Influence of the Surface Structure and Vibration Mode on the Resistivity of Cu Films

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The influence of the surface structure and vibration mode on the resistivity of Cu films and the corresponding size effect are investigated. The temperature dependent conductivities of the films with different surface morphologies are calculated by the algorithm based upon the tight-binding linear muffin-tin orbital method and the Green’s function technique. The thermal effect is introduced by setting the atomic displacements according to the Gaussian distribution with the mean-square amplitude estimated by the Debye model. The result shows that the surface atomic vibration contributes significantly to the resistivity of the systems. Comparing the conductivities for three different vibration modes, it is suggested that freezing the surface vibration is necessary for practical applications to reduce the resistivity induced by the surface electron-phonon scattering.

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I. INTRODUCTION

The study on the transport property of copper has been attracting much attentions of researchers\textsuperscript{1–8} since it often serves as a good conductor in devices either on macro or micro scales, such as the interconnect material of integrated circuits (IC). Reducing resistivity is highly demanded in IC technology to cut down the power consumption of micro-devices. Effort should be made to reach this goal theoretically and experimentally. It was found that the decreasing cross section of Cu wire would lead to the increase of the resistivity\textsuperscript{3,4,7}, which is the so called “size effect”. It may give rise to 100\% increase in the resistivity when the size of the sample is below 50 nm\textsuperscript{3,4}. This effect severely impacts the time delay of the interconnects of integrated circuits and thus represents a major challenge for the continuing evolution of the microelectronic devices.

Actually, the size effect is related to the increasing surface to bulk atomic number when the dimension of the cross section of thin films decreases to nanometer scale. Furthermore, experimental observations revealed that there was about −2.0\% contraction of the top-layer for Cu films when \( T \leq 305 \text{ K} \), and −2.3\% when \( T > 520 \text{ K} \). Generally, the total resistivity of Cu interconnect originates from several scattering mechanisms, including lattice vibrations, impurities, defects, surface roughness and grain boundaries, etc. Surface scattering is considered to play a key role in the increase in the resistivity of copper thin films\textsuperscript{7,10}. Therefore, investigating the influence of the surface structure and its vibration mode on the resistivity, i.e. the effect of the surface electron-phonon interaction, is a very important topic.

Many methods have been advanced to study the effect of the surface electron-phonon scattering on the resistivity. A widely used semiclassical model is the Fuchs-Sondheimer model\textsuperscript{11,12}, where a phenomenological parameter is used to characterize the electron scattering at the surface. Other more advanced analytic models\textsuperscript{13–15} have also been proposed in the general area of the thin-film resistivity, which take into account the quantum effects that may become prominent at very small film thickness. Recently, parameters free \textit{ab initio} methods\textsuperscript{16,17} have been used to directly calculate the resistivity of Cu films and nanowires, where a supercell approach was employed on periodic atomic structures. In an earlier work\textsuperscript{18}, we have developed an approach based upon a tight-binding muffin-tin-orbital implementation of the Landauer-Büttiker formulation of transport theory within the local-spin-density approximation of density-functional theory. It was used to calculate the resistivity due to
diluted impurities in alloys\textsuperscript{5} and good agreement with experiment\textsuperscript{19} was obtained. Unfortunately the code works only for occasions at zero temperature. In the current work, however, we are interested in the finite temperature effect of the surface electron-phonon scattering on the resistivity of thin films. Therefore the approach should be revised to include the thermal effect. It is achieved in this paper by sampling the disordered atomic configurations due to thermal vibration in the scattering region according to Gaussian distributions, where the temperature dependent mean-square amplitudes are estimated by the Debye model.

The rest of this paper is organized as follows. In Sec. II we describe the atomic structure of Cu films, the determination of the atomic displacements due to thermal vibration, and the computational method. The temperature dependent resistivity of the bulk and the film structures of copper are presented and discussed in Sec. III. A short summary is made in Sec. IV.

II. MODEL AND COMPUTATION METHOD

A. Geometry Structures

The geometry structure of the system studied in the current work is shown in Fig. 1. It consists of three parts, i.e. the two contacts regions denoted respectively by L and R, and a scattering region denoted by M. The L and R regions are Cu metals with perfect fcc structure, and the lattice constant $a$ is set to 3.61 Å. The $x$, $y$, and $z$ axes are along $\langle 10\bar{1} \rangle$, $\langle 010 \rangle$ and $\langle 101 \rangle$ directions, respectively. $d$ is the thickness of the Cu film.

The atomic structure is assumed to be a perfect crystal in the scattering region when the temperature is 0 K (see Fig. II(a)). For finite temperature, the atoms deviate from their equilibrium positions due to thermal vibration (as shown in Fig. II(b)), which can be simulated by random displacements.\textsuperscript{20} Actually, the temperature dependence of the mean-square displacement has been studied both theoretically\textsuperscript{21} and experimentally.\textsuperscript{22} Here we introduce it by a simple argument based upon the Debye model.

In the language of phonon, the lattice vibrations is described by the linear combination of collective oscillations with different frequencies. The energy of each atom contributed by one collective mode with frequency $\omega$ can be represented as $E = \frac{1}{2}m\omega^2A^2$ in average, which
FIG. 1. (Color online) The atomic structure of Cu film consisting of two lead regions (denoted by L and R) and one scattering region (denoted by M). (a) for $T = 0$ K, no disorder in the scattering region, except for the quantum fluctuation of lattice; (b) for $T \neq 0$ K, the atoms in scattering region violate the perfect crystal structure.

Given the square of atomic vibration amplitude

$$A^2 = \frac{2E}{m\omega^2}, \quad (1)$$

with the single atom mass $m$. On the other hand, the total energy $E$ in equation (1) can be estimated from the statistical average of phonon number $\langle n \rangle$

$$E = (\langle n \rangle + \frac{1}{2})\hbar\omega, \quad (2)$$

from the Planck distribution $\langle n \rangle \equiv \frac{1}{\exp(\hbar\omega/k_B T) - 1}$.

We further assume that the frequency distribution of the collective oscillations obeys the Debye model, and thus the mean-square amplitude can be expressed by

$$\langle A^2 \rangle = \frac{2}{m} \int_0^{\omega_D} D(\omega) \frac{E}{\omega} d\omega,$$

where $\omega_D$ is the Debye frequency, and $D(\omega)$ is the density of state for phonons. For our case, we have $D(\omega) = 3\omega^2/2\pi^2v^3$, where $v$ is the sound velocity in the system. Finally, we get the analytic expression for the mean-square amplitude, i.e.

$$\langle A^2 \rangle = \frac{6\hbar^2}{mk_B\theta_D} \left[ \frac{1}{4} + \left( \frac{T}{\theta_D} \right)^2 \Phi_1 \right], \quad (3)$$
where \( \theta_D \) is the Debye temperature, and \( \Phi_n \equiv \int_0^{\theta_D/T} dx \frac{x^n}{e^{x/T} - 1} \).

Now, the mean-square vibrational amplitudes \( \langle A^2 \rangle^{1/2} \) of the system at finite temperature can be calculated through equation (3), and the atomic positions in the scattering region in Fig. (b) can thus be determined through the random displacements satisfying the Gaussian distribution \( P(x) = (2\pi u^2)^{-1/2}e^{-x^2/2u^2} \), with the mean-square displacement \( u^2 = \langle A^2 \rangle/2 \). Here, our approach to describe the lattice vibration is more suitable for weakly correlated atoms, and is a rough approximation for the calculations below.

**B. Computational Method**

The transport property of the system is estimated by the first principle method developed in the previous works. In this approach, the electron structure is calculated through the tight-binding linear muffin-tin orbital method, where the atomic sphere potentials in the scattering region are determined by the self-consistent calculations based upon the Green’s function technique. The conductance is calculated by the Landauer- Büttiker formulism, and the resistivity is expressed explicitly in terms of the transmission matrix \( T \) as

\[
\rho \equiv \frac{SR_{L/R}}{\ell} = \frac{S}{\ell} \frac{h}{e^2} \left[ \sum T_{\mu\nu} - \frac{1}{2} \left( \frac{1}{N_L} + \frac{1}{N_R} \right) \right].
\]

Here, \( S \) is the interface area and \( \ell \) is the length of the lateral supercell, which is used to model the temperature induced disorder. The element \( T_{\mu\nu} \) is the transition probability from state \( |\nu\rangle \) in the left-hand lead to state \( |\mu\rangle \) in the right-hand lead, and \( N_L(N_R) \) is the number of conduction channels in lead L(R), which gives the Sharvin conductance. The transmission matrix can be obtained by the wave function matching at the interfaces between the leads and the scattering region defined in the previous subsection. In the numerical realization, to improve the accuracy, the resistivity at a given temperature is determined by the linear regression of the resistances obtained for different lengths.

The computational method described above is in the ballistic transport region, where there is no energy loss for electrons. However, the electron-phonon scattering should be an inelastic scattering processes. Thus one may question whether it is valid to describe the inelastic process by the current approach. This has in fact been discussed in the previous work in detail. The authors proved that the average conductivity over time-dependent configurations will give the same results as the static electron-phonon scattering method.
does. In the current work, we carry out the average of the conductivities obtained for different atomic configurations determined by the Gaussian distributions with different random number sequences.

III. RESULTS AND DISCUSSION

A. Bulk Cu

To test the validity of the approach in the current work, we calculate the temperature dependent resistivity of bulk copper for test purpose firstly. The Debye temperature in Eq. (3) is set to 315 K in the calculations. The theoretically estimated and the experimentally measured mean-square displacements of atomic vibration for different temperatures are listed in Table I for comparison. It is shown that the formers are at most 9% less than the latters due to the anharmonicity of the lattice potentials. Therefore we can use the theoretically estimated mean-square displacements in the current work.

TABLE I. The theoretically estimated and experimentally measured values of the mean-square atomic vibration displacements for different temperatures $T$ with $\theta_D = 315$ K.

| $T$ (K) | Theoretical Estimations ($\text{Å}$) | Experimental Measurements$^{22}$ ($\text{Å}$) |
|---------|-------------------------------------|-----------------------------------------------|
| 107     | 0.055                               | 0.055                                         |
| 305     | 0.086                               | 0.085                                         |
| 520     | 0.111                               | 0.115                                         |
| 685     | 0.127                               | 0.134                                         |
| 900     | 0.146                               | 0.160                                         |

For the bulk Cu structures, the transport is along the ⟨001⟩ direction, and the lateral supercell is 10 × 10 in size. The calculated resistivity is shown in Fig. 2 (see the red dot line). One may find that it increases linearly with the temperature when $T$ is above 100 K, and the slope is $9.32 \times 10^{-3} \, \mu\Omega\text{cm/K}$. The experimentally measured resistivity$^{26}$ (the black dot line in Fig. 2) shows a similar behavior to the calculated one, but with a 25% smaller slope, which is $7.02 \times 10^{-3} \, \mu\Omega\text{cm/K}$. We have to point out that the total resistivity no
FIG. 2. (Color online) Resistivity as a function of temperature. The theoretical results are show as red line, The experimental results are show as black line.

longer shows the linear relation at low temperature region, which is due to the fact that the energy equipartition theorem fails in this region.

One may notice that the calculated values of the resistivity are larger than the experimental ones, and is not zero at the zero-temperature as expected. This is understood from the atom vibration amplitude estimated by relation (3), which gives a non-zero vibration at zero-temperature. This comes from the zero-point energy of the phonons, and the non-zero resistivity at zero-temperature is from the quantum fluctuation of the crystal lattice. However the close slope of temperature dependence of the resistivity between the theoretical and experimental results suggests that the method employed in this work is able to capture the main physical picture of the electron-phonon scattering.

B. Cu Film

As shown in the previous works, the electrical resistivity is largely dependent on the surface scattering when materials are in nanometer scale. Thus we expect the significant contribution from the surface electron-phonon scattering to the resistivity in nanostructures. In this subsection, we calculate the temperature-dependent resistivity of thin films in the
same way as for the bulk samples. The films with different thicknesses \( d \), denoted by the number of monolayers (ML), are considered to study the size effect. In the scattering region, the lateral supercells is used to deal with the thermal vibrations, similar to the bulk copper.

We treat two outer MLs of the Cu films as its surface, and the other inner MLs as its ”middle part”. Three different situation for lattice vibrations are considered: (i) the amplitude of all the atom vibrations in the film is the same to that in the bulk case, estimated from Eq. 3; (ii) the surface atomic vibrations are decomposed into the in-plane surface vibration and the perpendicular component, and their amplitudes are taken from former experimental results\(^9,21,28\); the atom vibrations in the middle part is the same to the bulk case; (iii) freezing the surface atoms in their equilibrium positions, and treating the atoms in the middle part the same in bulk case.

The calculated results are presented in Fig. 3. It shows that the resistivity increases linearly with temperature for mode (i) and (iii), which is the same to that for the bulk one. The resistivity is slightly lower in mode (iii) than mode (i) due to the freezing of surface atoms. For mode (ii), the two components are unequal, and the ratios of the surface to bulk vibrational amplitudes are 1.71 (\( A_\parallel \)) and 1.53 (\( A_\perp \)) when \( T = 107 \) K. When the temperature is 685 K, they increase to 2.76 (\( A_\parallel \)) and 2.02 (\( A_\perp \)), respectively.\(^9\) Fig. 3 shows that the resistivities (the green lines) are largely increased when the surface vibration is considered. Furthermore, the resistivity increases non-linearly with the increasing of temperature, specially for \( d = 8 \) ML. These phenomena can be understood by the following arguments. The resistivity is heavily influenced by the surface atomic vibration, and the surface vibrational amplitudes used in our calculations are non-linearly depending on the temperature due to the reduced symmetry\(^9\). The surface atomic vibration dominates the contribution to the electron-phonon scattering because the surface to bulk ratio of the atomic numbers is very large for thin films. Therefore one observes the largest resistivity and the strongest non-linear temperature dependence in Fig. 3(a). As the increasing of the thickness, the ratio of the surface to bulk atomic number reduces and thus the contribution from the surface vibration shrinks. One may find that the temperature dependence of the resistivity becomes close to those of model (i) and (iii) as shown in Fig. 3(d).

The computational results mentioned above suggest that the non-linear temperature dependence of the resistivity might be observed in very thin films. Actually, it is not easy to obtain very thin films or wires in experiment. Recently, Plombon \textit{et al.}\(^3\) have observed a
FIG. 3. (Color online) The resistivity of Cu films with different thickness. The results for mode (i), mode (ii) and mode (iii) are represented by red, green, and black lines, respectively.

linear high-temperature dependence of the resistivity in the copper wires with the transversal dimensions ranging from 75 nm (about 400 MLs) to 520 nm (about 2880 MLs). This work implies that, to observe the nonlinear temperature dependence, more effort should be made to grow thin films or nanowires with smaller cross section.

In order to illustrate more clearly the effect of the surface electron-phonon scattering, we list the extra resistivity $\rho_s$ in table [II]. The extra resistivity is defined by $\rho_s \equiv \rho_{ii} - \rho_{iii}$, where $\rho_{ii}$ and $\rho_{iii}$ are the resistivities of Cu film for mode (ii) and mode (iii), respectively. It is the measure of the contribution due to the surface electron-phonon scattering. In the temperature range from 107 K to 685 K, the extra resistivity varies from $0.4192 \sim 18.5215 \mu\Omega cm$. 
TABLE II. The extra resistivity of Cu films due to surface electron-phonon scattering (defined by $\rho_s \equiv \rho_{ii} - \rho_{iii}$). The unit of $\rho_s$ is $\mu\Omega\text{cm}$.

| $T$(K) | $\rho_s$(8 ML) | $\rho_s$(12 ML) | $\rho_s$(16 ML) | $\rho_s$(20 ML) |
|--------|----------------|-----------------|-----------------|-----------------|
| 107    | 1.963          | 0.756           | 0.599           | 0.419           |
| 305    | 3.800          | 1.974           | 1.716           | 1.117           |
| 520    | 8.039          | 3.969           | 2.875           | 2.233           |
| 685    | 18.52          | 8.705           | 6.209           | 4.489           |

for the Cu films of different thicknesses. It is quite obvious that the surface electron-phonon scattering will become more and more important in the resistivity of Cu films when the temperature increases. This result is consistent with the experimental observation of Plombon et al. Their result showed that, for the copper wires with transverse dimension of 75 nm, the contribution from electron-phonon scattering increases from 16% to 63% when the temperature changes from $T = 20$ K to $T = 300$ K. Furthermore, we would also like to compare our result with the surface roughness contribution of the thin Cu films observed by Ke et al. They showed that the surface roughness dependent resistivity are about $2 \sim 14 \mu\Omega\text{cm}$, which falls in the above mentioned range of the extra resistivity. Thus one may conclude that the surface electron-phonon scattering plays a role at least as important as the surface roughness in the enhanced resistivity of Cu films.

It can also be found in table II that the extra resistivity $\rho_s$ decreases with the increase of the film thickness, which obviously shows the “size effect”. To make it clear, plotted in Fig. 4 is the thickness dependence of the resistivities for different models at $T = 520$ K. One may find that the value of $\rho_{iii}$ keeps almost unchanged for different thicknesses and even shows a slightly decrease as the thickness decreases, while $\rho_i$ and $\rho_{ii}$ increase with the decrease of the thickness. These results reveal that the surface atomic vibration dominates the contribution to the “size effect” of the overall resistivity.

Actually, the electron momentum can be decomposed into two components, i.e. the ones that are perpendicular and parallel to the surface, respectively. But only the perpendicular component affects the resistivity, which is called “specular electron scattering”. Chawla and Gall have showed that it is possible to reduce the surface scattering by realizing
FIG. 4. (Color online) The resistivity of Cu films as a function of thickness when the temperature is 520K.

the specular electron scattering at single-crystal Cu surface. As we have presented in the previous sections, model (iii) shows the smallest resistivity and weak size effect due to its specular surface feature. Here, we may suggest that freezing the surface vibration is also necessary for practical applications to reduce the resistivity induced by the surface electron-phonon scattering.

IV. SUMMARY

In summary, we have estimated the mean-square amplitude of atomic vibration based upon the Debye model. The mean-square amplitude was used to simulate the atomic displacements during lattice vibration in the bulk and film samples of Cu. The temperature dependence of the resistivity for bulk Cu was calculated and the result agrees reasonably well with the experiment one. The resistivity for three different Cu film models and various thicknesses were calculated and analyzed. The result shows that the surface electron-phonon scattering plays a key role in the enhancement of the resistivity at high temperature, especially for the thinner Cu films due to the quantum size effect. Comparing the conductivities for three surface vibration modes, we may suggest that freezing the surface vibration is nece-
necessary for practical applications to reduce the resistivity due to the surface electron-phonon scattering.

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