Initial stages of Cu growth on ordered Al$_2$O$_3$ ultrathin films

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The initial stages of Cu growth (up to 20 Å) on ordered Al$_2$O$_3$ ultrathin films (~20 Å thick) synthesized on a Re(0001) substrate are studied by low-energy ion scattering (LEIS) and x-ray photoelectron spectroscopy (XPS). LEIS results indicate that Cu grows as three-dimensional clusters on the Al$_2$O$_3$ films at both 80 and 300 K. XPS results show decreases in the Cu $2p_{3/2}$ binding energy and increases in the Cu $L_3M_{4,5}M_{4,5}$ kinetic energy as a function of coverage. Analysis of these results indicates that Cu is not oxidized at the interface. For the coverage-dependent shifts in the Cu $2p_{3/2}$ peaks, the initial-state and final-state contributions and their relation to Cu cluster size are discussed. © *1996 American Vacuum Society.*

I. INTRODUCTION

Metal/oxide interactions play essential roles in many applications, including thin film technology, semiconductor devices, and heterogeneous catalysis; the electronic and structural properties of various metal/oxide interfaces have been widely studied in recent years. Among metal/oxide systems, the Cu/Al$_2$O$_3$ interface is one of the more interesting, because Cu is an active component in many catalytic reactions (such as methanol synthesis and NO$_x$ reduction),[1,2] and metallization of Al$_2$O$_3$ is technically important in microelectronics applications.

Early results[3,4] using Auger electron spectroscopy (AES) to study the growth mode of Cu on Al$_2$O$_3$ indicated that Cu forms three-dimensional crystallites on oxidized Al surfaces, corresponding to the Volmer–Weber (VW) growth mode. However, formation of a uniform Cu monolayer on Al$_2$O$_3$ has also been reported by other groups working at room temperature[5] and 95 K,[6] indicating the Stranski–Krastanov (SK) growth mode. As discussed in Ref. 7, scatter in the data and changes in Auger line shapes may cause relatively large experimental error in the AES intensity plots, and make these plots inconclusive in distinguishing between growth modes. Surface-extended x-ray-absorption fine structure (SEXAFS) and x-ray absorption near-edge structure (XANES) results[8–10] indicate that Cu grows as three-dimensional particles on Al$_2$O$_3$ via the VW mode. Formation of a uniform Cu monolayer on the α-Al$_2$O$_3$(0001) surface is also reported from an angular resolved x-ray photoelectron spectroscopy (ARXPS) study,[11] but this conclusion may be influenced by the overlap of Al $2p$ and Cu $3p$ peaks.[10]

The chemical interaction of Cu with Al$_2$O$_3$ is believed to be weak.[3] High-resolution electron-energy-loss spectroscopy (HREELS) results indicate that the Al–O surface phonon mode is not affected by Cu adsorption.[6] Based on the small shifts of the Cu $3d$ peak in ultraviolet photoelectron spectroscopy (UPS) at low Cu coverages, Ohuchi *et al.*[12] propose a weak bonding interaction between Cu and Al$_2$O$_3$. *Ab initio*

calculations[12] indicate that Cu atoms preferentially bind to surface O atoms rather than Al atoms. From their AES, UPS, and electron-energy-loss spectroscopy (EELS) results, Guo and Møller[5,13,14] suggest the formation of Cu(I) on the Al$_2$O$_3$(0001) surface when the Cu overlayer is less than 2 Å thick. Based on the observed Auger parameter in x-ray photoelectron spectroscopy (XPS), Gautier *et al.*[8,9] also suggest the formation of Cu(I) on Al$_2$O$_3$ at low Cu coverages. Evidence for Cu(II) formation on a sapphire surface is reported based on XPS measurements.[11] However, no evidence for Cu oxidation is observed in the XANES and SEXAFS data.[10] Vijayakrishnan *et al.*[15] interpret the coverage-dependent shifts in the XPS $3d$, $2p$, and x-ray induced *LMM* peaks of a Cu overlayer on Al$_2$O$_3$ as the effects of final-state screening, rather than the oxidation of Cu.

In this study we use XPS and low-energy ion scattering spectroscopy (LEIS) to study the initial stages of Cu growth on ordered Al$_2$O$_3$ ultrathin films synthesized on a Re(0001) substrate. Because the Al$_2$O$_3$ films are very thin (~20 Å), static charging is minimized during the spectroscopic studies. Since LEIS with He$^+$ ions is an extremely surface-sensitive technique, it is very effective in distinguishing between the VW growth mode and other growth modes.[7,16] Our results clearly indicate that Cu grows initially as three-dimensional clusters on the Al$_2$O$_3$ films at both 80 and 300 K. When the Cu coverage increases, the binding energy of the Cu $2p_{3/2}$ core level decreases, and the kinetic energy of the x-ray induced Cu $L_3M_{4,5}M_{4,5}$ Auger peak increases. These observations may be explained by final-state screening effects as a function of Cu cluster size, and they are not consistent with the formation of Cu(I) or Cu(II). This indicates that Cu is not oxidized at the Cu/Al$_2$O$_3$ interface. In order to keep this manuscript concise, we report only selected results in this article; more experimental results and discussion may be found in Ref. 17.

II. EXPERIMENT

XPS and LEIS experiments are carried out in a stainless steel ultrahigh vacuum chamber with a base pressure of 3×10^{-11} Torr. Al $K\alpha$ x rays (1486.6 eV) are used as the

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excitation source for XPS, and photoelectrons are detected by a 100 mm radius concentric hemispherical analyzer (CHA) operated in the fixed analyzer transmission mode, with a pass energy of 25 eV. The axis of the entrance lens of the analyzer is 12° to the surface normal. A sputter ion gun, operated at 1 kV in a He atmosphere (usually 1×10^{-6} Torr), is used as the ion source for LEIS. The scattering angle is ~155° and the CHA analyzer is operated in the fixed retarding ratio mode with a retarding ratio of 5. Low-energy electron diffraction (LEED) is used to characterize the surface periodicity.

Ultrathin Al$_2$O$_3$ films are prepared by depositing Al onto a Re(0001) substrate in ambient O$_2$.[18] For sample cleaning, the Re crystal is annealed resistively at ~1000 K in 2×10^{-7} Torr oxygen for several h, and then flashed (by electron beam) to high temperatures (~2000 K) to desorb the surface oxygen. The Al is evaporated in a pressure of 5×10^{-6} Torr O$_2$ by heating a W wire wrapped with pure Al wires (99.999%, Johnson-Matthey). The evaporation rate is monitored by a quartz crystal microbalance (QCM) and is ~1–2 Å of Al$_2$O$_3$/min. During the deposition the Re substrate is kept at ~973 K; Al and O are codeposited until a 20 Å total average thickness film is deposited. LEIS results show that the Re substrate is completely covered by the films prepared in this way. For these films the XPS Al 2s peak is at 120.9 ±0.1 eV and the O 1s peak is at 532.7±0.1 eV; the Re 4f substrate peak is at 40.5 eV. These films display hexagonal (1×1) LEED patterns, indicating a similar crystalline structure to those of α- or γ-Al$_2$O$_3$.[18,19]

Cu is deposited by heating a W wire wrapped with pure Cu wires in a liquid-N$_2$-cooled evaporator. The Cu overlayer thickness is monitored by the QCM and the deposition rate is controlled at ~0.2–0.5 Å/min; all references to Cu coverage in this article are for the average values obtained from the QCM readings. The pressure increase is ~8×10^{-11} Torr during deposition. Cu is deposited onto the Al$_2$O$_3$ films at two different substrate temperatures, i.e., 300 and ~80 K (using LN$_2$ cooling). For the low-temperature deposition, the sample is kept at ~80 K during the XPS and LEIS measurements.

III. RESULTS AND DISCUSSION

A. Growth mode of Cu overlayers on the Al$_2$O$_3$ films

Figure 1 shows LEIS spectra from ultrathin Al$_2$O$_3$ films with successively increasing Cu coverages, measured when Cu is deposited at 300 K. The LEIS O and Al yields decrease as the Cu coverage increases, but these features are still clearly observed at a Cu coverage of 20 Å, indicating that the oxide surface is not completely covered by Cu. If Cu forms a uniform monolayer, it would completely cover the Al$_2$O$_3$ film at an average thickness of ~2.09 Å.[7] So our LEIS results indicate that Cu forms three-dimensional clusters on the Al$_2$O$_3$ film during the initial stages of growth, following the VW growth mode. Similar behavior is also observed for Cu overlayer growth at 80 K (data not shown).

Figure 2 is a plot of integrated LEIS O yield as a function of Cu coverage at 300 and 80 K; the scattering yields with
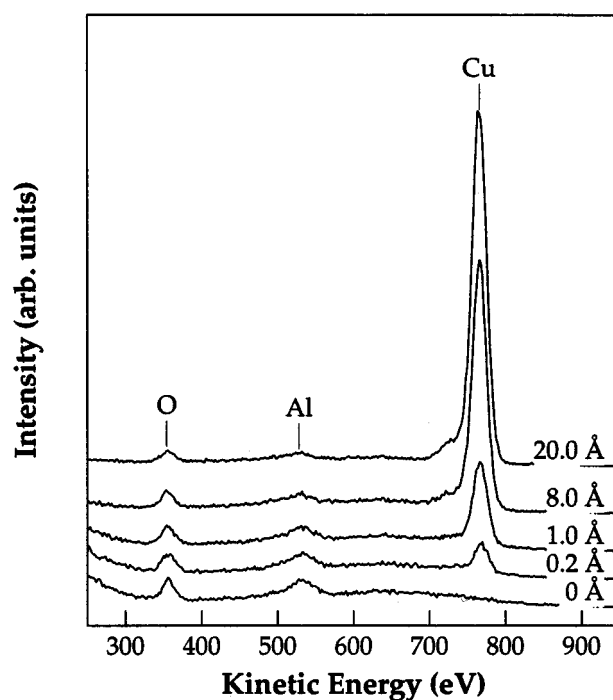

FIG. 1. LEIS spectra from an Al$_2$O$_3$ film with different Cu coverages when Cu is deposited at 300 K.

different Cu coverages are normalized to the value from the clean Al$_2$O$_3$ film. The O yields decrease slowly as smooth functions of the Cu coverage; similar behavior is also observed for the LEIS Al yields even though they decrease a little faster than the O yields, as shown by the dotted line in Fig. 2. These results indicate typical three-dimensional growth for the Cu overlayer[7]. In the case of Cu forming a smooth uniform monolayer, the O or Al yield would decrease much faster and be completely suppressed at ~2 Å, as schematically indicated by the dashed straight line in Fig. 2. The difference between the attenuation rates of the O and Al yields is outside the experimental uncertainty, and may imply that the Al$_2$O$_3$ ultrathin films synthesized in our study are O terminated.[20]

The growth behavior of a metal on an oxide surface is related to the surface free energies of the metal and the oxide, and the interfacial energy between them (see, e.g., Ref. 21). The surface energy of Cu (1300 erg/cm^2) (Ref. 22) is significantly larger than that of Al$_2$O$_3$ (~840 erg/cm^2).[23,24] This indicates that Cu is thermodynamically favored to form clusters unless the interfacial energy between Cu and Al$_2$O$_3$ is a large negative number. A negative interface energy implies that strong interaction exists between Cu and Al$_2$O$_3$; however, such an interaction is in contrast to our XPS observations (see Sec. II B). Because of the low oxygen affinity of Cu, the interaction between Cu overlayers and oxides is usually very weak,[7,25,26] and this is the reason why Cu forms clusters at many oxide surfaces.

In Fig. 2 it is found that the O yield decreases faster at 80 than at 300 K, indicating that at the same coverage, the Cu overlayers deposited at 80 K cover more oxide surface than
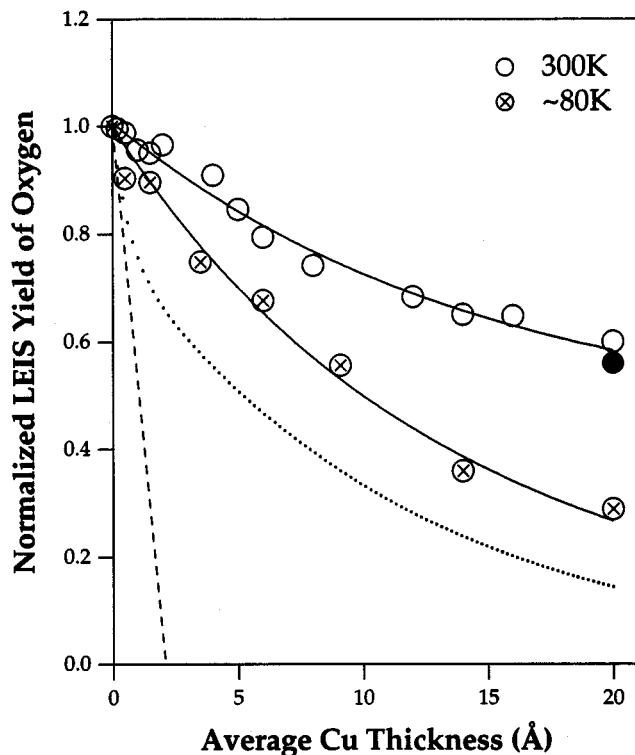
FIG. 2. Normalized LEIS O yields as a function of Cu coverage at 300 and 80 K. (●) Obtained after a 20 Å Cu film deposited at 80 K is annealed to 300 K. The dotted line indicates the decrease of normalized LEIS Al yield when the Cu overlayer grows at 80 K. The dashed straight line corresponds to the expected decrease of LEIS O or Al yield during the growth of a uniform Cu monolayer.

FIG. 3. XPS Cu $2p$ spectra from Cu overlayers deposited at 300 K; the average Cu coverages are indicated.

B. Chemical state of the Cu overlayers

Plotted in Fig. 3 are the XPS Cu $2p$ spectra of the deposited Cu overlayers, for different coverages, formed at 300 K. No shake-up satellite features characteristic of CuO are observed, even at the lowest coverages. This indicates that no Cu(II) is formed in our experiment, in contrast to the observations reported in Ref. 11. The positions of Cu core level peaks vary as a function of Cu coverage. The Cu $2p_{3/2}$ binding energy decreases from 933.7 to 932.7 eV when the Cu coverage increases from 0.2 to 20 Å. In addition, no shake-up peaks are observed for the Cu overlayers formed at 80 K (spectra not shown); at this temperature, the Cu $2p_{3/2}$ binding energy decreases from 933.8 to 932.7 eV as the Cu coverage increases from 0.5 to 20 Å. The shifts of the Cu $2p_{3/2}$ binding energy as a function of Cu coverage are summarized in Fig. 4. During the Cu overlayer growth, no changes are observed in the positions and line shapes of Re $4f$, O $1s$, and Al $2s$ peaks. The width of the Cu $2p_{3/2}$ peak is observed to become narrower as the Cu coverage increases. The peak-narrowing behavior is consistent with the results observed from Cu clusters on graphite,[28] and is generally observed for various metal clusters; contributing factors to broader peaks at lower coverage may include the cluster size inhomogeneity, lifetime broadening, and screening.[29]

Results in Fig. 4 indicate that at similar Cu coverages, the Cu $2p_{3/2}$ binding energy is smaller for the clusters formed at 300 K than those formed at 80 K. At both 300 and 80 K, the Cu $2p_{3/2}$ binding energy approaches 932.7 eV at very high coverages; this value is close to the tabulated value of 932.67 eV[29] of bulk Cu. The kinetic energy of the Cu x-ray induced $L_3M_{4,5}M_{4,5}$ Auger peak (data not shown) is observed to increase as the Cu overlayer grows at both 300 and 80 K; the magnitude of the shift in Cu $L_3M_{4,5}M_{4,5}$ kinetic energy is larger than the corresponding change in Cu $2p_{3/2}$ binding energy. At the same coverage the Cu $L_3M_{4,5}M_{4,5}$ peak has larger kinetic energy for the clusters formed at 300 K than those formed at 80 K, and at high coverages this peak approaches 918.6 eV at both temperatures, which is close to the

the overlayers formed at 300 K. At a Cu coverage of 20 Å, ~40% of the oxide surface is covered at 300 K, and ~60% of the oxide surface is covered at 80 K. Consistently, at the same coverage the LEIS Cu yield (not shown) is higher at 80 than at 300 K, indicating that the Cu clusters expose more surface area at the lower temperature. Moreover, when a 20 Å Cu overlayer deposited at 80 K is annealed to 300 K, the LEIS Cu yield decreases (not shown) and the O yield increases (a data point, after a 20 Å Cu overlayer deposited at 80 K is annealed to 300 K, is included in Fig. 2). These observations may be explained as follows. First, the growth of clusters may involve the hopping of Cu atoms at an island edge to upper layers of the cluster.[27] This process is more likely to occur at a higher temperature, so the aspect ratio of the Cu clusters should increase upon annealing. In other words, for the same total number of Cu atoms, more surface Cu atoms will be observed at 80 K. Second, at 300 K the average cluster size should be larger than at 80 K. Bigger clusters should form out of smaller ones ("Ostwald ripening"), as the isolated Cu atoms tend to adsorb on bigger clusters. Additionally, clusters can grow by agglomeration, causing the exposed Cu surface area to decrease. However, since we lack microscopic pictures of the Cu growth process, it is hard to confirm whether cluster shape changes or cluster size effects are more important.
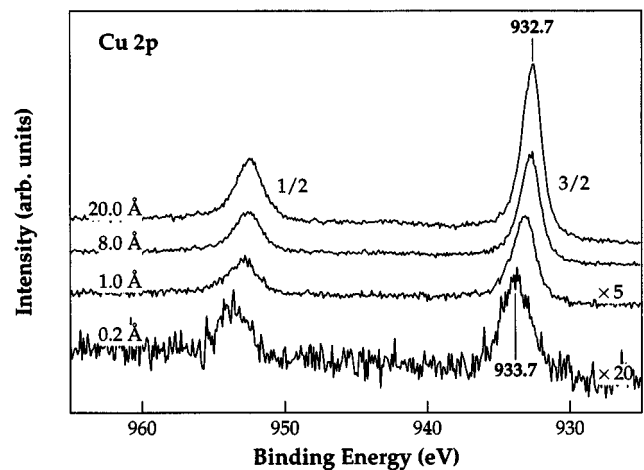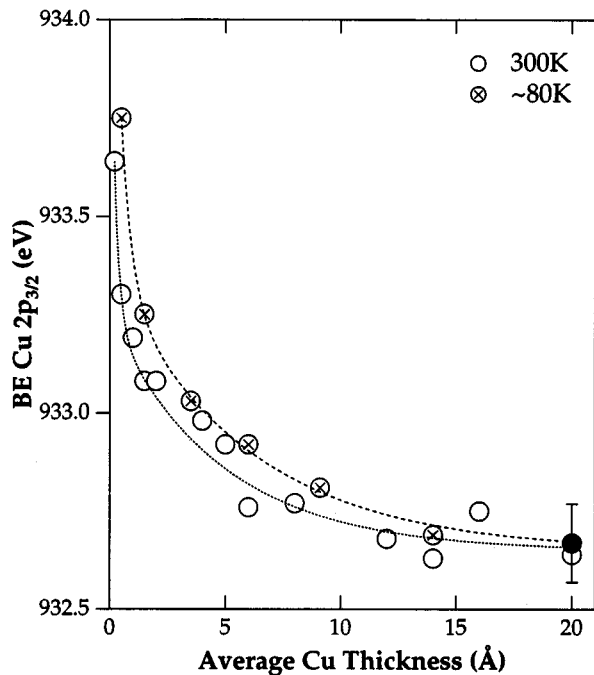
FIG. 4. The decrease of Cu $2p_{3/2}$ binding energies as a function of Cu coverage at 300 and 80 K. (●) Obtained after a 20 Å Cu overlayer deposited at 80 K is annealed to 300 K; the error bar indicates the experimental uncertainty for all these binding energy values.
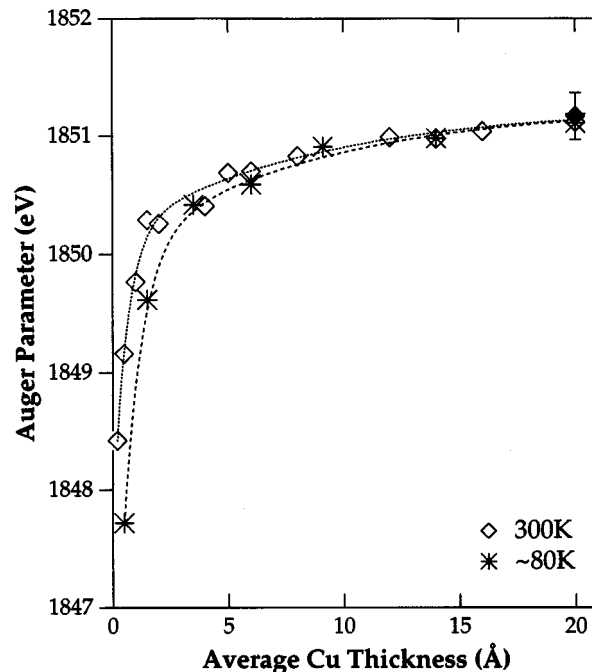
FIG. 5. The change of Auger parameter as a function of Cu coverage at 300 and 80 K. (◆) Obtained after a 20 Å Cu overlayer deposited at 80 K is annealed to 300 K; its error bar indicates the uncertainty for all data points.

tabulated value of 918.65 eV (Ref. 30) for bulk Cu.

Alternatively the data may be presented in terms of the Auger parameter, α, which is defined as[30]

$$\alpha = BE\ (Cu\ 2p_{3/2}) + KE\ (Cu\ L_3M_{4,5}M_{4,5}), \quad (1)$$

where BE (Cu $2p_{3/2}$) is the binding energy of the Cu $2p_{3/2}$ peak and KE (Cu $L_{4,5}M_{4,5}$) is the kinetic energy of the Cu $L_{4,5}M_{4,5}$ peak. The α values of the Cu clusters in our experiment are plotted in Fig. 5. Because the increase in KE (Cu $L_3M_{4,5}M_{4,5}$) is larger in magnitude than the corresponding decrease in BE (Cu $2p_{3/2}$) upon Cu overlayer growth, the α value increases continuously as a function of Cu coverage. At the low Cu coverage end (~0.5 Å), the α values range from 1847.8 eV at 80 K to 1849.2 eV at 300 K. Results in Fig. 5 agree qualitatively with those of Gautier et al.,[8,9] where the Auger parameter is used to study Cu clusters on single-crystal Al₂O₃(0001) surfaces because its value is insensitive to surface charging on insulating samples. In these studies, the gradual increase of α is related to the gradual increase in the Cu cluster size, and α values in the range of 1849–1850 eV are observed at low Cu coverages (~0.5 Å). Since these values at low coverage are close to that of Cu₂O [1849.4 eV (Ref. 29)], Cu(I) formation is proposed by Gautier et al.[8,9] at low coverages.

However, it is hard to believe that Cu(I) is formed at the Cu/Al₂O₃ interface, because this implies a *strong*, rather than weak, interaction between Cu and Al₂O₃. Since ultrathin Al₂O₃ films are employed in our study instead of single crystals, static charging is minimized. This gives us the ability to monitor the changes in the BE (Cu $2p_{3/2}$) and KE (Cu

$L_3M_{4,5}M_{4,5}$) separately. It is clear that the binding energy and kinetic energy values obtained at low Cu coverages are very different from the values corresponding to Cu(I). This point may be better seen in Fig. 6, where KE (Cu $L_{4,5}M_{4,5}$) is plotted vs BE (Cu $2p_{3/2}$) for the Cu clusters. The data corresponding to bulk Cu, Cu₂O, CuO, and Al₂Cu are obtained from Ref. 30 and are also included in Fig. 6. Figure 6 indicates that there exists a correlation between the KE (Cu $L_3M_{4,5}M_{4,5}$) and BE (Cu $2p_{3/2}$) values of the Cu clusters. The data point for bulk Cu may be nicely included in this correlation at the high coverage (low binding energy) end, but the point for Cu₂O does not fit this correlation. Therefore, Cu(I) does not appear to be a product at the Cu/Al₂O₃ interface. Similarly, CuO and Al₂Cu do not appear to be formed during the Cu growth. All these observations lead to the conclusion that the interaction between Cu and the Al₂O₃ films involves little ionic bonding and is indeed very weak. It also seems that while the Auger parameter is very useful in determining the chemical state of many substances, it may be misleading in cases such as Cu cluster growth.

Our XPS results are very similar to those of Vijayakrishnan et al.,[15] where Cu clusters are formed on thermally oxidized Al foils. In this study, the authors indicate that the binding and kinetic energy shifts are mostly due to final-state screening effects. As Cu overlayers grow, the average size of Cu clusters increases and the screening effects become more effective; therefore the Cu $2p_{3/2}$ binding energy is observed to decrease. At the same Cu coverage, the average cluster size may be smaller at 80 than at 300 K, so the Cu $2p_{3/2}$ binding energy should be higher at the lower temperature.
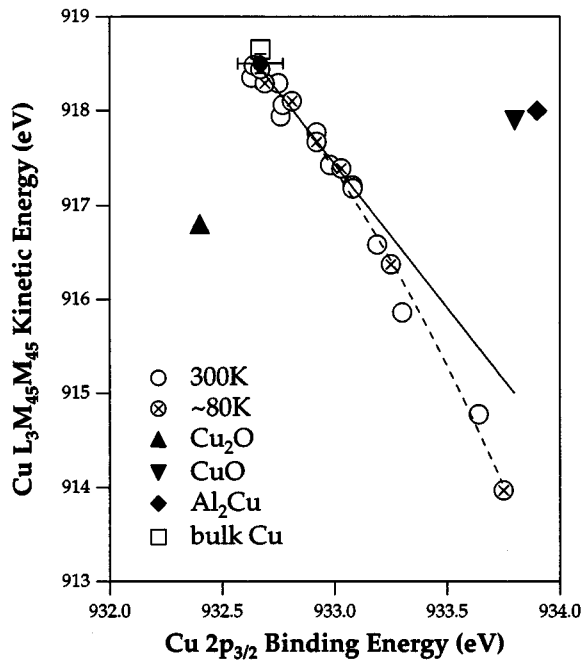
FIG. 6. The correlation between Cu $L_3M_{4,5}M_{4,5}$ kinetic energy and Cu $2p_{3/2}$ binding energy for Cu clusters deposited at 300 and 80 K. (●) Obtained after a 20 Å Cu film deposited at 80 K is annealed to 300 K; the error bars indicate the experimental uncertainty. (□), (▲), (▼), and (♦) Bulk Cu, Cu₂O, CuO, and Al₂Cu, respectively. The solid line corresponds to $\Delta KE/\Delta BE = -3.05$, and the dashed line indicates the deviation at low Cu coverages from this relation.

FIG. 7. Estimated initial-state contribution to the Cu $2p_{3/2}$ binding energy shifts.

Since in the Auger process the final state has two core holes and is doubly charged,[15,29] enhanced final-state screening should lead to shifts in the Cu $L_3M_{4,5}M_{4,5}$ peaks that are larger than the corresponding shifts in the Cu $2p_{3/2}$ peak.

If there is no initial-state contribution to the peak shifts, to a first-order approximation the correlation between these energies[28] should be

$$\Delta KE/\Delta BE = -3.0, \qquad (2)$$

where ΔKE and ΔBE are the changes in KE (Cu $L_3M_{4,5}M_{4,5}$) and BE (Cu $2p_{3/2}$), respectively. In Fig. 6 the data points at high Cu coverages (upper-left end) may be well fit with a slope of -3.05 (the solid line), indicating that Eq. (2) describes data at this end. However, at low Cu coverages, the data deviate from Eq. (2), indicating that the initial-state shift should not be neglected at this end. With several approximations,[29,31] the initial-state contribution, $\Delta \varepsilon_{2p}$, may be estimated by

$$\Delta \varepsilon_{2p} = \Delta BE + \Delta \alpha/2, \qquad (3)$$

where ΔBE and $\Delta \alpha$ are the shifts in the Cu $2p_{3/2}$ binding energy and Auger parameter of the of a Cu overlayer with respect to bulk Cu. The values of the Cu $2p_{3/2}$ binding energy and the Auger parameter of bulk Cu are given in Ref. 30 as 932.67 and 1851.32 eV, respectively, and the $\Delta \varepsilon_{2p}$ values estimated in our experiment are plotted in Fig. 7 as a function of Cu coverage. Due to the propagation of experimental uncertainty, the data in Fig. 7 are rather scattered. At a Cu
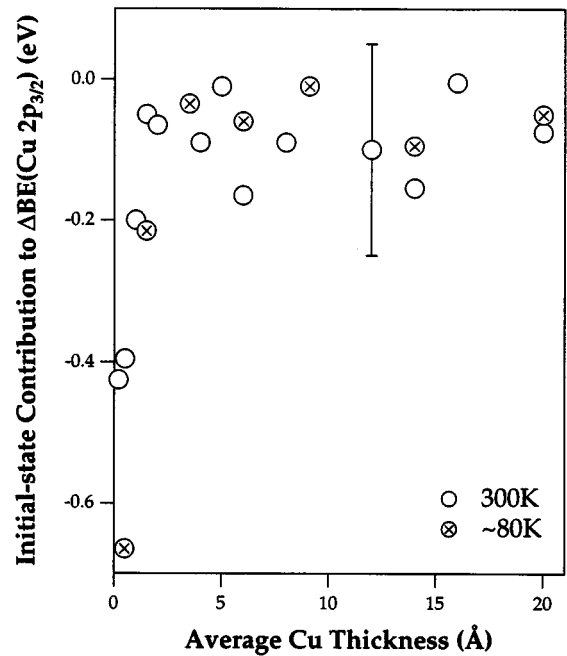
coverage of 0.5 Å, the initial-state shifts for the Cu clusters formed at 80 and 300 K are ~ -0.6 and ~ -0.4 eV, respectively. These values are compatible with the observed initial-state shifts (up to ~ -0.5 eV) of Cu clusters dispersed on carbon.[28] The direction of the initial-state shifts is consistent with the surface core level shift (SCLS) of Cu metal (-0.3 eV for polycrystalline Cu),[32] indicating a reduced average coordination number for Cu atoms in clusters. The larger initial-state effect for the Cu clusters formed at 80 K indicates that these clusters have more low-coordinated Cu atoms. This may be ascribed to a smaller average size of the Cu clusters formed at 80 K, though more "flat" island shapes may also contribute. Figure 7 also indicates that the initial-state effect diminishes rather rapidly as the Cu coverage increases. This reflects the quick increase in the average cluster size when the coverage becomes higher. The initial-state shift becomes very small at coverages above ~ 5 Å, and this is why our data points at high Cu coverages may be well described by Eq. (2) (see Fig. 6). The final-state contributions have positive values and are larger in magnitude than the initial-state shifts. At the coverage of 0.5 Å, the final-state contributions at 80 and 300 K are ~ 1.8 and ~ 1.1 eV, respectively. This difference is strong evidence that at 80 K the average size of Cu clusters is smaller than at 300 K, since the final-state effects are very sensitive to the cluster size (e.g., the final-state Coulomb energy is roughly proportional to $1/r$ where r is the average radius of Cu clusters[31]).

It should be noted that the separation into initial-state and final-state effects is only an approximation, because the conditions that lead to Eq. (3) may not be completely satisfied.[17,31] However, our results may be nicely interpreted in this way. Experimentally, static charging must be avoided

before any efforts are made to separate the initial-state and final-state effects; charging alters the measured binding energy values significantly but may have little effect on the Auger parameter. Our experiment demonstrates that the use of ultrathin oxide films as substrates is an excellent way to minimize charging.

IV. SUMMARY

LEIS results indicate that three-dimensional clusters are formed in initial stages of Cu growth on ordered Al$_2$O$_3$ films at both 80 and 300 K, following the Volmer–Weber growth mode. No evidence of Cu oxidation or a Cu–Al reaction is observed in our XPS experiment. At low Cu coverages the Cu $2p_{3/2}$ peak is observed at higher binding energies while the x-ray induced Cu $L_3M_{4,5}M_{4,5}$ peak occurs at lower kinetic energies relative to the values of bulk Cu. These shifts are related to the average sizes of the Cu clusters at different coverages. The correlation between the Cu $2p_{3/2}$ binding energy and the Cu $L_3M_{4,5}M_{4,5}$ kinetic energy indicates that little bonding occurs between Cu atoms and the oxide film. Using the Auger parameter, the initial-state and final-state contributions to Cu $2p_{3/2}$ binding energy shifts may be separated. The initial-state shifts measured upon the formation of small clusters are negative, reflecting the reduced average coordination number of Cu atoms. The final-state effects (relaxation and screening) have positive values and determine the direction of the Cu $2p_{3/2}$ peak shift. Both LEIS and XPS results support the interpretation that the average Cu cluster size is smaller at 80 than at 300 K.

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