Electron scattering at single crystal Cu surfaces

J.M. Purswani *, D. Gall

Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, NY 12180, USA

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Abstract

Epitaxial copper layers, 6.6 nm to 1.2 μm thick, were grown on MgO(001) by ultra-high vacuum magnetron sputter deposition at 100 °C. The surface morphology, as determined by in-situ scanning tunneling microscopy, exhibits a regular mound structure. The mounds grow in width \( w \) and height \( h \) as a function of layer thickness \( t \) from \( h=3 \) nm and \( w=20 \) nm for \( t=20 \) nm to \( h=5 \) nm and \( w=200 \) nm for \( t=1.2 \) μm. The resistivity increases with decreasing layer thickness from 1.70 μΩ-cm for \( t=1.2 \) μm to 8.35 μΩ-cm for \( t=6.6 \) nm. The resistivity increase is consistent with the Fuchs–Sondheimer model for completely diffuse surface scattering. The diffuse scattering is attributed to a high density of surface steps, which are separated by less than 1 nm.

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1. Introduction

The electrical resistivity of copper interconnects in micro-electronic devices increases with decreasing line widths. This so-called “size effect” [1] represents a major challenge for the continued down scaling of feature sizes in integrated circuits. The resistivity increase becomes larger than 10% when the line width of the conductor decreases to less than \( \sim 3 \times \) the electron mean free path for electron–phonon collisions, which is 39 nm for copper at room temperature [2]. There are three components which contribute to the size effect: surface scattering, grain boundary scattering, and surface roughness. Grain boundary scattering increases as the line width decreases [1–3]. This is attributed to the fact that the grain size scales with the feature width, resulting in a larger grain boundary density and, in turn, a higher resistivity for smaller line widths [4]. Surface roughness increases the line resistivity, due to purely geometric constraints [5]. This effect becomes more important with decreasing line thickness, yielding, for example, a 40% increase for a 5-nm-amplitude surface roughness on a 20-nm-thick layer [1,2].

Surface scattering is the least understood contribution to the size effect. It is typically described by a semi-classical model developed by Fuchs and Sondheimer [6,7], which divides the electron scattering at the surface into specular and diffuse events. Specular scattering refers to an elastic scattering event where the momentum perpendicular to the surface is reversed while the parallel component is conserved, causing no effect on the resistivity. In contrast, diffuse scattering results in a complete randomization of the electron momentum at the surface, corresponding to an inelastic scattering event which increases the resistivity. The Fuchs–Sondheimer equation predicts the effect of surface scattering on the resistivity \( \rho \) for a thin film with thickness \( d \) according to:

\[
\rho = \rho_0 \left[ 1 + \frac{3\lambda}{8d} (1 - p) \right],
\]

where \( \rho_0 \) is the bulk resistivity, \( \lambda \) the electron mean free path, and \( p \) the specularity parameter which ranges from 0 to 1 for completely diffuse to completely specular scattering, respectively [1,6–8]. Various reported studies have focused on the surface scattering in copper layers. While most researchers conclude that their surfaces yield completely diffuse scattering [1–3,9], a few studies report \( p > 0 \) values [10–13]. However, these latter reports use room-temperature bulk resistivity values that are several times larger than the commonly accepted value of \( \rho_0 = 1.67 \ \mu\Omega\cdot\text{cm} \), indicating that another scattering process dominates, which in turn, may falsify the \( p \)-determination due to multiple thickness-dependent scattering mechanisms. In contrast to the results on copper, various studies report partially specular scattering on gold surfaces, with \( p \) values ranging from 0.20 [14–16] to 0.64 [17,18] to 0.85, with the highest specularity reported for Au(111) grown
on freshly cleaved mica [18]. These results suggest that specular scattering is possible and may therefore also be feasible in Cu, given sufficient crystalline quality, surface smoothness, and the correct surface structure.

Electron scattering at copper surfaces is preferably studied using single crystal layers rather than the more commonly used polycrystalline films, since the absence of grain boundaries allows the direct determination of the specularity parameter from the resistivity versus thickness data, with \( p \) being the only fitting parameter. In addition, single crystal layers provide a more controlled surface structure since the orientation is fully controlled. Most work on copper epitaxy has focused on c-cut sapphire [19–21] or H-terminated Si(001) or Si(111) substrates [9,22–27], where the copper grows as \((111)_{\text{Cu}}||(0001)_{\text{MgO}}\) on sapphire, \((001)_{\text{Cu}}||(001)_{\text{Si}}\) and \((100)_{\text{Cu}}||(110)_{\text{Si}}\) on Si(001), and \((111)_{\text{Cu}}||(111)_{\text{Si}}\) on Si(111). For these systems, however, there are two possible orientations for copper nucleation, resulting in highly twinned layers which are not ideal for electron transport studies due to scattering at twin boundaries. The most promising substrate for single crystal Cu growth is MgO(001). We have recently demonstrated [28], in agreement with other studies [21,27,29–33], that copper grows with a cube-on-cube epitaxial relationship \((001)_{\text{Cu}}||(001)_{\text{MgO}}\) with \([100]_{\text{Cu}}||[100]_{\text{MgO}}\) where the misfit strain is relieved by \(7\times7\) Cu unit cells fitting on \(6\times6\) MgO cells.

Here we report on the surface morphology and the resistivity of single crystal Cu/MgO(001) layers, with the goal of providing insight into the atomic-level surface structure required for specular scattering. The layers, deposited by ultra-high vacuum (UHV) magnetron sputtering, are complete single crystals as confirmed by X-ray diffraction and scanning electron microscopy. In-situ scanning tunneling microscopy (STM) shows that the surfaces of 20-nm-thick layers exhibit a regular mound structure with mound widths and heights of 20 nm and 3 nm, respectively. With increasing thickness, the mounds broaden considerably and elongate along perpendicular \((110)\) directions, to form 80 to 400 nm wide and 5 nm high mounds for 1.2-\(\mu\)m-thick layers, which also exhibit a mound-formation on a shorter length-scale of \(\sim 5\) nm. The root-mean-square (RMS) surface roughness increases as a function of thickness, from 1.1 nm for \(t = 20\) nm to 1.8\(\pm\)0.5 nm for \(t = 1.2\) \(\mu\)m. Four point probe resistivity measurements show that the resistivity increases with decreasing thickness, from 1.70 \(\mu\)Ω\(\cdot\)cm at \(t = 1.2\) \(\mu\)m to 8.35 \(\mu\)Ω\(\cdot\)cm at \(t = 6.6\) nm. Interpreting the resistivity data with the Fuchs–Sondheimer model suggests that all layers exhibit completely diffuse scattering. This is attributed to the surface structure which, based on the STM results, is very rough on the atomic scale. The measured surface morphology provides an estimated width of 0.51–0.77 nm for the average terrace that exhibits an atomically smooth surface. We expect that considerably larger atomically smooth surfaces are required to yield coherent scattering, which is a requirement for specular scattering.

2. Experimental procedure

Copper layers were grown in a load-locked UHV dc magnetron sputtering system. The base pressure of the system is \(1.3\times10^{-7}\) Pa (\(1\times10^{-9}\) Torr), achieved through a 520 l s\(^{-1}\) turbomolecular pump. The substrates are \(10\times10\times0.5\) mm\(^3\) polished MgO(001) and were cleaned with successive ultrasonic rinses of trichloroethylene, acetone, and isopropanol, and then rinsed with distilled water and blown dried with dry N\(_2\) [34]. Samples were then clamped to stainless steel backing plates which were mounted to a molybdenum holder and inserted into the load lock chamber for transport to the growth chamber. The substrates were thermally degassed at 800 °C, as measured by a thermocouple located within the sample stage and confirmed with a pyrometer. Prior to deposition, Ar (99.999% purity) was further purified through a Micro Torr purifier and introduced into the system. The Ar pressure, as measured by a capacitance manometer, was kept constant at 0.33 Pa (2.5 mTorr). A 75-mm-diameter copper target (99.999% pure) faced the substrate, at a source-to-substrate distance of 12 cm. Just prior to deposition, a protective shutter was placed over the substrate and the copper target was sputter cleaned for 5 min. Films were grown by sputter deposition at a constant power of 150 W, which resulted in a growth rate of 40 nm/min. Copper layers were grown at a substrate temperature \(T_s = 100\) °C, with layer thicknesses \(t = 6.6\) nm to 1.2 \(\mu\)m. Two series of copper films were grown; one consisted of pure Cu, while the second set contained a controlled 1.1 wt.% oxygen impurity, introduced through a leak in the growth system.

Post deposition, the samples were allowed to cool to \(< 70\) °C before they were transported to the analysis chamber without breaking vacuum. The base pressure of the analysis chamber was less than \(1.3\times10^{-7}\) Pa (\(1\times10^{-9}\) Torr) maintained with a 300 l s\(^{-1}\) ion pump. The sample surface morphology was characterized by in-situ scanning tunneling microscopy (STM), using a commercially prepared tungsten tip. Samples were scanned at bias voltages of 0.1–5.1 mV and tunneling currents of 0.6–4.0 nA. Scan areas ranged from 5 nm to 1.0 \(\mu\)m. The layers were then transferred back to the load lock chamber, which was subsequently vented with dry N\(_2\). The resistivity of the copper layers was measured within 10 min after removal from the load lock, in order to minimize oxide formation. Measurements were made using a linear four point probe assembly with probe spacings of 1 mm and currents ranging from 1 \(\mu\)A to 20 mA. The resistivity was determined using geometrical correction factors according to Refs. [35,36], and using the layer thickness based on deposition rate calibrations obtained from cross-sectional scanning electron microscopy analyses.

3. Results and discussion

All layers are single crystals, with a cube-on-cube epitaxial relationship with the substrate, \((001)_{\text{Cu}}||(001)_{\text{MgO}}\) and \([001]_{\text{Cu}}||[001]_{\text{MgO}}\), as confirmed by X-ray diffraction \(\omega\)-20 scans, \(\omega\)-rocking curves, and pole figure analyses. This is consistent with results from our previous study on the epitaxial growth of Cu/MgO (001), showing the highest crystalline quality at a growth temperature \(T_s = 100\) °C [28]. The 1.1 wt.% oxygen doping, done for some samples for this study, did not result in any noticeable effect on the crystalline quality nor the surface morphological evolution, but affects the electron transport properties, as discussed below.

Fig. 1 is a typical cross-sectional scanning electron micrograph from a 220-nm-thick epitaxial copper layer on MgO(001),
Detailed analyses of this sample reveal no grain boundaries, confirming that the copper layer is a single crystal. The micrograph shows a relatively sharp MgO–Cu interface, with some residual intermixing attributed to ion-bombardment induced defects and redeposition that occurs during sample preparation by focused ion beam cross-sectioning. The layer surface exhibits a mound structure with a lateral mound width of \( \sim 20 \text{ nm} \) and a peak-to-valley roughness of \( \sim 5 \text{ nm} \). This is in agreement with the surface morphological analyses described below.

Fig. 2(a) shows an in-situ scanning tunneling micrograph from a 200 \( \times \) 200-nm\(^2\) surface area of a 19.6-nm-thick epitaxial Cu(001)/MgO(001) layer. The surface exhibits a regular mound structure, with approximately circular mounds that have an average peak-to-valley height of 3 nm and an average width of 20 \( \pm \) 3 nm, as determined by statistical analyses from multiple large-area scans involving more than 60 mounds. The resulting RMS surface roughness, as obtained using the Omicron SCALA \(^\circ\) software, is 1.1 nm. Fig. 2(a) also shows a plot of the \( z \)-height as a function of position corresponding to the dashed line marked in the micrograph. This line scan confirms that the mounds are \( \sim 20 \text{ nm} \) apart and that their average height is 3 nm. The mound shape is also illustrated in the schematic in Fig. 2(b), which is plotted with an undistorted \( z \)-to-\( x \) aspect ratio. The average slope \( \chi \) of the terminating mound surface is estimated from the height versus half-width ratio: \( \chi = \tan^{-1} \left( \frac{3 \text{ nm}}{10 \text{ nm}} \right) = 17^\circ \). We estimate the effect of this slope on the atomic-level surface structure, using a step height \( h_{001} = a/2 = 0.18 \text{ nm} \) along the vertical (001) direction, where \( a = 0.36149 \text{ nm} \) is the Cu lattice constant. This analysis shows that the average terrace is 0.60 nm wide. Considering single atom high steps along the close packed horizontal [110] direction, which has an interatomic spacing of \( a/\sqrt{2} = 0.25 \text{ nm} \), shows that the average terrace is less than 3 atoms wide, as also illustrated in Fig. 2(b). This limited size of the atomically smooth terrace is considered to be the primary cause for diffuse electron scattering, as discussed below.

Fig. 3(a) shows a 300 \( \times \) 300-nm\(^2\) scanning tunneling micrograph from a 1.2-\( \mu \text{m} \)-thick Cu(001) layer. This image has a \( z \)-height (black-to-white scale) of 20.6 nm. The surface morphology is dominated by wide mounds that are elongated along both perpendicular [110] and [1\( \overline{1} \)0] directions, as determined by large-area analyses (not shown). Such elliptically shaped mounds, elongated along \( \langle 110 \rangle \) directions have previously been reported for Cu/MgO(001) and are attributed to an anisotropic surface diffusion and/or an anisotropy in the 2D adatom adsorption on islands [31]. The mounds are 80 to 400 nm wide, with an average width of 200 nm. Their peak-to-valley height is \( \sim 5 \text{ nm} \), yielding an RMS surface roughness of 1.8 \( \pm \) 0.5 nm. Comparing these values to the 60 times thinner layer in Fig. 2 shows that both mound height and width increases with increasing thickness, which is attributed to coalescence during layer growth [37], while the height-versus-width aspect ratio decreases by nearly an order of magnitude from 0.15 to 0.025. That is, while the overall roughness increases, the slope of the mound decreases from \( \chi = 17^\circ \) to 3\(^\circ\).
as the layer thickness is increased from \( t = 19.6 \) to 1190 nm. Fig. 3(b) is a higher magnification STM micrograph from the same sample. It reveals a short wave-length surface modulation that is superimposed on the wide mounds discussed above, but is not observed in Fig. 3(a), due to limited \( x/y \) resolution in this lower magnification image. The submounds in Fig. 3(b) have an average width of 3.9±0.8 nm and a peak-to-valley height of 1 nm, yielding an RMS roughness of 0.4±0.1 nm. The latter value was obtained from a 25×25-nm² area, which is considerably smaller than a (large) mound, so that the value is not affected by the roughness due to the large mound. Fig. 3(c) summarizes the roughness analysis of the 1.2-µm-thick Cu layer, similar to that done in Fig. 2(b): The 200-nm-wide mounds lead to a relatively small average slope \( \chi = 3^\circ \), which, in turn, would result in 3.6-nm-wide (14 atoms wide) atomically smooth terraces. However, a shorter length-scale roughness with 3.9-nm-wide mounds yields an atomically rough surface with terraces that are in average 0.35 nm wide, which corresponds to less than 2 atoms.

Fig. 4 is a plot of the measured resistivity \( \rho \) as a function of layer thickness \( t \) for both pure and oxygen-doped Cu(001). The thickest layers, with \( t = 1.2 \) and 1.1 µm, show \( \rho \) values of 1.70 and 1.92 \( \mu\Omega \)-cm for pure and oxygen-doped copper, respectively. These values are close to the expected room-temperature bulk resistivities which are \( \rho_p = 1.67 \) \( \mu\Omega \)-cm for pure Cu and \( \rho_p^* = 1.91 \) \( \mu\Omega \)-cm for Cu containing 1.1 wt.% of oxygen doping [38], as also indicated by the horizontal dotted lines in Fig. 4. As the film thickness decreases, the resistivity increases up to 8.35 \( \mu\Omega \)-cm for \( t = 6.6 \) nm. This increase is attributed to surface scattering. The data points from the thinner layers exhibit a larger relative uncertainty (30% for \( t = 6 \) nm versus 1% for \( t = 100 \) nm), as indicated by the error bars in Fig. 4, which is dominated by the thickness determination which becomes less accurate for decreasing layer thickness.

The dashed lines in Fig. 4, obtained using Eq. (1), are the expected resistivities from the Fuchs–Sondheimer model for completely diffuse (\( \rho = 0 \)) scattering, using values for the room-temperature mean free path in pure Cu and O-doped Cu of \( \lambda = 39 \) and 32.7 nm, respectively [2,39]. The data points follow closely these lines and are, within the experimental uncertainty, in perfect agreement with the model for a completely diffuse surface scattering.

We attribute the diffuse scattering to the large atomic-scale surface roughness of our layers. Specular surface scattering requires coherent scattering within a single plane, that is, the surface needs to be atomically smooth within the electron coherence length. However, our surface morphological analyses, illustrated in Figs. 2(b) and 3(c), indicate that the copper layers are atomically smooth only over length scales ranging from 0.35 to 0.60 nm, which is expected to be much less than the (unknown) room-temperature electron coherence length in Cu. This roughness effect on resistivity is distinctly different from previously reported roughness considerations which focus on a purely geometrical effect within a classical electron-path model [1,2,5].

4. Conclusions

Single crystal Cu layers have been grown on MgO(001) substrates by magnetron sputter deposition with thicknesses ranging from 6.6 nm to 1.2 µm. The surface morphology exhibits a regular mound structure, with mound widths and heights increasing with layer thickness. Surface morphological analyses indicate that all layers exhibit an atomic-level roughness, with average (atomically smooth) terraces being 0.35 to 0.60 nm wide. The resistivity of both pure copper and oxygen-doped copper layers follow the expected values from the Fuchs–Sondheimer model for purely diffuse surface scattering. We attribute the diffuse scattering to the atomic-level roughness and expect that considerably larger atomically smooth surfaces would be required to observe specular scattering in copper.

Fig. 3. (a) In-situ STM micrograph from a 300×300-nm² surface area of a 1.2-µm-thick Cu film, (b) a higher magnification image of the same film, and (c) schematic of the mound structure, including the presence of submounds resulting in a relatively short terrace width.

Fig. 4. Plot of Cu resistivity for Cu/MgO(001) layers grown at 100 °C. The curves indicate the Fuchs–Sondheimer model for diffuse scattering (\( \rho = 0 \)) for pure Cu (\( \lambda = 39 \) nm) and Cu with 1.1 wt.% O (\( \lambda = 32.7 \) nm). The dotted lines indicate the corresponding bulk resistivities.
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