Ni doping on Cu surfaces: Reduced copper resistivity

P.Y. Zheng, R. P. Deng, and D. Gall

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

(Received 25 July 2014; accepted 22 September 2014; published online 1 October 2014)

The resistivity of 9.3-nm-thick epitaxial and polycrystalline Cu is reduced by 11%–13% when coated with 0.75 nm Ni. Sequential in situ and ex situ transport measurements show that this is due to electron surface scattering which exhibits a specularity \( p = 0.7 \) for the Cu-vacuum interface that transitions to completely diffuse \( (p = 0) \) when exposed to air. In contrast, Ni-coated surfaces exhibit partial specularity with \( p = 0.3 \) in vacuum and \( p = 0.15 \) in air, as \( \text{Cu}_2\text{O} \) formation is suppressed, leading to a smaller surface potential perturbation and a lower density of localized surface states, yielding less diffuse electron scattering.

Thus, it is still unclear if Cu-metal interfaces can lead to specular scattering and what interface properties are required to yield specular scattering. Ultimately, integration of a Cu-liner/barrier interface with specular electron scattering into integrated circuit wiring will lead to high-conductivity interconnects.

In this letter, we provide direct experimental evidence for partially specular scattering with \( p = 0.3 \pm 0.1 \) of Ni coated Cu(001) surfaces, as determined from thickness dependent resistivity measurements in vacuum. In addition, Ni-coated Cu surfaces retain some degree of specularity even after exposure to air, such that they exhibit a higher conductivity than uncoated Cu layers. This is demonstrated for both polycrystalline and epitaxial single crystal layers and is attributed to the lower localized density of states for NiO in comparison to \( \text{Cu}_2\text{O} \).

Layer deposition and transport measurements are done in a three chamber ultrahigh vacuum DC magnetron sputter deposition system with a base pressure \(< 10^{-10}\text{Torr}\). Epitaxial 9–25 nm thick Cu(001) layers are grown at 60°C on MgO(001) substrates following the procedure in Ref. 14. Polycrystalline Cu layers with 110 and 111 preferred orientation are deposited at 45°C on TiN/MgO(001) and TiN/SiO\(_2\)/Si(001) wafers, respectively, where SiO\(_2\) is a 285-nm-thick thermally grown oxide and TiN is a 2.5-nm-thick underlayer grown in situ by reactive sputtering at 900°C to facilitate substrate wetting and the subsequently deposited Cu. The in-plane and out-of-plane crystalline orientation is confirmed for all samples by x-ray diffraction \( \omega-2\theta \) scans, \( \omega\)-rocking curves, and \( \phi \) scans of Cu 111 reflections, indicating 001 single crystal and 011 and 111 textured polycrystalline layers with negligible strains (0.0%–0.5%). After deposition, the Cu resistivity is measured without breaking vacuum in an adjacent analysis chamber using a spring loaded linear four point probe. Some samples are transferred back for growth of a 0.75 or 0.15 nm thick Ni cap layer, deposited at 0.01 or 0.005 nm/s and \( T_s = 25^\circ \text{C} \), followed by additional in situ resistivity measurements. After removal from the deposition system, the samples are stored inside desiccators and the resistivity is measured at different time intervals to evaluate the effect of air exposure time. The thickness and roughness of each film are determined by x-ray reflectivity (XRR) using...
the fitting method described in Ref. 28. Measurements on all samples indicate a reproducibility variation of layer thickness of 1%, and a root-mean-square (rms) surface roughness \( \langle r \rangle = 0.6–1.2 \text{ nm} \), leading to negligible geometric roughness effects on the Cu resistivity as discussed below.

Figure 1 shows the measured resistivity \( \rho \) of 9-nm-thick Cu layers vs sequential experimental steps. There are two data sets corresponding to pristine and Ni-coated Cu layers for each of the three crystalline orientations, single crystal Cu(001) and 110- and 111-oriented polycrystalline Cu layers. The first data-points are the in situ measured \( \rho \) from as-deposited Cu layers. Two values are plotted for each orientation, as obtained from two nominally identical samples. These values agree to within 0.1%–2.7%, indicating the good reproducibility of sample preparation and electric transport measurements. The single crystal Cu(001) layers have a \( \rho = 3.75 \pm 0.05 \mu \Omega \cdot \text{cm} \), which is approximately twice the reported bulk resistivity of 1.71 \( \mu \Omega \cdot \text{cm} \), indicating considerable scattering at the surfaces, as discussed below. The polycrystalline 110 and 111 oriented layers have a 1.4 and 1.7 times higher \( \rho = 5.22 \pm 0.06 \) and \( 6.51 \pm 0.07 \mu \Omega \cdot \text{cm} \), due to additional electron scattering at grain boundaries. The difference between 110 and 111 orientations is attributed to a combination of the different grain size distributions\(^4\) and the different grain boundary types, which are expected to exhibit different specific resistances.\(^9\)

Transport within the 2.5 nm thick TiN wetting layer for the polycrystalline films is accounted for with a 2.5% and 1% resistivity correction based on a measured sheet resistance of 30 and 60 \( \Omega \cdot \text{cm} \) for 001, 110, and 111-oriented Cu, respectively. However, the corresponding increase for the Ni-coated layers is only 9%, 5%, and 7%, leading to an overall 11%–13% lower resistivity for the Ni-coated layers after air exposure. Continued exposure has little effect on the resistivity, as its change between 30 min and 48 h exposure is −0.8% to +3.5%, which is comparable to the experimental uncertainty of ±1.4%. These results suggest that Ni considerably reduces the negative effect of air exposure on the electron transport in thin Cu layers by preserving some degree of specular surface scattering, as evaluated in more detail in the following.

Figure 2 shows the in situ and ex situ measured resistivities of (a) pristine and (b) Ni coated epitaxial Cu(001) layers as a function of Cu thickness \( d \), and includes the results from data fitting which is used to determine the surface specularity parameter \( p \). The resistivity of the as deposited Cu in Fig. 2(a) increases from 2.54 \( \mu \Omega \cdot \text{cm} \) for \( d = 25.1 \text{ nm} \) to 3.75 \( \mu \Omega \cdot \text{cm} \) for \( d = 9.3 \text{ nm} \), which is attributed to electron scattering at the MgO-Cu and Cu-vacuum interfaces. This increase in \( \rho \) is well described by the Fuchs-Sondheimer

![FIG. 1. The resistivity vs experimental step for 9-nm-thick pristine and Ni-coated epitaxial Cu(001) and polycrystalline Cu(110) and Cu(111) layers.](image1)

![FIG. 2. Resistivity \( \rho \) of epitaxial (a) pristine and (b) Ni-coated Cu(001) vs layer thickness \( d \), for as-deposited, as-deposited including Ni coating, and air exposed samples. Solid lines indicate predictions from the F-S model for different \( p \) values, dashed and dotted lines are from the FS-Namba and Soffer models, and open symbols are the measured resistivity from air exposed Cu layers, corrected for oxidation.](image2)
model, as indicated by the line through the data points which is obtained by numerical integration of the FS prediction for two distinct surfaces, where the electron scattering at the Cu-vacuum interface is partially specular with $p_1 = 0.7$, and scattering at the MgO-Cu interface is completely diffuse ($p_2 = 0$). We note that other pairs of specular parameters including $p_1 = p_2 = 0.35$ would describe this in situ data with a comparable fitting quality. However, fitting of the $\rho$ for air exposed layers with the same F-S model, as also shown in Fig. 2(a), yields as the only parameter choice $p_1 = p_2 = 0$. Thus, the MgO-Cu interface exhibits completely diffuse scattering ($p_2 = 0$), and since the substrate-layer interface is not expected to be affected by air exposure, $p_2 = 0$ also in the as deposited state. This is consistent with other reports indicating diffuse scattering for the MgO-Cu interface\textsuperscript{14,28} and is attributed to a localized interfacial density of states which arises from the Cu-O orbital overlap and a perturbation potential due to local dipole moments at the interface which cause a lateral variation in the image potential.\textsuperscript{12} The $\rho$ after air exposure of pure Cu layers shown in Fig. 2(a) is 18\%–37\% higher than the in situ data. This increase is attributed to a decrease in the specular parameter from $p_1 = 0.7$ for the Cu-vacuum to $p_1 = 0$ for the Cu-air interface.

The data fits relatively well the prediction by the FS model, particularly considering that the specular parameter is the only fitting parameter, while the Cu bulk resistivity and mean free path are kept fixed at the literature values of $\rho_o = 1.71 \, \mu\Omega \cdot \text{cm}$ from bulk measurements and $\lambda = 39 \, \text{nm}$ from the free-electron-model. Nevertheless, the ex situ measured $\rho_{\text{air}}$ of Cu at $d = 9.3 \, \text{nm}$ is 9\% higher than the prediction from fitting. In order to investigate if this deviation could be explained by surface roughness which has a more dominant effect at small $d$, Fig. 2(a) also includes the resistivity predictions by the Soffer\textsuperscript{33} and FS-Namba\textsuperscript{34} models. The Soffer model determines $p$ as a function of $\langle r \rangle / \lambda_F$ where $\lambda_F = 0.46 \, \text{nm}$ is the Fermi wavelength for Cu (Ref. 29) and $\langle r \rangle = 0.90 \pm 0.05 \, \text{nm}$ is obtained by XRR on pristine air-exposed Cu layers and found to be independent of $d = 9\text{–}25 \, \text{nm}$. The FS-Namba model determines the increment in the resistivity from geometric surface roughness effects based on the ratio $h/\lambda$, where $h = \sqrt{2} \langle r \rangle$. The Soffer model systematically underestimates the resistivities at all thicknesses, while the FS-Namba model provides a small 1.6\% correction for $d = 9.3 \, \text{nm}$. Since there is no substantial improvement in the fit quality for both models, the FS model is chosen throughout the discussion. Another possible explanation for the apparently larger $\rho_{\text{air}}$ at $d = 9.3 \, \text{nm}$ is that Cu surface oxidation causes not only complete diffuse surface scattering but also reduces the total conducting thickness. To illustrate this effect, Fig. 2(a) includes as open symbols the resistivity obtained from the measured sheet resistance of air exposed Cu layers, using an effective Cu thickness that is reduced by 0.5 nm due to surface oxidation. The $0.5 \pm 0.1 \, \text{nm}$ thickness reduction is based on the molar amount of Cu present in a $1.4 \pm 0.1 \, \text{nm}$ thick surface layer consisting of 74 mol. % Cu(OH)$_2$ and 26 mol. % Cu$_2$O, as quantified from XPS measurements following the method outlined by Seah\textsuperscript{35} and Biesinger,\textsuperscript{36} using a weighted photoelectron inelastic mean free path of 1.45 nm for Cu 2p$_{3/2}$ electrons in the 0.03618 mol/cm$^3$ hydroxide/oxide mixture.\textsuperscript{37,38} The corrected data points match the F-S prediction for $p_1 = 0$ and $d = 9.3 \, \text{nm}$ and are slightly below the expected resistivity for $d \geq 15 \, \text{nm}$. We note here also that the measured $\rho$ for all sample sets shown in Fig. 2 exhibit a slightly stronger (larger curvature) dependence on $d$ than expected from the F-S model, similar to what has been reported recently for W.\textsuperscript{39} This suggests that the F-S model fails to correctly describe the electron scattering, which is likely related to the classical electron description within the F-S model and the related absence of correlated bulk and surface scattering events.

Fig. 2(b) shows the corresponding plot for Cu thin films that are coated with a 0.75 nm-thick Ni layer. The plotted resistivity values for the as deposited Cu prior to Ni coating are in excellent agreement ($\pm 0.4\%$–1\% deviation) with the sample set in Fig. 2(a) for all thicknesses, indicating good sample-to-sample reproducibility. After in situ deposition of a Ni coating, the measured resistivity increases by 10\%–14\% for $d_{\text{Cu}} = 9\text{–}25 \, \text{nm}$, corresponding to a decrease in the specularity of the top surface from $p_1 = 0.7$ to $p_1 = 0.3$. Subsequent exposure to air leads to a further decrease to $p_1 = 0.15$, which is, however, above the $p_1 = 0$ for uncoated air-exposed Cu layers in Fig. 2(a).

We attribute the relatively large specularity $p_1 = 0.7$ of the as deposited Cu-vacuum interface to constructive interference and therefore specular reflection of electron plane waves approaching the potential drop at the Cu-vacuum interface. For a pristine Cu surface, this potential drop is flat within the plane of the surface and exhibits periodic oscillations associated with the crystalline surface structure that do not affect specular reflection. However, the surface oxidation after air exposure perturbs the smooth potential drop of the original, atomically flat surface, yielding diffuse electron scattering with $p_1 = 0$. Similarly, adding a Ni coating to the Cu surface reduces the scattering specularity, in this case from 0.7 to 0.3. This decrease is attributed to (i) non-uniformly distributed localized surface charges arising from the Fermi level alignment of the metal-metal contact leading to a lateral perturbation of the surface potential drop that diffusely scatters or terminates the electron plane wave at the crystal surface\textsuperscript{40} and/or (ii) transitions of electrons near the Fermi level between delocalized states of the Cu layer and localized states of the Ni d-band, which effectively randomizes the electron momentum corresponding to diffuse surface scattering events. Nevertheless, electron scattering at Ni coated surfaces remains partially specular, which we attribute to a relatively small perturbation of the surface potential due to the similarity of the two elements, including a good miscibility, a small difference in atomic radii and atomic number, and a possible matching of the density of states.\textsuperscript{21} When the Ni coated Cu layer is exposed to air, the specularity is further reduced to $p_1 = 0.15$, which is attributed to localized states in the oxide, as discussed below. However, contrary to the Cu surface, electron scattering at the air exposed Ni surface retains some degree of specularly, which yields consistently lower ex situ resistivity values for Ni-coated vs uncoated Cu layers with different crystalline orientations and thickness shown in Figs. 1 and 2, respectively.

In order to explore possible reasons for the difference in electron scattering at the Cu-air and Ni-air interfaces, XPS
measurements were carried out using a PHI 5000 VersaProbe™. Fig. 3 shows the O 1s spectra from a pristine Cu surface and a Cu surface coated with approximately a monolayer (= 0.15 nm) of Ni, which have been exposed to atmospheric air for 280 and 190 h, respectively. The spectrum from the Cu surface in Fig. 3(a) exhibits a double peak feature which is well described by the data fitting using Voigt curves with a peak area ratio of 85:15, and binding energies $E_b = 531.6$ and 530.3 eV. These values are close to reported $E_b = 531.57$ and 530.20 eV (Ref. 41) for O 1s in hydroxide and copper oxide, respectively, indicating the formation of Cu(OH)$_2$ and Cu$_2$O on the Cu surfaces during air exposure. The formation of Cu(OH)$_2$ is also confirmed by Cu 2p$_{3/2}$ peaks at 934.8 eV and 932.7 eV (not shown), close to the reported values for Cu hydroxide at 934.75 eV and Cu(0) at 932.61 eV, while Cu$_2$O reported at 934.37 eV is overshadowed by Cu(0).41

The corresponding spectrum from the Ni-coated layer in Fig. 3(b) exhibits three peaks at $E_b = 531.5$, 531.1, and 529.3 eV, which are attributed to oxygen in Cu(OH)$_2$, Ni(OH)$_2$, and NiO, with reported $E_b = 531.57$, 531.10, and 529.30 eV.42 No Cu$_2$O or CuO formation can be detected for states at the Fermi level in Cu 2O vs NiO surface layers, two surfaces to the difference in the density of localized states.

This research was funded by the Semiconductor Research Corporation, under Tasks 1292.078 and 1292.094 and NSF grant Nos. 1309490 and 1234872.