Effects of interface scattering and carrier localization on conductance of Cu-based superlattices

Jiyoon Jessica Kim

University at Albany, State University of New York, jkim2158@gmail.com
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by

Jiyoon Jessica Kim

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Abstract

Ultra-thin films and multilayer structures are widely used in modern technologies such as semiconductor logic and memory devices. As film thickness decreases to a few nanometers or smaller, classical transport theories are no longer valid. In this study, we investigate transport properties of superlattices with layer thickness reduced to ~1 nm. The superlattices are made of alternating layers of Cu and a transition metal (Ru, Mo, and Co). The layers are deposited by physical vapor deposition and resistance changes during superlattice growth are measured. The observed resistance evolution reveals the effects of carrier scattering and localization at the interfaces.

The Fuchs model is used to analyze the effect of interface scattering in each layer and to determine the carrier mean free path, which can represent grain sizes. Cu is found to have a larger mean free path than the transition metals. The interfacial energy controls grain sizes; large grains contribute to a higher conductance.

A significant conductance drop is observed when a new interface is created during the superlattice growth, indicating carrier localization occurring due to the $s$-$d$ hybridization. The conductance drop is instant and strong when transition metal atoms are deposited on Cu, not vice versa, suggesting the $s$-$d$ resonance only occurs at partially filled $d$ states of the transition metal atoms. The density of localized states at three different interfaces is compared through the size of the conductance drop. Our measurements indicate that the Ru/Cu interface creates the strongest localization, followed by the Co/Cu and Mo/Cu interfaces.

The superlattices are annealed to 400 °C while the resistance change is monitored. Grain growth is observed in the Cu/Mo superlattice at $T > 100$ °C, and in the Cu/Ru superlattice at $T > 300$ °C. The annealing reveals more phonon activities in the Cu/Co superlattice.
Chapter 1

Introduction

Thin films are widely used in everyday applications such as semiconductor devices, data storage, optical coating, etc. As technology advances and the size of electronic devices shrinks, the films in circuits are reduced to tens of nanometers or less in thickness. At this thickness, material issues such as electron migration and Joule heating become significant. In addition to single-layer thin films, multilayer structures are used to achieve unique electric, magnetic, optical, and mechanical properties. For instance, metal and semiconductor superlattices are used in giant magnetoresistance devices, optical coatings, high mobility devices, quantum dots and arrays, etc.

As the film thickness reduces below the phonon scattering mean free path, scatterings at surfaces/interfaces, grain boundaries, and other defects would dominate the electrical conductivity. The effect of surface scattering was treated by Fuchs in 1938 [1], and Mayadas studied the grain boundary effects [2]. Kuan et al. verified the importance of surface scattering in Cu interconnects below 0.1 μm [3]. The effect of surface roughness has also been studied at thickness below 10 nm [4-6]. Classical transport theories become invalid as the film thickness approaches the electron Fermi wavelength, and quantum effects must then be considered. In this study, the conductivities of Cu-based superlattices with layer thickness about 1 nm are investigated.

The superlattices contain highly disordered interfaces which scatter as well as localize carriers. In this study, superlattices consisting of Cu and transition metal (Ru, Mo, and Co) layers are grown at a low deposition rate at room temperature. Throughout the growth, relative resistance change is monitored and recorded without breaking the vacuum. The resistance
change occurring when a new interface is introduced during the growth is analyzed based on the
hybridization-induced localization model.

Chapter 2 reviews classical transport theories and quantum effects expected in nm-thick
films. Chapter 3 simulates the conductance evolution in a superlattice growth using a set of
scattering and localization parameters. Chapter 4 describes the deposition processes and data
acquisition method used in this study. The measured data and analysis of Cu-based superlattices
are presented in Chapters 5 and 6, with conclusions summarized in Chapter 7.

References

Chapter 2  

Electrical transport in a thin film

The electrical properties of simple metals can be explained by a nearly-free-electron model. In a thin film, surface scattering of electrons becomes prominent, and electrical conductivity decreases drastically when film thickness decreases. Fuchs proposed a thin film conductivity theory based on surface scattering in 1938 [1]. Later experimentation supported the model very well for film thickness above 10 nm [2].

However, as the thickness decreases below 10 nm, conductivity drops to a value much lower than the Fuchs prediction, which can be attributed to small grain sizes, surface roughness, or other structure factors [3, 4]. Quantum effects need to be considered when the thickness is reduced further towards the carrier wavelength. At that distance, carriers can be localized among scattering sites, which causes an additional conductivity reduction [5].

2.1 Effect of surface scattering

When an electric field is applied to a metal, free electrons at the Fermi surface are accelerated at a uniform rate to occupy adjacent empty states. If the electrons do not dissipate their energies to the lattice, the Fermi surface would continue to drift in the opposite direction of the applied field. However, scatterings of electrons by phonons, grain boundaries, surfaces, and other defects will stop the drift of the Fermi sphere as shown in Fig. 2.1.

The effect of surface scattering on the motion of free electrons is termed the size effect, which can be calculated via the Boltzmann equation. Using this equation, Fuchs derived the conductivity in a thin film as a function of thickness \( t \) as the following [1]:

\[
\sigma(t) = \frac{e^2}{4\pi m^*} \left( \ln \left( \frac{t}{a} \right) + \frac{1}{2} \right)
\]
Figure 2.1. (a) The Fermi sphere is in equilibrium at time $t = 0$ in the absence of an electric field. (b) At time $t$, the Fermi sphere is displaced by $\delta k$ due to the applied electric field.

\[
\frac{\bar{\sigma}}{\sigma_0} = 1 - \frac{3}{2} \frac{l_0}{t} (1 - p) \int_0^{\pi/2} \sin^3 \theta \cos \theta \left[ 1 - \exp \left( -\frac{t}{l_0 \cos \theta} \right) \right] \frac{1 - \exp \left( -\frac{t}{l_0 \cos \theta} \right)}{1 - \exp \left( -\frac{t}{l_0 \cos \theta} \right)} d\theta,
\]  

(2.1)

where $\sigma_0$ and $l_0$ are the conductivity and carrier mean free path in a bulk metal, respectively. The parameter $p$ represents the probability of specular scattering at the surface.

The Fuchs model describes elastic scattering at the surface that could be either specular or diffuse as depicted in Fig. 2.2. The specular scattering ($\theta_i = \theta_r$) will conserve the carrier velocity in the $-E$ direction and leaves $\bar{\sigma} = \sigma_0$. The diffuse scattering causes $\bar{\sigma} < \sigma_0$ at any incident angle ($0 \leq \theta_i \leq \pi/2$) because of its isotropic scattering angle, according to the integration in Eq. (2.1).

Figure 2.2. Schematic diagrams of (a) specular scattering and (b) diffuse scattering at a surface.
The probability of specular scattering at a surface is denoted by $p$, and the diffuse scattering by $(1 - p)$. Specular scattering ($p = 1$) does not affect electrical resistivity as stated before, and diffuse scattering ($p = 0$) contributes the maximum amount of resistivity.

Fig. 2.3 (a) shows the effect of surface scattering on the conductivity of a thin film calculated by Eq. (2.1). Here it is seen that a large mean free path $l_0$ (from 1 nm to 5 nm) can lower $\bar{\sigma}/\sigma_0$ as significantly as a lower $p$ value ($p = 0.75$ to 0) as indicated by arrows in Fig. 2.3.

The Fuchs model assumes a phonon scattering mean free path, which is suitable for a single crystal thin film or a polycrystalline film with grain size much larger than $l_0$. However, additional physical effects such as surface roughness are not included in the model. Observed conductivity of single crystal Cu films with thickness down to 4 nm grown on Si indicated a large effect of surface roughness [4], as shown in Fig. 2.4.

The Fuchs model considers only phonon and surface scatterings and is not suitable for polycrystalline films with small grain size. To modify the Fuchs model for such fine grain polycrystalline films, a small mean free path $l_g$ corresponding to grain boundary scattering should be used along with a smaller bulk conductivity $\sigma_g$ representing the conductivity of the fine grain bulk material. Therefore, Eq. (2.1) becomes

$$\frac{\bar{\sigma}}{\sigma_g} = 1 - \frac{3}{2} \frac{l_g}{t} (1 - p) \int_0^\pi \sin^3 \theta \cos \theta \frac{1 - \exp(-t/l_g \cos \theta)}{1 - p \exp(-t/l_g \cos \theta)} d\theta.$$  \hspace{1cm} (2.2)

In Fig. 2.3 (b), we see that a smaller mean free path $l_g$, corresponding to a smaller grain size, shifts the size effect to a smaller film thickness region ($t < l_g$).
Figure 2.3. (a) Effect of surface scattering on the conductivity of a thin film at $l_0 = 5$ nm. (b) Effect of mean free path $l_0$ on the conductivity. The conductivity can be affected significantly by either $p$ or $l_0$. 
2.2 Effective surface scattering parameters

When a thin film is deposited on a substrate, or is a layer within a superlattice, the top and bottom surfaces often have different surface scattering parameters. Lucas introduced two scattering parameters $p$ and $q$ for the two surfaces [8], and the film conductivity Eq. (2.1) became

$$\frac{\bar{\sigma}}{\sigma_0} = 1 - \frac{3}{4\kappa l_0} \int \left( \frac{1}{\alpha^3} - \frac{1}{\alpha^5} \right) \left[ \frac{1 - e^{-\kappa \alpha}}{1 - pq e^{-2\kappa \alpha}} \left[ 2 - p - q + (p + q - 2pq) e^{-\kappa \alpha} \right] \right] d\alpha, \quad (2.3)$$

where $\alpha = 1/\cos \theta$ and $\kappa = t/l_0$. Experimentally it is difficult to measure the two parameters. In simulating the film conductivity, using an effective parameter $p'$ in the Fuchs model can result in the same conductivity as from $p$ and $q$ [2]. An example is shown in Fig. 2.5.

A real surface or interface in nm-thick films or superlattices often contains a high density
Figure 2.5. Identical conductivity can be produced by Lucas model (curve) with $p = 0.2$ and $q = 1$ or by an effective $p' = 0.55$ using Eq. (2.1) with $l_g = 10$ nm.

of defects such as vacancies, steps, dislocations, and grain boundaries. If the distance between defects is comparable to the carrier Fermi wavelength, then total diffuse scattering ($p = 0$) is expected at the interfaces [9].

2.3 Carrier localization

The phonon mean free path in most metals ranges from ~10 to ~50 nm at room temperature, and the grain boundary scattering mean free path is comparable to the grain sizes. When we grow a film to a few nm thick, and if the grain size is comparable to the film thickness, the scattering mean free path is then close to the film thickness. However, if the film contains a higher degree of disorder than fine grain size, electron wavefunctions can become localized due
to disorder scattering. Such localizations often occur at the edges of a narrow $d$ band, as depicted in Fig. 2.6. This phenomenon is termed Anderson localization \cite{5}.

Carrier localization can also occur when transition metals are adsorbed on a simple metal surface. The adsorbed atoms produce big potential perturbations, which can localize surface carriers as illustrated in Fig. 2.7. The localization involves $s$-$d$ hybridization occurring at a resonant energy $E_r$ \cite{10-12}. Surface carriers will be trapped if the resonant energy is within the

\[ E_r \]

\[ E_r \]

Figure 2.6. The density of $d$ states of the Anderson model in a 3-D highly disordered metal. Shaded regions are the localized states. Non-localized, extended states remain at the band center.

Figure 2.7. Potential variations due to surface adsorption of foreign atoms. Electron orbitals are localized at the high or low potentials \cite{13}.
energy band of the substrate, as shown in Fig. 2.8. This is often the case when a transition metal, such as Ru, is adsorbed on Cu surfaces. However, if Cu atoms are adsorbed on a transition metal substrate, the resonant energy may lie above the Fermi energy of the transition metal, and in this case, no localization of surface carriers would occur.

To summarize, disorder scattering can produce localization states if the density of defects is high enough. When transition metal atoms are adsorbed on a simple metal surface, the s-d hybridization can also produce localization states. The former process involves collective defect scatterings, and the latter depends on chemical interactions. Those electrons occupying the localized states will no longer contribute to the electrical conductance [5, 14-18], whereas electrons in the extended states remain as free carriers, whose mobility can be hindered by surface scatterings as described by the Fuchs model.

![Figure 2.8](image_url)

**Figure 2.8.** The localized states due to adsorbed atoms occurred at a resonant energy $E_r$ with a width of resonance $\Gamma$ [12].
References


Chapter 3

Simulation of conductance in a superlattice

Conductance of a thin film during growth can be simulated using a modified Fuchs model, and the method can be extended to a multilayer structure. In this chapter, the transport behavior during growth of a multilayer superlattice is simulated including the quantum effects. The localization of carrier wavefunctions during an interface creation is expected to cause a drop in the conductance. Diffuse scattering ($p = 0$) is assumed in all simulations in this chapter as discussed in section 2.2.

3.1 Conductance in a single layer

Conductance in a single layer is given by,

$$ G(t) = \sigma t, \quad (3.1) $$

where $G$ is the total conductance at thickness $t$, and $\bar{\sigma}(t)$ is the average conductivity of the thin film with thickness $t$. According to the Fuchs model with $p = 0$,

$$ \bar{\sigma} = \frac{1}{t} \int_0^t \sigma dt = \sigma_0 \left[ 1 - \frac{3}{2} \int_0^t \sin^3 \theta \cos \theta \left[ 1 - \exp(-t/l_\theta \cos \theta) \right] d\theta \right]. \quad (3.2) $$

The differential conductance $dG/dt = \sigma$ indicates the instantaneous conductivity $\sigma$ at thickness $t$, which can become negative due to the localization effect.

As discussed in section 2.2, diffuse scattering ($p = 0$) always produces the lowest $\bar{\sigma}$ at any thickness, however, a longer mean free path can also lower the $\bar{\sigma}/\sigma_0$. Fig. 3.1 (a) shows the effect of different mean free path on the conductance for $p = 0$. The differential conductance $dG/dt = \sigma$ exhibits a smaller curvature for a longer mean free path as shown in Fig. 3.1 (b).
Figure 3.1. (a) Conductance in a thin film ($p = 0$) with different mean free path. (b) The differential conductance $dG/dt$ at different mean free path are compared.
3.2 Effect of carrier localization

When a transition metal film is grown on a simple metal substrate with just a monolayer thickness, a new interface is created. Free carriers from the simple metal substrate can be localized via s-d hybridization at the interface. The localization produces a permanent conductance drop, as the localized states are formed and occupied. We have found that the conductance drop can be expressed as:

$$-\Delta G(1 - e^{-t/t_0})$$,  \hspace{1cm} (3.3)

where \(\Delta G\) represents the maximum drop and \(t_0\) is the thickness constant for the width of localization zone. The carrier localization adds a negative term,

$$-\frac{\Delta G}{t_0} e^{-t/t_0}$$,  \hspace{1cm} (3.4)

to the differential conductance \(dG/dt\), which represents the instantaneous conductivity drop due to localization.

As discussed in Chapter 2, surface carriers are localized when a transition metal is deposited on Cu. However, when Cu is deposited on transition metals, surface carriers are not localized. An example of the instant conductance drop due to localization at a new interface is shown in Fig. 3.2 (a), and the effect on \(dG/dt\) is shown in Fig. 3.2 (b). The conductance drop stays with the \(G\) curve, but the effect on \(dG/dt\) disappears above certain thickness as the localized states are totally filled.
Figure 3.2. The localized states due to the s-d hybridization at the interface can trap the carriers from the substrate and produce an instant conductance drop. The effects of localization on (a) $G$ and (b) $dG/dt$ are simulated using $\Delta G = 0.3 \, \text{k}\Omega^{-1}$ and $t_0 = 0.05 \, \text{nm}$. Here the conductance of the substrate is set to zero.
3.3 Electrical transport in multilayers

To simulate a multilayer grown with carrier localization at the interfaces, Eqs. (3.1) and (3.3) can be applied repeatedly:

\[ G = \sum t_i \bar{\sigma}_i t - \Delta G_i (1 - e^{-t_i/t_0}) . \]  

(3.5)

As mentioned in the beginning of this chapter, \( p = 0 \) is assumed for all layers. The average conductivity \( \bar{\sigma} \) is sensitive to mean free path \( l_g \) and the fine-grain bulk conductivity \( \sigma_g \), and the conductance drop \( \Delta G \) is determined by the strength of localization. Two types of interfaces are encountered in the superlattices growth: one involves a transition metal deposited on a simple metal, the other involves a simple metal on a transition metal. Only the former interface produces localized states.

Fig. 3.3 shows an example of simulated transport behavior in a superlattice with alternating transition metal A and simple metal B layers. We assume A layers have a mean free path \( l_g = 1 \text{ nm} \) with a bulk conductivity \( \sigma_g \), and B layers have a longer \( l_g = 5 \text{ nm} \) with a bulk conductivity \( 3\sigma_g \). The simulation shows more size effect in B layers with a larger mean free path than in A layers in Fig. 3.3 (b). Solid lines represent the simulation with localizations occurring at the A/B interfaces, using \( \Delta G = 0.3 \text{ k\Omega}^{-1} \) and \( t_0 = 0.05 \text{ nm} \). As expected, \( \Delta G \) drops stay with the conductance curve in Fig. 3.3 (a), while the conductivity \( dG/dt \) quickly recovers to non-localized dashed curve described by the Fuchs model in Fig. 3.3 (b).
Figure 3.3. Simulation for a $AB$-superlattice (dashed lines without localization and solid lines with localization). $A$ layers have $l_g = 1\ \text{nm}$ and a bulk conductivity $\sigma_g$, and $B$ layers have $l_g = 5\ \text{nm}$ and a bulk conductivity $3\sigma_g$. The localization parameters $\Delta G = 0.3\ \text{k}\Omega^{-1}$ and $t_0 = 0.05\ \text{nm}$ are used in $A$ layers.
Chapter 4

*Direct observation of conductance growth*

4.1 DC magnetron PVD

In this study, the Cu-based superlattices are grown by physical vapor deposition (PVD) using a magnetron. During the magnetron sputtering, an inert Ar gas is constantly flowed into the vacuum chamber, and a power supply delivers a potential difference between electrodes creating an electric field from anode to cathode. When free electrons accelerate towards the anode, they collide with the Argon gases and ionize the gas. The Ar cations are accelerated towards the cathode, colliding with the target material, sputtering the target atoms into the plasma. Ionized target atoms are accelerated toward and deposited on the substrate. A schematic of the setup is depicted in Fig. 4.1.

In a magnetron, a magnetic field is used to increase the plasma density and the sputtering efficiency. A set of magnets is located behind the target to create a magnetic field at the target

![Figure 4.1. A DC diode discharge setup.](image)
In a DC magnetron, a set of magnets is placed with the north pole in the center surrounded by the south poles, generating a B-field outwards from the center. An E×B drift path (magnetron tunnel) is created on top of the target. Surface as shown in Fig. 4.2, which confines electrons in an E×B drift path (or magnetron tunnel) near the target surface. More captured electrons in the drift path produce a higher plasma density.

4.2. Deposition rate calibration

One of the advantages DC magnetron PVD offers is an easy control of deposition rates. The deposition rate is proportional to input power. A very low power deposition rate is pre-calibrated using an atomic force microscope (AFM). A mask tape is applied on a part of a substrate prior to the calibration deposition. The mask tape is removed after the deposition, and a step height of the deposited film is measured by AFM. The step height can give an accurate calibration of the deposition rate. An example of the AFM step height profile for a Cu film is shown in Fig. 4.3. More than ten step height profiles are taken for each calibration sample to ensure accuracy. Table 4-1 lists the deposition rates for different targets under the sputtering conditions used in this study.
Figure 4.3. A typical step height profile obtained by *ex situ* AFM. The step height is used to calibrate the deposition rate. This is a profile of Cu deposited for 15 min under conditions of 50 mA/260 V/13 W.

Table 4-1. Deposition rates for different targets at a throw distance of 14.5 cm

<table>
<thead>
<tr>
<th>Material</th>
<th>Conditions (mA/V/W)</th>
<th>Deposition time (min)</th>
<th>Deposition rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta</td>
<td>200/230/46</td>
<td>10</td>
<td>3.4 ± 0.1</td>
</tr>
<tr>
<td>Ru</td>
<td>200/330/66</td>
<td>10</td>
<td>3.6 ± 0.1</td>
</tr>
<tr>
<td>Mo</td>
<td>200/280/56</td>
<td>10</td>
<td>3.9 ± 0.2</td>
</tr>
<tr>
<td>Co</td>
<td>200/315/63</td>
<td>10</td>
<td>2.3 ± 0.1</td>
</tr>
<tr>
<td>Cu</td>
<td>50/260/13</td>
<td>15</td>
<td>1.9 ± 0.1</td>
</tr>
</tbody>
</table>
4.3. Thin film deposition

A sequence of transition metal (TM) and Cu depositions resulting in a superlattice on a SiO₂/Si substrate is shown in Fig. 4.4 (a). The Si substrate is coated with 2.4 μm thermal oxide (SiO₂). Four Ta contact pads, 140 nm in thickness and 0.5 cm in diameter, are deposited onto SiO₂ prior to the superlattice growth as shown in Fig. 4.4 (b).

The substrate with Ta contact pads is loaded onto the sample holder. A ceramic ring with four affixed I-V probes is mounted onto the substrate and in contact with the Ta pads. A 1.8 cm diameter circular aperture over the ceramic ring confines the deposition to overlap partially with the contact pads. Fig. 4.5 shows the assembly of the substrate holder, isolated I-V leads, and a circular aperture. After the substrate is loaded, the PVD chamber is pumped down to a minimum base pressure of less than 5 × 10⁻⁷ Torr.

Ar gas is flowed into the vacuum chamber at 5 sccm, and the Ar pressure is maintained at

---

**Figure 4.4.** (a) A schematic of Cu-based superlattice structure on SiO₂/Si used for this study. Thickness for Ru, Mo, and Co are 1.3 nm, 2.2 nm, and 0.8 nm respectively. (b) A schematic of a SiO₂/Si substrate with Ta contact pads. A dashed circle, 1.8 cm in diameter, indicates where the superlattice is deposited.
Figure 4.5. (a) A schematic of the sample holder mounted inside the PVD chamber. The sample holder is assembled as following: (b) substrate with pre-deposited Ta contact pads is placed on a heating stage, (c) isolated I-V leads are connected to the contact pads, then (d) a circular PVD aperture is fixed on top [1].

2.1 mTorr. The superlattice structure is deposited at room temperature, and all electrical measurements are taken during the deposition without breaking the vacuum.

4.4. In situ resistance measurement

Because the film is prone to oxidize, the measurement must be done in situ. Current and voltage (I-V) measurements are taken continuously and recorded every two seconds by a LabVIEW program throughout the experiment, and the recorded data allow us to follow the evolution of conductance during growth.

Resistance or conductance of the film can be measured in two different ways: 4-point and 2-point methods. The 4-point method measures the relative change in resistance as depicted in Fig. 4.6 (a). The circuit of 4-point method is depicted in Fig. 4.6 (c). A fixed current is
applied between point 1 and point 2, and voltage drop is measured between point 3 and 4. Then the measured 4-point resistance is

\[
R_{\text{measured}} = \frac{V_{\text{measured}}}{I_{\text{applied}}} = \frac{I_R}{I_R + I_V} R - \frac{I_V}{I_R + I_V} (R_3 + R_4) \approx R, \tag{4.1}
\]

since \( R_V \gg R_3 + R_4, R_V \gg R \), and \( I_R \gg I_V \). The error size is related to those contact resistances, which is negligible in the calculation. Therefore, errors due to any change in contact resistance during the growth can be avoided in this method. Fig. 4.6 (b) shows a 2-point measurement, which measures the absolute value of the resistance. The current is applied at point 1 while the voltage is measured at point 1 and grounded at point 2. The measured 2-point resistance,

\[
R_{\text{measured}} = R_1 + R + R_2 > R, \tag{4.2}
\]

therefore includes resistances from the leads and the contact pads. The resistance of the Ta contact pad is \(~0.5 \, \Omega\) and the I-V lead is \(~0.1 \, \Omega\). Uncertainty in 2-point measurement is therefore within \( 1 \, \Omega \). Given a film resistance of \(~100 \, \Omega\), the 2-point method gives the absolute film resistance within \( 1 \% \) error.

When current flows in a circular film as shown in Fig. 4.6 (b), the measured resistance \( R \) of the film of radius \( r \) and thickness \( t \) is related to the material resistivity \( \rho \) by [2]:

\[
R = 2 \pi \rho \frac{r}{t}.
\]
$R = \frac{2 \rho}{\pi \delta} \ln \frac{2r}{\delta/2}$, \hspace{1cm} (4.3)

where $\delta$ is the contact length at the film edge. In the I-V measurement, we use samples with $r = 0.9$ cm and $\delta = 0.42$ cm, which give $R = 1.37 \rho/t$ in Eq. (4.3). Electrical resistivity in a metal is given by the Drude-Sommerfeld model:

$$\rho = \frac{m^* v_F}{n e^2 l}$$ \hspace{1cm} (4.4)

where $n$ is the electron density, $m^*$ is the effective mass of an electron, $l$ is the collision mean free path, and $v_F$ is the Fermi velocity.

During the in situ 4-point probe measurement, the electric current passing through the film can raise the film temperature. It is important to minimize the Joule heating to avoid alternating the properties of the film. A very low current $I = 1 \mu A$ is used for this study. The power carried by the current is small and any heat generated in the film is dissipated into the Si substrate. A thermocouple is affixed adjacent to the substrate (see Fig. 4.5) to measure the temperature, and no temperature raise is observed throughout the deposition.

Prior to experiments, the substrate is preheated to 300 °C for 30 min to eliminate any contaminants on the substrate surface. After the superlattice growth is complete, an annealing experiment is carried out with the superlattice/substrate heated from room temperature to 400 °C with conductance fully monitored during the heating and cooling periods. The heating coil has a resistance of 25 Ω, and it heats up the film/substrate to 400 °C in approximately 40 mins at 71 W. The heating rate is kept constant to enable direct comparisons between the experiments.
4.5 Surface morphology by *ex situ* AFM

An atomic force microscope (XE-100 AFM by Park Systems, Inc.) is used to study the surface morphology of the superlattices after annealing. The AFM works by scanning a fine probe over a sample surface. A piezoelectric scanner moves the sample in the $x$ and $y$ directions. A probe tip is mounted on the end of a cantilever ensemble which can move in the $z$ direction. A laser beam incident on the cantilever is reflected to a photodiode to measure the bending angle of the cantilever. The bending angle is proportional to the force between the probe tip and the surface. The feedback control connected to the photodiode feeds the signal to adjust the height of the tip/cantilever ensemble to maintain a constant force on the tip. The $(x, y)$ and $\Delta z$ signals generate a 3-D map of the surface topography. Fig. 4.7 shows the schematic of the AFM operation and system.

The AFM analysis utilizes two different force modes, contact or non-contact mode, as shown in Fig. 4.8. The contact mode operating in the repulsive regime is used for this study. In this mode, the tip is in contact with the sample surface during the scan to produce a high-resolution image.

![AFM Feedback System Diagram](image)

*Figure 4.7. A schematic of the AFM feedback system [3].*
Figure 4.8. Force regimes for different AFM modes. In the contact mode, the tip makes soft contact with the sample and the force between the tip and the surface is maintained constant [3].

References


Chapter 5

Measurement of electrical conductance during superlattice growth

Effects of carrier scattering and localization on electrical conductivity were measured \textit{in situ} during the growth of superlattices of Cu and transition metals (Ru, Mo, and Co). The superlattices were prepared by a physical vapor deposition (PVD) process. The first layer of transition metal was deposited on a SiO$_2$/Si substrate until its resistance reached about 2 kΩ, to ensure a continuous and uniform film. Subsequent layers were deposited with their deposition rates listed in Table 4-1. In this chapter, measurement results on superlattices of Cu with Ru, Mo and Co are presented.

5.1 Cu/Ru superlattice

To facilitate the I-V measurement, the PVD is interrupted for ~40 seconds after each 2-second or 3-second deposition, as shown in Fig. 5.1 (a). For the first Cu layer, the interruptions are longer than 40 seconds to allow for grain growth to be stabilized. During the interruption the incoming beam is blocked by a shutter in front of the magnetron gun, so that the I-V measurement will not be interfered by the charges carried in the incoming beam. The subsequent Ru layers are grown through a sequence of eleven 2-second depositions, yielding 1.3 nm in total thickness. The measurements taken during the interruptions show the evolution of resistance during the growth of that layer. The 1.1-nm-thick Cu layers are grown through eleven 3-second depositions. The superlattice has a structure of four Ru layers separated by three Cu layers, with a total thickness of 8.5 nm.

A 2-point I-V resistance measurement is taken after the last layer deposition to calibrate the 4-point I-V measurements taken during the growth, since the 4-point method measures the
Figure 5.1. (a) The measured 4-point relative resistance data versus real deposition and interruption time. The resistance spikes up at every deposition due to charges in the beam. Clear resistance value is obtained during the ~40 sec growth interruption. (b) The normalized resistance versus film thickness.
relative change in resistance whereas the 2-point method measures the absolute value. The normalized resistance is presented in Fig. 5.1 (b).

Significant resistance decrease due to grain growth in Cu was observed during the first few long interruption periods (~200 sec) in the growth of the first Cu layer, as indicated by arrows in Fig. 5.1 (a). To analyze the effects of carrier scattering and localization on the conductance of the superlattices, it is desirable to separate the factor due to grain growth. Such correction is easily done in the conductance $G$, since conductance of parallel layers are additive, and the grain growth component can be deducted directly from the measured total. The reconstructed conductance of the Cu/Ru superlattice is shown in Fig. 5.2 (a). It is noted that a grain growth correction is required only in the first Cu layer. In Fig. 5.2 (b), the derivative of $G$ with thickness ($dG/dt$) is plotted. The derivative represents the instantaneous conductivity during the growth of the superlattice.

Two interesting features are observed in the conductance plot in Fig. 5.2 (a). First, conductance drops are observed at the beginning of each Ru layer deposition and the amount of $\Delta G$ drops are listed in Table 5-1. No drops are observed during the growth of Cu layers.

<table>
<thead>
<tr>
<th>Layer</th>
<th>$\Delta G$ (k$\Omega^{-1}$)</th>
<th>$dG/dt_{\text{max}}$ (µ$\Omega^{-1}$cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (2)</td>
<td>-</td>
<td>0.016</td>
</tr>
<tr>
<td>Cu (4)</td>
<td>-</td>
<td>0.024</td>
</tr>
<tr>
<td>Cu (6)</td>
<td>-</td>
<td>0.027</td>
</tr>
<tr>
<td>Ru (3)</td>
<td>0.24</td>
<td>0.013</td>
</tr>
<tr>
<td>Ru (5)</td>
<td>0.54</td>
<td>0.012</td>
</tr>
<tr>
<td>Ru (7)</td>
<td>0.61</td>
<td>0.012</td>
</tr>
</tbody>
</table>
Figure 5.2. (a) The original \textit{in situ} conductance measured during the Cu/Ru superlattice growth (dashed line) and reconstructed data with grain growth component deducted (symbols). (b) $dG/dt$ of the Cu/Ru superlattice during growth.
Second, $dG/dt$ reaches a significantly higher value in Cu layers than in Ru layers. The first Ru layer grown on SiO$_2$/Si is not listed and its unique growth conditions will not be considered.

5.2 Cu/Mo superlattice

The first Mo layer is grown on SiO$_2$/Si through nine 3-second depositions, yielding 1.8 nm in total thickness. Subsequent Mo layers are deposited to a thickness of 2.2 nm. The 1.1-nm-thick Cu layers are deposited through eleven 3-second depositions. The superlattice of four Mo layers and three Cu layers has a total thickness of 11.4 nm. The measured relative resistance and the normalized resistance data are plotted in Fig. 5.3.

As in the Cu/Ru superlattice, some Cu grain growth occurred during the long growth interruptions in the first Cu layer (~100 sec), as indicated by arrows in Fig. 5.3 (a). The conductance, with grain growth components deducted, is shown in Fig. 5.4 (a).

The two features observed in the Cu/Ru are also present in the Cu/Mo superlattice. A $\Delta G$ drop occurs at the initial growth of Mo on Cu, and no $\Delta G$ drops are observed when Cu is deposited on Mo. The $\Delta G$ drop during Mo growth is much smaller than the drop observed in Ru

<table>
<thead>
<tr>
<th>Layer</th>
<th>$\Delta G$ ($\text{k}\Omega^{-1}$)</th>
<th>$dG/dt_{\text{max}}$ ($\mu\Omega^{-1}\text{cm}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (2)</td>
<td>-</td>
<td>0.010</td>
</tr>
<tr>
<td>Cu (4)</td>
<td>-</td>
<td>0.012</td>
</tr>
<tr>
<td>Cu (6)</td>
<td>-</td>
<td>0.015</td>
</tr>
<tr>
<td>Mo (3)</td>
<td>-</td>
<td>0.0057</td>
</tr>
<tr>
<td>Mo (5)</td>
<td>0.062</td>
<td>0.0059</td>
</tr>
<tr>
<td>Mo (7)</td>
<td>0.099</td>
<td>0.0051</td>
</tr>
</tbody>
</table>
Figure 5.3. (a) The measured 4-point relative resistance data and (b) the normalized resistance versus thickness of the Cu/Mo superlattice during growth.
Figure 5.4. (a) The measured conductance (dashed line) and the conductance with the grain growth component deducted (symbols). The grain growth component is very small (< 5 %). (b) $dG/dt$ of the Cu/Mo superlattice during growth.
growth. The $dG/dt$ plotted in Fig. 5.4 (b) shows similar features as in the Cu/Ru superlattice, but with significantly lower $dG/dt$ values. The $dG/dt$ in Cu is roughly three times of that in Mo.

### 5.3 Cu/Co superlattice

In this superlattice, each Cu layer is grown with eleven 3-second depositions for 1.1 nm in thickness, and the Co layer with eleven 2-second depositions for 0.8 nm in thickness. The superlattice has 4 Co layers and 3 Cu layers with a total thickness of 7.3 nm. The measured relative resistance and normalized resistance are plotted in Fig. 5.5.

Significant resistance decrease due to grain growth was observed during the long growth interruptions (~300 sec) in the first Cu layer as indicated by arrows in Fig. 5.5 (a). The conductance with the grain growth component deducted in the first Cu layer is shown in Fig. 5.6 (a).

The $\Delta G$ conductance drops observed at the beginning of each Co layer deposition are comparable to those in the Ru layers. The $dG/dt$ plot in Fig. 5.6 (b) shows a sharp peak in Co layers after the $\Delta G$ drop that are not observed in Ru or Mo. Further analysis will be discussed in Chapter 6.

**Table 5-3. Conductance drop and $dG/dt$ observed in the Cu/Co superlattice**

<table>
<thead>
<tr>
<th>Layer</th>
<th>$\Delta G$ (kΩ⁻¹)</th>
<th>$dG/dt_{\text{max}}$ (μΩ⁻¹cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (2)</td>
<td>-</td>
<td>0.022</td>
</tr>
<tr>
<td>Cu (4)</td>
<td>-</td>
<td>0.025</td>
</tr>
<tr>
<td>Cu (6)</td>
<td>-</td>
<td>0.029</td>
</tr>
<tr>
<td>Co (3)</td>
<td>0.027</td>
<td>0.017</td>
</tr>
<tr>
<td>Co (5)</td>
<td>0.32</td>
<td>0.019</td>
</tr>
<tr>
<td>Co (7)</td>
<td>0.36</td>
<td>0.021</td>
</tr>
</tbody>
</table>
Figure 5.5. (a) The measured 4-point relative resistance data and (b) the normalized resistance of the Cu/Co superlattice during growth.
Figure 5.6. (a) The reconstructed conductance (symbols) without grain growth component and the original *in situ* conductance (dashed line). (b) $dG/dt$ of the Cu/Co superlattice during growth.
5.4 Observations of grain growth during annealing

The Matthiessen rule states that the total resistivity of materials is the sum of contributions from phonon scattering in the lattice and from scattering at impurities, defects, surfaces, and grain boundaries. The phonon contribution to the resistivity is linear with temperature because there are more phonons at a higher temperature. Since the number of surfaces and defects are constant, the resistivity from those is temperature independent. In thin films or superlattices, phonon contribution to resistance is less important. The small phonon contributions, however, can be detected by annealing.

Phase diagrams of Cu alloyed with three transition metals (Ru, Mo, and Co) are shown in Fig. 5.8. No chemical compounds are expected in the alloys up to melting temperatures. The superlattices were annealed from RT to 400 °C at a uniform heating rate (9 °C/min) and cooled down to RT in an Ar ambient at 10⁻³ Torr. Resistance was monitored in situ during this process, as shown in Fig. 5.7. During the heating, resistance decreases due to grain growth are observed in Cu/Ru and Cu/Mo superlattices. The grain growth starts at ~100 °C in the Cu/Mo superlattice, and at ~300 °C in the Cu/Ru superlattice, indicating a stronger driving force for grain growth in the Cu/Mo superlattice. The resistance of both superlattices drops about 7.5 % at 400 °C due to grain growth. The resistance in the Cu/Co superlattice is observed to increase linearly from RT to 300 °C suggesting no grain growth and presence of phonon activities.

During cooling, a steady but small decrease in resistivity is observed in all three superlattices. Since additional grain growth is unlikely during the cooling, the slight decrease in resistance must be due to the phonon activities. Much stronger phonon activity is observed in the Cu/Co superlattice.
Figure 5.7. Phase diagrams of Cu alloyed with three transition metals [1].
Figure 5.8. Resistance change in three superlattices during annealing and cooling.

5.5 Surface morphology

The superlattice surfaces are analyzed after annealing by AFM. The measured surface morphologies and profiles are plotted in Fig. 5.9. The surface roughness is calculated by root-mean-square (RMS), which is

$$\text{RMS} = \sqrt{\left(\Delta Z_1^2 + \Delta Z_2^2 + \cdots + \Delta Z_N^2\right)/N} = \sqrt{\langle \Delta Z^2 \rangle},$$

(5.1)

for a $N$ pixel AFM image with deviation $\Delta Z$ from an average height. The images in Fig. 5.8 are 256 by 256 pixels. The surface morphologies of all superlattices have RMS roughness of the order of monolayer thickness (~0.3 nm), as shown in Fig. 5.9. The interface roughness in the superlattices should also be within a monolayer thickness.
Figure 5.9. *Ex situ* AFM surface images and profiles of the (a) Cu/Ru, (b) Cu/Mo, and (c) Cu/Co superlattices taken at RT.
References

Chapter 6

Analysis of carrier scattering and localization in superlattices

Following the discussions in Chapter 3, the measured conductance in the superlattices can be analyzed using the formula with parameters $l_g$, $\sigma_g$, $\Delta G$, and $t_0$:

$$ G = \sum_i \bar{\sigma}(l_g, \sigma_g, t_i)T_i - \Delta G (1 - e^{-l_g/l_0}) , $$

(6.1)

where the average conductivity $\bar{\sigma}$ is calculated using the Fuchs model with $p = 0$:

$$ \frac{\bar{\sigma}}{\sigma_g} = 1 - \frac{3}{2} \int_0^\pi \frac{l_g}{2} \sin^3 \theta \cos \theta \left[1 - \exp(-t/l_g \cos \theta)\right] d\theta . $$

(6.2)

Following the strategies discussed in section 3.3, the four parameters can be determined uniquely from the measurements:

1) As discussed in section 3.1, the measured curvature of $dG/dt$ dictates the size of $l_g$.

2) The mean free path $l_g$ and the fine grain conductivity $\sigma_g$ are correlated. Once the $l_g$ is set, $\sigma_g$ is determined accordingly.

3) The localization factors $\Delta G$ and $t_0$ are obtained by fitting the known $(G - \bar{\sigma}t)$ vs. $-\Delta G (1 - e^{-t/l_0})$ using MATLAB. The base transition metal layer is not fitted because of different growth conditions on SiO$_2$.

6.1 Cu/Ru superlattice

An optimum fit to the measured conductance of the Cu/Ru superlattice is achieved using parameter values listed in Table 6-1, and the fitting is shown in Fig. 6.1. $R^2$ correlation coefficient in the conductance curve fitting is also listed in Table 6-1. Diffuse scattering ($p = 0$) is assumed for all simulations. As a smaller curvature in $dG/dt$ indicates a larger mean free path, the mean free path $l_g = 1$ nm for Ru and 5 nm for Cu are used with an exception of the first Cu
layer which is fitted with $l_g = 1$ nm. The mean free path is proportional to the grain size in that layer. Active grain growth observed in the first Cu layer during growth suggests that the layer must contain small initial grain size. Large grain size (~5 nm) reached in the second and third Cu layers brings about no more grain growth. The curvature of $dG/dt$ is fitted well with the parameters as shown in Fig. 6.1 (b).

A large drop in conductance suggests an instant localization at the newly formed Ru/Cu interface. There is no drop when Cu is deposited on Ru. The $\Delta G$ from the curve fitting is slightly larger than those listed in Table 5-1 because of the $\sigma t$ term in Eq. (6.1).

The sudden drop due to the strong localization at the Ru/Cu interface is fitted with very small $t_0$. The localization thickness $t_0$ below 0.05 nm produces a good $dG/dt$ fit in the Ru layers ($R^2 > 0.99$) as shown in Fig. 6.1 (b). The $R^2$ values are calculated by

$$R^2 = 1 - \frac{\sum (y - f)^2}{\sum (y - \bar{y})^2}$$

(6.3)

where $y$ is the measured variable, $\bar{y}$ is an average of variables, and $f$ is the fitted curve.

<table>
<thead>
<tr>
<th>Table 6-1. Fitting parameters for the Cu/Ru superlattice</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l_g$ (nm)</td>
</tr>
<tr>
<td>------------</td>
</tr>
<tr>
<td>Cu (2)</td>
</tr>
<tr>
<td>Cu (4)</td>
</tr>
<tr>
<td>Cu (6)</td>
</tr>
<tr>
<td>Ru (3)</td>
</tr>
<tr>
<td>Ru (5)</td>
</tr>
<tr>
<td>Ru (7)</td>
</tr>
</tbody>
</table>
Figure 6.1. (a) Conductance fitting with measurements and (b) differential conductance with fitting curves for the Cu/Ru superlattice during growth.
6.2 Cu/Mo superlattice

The conductance of the Cu/Mo superlattice is fitted using the same Eqs. (6.1) and (6.2) with parameters listed in Table 6-2. The mean free path $l_g = 1$ nm is used for all Mo and Cu layers. In the Cu/Ru superlattice, a larger mean free path $l_g = 5$ nm was used in the Cu layers in order to fit the small curvature in $dG/dt$. In the Cu/Mo superlattice, however, a small mean free path ($l_g = 1$ nm) is used for Cu to fit the $dG/dt$ with a larger curvature. The small Cu $\sigma_g$ values ($\sim 0.02 \, \mu\Omega^{-1} \text{cm}^{-1}$) in this superlattice also confirm the small mean free path, as compared to the larger $\sigma_g$ values ($\sim 0.06 \, \mu\Omega^{-1} \text{cm}^{-1}$) in the Cu/Ru superlattice.

The fitting of conductance $G$ and $dG/dt$ for the Cu/Mo superlattice are shown in Fig. 6.2. The $\Delta G$ values in Mo are smaller than that in Ru. Both $\sigma_g$ and $\Delta G$ increase in upper layers, and the localization in Mo layers happens instantly with $t_0$ less than 0.015 nm. The fitted $\Delta G$ is again, larger than the direct $\Delta G$ measurement listed in Table 5-2.

Table 6-2. Fitting parameters for the Cu/Mo superlattice

<table>
<thead>
<tr>
<th></th>
<th>$l_g$ (nm)</th>
<th>$\sigma_g$ ($\mu\Omega^{-1} \text{cm}^{-1}$)</th>
<th>$\Delta G$ (k$\Omega^{-1}$)</th>
<th>$t_0$ (nm)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (2)</td>
<td>1</td>
<td>0.017</td>
<td>-</td>
<td>-</td>
<td>0.99</td>
</tr>
<tr>
<td>Cu (4)</td>
<td>1</td>
<td>0.018</td>
<td>-</td>
<td>-</td>
<td>0.99</td>
</tr>
<tr>
<td>Cu (6)</td>
<td>1</td>
<td>0.021</td>
<td>-</td>
<td>-</td>
<td>0.99</td>
</tr>
<tr>
<td>Mo (3)</td>
<td>1</td>
<td>0.0074</td>
<td>0.043</td>
<td>0.0022</td>
<td>0.99</td>
</tr>
<tr>
<td>Mo (5)</td>
<td>1</td>
<td>0.0078</td>
<td>0.094</td>
<td>0.0063</td>
<td>0.98</td>
</tr>
<tr>
<td>Mo (7)</td>
<td>1</td>
<td>0.0080</td>
<td>0.13</td>
<td>0.014</td>
<td>0.98</td>
</tr>
</tbody>
</table>
Figure 6.2. (a) Conductance fitting with measurements and (b) differential conductance with fitting curves for the Cu/Mo superlattice during growth.
6.3 Cu/Co superlattice

The conductance of the Cu/Co superlattice is fitted using parameters listed in Table 6-3, and the fitted $G$ and $dG/dt$ curves are shown in Fig. 6.3. The $dG/dt$ curvature dictates a large mean free path $l_g = 5$ nm in the second and third Cu layers and a small $l_g = 1$ nm in all Co layers. The first Cu layer with a large $dG/dt$ curvature is fitted with $l_g = 1$ nm for initially small grains. The conductivity $\sigma_g$ increases in upper Cu layers, indicating larger grain sizes.

The conductance drop due to carrier localization at the Co/Cu interface happens instantly with $t_0 = 0.01$ nm. The drop does not occur when Cu is deposited on Co, confirming again that localization only occurs around transition metal atoms. The fitted $\Delta G$ is larger than the direct $\Delta G$ measurement listed in Table 5-3.

Cobalt exhibits magnetic properties unlike the other two transition metals. The Co layers also exhibit large fluctuations in $dG/dt$. These factors are not considered in the analysis.

Table 6-3. Fitting parameters for the Cu/Co superlattice

<table>
<thead>
<tr>
<th></th>
<th>$l_g$ (nm)</th>
<th>$\sigma_g$ ($\mu\Omega^{-1}cm^{-1}$)</th>
<th>$\Delta G$ (k$\Omega^{-1}$)</th>
<th>$t_0$ (nm)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu (2)</td>
<td>1</td>
<td>0.035</td>
<td>-</td>
<td>-</td>
<td>0.99</td>
</tr>
<tr>
<td>Cu (4)</td>
<td>5</td>
<td>0.067</td>
<td>-</td>
<td>-</td>
<td>0.99</td>
</tr>
<tr>
<td>Cu (6)</td>
<td>5</td>
<td>0.076</td>
<td>-</td>
<td>-</td>
<td>0.99</td>
</tr>
<tr>
<td>Co (3)</td>
<td>1</td>
<td>0.033</td>
<td>0.06</td>
<td>0.01</td>
<td>0.97</td>
</tr>
<tr>
<td>Co (5)</td>
<td>1</td>
<td>0.035</td>
<td>0.35</td>
<td>0.01</td>
<td>0.90</td>
</tr>
<tr>
<td>Co (7)</td>
<td>1</td>
<td>0.041</td>
<td>0.40</td>
<td>0.01</td>
<td>0.90</td>
</tr>
</tbody>
</table>
Figure 6.3. (a) Conductance fitting with measurements and (b) differential conductance with fitting curves for the Cu/Co superlattice during growth.
6.4 Comparison and analysis

A. Correlations between grain size, mean free path, and conductivity

Fig. 6.4 shows the conductance of the three superlattices plotted together for comparisons. The Cu/Co superlattice has the highest conductance, followed by the Cu/Ru and Cu/Mo superlattices. This order is expected since the Co layers have the highest conductivity $\sigma_g$, followed by the Ru and Mo layers. The Cu layers also have the highest $\sigma_g$ in the Cu/Co superlattice and the lowest in the Cu/Mo superlattice. Since all three transition metals have similar grain size (~1 nm), and do not participate in carrier localization, their conductivities must be related to the number of $s$ and $d$ electrons: Co has 9, followed by 8 in Ru and 6 in Mo.

The Cu conductivity $\sigma_g$ is sensitive to the grain size. Our fitting indicates a large Cu grain size ($l_g = 5 \text{ nm}$) in the Cu/Co and Cu/Ru superlattices and a small Cu grain size ($l_g = 1 \text{ nm}$)

Figure 6.4. Conductance of the three superlattices plotted on the same scale.
Table 6-4. Comparison of three interfaces

<table>
<thead>
<tr>
<th>Interface</th>
<th>Interfacial energy $\gamma$ (ergs/cm$^2$) [1]</th>
<th>Cu $l_g$ (nm)</th>
<th>Cu $\sigma_g$ ($\mu\Omega^{-1}cm^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/Mo</td>
<td>2100</td>
<td>1</td>
<td>0.02</td>
</tr>
<tr>
<td>Cu/Ru</td>
<td>1800</td>
<td>5</td>
<td>0.06</td>
</tr>
<tr>
<td>Cu/Co</td>
<td>1450</td>
<td>5</td>
<td>0.07</td>
</tr>
</tbody>
</table>

in the Cu/Mo superlattice. A large interfacial energy $\gamma$ can suppress grain growth. Table 6-4 lists the correlations between the interfacial energy, Cu mean free path and conductivity. Here we see that a larger $\gamma$ value gives rise to a smaller grain size and a smaller $\sigma_g$ value.

**B. Correlations between conductance drop and the density of localized states**

The observed conductance drops are due to carrier localization via $s$-$d$ hybridization at the transition metal/Cu interfaces. The conductance drop is fully achieved before a monolayer of transition metal is deposited on Cu. Similar localization has been observed at solute atoms in Cu-alloys.

Without any localizations, the total conductance in a Cu layer is given by

$$G = \bar{\sigma}t = ne\mu t ,$$

where $n$ is the carrier density and $\mu$ is the carrier mobility. When $\Delta n$ electrons are localized, the conductance is reduced by

$$\Delta G = \Delta ne\mu t .$$

Hence the percentage of carriers localized is given by:

$$\frac{\Delta n}{n} = \frac{\Delta G}{G_{Cu}} .$$

The $\Delta G/G_{Cu}$ ratios observed at the three transition metal interfaces are plotted in Fig. 6.5. Here it
is noticed that the $\Delta G/G_{Cu}$ ratio approaches to a constant as the number of layers increases.

The Ru/Cu interface has the highest localization ratio ($\sim 40 \%$), followed by the Co/Cu interface ($\sim 20 \%$), and the Mo/Cu interface ($\sim 12 \%$). The Cu/Co superlattice has previously been measured by Bailey et al. with a $\Delta G/G_{Cu}$ ratio of 20 % [2]. Our observation is in good agreement with their result.

The density of localized states $\Delta n$ is calculated using the ratio in Eq. (6.6). With atomic concentration of Cu $8.45 \times 10^{22}$ cm$^{-3}$ [3], the density of carriers $n$ per unit area in the Cu layer is

$$n = (\text{atomic density})(\text{valency})(\text{thickness})$$

$$= (8.45 \times 10^{22} \text{ cm}^{-3})(1)(1.1 \text{ nm}) = 9.02 \times 10^{15} \text{ cm}^{-2}.$$  

(6.7)

The $\Delta n$ values calculated for the three superlattices are listed in Table 6-5. Assuming close-packed planes at the interface, (0001) for hcp and (110) for bcc, the number of atoms per unit

Figure 6.5. The $\Delta G/G_{Cu}$ ratios measured at the transition metal/Cu interfaces in three superlattices.
Table 6-5. Density of localized states at the transition metal/Cu interfaces

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Lattice parameter $a$ (Å)</th>
<th>Density of surface atoms ($10^{16}$ cm$^{-2}$)</th>
<th>$\Delta n/n$</th>
<th>$\Delta n$ ($10^{15}$ cm$^{-2}$)</th>
<th>Localized states per atom</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>bcc</td>
<td>3.15</td>
<td>0.14</td>
<td>1.08</td>
<td>0.76</td>
</tr>
<tr>
<td>Co</td>
<td>hcp</td>
<td>2.51</td>
<td>0.18</td>
<td>1.80</td>
<td>0.98</td>
</tr>
<tr>
<td>Ru</td>
<td>hcp</td>
<td>2.71</td>
<td>0.16</td>
<td>3.70</td>
<td>2.36</td>
</tr>
</tbody>
</table>

The formation of localized states is due to a resonance between the $d$ states of adsorbed transition metal atoms and the $s$ carriers at the Cu surface, as discussed in Chapter 2. The location of the resonant energy $E_r$ and the width of resonance $\Gamma$ determine the strength of the $s$-$d$ hybridization [4-6]. We found that the adsorbed Ru atoms produce more than twice the number of localized states than the adsorbed Co and Mo atoms on the Cu surface. The $s$-$d$ hybridization is pertinent to the difference in electronegativity between the adsorbed transition metal atoms and Cu. Ru has the highest electronegativity (2.2), followed by Cu (1.9), Co (1.8), and Mo (1.8) [7]. Ru and Cu has the biggest difference in electronegativity, and hence the strongest resonance. The $s$-$d$ hybridization is observed to occur only when transition metal atoms are deposited on Cu surface as no localization is observed when Cu is adsorbed on transition metal surfaces. This may suggest that the resonant energy $E_r$ of adsorbed Cu atoms is higher than the Fermi energy of the transition metals.
References


Chapter 7

Conclusion

Carrier localization in Cu-based superlattices are observed at room temperature through the conductance drop occurred when an interface is introduced during the growth. Such conductance drop is observed at sub-monolayer (0.1 – 0.2 nm) coverage of transition metals on Cu, indicating that Cu carriers are instantly localized at the transition metal atoms adsorbed on the Cu surface via s-d hybridization. No conductance drop is observed when Cu is deposited on a transition metal surface. Our measurements show that the localization effect is the strongest at the Ru/Cu interface, followed by the Co/Cu and Mo/Cu interfaces.

Analysis of conductance rise during the growth of each layer using the Fuchs model indicated that the mean free path is larger in Cu (5 nm) than in transition metals (1 nm). A larger mean free path in Cu could be due to a larger grain size, or weaker scattering at grain boundaries.

The resistance decrease observed during annealing of superlattices shows that grain growth starts at ~100 °C in the Cu/Mo superlattice and at ~300 °C in the Cu/Ru superlattice. No grain growth is observed in the Cu/Co superlattice during annealing. During cooling, slight decrease in resistance suggests phonon activities in the Cu/Co superlattices.

This study shows that in situ transport measurement is sensitive enough to directly observe the s-d hybridization occurring when transition metal atoms are adsorbed on a simple metal surface. This technique may prove to be a powerful tool to study electrochemistry involving adsorption of individual atoms.