The anisotropic size effect of the electrical resistivity of metal thin films: Tungsten

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The resistivity of nanoscale metallic conductors is orientation dependent, even if the bulk resistivity is isotropic and electron scattering cross-sections are independent of momentum, surface orientation, and transport direction. This is demonstrated using a combination of electron transport measurements on epitaxial tungsten layers in combination with transport simulations based on the ab initio predicted electronic structure, showing that the primary reason for the anisotropic size effect is the non-spherical Fermi surface. Electron surface scattering causes the resistivity of epitaxial W(110) and W(001) layers measured at 295 and 77 K to increase as the layer thickness decreases from 320 to 4.5 nm. However, the resistivity is larger for W(001) than W(110) which, if describing the data with the classical Fuchs-Sondheimer model, yields an effective electron mean free path $\lambda^*_{\text{ph}}$ for bulk electron-phonon scattering that is nearly a factor of two smaller for the 110 vs the 001-oriented layers, with $\lambda^*_{\text{ph}}(110) = 18.8 \pm 0.3 \text{ nm}$ vs $\lambda^*_{\text{ph}}(001) = 33 \pm 0.4 \text{ nm}$ at 295 K. Boltzmann transport simulations are done by integration over real and reciprocal space of the thin film and the Brillouin zone, respectively, describing electron-phonon scattering by momentum-independent constant relaxation-time or mean-free-path approximations, and electron-surface scattering as a boundary condition which is independent of electron momentum and surface orientation. The simulations quantify the resistivity increase at the reduced film thickness and predict a smaller resistivity for W(110) than W(001) layers with a simulated ratio $\lambda^*_{\text{ph}}(110)/\lambda^*_{\text{ph}}(001) = 0.59 \pm 0.01$, in excellent agreement with 0.57 ± 0.01 from the experiment. This agreement suggests that the resistivity anisotropy in thin films of metals with isotropic bulk electron transport is fully explained by the non-spherical Fermi surface and velocity distribution, while electron scattering at phonons and surfaces can be kept isotropic and independent of the surface orientation. The simulations correctly predict the anisotropy of the resistivity size effect, but underestimate its absolute magnitude. Quantitative analyses suggest that this may be due to (i) a two-fold increase in the electron-phonon scattering cross-section as the layer thickness is reduced to 5 nm or (ii) a variable wave-vector dependent relaxation time for electron-phonon scattering. Published by AIP Publishing.

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I. INTRODUCTION

Electron scattering at surfaces of narrow conductors causes an increase in the electrical resistivity $\rho$, which is typically described within the framework developed by Fuchs and Sondheimer (FS model). The FS model and its extensions assume a spherical Fermi surface and utilize a phenomenological specularity parameter $p$, which quantifies the probability for electrons being elastically reflected by the surface (i.e., specularly scattered). Some authors have theoretically considered ellipsoidal Fermi surfaces and predicted that this could lead to an anisotropic resistivity for the case of thin films or wires. Experimentally, an anisotropic size effect has been measured for Al, using single crystal rods with different major surface orientations and in-plane transport directions. However, the results did not match the theoretical expectations, such that it is unclear if the observed effect is related to the anisotropy in the Fermi surface, anisotropic electron scattering at different crystal facets, or impurities that change the carrier relaxation time near zone boundaries. This question regarding the physical origin for the anisotropy in the size effect is the primary motivation for the study presented in this article, which tests the hypothesis that the resistivity anisotropy is primarily due to the anisotropy in the Fermi surface. This is done by comparing the experimentally measured resistivity with results from a Boltzmann transport model that uses the electronic structure calculated from first-principles and therefore correctly accounts for the anisotropy in the Fermi surface and velocity. We envision that such a quantitative transport model that uses the correct bulk Fermi surface of specific metals will be useful to evaluate potential candidate material systems for high-conductivity nanowires, facilitating the development of advanced integrated circuits, flexible transparent conductors, thermoelectric power generation, magnetic sensors, and spintronics, and also help to improve the fundamental understanding of the resistivity size effect to answer questions like why the Fermi surface area obtained from size effect measurements is smaller than expected and why the experimental $\rho$ at small lengthscales is considerably larger than expected from F-S and related models.

Tungsten is an ideal candidate to study the anisotropic size effect since it has a highly anisotropic Fermi surface.
and has recently been reported to exhibit a $\rho$ for narrow single crystal wires that is dependent on the crystalline orientation. Investigations on the resistivity size effect in W are contradictory, with reported values for the bulk mean free path $\lambda$ at room temperature ranging from 10 to 54 nm for polycrystalline samples, while bulk density functional calculations suggest $\lambda = 19.1$ or 15.5 from Refs. 32 or 33, respectively, and fitting of measured resistivities of epitaxial tungsten layers yields $\lambda = 39.6$ nm with partial specular scattering for W(001), while the measured resistivity of single-crystal W(001) layers is consistent with the theoretical $\lambda = 19.1$ nm for nearly completely diffuse scattering $p = 0.11$. In addition, a report on a single crystal W foil suggests a larger degree of specular scattering for the (110) than the (100) surface at 4 K. It is completely unknown to what extent the apparent differences in $\lambda$ are a consequence of (i) the anisotropy of the W Fermi surface, (ii) variations in scattering probabilities at different surfaces, or (iii) differences in grain boundary scattering in polycrystalline samples. Furthermore, electron transport in narrow W wires has technological significance because W is a possible barrier-free candidate to substitute $<10$-nm-wide copper lines in future integrated circuits because of a potentially lower effective resistivity, better reliability, superior electromigration resistance, and good process compatibility with CMOS devices.

In this paper, we present a combination of experimental and computational results that demonstrate that the resistivity anisotropy in W layers can be explained by the anisotropy of the Fermi surface and velocity. The resistivity of W layers is simulated with a semi-classical Boltzmann transport model which utilizes the Fermi surface and Fermi velocity as a function of wave vector obtained from first principles calculations for bulk W. The simulations show a considerable resistivity anisotropy even if electron scattering at surfaces and phonons is assumed to be completely isotropic, with the predicted $\rho$ decreasing from W(001) to W(111) to W(110) layers. Epitaxial single-crystal W(001) and W(011) layers are deposited on MgO(001) and Al$_2$O$_3$(1120) substrates, respectively, and their resistivity measured in situ at room temperature and at 77 K. The resistivity of W(001) layers is larger than of W(011) layers, in agreement with the simulations. More importantly, quantifying the resistivity size effect with an effective mean free path indicates good quantitative agreement between experiment and simulation for the anisotropy effect, suggesting that the resistivity anisotropy is well explained with the anisotropy of the Fermi surface. However, the absolute resistivity increase for thin films is larger in experiment than in simulations, suggesting an increasing electron-phonon coupling for thin layers and/or a considerable effect of a wavevector-dependence in the carrier relaxation time.

II. THEORETICAL FRAMEWORK

We consider a homogeneous conducting film with an arbitrary crystalline orientation and thickness $d$, a coordinate system with the $z$-axis normal to the film surface, and an applied electric field in the $x$-direction, corresponding to the transport direction. The electron distribution function $n_q(z,k)$ for band with index $q$ is a function of wave vector $k$ and real-space position $z$ and is defined as the deviation from the equilibrium electron density $N_{eq}(k)$ in the absence of an electric field $E$. Electron scattering in the bulk, which is typically dominated by phonon scattering, is described by a carrier relaxation time $\tau_q(z,k)$ such that steady state Boltzmann transport yields

$$0 = \frac{eE}{h} \frac{\partial N_{eq}}{\partial k_x} - n_q \frac{\partial n_q}{\partial z} - v_x \frac{\partial n_q}{\partial k_x},$$

where the electron velocity perpendicular to the film surface $v_{z,q}(k) = (\hbar/v) \partial E_q(k)/\partial k_z$, $E_q(k)$ is the bulk energy vs $k$ curve for band index $q$. That is, quantum size effects on $E_q(k)$ are neglected such that $v_{z,q}(k)$ is independent of $z$. Electron scattering at the top and bottom surfaces is described by specular parameters $p_1$ and $p_2$ which define the probability for specular electron scattering at $z = d$ and 0, respectively. These parameters are in the most general case a function of $k$, $q$, the crystalline orientation relative to the $z$ axis, and particulars of the terminating surface including reconstructions, atomic-level roughness, or interfaces with adjacent layers. We choose distinct parameters for top and bottom surfaces because the experimental realization results in different surfaces, in particular, a metal-vacuum interface at the top and a layer-substrate interface at the bottom. The surface scattering defines the boundary conditions for Eq. (1), since specular scattering results in a reversal of $v_z$, such that, for example, $n_q(z = d, k_x, k_y, k_z)$ with $v_z < 0$ is set equal to $n_q(z = d, k_x, k_y, -k_z)$, similar to the original work by FS. The original work by Lucas and the current determined by integration of $n$ over both real and reciprocal space, where integration through $k$-space is transformed into an integration over the Fermi surface. Integration over $z$ is solved explicitly such that the conductivity $\sigma$ of a thin film becomes

$$\sigma = \frac{2e^2}{8\pi^2 h} \int_{FS} \left[ \frac{v_z^2}{|v|} \left[ 1 + \frac{2 - p_1 - p_2 + e^{-\eta}(p_1 + p_2 - 2p_1p_2)}{1 - p_1p_2e^{-2\eta}} \right] \times e^{-\eta} - 1 \right] dS,$$

where $\eta = \frac{d}{\tau_{q,0}}$.

Here, the factor of two accounts for the two spin directions and the integral is over the total Fermi surface (FS) of all bands. That is, summation over the band index $q$ is implied within the integral. In Eq. (2), the relaxation time $\tau$, the velocities $v_x$, $|v_z|$, $|v|$, and therefore also $\eta$, as well as $p_1$ and $p_2$ are all functions of the wavevector $k$. The original work by Fuchs and Sondheimer as well as other researchers has assumed a constant specularity parameter $p = p_1 = p_2$. For that case, Eq. (2) simplifies to

$$\sigma = \frac{2e^2}{8\pi^2 h} \int_{FS} \left[ \frac{v_z^2}{|v|} \left[ 1 + \frac{(1 - p)(e^{-\eta} - 1)}{1 - pe^{-\eta}} \right] \right] dS.$$

In the present work, we do all transport simulations for the case of completely diffuse surface scattering, that is,
\[ p_1 = p_2 = 0. \] In addition, approximating bulk electron scattering using a constant \((k\text{-independent})\) \(\tau\) results in

\[
\sigma = \frac{2e^2\tau}{8\pi^3h} \int_{FS} \frac{v^2}{j} \left[ 1 + \left( e^{-q} - 1 \right)/q \right] dS. \tag{4}
\]

That is, Eq. (4) is the conductivity of a thin film within a constant relaxation time approximation and for completely diffuse surface scattering. An alternative choice for bulk scattering is to assume a constant \((k\text{-independent})\) electron mean free path \(\lambda\). In that case, \(\tau_q(k) = \lambda/|v_q(k)|\) and the thin film conductivity becomes

\[
\sigma = \frac{2e^2\lambda}{8\pi^3h} \int_{FS} \frac{v^2}{j} \left[ 1 + \left( e^{-q} - 1 \right)/\chi \right] dS, \tag{5}
\]

where \(\chi = \frac{|v|}{|v|^2}\).

Equation (5) is for a constant mean-free-path approximation and, again, completely diffuse surface scattering.

The integrations in Eqs. (4) and (5) are done numerically, using the band structure obtained from first principles, as described in more detail in Sec. III B. This is done with scaled variables, which are independent of the choice of the constants \(\tau\) or \(\lambda\), respectively. More specifically, for the case of a constant relaxation time \(\tau\), the bulk conductivity \(\sigma_o\), or also the inverse of the bulk resistivity \(1/\rho_o = \sigma_o\) is proportional to \(\tau\) according to Eq. (4), when setting the thickness \(d\), and therefore \(\eta\), to infinity. Thus, \(\rho_o\) depends on the scattering cross-section, while, in contrast, the product \(\rho_o \times \tau\) is a constant, which only depends on the calculated electronic structure and is therefore independent on the bulk electron scattering cross section which is a function of temperature as well as impurity and defect concentrations.\(^{53}\) For simulation of a layer with finite thickness \(d\), the value of \(\tau\) is expressed in terms of the calculated constant \(\rho_o \times \tau\). Thus, the resistivity \(\rho\) of a thin film is expressed as the ratio \(\rho/\rho_o\) and calculated as a function of the product \(d \times \rho_o\), which can be done purely from first-principles without assuming any value of \(\tau\) or requiring an experimental value for \(\rho_o\). Correspondingly, for the case of a constant mean free path, \(\rho_o \times \lambda\) is independent of the scattering cross-section such that \(\rho/\rho_o\) vs \(d \times \rho_o\) can be directly obtained using Eq. (5) and the calculated bulk electronic structure.

### III. PROCEDURE

#### A. Sample preparation and analysis

Epitaxial tungsten films, 4–320 nm thick, were deposited by DC magnetron sputtering on MgO(001) or Al₂O₃(1120) substrates at 900 and 1050 °C, respectively. Deposition was done from a 5-cm-diameter 99.95% pure W target in a multi-chamber ultra-high vacuum deposition system with a base pressure <10⁻⁹ Torr, as described in more detail in Ref. 49. After deposition, all samples were annealed in vacuum at 1050 °C for 2h, followed by in-vacuum transport to the analysis chamber for in situ room-temperature resistivity measurements with a linear 4-point probe, as described in Ref. 50. Subsequently, samples were removed from the chamber through a load-lock that was vented with dry N₂ and dropped into liquid N₂ within 2 s after air exposure to minimize possible surface oxidation. The resistivity at 77 K was measured while keeping the samples immersed in liquid N₂. They were blown dry with commercial grade N₂ during subsequent warm up to 295 K, followed by X-ray reflectivity measurements in air, as described below, and 4-point probe measurements in air at 295 K, all done within 1 h after sample exposure to air. Samples were stored for 48 hours in a desiccator with <5% humidity, followed by another set of resistivity measurements at 295 and 77 K to evaluate changes in \(\rho\) during air exposure. A combination of X-ray diffraction \(\theta-\phi\) scans, \(\omega\)-rocking curves, and \(\phi\) scans of W 110 or 002 reflections was used to confirm that the layers deposited on MgO(001) and Al₂O₃(1120) are epitaxial W(001) and W(011), respectively, following a procedure similar to that described in Refs. \(^{49, 51}\) and \(^{52}\) for epitaxial W(001), ScN(001), and Sc₁₋₅Al₅N(001) layers, respectively. The out-of-plane strain of W(001) layers is 0.8%–0.2% for \(d = 4.5–320\) nm, while it is 0.2%–0.1% for 5.7–320 nm thick W(011) layers. The full-width at half-maximum of the rocking curves is \(\Delta\omega = 0.13°\) and 0.01° for W(001) and W(011) at \(d = 320\) nm, respectively, suggesting better crystalline quality for the W(011) films deposited on Al₂O₃(1120). However, this difference has no detectable (<0.3%) effect on the bulk \(\rho_o\) of W(001) vs W(011), as shown below, and is therefore assumed to have no effect on the resistivity of all samples in this study.

The layer thickness and surface roughness of samples thinner than 50 nm were determined from X-ray reflectivity (XRR), using a Panalytical X’pert PRO MPD system with a scintillator point detector with a 0.27° parallel collimator and a Cu source with a two-crystal Ge(220) two bounce monochromator which yields a \(\lambda_{\text{FeK}} = 1.5406\) Å beam with a 0.0068° divergence, as described in more detail in Ref. 49. Fitting of the \(\theta-\phi\) XRR spectra using the recursive theory of Parrat\(^{53}\) and assuming a Gaussian distribution to model the surface and interface roughness yields values for the W layer thickness and suggests fully dense W \((19.3\, \text{g/cm}^3)\) which is covered by a 0.6 ± 0.1 nm thick WO₃ surface oxide \((7.13\, \text{g/cm}^3)\) which is independent of the W thickness, assuming that the oxide-air surface and the W-WO₃ interface have the same roughness. The root-mean-square (rms) surface roughness \((\sigma)\) of W(001) increases from 0.29 ± 0.03 to 0.44 ± 0.02 to 0.80 ± 0.05 nm for \(d = 4.5 ± 0.1\) to 9.3 ± 0.1 to 18.7 ± 0.1 nm. The surface roughness for the W(110) layers is similar, with \((\sigma) = 0.19 ± 0.02\) to 0.44 ± 0.05 to 0.83 ± 0.05 nm for \(d = 5.7 ± 0.1\) to 9.3 ± 0.1 to 18.7 ± 0.1 nm. In addition, the two sample sets have a comparable film-substrate interface roughness of 0.46 ± 0.06 and 0.39 ± 0.04 nm for the W-MgO and W-Al₂O₃ interfaces, respectively. The thickness of the thicker (\(d > 50\) nm) samples is determined using the deposition rate, as calibrated from the thinner samples. X-ray photoelectron spectroscopy (XPS) was carried out to confirm the presence of WO₃ by the chemical shift of W 4f₇/₂ and 4f₅/₂ peaks, using a PHI 5000 Versaprobe™ with an Al Kα source (1486.6 eV). The surface chemistry is studied in more detail by area and line scans using Auger electron spectroscopy (ULVAC-PHI 700).
to confirm the absence of segregated surface impurities such as Mg from the substrate which may have out-diffused during annealing. Atomic force microscopy (AFM) was used to further examine the surface morphology, using a Digital Instruments Multimode III-a microscope. The rms surface roughness $\langle r \rangle$ and the lateral correlation length $L$ are obtained by quantitative analyses of the AFM data with the height-height correlation function using the GWYDDION software package, as previously done for epitaxial CrN(001)\cite{54} and Cu(001).\cite{55} This yields $\langle r \rangle = 0.29 \pm 0.02$ and $0.44 \pm 0.02$ nm with $L = 13.2 \pm 0.5$ and $14.6 \pm 0.5$ nm for W(001) layers with $d = 4.5$ and $9.3$ nm, respectively, and $\langle r \rangle = 0.16 \pm 0.03$ and $0.37 \pm 0.02$ nm with $L = 10.4 \pm 1.7$ to $8.6 \pm 0.7$ nm for W(011) layers with $d = 5.7$ and $9.3$ nm. The $\langle r \rangle$ values determined by AFM and XRR are in excellent agreement, with typical deviations of 7%-16%, which is within the measurement uncertainty.

B. Computational approach

The electronic structure of tungsten is obtained from density functional calculations using the Vienna ab initio simulation package (VASP), employing periodic boundary conditions, a plane wave basis set with an energy cutoff of 223 eV, the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) exchange correlation functional,\cite{56} and the projector-augmented wave method.\cite{57} The W 5p electrons are explicitly calculated, i.e., they are not included in the pseudopotential. Calculations are done using a one-atom primitive bcc unit cell with a lattice constant of 3.1652 Å, which corresponds to the established experimental room temperature value for W and is close to 3.17 Å, the minimum of the calculated energy vs lattice parameter curve. Self-consistent calculations using a Γ-centered 40 × 40 × 40 k-point grid are used to determine the charge distribution, which is subsequently used for non-self-consistent calculations with a finer 200 × 200 × 200 k-point mesh. Such a fine k-point sampling is required for convergence of the numerical integration across the Fermi surface, which is very sensitive to band crossings. The chosen 200\(^3\) k-points yield a computational accuracy for all reported values in this paper of ±1%.

The Fermi surface and the Fermi velocity as a function of $k$-vector are determined from the calculated bands, i.e., the calculated electron energy vs $k$ curves $E_q(k)$ where $q$ is the band index.\cite{33} This is done by dividing the Brillouin zone into irregular tetrahedra that are defined by four neighboring k-points. The intercepts of the Fermi surface with the tetrahedron edges are obtained by linear interpolation between the corners. This results in three or four intercepts per tetrahedron which define one or two triangles of the Fermi surface, respectively.\cite{37} For each triangle, the electron velocity $v_q(k) = \frac{1}{h} \nabla_k E_q(k)$ is calculated from the energy difference at the tetrahedron corners, resulting in an array of approximately $1.06 \times 10^6$ triangles and their corresponding velocity vectors that define the tungsten Fermi surface for the subsequent transport simulations.

The electron transport is simulated by numerical integration over the Fermi surface using either a constant $\tau$ or $\lambda$ approximation, as specified with Eqs. (4) and (5), respectively. More specifically, the integration in these equations becomes a sum over all triangles, where $dS$ corresponds to the triangle area in reciprocal space and the velocity components $v_x$ along the transport direction and $v_z$ perpendicular to the film surface are obtained from the dot product of the unit vectors in these directions and the velocity vector, which is expressed in a Cartesian coordinate system of the bcc crystal. In this study, we choose to calculate the thin film vs bulk resistivity ratio $\rho/\rho_o$ for three layer orientations with low index surfaces (001), (011), and (111) corresponding to the major axes in reciprocal space, and two in-plane transport directions for each layer orientation, for thousand $d \times \rho_o$ values that span over four orders of magnitudes that are experimentally relevant, i.e., exhibit an approximately negligible to 100-fold resistivity increase. These layer orientations and transport directions are chosen to quantitatively illustrate the anisotropic size effect and to directly compare the simulation results with our experimental measurements.

IV. RESULTS

A. Simulated resistivity

Figure 1 is a plot of the calculated tungsten resistivity as a function of film thickness $d$. The data are plotted as the thin film to bulk resistivity ratio $\rho/\rho_o$ vs. the product $d \times \rho_o$, as directly obtained from the first-principles calculations assuming completely diffuse surface scattering on both surfaces, i.e., $p_1 = p_2 = 0$. The curves are directly applicable to W with any given bulk resistivity $\rho_o$, which is primarily controlled by the temperature (due to phonon scattering) and is experimentally known for $T = 1–1600$ K.\cite{58} This is illustrated with the right $y$-axis and the top $x$-axis which indicate the absolute thin film resistivity $\rho$ for thickness $d = 3–1000$ nm, for the case of room temperature tungsten with a bulk resistivity $\rho_o = 5.33 \mu\Omega$ cm. The plot shows data for three layer orientations with two in-plane transport directions each. In

![FIG. 1. The simulated electrical resistivity $\rho$ of W thin films normalized by the bulk resistivity $\rho_o$, as a function of the product $\rho_o d$ for room temperature W. The inset shows the W Fermi surface colored according to the magnitude of the electron velocity.](image-url)
particular, W(001) with transport along [100] and [110], W(011) with transport along [100] and [011], and W(111) with transport along [011] and [211]. The solid lines (with symbols) indicate the results for the constant mean free path approximation, while the dotted lines are for a constant relaxation time.

All lines converge to a single bulk resistivity value for large thicknesses, consistent with W exhibiting a crystal structure with cubic symmetry, which results in an expected isotropic bulk resistivity. The thin film resistivity increases with decreasing d. This is due to diffuse surface scattering as predicted from the conventional FS-model. However, the magnitude of this increase depends on the transport direction and crystalline orientation of the layer. The transport direction has a negligible effect for the W(001) and W(111) layers. This is evident from the corresponding curves in Fig. 1, where the two brown curves labeled with up and down triangles for the W(001) layer with [100] and [110] transport directions, respectively, lay undistinguishably on top of each other. Thus, the resistivity of a W(001) layer is independent of the in-plane transport direction. We attribute this to the four-fold in-plane symmetry such that orthogonal [100] and [010] directions and therefore any other in-plane direction including the [110] have the same resistivity. Similarly, the W(111) layer exhibits a resistivity increase that is independent of the in-plane direction, with calculated values for W(111) layer exhibits a resistivity increase that is independently to a minimum $\nu_f = 2 \times 10^3 \text{m/s}$ in the electron knobs that extend along the [100] directions, $\nu_f = 9-18 \times 10^3 \text{m/s}$ for the hole octahedron and $\nu_f = 7-11 \times 10^3 \text{m/s}$ for the hole ellipsoid near the zone boundary along [100] and [110], respectively, and small hole pockets between the octahedron and the ellipsoid with $\nu_f$ of only $1-2 \times 10^5 \text{m/s}$.

We interpret the transport simulation results presented in Fig. 1 using an effective mean free path $\lambda^*$. The concept of an effective mean free path has previously been introduced to describe experimentally measured resistivity size effects that deviate from the expected bulk mean free path. Here we define the effective mean free path as the $\lambda^*$-value for which the classical Fuchs-Sondheimer model with a spherical Fermi surface predicts the same resistivity as obtained from our ab initio calculations. More specifically, the simulated room temperature resistivity data for $d = 3-1000 \text{nm}$ are fitted using the expression from the F-S model, where $\lambda$ is the only fitting parameter while $p = 0$ for both the first-principles simulations and the F-S model. We find $\lambda^*_{(001)} = 19.1 \pm 0.1 \text{nm}$ for the effective mean free path for a W(001) layer simulated using the constant $\lambda$ approximation. The fit matches well the simulated data, with deviations in $\rho$ of less than 0.5% over the entire $d = 3-1000 \text{nm}$ range, suggesting that the introduction of an effective mean free path is well suited to quantitatively describe the resistivity size effect. The corresponding value for the constant $\tau$ approximation is $23.4 \pm 0.1 \text{nm}$, which is 23% above the constant-$\lambda^*$-approximation value. Similarly, we obtain $\lambda^*_{(111)} = 16.1 \pm 0.1$ and $17.4 \pm 0.1 \text{nm}$ for the W(111) layer using constant $\lambda$ and $\tau$ approximations, respectively, with the deviation in $\rho$ between first-principles prediction and FS-fit being $<1.5\%$. For the W(011) layer, we use the average of the simulated conductivities along [100] and [011] and find $\lambda^*_{(011)} = 11.2 \pm 0.2 \text{nm}$ for the constant-$\lambda^*$-approximation and $\lambda^*_{(011)} = 10.7 \pm 0.3 \text{nm}$ for the constant-$\tau$-approximation. For this case, the deviation between simulation and FS-fit is larger, up to 5% within $d = 4-1000 \text{nm}$. This larger deviation is the result of a weaker (smaller curvature) $\rho$ vs $d$ dependence from the $ab$ initio calculations than from the analytical FS solution, which may be related to the in-plane anisotropy of the W(011) layer that exhibits a transport direction dependent size effect and is therefore less free-electron-like. Comparing the $\lambda^*$ for the different layer orientations quantitatively illustrates the above discussed anisotropy of the resistivity size effect: $\lambda^*_{(001)}$ is 19% and 71% larger than $\lambda^*_{(111)}$ and $\lambda^*_{(011)}$ within the constant mean free path.
approximation, while it is 34% and 119% larger for the constant relaxation time approximation, consistent with the highest resistivity for the W(001) layer and the lowest resistivity for the W(011) layer.

B. Measured resistivity

Figure 2 is a plot of the measured resistivity ρ vs layer thickness \( d = 5–320 \text{ nm} \) of single crystal W(001) and W(011) layers grown on MgO(001) and Al₂O₃(1120) substrates, respectively, as measured in situ in vacuum at 295 K. The corresponding ρ at 77 K obtained by sample immersion in liquid nitrogen is shown in the inset. At large thickness \( d = 320 \text{ nm} \), the measured ρ is independent of layer orientation. More specifically, \( \rho_{(011)} = 5.75 \pm 0.02 \) and \( \rho_{(001)} = 5.76 \pm 0.02 \, \mu\Omega \text{ cm} \), respectively, which is 8% larger than the reported room-temperature bulk resistivity \( \rho_{295 \text{ K}} = 5.33 \, \mu\Omega \text{ cm} \).\(^{56}\) This deviation is attributed to a combination of electron scattering at surfaces (2%) and at residual impurities and/or defects (6%), which is independent of layer orientation and is therefore assumed to be constant for all layers in this study. As \( d \) decreases, the resistivity increases for both sample sets, reaching 13.2 ± 0.2 \( \mu\Omega \text{ cm} \) for W(011) at \( d = 5.7 \text{ nm} \) and 24.4 ± 0.6 \( \mu\Omega \text{ cm} \) for W(001) at \( d = 4.5 \text{ nm} \). This increase is attributed to electron surface scattering, as discussed below, and is more pronounced for the W(001) than the W(011) layers. For example, \( \rho_{(001)} \) is 14% larger than \( \rho_{(011)} \) at \( d = 18.7 \), and 30% larger for \( d = 9.3 \text{ nm} \). This is in good agreement with the simulation results in Fig. 1, which predict \( \rho_{(001)} \) to be 10% and 23% larger than the average \( \rho_{(011)} \) at \( d = 18.7 \) and 9.3 nm, respectively. The 77 K data in the inset confirm that the resistivity of W(001) and W(011) layers diverges with decreasing \( d \), with \( \rho_{(001)} \) being approximately two times larger than \( \rho_{(011)} \) for \( d \sim 5 \text{ nm} \).

Surface oxidation experiments (not shown) are performed to explore potential changes in the scattering specularity upon oxidation, as has previously been observed for Cu(001) layers.\(^{12,36,60,61}\) More specifically, after resistivity measurements at 295 and 77 K, the W layers are exposed to air and additional resistivity measurements are done after 1 and 48 h. Air exposure for 1 h yields \( \rho_{(001)} \) and \( \rho_{(011)} \) values that are increased by 0.1%–2% and 0.1%–3.3%, respectively, over the entire thickness range \( d = 4–320 \text{ nm} \). This increase is of comparable magnitude as the experimental uncertainties of 0.4%–1.3% and 0.1%–1.8%, respectively, indicating a negligible (\( \Delta \rho < 0.06 \)) change in the surface specularity parameter. Prolonged 48 h air exposure of the two sets of samples still shows negligible changes of their resistivity measured at both 295 and 77 K, with the exception of the thinnest W layers with \( d = 4.4 \) and 5.7 nm, which exhibit a slight increase in \( \rho \) of 6.2 and 5.2%, respectively. This increase is attributed to the reduction of the effective conducting cross section due to W surface oxidation. The overall observation that surface oxidation has no effect on the scattering specularity suggests that electron scattering at the W-vacuum and W-liquid nitrogen interfaces is completely diffuse. This is because the scattering specularity is expected to decrease upon oxygen chemisorption\(^{56,66}\) and subsequent surface oxidation.\(^{36,66}\) In turn, the absence of a decrease in the specularity upon oxidation indicates that the specularity is already zero at the beginning. In addition, the difference between \( \rho_{(001)} \) and \( \rho_{(011)} \) is independent of air exposure time, indicating that the size effect anisotropy is unaffected by surface oxidation. The completely diffuse electron scattering at the W-vacuum and W-liquid nitrogen interfaces is consistent with previous reports on the size effect in tungsten\(^{26}\) and is attributed to atomic surface roughness and the related local surface/interface charges,\(^{62}\) which (1) cause a lateral perturbation of the flat surface potential drop, resulting in destructive interference of electron waves after reflection\(^{36,63}\) and/or (2) terminate the electron plane wave at the crystal surface,\(^{64}\) both leading to a randomization of the electron momentum. The surface charge is the result of the narrowing of the \( d \) bands at the surface layer due to the reduced number of neighboring atoms, which pushes the occupied states above the bulk Fermi level. Therefore, electrons must flow away from these occupied states leaving the surface with a net positive charge relative to the bulk and causing a surface core level shift which has been experimentally observed and quantified for W.\(^{65}\) When the W surface layer is oxidized, the completely diffuse scattering at W-WO₃ is the consequence of transitions of electrons at the Fermi level between delocalized states of the W layer and localized surface states in WO₃, which effectively randomize the electron momentum corresponding to diffuse surface scattering events.\(^{36,62}\) This mechanism is the same as the completely diffuse scattering reported for the Cu-Cu₂O interface,\(^{36}\) where the density of localized states of \( 1 \times 10^{19} \text{ eV}^{-1} \text{ cm}^{-3} \) at the Fermi level in WO₃ (Ref. 66) is comparable to the hole concentration of \( 1.11 \times 10^{19} \text{ cm}^{-3} \) in Cu₂O.\(^{67}\)

The solid lines in Fig. 2 are obtained by curve fitting to the measured resistivity. This is done using the conventional Fuchs-Sondheimer analytical solution for a spherical Fermi surface and completely diffuse surface scattering \( (p = p_1 = p_2 = 0) \), where the mean free path is a free fitting parameter which is independently determined for each layer orientation. That is, effective mean free paths \( \lambda_{(001)}^\ast \) and \( \lambda_{(011)}^\ast \) are
obtained independently for the W(001) and W(011) layers. For the fitting procedure, the bulk resistivity is kept fixed at the reported room temperature value of \( \rho_{o,295K} = 5.33 \) \( \mu \Omega \) cm. The assumption of \( p_1 = 0 \) is based on the above described oxidation experiments which suggest completely diffuse electron scattering at the W-vacuum and W-liquid N\(_2\) interfaces, while \( p_2 = 0 \) corresponds to diffuse scattering at the W-MgO and W-Al\(_2\)O\(_3\) interfaces and is expected based on reported studies of metal-MgO\(^ {36,68}\) and W-Al\(_2\)O\(_3\) interfaces.\(^ {32}\) We note here that the experimental evidence for \( p_1 = p_2 = 0 \) can be questioned and that non-zero values for \( p_1 \) and/or \( p_2 \) would increase the effective mean free path without considerably affecting the quality of the fit. Correspondingly, the \( \lambda^* \) values presented in the following can either be considered a lower bound for the experimental mean free path or may be defined to include a possible non-zero specularity. However, these subtle differences in the definition of \( \lambda^* \) do not affect the quantitative conclusions on the anisotropy of the size effect presented in this paper.

The curve fitting yields effective mean free paths of \( \lambda^{*}_{(001)} = 33.0 \pm 0.4 \) nm and \( \lambda^{*}_{(011)} = 18.8 \pm 0.3 \) nm for the W(001) and W(011) layers at 295 K. The corresponding values at 77 K are directly determined from the reported W bulk resistivity of 0.549 \( \mu \Omega \) cm\(^ {77K}\) at 77 K and using the fact that the product \( \rho_0 \lambda \) is independent of temperature as previously done in studies on TiN\(^ {59}\) and W,\(^ {32}\) yielding \( \lambda^{*}_{(001)} = 320 \pm 4 \) nm and \( \lambda^{*}_{(011)} = 182 \pm 3 \) nm. Correspondingly, the solid lines plotted in the inset are obtained using these \( \lambda^{*} \) values without any fitting parameters. They match the measured data very well, confirming that the electron scattering specularity at the W-vacuum and the W-liquid N\(_2\) interfaces is identical. This analysis confirms the considerably larger resistivity size effect for the W(001) than the W(011) layers. We calculate a ratio \( \lambda^{*}_{(011)}/\lambda^{*}_{(001)} = 0.57 \pm 0.01 \). This value agrees well with the results from the \textit{ab initio} calculations which predict \( \lambda^{*}_{(011)}/\lambda^{*}_{(001)} = 0.59 \pm 0.01 \) and 0.46 \( \pm 0.01 \) for the constant \( \lambda \) and \( \tau \) approximations, respectively. In addition, in order to determine to what extent the assumption of \( p_1 = 0 \) affects this good agreement, we have done alternative data fitting assuming \( p_1 = 0.11 \), which is the value from Ref.\(^ {32}\). This yields \( \lambda^{*}_{(011)} = 20.1 \pm 0.3 \) nm and \( \lambda^{*}_{(011)}/\lambda^{*}_{(001)} = 0.61 \pm 0.01 \), which is close to 0.57 \( \pm 0.01 \), suggesting that small variations in \( p_1 \) have a negligible effect of the measured anisotropy. We note here that the in-plane anisotropy that is predicted in Fig.\(^{1}\) for W(011) layers with different transport directions cannot be experimentally verified with our \textit{in situ} linear 4-point probe setup, which uses unpatterned as-deposited samples and therefore effectively measures approximately an average over all in-plane directions. The reader is referred to Ref.\(^ {30}\) which presents a study on this in-plane anisotropy. However, this previous study cannot be quantitatively compared to our simulation results, because of the complicating fact that the studied wires exhibit two pairs of terminating surfaces, such that they no longer represent a thin film conductor. We also note that our analysis uses previously reported values for the bulk resistivity at 295 and 77 K. This approach neglects the effect of impurity scattering on the resistivity. Using an alternative fitting approach suggests that the resistivity due to impurity scattering in our samples is 0.33 \( \pm 0.05 \) \( \mu \Omega \) cm, and results in a correction to the reported \( \lambda^* \) values of 4\%–6\%, which is comparable to the quoted experimental uncertainty and is therefore neglected.

V. DISCUSSION

Here we present first a discussion on the physical origin for the anisotropy of the resistivity size effect, based on the good quantitative agreement in the magnitude of the anisotropy from computational and experimental data for W(001) and W(011) layers. Second, we discuss the effective bulk electron mean free path for tungsten, including possible reasons for the difference in the absolute \( \lambda^* \) values between experiment and simulations. Last, we briefly discuss how the findings in this paper may affect the search for metals that exhibit a high conductivity at small dimensions.

A. Resistivity anisotropy

In Sec. IV, we have presented the resistivity of tungsten layers vs their thickness from both first-principles simulations and experimental measurements, with the goal to determine the physical origin for the resistivity anisotropy effect. The data from simulations and experiments can be directly and quantitatively compared for the case of the room temperature resistivity of W(001) and W(011) layers. Both simulations and experiments quantitatively show an anisotropy in the resistivity with a considerably larger \( \rho \) for W(001) than W(011) layers. To facilitate the understanding of this effect and comparison between simulation and experimental results, the \( \rho \) vs \( d \) data have been fitted using the classical Fuchs-Sondheimer model with an effective orientation-dependent mean-free path, yielding \( \lambda^{*}_{(011)} = 33.0 \pm 0.4 \) nm and \( \lambda^{*}_{(001)} = 18.8 \pm 0.3 \) nm from experiment, and \( \lambda^{*}_{(011)} = 19.1 \pm 0.1 \) nm and \( \lambda^{*}_{(001)} = 11.2 \pm 0.2 \) nm from the simulation with a constant-\( \lambda \)-approximation. While the values from the simulations are smaller than that from the experiment (as discussed in Section VB), the anisotropy effect from experiment and simulation agrees very well, with \( \lambda^{*}_{(011)}/\lambda^{*}_{(001)} = 0.57 \) and 0.59 from experiment and simulation, respectively. This excellent quantitative agreement in the magnitude of the anisotropy effect indicates that the simulation correctly describes the resistivity anisotropy in tungsten layers. Therefore, we postulate that the simulations can be directly used to determine the physical origin of the anisotropy effect. More specifically, the simulations account for the correct anisotropic Fermi surface and \( k \)-vector-dependent electron velocity, but consider the electron scattering at surfaces and in the bulk to be completely independent on surface orientation and \( k \)-vector. Thus, we conclude that the anisotropy of the resistivity in W layers is purely due to the orientation of the Fermi surface relative to the layer orientation and transport direction, while the actual scattering events at different surfaces as well as the anisotropy in electron-phonon scattering have a minor/negligible effect on the resistivity anisotropy. This conclusion answers the open question regarding the physical origin of the anisotropic size effect of the electrical resistivity, as introduced in Sec. I, which is expected to affect the resistivity of most elemental metals based on their non-spherical Fermi surface shape.\(^ {33}\)
We note here that the quantitative agreement between experiment and simulations does not preclude the possible anisotropic electron scattering at surfaces, at phonons, and/or at grain boundaries in other material systems. The agreement simply suggests that the anisotropic Fermi surface correctly accounts for the anisotropy in the resistivity, without the need for the electron scattering itself to be anisotropic.

In order to gain direct qualitative insight into why the resistivity of thin W(001) layers is larger than of corresponding W(011) layers, we evaluate Eq. (5) in the limiting case of small and large layer thickness \(d\), corresponding to \(\chi \ll 1\) and \(\chi \gg 1\), respectively. A second order expansion of the exponential in Eq. (5) results in the integrand being proportional to \(|v_z|/v\). Here we use the qualifier “approximately” because the integrand also includes a weighting term \(v_z^2/v^2\) which depends on the transport direction. Similarly, for large thicknesses, the resistivity becomes constant plus a term that is proportional to \(|v_z|/v\). Therefore, for all \(d\), the resistivity size effect increases monotonically with \(|v_z|/v\). This ratio is proportional to the projection of the Fermi surface onto a plane that is parallel to the thin film surface. Thus, we expect the highest resistivity for the layer orientation with the largest projected Fermi surface. This qualitative argument is directly verified by numerically determining the projection of the Fermi surface onto (001), (011), and (111) planes, yielding 9.72, 8.91, and 9.34 Å\(^2\), respectively. That is, this argument predicts \(\rho_{(001)}>\rho_{(111)}>\rho_{(011)}\), where the subscript refers to the thin film orientation (not the transport direction). This resistivity ranking matches the predicted resistivities shown in Figs. 1 and 2, confirming the applicability of this qualitative argument. In addition, the argument also makes intuitive sense: The Fermi surface projection onto the film surface plane is proportional to the ballistic (Sharvin) conductance perpendicular to the film surfaces, which are calculated to be: 9.53 \(\times 10^{14}\), 8.74 \(\times 10^{14}\), and 9.17 \(\times 10^{14}\) \(\Omega^{-1}\) m\(^{-2}\) for (001), (011), and (111) directions of W, respectively, where the values include both spin directions. The largest ballistic conduction for the (001) direction leads to the largest flux of electrons impinging on the W(001) surface, causing most surface scattering and, in turn, the highest resistivity for the W(001) layers. We note that these arguments are done using the constant free-path approximation with a conductivity based on Eq. (5). This expression is not directly dependent on the electron velocity but only on the ratios \(v_z/v\) and \(v_z/\hbar\). Therefore, the resistivity size effect in the constant-\(\lambda\)-approximation is only dependent on the shape of the Fermi surface, but unaffected by the magnitude and/or anisotropy of the Fermi velocity. In contrast, the velocity explicitly enters the conductivity formula for a constant relaxation time approximation in Eq. (4), as the expression contains \(v_x\) as well as \(v_z\) through the parameter \(\eta\). Therefore, a qualitative argument for the resistivity size effect in the constant-\(\tau\)-approximation needs to also include the variation in the electron velocity, as indicated by the color coding in the inset in Fig. 1. In particular, the size effect is expected to be most pronounced for layer orientations which result in a large Fermi velocity component perpendicular to the surface, which correspondingly leads to more pronounced surface scattering in the case of a constant \(\tau\). To test this argument, we use numerical integration over the Fermi surface to calculate the average of the Fermi velocity component along certain crystalline directions and find \(v_{(001)}=5.17 \times 10^5\) m/s, \(v_{(011)}=4.55 \times 10^5\) m/s, and \(v_{(111)}=4.84 \times 10^5\) m/s. Here, the Fermi velocity is largest along the (001) direction, which leads to the largest resistivity for the W(001) layer, as indicated by the brown dotted line in Fig. 1 for the simulated resistivity of the W(001) layer using a constant \(\tau\) approximation. Conversely, the resistivity of W(011) is smallest because of the small Fermi velocity component along (011). This can be observed in the inset of Fig. 1, which shows particularly slow electrons with a blue contrast (2 \(\times 10^5\) m/s) in the electron knobs. Each knob has four dark blue patches when the Fermi surface is perpendicular to (011). We note that observing the plotted Fermi surface and then correctly predicting the resistivity anisotropy are, however, not trivial, particularly since the velocity vector is not proportional to the wave vector but is perpendicular to the Fermi surface, such that local curvatures considerably affect the ultimate transport properties but may not be evident when just “looking” at the plotted Fermi surface.

### B. Tungsten mean free path

In this section, we discuss the quantitative values for the tungsten electron mean free path \(\lambda\) as summarized in Table I, and possible causes for the quantitative deviation between experiment and simulation. Conceptually, the mean free path is the distance that an electron travels between two scattering events. However, consistent with most literature in the field of the resistivity size effect, electron scattering at surfaces is not considered to affect \(\lambda\). That is, \(\lambda\) is defined as a bulk property that quantifies the distance that an electron travels between two electron-phonon scattering events, including other (typically negligible) bulk scattering events. In addition, we also define an effective mean free path \(\lambda^*\), which corresponds to the characteristic length scale that quantifies

<table>
<thead>
<tr>
<th>Method</th>
<th>(\lambda^*) (001)</th>
<th>(\lambda^*) (011)</th>
<th>(\lambda_{min}) (001)</th>
<th>(\lambda^*) (111)</th>
<th>(\rho)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
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<td>Constant mean free path</td>
<td>19.1</td>
<td>18.8 ± 0.3</td>
<td>0.57</td>
<td>16.1 ± 0.1</td>
<td>0.11</td>
<td>Reference 32</td>
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<tr>
<td></td>
<td>39.6</td>
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<td></td>
<td>0.3</td>
<td>Reference 35</td>
</tr>
<tr>
<td></td>
<td>33.0 ± 0.4</td>
<td>11.2 ± 0.2</td>
<td>0.59</td>
<td>17.4 ± 0.1</td>
<td>0</td>
<td>Experimental results from this study</td>
</tr>
<tr>
<td></td>
<td>19.1 ± 0.1</td>
<td>10.7 ± 0.3</td>
<td>0.46</td>
<td></td>
<td>0</td>
<td>Simulation results from this study</td>
</tr>
</tbody>
</table>

TABLE I. The effective electron mean free path \(\lambda^*\) for W(001), W(110), and W(111) layers. The listed \(\rho\) indicates the surface scattering specularit.
the resistivity size effect. That is, $\lambda^*$ is a fitting parameter that is determined by describing resistivity vs thickness data with the conventional Fuchs-Sondheimer model. In the classical isotropic limit, $\lambda^*$ should be equal to $\lambda$.

For bulk tungsten, our simulations yield a room temperature $\lambda$ of 15.4 nm, as obtained from the calculated Fermi surface by setting $d = \infty$ in Eq. (5) and using the reported 5.33 $\mu\Omega$ cm for the bulk resistivity of W at 295 K. This $\lambda = 15.4$ nm is reasonably close to previously reported values of 15.4 nm$^{33}$ and 19.1 nm$^{32}$ and is identical ($\pm$1%) to the average of the three effective mean free paths $\lambda^*_{(001)} = 19.1 \pm 0.1$ nm, $\lambda^*_{(011)} = 11.1 \pm 0.2$ nm, and $\lambda^*_{(111)} = 16.1 \pm 0.1$ nm calculated using the constant-$\lambda$-approximation, while the corresponding values for the constant-$\tau$-approximation of 23.4 $\pm$ 0.1 nm, 10.7 $\pm$ 0.3 nm, and 17.4 $\pm$ 0.1 nm yield a slightly larger average of 17.2 nm. The considerable variation of $\lambda^*$ with layer orientation and chosen electron-relaxation-approximation may be the reason for the large range of reported mean free paths determined from polycrystalline$^{29,30}$ and single crystal W with different orientations$^{32,33}$ and different specularity parameters reported for W(001) and (011) surfaces.$^{35}$ Furthermore, the reported failure of the FS analytical solution$^{26}$ may be caused by a change in the effective mean free path associated with changes in the grain orientation distribution parallel to the surface.

Our measured $\lambda^* = 33.0 \pm 0.4$ and 18.8 $\pm$ 0.3 nm for W(001) and W(011) layers, respectively, is 45%–74% larger than the corresponding values from our ab initio simulations using constant $\tau$ or $\lambda$ approximations. In the following, we discuss possible reasons for this considerable quantitative disagreement: First, the deviation may be due to a possible thickness-dependence in the electron-phonon scattering cross-section $\sigma_p$. Previous reports have suggested that the electron-phonon coupling increases with decreasing thickness$^{69,70}$ which, in turn, leads to a decrease in $\lambda$ with decreasing $d$.$^{71}$ In order to explore this possible explanation, we treat $\lambda$ in Eq. (5) as a free thickness-dependent variable such that the simulated resistivity in Fig. 1 matches the measured values in Fig. 2. This leads to an electron-phonon scattering cross-section $\sigma_p$ for thin films that is larger than the bulk value $\sigma_p^{\infty}$. Figure 3(a) shows the increase in the electron-phonon scattering cross section as a plot of the ratio $\sigma_p/\sigma_p^{\infty}$ vs layer thickness $d$ for W(001) and W(011) layers. Both W(001) and (011) exhibit a similar trend, with $\sigma_p/\sigma_p^{\infty}$ increasing to 2.44 for W(001) with $d = 4.5$ nm and to $\sigma_p/\sigma_p^{\infty} = 1.64$ for W(011) with $d = 5.7$ nm. This increase by a factor of two for layers with a thickness of $\sim5$ nm is in reasonable agreement with a reported two times higher electron-phonon scattering rate for 4 nm thick epitaxial Cu(001) layers than for bulk Cu.$^{72}$

A second possible reason for the quantitative difference in the simulated and measured effective W mean free paths is the approximation in our calculations of an isotropic bulk electron scattering, that is a wave-vector independent carrier relaxation time $\tau$. It is beyond the computational scope of this work to explicitly determine the wave-vector dependence of the electron-phonon coupling. Thus, in a first level-attempt to explore the effect of a varying $\tau$, we replace the constant $\tau$ with a log-normal distribution which is identical for all $k$-vectors. This is illustrated in the inset of Fig. 3(b) showing the probability distribution $P$ vs $\tau$ for an average $\bar{\tau} = 1.58 \times 10^{-14}$ s and a logarithmic standard deviation scale factor $\sigma_s = 1.18$. Here, we choose the average relaxation time $\bar{\tau}$ to be identical to the relaxation time calculated from Eq. (4) for bulk W. This is because for the limiting case of large $d$, and therefore large $\eta$, the $\sigma$ calculated in Eq. (4) becomes proportional to $\tau$ such that the simulated bulk conductivity is only dependent on the average $\tau$ but is independent on the distribution of $\tau$. In contrast, for thin films, surface scattering more strongly affects the current carried by electrons with a large $\tau$ which also have large mean free paths. Thus, replacing a constant $\tau$ with a distribution of $\tau$-values that have the same average $\tau$ does not affect the bulk resistivity but increases the resistivity for thin films, where the width of the distribution is a free parameter that defines the magnitude of this effect. Correspondingly, we choose $\sigma_s$ such that the simulated resistivity most closely matches the experimentally measured $\rho$. The result is shown in Fig. 3(b). The plotted data points are the measured resistivity of W(001) and W(011) layers reproduced from Fig. 2, the dotted lines indicate the original simulated resistivity for a constant $\tau$ for W(001) and W(011) with averaged transport directions, and the solid lines are the new predicted resistivity for a variable $\tau$ with the log-normal probability distribution shown in the inset. The solid lines for a variable $\tau$ match the measured data considerably better than the dotted lines.

FIG. 3. (a) The electron-phonon scattering cross section $\sigma_p$ in W(001) and W(011) thin films vs thickness $d$, normalized by the bulk cross section $\sigma_p^{\infty}$.
(b) Resistivity vs thickness $d$ of W(001) and W(011) layers. The data points are measured values, the dotted lines are from a constant $\tau$ simulation, and the solid lines from a simulation using a log-normal distribution for $\tau$, which is shown in the inset.
In particular, the variable $\tau$ increases the simulated $\rho$ for all finite thicknesses, removing the systematic underestimation of $\rho$ by the constant-$\tau$ simulation. For small layer thickness $d < 10$ nm, the agreement is not good, indicating the limits of this approach. In particular, the approach of a variable $\tau$ that is identical for all $k$-vectors is different from the expected variation in $\tau$, which is expected to be a function of $k$. Thus, the curves presented in Fig. 3(b) primarily illustrate that a variable $\tau$ leads to an increase in the simulated resistivity size effect which can explain the deviation of the measured and simulated data presented in Figs. 1 and 2, and may possibly also explain the reported$^{26}$ underestimation by the FS model of the thin film resistivity for small feature sizes ($d < 10$ nm).

Lastly, we discuss if surface roughness effects may explain the difference in the measured and simulated $\lambda^*$ values in this study. As presented in Sec. III A, the deposited W layers exhibit an rms surface roughness $\langle r \rangle$ that increases with the layer thickness, while the lateral correlation length $L$ remains approximately constant with increasing $d$. The two sample sets have similar values ($\pm 10\%$) for $\langle r \rangle$, $L$, and the substrate-layer interface roughness, indicating that the contribution to $\rho$ due to the surface roughness is comparable for the two layer orientations and therefore the surface roughness does not explain the resistivity anisotropy measured in our samples. In fact, applying a recent quantum model for the resistivity roughness effect by Chatterjee and Meyerovich$^{74}$ to our 5 to 9 nm thick W(001) and W(011) layers with measured $\langle r \rangle$ and $L$ values suggest that surface roughness effects would cause a slightly lower resistivity for the W(001) layers than the W(011) layers, in direct contradiction with the measured results. This is consistent with our discussion in Sec. VA, which attributes the resistivity anisotropy to the anisotropy in the Fermi surface. We note that strong interference between bulk and surface scattering is not expected in our films because the measured $L \approx 10$ nm is much larger than the critical value $l$ of 1.8 nm, estimated based on the reported relation $l^2 \sim a \lambda$, where $a$ is the atomic size.$^{74}$ In addition, the surface roughness causes a variation in the film cross section which increases the mean $\rho$. This is known as geometrical effect$^{75}$ and is quantified for our samples using the Namba model.$^3$ However, the corrections to the resistivity are very small ($<1\%$), due to the relatively smooth W(001) and W(011) surfaces with a small measured $\langle r \rangle < 1$ nm.$^{36,74,76}$ On the other hand, multi-scattering model calculations suggest that surface mounds with successive steps can act as multiple scattering centers such that, for example, a single step is predicted to cause a 1.5 times larger surface resistivity than atomic roughness.$^{77}$ Similar effects may also affect our W samples such that the difference in $\lambda^*$ values from simulation and experimental measurements presented in Secs. IV A and IV B could possibly be attributed to surface morphology effects.$^{78}$ A good review of such surface morphology effects on the resistivity can be found in Ref. 79. In contrast, as discussed, the measured resistivity anisotropy between our W(001) and W(111) layers cannot be easily attributed to surface morphological effects because their measured surface morphological parameters are very similar.

C. Implications for nanoscale interconnects

The most prominent technological need for metallic conductors with nanoscale ($<10$ nm) width is integrated circuits,$^{13–17}$ followed by other emerging technologies including transparent flexible conductors,$^{18–20}$ thermoelectrics,$^{21,22}$ magnetic sensors,$^{23}$ and spintronics.$^{24}$ The International Technology Roadmap for Semiconductors (ITRS) states in its 2013 interconnect summary that the biggest near term challenge for interconnects is the introduction of new materials that meet wire conductivity requirements, while the 2015 ITRS report becomes even more explicit, specifying the need to replace copper as interconnect material to limit the resistance increase at reduced scale in order to minimize both power consumption and signal delay. The implication of the results from our study on the search for metals to replace Cu nanowires can be summarized in two ways: (1) The orientation of the Fermi surface relative to the layer orientation and transport direction determines the actual increase in the resistivity at reduced dimension. Therefore, instead of considering a new material with a smaller bulk mean free path$^{26,34}$ or engineering the surface to increase its scattering specularity,$^{12,45}$ it may become more practical to increase nanowire conductivities by texturing the microstructure such that the surface orientation corresponds to the smallest projected Fermi surface orientation and that the Fermi velocity component perpendicular to the surface is minimized. It is noteworthy that a U.S. patent (9117821) about orientated crystal nanowire interconnects has already been granted to Barmak et al. and the anisotropic effect has been reported on W nanowires with transport directions (001) and (110) vs (111),$^{30}$ The results presented in this paper clearly demonstrate that the correct choice of crystalline orientation has the potential to reduce nanowire resistance, by approximately a factor of two for the case of tungsten. More importantly, the combined experimental and computational results show that the anisotropy effect can be explained using the bulk calculated electronic structure, without the need to consider electron scattering cross sections. Therefore, we expect that the anisotropy effect can be accurately predicted for any metal and any wire orientation using the computational approach presented in this paper, which may be extended to include the orientation distribution of, for example, textured polycrystalline wires or electron scattering at grain boundaries$^{38,40}$ where the latter is expected to add an additional anisotropy effect. In contrast, first-principles methods that quantitatively predict the electron scattering specularity at metal-barrier interfaces are still limited,$^{44}$ and experimentally, it has been found that electron scattering at heterogeneous interfaces between wires and metallic barrier layers is mostly diffuse.$^{4,11,12,81}$ We envision that the proposed textured nanowires that will take the advantage of the resistivity anisotropy can be achieved by engineering interface and strain energy,$^{82,83}$ local epitaxy to an under layer,$^{68,84}$ alloying,$^{85,86}$ and appropriate choice of processing parameters and method,$^{87}$ as previously demonstrated for a tungsten nanowire formed by subtractive patterning of an epitaxial W(011) film.$^{30}$ (2) The second result of this study affecting the search for a metal to replace Cu
for nanoscale wires is discussed in Sec. V B: In particular, the effective mean free path $\lambda^*$ which defines the length scale that determines the resistivity increase due to surface scattering is considerably larger than the theoretical effective (bulk) mean free path $\lambda$. The former value is obtained from experimentally measured $\rho$ vs $d$ curves and is the key parameter to determine the resistivity increase of metal nanowires, while the latter is obtained from electronic structure calculations in combination with the known experimental bulk resistivity. For tungsten, the example metal investigated here, $\lambda^*$ is 45%-74% larger than $\lambda$, which means that the experimental resistivity of a 5-nm-wide W wire is nearly twice as high as expected from the theoretical mean free path. Based on quantitative analyses above, this is likely due to the $k$-dependence of electron-phonon scattering, which always results in an increase (i.e., $\lambda^* > \lambda$) rather than a decrease of $\lambda$. This increase is expected to negatively affect the conductivity of most metal candidates that may replace Cu for narrow interconnects. More specifically, Rh, Ir, and Ni are predicted to be up to 2-times more conductive than Cu in the limiting case of narrow wires, based on the calculated product of $\lambda$ times $\rho$. However, as their Fermi surface is less spherical than that of Cu, we also expect the electron-phonon scattering to be less isotropic, such that $\lambda^* > \lambda$ and therefore the envisioned conductivity advantage may be smaller than predicted.

VI. CONCLUSIONS

Transport simulations based on the electronic structure calculated from first-principles as well as resistivity measurements on epitaxial layers both show that the resistivity of thin W(011) layers is considerably smaller than that of W(001) layers. This effect is quantified by fitting the predicted and measured resistivity vs thickness data using the classical Fuchs-Sondheimer model for a spherical Fermi surface, but with an effective orientation-dependent bulk electron mean free path $\lambda^*$. There is excellent quantitative agreement between experiment and simulation for the magnitude of the anisotropy of the resistivity size effect, expressed as the ratio $\lambda^*_{(011)}/\lambda^*_{(001)}$ which is 0.57 from experiment and 0.59 from simulations. The good agreement suggests that the simulations accurately capture the primary reason for the anisotropy in the resistivity size effect in tungsten: It is the anisotropy in the Fermi surface and velocity, or more specifically, the projected area of the Fermi surface onto the layer surface plane and the Fermi velocity component perpendicular to the layer surface. In contrast, we conclude that a possible anisotropy in electron-phonon scattering and/or electron scattering at different terminating surfaces has a negligible impact on the observed resistivity anisotropy, because the simulations accurately predict the measured $\lambda^*_{(011)}/\lambda^*_{(001)}$ despite that they assume all electron scattering events to be isotropic and surface scattering to be completely diffuse for both W(100) and W(011) and for both measured temperatures.

While there is good agreement between simulation and experiment for the anisotropy of the resistivity size effect, there is disagreement regarding the magnitude of the size effect. In particular, the simulations using constant relaxation time or mean free path approximation underestimate the measured resistivity. Quantitative analyses suggest that this deviation can be explained by an electron-phonon coupling that increases in strength with decreasing layer thickness, or also by a variable bulk carrier relaxation time that effectively increases the resistivity of thin films.

This study provides insight into important considerations in the search of metal nanowires that exhibit a high conductance, including (a) engineering the crystalline orientation relative to terminating surfaces has the potential to considerably ($2 \times$ for the case of tungsten) increase the conductivity of narrow wires and (b) the effective mean free path is considerably larger than the theoretically predicted bulk mean free path, which leads to a larger resistivity size effect and therefore a larger experimental resistance than predicted based on simulations with a bulk mean free path that assume electron-phonon scattering to be independent of wire dimensions and electron momentum.

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