Resistivity and Surface Scattering of (0001) Single Crystal Ruthenium Thin Films

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The resistivity size effect in nanoscale metals is of both scientific and technological interest, the latter due to its importance to interconnects between transistors in integrated circuits. In this work, we report the variation of resistivity with film thickness and with changes in surface scattering of ex-situ annealed single crystal Ru thin films grown on sapphire substrates by sputter deposition. The room temperature deposition of SiO$_2$ on the Ru sample surface was observed to increase the resistivity of films that had previously been subjected to annealing in a reducing gas ambient. These overcoated samples were also found to increase in resistivity as a result of an oxidizing anneal and reduce in resistivity as a result of a subsequent reducing gas (Ar + H$_2$) anneal. To a large extent, the surface structure and electron scattering characteristics were found to be reversible between oxidizing and reducing gas anneals. The chemistry and structure of the Ru upper surface was characterized by low energy electron diffraction (prior to the SiO$_2$ overcoat deposition), X-ray reflectivity, X-ray photoelectron spectroscopy and resistivity measurements. The changes in surface structure and chemistry were related to the changes in the specularity of the Ru surface for electron scattering in the context of the Fuchs-Sondheimer semi-classical model of the resistivity size effect, and in this context a mostly specular metal/dielectric interface is reported.
I. INTRODUCTION

The observation of the resistivity size effect for metallic conductors dates back to 1901 and was described by semi-classical models in the middle of the last century. These models attributed the resistivity increase to additional electron scattering from conductor interfaces (surfaces and grain boundaries) when the spacing between such events approaches the electron mean free path (EMFP) associated with phonon scattering. Recently, interest in this phenomenon has been renewed as the dimension of the wires interconnecting transistors in integrated circuits approach the EMFP (which for Cu at room temperature is 39 nm). The resistivity effects due to grain boundaries, surface roughness, and scattering at the conductor surfaces have been previously described and there is significant interest in obtaining “specular” metal surfaces with reduced surface scattering to minimize the size effect resistivity increase. In the current work, we report a study of variations in scattering from the surface of single crystal Ru metal films with variation of the structure and chemistry of the surface. We observe interfaces that are significantly specular, air-stable, and resilient to non-reversible changes, even when encapsulated beneath a dielectric. Within the surface science literature there are similar studies of resistivity effects due to surface scattering at metal/vacuum interfaces wherein the adsorption of atoms or molecules on the surface increase the electrical resistivity of the thin films. These chemical and structural modifications to the surface are known as adsorbate-induced changes where the electrical resistivity increases with increased coverage of the adsorbate species on the surface. This increased coverage is understood to increase the density of scattering sites on the surface. The adsorbate species can also form molecular compound complexes with the metallic thin films and thereby change the electronic states at the surface.
These prior studies typically explored variations in surface chemistry or structure at an exposed metal/vacuum or metal/vapor interface. Other prior work includes studies of large scale roughness and atomic scale roughness induced resistivity wherein the presence of atomically flat regions on the metal surface were found to reduce surface scattering. In the current work, resistivity measurements as a function thickness and as a function of chemical and/or structural changes at a buried metal/dielectric oxide interface are reported. X-ray photoelectron spectroscopy (XPS) is used to determine the chemical bonding at the buried interface, while X-ray reflectivity (XRR) is used to determine interfacial roughness of metal upper surface. For the metal/dielectric interface study, we focus on single crystal 20 nm Ru on sapphire as our conductor and amorphous SiO$_2$. Our choice of the metal and dielectric is motivated by the different oxygen affinities of Si and Ru, which allows desirable control of experimental conditions at the metal/dielectric interface.

The surface adsorption of atomic and molecular gaseous species on transition metals (i.e., Cu and Ni) were studied extensively in the past. The atomic adsorbate species examined include H, N, O, S, and C, while the molecular species include N$_2$, CO, NO, NH$_3$, and HCN. The local potential at the metal surface created due to the adsorbate is believed to increase the scattering of conduction electrons. Ru, being a nearly noble metal from the platinum group, is being investigated by researchers for semiconductor applications. Ru has desirable properties that may allow it to replace Cu as an interconnect metal, such as high electrical conductivity, large work function, and small resistivity size effect. Nanoscale Ru may have lower resistivity than nanoscale Cu and can be expected to have greater stability due to its higher melting point. Ruthenium has also been studied as a diffusion barrier in the copper metallization process and has potential for integration in semiconductor manufacturing. The electrical resistivity of RuO$_2$ is about 35.2 $\mu\Omega\cdot$cm at room temperature and higher than that of polycrystalline metallic ruthenium (about 7.2
µΩ·cm). The encapsulation material used in our studies, SiO₂, has been used in many modern technologies and is studied here as an example of an amorphous dielectric. Recent studies of thin ordered silicon dioxide films grown on Ru (0001) have used XPS, low energy electron diffraction (LEED), and scanning tunneling microscopy wherein these techniques were used to study the epitaxial growth of SiO₂ layers on Ru. In the present paper, we study amorphous SiO₂ grown in vacuum at room temperature on epitaxial Ru (0001)/sapphire (0001) and focus on the interaction of deposition and oxidizing and reducing gases on the buried SiO₂/Ru interface and relate these to changes in surface scattering.

II. EXPERIMENTAL - SAMPLE PREPARATION

The deposition and annealing of four series of Ru and Ru/SiO₂ thin film samples are described in this section. The first and second sample series are variations in thicknesses for Ru films on sapphire while the third and fourth series utilize bilayered Ru/SiO₂ bilayer film structures at a single Ru thickness to elucidate surface scattering phenomena.

A. Ru single crystal film deposition

The Ru thin films were sputter deposited on single-side polished two-inch diameter (0001) Al₂O₃ sapphire substrates obtained from MTI Corporation. Prior to deposition, the as-received sapphire substrates were pre-conditioned by heating in a tube furnace in air at 1000°C for 30 minutes to remove adsorbed contaminants and loaded within the deposition chamber within 5 minutes to minimize the possibility of recontamination. The deposition system used was an ATC2200 UHV sputtering system obtained from AJA International Inc. equipped with a loadlock
chamber for sample introduction and operated with a base vacuum in the low 10⁻⁸ Torr range. DC magnetron sputtering in a point-of-use purified Ar gas ambient at 4 mTorr from a two-inch diameter Ru (99.95%) target was used for the Ru film depositions. The Ru deposition power of 200W was used to obtain a deposition rate 0.13 nm/s. In the deposition chamber, the sapphire substrates were heated to 350°C (for sample series one) or 700°C (for sample series two, three, and four) for 20 minutes prior to deposition and maintained at that temperature during the deposition process. The deposition time was varied to obtain Ru films of the desired thickness. Four series of samples were prepared, as described in Table 1. Sample series one was made in the thickness range of 8 nm to 124 nm. Sample series two was made in the thickness range of 20 nm to 80 nm. The third and fourth experimental series each consisted of samples cut from a single wafer, both having a deposited thickness of 20 nm. After the initial Ru sputter deposition, the ruthenium thin films were allowed to cool to room temperature in the sputter deposition chamber and removed from the vacuum system and exposed to the ambient laboratory atmosphere. The sapphire wafers with deposited ruthenium thin films were subsequently cut into 7 mm by 7 mm square pieces by a CO₂ laser incident upon the back side of the wafer.

### Table I – Listing of sample series studied.

<table>
<thead>
<tr>
<th>Sample Series</th>
<th>Ru Layer Thickness, nm</th>
<th>Dielectric Overlayer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8 to 124</td>
<td>None</td>
</tr>
<tr>
<td>2</td>
<td>20 to 80</td>
<td>None</td>
</tr>
<tr>
<td>3</td>
<td>20</td>
<td>SiO₂</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>SiO₂</td>
</tr>
</tbody>
</table>

**B. Step anneal to 950°C**

After cutting, all the samples were annealed (ex-situ) step-wise in one atmosphere of flowing Ar/H₂ 3% to a maximum temperature of 950°C. The annealing temperature was increased from room temperature to 350°C and stabilized at 350°C for 30 minutes. After that the temperature was further increased in steps of 100°C and held for 30 minutes at each temperature. This increasing
temperature portion of the anneal continued up to the maximum temperature of 950°C, at which temperature the sample was held for 30 minutes. Subsequently, the temperature was decreased in steps of 100°C and held at each temperature for 60 minutes until 150°C was reached, after which the sample was allowed to cool to room temperature. This was the basic processing (Ru film deposition and ex-situ 950°C Ar/H₂ step anneal) which was performed for all four of the sample series.

C. **SiO₂ overlayer depositions**

For the third sample series, the Ru film coupons were overcoated with electron beam evaporated SiO₂ of thicknesses from 0.5 nm to 30 nm using an ATC2600 UHV evaporation system obtained from AJA International Inc. equipped with a loadlock chamber for sample introduction and operated with a base vacuum in the 10⁻⁸ Torr range. The deposition thickness and rate were monitored by a calibrated quartz crystal microbalance.

For the fourth sample series, the Ru film coupons were overcoated with a single 5 nm thickness of sputter deposited SiO₂ via radio frequency (RF) sputtering in 4 mTorr of argon at room temperature with 165 W of power using a two-inch diameter SiO₂ (99.95%) target. The rate of deposition for SiO₂ on the ruthenium thin films was 0.03 nm/s. The thickness of the overlayer was chosen to be sufficiently thin to allow subsequent XPS characterization of the buried Ru/SiO₂ interface.

D. **Additional anneals for series four**

The fourth sample series was also subjected to subsequent additional oxidizing and reducing annealing treatments of the Ru/SiO₂ bilayer films, including a repeat of the 950°C Ar/H₂ step
anneal. The lower temperature anneals were in one atmosphere of one of the following gases: flowing Ar/H₂ 3%, Ar/O₂ 20%, or air, at temperatures 300°C, 400°C, or 500°C wherein the desired temperature was held for 2 hours, and then furnace cooled to room temperature. These anneals and the sequence in which they were performed is described in Table 2.
Table II - Process sequence with the primary characterization results for the fourth sample series consisting of 20 nm Ru films deposited at 700°C. Data from the five samples are shown in a consistent sequential order in each cell of the table, except for the Ru$^\delta$/Ru$^0$ ratios determined from XPS where only the same two of the five samples were characterized.

<table>
<thead>
<tr>
<th>Process Step</th>
<th>Process</th>
<th>Resistivity ($\mu\Omega$-cm)</th>
<th>Ru Thickness (nm)</th>
<th>Ru Roughness (nm)</th>
<th>Ru Oxide Thickness (nm)</th>
<th>SiO$_2$ Thickness (nm)</th>
<th>XPS Ru$^\delta$/Ru$^0$ Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Deposit Ru</td>
<td>9.41, 9.43, 9.38, 9.41, 9.46</td>
<td>20.74, 20.77, 20.73, 20.88, 20.55</td>
<td>0.25, 0.28, 0.26, 0.30, 0.23</td>
<td>0.29, 0.29, 0.30, 0.14, 0.36</td>
<td>-</td>
<td>0.17, 0.18</td>
</tr>
<tr>
<td>2</td>
<td>950°C Ar/H$_2$</td>
<td>8.96, 8.92, 8.93</td>
<td>20.88, 20.89, 20.59</td>
<td>0.13, 0.15, 0.11</td>
<td>0.24, 0.24, 0.26</td>
<td>-</td>
<td>0.07, 0.05</td>
</tr>
<tr>
<td>3</td>
<td>Deposit SiO$_2$</td>
<td>9.41, 9.42, 9.49, 8.93, 8.97</td>
<td>20.81, 20.81, 20.82, 20.80</td>
<td>0.04, 0.04, 0.14, 0.10</td>
<td>0.27, 0.25, 0.25, 0.26</td>
<td>0.30, 0.26, 0.26, 0.26</td>
<td>5.04, 4.83, 4.78, 4.99</td>
</tr>
<tr>
<td>4</td>
<td>500°C Ar/H$_2$</td>
<td>8.95, 8.89, 8.92</td>
<td>20.80, 20.88, 20.61</td>
<td>0.08, 0.11, 0.09</td>
<td>0.25, 0.26, 0.26, 0.26</td>
<td>0.25, 0.25, 0.26, 0.26</td>
<td>4.78, 4.64, 4.74, 4.79</td>
</tr>
<tr>
<td>5</td>
<td>500°C Air</td>
<td>9.38, 9.45, 9.63</td>
<td>20.39, 20.45, 20.23</td>
<td>0.19, 0.26, 0.32</td>
<td>1.17, 1.20, 1.97</td>
<td>0.27, 0.27, 0.27, 0.27</td>
<td>4.80, 4.78, 4.82</td>
</tr>
<tr>
<td>6</td>
<td>500°C Ar/H$_2$</td>
<td>9.10, 9.01</td>
<td>20.81, 20.80</td>
<td>0.11, 0.11</td>
<td>0.28, 0.29, 0.28, 0.29</td>
<td>0.27, 0.27, 0.27, 0.27</td>
<td>4.67, 4.75, 4.60, 4.57</td>
</tr>
<tr>
<td>7</td>
<td>950°C Ar/H$_2$</td>
<td>9.09, 9.04, 8.98, 8.89, 8.95, 9.53, 9.41</td>
<td>20.84, 20.84, 20.95, 20.93, 20.79, 20.75</td>
<td>0.05, 0.06, 0.05, 0.07, 0.19, 0.24</td>
<td>0.26, 0.27, 0.27, 0.25, 0.53, 0.50</td>
<td>0.27, 0.27, 0.27, 0.27</td>
<td>4.57, 4.55, 4.77, 4.54</td>
</tr>
<tr>
<td>8</td>
<td>400°C Ar/O$_2$</td>
<td>9.24, 9.21, 9.22, 9.33, 9.22</td>
<td>20.67, 20.79, 20.47, 20.80, 20.83</td>
<td>0.21, 0.28, 0.22, 0.10, 0.11</td>
<td>0.48, 0.43, 0.52, 0.25, 0.26</td>
<td>0.27, 0.27, 0.27, 0.27</td>
<td>4.91, 4.91, 4.94, 4.79, 4.66</td>
</tr>
<tr>
<td>9</td>
<td>500°C Ar/H$_2$</td>
<td>9.08, 9.02, 9.04, 9.43, 9.33</td>
<td>20.83, 20.90, 20.61, 20.72, 20.83</td>
<td>0.13, 0.10, 0.15, 0.15, 0.13</td>
<td>0.23, 0.20, 0.20, 0.23, 0.20</td>
<td>0.28, 0.28, 0.28, 0.28</td>
<td>4.73, 4.71, 4.67, 5.31, 5.48</td>
</tr>
<tr>
<td>10</td>
<td>300°C Ar/O$_2$</td>
<td>9.11, 9.02, 9.07</td>
<td>20.79, 20.69, 20.56</td>
<td>0.13, 0.15, 0.10</td>
<td>0.24, 0.24, 0.24</td>
<td>0.24, 0.24, 0.24</td>
<td>5.44, 5.09, 5.15</td>
</tr>
<tr>
<td>11</td>
<td>950°C Ar/H$_2$</td>
<td>8.92, 8.96, 8.95</td>
<td>20.94, 20.99, 20.72</td>
<td>0.09, 0.12, 0.17, 0.13</td>
<td>0.25, 0.25, 0.20, 0.20</td>
<td>0.12, 0.12, 0.20, 0.20</td>
<td>4.81, 4.91, 5.20, 4.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.06, 0.04</td>
</tr>
</tbody>
</table>
III. EXPERIMENTAL- SAMPLE CHARACTERIZATION

The characterizations of the Ru and Ru/SiO₂ thin film samples by X-ray diffraction (XRD), XRR, XPS, LEED, and four-point sheet resistance measurements are described in this section. The sheet resistance measurements were performed once on the samples of series one, two and three, (after processing was completed) and were performed on the samples of series four, after each of the processing steps listed in Table 1. The XRD and LEED characterization were performed on selected samples sharing the common basic processing. The XRR and XPS characterization was also performed for the series four samples after each of the processing steps listed in Table 1. XRR was used for the samples of series one, two, and three to establish the Ru layer thicknesses to calculate resistivity.

A. XRD and XRR characterization

The XRD studies were performed using a Panalytical X’pert3 MRD system with a copper source with a graded multilayer mirror for the incident beam and the 1D PIXcel detector for the diffracted beam. The layer thicknesses and roughnesses were characterized by XRR with same X-ray optical configuration used for the XRD measurements. The XRR data were interpreted using the PANalytical X’Pert Reflectivity software. The samples without a SiO₂ overlayer were modeled as a sapphire/Ru/RuO₂ structure, and the samples with the SiO₂ overlayer as sapphire/Ru/RuO₂/SiO₂. Bulk density values of 3.989 g/cm³, 12.4 g/cm³, 6.97 g/cm³, and 2.196 g/cm³ were used for the sapphire, Ru, RuO₂, and SiO₂, respectively.

B. XPS characterization
The chemistry of the film surface and Ru/SiO$_2$ interfacial region was studied by XPS, collected under ultra-high vacuum (base pressure ~ $5 \times 10^{-10}$ Torr) conditions using a SPECS Electron Spectrometer with a PHOIBOS 100 Hemispherical Energy Analyzer and XR 50 Al K$_\alpha$ X-ray source (1486.67 eV).

An example of the XPS characterization is shown in Fig. 1, which shows representative XPS data taken from the same sample at three different steps along the 11-stage process shown in Table 1. The XPS spectra were collected at a pass energy of 20 eV with energy resolution of 0.1 eV.
The XPS spectra were fitted using XPSPEAK 4.1 program with Gaussian/Lorentzian mixed peak shape and with Shirley background correction. The normalized Ru 3d5/2 peak heights allowed interpretation by fitting to two components, Ru0 and oxidized Ruδ+, at binding energies (BEs) consistent with metallic Ru and RuO2, respectively. In addition, C 1s features have also been included as needed to fit the data, and angle-dependent measurements (not shown) have been employed to confirm the enhanced surface preference of the C and Ruδ+ species relative to Ru0 in select samples. To generate the fits, we first established an empirical line shape for the metallic Ru (Ru0), using a rigorously cleaned Ru (0001) single-crystal kept within the vacuum system. With the shape, width, and position of this peak constrained to fixed values equivalent to those from the control sample, a second peak associated with RuO2 (Ruδ+) was added to the experimental spectra of each sample as needed to ensure proper fitting of the 5/2 spin-orbit splitting components, where the C 1s signal is not expected to contribute to the XPS intensity. With the 5/2 component fit as well as possible by the two features associated with oxidized and unoxidized Ru, residual differences between the data and the fitting in the Ru 3d 3/2 component region of the spectra, the higher binding energy (BE) feature present in each, were fit to a single unconstrained C 1s peak.

Noting large variations in both the position and intensity of the C 1s features needed to accurately fit our data as a function of condition, we obtained XPS spectra associated with step 7 for two samples exposed to air for drastically different periods of time between annealing and vacuum introduction, which was an uncontrolled (but measured) variable throughout the remainder of the data set. This variable results in clear changes to the amount of C detected by XPS, but does not result in changes to the Ruδ+:Ru0 XPS intensity ratio. To provide further insight into the nature of the spurious carbon species on the samples, we also provide O 1s and Si 2p
regional XPS plots from the 4th and 5th process steps in Fig. 1. Interestingly, the same ~1 eV shift to lower binding energy (BE) noted for the C 1s contribution to the Ru 3d region is also noted in both the O 1s and Si 2p data when transitioning from step 4 (Ar/H₂ annealing) to step 5 (air annealing) in our multi-step process sequence. This combination of data is consistent with carbon on or within the SiO₂ layer present at the interface of Ru undergoing changes in work-function as the interfacial oxidation state of the metal transitions from Ru to RuO₂, which then results in equivalent band-bending shifts to the BEs associated with all elements present within the insulating oxide layer. Since oxidation is known to increase the work-function of Ru, band-bending effects near the surface are expected to concomitantly decrease the BE of core-levels in the supported oxide when oxidizing the Ru metal. , and similar rationalizations have been used to explain core-level shifts observed in other Ru-supported, silicate thin-films following the deliberate intercalation of a number of atomic species, such as: O, Au, Pd, and Cu⁴⁹,⁵⁰.

C. LEED and resistance characterization

Back-view LEED (OCI, Microengineering) was used to assess the surface structure of the Ru films in UHV conditions. The LEED patterns were obtained with a primary electron beam energy of 68 eV.

The sheet resistance of all the ruthenium thin film samples was measured by a Van der Pauw technique, contacting the four corners of the square samples with tungsten wire probes at each process step. The resistivity measurements were made in laboratory air at room temperature (23°C).
IV. MODELLING

The influence of the thickness of a Ru film and the influence of its surface characteristics upon the resistivity of the film can be described by the Fuchs-Sondheimer (FS) model of surface scattering \(^2,^3\), given in a simplified version \(^8,^{51}\) by the equation below:

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

where \(\rho_{FS}\) is the film resistivity, \(\rho_0\) is the thick film resistivity of the material (absent of a surface scattering contribution), \(\lambda\) is the electron mean free path for scattering in thick films, \(p\) is the average of the specular scattering coefficients (probabilities) of the upper \((p_u)\) and lower \((p_l)\) surfaces of the film \(^{51}\) and \(h\) is the thickness of the film. In this model, changes in resistivity for a common material and constant thickness are associated with changes in the surface scattering specularity, \(p\). From inspection, it is clear that \(\lambda\) and \(p\) can be varied over a range of values and not result in a change to the model’s prediction of resistivity versus thickness \((\rho_{FS} \text{ versus } h)\), as long as the product of \((1-p)\) and \(\lambda\) is maintained constant, i.e. they cannot be uniquely determined by fitting to
Fig. 2. Representative (a) XRD for a Ru film on sapphire (0001) deposited at 700°C with thickness $d = 39.8$ nm, (b) an XRD $\phi$ scan of the Ru $\{11\bar{2}2\}$ peaks overlaid with a scan of the sapphire $\{11\bar{2}6\}$ peaks.

Given a value chosen for $\lambda$, then the average value of $p$ can be determined from the experimental fitting (for example as $p = 50\%$), but this is still not unique as this may be interpreted as both upper and lower surfaces having a 50% probability of specular reflection, or as one surface having a 0% probability and the other having a 100% probability of specular reflection of electrons. The assumption of fully diffuse surface scattering from both upper and lower surfaces ($p = 0\%$), is often made in the interpretation of experimentally measured results, particularly for studies of Cu films and lines. In this work, we will study variations of resistivity as a result of changes in surface scattering, and, hence, will need a range of specularity values to correspond to the range of resistivity observed. In this case we will necessarily deviate from the $p = 0\%$ assumption.

V. RESULTS AND DISCUSSION
A. Single crystal Ru films

For selected samples, their single crystal nature was confirmed by X-ray diffraction (XRD) with specular theta-2theta scans exhibiting the Ru (0002) and (0004) peaks and the sapphire (0006) and (00012) peaks (shown in Fig. 2a) and by non-specular phi scans at chi equal to 57.71° and two-theta equal to 84.68° to observe the six fold symmetry of the Ru \{11\bar{2}2\} peaks, and at chi equal to 42.3° and two-theta equal to 57.499° to observe the six fold symmetry of the sapphire \{11\bar{2}6\} peaks. These are shown in Fig. 2b.

A 30° offset in the phi positions of these peaks was observed as expected for the 30° rotational honeycomb epitaxial relationship of (0001) Ru || (0001) sapphire and \langle11\bar{2}0\rangle_Ru ||\langle10\bar{1}0\rangle_sapphire that has been previously reported\textsuperscript{43,53}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig3.png}
\caption{LEED images at 68 eV for an air exposed Ru film (a) after deposition at 350°C, (b) after deposition at 700°C, (c) after deposition at 700°C and ex-situ annealing to 950°C in Ar/3%H\textsubscript{2}, and (d) a sample Ar ion beam cleaned and annealed to 1,000°C in UHV conditions with an H\textsubscript{2} background.}
\end{figure}
The LEED characterization of the films also confirms their single crystal nature. Figure 3 provides LEED images from selected Ru films at different process steps prior to SiO\textsubscript{2} deposition. Figure 3d is of a Ru film whose surface was cleaned by Ar ion beam sputtering and annealing in a H\textsubscript{2} background in the UHV system used for LEED image acquisition. This image clearly displays the six-fold symmetry expected of the single crystal Ru (0001) surface. Images 3a to 3c were obtained from air exposed Ru film surfaces without any in-situ UHV cleaning or annealing. Figure 3c) is of a 20 nm-thick sample, deposited at 700°C, lab air exposed, and step annealed to 950°C in Ar/H\textsubscript{2} 3% and imaged without the surface being cleaned, annealed, or prepared in any way other than by introduction to the ultra-high vacuum chamber. Notably, the six-fold symmetry expected of the Ru (0001) surface is present and qualitatively similar to that of Fig. 3d. While it is not clear if the LEED image of Figs. 3a to 3c are the result of low energy electrons reflecting from the Ru atoms directly, or from an absorbed gas layer on the Ru surface, it is clear that an ordered surface structure is, surprisingly, observable after the exposure of the Ru film to ambient air. This also indicates that a relatively well atomically ordered Ru (0001) surface resulted from the deposition and ex-situ 950°C Ar/H\textsubscript{2} 3% anneal processing of the Ru single crystal films and that this high degree of atomic surface order persists during laboratory air exposure. Figures 3a and 3b are from samples as deposited at 350°C and 700°C, respectively, and imaged without the 950°C Ar/H\textsubscript{2} 3% anneal. A qualitatively weaker six-fold pattern is present in Fig. 3b and is essentially absent in Fig. 3a. A LEED image was also obtained from a sample overcoated with 5 nm of SiO\textsubscript{2} (not shown) and, as expected, no spot pattern was present due to the amorphous nature of the SiO\textsubscript{2} layer.
B. XRR layer thickness

An example of the XRR experimental data and corresponding model fit is shown in Fig. 4.

FIG. 4. shows representative XRR data from a 4.6nm thick SiO$_2$ on a 20.8nm-thick Ru(0001) layer. (a) upper (black) curve is for measured data shifted by a factor of 10 for clarity and (b) the lower (red) curve is the model prediction.

The Ru layer thicknesses obtained from modeling this data are used with the sheet resistance measurements to calculate sample resistivity. For sample series four, XRR characterization was performed at each processing step on each sample coupon and these results are summarized in Table 1. It should be noted that the very thin (~ 0.2 nm or less) RuO$_2$ layers resulting from this modeling of XRR data may represent a physiosorbed gas layer and/or a short wavelength roughness of the Ru metal surface, rather than a distinct oxide layer.

C. Resistivity – Sample series 1 and 2
Figure 5 shows the resistivity associated with the variation in film thickness for sample series 1 and 2, deposited at 350°C and 700°C, respectively.

![Resistivity versus thickness for c-axis single crystal Ru films deposited at 350°C (circles) and 700°C (squares) and ex-situ step-annealed to 950°C in Ar/H₂ 3%. The solid line is the calculation of the FS model.]

These resistivity measurements were made after Ru deposition, ambient lab air exposure, and an Ar/H₂ 3% step anneal to 950°C, but without any SiO₂ overlayer. The lower deposition temperature of 350°C was found useful to provide thinner films without dewetting during the subsequent 950°C step annealing process while slightly lower resistivity values are observed for the films deposited at 700°C. The resistivity versus thickness trends of both sample series are similar and can be described with a single set of FS model parameters. Recently, it was proposed to use an EMFP of 6.7 nm in a report for similar (0001) Ru films prepared in UHV conditions wherein the resistivity increase with thickness of their films was described using FS

<table>
<thead>
<tr>
<th>EMFP λ, nm</th>
<th>Thick Film Resistivity ρ₀, μΩ-cm</th>
<th>Average Surface Specularity, p</th>
<th>Upper Surface Specularity p_U</th>
<th>Lower Surface Specularity p_L</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.7</td>
<td>8.0</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>11.0</td>
<td>8.0</td>
<td>39%</td>
<td>39%</td>
<td>39%</td>
</tr>
<tr>
<td>11.0</td>
<td>8.0</td>
<td>39%</td>
<td>78%</td>
<td>0%</td>
</tr>
<tr>
<td>30.8</td>
<td>8.0</td>
<td>39%</td>
<td>78%</td>
<td>78%</td>
</tr>
</tbody>
</table>

Table III – Listing of FS model parameters.
model parameters of $\rho_0 = 7.6 \ \mu\Omega\cdot\text{cm}$, $p = 0\%$ and $\lambda = 6.7 \ \text{nm}$. Using the same EMFP of 6.7 nm, the least squares fitting of the combined data for series 1 and 2 resulted in FS model parameters of $\rho_0 = 8.0 \ \mu\Omega\cdot\text{cm}$, $p = 0\%$ and $\lambda = 6.7 \ \text{nm}$. This is shown as the solid line if Fig. 5 for comparison to the experimental data. Using this EMFP we find a similar result of fully diffuse surface scattering, but a slightly higher thick-film resistivity value $8.0 \ \mu\Omega\cdot\text{cm}$. This thick film resistivity is intermediate to that reported for a-plane resistivities of 7.5 and 8.2 $\mu\Omega\cdot\text{cm}$ in bulk single crystal Ru samples $^{54-56}$. In the current study, we find that additional modifications to the surfaces of samples in series 3 and 4, prepared identically to those of series 2, result in increases in film resistivity. This cannot be accommodated by this set of FS model parameters as it has the Ru surfaces already fully diffuse ($p = 0\%$). A larger EMFP value is needed to allow variations in specularity (i.e., $100\% > p > 0\%$) while maintaining the product, $(1-p)\lambda = 6.7 \ \text{nm}$, constant to be consistent with the data and fitting of Fig. 5. Table 3 lists some of the possible alternative assumptions of FS model parameters that maintain this product constant. While every set of model parameters shown in Table 3 can equally provide the FS prediction shown in Fig. 5, we choose to use the set of $\rho_0 = 8.0 \ \mu\Omega\cdot\text{cm}$, $\lambda = 11 \ \text{nm}$, and $p_l = 0\%$ and $p_u = 78\%$ as these provide for variations of resistivity associated with changes to the upper Ru surface while avoiding large values for the EMFP that are inconsistent with the previous work.

The high specularity $p_u = 78\%$, of the air-exposed Ru surface is surprising in light of prior UHV experiments for single crystal Ni and Cu surfaces where ambient air and sub-monolayer gas exposure were found to induce fully diffuse scattering $^{19}$. However, the high specularity of the top Ru surface is consistent with the air-exposure stability of the highly ordered surface structure of these films evidenced in the LEED images of Fig. 3, and is also consistent with the report of no increase in the resistivity of similar single crystal Ru samples measured ex-situ as compared to
their resistivity measured in-situ after deposition and annealing in ultra-high vacuum conditions.

**D. Resistivity and specularity- sample series 3**

The third sample series explored the effect of UHV evaporation of SiO$_2$ on coupons having 20 nm-thick Ru films that had been step annealed to 950°. One sample from the wafer was not overcoated (0 nm) to allow comparison of resistivities, one was coated with 0.5 nm, and two coupons were overcoated with 5 nm and another two with 30 nm of SiO$_2$. Figure 6 shows the increase in resistivity and the drop in upper surface specularity, $p_u$, associated with the UHV evaporation of SiO$_2$ onto the sample surface.

![Graph showing resistivity and calculated upper surface specularity for the FS model as a function of evaporated SiO$_2$ thickness for 20 nm thick Ru samples.](image)

**Fig. 6.** – Resistivity and calculated upper surface specularity for the FS model as a function of evaporated SiO$_2$ thickness for 20 nm thick Ru samples.

The error bars shown in Fig. 6 reflect the estimated error in thicknesses of the individual coupons in the absence of individual XRR characterization of each (only the full as-deposited wafer was measured).

It is clear that even the thinnest SiO$_2$ deposit of 0.5 nm results in an increase in resistivity that can only be accounted for by an increase in diffuse scattering of the upper Ru metal surface. We conclude that the specularity and surface order present after the 950°C step anneal in Ar + H$_2$
3% (e.g., as evidenced in Fig. 3c) is degraded by the SiO$_2$ deposition, which brings reactive Si and O adatoms and SiO$_x$ molecules to the sample surface, and apparently is more disruptive to specular scattering than the ambient air exposure of predominantly stable gaseous species (N$_2$, O$_2$, others). The upper surface specularity change is shown in Fig. 6 as well, using the FS model with $\rho_0 = 8.0$ $\mu\Omega$-cm, $\lambda = 11$ nm, and $p_l = 0\%$. The increase in resistance and decrease in specularity is associated only with changes in the specularity of the upper Ru surface as the room temperature SiO$_2$ deposition is not expected to change scattering within the Ru layer or scattering at the lower Ru/sapphire interface.

**E. Resistivity and specularity- sample series 4**

Experimental characterization data of the five samples of the fourth sample series are summarized in Table 2 along with the identification of the process steps after which the data was taken and the overall sequence of the process steps. It should be noted that the five samples were subjected simultaneously to all of the processing steps shown in the table, including the sputter deposition of a single 5 nm-thick layer of SiO$_2$. The data from each coupon are listed in a consistent order in each cell of Table 1, and the minimum and maximum value of each cell is used to provide the error estimations shown in Figs. 7 and 8. The resistivity values shown were calculated from the sheet resistance measured for each sample (not shown) and the Ru metal layer thickness for each sample, both parameters measured at each process step to eliminate this source of variability (shown as the error bars in Fig. 6). The simple trend readily apparent in the table is for the resistivity to decrease as a result of a reducing anneal and to increase as a result of the SiO$_2$ overlayer deposition or as the result of an oxidizing anneal.
Figure 7 shows the resistivity changes (left-hand axis) resulting from each processing step. Also observed here is the increase in resistivity resulting from the deposition of an amorphous 5 nm-thick SiO$_2$ overlayer on top of the Ru films that had been previously step annealed to 950°C in Ar + H$_2$ 3%. As above, these resistivity changes are described by the FS model with $\rho_0 = 8.0$ $\mu$Ω-cm, $\lambda = 11$ nm, and $p_l = 0\%$. As with sample series 3, an increase in surface roughness, a change in defect-related scattering within the layer, or a change in the lower Ru/sapphire interface cannot be expected from the room temperature SiO$_2$ overlayer deposition. The addition of the amorphous overlayer is understood to have increased surface scattering of the upper Ru surface, by an increase in the diffuse scattering fraction, from a surface that was largely specular. This increase in diffuse scattering can be understood as resulting from localized surface states that scatter electrons$^{15,19}$. These states are likely associated with atomic scale defects and/or the irregular bonding of Si and O adatoms and SiO$_x$ molecules at the Ru metal surface. The variations of the specularity of the upper surface are also shown in Fig. 7 using the right-hand axis and exhibit a variation in specularity of approximately 60%. Figure 7 plots the average value and presents the minimum and maximum values of the five samples as error bars. It is evident that the difference between
the maximum and minimum values in resistivity (and hence specularity) tends to increase with additional processing steps. We attribute this to the physical damage (i.e., scratches) imparted by the repeated probing of the sample surface by the sharp W wire contacts for the Van der Pauw sheet resistance measurements.

Figure 8 summarizes the trend of several of the measured sample characteristics from Table 1 as a function of processing step and compares these to the changes in FS model specularity. Shown are the changes in the Ru metal layer thickness (from the as-deposited state), the RuO$_2$ layer thickness, the XPS Ru$^+$/Ru$^0$ ratio, the Ru upper surface roughness, and the calculated
specularity. It is evident that the oxidizing anneals, steps 5 and 8, at 500°C and 400°C respectively, provided a significant increase in the RuO₂ thickness with corresponding decreases in the Ru metal thickness that are consistent with the expected variations in stoichiometry and density in the two layers. A much weaker effect was observed for step 10, an oxidizing anneal at 350°C. The higher temperature oxidizing anneals also destroyed the relatively specular scattering of the Ru upper surface to values similar to that immediately following SiO₂ overlayer deposition. A surprising observation is that, in all cases, the higher surface specularity immediately following the first 950°C step anneal in Ar + H₂ 3% (process step 2, with surface quality as imaged in Fig.5c) could be restored by a subsequent Ar + H₂ 3% anneal, at temperatures as low as 500°C, even with the amorphous SiO₂ overlayer present. In other words, the transition between mostly specular and mostly diffuse scattering from the upper surface was found to be reversible. The oxidizing anneals also resulted in a reversible increase in the roughness of the Ru upper surface, but these changes are small and would only account for a small fraction of the resistivity changes observed⁹,⁴³.

VI. CONCLUSIONS

The (0001) surfaces of single crystal Ru thin films ex-situ annealed at 950°C in Ar + H₂ 3% were found to form a highly ordered atomic surface structure that was stable to subsequent air exposure, as evidenced by LEED. Films with this structure for the upper Ru surface were found to have a relatively low resistivity that was correlated to a relatively high specular scattering probability, i.e., largely specular surface, for the upper surface in the context of the FS semi-classical model of the resistivity size effect. The deposition of SiO₂ on this surface, by sputtering or evaporation, was found to increase the resistivity and reduce the specularity of the surface. A subsequent anneal at 500°C in Ar + H₂ 3% was found to restore the low resistivity and high
specularity of the upper surface. Subsequent oxidizing anneals at 500°C and 400°C were again found to reduce the specularity of the upper surface while intermediate Ar + H\textsubscript{2} 3\% anneals were found to restore it. For the 20 nm thick Ru (0001) single crystal films, the relatively low and high specular scattering probabilities for the upper Ru surface were found to differ in magnitude by approximately 60\% and to be substantially reversible. This work clearly illustrates that improvement of specular scattering at a metal/dielectric interface is possible, thereby motivating the exploration of similar processing and/or processing at lower temperatures to achieve reduced resistivity for interconnect metals.

VII. ACKNOWLEDGEMENTS

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Figure captions

Figure 1
XPS data for Ru 3d (a), Si 2p (b), and O 1s (c) for the same sample following the 2nd (blue) 4th (green), and 5th (red) stage in the annealing process described in Table 1. Ru⁰ and Ru⁶⁺ in fig. 1(a) correspond to metallic ruthenium and ruthenium oxide (RuO₂) respectively.

Figure 2
Representative (a) XRD for a Ru film on sapphire (0001) deposited at 700°C with thickness d = 39.8 nm, (b) an XRD φ scan of the Ru {1122} peaks overlaid with a scan of the sapphire {1126} peaks.

Figure 3
LEED images at 68 eV for an air exposed Ru film (a) after deposition at 350°C, (b) after deposition at 700°C and ex-situ annealing to 950°C in Ar/3%H₂, and (d) a sample Ar ion beam cleaned and annealed to 1,000°C in UHV conditions with an H₂ background.

Figure 4
Shows representative XRR data from a 4.6nm thick SiO₂ on a 20.8nm-thick Ru(0001) layer. (a) upper (black) curve is for measured data shifted by a factor of 10 for clarity and (b) the lower (red) curve is the model prediction.

Figure 5
Resistivity versus thickness for c-axis single crystal Ru films deposited at 350°C (circles) and 700°C (squares) and ex-situ step-annealed to 950°C in Ar/H₂ 3%. The solid line is the calculation of the FS model.

Figure 6
Resistivity and calculated upper surface specularity for the FS model as a function of evaporated SiO₂ thickness for 20 nm thick Ru samples.

Figure 7
Film resistivity and FS model upper surface specularity (p_u) as a function of sample processing. Shown are average values for the five samples with error bars to reflect the extreme values amongst the five.

Figure 8
Shows (a) Ru metal thickness change, (b) RuOₓ, (c) Ru oxide to Ru metal ratio, (d) Ru roughness and (e) surface specularity (p) processing as a function of sample shown are average values for the five samples with error bars to reflect the extreme values amongst the five.