Surface Oxidation and Reduction of CuO and Cu₂O Studied Using XPS and XAES

S. Poulston, P. M. Parlett, P. Stone and M. Bowker*

Reading Catalysis Centre, University of Reading, Department of Chemistry, Whiteknights, Reading, UK

Using XPS and x-ray-excited Auger electron spectroscopy (XAES), we have studied the variation in surface composition of CuO and Cu₂O with a variety of high-vacuum treatments, including vacuum annealing, oxidation and hydrogen reduction. Prolonged annealing of CuO results in the formation of a thick layer of Cu₂O at the surface whilst vacuum annealing of Cu₂O produces a thin (possibly one monolayer) film of Cu metal. Both bulk Cu₂O and the thick Cu₂O film generated from vacuum-annealed CuO were oxidized to CuO by heating at 800 K in 1×10^{-4} mbar O₂, the original surface being regenerated with vacuum annealing at the same temperature. Both CuO and Cu₂O are reduced to metal at the surface by heating in 1×10^{-4} mbar hydrogen at 400 K. In the case of CuO, the extent of reduction varies with the thermal history of the sample, with prolonged vacuum annealing producing a more reducible surface. Hydrogen-reduced CuO and Cu₂O were both reoxidized on vacuum annealing, demonstrating the diffusion of lattice oxygen to the surface.

INTRODUCTION

The study of copper oxide is motivated by both fundamental and applied considerations. First, there is an interest in understanding the unusual structural[1] and electronic properties[2–4] of copper oxides. Secondly, there is the use of copper and its oxides in catalytic applications. In particular, many studies have been prompted by the use of copper in methanol synthesis catalysts[5] and to a lesser degree for the possible use in zeolite catalysts for the reduction of NO by CO in relation to automotive catalytic converters.[6,7]

Under catalytic operating conditions or during activation, the copper component of catalysts may be modified on exposure to oxidizing and reducing environments. For example, partial surface reduction of Cu₂O single-crystal surfaces to Cu° has been observed by dosing with acrolein.[8] The reduction was attributed to consumption of lattice oxygen to burn off hydrogen and surface carbon. An investigation of the oxidation and reduction behaviour of copper oxides could therefore be of catalytic interest. Furthermore, modifications of surface composition easily accessible under ultra-high vacuum (UHV) conditions are of clear importance to the preparation of copper oxide surfaces for surface science studies. Several investigations have been carried out into the oxidation and reduction behaviour of copper oxides using surface science techniques. These studies have used oxide films on planar copper substrates (single crystal[9] and polycrystalline[10–12]) and copper field emitter tips,[13] together with bulk copper oxide in the form of powdered catalysts[14,15] and Cu₂O single crystals.[16] In many of these studies a particularly interesting feature of copper oxide systems is exhibited, namely the relative ease with which the surface composition can be modified. However, a systematic study into the modification of surface composition by oxidation and reduction procedures of bulk copper oxides under UHV conditions is not available. In this paper we present such a study of the *in situ* oxidation and reduction (using hydrogen) of both CuO and Cu₂O, together with data on the thermal stability of the surfaces produced.

EXPERIMENTAL

The XPS and XAES measurements were carried out in a UHV chamber (base pressure $\sim 1 \times 10^{-10}$ mbar) using a VSW system with a 100 mm radius hemispherical analyser and Al Kα photons (1486.6 eV) from a dual-anode x-ray source run at 180–300 W power; under these conditions no significant changes in the spectra were observed over the time scale of the experiment. Powdered CuO and Cu₂O were obtained from BDH Ltd. The sample was pressed onto a stainless-steel mesh (40 × 40 wires/inch, 0.25 mm diameter) with a chromel–alumel thermocouple attached, and this was mounted on a manipulator that could be retracted into a separately pumped chamber where higher pressure ($> 1 \times 10^{-5}$ mbar) gas treatments were carried out. The spectra were referenced to adventitious C 1s at 284.5 eV binding energy (BE). Heating of the sample was performed using radiative heating from a tungsten filament heater situated close (~ 1–2 mm) to the rear of the sample. The weight of the catalyst used was typically 0.2 g. Gas exposures were carried out by backfilling a sample preparation chamber that could be isolated from the main analysis chamber. Exposures are quoted

* Author to whom correspondence should be addressed.

in Langmuirs (L), where $1 \; L = 1 \times 10^{-6}$ Torr s^{-1}. Atomic sensitivity factors for Cu and O were taken as 4.798 and 0.711, respectively.[17]

The powder x-ray diffraction (XRD) data were recorded with Cu Kα radiation using an Inel Spectrolab CPS 120 operated at 40 kV and 40 mA.

RESULTS

X-ray diffraction spectra of the CuO and Cu$_2$O (see Table 1) used in this study conformed extremely well with previously published standard spectra of these materials. However, a feature not observed in XRD is that the fresh samples were both found to be extensively covered by a surface hydroxide. We have clearly observed this during inelastic neutron scattering (INS) experiments of samples similar to the ones used in this study.[18] Both Cu$_2$O and CuO annealed to 420 K in a vacuum of $\sim 10^{-6}$ mbar showed a broad intense feature between 500 and 1000 cm^{-1} characteristic of an M–O–H bending mode.[19] Vacuum annealing of CuO to 670 K resulted in the complete removal of the O–H-related features. Fresh samples were therefore initially annealed in vacuum to 800 K for ~ 20 min in order to remove surface contamination. Following this procedure, the only surface contaminant observed with XPS was atomic carbon.

It is generally agreed that XPS and XAES can be used to distinguish between Cu metal, Cu$_2$O and CuO: The CuO is characterized by high-intensity shake-up satellites at ~ 9 eV higher binding energy than the main 2p$_{3/2}$ and 2p$_{1/2}$ peaks, which are in addition considerably broader than in the case of bulk Cu$_2$O and Cu metal; this broadening has been attributed to a shake-up process.[20] The Cu metal and Cu$_2$O are best distinguished from the x-ray-excited Cu LMM Auger spectra. The characteristic kinetic energy for this transition and Cu 2p$_{3/2}$ with different oxidation states of Cu are shown in Table 2.

Vacuum annealing and reoxidation of CuO

Fully oxidized. In agreement with hydroxide seen in INS,[18] the fresh CuO sample exhibited a lattice O 1s peak at 530.3 eV BE with a second peak at higher binding energy (531.8 eV) associated with the surface

Table 1. Relative intensities of main XRD peaks for untreated CuO and Cu$_2$O compared with vacuum-annealed CuO, showing formation of the Cu$_2$O phase

d Spacing (Å)	CuO before vacuum treatment	CuO after prolonged vacuum heating	Cu$_2$O before vacuum treatment
2.52	93.17	100	
2.32	100.0	98.6	
1.86	21.1	29.4	
1.41	16.2	12.0	
1.38	17.1	19.2	
2.46		26.2	100.0
2.13		12.4	35.2
1.51		27.6	33.0
1.29		6.9	24.8

Table 2. Values of the Cu 2p$_{3/2}$ binding energy and Cu LMM Auger transition kinetic energy for Cu metal, CuO and Cu$_2$O taken from Tobin *et al.*,[15] with peaks referenced to C 1s at 284.6 eV BE

	Cu 2p$_{3/2}$ binding energy	Cu LMM kinetic energy
Metallic copper	932.6	918.4
Cu$_2$O	932.4	916.5
CuO	933.6	917.8

hydroxide, as shown in Fig. 1(a). In addition the Cu 2p XPS peak in Fig. 1(b) showed only a low-intensity satellite structure. Vacuum annealing of the sample up to 870 K led to a gradual loss of the O 1s hydroxide
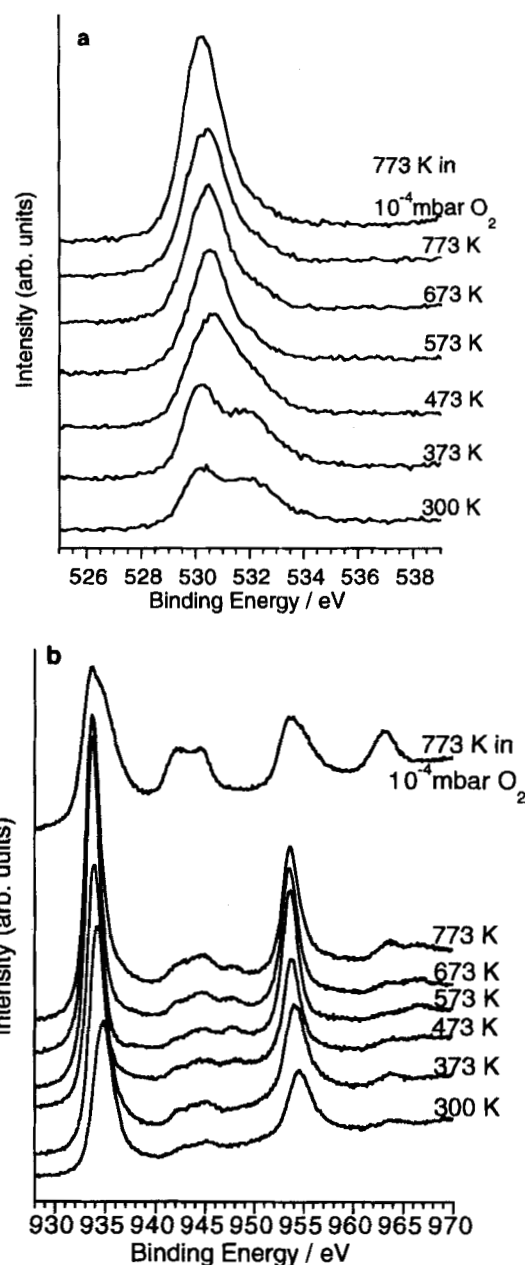

Figure 1. Changes in the XPS spectrum of CuO on initial vacuum annealing. Samples annealed for 5 min at temperature indicated: (a) O 1s; (b) Cu 2p. In both (a) and (b) the final spectrum shows the result of heating the sample at 773 K in 1×10^{-4} mbar O$_2$ for 15 min.

shoulder. Following this procedure the sample was not fully oxidized, with the Cu 2p spectrum showing only a weak satellite structure. To obtain the fully oxidized Cu(II)O surface, the sample was subsequently annealed to 773 K in 1×10^{-4} mbar O_2, also shown in Fig. 1. The fully oxidized CuO surface exhibits a Cu $2p_{3/2}$ peak at a binding energy of 933.6 eV together with intense satellite peaks at 942.4 and 944.6 eV, these two peaks overlapping, and 963.3 eV. The Cu LMM peak for this surface occurs at a kinetic energy of 917.1 eV (569.5 eV BE).

Vacuum reduced. Extensive vacuum annealing of CuO (~8 h at 800 K) led to a Cu 2p XPS spectrum generally associated with a Cu_2O surface with no satellite struc-

ture to the main peaks. Thus a sufficiently thick layer of Cu_2O could be generated at the surface so that reoxidation by oxygen diffusion from the bulk was not significant. The reduction of the CuO surface on vacuum annealing is, at least to some extent, reversible. The CuO surface could be returned to the fully oxidized state, with a high-intensity satellite structure in the Cu 2p spectra, by heating at 773 K in 1×10^{-4} mbar oxygen for 15 min. The surface can therefore be cycled between the fully oxidized state (characterized by a highly intense Cu 2p XPS peak satellite structure) and the reduced state (where this is absent) by heating in oxygen and vacuum annealing, respectively. The transition between these two states is clearly illustrated in Fig. 2(a), which shows the development of the Cu 2p
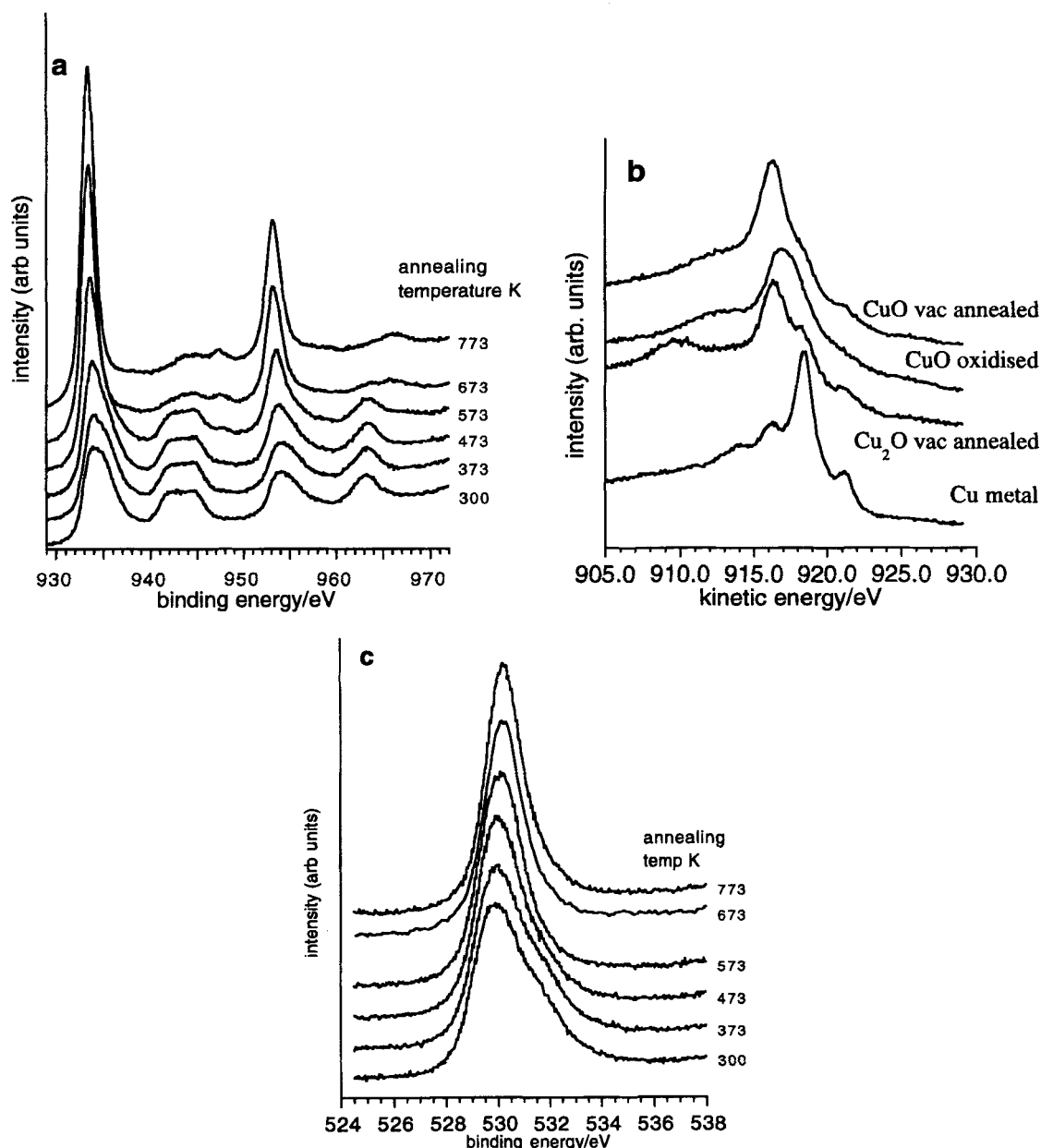

Figure 2. Vacuum annealing of heavily annealed CuO oxidized in 1×10^{-4} mbar O_2 at 773 K for 15 min. Samples annealed for 5 min at temperature indicated. (a) Cu 2p XPS. (b) Cu LMM XAES, showing only the two extreme cases of the annealing procedure represented in (a), i.e. immediately after oxidation and with annealing to 773 K (top two spectra). Also shown (bottom two spectra) are spectra for Cu_2O vacuum annealed to 800 K and Cu metal. (c) O 1s XPS.
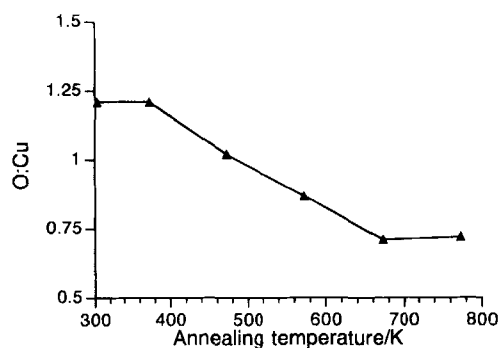
Figure 3. The O 1s /Cu 2p XPS peak area ratio as a function of annealing temperature for heavily annealed CuO oxidized in 1×10^{-4} mbar O_2 at 773 K for 15 min (from spectra shown in Fig. 2).

XPS spectra with vacuum annealing (5 min at a base pressure of $\sim 2 \times 10^{-9}$ mbar at the maximum temperature indicated) following oxidation. The bottom spectrum is characteristic of fully oxidized CuO with a
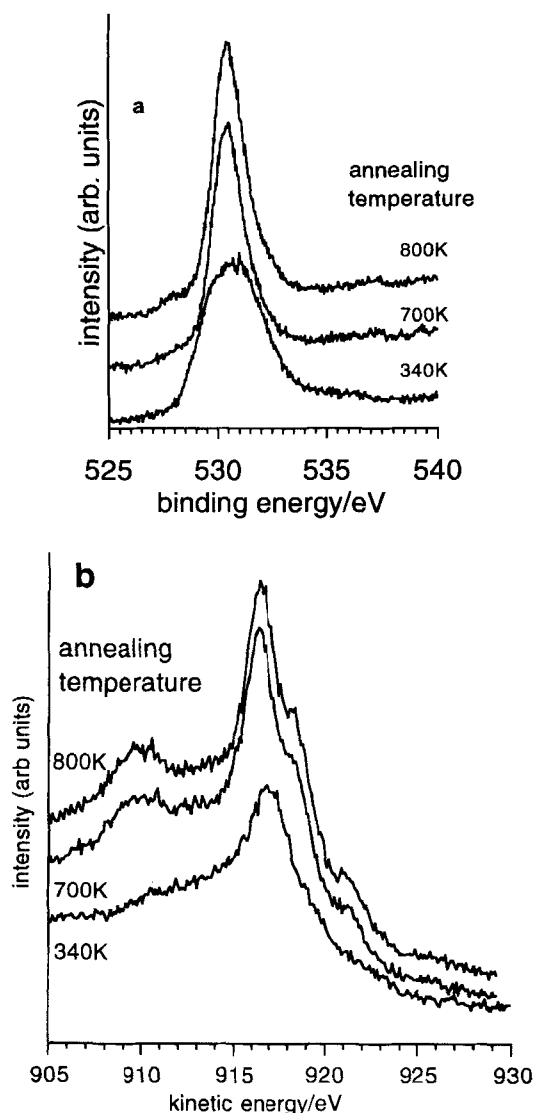

Figure 4. Changes in the XPS and XAES spectra of a fresh Cu_2O sample on initial vacuum annealing: (a) O 1s; (b) Cu LMM XAES.

Cu $2p_{3/2}$ binding energy of 933.8 eV. Annealing to 673 K results in the satellite intensity being significantly reduced, and by 773 K completely extinguished. Further, prolonged annealing at up to 820 K led to no further change in the Cu 2p spectrum. Together with the loss of Cu 2p satellite intensity on annealing, there is a reduction in the O:Cu ratio to $\sim 60\%$ of its initial value, as shown in Fig. 3. It should be noted that the y-axis in this figure is only intended to give a relative measure of the O:Cu ratio in the analysed region and not to represent the real stoichiometry of the surface. The binding energy in the spectrum of the most reduced surface is shifted to 933.3 eV. This value is higher than the value for Cu_2O quoted in Table 1, which may be an indication that the Cu_2O like layer is not fully stoichiometric at the surface. However, there is considerable variation in the literature of the binding energy quoted for Cu_2O and so comparison with a standard literature value is difficult.

The extent of the oxidation produced by *in situ* oxygen treatments of the heavily vacuum-annealed sample was dependent on the oxidation conditions with a higher or lower temperature lessening the extent of oxidation. Formation of CuO by heating Cu metal in oxygen is frequently reported in the literature, although the conditions employed are usually more severe in either pressure and/or temperature than reported here (see, for example, Jernigan and Somorjai[16] and Cocke *et al.*[13]). In this respect it is interesting to note that Ramanarayanan and Alonzo[12] have reported that surface oxidation of Cu metal at 1073 K in subatmospheric pressures of oxygen led to the formation of Cu_2O and not CuO, suggesting that oxidation at too high a temperature prevents CuO formation.

X-ray diffraction of a CuO sample taken after prolonged vacuum annealing at 770 K resulted in the appearance of additional diffraction features that can be associated with the formation of the Cu_2O phase. The most intense of these additional peaks occur at d spacings of 2.46 and 1.51 Å, corresponding to the two most intense peaks in the spectrum of bulk Cu_2O. The XRD data are summarized in Table 1, where the vacuum-annealed CuO sample is compared with untreated CuO and Cu_2O.

In order to determine if Cu metal was formed, x-ray-excited Auger spectra (XAES) were also recorded, Cu metal being distinguishable from Cu_2O by the Cu LMM spectra, a distinction that is more difficult from the Cu 2p spectra alone. Figure 2(b) shows the Cu LMM spectra for the two extreme cases shown in Fig. 2(a) together with that of a thick Cu metal film formed by hydrogen reduction (described in detail below). The kinetic energy of the Cu LMM transition in the thick Cu metal film is 918.5 eV, (568.1 eV BE), in agreement with literature values. The oxidized CuO-like surface has a Cu LMM peak maximum at a kinetic energy of 917.0 eV (569.6 eV BE), which is very close to the value for the CuO described above, and the vacuum-annealed Cu_2O-like surface has a peak maximum at a kinetic energy of 916.3 eV (570.3 eV BE), the general trend though not the exact values agreeing with literature data such as in Table 2.

Annealing of the CuO surface leads to some changes in the O 1s XPS spectra, as shown in Fig. 2(c). The O 1s spectrum associated with CuO is significantly
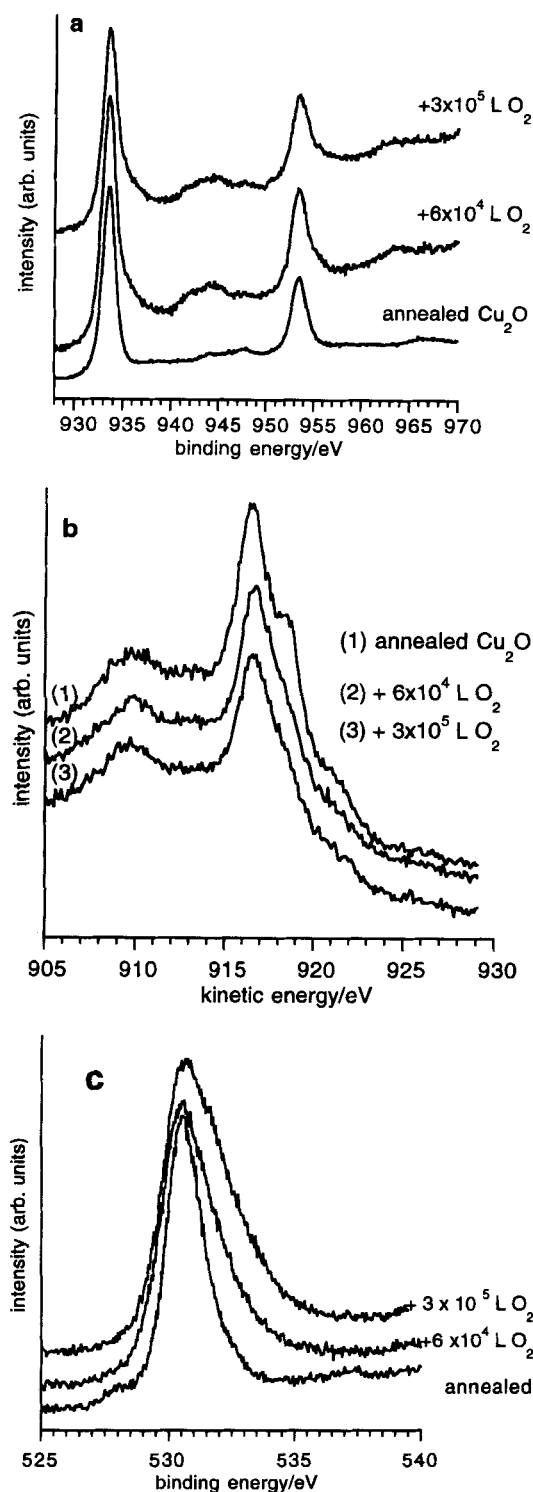
Figure 5. Vacuum-annealed Cu$_2$O exposed to oxygen at 300 K:
(a) Cu 2p XPS; (b) Cu LMM XAES; (c) O 1s.

Figure 6. Vacuum annealing of Cu$_2$O oxidized in 1 × 10^{-4} mbar O$_2$ at 773 K for 10 min. Samples annealed for 3 min at temperature indicated: (a) Cu LMM XAES; (b) Cu 2p XPS.

broadened to higher binding energy. This broadening is largely removed with annealing to 800 K, leaving a far more symmetric peak associated with the reduced surface.

These spectra indicate that the surface is reduced with annealing from an essentially fully oxidized state, after heating in oxygen, through to a Cu$_2$O-like state with relatively little Cu metal being formed at the surface; the small shoulder at lower binding energy to the main
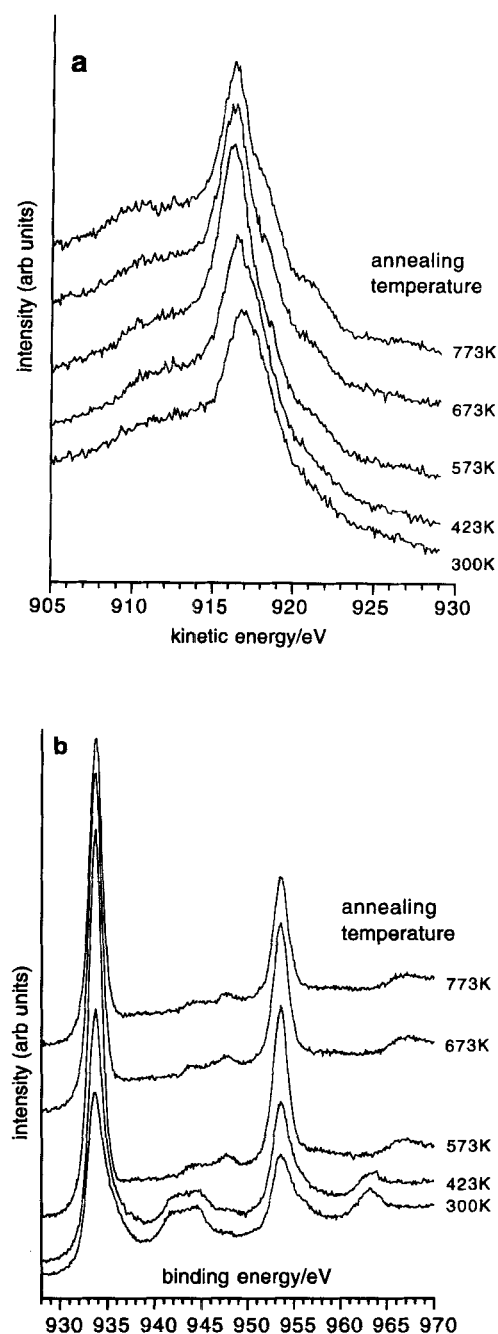
Cu LMM of the vacuum-annealed surface could, however, indicate a small amount of Cu metal.

Vacuum annealing and reoxidation of Cu$_2$O

Vacuum annealing of Cu$_2$O to 700 K led to the removal of surface hydroxide species characterized by a sharpening of the O 1s XPS peak and a shift in the peak maximum to lower BE [Fig. 4(a)]. The Cu 2p spectra
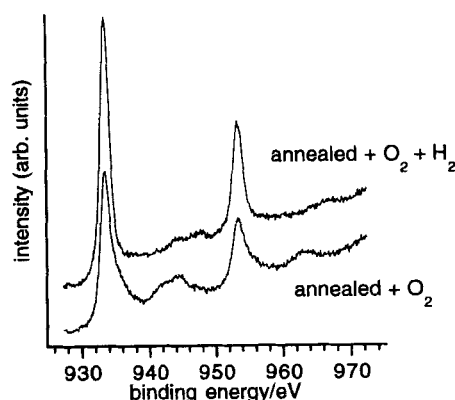
Figure 7. The Cu 2p spectra of annealed Cu₂O: (i) exposed to O₂ (3 × 10⁶ L) at 300 K; (ii) then exposed to 1 × 10³ L H₂ at 300 K.

showed no sign of the CuO-related satellite structure. Annealing also led to the formation of Cu metal at the surface. This is clearly distinguished in the Cu LMM x-ray-excited Auger transition by the formation of a
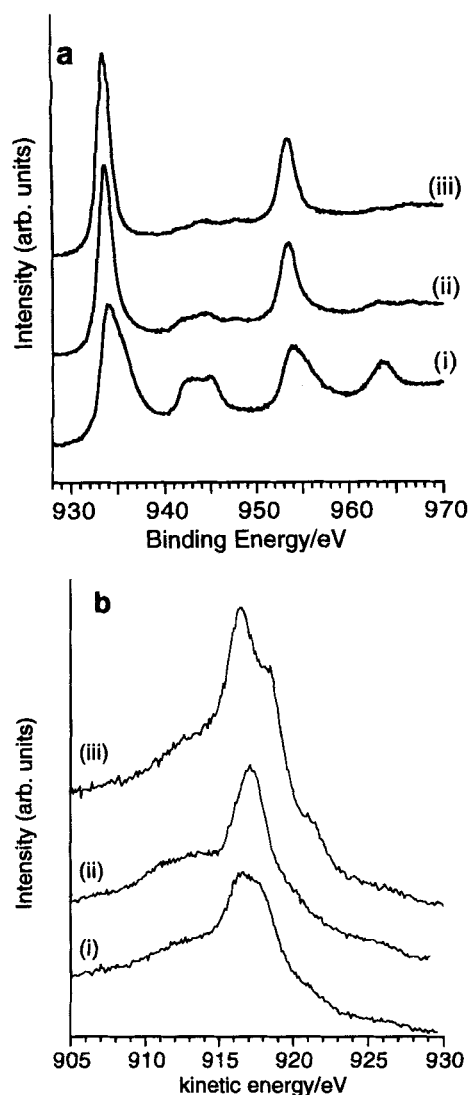

Figure 8. Reduction of CuO by exposure to 1 × 10⁻⁴ mbar H₂ at 300 K for 10 min (ii) and 420 K for 10 min (iii); also shown are the spectra for fully oxidized CuO (i). (a) Cu 2p XPS. (b) Cu LMM XAES.

lower binding energy shoulder to the main Cu₂O transition [Fig. 4(b)]. This additional peak at 568.3 eV BE (918.3 eV kinetic energy) is characteristic of Cu metal. Heating therefore led to decomposition of Cu₂O to form metallic Cu at the surface.

X-ray diffraction of a Cu₂O sample taken after an extensive series of treatments in vacuum indicated no significant alteration from that of the fresh sample.

The metallic layer formed on vacuum annealing of Cu₂O was highly susceptible to oxidation. This is illustrated in Fig. 5(a) and (b), which respectively show the Cu 2p and Cu LMM peaks after room temperature oxygen dosing (2 × 10⁻⁴ mbar). The shoulder at 568.3 eV BE to the main feature in the Cu LMM spectrum was substantially reduced by oxygen exposures of 6 × 10⁴ L (1 × 10⁻⁴ mbar, 10 min), indicating oxidation of the metal. From the simultaneous development of satellite structure in the Cu 2p spectra it is clear that the metal is oxidized to CuO. The O 1s peak similarly shows signs of CuO formation as it is broadened to higher BE [Fig. 5(c)]. The oxidation of the surface can be reversed by vacuum annealing, which regenerates the metal overlayer. The oxidation behaviour of this thin Cu metal layer has some similarities with the behaviour of bulk Cu metal, although it is much more readily oxidized to CuO. For example, Cu(110) forms a thin oxide-like layer, the so-called c(6 × 2) reconstruction, when exposed to ∼10⁴ L oxygen at room temperature that has structural similarities to Cu₂O.[9] Cocke et al.[13] report that exposure of Cu metal to oxygen (0.3 Torr, 30 min) at 300 K results in the formation of a thin oxide layer identified by XPS to consist of Cu(I) oxide. Formation of CuO at the surface of Cu(100) with oxygen exposure at 300 K is, however, reported by Braithwaite et al.[21], although the required exposure is many orders of magnitude higher, 5 Torr for 16 h.

Vacuum annealed CuO with a Cu₂O-like surface was not oxidized back to CuO by similar exposure to oxygen at 300 K. The extent of oxidation achieved by exposure to oxygen at 300 K is therefore highly dependent on the state of the initial surface.

More extensive oxidation of the surface was achieved by heating the Cu₂O in 1 × 10⁻⁴ mbar oxygen at 773 K for 10 min. The result on the Cu LMM and Cu 2p spectra can be seen in Fig. 6(a) and (b) together with the effect of subsequent vacuum annealing. Prior to vacuum annealing the O 1s, Cu 2p and Cu LMM spectra showed significant changes compared with the vacuum-annealed Cu₂O sample, indicating the formation of a CuO layer that is thicker than the one formed with room-temperature oxygen exposure. The changes with respect to vacuum-annealed Cu₂O were as follows: first, the O 1s spectra were considerably broadened; secondly, the Cu LMM XAES spectra showed no sign of Cu metal and was shifted to lower binding energy [Fig. 6(a)]; third, the Cu 2p spectra had a well-developed shake-up satellite structure and broader Cu 2p peaks [Fig. 6(b)]. Vacuum annealing to 573 K removes the Cu 2p satellite structure [Fig. 6(b)], indicating reduction to Cu(I) or Cu metal; similarly the O 1s peak narrows noticeably. However, at this temperature there are no signs of significant Cu metal in the Cu LMM spectra, indicating that the overlayer requires further annealing for metal to be regenerated. By 773 K signs of Cu metal in the Cu LMM spectra [Fig. 6(a)] were more
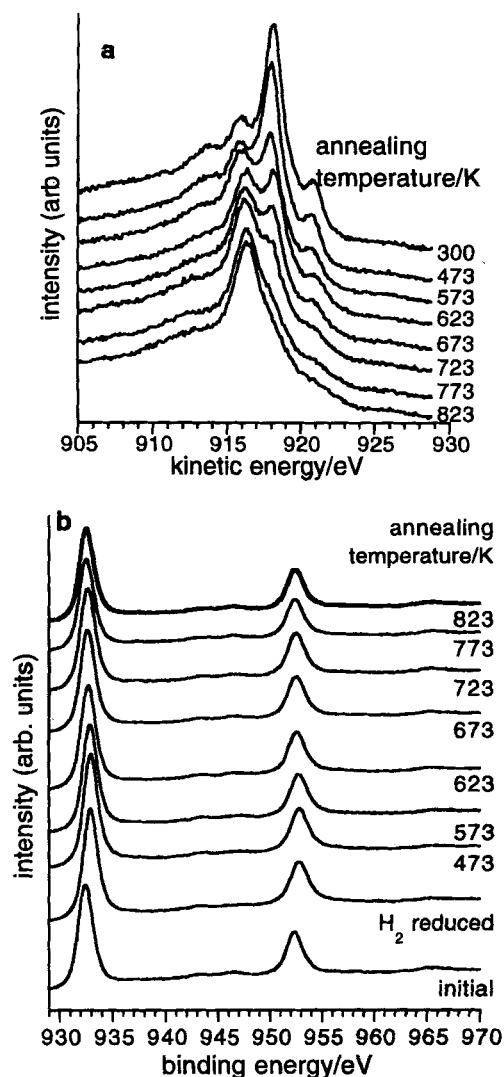
Figure 9. Heavily annealed CuO reduced in 5 × 10⁻⁵ mbar H₂ at 420 K for 10 min and subsequent vacuum annealing: (a) Cu LMM XAES; (b) Cu 2p XPS.

clearly observed but further prolonged annealing at this temperature or above was required to return the surface to its initial state.

Hydrogen reduction of CuO and Cu₂O

As indicated above, exposure of vacuum-annealed Cu₂O to oxygen led to the formation of a thin layer of CuO, indicated by a strong Cu 2p satellite intensity. Exposure of this surface to hydrogen at 300 K (5 × 10⁻⁵ mbar, 10 min) led to the complete removal of the satellite structure associated with the Cu 2p signal (Fig. 7), demonstrating that reduction can occur even at 300 K. The reduction is, however, limited as corresponding changes in the Cu LMM spectra showed that very little Cu metal is formed under these conditions.

Exposure of fully oxidized CuO to hydrogen at 300 K (10⁻⁴ mbar, 10 min) also led to some reduction, as indicated by a loss of intensity in the Cu 2p satellites, as
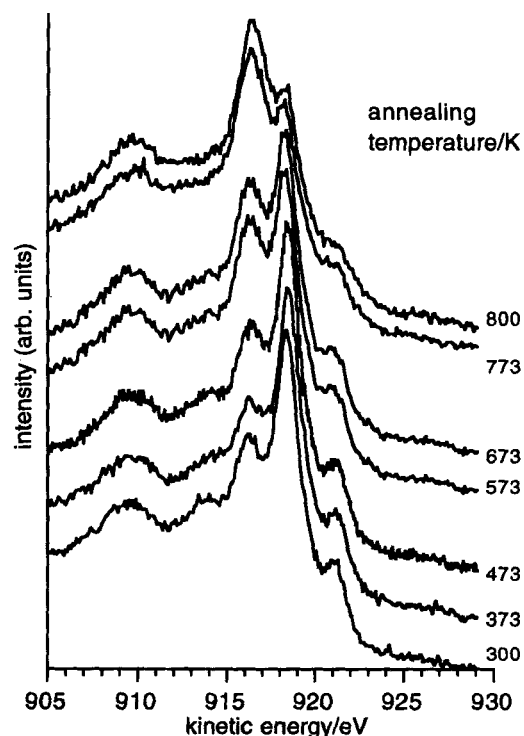

Figure 10. The Cu LMM XAES spectra of Cu₂O reduced in 5 × 10⁻⁵ mbar H₂ at 420 K for 10 min and subsequently vacuum annealed.

shown in Fig. 8(a) (ii). Hydrogen treatment of the fully oxidized CuO at 400 K in 1 × 10⁻⁴ Torr H₂ resulted in more extensive reduction with a further reduction in the Cu 2p satellite intensity [Fig. 8(a) (iii)]. Evidence for Cu metal can be seen from the lower binding energy shoulder at 568.3 eV on the Cu LMM peak in Fig. 8(b) (iii). The fully oxidized CuO surface could be regenerated by vacuum annealing to 773 K for several minutes.

In the case of the heavily annealed CuO sample, reduction to metal was found to proceed at 420 K with a hydrogen pressure of only 5 × 10⁻⁵ mbar H₂ for 10 min. The Cu metal layer formed under these conditions was noticeably thicker than that formed by the fully oxidized Cu. This is clearly demonstrated in Fig. 9(a), which shows the Cu LMM Auger region dominated by Cu metal transitions, the dominant peak at 568.4 eV BE being characteristic of Cu metal. Figure 9(a) also shows that the oxidized surface could be recovered by subsequent vacuum annealing, the final spectrum in the sequence showing a Cu₂O-like Cu LMM peak after annealing at 823 K. Changes in the Cu 2p spectra are less pronounced on hydrogen reduction and reoxidation, although for the reduced surface the Cu metal $2p_{3/2}$ BE was at ~0.4 eV higher BE than the Cu₂O-like surface [Fig. 9(b)]. This shift is consistent with literature reports of the Cu 2p BE difference between Cu₂O and Cu°. For example, Tobin et al.[15] report 932.6 eV for Cu° and 932.4 eV for Cu₂O. Subsequent vacuum annealing of the reduced surface led to a return to the initial Cu₂O-like Cu $2p_{3/2}$ BE.

Hydrogen reduction of Cu₂O under the same conditions as those employed for CuO (420 K, 5 × 10⁻⁵ mbar H₂, 10 min) again resulted in the formation of a metallic overlayer, clearly demonstrated by the alteration in the Cu LMM spectrum (Fig. 10). With vacuum

annealing the Cu metal was again reoxidized to Cu_2O (Fig. 10). The principle difference between the thermal stability of H_2-reduced Cu_2O and CuO is that the former retained a significant metal coating even after prolonged annealing to 800 K. This is in line with the reducibility of the fresh Cu_2O material, which, as shown above, forms a thin metal layer at the surface on vacuum annealing.

DISCUSSION

To assist the following discussion, Fig. 11 presents a schematic representation of the changes in surface composition for CuO and Cu_2O with the oxidation and reduction treatments described above.

Two types of surface composition were generated from CuO samples. The first was a fully oxidized CuO surface not subjected to prolonged vacuum annealing and characterized by high-intensity Cu 2p satellites. The second produced after prolonged vacuum annealing contained a thick surface layer of Cu_2O and was characterized by the absence of an intense Cu 2p satellite structure. The first of these, the fully oxidized surface,

was partly reduced to Cu_2O at 300 K in hydrogen as outlined above. Subsequent vacuum annealing regenerated the fully oxidized surface. This behaviour has some similarity to the behaviour of CuO reported by Tobin *et al.*,[15] who found that following reduction of CuO to Cu_2O (which occurred with annealing at 473 K), prolonged annealing at 673 K led to significant reoxidation to CuO. The reoxidation of the surface can be attributed to net migration of lattice oxygen to the surface and was observed in this work for a number of different surfaces, including CuO. This process occurs in a number of oxide systems to reoxidize a reduced surface, e.g. sputter-reduced TiO_2.[22]

The second type of surface obtained after prolonged vacuum annealing was characteristic of Cu_2O. Several authors have reported on the reduction of CuO to form a surface layer of Cu_2O during vacuum annealing monitored with XPS. Jernigan and Somorjai[6] report that UHV annealing of CuO at 773 K led to the formation of Cu_2O only, with no report of reoxidation to CuO. The reduction of CuO to Cu_2O with annealing would be expected from the behaviour of bulk CuO, which decomposes to Cu_2O above 1073 K.[23] It is, however, suggested from this previous work that reduction of the surface region begins at considerably lower tem-
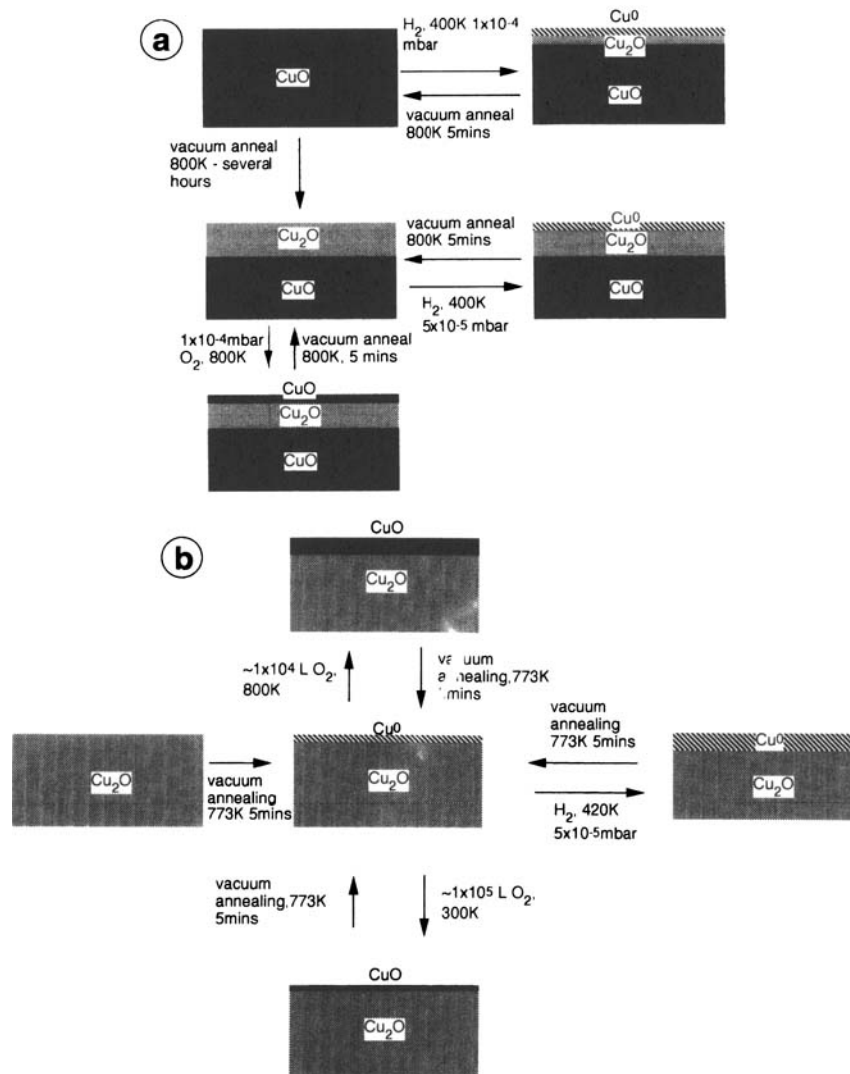

Figure 11. Schematic representation of the changes in surface composition of CuO (a) and Cu_2O (b), with a variety of oxidation and reduction treatments employed in this work.

perature. Both bulk Cu_2O and the Cu_2O-like surface obtained from CuO can be cycled between fully oxidized and reduced states by heating in O_2 and annealing.

The decomposition of Cu_2O to metallic Cu reported here has also been observed by Yoon and Cocke[10] on thin Cu_2O films, although to a very different extent and under different conditions. Yoon and Cocke formed thin Cu(I) oxide layers by exposing polycrystalline Cu to air. The reduction of the oxide layer to metal was reported to occur on heating the sample in 4×10^{-3} Pa oxygen for 30 min. After heating in oxygen to 530 K the Cu LMM spectrum was essentially completely metal-like. Reduction of the Cu_2O was attributed to oxygen dissolution into the bulk. The extent of reduction reported by Yoon and Cocke is therefore much greater than that observed here, where the Cu_2O signal still dominates the Cu LMM spectra even after annealing to 820 K. The difference between the two cases could be explained by the more effective dissolution of O^{2-} ions into the bulk of the metal when Cu metal is used as the substrate than is the case for the bulk oxide employed in this work. It is also interesting to note that the formation of the thin metal layer observed after vacuum annealing of Cu_2O was not observed for heavily annealed CuO where the surface region was reduced to a Cu_2O-like state by vacuum annealing. This type of behaviour is much closer to that observed by Schultz and Cox[16] for Cu_2O single-crystal samples. They found no evidence of Cu^{2+} or Cu° at the surface after Ar^+ bombardment or annealing up to 1000 K. They did, however, observe a history-dependent lattice oxygen mobility due to depletion of lattice oxygen, which with time led to a reduction in the Cu:O ratio at the surface.

Our observations of differences in the surface composition of bulk Cu_2O and Cu_2O-like vacuum-annealed CuO are consistent with the very different reactivity of vacuum-annealed CuO and Cu_2O towards methanol that we have observed using temperature-programmed desorption measurements.[24] Fully oxidized and heavily annealed CuO (to give a Cu_2O-like surface) adsorbed methanol readily, whereas Cu_2O with its thin metal overlayer did not. This is in agreement with the much lower sticking probability and reactivity of methanol on clean Cu(110) metal compared with oxygen-precovered Cu(110).[25] The inactivity of annealed Cu_2O towards methanol indicates that the surface is completely covered in metallic Cu; however, the Cu LMM signal is still dominated by Cu(I) transitions so the metal layer is thin. We estimate the coverage of the continuous metallic layer to be ~ 1 ML, although the presence of additional copper metal in clusters, which contribute little to the overall signal, cannot be ruled out.

Reduction of copper oxide can also be achieved using hydrogen. The number of surface science studies of the interaction of hydrogen with copper oxides is rather limited. Schulz and Cox[26] found no observable hydrogen uptake on $Cu_2O(100)$ under UHV conditions, although atomic hydrogen predissociated on a Pt filament could be adsorbed. Subsequent annealing led mostly to hydrogen recombination and desorption rather than surface reduction. Reduction of polycrystalline CuO and Cu_2O by UV irradiation and by atomic hydrogen at room temperature was observed by Fleisch and Mains.[27] As all the Cu within the sampling

depth of XPS was present as metal, the authors concluded that at least the top 30 Å of the material had been reduced down to metal. Although there are no reports that copper oxide is reduced by molecular hydrogen at room temperature, it can be reduced at elevated temperature (1070 K) even at subatmospheric pressure.[12]

It is clear from this work that reduction of Cu oxides to form thin films of Cu at the surface can be achieved by heating in hydrogen. Furthermore, fully oxidized surfaces of CuO and Cu_2O (i.e. for samples heated to 770 K in oxygen) can be partially reduced on exposure to hydrogen at 300 K, this reduction being characterized by the loss of the Cu 2p satellite structure. Full reduction to Cu metal was not, however, observed at 300 K. As mentioned above Schulz and Cox[26] found no observable hydrogen sticking on $Cu_2O(100)$ at 300 K, suggesting that a fully oxidized surface is required for interaction with hydrogen to occur at 300 K. The most likely explanation for the surface reoxidation on annealing following hydrogen reduction is again the diffusion of lattice oxygen to the surface to reoxidize the metal overlayer.

It is interesting to compare the reduction of CuO by hydrogen observed here with the titration of adsorbed oxygen from Cu(110) by hydrogen. Reported reaction probabilities are in the range 10^{-7} at 500 K and 10^{-5} at 800 K.[28,29] For example, Campbell and Campbell[28] measured a reaction probability for a sample temperature of 623 K as $\sim 1 \times 10^{-6}$, whilst Hayden et al.[29] report no detectable reaction at 400 K using a supersonic molecular beam of hydrogen with translational beam energies < 200 meV. As shown above, the surface film of CuO, formed from dosing vacuum-annealed Cu_2O with oxygen, can be reduced with hydrogen exposures of < 1200 L, suggesting a reaction probability and therefore hydrogen adsorption probability at 300 K of the order 10^{-3}, which is substantially higher than for the O/Cu(110) system. Heating Cu_2O and heavily annealed CuO in hydrogen at 420 K again results in a hydrogen-lattice oxygen reaction probability of $\sim 10^{-3}$ with exposures of $\sim 10^3$ L, resulting in the formation of Cu metal films several monolayers thick.

A reduction in the Cu 2p satellite intensity of the oxidized surface of vacuum-reduced Cu_2O was also observed to occur readily with exposure to methanol or even by exposure overnight to background gases in the vacuum chamber. This is surprising for a lower power reductant such as methanol at ambient temperature. One explanation is that even a several monolayer thick CuO film can be reduced at 300 K, as observed for the CuO surface shown in Fig. 8. An alternative explanation is that the satellite structure is not a good signature of Cu^{2+} in this case but is actually the result of interaction of the outgoing 2p photoelectron with a surface state of the Cu^{2+}. The methanol then interacts with the surface state by adsorption, eliminating it and thereby removing the satellite structure.

CONCLUSIONS

(1) Bulk powder samples of CuO and Cu_2O can be reduced on vacuum annealing to 800 K. Prolonged

annealing of CuO led to a loss of the intense satellite structure associated with fully oxidized CuO and the formation of a thick Cu_2O layer. With vacuum annealing, Cu_2O forms a Cu metal film at the surface of ~ 1 ML thickness.

(2) Fresh samples of CuO exhibit considerable lattice oxygen mobility, which allows reoxidation of a reduced surface region to CuO on annealing in vacuum. The thick Cu_2O layer formed by prolonged annealing of CuO could not, however, be returned to CuO by vacuum annealing, heating in 1×10^{-4} mbar O_2 at 800 K being required to generate a CuO surface.

(3) The Cu metal film formed by vacuum annealing Cu_2O was readily oxidized to CuO by exposure to oxygen at 300 K. More extensive oxidation of the underlying Cu_2O to CuO could be achieved by heating to 800 K in 1×10^{-4} mbar O_2.

(4) Hydrogen can reduce surface CuO to Cu_2O even at 300 K by exposure to 5×10^{-5} mbar H_2 for 10 min.

This suggests an average hydrogen reaction probability in the region of 1×10^{-3}. At 420 K, Cu_2O and heavily annealed CuO can be reduced to metal with similar reaction probabilities. These reaction probabilities are substantially higher than the value of $\sim 10^{-6}$ measured for titration of $O_{0.5}/Cu(110)$ at 623 K.

(5) Relatively mild reduction conditions are required to produce a several monolayer thick layer of Cu metal on Cu_2O and extensively annealed CuO with a Cu_2O-like surface: 5×10^{-5} mbar H_2, 420 K, 10 min.

(6) The oxidation/reduction behaviour and thermal stability of bulk CuO and Cu_2O powder show significant variations from those reported for both Cu oxide films prepared from oxidizing Cu metal and bulk Cu_2O single crystals. This could be accounted for by a dependence on lattice oxygen mobility, which varies significantly in the different materials and also varies with sample history.

REFERENCES

1. N. E. Brese, M. O'Keeffe, B. L. Ramakrishna and R. B. von Dreele, *J. Solid State Chem.* **89**, 184 (1990).
2. M. Grioni, J. F. van Acker, M. T. Czyzyk and J. C. Fuggle, *Phys. Rev. B* **45**, 3309 (1992).
3. J. Ghijsen, L. H. Tjeng, H. Eskes, G. A. Sawatzky and R. L. Johnson, *Phys. Rev. B* **42**, 2268 (1990).
4. J. Ghijsen, L. H. Tjeng, J. van Elp, H. Eskes and M. T. Czyzyk, *Phys. Rev. B* **38**, 11322 (1988).
5. J. C. J. Bart and R. P. A. Sneeden, *Catal. Today* **2**, 1 (1987).
6. G. G. Jernigan and G. A. Somorjai, *J. Catal.* **147**, 567 (1994).
7. R. Hierl, H. P. Urbach and H. Knozinger, *J. Chem. Soc. Faraday Trans.* **88**, 355 (1992).
8. K. H. Schulz and D. F. Cox, *J. Phys. Chem.* **97**, 3555 (1993).
9. R. Feidenshans'l, F. Gray, M. Nielsen, F. Besenbacher, F. Jensen, E. Laegsgaard, I. Stensgaard, K. Jacobsen, J. Norskov and R. Johnson, *Phys. Rev. Lett.* **65**, 2027 (1990).
10. C. Yoon and D. L. Cocke, *J. Electrochem. Soc.* **134**, 643 (1987).
11. T. Robert, M. Bartel and G. Offergeld, *Surf. Sci.* **33**, 123 (1972).
12. T. A. Ramanarayanan and J. Alonzo, *Oxid. Met.* **24**, 17 (1985).
13. D. L. Cocke, G. K. Chuah, N. Kruse and J. H. Block, *Appl. Surf. Sci.* **84**, 153 (1995).
14. G. Schon, *Surf. Sci.* **25**, 96 (1973).
15. J. P. Tobin, W. Hirschwald and J. Cunningham, *Appl. Surf. Sci.* **16**, 441 (1983).
16. K. H. Schulz and D. F. Cox, *Phys. Rev. B* **43**, 1610 (1991).
17. J. Chastain (ed.), *Handbook of X-ray Photoelectron Spectroscopy.* Perkin-Elmer, Eden Prairie, MN (1992).
18. R. P. Holroyd, S. Poulston, M. Bowker and P. C. H. Mitchell, ISIS 1996 Rutherford Appleton Laboratory Annual Report, RB Number 7159.
19. K. Nakamoto, in *Infrared Spectra of Inorganic and Coordination Compounds.* pp. 227–231. Wiley, New York (1963).
20. K. S. Kim, *J. Electron Spectrosc.* **3**, 217 (1974).
21. M. J. Braithwaite, R. W. Joyner and M. W. Roberts, *Faraday Discuss.* **60**, 89 (1975).
22. H. Idriss and M. A. Barteau, *Catal. Lett.* **26**, 123 (1994).
23. F. A. Cotton and G. Wilkinson, in *Advanced Inorganic Chemistry.* p. 768. Wiley, Chichester (1988).
24. S. Poulston, P. Parlett, E. Rowbotham and M. Bowker, to be published.
25. S. M. Francis, F. M. Leibsle, S. Haq, N. Xiang and M. Bowker, *Surf. Sci.* **315**, 284 (1994).
26. K. H. Schulz and D. F. Cox, *Surf. Sci.* **278**, 9 (1992).
27. T. H. Fleisch and G. J. Mains, *Appl. Surf. Sci.* **10**, 51 (1982).
28. J. M. Campbell and C. T. Campbell, *Surf. Sci.* **259**, 1 (1991).
29. B. E. Hayden and C. L. A. Lamont, *J. Phys.: Condens. Matter* **1**, SB33 (1989).