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Different effects of grain boundary scattering on charge and heat transport in polycrystalline platinum and gold nanofilms*

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The in-plane electrical and thermal conductivities of several polycrystalline platinum and gold nanofilms with different thicknesses are measured in a temperature range between the boiling point of liquid nitrogen (77 K) and room temperature by using the direct current heating method. The result shows that both the electrical and thermal conductivities of the nanofilms reduce greatly compared with their corresponding bulk values. However, the electrical conductivity drop is considerably greater than the thermal conductivity drop, which indicates that the influence of the internal grain boundary on heat transport is different from that of charge transport, hence leading to the violation of the Wiedemann–Franz law. We build an electron relaxation model based on Matthiessen's rule to analyse the thermal conductivity and employ the Mayadas & Shatzkes theory to analyse the electrical conductivity. Moreover, a modified Wiedemann–Franz law is provided in this paper, the obtained results from which are in good agreement with the experimental data.

Keywords: polycrystalline nanofilm, grain boundary scattering, thermal and electrical conductivities, Wiedemann–Franz law

PACC: 7360D, 7215E, 7210

1. Introduction

As semiconductor/electronics technologies and micro/nano-electromechanical systems (MEMS/NEMS) rapidly progress, metallic thin films are widely used as interconnecting wires in ultra-large-scale-integrated (ULSI) and giga-scale-integrated (GSI) circuits[1,2] and the grain boundary of nanofilms is one of the key factors.[3,4] To ensure the capability and the reliability of these delicate circuit systems, a deep insight into the electrical and thermal properties of metallic nanofilms is a must.

Sharp declines of electrical and thermal conductivities can be observed when the dimensions of metallic films approach the bulk electron mean free path (MFP). To figure out their causes, some efforts have been made. Fuchs and Sondheimer (FS),[5,6] and Mayadas and Shatzkes (MS)[7,8] studied the effects of surface and grain boundary scattering on the electrical conductivity, respectively. According to the FS theory and the MS theory, Tien *et al*[9] and Qiu and Tien[10] first studied the effects of surface and grain boundary on thermal conductivity by applying the electrical–thermal analogy: the Wiedemann–Franz (WF) law.[11]

Matthiessen's rule (MR)[12,13] is usually used to estimate the relative magnitudes of different scattering mechanisms. It states that the total scattering rate is a sum of all different scattering processes, including the background scattering, the impurity scattering, the boundary scattering, etc, on the underlying assumption that the scattering processes do not interact with each other. Recent studies[14] on the in-plane thermal conductivity of polycrystalline platinum nanofilms show that by considering the background scattering and the grain boundary scattering Matthiessen's rule is still valid.

In view of the fact that an electron is a mutual carrier of charge and heat in metal, Wiedemann and Franz[11] first found the ratios between thermal and electrical conductivities were very similar for most metals at room temperature. Lorenz[15] later discov-

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ered that such a ratio was proportional to the absolute temperature and the coefficient was relevant to two fundamental constants: the quantum of electrical charge, e, and the quantum of entropy, k_B. This is the well-known Wiedemann–Franz law, which has provided much of the credibility for the free-electron theory and also has been proven to be one of the basic properties of a Fermi liquid.

However, recent studies[16,17] have shown that the WF law may become invalid in metallic thin films. Zhang *et al* studied the thermal and the electrical conductivities of three platinum nanofilms and deduced a modified Wiedemann–Franz law based on Matthiessen's rule and the Mayadas & Shatzkes theory.[18] In the present paper, the electrical and thermal conductivities of several platinum and gold nanofilms in a large temperature range from 80 to 300 K are measured simultaneously by using the direct current heating method.[16] The result shows that the Wiedemann–Franz law is violated due to different effects of grain boundary scattering on heat and charge transport properties. From statistical analysis, it can be found that variations of both the film thickness and temperature lead to different ratios between the grain size in nanofilm and the corresponding bulk mean free path, which determines the thermal and the electrical properties of the polycrystalline films and has been studied by using Matthiessen's rule and the Mayadas & Shatzkes theory, respectively.

2. Experiment

The platinum and gold used in this study are of high purity (99.98%), and they are fabricated into suspended nanofilms with electron beam-physical vapour deposition under vacuum conditions, assisted with the electron beam lithography and the isotropic/anisotropic etching techniques. A sample of the fabricated nanofilm is shown in Fig.1, which is obtained by scanning electron microscopy (SEM). The fabrication processes in detail can be found in Ref.[14]. The average grain diameter of the nanofilms is investigated by x-ray diffraction (XRD); Figure 2 shows the diffraction spectra of gold and platinum nanofilms. The dimensions and the average grain size are listed in Table 1.

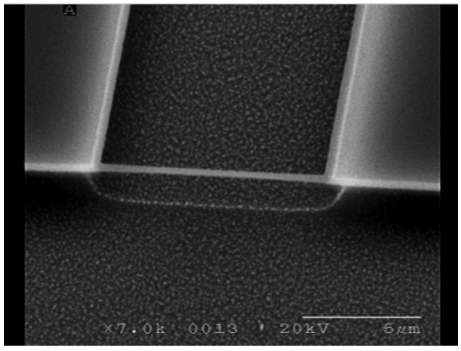


Fig.1. Scanning electron micrographs of the suspended nanofilm.

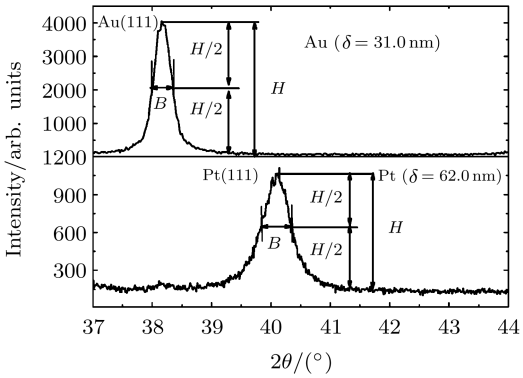


Fig.2. X-ray diffraction spectra of platinum and gold nanofilms.

Table 1. Size parameters of fabricated platinum and gold nanofilms.

nanofilm sample	platinum					gold			
	a	b	c	d	e	a	b	c	d
thickness/nm	22.0	24.0	62.0	62.0	63.0	20.0	31.0	36.0	54.0
width/nm	479.6	491.1	1383.4	1228.0	696.8	371.0	371.0	329.5	378.0
length/μm	5.56	5.83	9.21	8.87	6.23	10.03	9.91	10.23	10.26
grain diameter/nm	11.4	11.6	16.3	14.8	17.6	18.2	29.2	29.3	38.3

In measurement, the silicon chip with the suspended nanofilm is mounted on a sample holder of a liquid nitrogen cryostat (Oxford Instruments, Optistat DNV). The sample chamber is continuously evacuated by a two-stage vacuum-pumping system composed of a roughing pump and a high-vacuum pump (turbo molecular pump) in order to obtain and maintain a high vacuum level of 1×10^{-4} Pa. The tem-

perature of the sample holder can be adjusted to any point between 77 and 500 K by using the intelligent temperature controller (ITC 503, Oxford Instruments DNV). The measurement system consists of the nanofilm sample, two high precision digital multimeters (Keitheley 2002, 8.5 digits) and a standard resistance (Yokogawa 2792), which are used to measure the resistance of the nanofilm exactly so as to obtain the corresponding electrical conductivity directly. The thermal conductivity of the film can also be obtained from the analysis of its resistance, which is very sensitive to temperature. For further details about the measurement in data refer to Ref.[14].

3. Result and discussion

As indicated in Ref.[19], grain boundary scattering dominates the combined scattering process for all studied nanofilms in the whole temperature range, while the contribution of surface scattering is rather less important. Hence, in this study, we lay emphasis on the effects of the gain boundary scattering.

As the metallic thin films are polycrystalline and the mean grain size is comparable with or even less than the electron MFP, the effects of grain-boundary scattering on electrical and thermal conductivities must be included. On the assumption that the grain boundary can be represented by a δ-function potential, Mayadas and Shatzkes[7,8] studied the grain-boundary effects on the electrical conductivity of polycrystalline metals within the framework of the Boltzmann transport equation and obtained the following expression:

$$\sigma_{\mathrm{rel}} = \frac{\sigma_{\mathrm{f}}}{\sigma_{\mathrm{b}}} = 1 - \frac{3}{2}\alpha + 3\alpha^2 - 3\alpha^3 \ln\left(1 + \frac{1}{\alpha}\right) = f(\alpha), \tag{1}$$

where dimensionless parameter σ_{rel} is defined as the relative electrical conductivity, σ_{f} and σ_{b} represent the polycrystalline and corresponding single-crystal bulk electrical conductivities, respectively, and α is a combined parameter written as $\alpha = l_{\mathrm{b}}R/d(1-R)$, which includes the relative magnitude of the mean grain diameter d, the bulk electron MFP l_{b}, and the reflection coefficient of the electrons striking the grain boundary, R.

However, from the experimental result it can be found that the heat transfer cannot be analysed simply on the analogy of charge transport, for the reflected electrons can deliver energy to the phonons at the grain boundary, even very little, but they make no contribution to the charge transport.

For the thermal conductivity of the nanofilms, we built an electron relaxation model based on Matthiessen's rule, thus the total relaxation time could be written as[18]

$$\frac{1}{\tau_{\mathrm{e}}} = \frac{1}{\tau_{\mathrm{b}}} + \frac{1}{\tau_{\mathrm{g}}} + \frac{1}{\tau_{\mathrm{s}}} + \frac{1}{\tau_{\mathrm{i}}}, \tag{2}$$

where τ_{e} is the combined relaxation time of electrons, τ_{b} is the relaxation time caused by background scattering, τ_{g} by grain boundary, τ_{s} by surface, and τ_{i} by impurity. Because of the high purity (99.98%) of the platinum and the gold, the contribution made by the impurity scattering can be neglected. Moreover, the influence of surface scattering can also be neglected due to its little importance compared with grain boundary scattering.[19]

The electrons passing through the grain boundary have a relaxation time determined only by the background scattering as

$$\frac{1}{\tau_{\mathrm{e1}}} = \frac{1}{\tau_{\mathrm{b}}}. \tag{3}$$

The electrons elastically reflected have a relaxation time determined by both the background scattering and the grain boundary scattering as

$$\frac{1}{\tau_{\mathrm{e2}}} = \frac{1}{\tau_{\mathrm{b}}} + \frac{1}{\tau_{\mathrm{g}}}. \tag{4}$$

Considering the reflection coefficient R in the MS theory when analysing the charge transport, the probability of electrons passing through the grain boundary is $T^* = 1 - R$, where R is the probability for those electrons to be reflected. The relaxation time for the film, τ_{f}, can be calculated as[18]

$$\frac{1}{\tau_{\mathrm{f}}} = T^*\frac{1}{\tau_{\mathrm{e1}}} + R\frac{1}{\tau_{\mathrm{e2}}}. \tag{5}$$

Submitting $\tau_{\mathrm{f}} = l_{\mathrm{f}}/v_{\mathrm{F}}$, $\tau_{\mathrm{b}} = l_{\mathrm{b}}/v_{\mathrm{F}}$ and $\tau_{\mathrm{g}} = d/v_{\mathrm{F}}$ into expression (5) yields

$$\lambda_{\mathrm{rel}} = \frac{\lambda_{\mathrm{f}}}{\lambda_{\mathrm{b}}} = \frac{l_{\mathrm{f}}}{l_{\mathrm{b}}} = \frac{1}{1 + T^*\alpha} = g(\alpha), \tag{6}$$

where l_{f} and l_{b} are the film and bulk mean free paths, v_{F} is the Fermi speed, and $\alpha = (l_{\mathrm{b}}/d)(R/T^*)$ is the same as that in the MS theory.

From expressions (1) and (6) it can be found that the relative electrical conductivity σ_{rel} and the relative thermal conductivity λ_{rel} are univariant functions of α. In other words, σ_{rel} and λ_{rel} will vary only with the ratio of the grain diameter d to the MFP l_{b} on the assumption that the reflection coefficient of electrons is almost invariable for each given metal. So

when the ratio of d to l_b varies, we obtain different values of σ_{rel} and λ_{rel}. The grain diameter d is considered to be proportional to the film thickness (de Vries, 1988), which has also been proven by XRD studies. The corresponding single crystalline MFP l_b indicated in the literature tends to increase as temperature decreases. Therefore, to change the ratio of d to l_b (d/l_b), there are two methods available: one is to change the grain diameter d by preparing films of different thicknesses; the other is to change the MFP l_b by changing the temperature. The values of MFP l_b at different temperatures, the electrical and thermal conductivities (σ_b, λ_b) of the bulk metal can be found in the literature, whereas the electrical and the thermal conductivities of the films are measured directly in experiment. Thus, a series of d/l_b and the corresponding relative electrical and thermal conductivities (σ_{rel} and λ_{rel}) can be obtained.

Figures 3 and 4 show the experimental data of the platinum nanofilms and the gold nanofilms and the prediction lines provided by the MS theory and Matthiessen's rule. It can be easily found that for each value of d/l_b, the relative thermal conductivity is larger than the relative electrical conductivity.

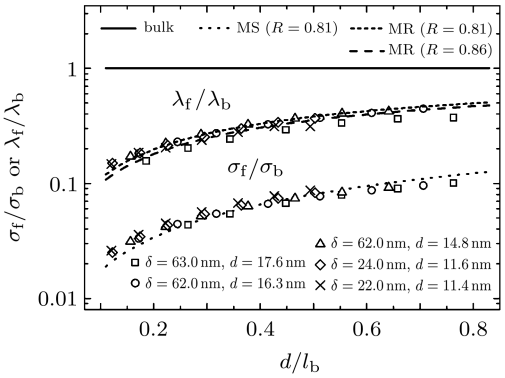


Fig.3. The grain size parameter-dependent relative electrical and thermal conductivities of platinum nanofilms.

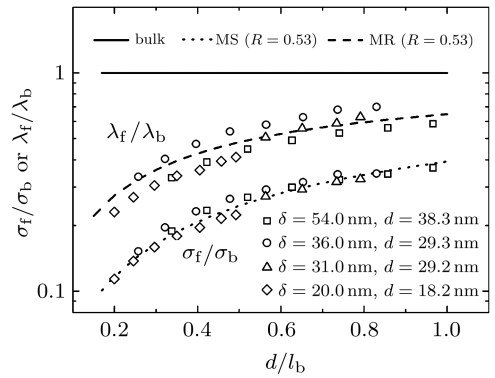


Fig.4. The grain size parameter-dependent relative electrical and thermal conductivities of gold nanofilms.

For the platinum nanofilms in Fig.3, when the reflection coefficient R is taken as 0.81, the electrical conductivity predicted from the MS theory is the best fitting to experimental data by the least squared criterion. However, for thermal conductivities, to fit the experimental data best by Matthiessen's rule, the reflection coefficient R should be 0.86 but not 0.81, both of which are plotted in Fig.3. Fortunately, the difference between them is not significant and the relative difference is 6%. For the gold nanofilms in Fig.4, when the reflection coefficient R is taken as 0.53, both electrical conductivities predicted from the MS theory and thermal conductivities predicted from Matthiessen's rule are the best fittings to the experimental data by least squared criterion.

Since the values of reflection coefficient R taken in the MS theory and in Matthiessen's rule for each given metallic film are very close, we have a good reason to say that under the grain size effects, the MS theory can be used to explain the charge transfer and Matthiessen's rule the heat transfer. As stated above, the same probability for electrons to be reflected at the grain boundaries leads to different effects on thermal and electrical conductivities.

According to the WF law[11] the ratio between thermal and electrical conductivities of bulk single-crystalline metals can be expressed in terms of the ratio as

$$L_0 = \lambda_b/(\sigma_b T) = \pi^2 k_B^2/(3e^2), \tag{7}$$

which may be called the Wiedemann–Franz ratio or the Lorenz ratio.

In our discussion on the experimental result, the ratio of thermal to electrical conductivities of polycrystalline nanofilms can be expressed as

$$L_f = \lambda_f/(\sigma_f T). \tag{8}$$

Combining expressions (7) and (8), the ratio between the Lorenz ratio of the polycrystalline film L_f and the corresponding bulk L_0 can be obtained as

$$\frac{L_f}{L_0} = \frac{\lambda_f/(\sigma_f T)}{\lambda_b/(\sigma_b T)} = \frac{\lambda_f/\lambda_b}{\sigma_f/\sigma_b}. \tag{9}$$

The ratios of film to bulk thermal and electrical conductivities, i.e. λ_f/λ_b and σ_f/σ_b, can be obtained by the MS theory and Matthiessen's rule from expressions (1) and (6) as

$$\frac{L_f}{L_0} = \frac{1}{[1 - 3\alpha/2 + 3\alpha^2 - 3\alpha^3 \ln(1 + 1/\alpha)](1 + T^*\alpha)}. \tag{10}$$

Figures 5 and 6 show the ratios of L_f/L_0 of platinum and gold respectively. The discrete points represent experimental data and the lines denotes predictions from expression (10). It can be found that the ratio is larger than 1 and varies with the ratio d/l_b, which means that the Wiedemann–Franz ratio is not a constant and the WF law is no longer valid. The predictions from the MS theory and Matthiessen's rule, which take into account different effects of boundary scattering on heat and charge transfer properties, accord well with the experimental data.

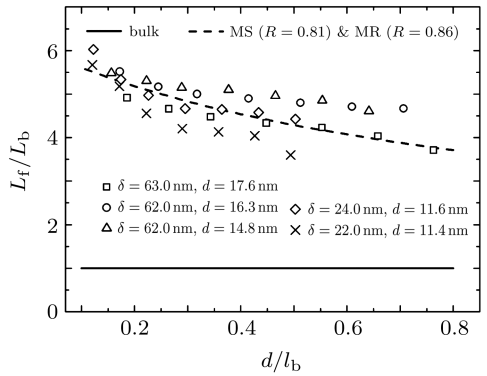


Fig.5. The grain size parameter-dependent relative Lorenz ratio of platinum nanofilms.

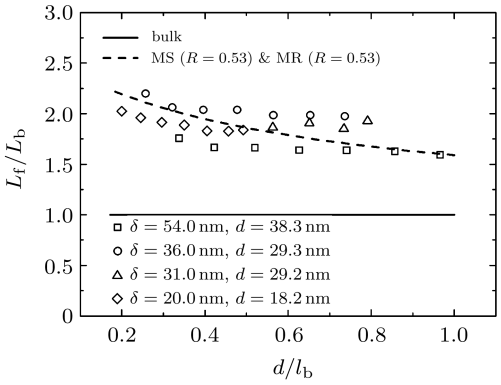


Fig.6. The grain size parameter-dependent relative Lorenz ratio of gold nanofilms.

Thus, when the reflection coefficients of electricity-/heat-conducting electrons are taken as $R = 0.81$ and 0.86 for platinum and $R = 0.53$ for gold, the predictions coincide well with experimental data for all properties of polycrystalline thin films, i.e. electrical conductivity σ_f, thermal conductivity λ_f, and WF ratio L_f in Figs.3–6.

The Wiedemann–Franz law which is based on the fact that an electron is a mutual carrier of charge and heat[11] may be a very good approximation of what actually happens in bulk or single crystalline materials. However, charge and heat transfer are not the same things in essence: charge is in a form of mass and heat is in a form of energy, and hence these two transfers are different especially in polycrystalline nanofilms. Since the reflected electrons can deliver energy to the phonons at the grain boundary, even if they make no contribution to the charge transport. The effects of grain boundary scattering on thermal and electrical conductivities will be different, which leads to the violation of the Wiedemann–Franz law.

Transforming expression (10), we have the modified Wiedemann–Franz law, which can be expressed as

$$L_f = \frac{L_0}{[1 - 3\alpha/2 + 3\alpha^2 - 3\alpha^3 \ln(1 + 1/\alpha)](1 + T^*\alpha)}. \tag{11}$$

Thus, if the electrical conductivity of the polycrystalline metallic nanofilm has been obtained, which is much more easily obtained than thermal conductivity, the reflection coefficients at grain boundary scattering can be obtained from the MS theory or measured directly with scanning tunnelling potentiometry.[20] Hence, the Lorenz ratioand the thermal conductivity can be predicted by expression (11).

4. Conclusions

In this paper, the electrical and the thermal conductivities of platinum and gold nanofilms with different thicknesses are measured at different temperatures from 80 to 300 K.

The electrical and the thermal conductivities reduce greatly compared with their corresponding bulk values. However, their reduction ranges, dependent on the ratio of the grain diameter to the MFP, are different due to the effects of grain boundary scattering. Moreover, we develop a new method, independent of WF law, to study the thermal conductivities.

Because the different effects of grain boundary scattering on heat and charge transport properties lead to the violation of the Wiedemann–Franz law, a modified Wiedemann–Franz law is derived based on the MS theory and Matthiessen's rule. Hence, the thermal conductivity of nanofilms can be predicted by measuring electrical properties only.

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