[11–13] held that the reflection coefficient R for the electronic thermal transport was the same as that for the charge transport in polycrystalline metallic films. The underlying assumption is that the WF law, which is widely used to relate the electronic thermal conductivity and the electrical conductivity in bulk metals, is still valid in the polycrystalline metallic thin films. Recent theoretical studies on the disordered metals[14] and experimental studies on the copper-oxide superconductor[15] both lead to a violation of the WF law. It is still an open question whether the WF law is valid in the polycrystalline metallic thin films. Zhang *et al.*[16–18] studied the thermal and electrical conductivities of Pt nanofilms simultaneously with a direct current heating method. It is found that the relationship between the thermal and electrical conductivities does not follow the WF law and the Lorenz numbers for the Pt nanofilms are even several times over the bulk value. Choi *et al.*[19] measured the thermal conductivities of polycrystalline Au, Sn, and Mo films with the ac calorimetric method, and then compared them with the corresponding electrical conductivities obtained by the four-probe technique. The results show that the variation of thermal and electrical conductivities in the case of Au and Sn films follows the WF law, while the thermal conductivity drop in the Mo film is found to be much smaller than the electrical conductivity drop and hence leads to a violation of the WF law. It should be noted that the thicknesses of the Au and Sn films are $1-2$ μm and the mean grain sizes are approximately 200–2000 nm. These dimensions are much larger than the corresponding electron MFP. We consider that this makes the obtained thermal and electrical conductivities very close to the corresponding bulk values in Ref. 19 and then the WF law is still valid in these metallic thin films. It is a pity that the information about the Mo film microstructure has not been provided in detail. The slight thermal conductivity drop in the Mo film was attributed to the contribution of the phonon heat transfer.[19] Situations are quite different in the Pt nanofilms.[18] The mean grain sizes in the Pt films are

TABLE I. The dimensions of the fabricated gold nanofilms.

Nanofilm samples	(a)	(b)	(c)	(d)	(e)
Thickness δ [nm]	21.0	21.0	23.0	23.0	37.0
Width w [nm]	471.6	537.0	450.8	455.2	556.8
Length l [μm]	5.53	5.50	5.46	5.62	5.43

about 20.0 nm, which are comparable to the electron MFP. The invalidity of the WF law was attributed to the effect of the grain boundary, but the mechanism is not very clear yet.

In this paper we study the electrical and thermal conductivities of polycrystalline Au films with the thickness of 21.0–37.0 nm. The electrical and thermal conductivities are measured simultaneously by a direct current heating method. The experimental results are compared with the Mayadas and Shatzkes (MS) theory[3,4] to find out the reflection coefficient R not only for the charge transport but also for the thermal transport. With the obtained electrical and thermal conductivities, it is ready to find out whether the WF law is valid in the polycrystalline gold nanofilms, and the underlying mechanisms leading to the violation of the law are further discussed.

II. EXPERIMENT

In order to measure the electrical and thermal conductivities simultaneously with the direct current heating method, the Au nanofilms are required to be suspended from the substrate. The nanofilm fabrication method includes electron beam lithography, electron beam-physical vapor deposition (EB-PVD) and isotropic/anisotropic etching techniques. The corresponding fabrication processes in detail can be found in Ref. 18 and one different step is that the Cr film with 5.0 nm in thickness is used for adhesion instead of Ti film. The dimensions of the fabricated Au nanofilms have been listed in Table I. The microstructure of the Au nanofilms has been investigated by the x-ray diffraction (XRD). It is found that the nanofilms are polycrystalline and the out-of-plane mean grain size obtained from the XRD studies tends to increase with increasing the thickness, as shown in Fig. 1. Since the thicknesses of the studied nanofilms are below 40.0 nm, the out-of-plane mean grain sizes are comparable to the corresponding thicknesses. The investigations made by the transmission electron microscope (TEM) (Ref. 5) and atomic force microscope (AFM) (Ref. 13) show that the in-plane mean grain size approximates to the corresponding thickness as the thickness is about 30.0 nm for gold thin films. In the following calculations, therefore, we take the in-plane mean grain size to be the corresponding thickness. It should be noted that the effects of the substrate on the measured electrical and thermal conductivities can be neglected in view of the suspended structure. The principle of measuring the electrical and thermal conductivities can be referred in Refs. 16 and 17. In the measurements, the silicon chip with the suspended gold nanofilm is mounted on the sample holder of a liquid nitrogen cryostat (Oxford Instruments, Optistat DN-V). The sample chamber is continuously evacuated by a vacuum pump and a molecular pump, and the temperature of the sample holder can be controlled continuously from 77 K to 500 K. The measurement system consists of the nanofilm sample, two high accuracy digital multimeters (Keitheley 2002, 8.5 digits), a standard resistance (Yokogawa 2792), and a high accuracy power supply (Advantest R6243).

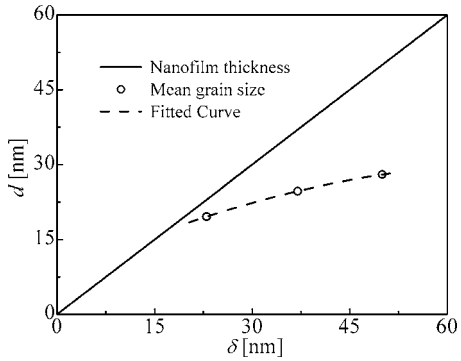

FIG. 1. The mean grain sizes studied by XRD for three different thicknesses of gold nanofilms.

III. RESULTS AND DISCUSSION

The measured electrical and thermal conductivities of Au nanofilms with the thickness of 21.0 nm, 23.0 nm, and 37.0 nm at 300 K are shown in Fig. 2, and the temperature dependent conductivities of the nanofilm with the thickness of 37.0 nm are shown in Fig. 3. It is found that both the

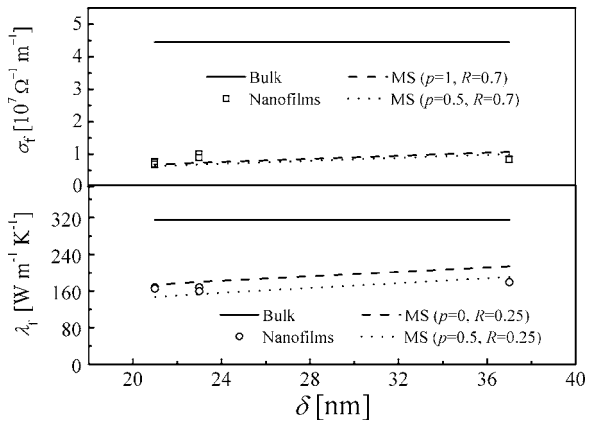

FIG. 2. The thickness-dependent electrical and thermal conductivities of gold nanofilms at 300 K.

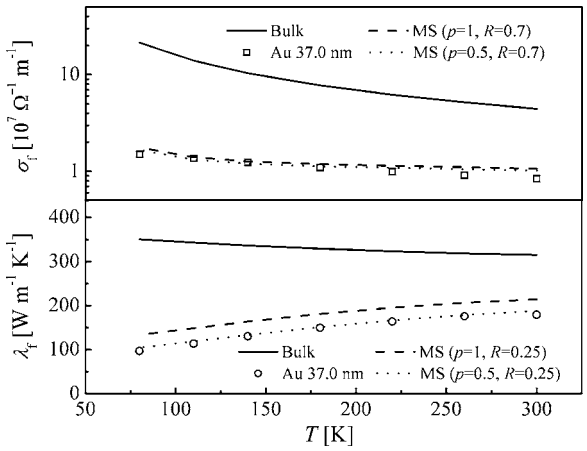

FIG. 3. The temperature-dependent electrical and thermal conductivities of gold nanofilms with the thickness of 37.0 nm.

electrical and thermal conductivities are greatly reduced from the corresponding bulk values. The reduction becomes more evident as the temperature decreases from 300 K to 80 K, since the electron MFP increases with decreasing the temperature and the size effects are then expected to be strengthened. In consideration that the present thickness and the mean grain size are both comparable to the electron MFP of Au (~40 nm at 300 K), both surface and grain boundary scatterings are considered to reduce the electrical and thermal conductivities. By introducing a simple δ-function potential to represent the grain boundary and by imposing a boundary condition due to the external surfaces, Mayadas and Shatzkes[3,4] solved the Boltzmann equation to obtain the total electrical conductivity of a polycrystalline metallic film as follows:

$$\frac{\sigma_f}{\sigma_0} = 1 - \frac{3}{2}\alpha + 3\alpha^2 - 3\alpha^3 \ln(1 + 1/\alpha) - \frac{6(1-p)}{\pi k_0}\int_0^{\pi/2} d\varphi \int_1^{\infty} dt \frac{\cos^2\varphi}{H^2(t,\varphi)} \times \left(\frac{1}{t^3} - \frac{1}{t^5}\right)\frac{1 - e^{[-k_0 t H(t,\varphi)]}}{1 - p e^{[-k_0 t H(t,\varphi)]}}, \quad (1)$$

where $\alpha = l_0 R/d(1-R)$, $k_0 = \delta/l_0$, $H(t,\varphi) = 1 + \delta/\cos\varphi(1 - 1/t^2)^{1/2}$, σ_f and σ_0 are the film and bulk conductivities respectively, l_0 is the MFP within a grain, δ is the film thickness, d is the mean grain size, p is the specular reflection parameter of electrons at film surfaces, R is the electron reflection coefficient at grain boundaries. Equation (1) can be further approximated[20] by

$$\frac{\sigma_f}{\sigma_0} = \left[1 + \frac{3(1-p)}{8k_0} + \frac{7}{5}\alpha\right]^{-1}, \quad (2)$$

within 9% error when the film thickness and the grain diameter are not too small compared with the electron MFP, i.e., $\alpha < 10$ and $k_0 > 0.1$. There are altogether four unknown parameters in Eq. (2): σ_0, l_0, p, and R. In consideration that $\sigma_0/l_0 = 1.2 \times 10^{15}\ \Omega^{-1}\ m^{-2}$ for Au,[21] and the electrical conductivity σ_0 can be referred in the literature, only two are unknown. As stated above, the specular reflection parameter p of electrons at Au film surfaces is usually taken to be 0.5.[3,7,9] Therefore, there is only the reflection coefficient R left to be determined. It is found that the electrical conductivities predicted by the MS theory can agree well with the measured results as the reflection coefficient R is taken to be 0.7, as shown in Figs. 2 and 3. In order to estimate the relative magnitude of the surface effect and the grain boundary effect, we also plot the thickness and temperature-dependent conductivities in terms of only grain boundary scattering by assuming the specular reflection parameter p to be 1.0. It is found from Figs. 2 and 3 that the reduced electrical and thermal conductivities are strongly dominates by grain boundary scattering, while the contribution of surface scattering is rather less important. The obtained reflection coefficient $R = 0.7$ agrees well with a previous scanning tunneling potentiometry study on the current transport through single grain boundaries,[8] which indicates that the reflection coefficient R depends on the grain orientation and varies between 0.7 and 0.9. Another study on the size effects in the electrical resistivity of polycrystalline nanowires[9] obtains an average value of $R = 0.9$. As stated above, however, some earlier studies[5–7] have obtained much smaller reflection coefficients from 0.10 to 0.35. The possible reason for the discrepancy was given in Ref. 8 that for the current it is much more favorable to take a longer path in a grain than to pass a grain boundary. Therefore, a macroscopic averaging measurement of the resistivity of the sample may be dominated by low-resistivity paths and then leads to a lower reflection coefficient in Refs. 5–7. In consideration that the mean grain size is comparable to the width of the nanowires in Ref. 9, the current will have to pass through more grain boundaries and hence leads to a much higher reflection coefficient. A value of $R = 0.7$ for our nanofilms is reasonable, since the widths of the present studied nanofilms are several hundred nanometers, which are much smaller than those in Refs. 5–7 but greater than those in Ref. 9. With the same reflection coefficient for the current transport $R = 0.7$, however, the predicted thermal conductivities must be markedly underestimated. As the reflection coefficient is taken to be 0.25, the theoretical predictions coincide well with the observed thermal conductivities, as shown in Figs. 2 and 3. The studies on the electron-phonon coupling factor in Au films show that as the reflection coefficient R is taken to be 0.17 and the specularly reflected parameter p is taken to be zero, the theoretical prediction can agree with the experimental results.[13] If p is taken to be 0.5 as we choose, the value of R will also approximate to be 0.25. Different reflection coefficients R for the electrical and thermal conductivities indicates that the electron scatterings on the grain boundaries can exert distinct influences on the current and heat transport in the polycrystalline gold nanofilms. This will be further explained in the following discussion.

The relative magnitudes of the nanofilm electrical and thermal conductivities to the corresponding bulk values have been plotted along the thickness in Fig. 4 and along the temperature in Fig. 5. It is clearly found that the electrical conductivity drop is considerably larger than the thermal conductivity drop. This discrepancy must lead to the violation of the WF law, which states that the Lorenz number defined as

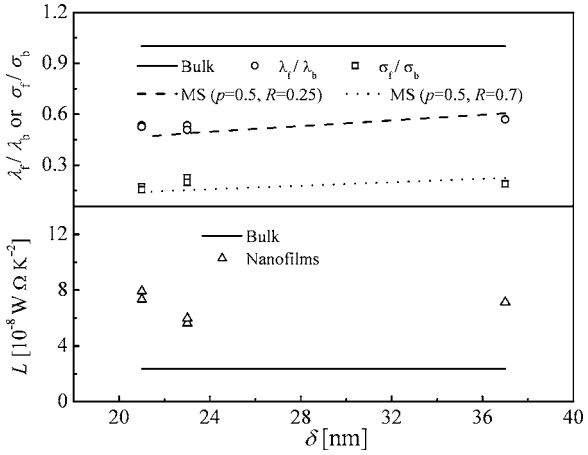

FIG. 4. The relative thickness-dependent electrical and thermal conductivities of gold nanofilms at 300 K and the corresponding Lorenz numbers.

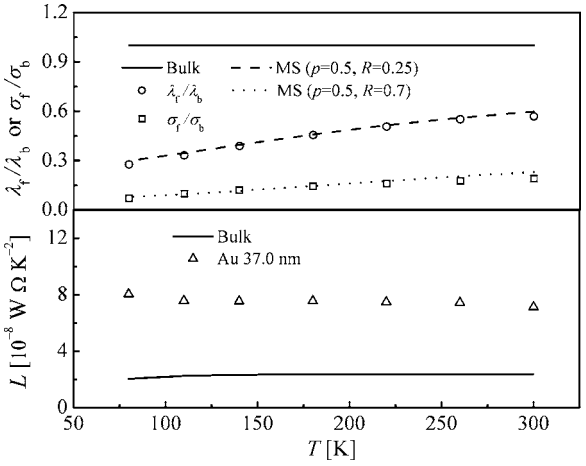

FIG. 5. The relative temperature-dependent electrical and thermal conductivities of gold nanofilms with the thickness of 37.0 nm and the corresponding Lorenz numbers.

$L_0=\lambda_0/\sigma_0 T$ equals 2.45×10^{-8} W Ω K^{-2} as the temperature is not too low compared with the Debye temperature (165 K for Au).[10] The thickness and temperature-dependent Lorenz numbers of the nanofilms have been calculated and plotted in Figs. 4 and 5. It is found that the Lorenz number for the nanofilms is around 7.0×10^{-8} W Ω K^{-2}, which is almost three times of the value predicted by the WF law and keeps almost invariant with decreasing the temperature from 300 K to 80 K. It is considered that observed thermal conductivity includes the contributions of both the electronic thermal transport and the phonon transport, and heat conduction by phonons can no more be neglected in metallic thin films.[19] However, the thermal conductivity caused by the phonon-phonon interactions cannot be twice of the electronic thermal conductivity in metallic films, since the former is usually one or tow order of magnitude less than the latter in pure bulk metals.[10] There must be other mechanisms leading to so high Lorenz numbers in present polycrystalline gold films.

Vancea *et al.*[21] studied the charge transport in several polycrystalline metallic thin films in order to separate volume and surface effects on the electrical conductivity as well as to separate the scattering of electrons inside the crystallites from the reflections of electrons by the crystallite boundaries. They found that a fraction of the electrons is elastically reflected from the boundaries of the crystallites, which reduces the electrical conductivity through an apparent reduction in the density of the effective electrons. Only those electrons which quantum mechanically pass over all the boundaries along the background MFP contribute to the charge transport. The effective density of electron electrons n_g in polycrystalline metals has been expressed as

$$n_g = n_0 T^{*l_g/d}, \tag{3}$$

here n_0 is the density of conduction electrons in single-crystal bulk metals, $T^*=1-R$ is the mean quantum mechanical transmission coefficient, l_g is electron MFP of polycrystalline bulk metals. Vancea *et al.*[22] pointed out later that it is impossible to define a MFP for the whole polycrystal, especially if the resistivity is governed by grain-boundary scattering. Only the background scattering MFP, which is mainly caused by the phonons and the defects in the volume of the crystallies, can be defined in a polycrystal and is responsible for the observed size effect. Therefore, in the discussions it is assumed that $l_g=l_0$. Eq. (3) indicates that the effective density of the conduction electrons is proportional to the mean probability for electron transmission through the l_g/d grain boundaries along one MFP. In the present studies, $l_g/d \approx 1.0$, $T^*=0.30$, and then the effective density of the conduction electron is found to be 30% of that in the single-crystalline metal. The situation in the thermal transport, however, is quite different. We hold that those conduction electrons contributing to the charge transport contribute to the heat transport as well and can be estimated by the WF law. Those electrons elastically reflected from the grain boundaries do not contribute to the charge transport but do have energy exchange with the phonons on the grain boundaries. Therefore, the grain boundaries are transparent to some extent for those electrons if they are considered as thermal carriers. The total reflection coefficient R for electronic thermal transport is then decreased and the WF law becomes invalid in such a situation.

IV. CONCLUSION

We have investigated the electrical and thermal conductivities of polycrystalline gold nanofilms experimentally and theoretically. It is found that the grain boundary can exert very different influences on the charge and electronic thermal transport. The conduction electrons can be divided into two parts: one is those quantum mechanically passing over all the boundaries along the background MFP, which contributes to both charge and electronic thermal transport and their relations can be described by the WF law; the other is those elastically reflected from the grain boundaries, which does not contribute the charge transport but enhances the thermal transport and their relations cannot accordingly be predicted by the WF law.

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