Scanning tunneling microscopy characterization of the surface morphology of copper films grown on mica and quartz

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Abstract

The morphology of copper films grown on quartz, mica, and Ti/quartz has been investigated by means of scanning tunneling microscopy (STM). Films grown on quartz, both bare and pre-plated with titanium, are characterized by self-affine fractal scaling behavior over the length scale of 10−500 nm, while films grown on mica are not. Annealing of the films to 340 °C reduces the root-mean-square (RMS) roughness values, despite the overall scaling behavior remains the same. Films grown on bare quartz have significantly larger RMS roughness than those grown on mica, or quartz pre-plated with titanium. For the latter two cases, the RMS roughness is very low, 1–4 nm for the length scale of $L=500$ nm. The overall dependence of copper film morphology on various substrates were discussed in terms of interfacial reaction, lattice mismatch, and surface energy difference of interface surfaces.

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1. Introduction

In deposition processes used to fabricate thin solid films, there is a very strong dependence of the film microstructure and surface roughness on the growth conditions, particularly the temperature and substrate material upon which the film is deposited. Mica is a substrate that cleaves easily, yielding an atomically smooth surface that is stable up to 500 °C. It has been widely used as a substrate to grow atomically flat metal films such as Au, Ag, Al or Ti, which typically form flat terraces separated by single steps or step bunches [1,2] when deposited at elevated temperatures (350−500 °C). But despite the high degree of crystallinity, films prepared on mica surfaces are not necessarily amenable to surface science studies involving experimental probes that require large-scale flatness, for example ellipsometry. The mica bends too readily. Moreover, it has a relatively large thermal expansion coefficient, which can cause a metal film to detach from it upon cooling.

We examine here whether atomically flat films of copper can be grown on a more rigid substrate, namely piezoelectric crystalline quartz (QC). This material resists bending and can also be employed for active monitoring of gas uptake, tribology, etc. of materials deposited on its surface electrodes [3]. Since an epitaxial relationship does not exist between copper and quartz, we have explored the grown of copper films on both bare quartz and quartz pre-plated with titanium. The latter has been associated with flat film formation for a variety of materials, including gold and aluminum [4−7].

Films deposited under nonequilibrium conditions have been the subject of many atomic-scale computer simulations and applications of the scaling theory [8–12]. In many cases, interfaces growing under nonequilibrium conditions (which is the case for most thin-film deposition processes) evolve into self-affine surfaces [13–16]. A self-affine surface is distinguished from self-similar fractal by an asymmetry in the scaling behavior perpendicular to the
surface. It is generally manifested by an absence of surface overhangs [17]. The root-mean-square (RMS) roughness \( \sigma = \langle h(x,y) - \bar{h} \rangle^{1/2} \), where \( h(x,y) \) is the height function and \( \bar{h} \) is the average height of a self-affine fractal surface, increases with the length scale \( L \) of the surface as \( \sigma(L) \propto L^H \). Here, the scaling exponent \( H \ (0 \leq H \leq 1) \) is the indicative of the texture of the surface [18]. This regime of self-affine fractal behavior is valid only for length scales smaller than a correlation length \( \xi \), beyond which the RMS roughness \( \sigma \) no longer scales as \( L^H \). At length scales \( L \geq \xi \), the RMS roughness \( \sigma \) reaches a saturation value \( \sigma_s \) [19].

Many techniques, such as X-ray reflectivity [20,21], STM [22,23], electron diffraction [24,25], electron microscopy [26], and adsorption [27] have been employed to characterize sub-micron surface morphologies. STM provides a direct measurement of topographic information in real space to the nanometer scale, and we have employed it here to study the topography and the self-affine nature of the various Cu films.

2. Experimental details

Two ultra-high vacuum (UHV) STM systems (McAllister 525DT and RHK UHV300) were used for the measurements of film morphology. The UHV chamber with McAllister 525DT has a thermal evaporator with W-boat, while the chamber with RHK UHV300 system has Telemark e-beam evaporator with three crucibles enabling the in situ deposition of multiple materials. The Cu films were deposited onto various substrates – quartz crystal (QC), mica, and Ti film on top of quartz crystal (Ti/QC) – using 99.999 % pure Cu shot and transferred in situ to the STM sample holder for STM morphology analysis.

Samples of Cu/QC and Cu/mica were deposited by thermal evaporation and analyzed with McAllister STM system. Overtone polished AT-cut 8 MHz quartz crystals from Colorado Crystal were cleaned with acetone using an ultrasonic cleaner and rinsed with methanol and deionized water before being introduced to the vacuum chamber. The mica was cleaved in ambient and mounted on a sample holder within the vacuum chamber. The mica was heated at 340 °C for 3 h to recover its original surface properties. As for Cu/Ti/QC, a Ti-film of 20 nm thickness was deposited by e-beam evaporation of 99.995 % pure Ti pellets on to the bare quartz crystal. Cu was then deposited on top of the Ti-film surface using the same technique. This sample was analyzed with RHK UHV STM system. The thickness of Cu-film was fixed to be 60 nm for all substrates, which is the typical thickness of the metal electrode for QC.

During the film deposition, the chamber pressure was near \( 3 \times 10^{-7} \) Torr and the deposition rate was 1.5 nm/min for all samples. The material being deposited by both techniques (e-beam and thermal evaporation) has the similar final arriving kinetic energies at the substrate. Therefore the effects from the different deposition techniques to the film morphology are expected to be very little. After the deposited samples were imaged by STM, those on mica and Ti/QC were vacuum annealed at 340 °C for 1 h to investigate the annealing effects to the surface morphology of these films.

The STM measurements were performed with mechanically prepared Pt/Rh tips in the constant-current mode at a bias voltage of 100–300 mV and tunneling current of 0.3–1.0 nA. For the morphology analysis, 5–10 images from different areas of the sample were obtained for each imaging length scale \( L \). Then, the RMS roughness value \( \sigma \) was obtained by the instrument software and averaged over the number of images obtained from different areas of the sample surface. This procedure was repeated for 5–7 different scan sizes, generating a set of averaged RMS roughness \( \sigma \) values as a function of the length scale \( L \). The data was then plotted in a \( \log_{10}(\sigma) \) versus \( \log_{10}(L) \) graph and a least-square fit to the data points was performed for the linear regime of each plot. The slope of the fitted curve determines the roughness exponent \( H \) according to the scaling behavior of self-affine fractal films as described above. For all images, the plane subtraction was performed as background correction, and 11 point line smoothing was applied to improve the image quality before any mathematical treatment.

3. Results

The STM measurements of the surface morphology of Cu-films on various substrates demonstrate that most of the films have features that are typically 10–30 nm in extent (Fig. 1 (a), (c), and (e)). The morphology in large scale shows clear dependence on substrate (Fig. 1 (b), (d), and (f)). In \( \log_{10}(\sigma) \)–\( \log_{10}(L) \) plotting, the \( \sigma \) of Cu/QC and Cu/Ti/QC increase linearly with length scale \( L \) for the regime studied in this paper, which implies those films have self-affine fractal surfaces [19]. While the roughness exponent values \( H \) of Cu/QC and Cu/Ti/QC are similar to each other \( (H=0.65 \pm 0.05) \), their RMS roughness \( \sigma \) is significantly different. For \( L=500 \) nm, the RMS roughness \( \sigma \) is \( \sim 16 \) nm for Cu/QC and \( \sim 4 \) nm for Cu/Ti/QC. Since the saturation of the RMS roughness \( \sigma \) was not observed, the correlation length \( \xi \) should be larger than the scale studied here. On the other hand, the dependence of \( \sigma \) on \( L \) for Cu/mica doesn’t show the characteristics of the self-affine fractal structure over the length scale of \( 10\sim 500 \) nm. The RMS roughness \( \sigma \) of the film seems to exponentially saturate to 2.4 nm at \( L\sim 100 \) nm, which implies that this film may have a relatively small correlation length \( \xi \).

The Cu/mica and Cu/Ti/QC were vacuum annealed at 340 °C for 1 h. While the overall scaling behavior of RMS roughness \( \sigma \) stays almost unchanged, the surfaces of those films become flatter for the studied length scales.
values of the measured parameters ($H$, and $\sigma$ at $L=500$ nm) are summarized in **Table 1**.

4. Discussion

For Cu/QC, which demonstrates the largest RMS roughness value $\sigma$ studied, the formation of copper oxide at its interface with SiO$_2$ was reported to be very little ($<0.1$ monolayer) [28]. This is because the heat of formation ($\Delta H_f^0$) of silicon oxide ($\approx 450$–$500$ kJ) is about three times larger than that of copper oxide ($\approx 150$–$200$ kJ).

This was reported to explain the very poor adhesion strength of Cu film on QC [29]. The lattice mismatch between Cu (0.361 nm) and SiO$_2$ (0.160 nm) is relatively large, however the surface energy difference at the interface is not significant ($\approx 1300$ ergs/cm$^2$ for Cu and $\approx 1500$ ergs/cm$^2$ for SiO$_2$).

The interfacial properties of Cu/mica are similar to those of Cu/QC in many aspects. There is little chemical reaction at the interface due to the inertness of mica surface to Cu [30], and the relatively large lattice mismatch between Cu and mica — 0.361 nm for Cu and 0.195 nm (Si/Al–O bonding) for mica. Despite these similarities, the surface of Cu/mica demonstrates non self-affine fractal morphology and Cu/mica provides significantly flatter surface morphology of Cu-film. The large scale images clearly demonstrate the difference in surface morphology of Cu/QC and Cu/mica. While the 10–30 nm size grains are sitting on non-flat underlying basal plate in Cu/QC, the similar size grains are closely packed on very flat basal plate in Cu/mica (Fig. 1 (a), (b), (d), and (e)). This difference in morphology may be attributed to the surface energy difference between Cu and mica. The surface energy of mica in vacuum ($10\,000$ ergs/cm$^2$) is substantially larger than that of Cu ($1300$ ergs/cm$^2$) [31,32]. This can be a driving force of better wetting of the

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$H$</th>
<th>$\sigma$ at $L=50$ nm</th>
<th>$\sigma$ at $L=500$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>QC</td>
<td>0.65±0.03</td>
<td>4.3 nm</td>
<td>16.1 nm</td>
</tr>
<tr>
<td>Mica-I</td>
<td>not self-affine</td>
<td>2.2 nm</td>
<td>2.3 nm</td>
</tr>
<tr>
<td>Mica-II</td>
<td>not self-affine</td>
<td>1.3 nm</td>
<td>1.3 nm</td>
</tr>
<tr>
<td>Ti/QC-I</td>
<td>0.59±0.04</td>
<td>1.0 nm</td>
<td>3.7 nm</td>
</tr>
<tr>
<td>Ti/QC-II</td>
<td>0.45±0.02</td>
<td>0.8 nm</td>
<td>2.5 nm</td>
</tr>
</tbody>
</table>

Substrates marked with – I are as was deposited, while those with – II are annealed ones.

Fig. 1. STM images of 60 nm Cu-films on various substrate. (a)–(f): from pre-annealing surfaces, and (g)–(j): from post-annealing surfaces.
mica substrate by Cu-film, which may lead to the smoother film morphology.

Ti has been mainly used as a bonding layer between metal film and oxide substrates to improve the interfacial adhesion strength [29]. When Ti is deposited on top of SiO$_2$ at room temperature, Ti bonds strongly to the oxygen in SiO$_2$. This phenomenon can be understood by considering the thermodynamic stability of the oxides based on the standard heat of formation ($\Delta H_f^0$): $-500 \leq \Delta H_f^0 \leq -550$ and $-450 \leq \Delta H_f^0 \leq -500$ for titanium and silicon oxide respectively. With the formation of a strongly bound interfacial oxide layer, Ti is known to grow in Stranski–Krastanov mode on silicon oxide [33], despite the large lattice mismatch between Ti (0.295 nm) and SiO$_2$ (0.160 nm). Regarding the interface between Cu and Ti, Cu-film on Ti was reported to form an amorphous alloy at ambient temperature whose thickness is about 10 monolayers [34]. This interfacial layer is expected to work as a buffer layer reducing the interfacial stress through the interface energy minimization process [35], and resulted in a relatively flat surfaces compared to the film on QC.

The roughness exponent value $H$ of Cu/QC and Cu/mica are similar, however their $\sigma$ values are significantly different. The implication of this observation is that the roughness of these films largely depends on the interfacial interaction, while the film growth mode is not affected. The major intrinsic parameters at the interface of each system, which were summarized from the previous work of other groups, are presented in Table 2.

With the vacuum annealing (340 °C, 1 h), the surfaces of Cu/mica and Cu/Ti/QC are flattened significantly. In the case of Cu/mica, the thermodynamic rearrangement of the film should have released the kinetically built-in stress during the ambient temperature growth, which should have lead to the flatter surface morphology. Fig. 2 indicates the significant decrease in $\sigma$ after the annealing treatment. The change in morphology is reflected in z-scale of actual film images, Fig. 1 ((c), (d), (g), and (h)).

For Cu/Ti/QC, the surface keeps its self-affine fractal structure while its roughness exponent $H$ and the RMS roughness $\sigma$ are reduced by $\sim 25\%$ and $\sim 50\%$ respectively. In their study of Cu-Ti using X-ray photoelectron spectroscopy (XPS), Geng et al. reported the formation of crystalline Cu$_3$Ti$_2$ alloy when Cu-Ti sample was annealed at 300 °C for 10 min [34]. Therefore, it is possible that the observed changes of the post-annealed Cu/Ti/QC actually come from the alloy formation of these two components.

The larger grain size and cloudy image of post-annealed Cu/Ti/QC may indicate the formation of this alloy (Fig. 1 (h) and (j)), which needs further investigation using other surface analysis tools such as Auger electron spectroscopy and XPS.

5. Conclusion

The morphology of Cu-film depends not only on the type of substrate but on the post-deposition thermal treatment. While Cu/QC and Cu/Ti/QC substrates have self-affine fractal surface morphology, Cu/mica shows non-fractal surface morphology over the length scale studied (10 nm $\leq L \leq 500$ nm). The QC substrate gives the largest RMS roughness among the substrates studied. On the other hand, the Cu/mica and Cu/Ti/QC demonstrate flatter surface morphology whose RMS roughness $\sigma$ is only 2.3 $\sim$ 3.7 nm.
for the length scale $L = 500$ nm. The observed dependence of surface morphology on substrate can be understood in terms of the interfacial interaction between film and substrate materials, including lattice mismatch, interfacial reaction, and surface energy difference. The annealing of Cu-films on mica and Ti/QC at 340 °C for 1h substantially reduces the film roughness, while their scaling behavior remains the same. The atomically flat terraces were not available with the experimental conditions studied here.

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References