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The Chemisorption of CO on Cu Films on ZnO(0001)–O

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The adsorption of CO on Cu films grown on the oxygen-terminated ZnO(0001)–O surface has been studied with temperature-programmed desorption (TPD) and XPS. At 130 K, submonolayer Cu films can be grown which cover about 50% of the surface in two-dimensional islands, in intimate contact with the ZnO. These films adsorb CO very much like the Cu(110) surface, producing strong satellite structure in the C(1*s*) and O(1*s*) spectra, and CO TPD spectra dominated by a peak at 220 K. These results imply that this 2D Cu is metallic in character, consistent with earlier measurements of its electronic properties. An explanation for the lack of evidence for CO adsorption by submonolayer Cu in an earlier study is offered. Multilayer Cu films, or submonolayer films which have been forced to form thicker, smaller islands by annealing at high temperatures, show CO TPD spectra with a strong peak at ~160 K, characteristic of Cu(111)-like sites, consistent with earlier LEED and ARXPS results. The loss in CO adsorption capacity of submonolayer Cu films caused by annealing is not as great as the loss in Cu surface area measured by He^+ ion scattering spectra. This is interpreted in terms of a CO-induced redispersion of 3D Cu clusters into 2D islands.

I. INTRODUCTION

The interaction of CO with films of Cu on ZnO is a subject of considerable catalytic interest since Cu/ZnO catalysts find widespread application in the hydrogenation of CO to methanol and in the water-gas shift reaction. The adsorption of CO on vapor-deposited films of Cu has been studied on several different single crystal surfaces of ZnO by Didziulis *et al.* (*1*). They found that CO would adsorb to Cu on the $(10\bar{1}0)$– and (0001)–Zn surfaces with about the same strength as on Cu metal. However, they concluded that submonolayer Cu films on the oxygen-terminated (0001)–O surface would not adsorb CO, even at 130 K and ambient pressures up to 5×10^{-6} Torr, based on a lack of observable changes in the valence band spectrum. Since metallic Cu adsorbs CO quite readily at these conditions (*2–8*), this conclusion would indicate that submonolayer Cu on ZnO(0001)–O is not very metallic in character. In contrast, we show here using temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) that CO readily adsorbs on submonolayer Cu films on this surface at 130 K, with high probability and a heat of adsorption similar to that of the Cu(110) surface. We further show that this adsorbed CO has an electronic structure very similar to that of CO on Cu(110). A few sites, which are populated at the lowest exposures, bind CO even more strongly than metallic Cu.

We (*9, 10*), and others (*1*), have studied the growth of vapor-deposited Cu on this ZnO(0001)–O surface. We have recently extended these studies to elucidate the structural and electronic properties of Cu films vapor-deposited on the oxygen-terminated ZnO(0001)–O surface at 130 K (*10*). The films were characterized using XPS, XAES, He^+ low-energy ion scattering spectroscopy (LEIS), LEED, work function and band-bending measurements, and angular resolved XPS. The electron spectroscopic results showed that Cu is cationic at tiny coverages, but becomes nearly neutral at coverages beyond a few percent. The Cu must cluster into islands at this point, since isolated Cu adatoms would be cationic. The

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XPS and LEIS signals versus Cu dose show that further deposition of Cu leads to spreading of these islands without forming thicker layers, until about 55% of the surface is covered. At this point the Cu coverage is about 1.1×10^{15} cm^{-2}, which we define for this paper as N_1. The magnitude of the XPS and LEIS signals prove that these islands must be two-dimensional in character (i.e., 2.2–2.6 Å in thickness). Thereafter, these Cu islands grow thicker without filling the gaps between the islands except at a rate much slower than the rate at which Cu is deposited into these clean spaces. The annealing behavior of these films have also been studied between 130K and 880K. These results show that the Cu has a thermodynamic tendency to cluster into thick 3D islands which only cover a small fraction of the surface. We presented a new model there based on the energetics of the system which readily explains the apparent contradiction between this thermodynamic tendency for nonwetting, and the dynamical effect which leads to such efficient wetting at coverages up to 1/2 monolayer (*10*).

The CO chemisorption amount and desorption temperature are also used in the present study to probe the character of these submonolayer and multilayer Cu films after they have been annealed to increasing temperatures. The results suggest that the films which have started to cluster into smaller, thicker islands can to some extent be redispersed by the adsorption of CO. Thin islands have Cu(110)-like sites for adsorbed CO. The very thick islands have Cu(111)-like sites for adsorbed CO, provided they have been annealed briefly to above 373 K for ordering. Our recent study of H_2O chemisorption on these films also confirms this picture (*11*).

II. EXPERIMENTAL

The experiments were performed in an ultrahigh vacuum apparatus described previously (*10*), with a base pressure of 10^{-10} Torr. It had capabilities for X-ray photoelectron spectroscopy (XPS), LEED, ion scattering spectroscopy (ISS), and temperature-programmed desorption spectroscopy (TPD) using a quadrupole mass spectrometer interfaced to a computer for multiplexing masses. All XPS spectra reported here use Al K_α radiation (1486.6 eV).

The preparation, mounting, and cleaning procedures for the ZnO samples used in this study are described elsewhere (*10*), as are the control experiments we performed to insure that our thermocouple was truly monitoring the sample temperature during TPD. The results below were also independent of the crystal used.

Copper was vapor deposited as described previously (*10*). Dose rates were found to be reproducible to better than 10% from day to day, judging by XPS signals. The purity of the research-grade CO used in this study was routinely verified to be better than 99% in the vacuum chamber using a mass spectrometer.

III. RESULTS

The study of CO adsorption on these Cu films is greatly complicated by the agglomeration that occurs in the films upon heating (see above). Thus, the surface had to be sputtered, annealed and redosed with Cu after every CO TPD heating that extended to a higher temperature than that to which we wished to anneal the Cu film.

The clean, Cu free ZnO(0001)–O surface does not adsorb CO at 130 K, as found earlier (*1*). However, clear TPD features associated with CO desorption could be seen after dosing small amounts of Cu to this surface. Figure 1a shows CO TPD spectra following various CO exposures to freshly dosed Cu at 130 K. In each experiment, the Cu coverage was within 10% of N_1, where N_1 was defined in the Introduction as 1.1×10^{15}/cm^2. This surface saturates after about 0.4 L of CO. As can be seen, the CO TPD peak broadens considerably to lower temperature with increasing CO coverage, finally showing a clear shoulder about 50 K below the main peak at ~220 K. This broadening suggests a distribution of Cu sites with different CO desorption temperatures, with

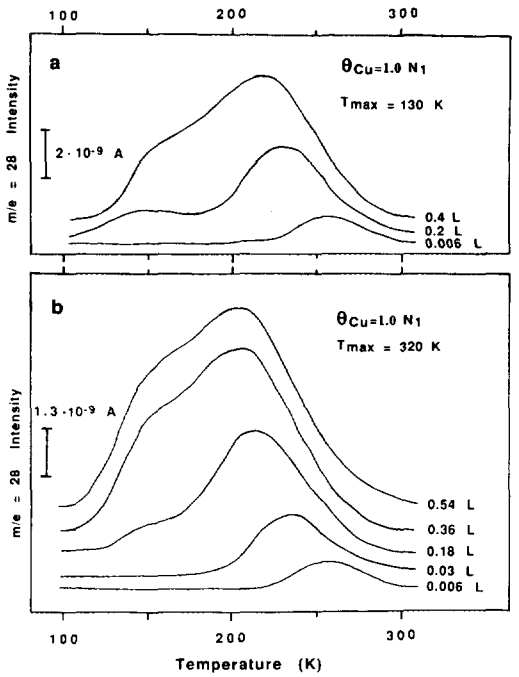


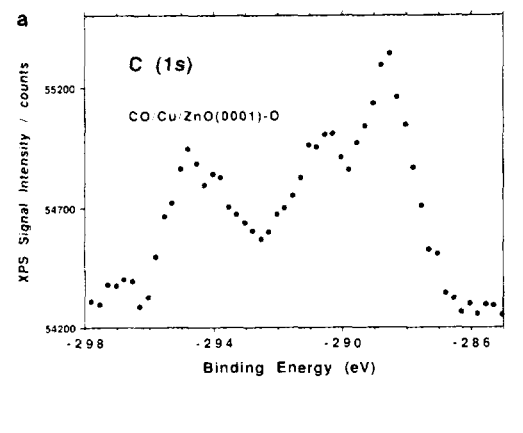
FIG. 1. Temperature-programmed desorption (TPD) curves for CO as a function of the CO exposure at 130 K to ZnO(0001)–O surfaces containing (a) freshly deposited films of Cu at 130 K and (b) a Cu film that had been briefly flashed several times to 320 K. The Cu coverages were $1.0N_1$, or about 1.1×10^{15} cm^{-2}, in all cases. Note the difference in current scales in parts (a) and (b) of this figure.

the most stable sites populating first. Alternatively, it could be due to repulsive lateral interactions between CO adspecies, all in similar sites. The main peak at 220 K is nearly identical in temperature to the peak for CO seen from metallic Cu(110) (*2, 3*), and from multilayer Cu deposited cold (see below). The shoulder at 170 K is close to the peak temperature seen for CO desorption from Cu(111) (*7, 8*).

Figure 1b shows the same type of TPD data, except here a single Cu film of coverage N_1 had been preannealed to 320 K (during previous CO TPD experiments) prior to each CO exposure. As can be seen, preheating the Cu film to 320 K has only minor influences on the CO TPD spectra. The increase in CO peak area with exposure is about the same in both cases, indicating that the sticking coefficient and saturation coverage for CO_a is about the same for both films. There is a slight shift of the high-temperature CO peak to lower temperature after annealing to 320 K.

The CO TPD spectra were also recorded after a 0.4-L CO exposure to Cu coverages of $0.3N_1$ and $0.6N_1$ that had been preannealed to 320 K, and found to be quite similar in lineshape to those shown in Fig. 1b for exposures of CO exceeding 0.36 L. However, the overall intensity was reduced, such that the total CO peak area was roughly proportional to the Cu coverage.

The nature of CO adsorbed on the submonolayer, unannealed (130 K) Cu film was also investigated with XPS. Here, a Cu coverage of N_1 and a CO exposure of 1 L were used. The resulting C(1*s*) and O(1*s*) spectra are presented in Fig. 2. A difference spectrum (minus the scaled O(1*s*) spectrum of the clean surface) is presented here, to remove the dominating signal from the oxygen of the substrate. These spectra closely resemble those previously published for CO adsorbed at 110 K on Cu(110) (*3*), at 120 K on Cu(100) [6,25], and at 77 K on bulk Cu (*12*). The broadness of these spectra have been attributed to strong shake-up transitions (*6, 12, 13, 25*). The magnitude of the integrated O(1s) and C(1s) signals relative to the clean substrate's Zn($2p_{3/2}$) signal (about 0.3 and 0.1%, respectively) also indicate a coverage of CO that is within 20% of that seen for saturation CO on Cu(110) (or $\sim 8 \times 10^{14}$ per cm^2 of Cu surface (*2*)) based on previous calibrations of the O/Cu and C/Cu XPS ratios for known overlayers on Cu(110) (*3*), and the reported differences in densities, sensitivity factors (*14*) and mean free paths (*15*) of Cu in bulk Cu versus Zn in ZnO. For this comparison, one must remember that only about 55% of the geometric surface area of the ZnO was covered by Cu at this coverage (see above). There was less than a 0.05 eV shift in the Zn($2p_{3/2}$) and O(1*s*) peak positions of the ZnO due to CO adsorption, indicating no significant CO-



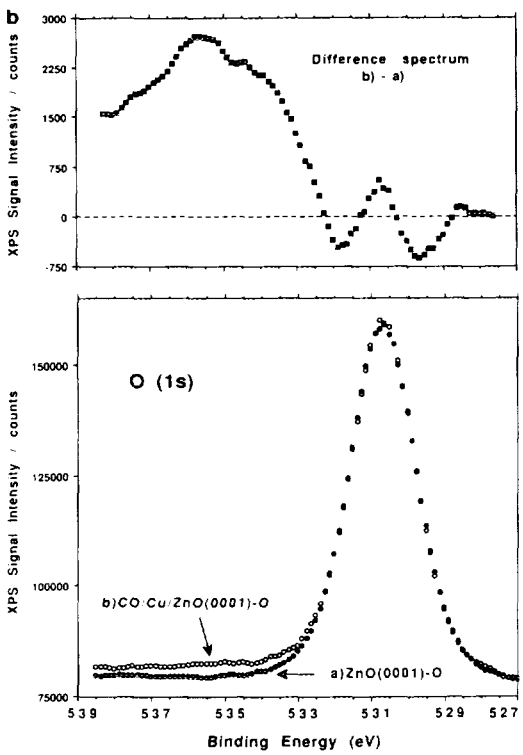


FIG. 2. XPS spectra in the C(1*s*) and O(1*s*) regions of adsorbed CO on a Cu film of coverage $1.0N_1$, freshly deposited at 130 K. The CO exposure was 1.0 L. The large O(1*s*) peak from the clean substrate has been subtracted from the O(1*s*) spectrum to show only those features due to CO. To do this, the clean surface peak had to be shifted (due to Cu-induced band bending (*10*)) and scaled down slightly (due to attenuation of the signal by the Cu and CO). The oscillations between 528.5 and 532.5eV in this difference spectrum are not due to CO itself, but result from subtracting these two very large substrate peaks which had slightly different widths.

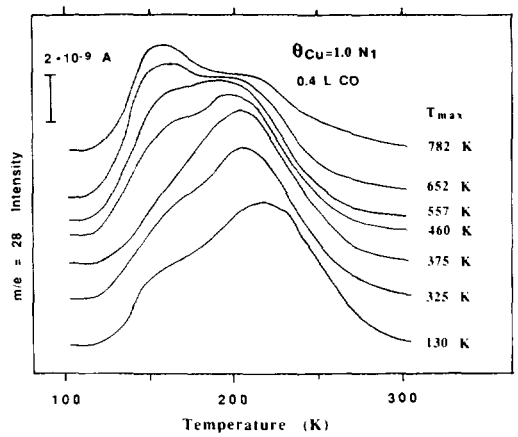


FIG. 3. CO TPD curves following a 0.4-L CO exposure at 130 K to a Cu film of coverage N_1, deposited at 130 K, which had been briefly flashed to the indicated maximum temperatures.

induced band-bending. Of course, the Cu deposition induced about a 0.3eV downward band bending as reported previously (*10*).

Figures 3 and 4 show the changes in the CO TPD spectrum which result from preannealing a Cu film to successively higher temperatures prior to the CO dose. In Fig. 3, the Cu coverage is N_1, while in Fig. 4 it is $6N_1$. In both cases the Cu was initially

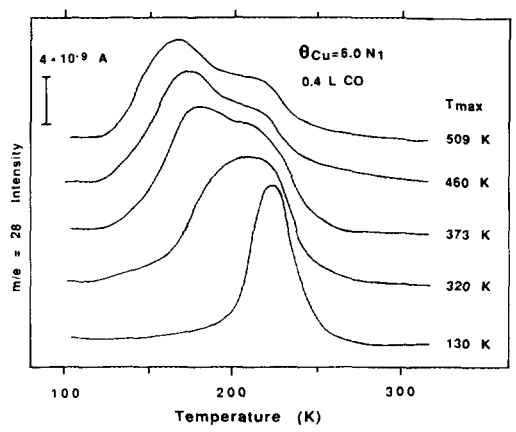


FIG. 4. CO TPD curves following a 0.4-L CO exposure at 130 K to a Cu film of coverage $6N_1$, deposited at 130 K, which had been briefly flashed to the indicated maximum temperatures.

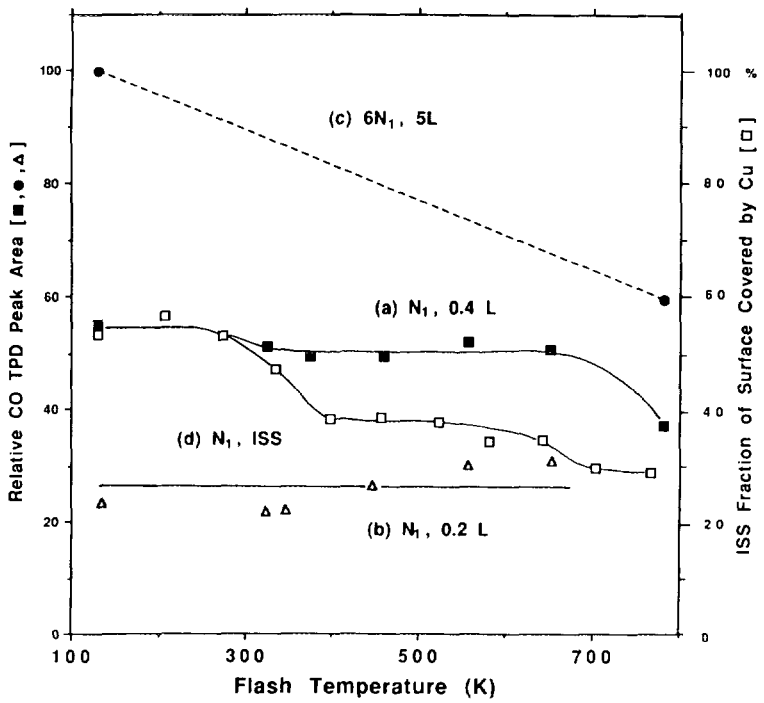


FIG. 5. Time-integrated CO TPD intensities from Cu films on ZnO(0001)–O versus the temperature to which the film had been preflashed for (a) a 0.4-L CO exposure at 130 K to a film of coverage N_1, (b) a 0.2-L CO exposure at 130 K to a film of coverage N_1, and (c) a 5-L CO exposure at 130 K to a film of coverage $6N_1$. Also shown for comparison to curve (a) is curve (d), which shows the fraction of the ZnO surface which is covered by Cu in this N_1 film versus flash temperature, as measured by the substrate's oxygen ISS signal (see text).

deposited at 130 K, and the CO exposure was 0.4 L, which is sufficient to saturate the surface at the lower Cu coverage (Fig. 3), as noted above. At this Cu coverage, the annealing had only the minor effect of slightly shifting the high-temperature CO TPD peak (at ~220 K) to lower temperatures for flashes up to 375 K. By 460 K and above, the area of this high-temperature peak begins to decrease markedly, and the low-temperature CO TPD peak (at ~160–170 K) begins to grow in intensity. The total CO TPD area remained nearly constant up to 500 K, but began to decrease noticeably for annealing temperatures above 650 K (see Fig. 5, curve a). At a 0.2-L CO exposure, the peak area remained nearly constant up to the maximum temperature studied, or 650 K (see Fig. 5, curve b).

The same types of lineshape changes in the CO TPD are seen upon annealing higher coverage Cu layers (see Fig. 4), except here the changes are very obvious already by 320 K. Again, there is an increase in intensity in a peak at ~160 K at the expense of the peak at ~220 K as the flash temperature increases. The exposure of 0.4 L of CO used here is sufficient to saturate this annealed multilayer Cu film, but not the unannealed film, as can be seen in Fig. 6. Similar lineshape changes can also be seen for saturation CO exposures to this multilayer Cu (5 L) by comparing the top curves in Fig. 6a and Fig. 6b. The CO peak area at saturation decreases to about 60% of its initial value for the fresh multilayer of Cu after it had been annealed to above 700 K (see Fig. 5, curve c).

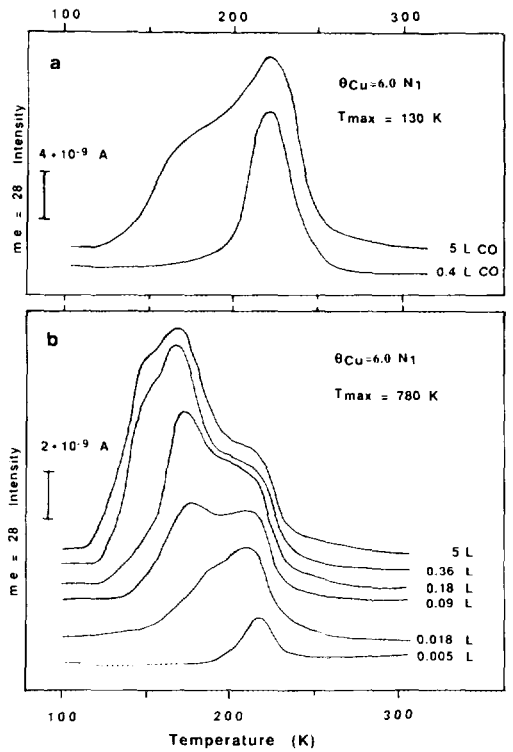


FIG. 6. CO TPD curves as a function of CO exposure at 130 K to Cu films of coverage $6N_1$ which were (a) freshly deposited at 130 K and (b) briefly flashed several times to 780 K.

IV. DISCUSSION

The present TPD and XPS results clearly show that CO adsorbs at 130 K on submonolayer Cu films on ZnO(00001)–O with a sticking probability near unity, and that it desorbs at temperatures between 150 and 280 K, comparable to those for metallic Cu (*2–8*). This is in contradiction to the conclusion of Didziulis *et al.* (*1*) that CO will not adsorb on such Cu films at 130 K even in an ambient of 5×10^{-6} Torr. That conclusion was based entirely upon the absence of clearly resolvable features due to CO exposure in the valence band photoemission (UPS) spectrum, except for a small peak which they assigned to the 4σ level of CO at ZnO step sites. There are problems with this method that could render the CO-derived peaks unresolvable, and possibly explain this discrepancy. They were comparing to peak intensities for CO on ZnO($10\bar{1}0$), which gives very sharp peaks for CO (*1*). The relative intensities for CO on this ZnO reference surface compared to CO on some metallic Cu surface are not known, but the latter could be considerably weaker due to the more efficient loss processes on metals. Furthermore, the CO-derived peaks might have strong shake-up satellites such as those observed in its core-level spectra of Fig. 2. Indeed, strong shake-up satellites are observed in the UPS spectrum of CO adsorbed on Cu(100) (*6*) and polycrystalline Cu (*12*), which steal large amounts of intensity from the main peaks. Furthermore, the peaks for CO on metallic Cu (*6, 12, 16*) are much broader than those of CO on the ZnO reference surface (*1*), which will also make them harder to see. Importantly, the CO 4σ peak, which is the sharpest and strongest and usually used for identification of CO, is located at a 2.7–3.0 eV lower binding energy on metallic Cu (*6, 12, 16*) compared to ZnO (*1*). This shifts this peak right into the energy range of the much, much stronger Zn($3d$) peak of the substrate, which would render it difficult or impossible to see. Finally, these CO-derived intensities are a strong function of detection angle and orientation on the surface (*16, 17*), so relative intensities for different structures at one angle could be very misleading. Since an exposure of only ~0.2 liter of CO would have saturated their Cu film, the possibility also exists that CO was already on the surface in ref. (1) before intentional CO exposure.

The O(1s) and C(1s) spectra of CO adsorbed on the submonolayer Cu film very much resemble those for CO on bulk, metallic Cu samples in their peak positions and shake-up satellite structure (see above). This shake-up structure is a very sensitive probe of the nature of the chemical bond to the CO (*6, 13, 25*), and changes greatly between one metal surface and that of another metal element (*6, 12, 25*). Only a single sharp peak, without strong shake-up structure, is seen for CO adsorbed on the cationic

Zn^{2+} sites of ZnO(10$\bar{1}$0) (*24*). The Cu^{+1} sites of CuCl(111) show a single strong satellite peak shifted by ~5.2 ± 0.4 eV (*24*), quite different than in the present case. The observed strong similarity in the present spectra with those on bulk Cu strongly suggests that this submonolayer Cu is very metallic in character. This conclusion of its metallic character is quite interesting since this submonolayer Cu is in 2D islands and therefore in intimate bonding contact to the ZnO below, according to ISS, XPS, and LEED results (*10*). This agrees with the fact that this Cu has been found to be neutral in charge, based on resonance photoemission (*1*) and work function measurements (*10*), and the appearance of delocalized-like Cu(4*s*) features in UPS even for much lower coverages of Cu (*1*). The previously reported inability of this Cu to chemisorb CO (*1*) was a major obstacle to characterizing it as metallic in nature, but we show here that this Cu actually adsorbs CO much like Cu(110). One must therefore conclude that this 2D film is very metallic in character. We show elsewhere that this film adsorbs H_2O and O_2 much like bulk metallic Cu as well (*11*).

The gradual loss in CO chemisorption capacity of this submonolayer Cu film (Figs. 3 and 5), and of thick Cu films (Fig. 5) after briefly annealing them to higher temperatures agrees with ISS studies of this system (*10*), which showed that the Cu has a thermodynamic tendency to cluster into 3D islands which cover less of the ZnO surface. Below about 270 K, this process is kinetically prevented. It occurs with sizeable rates by 320 K, but the clustering rate increases only gradually as the temperature is increased in the range 350 to 800 K (*10*). This behavior depended somewhat on the sample history (*10*). For the times when this CO adsorption study were performed, the sample was labelled as "new" in that ISS study. This sample condition gave a fairly dramatic gain in substrate oxygen signal between 130 and a 360 K flash for a film of coverage N_1, indicating that about one-third of the Cu in this 2D film at 130 K moved up into the second layer after the flash to 360 K (*10*). The loss in Cu surface area with flash temperature, based on these ISS signals, is also plotted in Fig. 5 as curve (d) for comparison to the CO adsorption data of curve (a). The loss of CO chemisorption capacity is less dramatic than is the loss in Cu surface area based on ISS. We interpret this to indicate that CO adsorption can induce the Cu to redisperse into 2D islands even at 130 K. We argue that this is thermodynamically reasonable elsewhere (*10*), where we presented an energetic model to explain the unusual growth and annealing behavior of this system. There, we also show (*10*) that the activation energy for this CO-induced spreading of Cu is small enough to be accessible at 130 K, and that the driving force for this redispersion of Cu is the ~50 kJ/mol heat of CO adsorption (*2*, *4*, *5*).

Such CO-induced spreading of Cu onto ZnO has been postulated for high-surface-area Cu/ZnO catalysts in order to explain changes in the Cu surface area of those catalysts under methanol synthesis conditions (*18*). It of course has serious implications concerning the accuracy of methods used to assess the Cu surface areas of such catalysts. This 2D-metallic Cu may have some interesting catalytic properties either associated with the dynamic character of its distribution on the ZnO, or due to its subtly different electronic properties compared to bulk metallic Cu, associated with its 2D nature or its intimacy to ZnO.

Interestingly, the TPD peak at the lowest CO coverage occurs at a temperature (260 K) very close to that seen from the Cu-terminated Cu_2O(100) surface (*19*). Indeed, work function and band-bending measurements indicate that the first few percent of the Cu which is dosed to this ZnO surface goes down as cationic Cu, and that the remaining Cu is neutral only above this first few percent (*10*). Thus there may also be a few cationic Cu sites for CO adsorption on this surface.

Changes in the CO TPD lineshapes occur after annealing these films, both at sub-

monolayer and multilayer Cu coverages. The dominant effect is a shift of intensity from the peak at 220 K into the peak at 160 K (Figs. 3 and 4). It has been reported that CO desorbs in a peak at 215 K from Cu(110) (*2*, *3*), but at 155–175 K from Cu(111) (*7*, *8*). This indicates that the Cu film converts partially from Cu(110)-like to Cu(111)-like in its chemisorption character after annealing. A similar conclusion has been reached from our studies of H_2O adsorption on these films. Thick Cu films ($>4N_1$ in coverage) grown at room temperature or flashed to higher temperatures show Cu(111) LEED spots and Cu(111) structure in angular-resolved XPS (*9*, *10*), consistent with these conclusions. Coupled with the evidence for thickening of the Cu islands (see above), these results suggest that the Cu(111) structure can only be assumed when the clusters of Cu are at least three layers removed from the ZnO interface.

Evidence for similar structural changes after annealing can be seen in the CO TPD spectra reported for submonolayer Pt films on this same ZnO(0001)–O face by the Gorte group (*20*). There, the dominant peak is at ~530 K for a film grown at 300 K, which is where CO desorbs from Pt(110) (*21*). After annealing to 923 K, this peak is decreased greatly in intensity, and a peak at 430 K dominates the TPD (*20*). From Pt(111), CO shows its main peak at 430 K (*22*). These TPD lineshape changes therefore suggest a change from (110) to (111) character of the Pt films, as we propose here for Cu films.

Kessler and Thieme (*8*) have concluded that vapor-deposited Cu films on glass and mica show a combination of two desorption states for adsorbed CO: one more weakly bonded which resembled desorption from Cu(111), and another considerably more strongly bonded which they attributed to Cu(100)-like sites. The kinetic parameters of Ref. (*4*) for CO desorption from Cu(100) imply via the Redhead equation (*23*) that the CO TPD from Cu(100) at a coverage of 0.2 and a heating rate of 5 K/s would peak at ~180 K. This is closer to the lower temperature peak seen in the present study, which suggests that some (100)-like sites may also be contributing to the spectrum in that region.

IV. CONCLUSIONS

Submonolayer Cu films on ZnO(0001)–O form 2D islands that are one atom thick at low temperatures. These adsorb CO in a manner which is very similar to Cu(110) surfaces in terms of their TPD behavior and the C(1*s*) and O(1*s*) satellite structure. These films also offer a few Cu sites that bond CO even more strongly than Cu(110), which may be cationic in character. Thicker Cu films, or submonolayer films that have been annealed to high temperatures to induce 3D clustering, show adsorption sites for CO that are Cu(111)-like. Exposure of these annealed Cu films to CO at 130 K can cause some of the Cu in these 3D clusters to respread across the ZnO surface.

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