Metal deposition onto oxides: An unusual low initial sticking probability for copper on SiO₂

Xueping Xu and D. Wayne Goodman
Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

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The initial sticking probability of copper on a thin silica film has been measured in the temperature range 90–700 K using temperature programmed desorption. The copper sticking probability depends markedly on the surface temperature, varying from 0.6 ± 0.1 at 90 K to less than 0.1 above 400 K. Upon covering the silica surface with multilayer water, the sticking probability of copper increases to ~1.0. These results imply that using a quartz crystal microbalance, even at 90 K, to monitor Cu deposition on silica (and likely other similar oxides) may lead to a significant error in the estimation of metal growth rate.

Metallization of silica is an important process in microelectronics. Copper has an extremely low electrical resistivity, 1.72 μΩ cm, however, it is not the choice for first-level metallization of silicon integrated circuits because of the rapid diffusion of copper into silicon. The utilization of copper thin films is being considered as an upper-level interconnect in very large-scale integrated circuits in which copper is not contiguous with silicon. Evaporation techniques are commonly used to prepare copper films, however, chemical vapor deposition (CVD) using volatile copper precursors also have been employed.

The initial stage of copper nucleation and growth on the substrate is critical in defining the film growth rate and morphology; however, the details of these steps have not been investigated in previous Cu deposition studies. A focus of our recent work has been to model the initial growth of copper on silica thin films via evaporative copper deposition.

In this letter we report an unusual low initial sticking probability of copper on a thin silica film in the temperature range 90–700 K. The sticking probability is found to vary with the surface temperature and the surface pretreatment. Since quartz crystal microbalances are frequently employed to monitor the flux and growth rate from metal evaporation sources, the results of the present study have significant implications. For example, metal deposition rates measured via a quartz microbalance, where the metal sticking probabilities are unity, transferred directly to oxide surfaces, where the sticking probabilities can be much smaller, could lead to a significant error in the estimated growth rates.

These experiments were performed in an ultrahigh vacuum chamber with a base pressure of 2 × 10⁻¹⁰ Torr. The chamber is equipped with an UTM quadrupole mass spectrometer, a CMA Auger electron spectroscopy, and a Mattson Cygnus 100 FTIR spectrometer. Gas dosing and metal evaporation capabilities are also available.

The Mo(110) substrate was cleaned by annealing in oxygen at 1200 K and flashing to 2200 K in vacuo. The preparation of thin SiO₂ films on Mo(110) has been reported previously. Briefly, the thin SiO₂ films (~100 Å) were deposited by evaporating silica in an oxygen environment. The films then were characterized with Au-electron, x-ray photoelectron, electron energy loss, infrared reflection-absorption, and thermal desorption spectroscopies.

After annealing to 1500 K, the SiO₂ films were stable up to 1600 K, exhibiting properties of vitreous silica. Accordingly, a SiO₂ film prepared in this manner is believed to be a valid model for the silica surface.

Copper was evaporated from a copper-wrapped (0.25 mm OFHC) tungsten filament (0.50 mm), while a line-of-sight quadrupole mass spectrometer (QMS) was used to monitor continuously the flux. At steady state, the copper flux as determined by the QMS was stable to within 5%. During the course of these studies the Cu evaporation rates based on the QMS signal were found to be reproducible within ±10%.

The absolute Cu flux was calibrated using temperature programmed desorption of Cu from Mo(110) (the inset of Fig. 1). Two peaks, the multilayer sublimation and monolayer desorption, are evident. The monolayer peak at ~1200 K saturates at the onset of the appearance of the sublimation peak at ~1100 K. Based on previous work, it is assumed that the sticking probability of Cu is near unity on the clean Mo(110). The time required to deposit one monolayer of Cu onto Mo(110) is used to calibrate the evaporation flux during the course of these experiments.

The TPD of copper from silicon dioxide films, which is used in this study to determine the Cu sticking probabilities, has been described elsewhere and is shown in Fig. 1 for reference. Briefly, multilayer copper on silica exhibits a low-temperature desorption feature at 1000–1100 K and a higher-temperature desorption feature at 1200–1400 K. The low-temperature feature (1000–1100 K) is attributed to sublimation from three-dimensional (3D) particles, whereas the higher-temperature (~1300 K) feature is believed to correspond to Cu desorption from a strongly bound Cu-SiO₂ species. The desorption of Cu is complete at ~1500 K, therefore, the integrated Cu desorption intensity in the TPD corresponds quantitatively to the amount of Cu on the silica.

Figure 2 shows the integrated Cu TPD area as a function of the Cu deposition time onto clean Mo(110), and onto silicon dioxide films at two different temperatures, 100 and 700 K. The Cu TPD area is approximately linear with deposition time, suggesting a constant copper sticking...
probability within the coverage range of these experiments. The slopes of these plots are proportional to the Cu sticking probabilities. The Cu coverage for the data in Fig. 2 is less than 2 monolayers (ML) for Cu/Mo(110) and less than 1 ML for Cu/SiO₂. Thus, the measured sticking probability correctly represents the initial stage of copper growth on the SiO₂ films. It is clear that the sticking probability of Cu onto the silica film is markedly smaller than on clean Mo(110).

The sticking probability for copper on the SiO₂ film of Fig. 2 is 0.6±0.1 at 90 K, and decreases dramatically with an increase in the surface temperature (Fig. 3). For example, Fig. 3 shows that less than 10% of the Cu atom flux remains adsorbed on the silica at a surface temperature of >400 K. This behavior is quite contrary to the sticking probabilities of unity typically observed for metals on metals, e.g., Cu on Mo(110).³

It is noteworthy that the initial sticking probabilities of Cu are only 0.6 at 90 K, and drop to less than 0.1 at temperatures above 400 K. It is commonly assumed that sticking probabilities during metallization of oxides are near unity. The measured sticking probabilities reported here are an average value for Cu coverages less than 1 ML (Fig. 2). The true initial sticking probabilities at zero coverage are likely smaller, since the sticking probabilities of copper onto a partially covered copper surface are anticipated to be significantly enhanced relative to the bare silica surface.

Experiments were carried out to address the possibility that copper diffuses into silica during the TPD process. A Cu film was deposited onto the silica substrate at 100 K and then annealed at 700 K for 30 min. In a subsequent TPD experiment the intensity of the desorbing Cu does not decrease relative to the Cu TPD intensity observed in the unannealed case. Furthermore, no copper signal was detected by AES or XPS following TPD measurements to 1500 K.

Careful checks were made to exclude any experimental artifacts that might contribute to the unusually low sticking probabilities. For example, the stability of the Cu source during evaporation was confirmed as follows to ensure that reproducibility of the flux during the metallization was not a source of error. Two consecutive Cu TPD experiments were carried out subsequent to Cu metallization at identical deposition times and with identical evaporation rates as measured with an in-line quadrupole mass spectrometer. For the first, Cu was deposited onto a SiO₂ film at 90 K; for the second, the SiO₂ films were first dosed with multilayer water then Cu deposited at 90 K. The ratio of the integrated Cu intensity from the TPD traces of these two experiments was 0.6:1.0, respectively, demonstrating
that with complete accommodation, the Cu sticking probability did indeed increase to unity.

The results presented in the preceding section clearly indicate that the initial sticking probability of Cu on a silica surface is significantly less than 1.0 at 90 K and falls markedly with an increase in the surface temperature. The origin of the relatively low sticking probability is not well understood and a thorough understanding must await an in-depth theoretical treatment. However, a cursory examination of the temperature dependence suggests simple competition between adsorption and desorption from a mobile precursor state of Cu. A decrease in the sticking probability with temperature further suggests that the barrier to adsorption from the precursor state is lower than the barrier to desorption, i.e., the sticking probability decreases with increasing temperature. Many nonactivated adsorption processes also exhibit a similar temperature dependence.\textsuperscript{17} Since the sticking probability of Cu on copper clusters should approach unity, the data of Fig. 2, at the high-Cu coverage limit, it should approach 1.0. Recent ancillary studies of the dispersion of Cu on SiO\textsubscript{2} at temperatures in excess of 200 K (Ref. 18) indicate that Cu does not wet the surface but rather nucleates into 3D clusters. This clustering behavior is consistent with the invariant slope of the plot corresponding to 700 K in Fig. 2. On the other hand, the upward curvature of the 100 K plot of Fig. 2 is consistent with minimal 3D nucleation of the deposited Cu at this temperature.

Based on the precursor model,\textsuperscript{17} the initial sticking probability \( S_0 \) can be expressed as

\[
S_0 = \frac{\alpha}{1 + \frac{(v_e - E_d - RT)}{(v_e - E_d - RT)}},
\]

where \( E_d \) and \( E_a \) are the activation energies of desorption and adsorption from the precursor state, \( v_d \) and \( v_a \) are the respective preexponential factors, and \( \alpha \) is the trapping probability for the incident copper atom into the precursor state. For the nonactivated adsorption (\( E_d > E_a \)), Eq. (1) predicts a low temperature limit for \( S_0 \) to be

\[
\lim_{T \to 0} S_0 = \alpha.
\]

In addition, a rearrangement of Eq. (1) yields

\[
\ln\left(\frac{S_0}{S_0 - 1}\right) = \ln\left(\frac{v_d}{v_a}\right) - \frac{(E_d - E_a)}{RT}.
\]

Using the data in Fig. 3, \( (E_d - E_a) \) is estimated to be 2.4 ± 0.4 kcal/mol, \( \ln\left(\frac{v_d}{v_a}\right) = 4.5 ± 0.5 \), and \( \alpha = 0.6 ± 0.1 \). The solid line in Fig. 3 corresponds to the calculated values of the initial sticking probability as a function of surface temperature. The calculated curve is in excellent agreement with the experimental data, strongly supporting a precursor mechanism as described above for Cu adsorption.

The low trapping probability of ~0.6 for copper into a precursor state on silica may be attributed to elastic scattering or inefficient energy transfer between the incident copper atom and the silica surface. The trapping probability of an incident atom depends on the precursor potential well depth and momentum transfer,\textsuperscript{19,21} that is, the incident atom must lose its translational energy before it is trapped. The dynamic details of the trapping processes for copper on silica await theoretical investigations; however, the sharp increase in the sticking probability and trapping probability following the addition of water indicates that the adsorbed water promotes efficient translational energy accommodation between Cu and silica.

The fact that the initial sticking probabilities of Cu on silica at ~400 K are low and can be enhanced significantly with surface treatment has practical implications. For example, on a silica surface selectively patterned with ion or light beams, the sticking probability of Cu might increase to unity on the modified surface, yet remain low on the untreated surface. This then could provide a convenient route to selective metallization.

It is also worthy to reiterate that if the sticking probabilities of metal on oxides and ceramic materials, in general, deviates significantly from one, then the utilization of a quartz crystal microbalance to measure the metal growth rate on these materials could lead to erroneous results.

The initial sticking probability of copper on a silica surface is found to be 0.6 at 90 K and less than 0.1 at temperatures >400 K. Pretreatment of the surface with adsorbed water enhances markedly the initial sticking probability to ~1.0. These results suggest that using a quartz crystal microbalance to measure the growth rate of metal deposition on oxides or ceramic materials could significantly overestimate the initial metal growth rate.

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