Non-monotonic boundary resistivity for electron transport in metal nanowires

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ABSTRACT

Boundary scattering is the most widely encountered size effect in nanoscale transport phenomena, and the scattering rate is usually regarded as a constant that is proportional to the ratio of carrier velocity to the characteristic size. Here, through combined experimental measurements and numerical modeling, we show non-monotonic variations of the boundary scattering rate for free electrons in metal nanowires as temperature escalates. This observation is attributed to the change of electron-phonon (e-ph) scattering angle as temperature reduces, which alters the surface scattering rate. In particular, at low temperatures, electrons traveling along the wire axis have to be first relaxed by e-ph scattering before they collide with the nanowire surface. Theoretical analysis indicates a transition temperature of 0.29 times Debye temperature. A theoretical model considering the effects of scattering angle is proposed that can fit the measured experimental data for both copper and silver nanowires over a wide temperature range.

The classical size effect, i.e., scattering of charge and/or energy carriers from materials boundaries, is the most widely encountered phenomenon in nanoscale transport studies.[1-9] It plays a critical role in electrical transport through metal thin films and nanowires, which are ubiquitous in modern electronic devices. In fact, in 2004, the International Technology Roadmap for Semiconductors implemented size-dependent values for the resistivity of copper conductors instead of listing a single bulk value.[10]

Fuchs[11] and Sondheimer[12] pioneered the study of the classical size effect on free electrons, and introduced the framework of modifying the bulk electrical conductivity with the Fuchs-Sondheimer (F-S) reduction function. The reduction function is derived based on the limitation of surface scattering on electron mean free path (MFP) and initially, the theory was applied to electron transport at ultra-low temperatures where the electron MFP is comparable to rather large sample sizes. Later the model was directly applied to transport in metal thin films and nanowires at higher temperatures as it was believed that the underlying physics remained the same.[13-15] The approach is in general highly effective and in fact, has also been extended to phonon transport in nanostructures.[16]

An alternative approach was developed through adding a surface resistivity term in the famous Bloch-Grüneisen (B-G) model, which includes the contributions of defects and e-ph scattering to the bulk resistivity of metal.[17] Many studies concluded that the B-G model could be used directly to predict the electrical resistivity of metal thin films[1,18,19] and nanowires[1-3,15] based on the finding that the model could fit the experimental data very well in a wide temperature range. It is believed that this is because the surface resistivity could be combined with the residue defect resistivity in the B-G formula as surface scattering simply adds a temperature-independent resistivity that can be absorbed into the defect scattering term.[2,3]

One general observation when using the B-G model to fit the electrical resistivity of metal thin films or wires is that the Debye temperature from the best fitting result is significantly lower than the corresponding value derived from heat capacity.[1-3,15,19] This is true even when the Fuchs-Sondheimer (F-S) model is combined with the B-G model to fit the electrical resistivity.[4-6,14,15,20] While some studies simply applied a correction factor to or adopted a semi-empirical expression for the Debye temperature used in the fitting,[1,7,8] others put forward various hypotheses to account for the decrease of the Debye temperature. For example, the lower Debye temperature has been attributed to softening of phonon modes at the surface,[5,9,14,15,18,20-25] or at the twin boundary.[4] However, this is not consistent with the observed increase in the Young's modulus of metal nanowires as a result of elastic stiffening.[26-29]

Recently Kojda *et al.*[7] noticed the discrepancy in the Debye temperature when modeling

silver nanowires and they showed that it could be reconciled by introducing a temperature dependent surface resistivity below a threshold temperature to replace the constant value at higher temperatures. In this way, they could fit the experimental electrical resistivity almost perfectly from 1.4 K to room temperature. One issue with the approach is that the temperature dependent surface resistivity below the threshold temperature was derived through assuming that the scattering angle for electrons at the wire surface could be derived in the same way as that for e-ph scattering, which is questionable.

In view of the remaining puzzle related to the classical size effect of electron transport in metal nanostructures, here we present a combined experimental and modeling effort to understand how surface scattering alters the electrical resistivity of silver and copper nanowires. The systematic study discloses the importance of coupling between small angle e-ph scattering and surface effect, which provides previously missing insights into the widely encountered classical size effect.

The electrical resistivity of copper and silver nanowires is measured using the four-probe method[13] from 20 K to 340 K in a cryostat, as shown in the scanning electron microscopy (SEM) image of Fig. 1a. These penta-twinned metal nanowires have a pentagonal cross-section and we characterize the wire size with its hydraulic diameter D_h,[13,30] four times the reciprocal of the surface-area-to-volume ratio, which is measured through cutting open the cross-section as shown in the inset of Fig. 1a. The contacts between the nanowires and the electrodes are treated with electron beam induced deposition (EBID) of Pt/C to achieve good electrical contacts. Both the copper and silver nanowires have an fcc crystalline structure and grow along the [110] direction, as shown in the high-resolution transmission electron microscopy (HRTEM) image of a representative copper sample in Fig. 1b. More details of the experimental procedure can be found in the supplementary material.

The measured electrical resistivity of copper and silver nanowires is shown in Fig. 1c and 1d, respectively. The data for both types of wires clearly indicate that the electrical resistivity shows a different trend at low temperatures from the well-expected linear increasing profile at high temperatures. The distinction is more obvious for thinner wires, which suggests that it is likely due to certain size effect. It is worth noting that several studies have reported the same observation for thin metal nanowires,[3,4,7,13,31] and even for thin metal films.[5,20] However, no satisfactory explanation of this phenomenon has been given in the literature. For example, Koleśnik-Gray *et al.*[4] suspected that the different slopes might be due to higher surface-scattering specularity at high temperatures; however, they also pointed out that it is physically unreasonable for the specularity parameter to become smaller at lower temperatures. As

mentioned previously, Kojda *et al.*[7] assume that in the low temperature regime, more forward surface scattering occurs as temperature drops; however, it is difficult to explain why the surface scattering has such a strong temperature dependence.

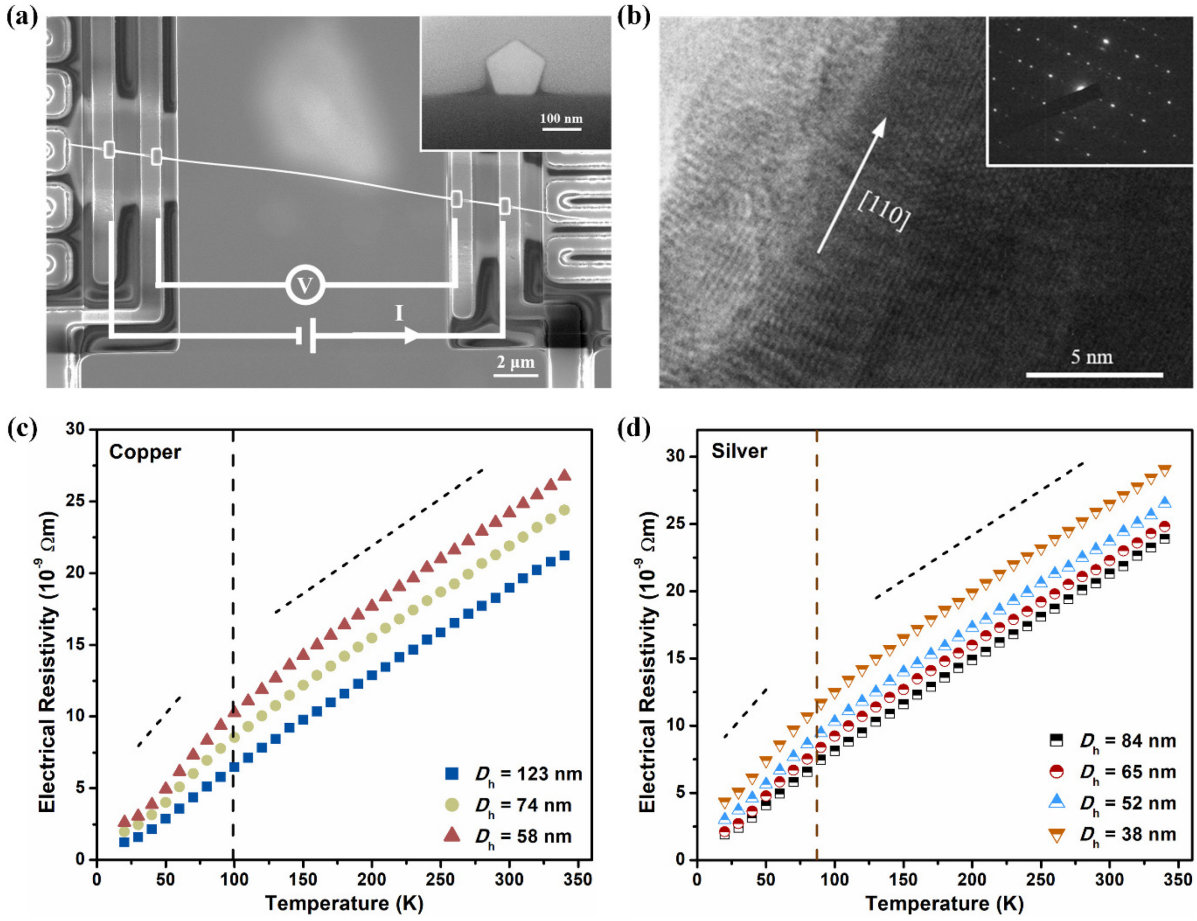

FIG. 1. (a) The SEM micrograph of a copper nanowire on the measurement device. The inset shows the cross-section of the nanowire with $D_h = 123\ nm$. (b) The HRTEM micrograph of a copper nanowire. The inset shows the selected area electron diffraction pattern. The measured electrical resistivity of (c) copper nanowires and (d) silver nanowires with different hydraulic diameters. The data for silver nanowires at temperatures above 50 K are taken from Ref. 13 with permission. Copyright 2020 American Society of Chemistry.

To explore the underlying mechanism for the distinct slope change in the nanowire resistivity, we conducted Monte Carlo (MC) simulation of electron transport under the free-electron assumption (see supplementary material for details). The resulting electrical resistivity for copper wires is presented in Fig. 2a, which demonstrates a slope change at ~100 K, consistent with the experimental data. The fact that MC modeling without adjusting the Debye temperature recaptures the experimental trend suggests that surface-induced phonon softening is not necessary to account for the electrical resistivity of metal nanowires, different from what

has been speculated in previous studies.[3-5] One more observation is that below ~100 K, the resistivity of bulk copper only changes marginally as defect scattering becomes more important than e-ph scattering, which is in sharp contrast to the behavior of the resistivity of the nanowire with a 50 nm × 50 nm square cross-section. Importantly, the only difference between the nanowires and the bulk in the MC simulations is whether surface scattering is taken into account. Therefore, the different behaviors are indeed due to the classical size effect instead of other factors such as twin boundary scattering as suggested in a previous study.[4]

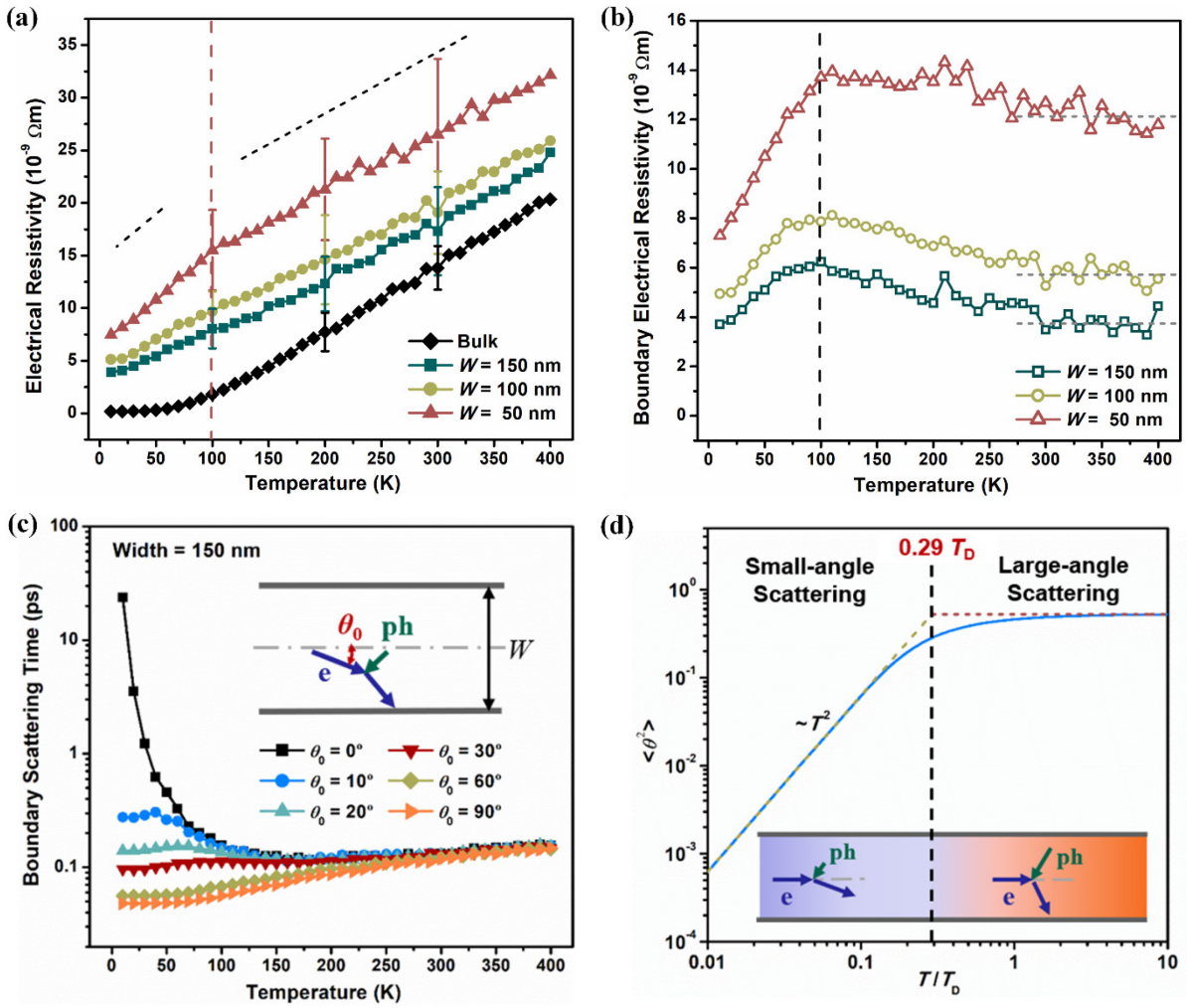

FIG. 2. (a) The electrical resistivity of copper nanowires with different widths based on the MC simulation. (b) The boundary electrical resistivity of copper nanowires with different widths based on the MC simulation. (c) The boundary scattering time of the electrons emitted with different initial emission angles θ_0, which is defined as the included angle between the wavevector of electrons and the nanowire axis as shown in the inset. (d) $\langle\theta^2\rangle$ as a function of temperature.

Based on the Matthiessen's rule,[32] we can extract the boundary electrical resistivity through subtracting the bulk resistivity from those of nanowires, as shown in Fig. 2b. The

results indicate that below ~ 100 K, the boundary resistivity of each nanowire first increases with temperature, and after reaching a peak value, it gradually declines till ~300 K and remains a plateau value for even higher temperatures. The strong variation of the boundary resistivity, especially below ~ 100 K, indicates that it cannot be combined with the defects resistivity as suggested in a few studies.[2,3] In addition, the boundary resistivity does not approach zero as the temperature drops to 0 K, which is different from the expression in Ref. 7.

To understand the interesting temperature dependence of boundary resistivity, we calculated the boundary scattering time, i.e., the average time for electrons to collide with the wire surface, for electrons emitted at different angles with the wire axis from the center line of the nanowire, as shown in Fig. 2c. Note that before the collision, the electrons may experience multiple scattering events with phonons. One important factor that has been considered in the MC simulations is the temperature-dependent phonon wave-vector distribution and the resulting variations of the probabilities for large and small angle e-ph scattering at different temperatures (see supplementary material for details).

Fig. 2c indicates that when the temperature is higher than 300 K, the boundary scattering time for electrons emitted at different angles is almost the same. This is because in this temperature regime, e-ph scattering is dominated by the large-angle scattering,[32] which leads to significant change of the electron traveling direction. As a result, electrons quickly lose the information of their initial emission angles, and the boundary scattering time is not sensitive to the emission angle.

Fig. 2c also indicates that in the regime of 100 to 300 K, the boundary scattering time for electrons with large emission angles (e.g., 60° and 90°) decreases as temperature drops, which means higher boundary scattering rates for these electrons and hence enhanced boundary electrical resistivity. It is known that the e-ph scattering rate becomes lower as temperature reduces, which renders longer intrinsic electron MFP in bulk copper. As the intrinsic MFP increases, it is more likely that electrons with large emission angles directly strike the nanowire surface, leading to enhanced boundary resistivity as the temperature reduces. Noted that this trend only holds for copper wires with diameters > 30 nm. For even thinner wires, almost all electrons with large emission angles would collide with the wire surface directly without the interference from e-ph scattering. In this case, the boundary resistivity remains approximately the same in this temperature range (see supplementary material for details).

As the temperature further drops below ~100 K, the decline of the boundary scattering time saturates as most electrons with relatively large emission angles directly strike the nanowire surface; however, the boundary scattering time for electrons with small emission

angles increases rapidly with decreasing temperature. This is because in this temperature regime, e-ph interactions are dominated by small-angle scattering without significantly altering the electron propagation direction. As such, it takes many times of e-ph scattering to deflect the electrons emitted at a small angle from the nanowire axis to collide with the nanowire surface. This effect becomes more significant at lower temperature, which renders a reducing boundary resistivity as temperature decreases. In fact, Fig. 2c indicates that the boundary scattering time for electrons emitted along the wire axis can increase by more than two orders of magnitude as the temperature drops from 100 K to 10 K.

Note that while Fig. 2c only illustrates the case for electrons emitted from a location in the centerline of the nanowire, the trend remains valid for electrons emitted at other locations in the nanowire cross-section. The above physical picture is different from that proposed by Kojda *et al.*[7] in terms that the surface scattering angle does not change with temperature but the surface scattering rate varies with temperature. Moreover, unlike the argument of Kojda *et al.*[7], the boundary electrical resistivity does not decrease to zero as the temperature approaches 0 K since the nanowire surface still limits the mean free path of electrons with large emission angles.

Now we consider the difference in the transition temperature for the electrical resistivity escalation slope for copper and silver nanowires. Fig. 1c and 1d indicate that copper nanowires have a higher transition temperature than silver nanowires and it would be highly desirable to understand the underlying mechanism for this. As the different slopes come from coupling between surface scattering and temperature-dependent electron momentum change during e-ph scattering, we consider the variance of the electron scattering angle (θ) as a function of temperature (T) as (see supplementary material for details):

$$\langle\theta^2\rangle = \frac{q_D^2}{k_F^2}\left(\frac{T}{T_D}\right)^2 \frac{\int_0^{\frac{T_D}{T}} \frac{x^3}{e^x-1}dx}{\int_0^{\frac{T_D}{T}} \frac{x}{e^x-1}dx}. \quad (1)$$

Here q_D and k_F are the Debye and Fermi wavevectors for phonons and electrons, respectively; and T_D is the Debye temperature. Fig. 2d plots $\langle\theta^2\rangle$ *versus* T and the high and low temperature limits of $\langle\theta^2\rangle$ can be expressed as:

$$\langle\theta^2\rangle \approx \frac{q_D^2}{3k_F^2} \approx 0.52 \quad for\ T \gg T_D, \quad (2)$$

$$\langle\theta^2\rangle \approx \frac{2\pi^2 q_D^2}{5k_F^2}\left(\frac{T}{T_D}\right)^2 \approx 6.16\left(\frac{T}{T_D}\right)^2 \quad for\ T \ll T_D. \quad (3)$$

Note that in the derivation of Eqs. 2 and 3, $q_D/k_F = 2^{\frac{1}{3}} \approx 1.26$ is adopted, which is valid for free electron gas in monovalent metals.[32] If we define the temperature corresponding to the intersection of the two lines described by Eqs. 2 and 3 in Fig. 2d as the transition temperature, T_{tr}, it can be estimated as:

$$T_{tr} = \frac{\sqrt{30}}{6\pi} T_D \approx 0.29 T_D. \quad (4)$$

According to Eq. 4, the transition temperature of copper nanowires can be estimated as 99 K, which matches the slope change point very well. Note that the copper nanowires we studied are of relatively large diameters and their Debye temperature is taken as the bulk value of 343 K due to the negligible elastic stiffening effects for wires of > 20 nm diameters.[29,33,34] For silver nanowires, however, the elastic stiffening effect cannot be neglected for smaller nanowires and for $D_h = 38\ nm$, the wire Debye temperature is estimated as 300 K,[13,26] which is significantly higher than the bulk value of 230 K. The corresponding transition temperature is 87 K, which again separates the two regimes where small and large angle e-ph scattering dominates very well.

The physical picture disclosed above indicates the critical role of the e-ph scattering angle; however, this effect has not been included in the theoretical models for the electrical resistivity of metal nanowires or films in the literature.[1,4,7,8,10] To reflect the coupling between surface scattering and temperature-dependent e-ph scattering angle, we propose a model to calculate the temperature-dependent electrical resistivity of metal nanowires. In constructing the model, we separate the boundary resistivity for two groups of electrons, i.e., those emitted with small and large angles from the nanowire axis. For electrons emitted at a large angle from the wire axis, it is likely that the electrons collide with the nanowire surface directly before their distributions are fully relaxed by enough e-ph scattering, as schematically shown in Fig. 3 (e). In this case, boundary scattering adds a residue resistivity that is only weakly dependent on temperature. On the other hand, for electrons emitting at a small angle from the wire axis, at low temperatures where small angle e-ph scattering dominates, it will take many e-ph scattering events before the electrons can be deflected by a large enough angle and collide with the nanowire surface. In other words, these electrons can only collide with the nanowire surface after they transport for an e-ph relaxation time (τ_{ep}) when their distributions of traveling directions are significantly relaxed by several collisions with phonons.[32] Since the probability of small-angle scattering is a strong function of temperature, the boundary resistivity for these

electrons varies significantly at low temperatures. The boundary scattering rate for these electrons can be expressed as $1/\left(D_h/(v_F \cdot sin\theta_D) + \tau_{ep}\right)$, where v_F is the Fermi velocity. θ_D represents the average angle that the electrons collide with the nanowire surface after experiencing enough e-ph scattering, as schematically shown in Fig. 3d. According to $\tau_{ep} = \tau_c/(1 - \langle\cos(\theta)\rangle) \approx 2\tau_c/\langle\theta^2\rangle$ (τ_c is the e-ph collision time),[32] at low temperatures the small $\langle\theta^2\rangle$ leads to extremely long time to relax the axial electrons, while this effect is negligible at high temperatures.

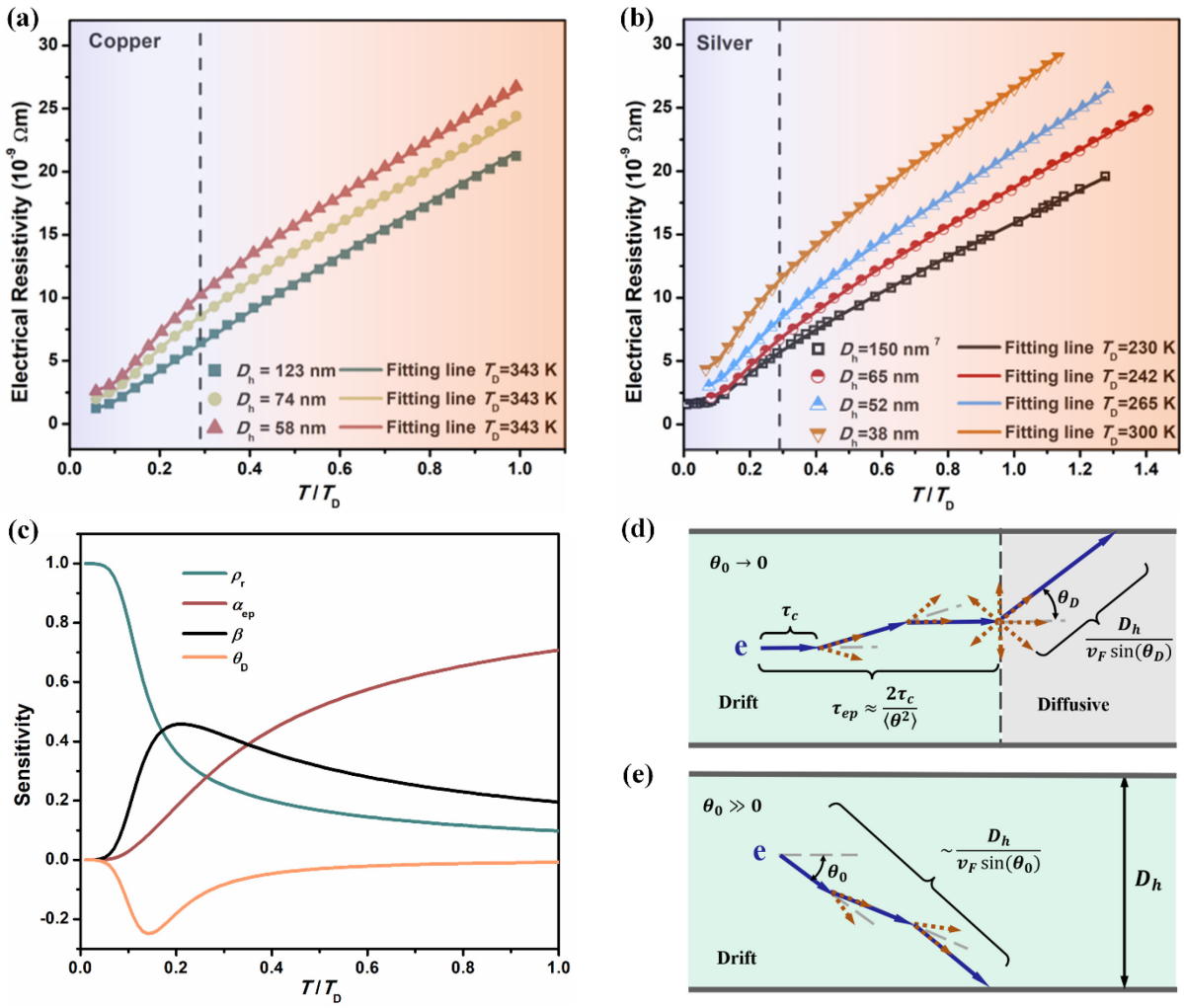

FIG. 3. Electrical resistivity of (a) copper and (b) silver nanowires with different diameters. The solid curves represent the best fitting results by using Eq. 5. (c) Sensitivity analysis for the electrical resistivity of metal nanowires in Eq. 5. Schematic illustrations of transport process in the metal nanowire for electrons with (d) small emission angles and (e) relatively large emission angles.

Based on the revealed physical picture, the temperature-dependent electrical resistivity of metal nanowires can be written as

$$\rho = \rho_r + \frac{\beta}{D_h/(v_F \cdot sin\theta_D)+\tau_{ep}} + \alpha_{ep}\left(\frac{T}{T_D}\right)^5 \int_0^{\frac{T_D}{T}} \frac{x^5 e^x}{(e^x-1)^2} dx. \quad (5)$$

Here ρ_r is the total residual resistivity, which includes both the impurity/defect resistivity and the boundary residual resistivity for electrons emitted at a large angle from the wire axis. In this simplified model, we neglect the weak temperature dependence of the boundary scattering rate for these electrons and treat ρ_r as a constant. The second term represents the boundary resistivity for those electrons emitted at a small angle from the wire axis with β as a fitting parameter. The last term is the resistivity due to e-ph scattering with α_{ep} as a constant characterizing the e-ph coupling strength according to the B-G model.[32] Taking ρ_r, α_{ep}, β, θ_D as four fitting parameters, Eq. 5 fits the experimental results extremely well as shown in Fig. 3a and 3b. In this fitting, the Debye temperature for copper wires is taken as the bulk value, while the Debye temperature for silver wires is extracted from the measured Young's modulus considering the elastic stiffening effect, as we have done previously.[20] In addition, the sensitivity coefficients (S_α), defined as the fractional variation of ρ with respect to each fitting parameter (α) as $S_\alpha = \partial \ln(\rho)/\partial \ln(\alpha)$, reveal the relative contribution of different mechanisms at different temperatures, as shown in Fig. 3c, which also reflect the relative importance of different scattering mechanisms in different temperature regimes.

In summary, systematic studies of the electrical resistivity of metal nanowires disclose an interesting transition of the escalation slope as temperature increases, which reveals a previously unrecognized coupling effect between boundary scattering and e-ph scattering. The increasing importance of small angle e-ph scattering at low temperatures renders the electrons emitted at a small angle from the wire axis much reduced boundary resistivity and alters the temperature dependence. Analysis suggests a transition temperature of $0.29T_D$, demarcating where this recognized regime has to be considered. A theoretical model that can fit the electrical resistivity over the entire temperature range was proposed, which provides a means of evaluating the electrical resistivity of various metal wires.

See supplementary material for the experimental details, the estimated boundary electrical resistivity, Monte Carlo simulation technique, the detailed derivation of the average scattering angle, the fitting parameters to recapture the experimental data, and a note about the Matthiessen's rule in the theoretical model.

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