Pressure and temperature dependence of cuprous oxide nucleation on Cu(410)

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Abstract
We studied the oxidation of Cu(410) during thermal O_2 exposure using high-resolution electron energy-loss spectroscopy. Cu_2O is identified by loss peaks at 19 and 79 meV. By monitoring the intensity of the latter, we find that Cu_2O formation depends strongly on the surface temperature *and* on the O_2 pressure and is kinetically limited by the impinging O_2 flux. Thermally activated step roughening, leading to detachment of Cu adatoms from the step edge, acts as a source of mobile Cu atoms, allowing for subsequent nucleation of Cu_2O patches.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Since the discovery of high-T_c superconductivity in oxygen-doped cuprate materials, the study of Cu–O bonding has attracted enormous interest [1]. In particular, cuprous oxide (Cu_2O) is regarded as a meaningful benchmark material for theories and experiments. Cu_2O, an industrially important direct-gap semiconductor with a band-gap energy of 2.0 eV, is considered as one of the most promising materials for application to photovoltaic cells [2–5]. Both higher carrier density and lower leakage currents are required for improved performance in terms of energy conversion in Cu_2O-based photovoltaic devices.

Recently, some of us reported on the hyperthermal-oxygen-beam-induced oxidation of room-temperature Cu(100) [6], Cu(111) [7], and Cu(110) [8] surfaces. A collision-induced absorption (CIA) mechanism was proposed both for Cu(100) and Cu(111), while for Cu(110) an additional mechanism involving mobile Cu adatoms is operative. In these studies, however,

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the role of defects in the oxidation process and, especially, in Cu_2O formation was not considered. One possible way to gain such information is by studying the oxidation of stepped Cu surfaces. The present study was stimulated by recent papers trying to assess the adsorption sites [9] and the vibrational properties [10] of atomic oxygen on Cu(410) and by previous investigations of oxygen adsorption on the similar, but less reactive, Ag(410) surface [11]. The initial stages of Cu(410) oxidation, corresponding to an oxygen coverage below 0.5 ML and to Cu_2O formation, will be presented elsewhere [12].

Herein we report on the results of our experimental investigation on Cu_2O nucleation on Cu(410) for thermal O_2 exposure. When dosing O_2 by backfilling the chamber, cuprous oxide formation occurs in ultra-high-vacuum (UHV) conditions at high surface temperature (500–700 K) and for large O_2 exposure ($>$1000 L). Cu_2O is identified thereby by high-resolution electron energy-loss spectroscopy (HREELS). We show that the oxidation process is kinetically limited by the impinging O_2 flux, since the amount of oxide formed depends, for fixed exposure and surface temperature, on the O_2 partial pressure.

2. Experimental details

HREELS experiments were performed in the Genoa laboratory employing an ultrahigh-vacuum apparatus equipped with a home-built HREEL spectrometer, a low-energy electron diffraction (LEED) optics, a cylindrical mirror analyser for Auger spectroscopy and an ion gun for *in situ* cleaning and preparation of the sample [13].

The sample was a 10 mm diameter disc, cut within 0.1° off the [410] direction. It was mounted onto a molybdenum sample holder and could be heated by electron bombardment and cooled by fluxing liquid nitrogen through a cryostat. It was cleaned by cycles of 1.5 keV sputtering with Ne ions followed by annealing for 3 min to a crystal temperature $T = 900$ K until clean Auger and HREEL spectra and a sharp LEED pattern were obtained. The surface geometry is shown in the inset of figure 1 and consists of three-atom-row wide (100) terraces alternating with mono-atomic steps running in a $\langle 001 \rangle$ direction. In spite of this ideal picture, however, a previous scanning transmission microscopy (STM) investigation [14] showed step fuzziness, indicating that step roughening occurs already at room temperature on the clean surface. Oxygen adsorption stabilizes the step atoms by the formation of Cu–O chains.

Thermal O_2 exposure was obtained by backfilling the chamber, thus taking advantage of the possibility to vary the impinging O_2 flux by more than one order of magnitude. HREEL spectra were always acquired at a base pressure better than 1×10^{-7} Pa and with the sample at room temperature, although the preparation occurred at higher temperature. Most spectra were recorded in specular geometry with an angle of incidence of the electron beam $\vartheta_e = 60°$. The selected primary electron energy was $E_e = 3.6$ eV because the cross section of the oxide loss feature is then at a maximum.

3. Results and discussions

Figure 1 shows HREEL spectra recorded after dosing different amounts of O_2 while keeping the sample at $T = 700$ K. The O_2 pressure was 5×10^{-4} Pa. It is apparent that for oxygen exposures exceeding 1000 L (1 L $= 1.33 \times 10^{-4}$ Pa s) the peak at 38 meV has reached saturation. In contrast, a loss at[7] 79 meV shows up and increases significantly with increasing oxygen exposure.

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[7] The frequency of the 79 meV mode varied in fact between 78 and 84 meV depending on the measurement conditions. We note also that the intensity of the loss was lower in our second run of experiments then in the first when the crystal was first inserted into the vacuum chamber and prepared for the first time. The origin of these effects was not investigated further.
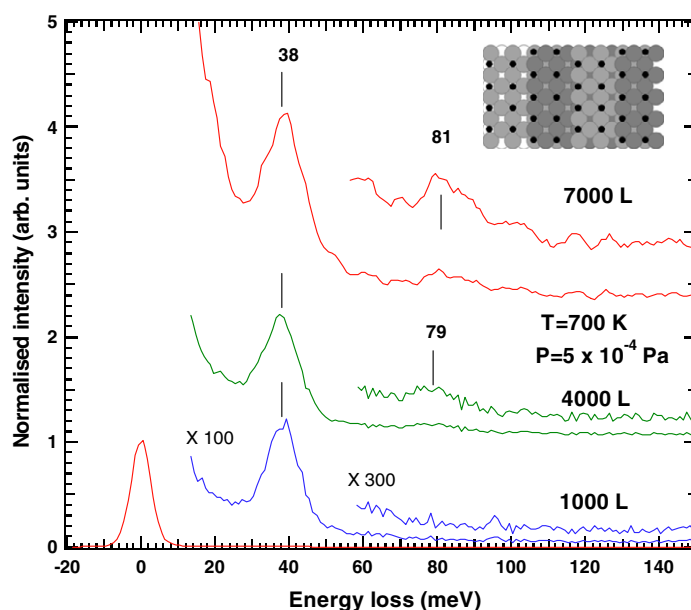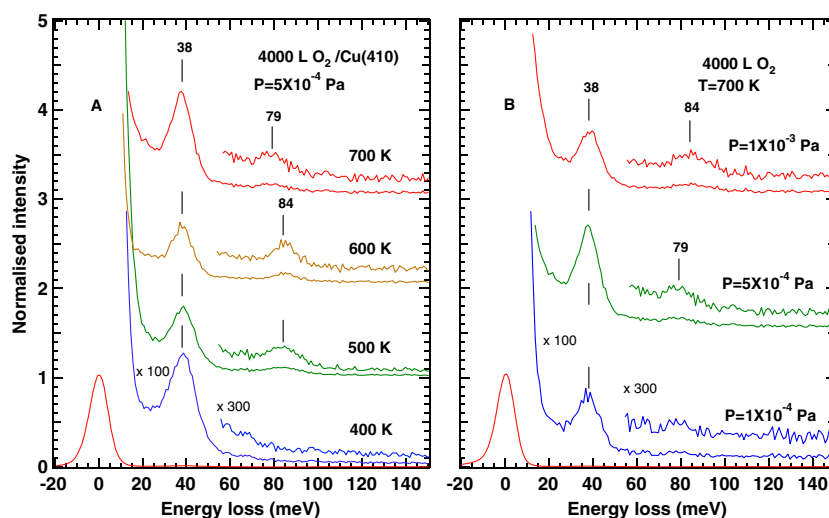
Figure 1. HREEL spectra recorded after different O_2 exposures on Cu(410) at $T = 700$ K. Oxygen was dosed by backfilling the chamber at a fixed pressure of 5×10^{-4} Pa for different time intervals. The inset shows a schematic picture of the Cu(410) surface with the ordered ('modified c(2 × 2)' [13]) superstructure.

The peak at 38 meV was also observed [12] for a much lower exposure (108 L), performed following the procedure indicated by Vlieg *et al* [9] and leading to the formation of an ordered structure initially identified by Thompson and Fadley as a 'modified c(2 × 2)' structure [15] (observed also during the present investigation) and corresponding to an oxygen coverage $\Theta_O = 0.5$ ML.

Vlieg *et al* characterized this ordered structure using x-ray diffraction [9]. In the proposed structural model, the metal-substrate is unreconstructed, with oxygen arranged in an overlayer consisting of 0.25 ML O at the step-edges, forming Cu–O chains with the oxygens nearly collinear with the Cu atoms, and of 0.25 ML O at mid-terrace hollow sites. Since there are two non-equivalent atoms per unit cell, two dipole-active vibrations are expected so that the sharp HREELS feature at 38 meV must be composed of two unresolved contributions. We note that such a feature remains narrow even at higher exposure, thus ruling out the possibility that the absence of a second peak is due to an incomplete c(2 × 2).

The appearance of the peaks at ∼79 meV at the surface temperature of 700 K is indicative of Cu_2O formation, since in bulk Cu_2O, two infrared-active modes are present at 18.1 and 75.5 meV [16]. A low-intensity peak at 19 meV is indeed also observed in our experiment under conditions for which the 79 meV peak intensity is maximum (see figure 4). Similar modes are present also for Cu_2O films grown on Cu(111) [17] and on Cu(110) [18]. It should be noted that no Cu_2O energy-loss peaks are observed on Cu(410) even after very large O_2 exposures performed at room temperature and for pressures as high as 10^{-3} Pa. This underlines the active role of crystal temperature in the Cu_2O formation process.

According to x-ray photoemission measurements [19], the O coverage after an exposure of 3000 L is only 20% higher than the 0.5 ML coverage proper of a well-developed c(2 × 2) structure, obtained after an exposure of only 108 L. This indicates that only islands of Cu_2O can form under such conditions and that the process of Cu_2O formation is kinetically limited [20].

Figure 2. Panel A: spectra recorded after dosing 4000 L of O_2 at a background pressure of 5×10^{-4} Pa and at different surface temperatures. Panel B: spectra recorded after an exposure of 4000 L at 700 K, at different background pressures.

In order to unravel the role of surface temperature and O_2 pressure in the nucleation of cuprous oxide patches at Cu(410), we performed the experiments reported in figure 2. Panel A shows HREEL spectra recorded after exposing the pristine Cu(410) surface to 4000 L O_2 at different surface temperatures, ranging from 400 to 700 K. The pressure was fixed at 5.0×10^{-4} Pa during the dose. The data show that at 400 K the amount of Cu_2O produced (if any) is negligible while a significant amount of cuprous oxide is detected for a surface temperature between 500 and 700 K.

Panel B shows the results when the sample was exposed to identical amounts of O_2 (4000 L) obtained by dosing at different O_2 pressures for different time intervals. The temperature was fixed at 700 K. It is evident that for $P = 1.0 \times 10^{-4}$ Pa, the oxide peak around 79 meV is quite small; however, when the pressure is increased by factors of 5 (intermediate spectrum) or 10 (upper spectrum) the oxide peak is clearly visible.

These data unambiguously show that *both* high temperature *and* a minimal O_2 pressure are required to initiate the formation of Cu_2O. Notably, when the temperature is high enough to allow the formation of a c(2 × 2) structure, testified by a loss peak at 38 meV, oxide formation is allowed only provided that the O_2 pressure is also high enough.

By monitoring the energy-loss peak at ∼79 meV, we can evaluate the efficiency of Cu_2O formation versus surface temperature *and* O_2 pressure. This analysis is shown in figure 3. In order to reduce the scattering of the data points due to the absolute intensities of the loss peaks in different experiments, we plot the ratio between the intensity of the 79 meV and that of the 38 meV peak. The implicit assumption of a constant coverage of adatoms when different amounts of cuprous oxide are present is justified by the comparable intensities of the oxygen-related transition in the Auger spectra (not shown) and by the fact that oxide nucleation can start only on surface sites that have been saturated, i.e. at a coverage of adatoms of 0.5 ML.

We note that, in accord with the spectra in figure 2(A), no detectable Cu_2O formation was found at $T = 400$ K, independently of pressure. On increasing the surface temperature to 500 K, Cu_2O formation could be easily observed. The peak intensity strongly increases with
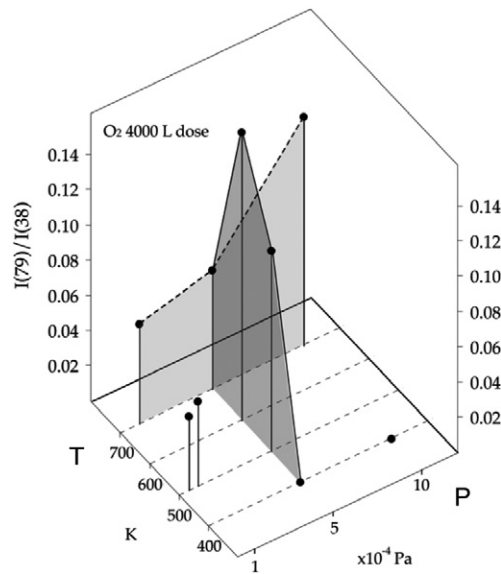
Figure 3. Ratio between the intensities of the 79 meV and of the 38 meV peaks versus temperature and background pressure P after an exposure of 4000 L. The EELS peaks were fitted by Gaussian functions on a exponential background. The peak intensity was estimated by the height of the fitted Gaussian peak. The normalization to the intensity of the 38 meV peak reduces the scatter of the absolute loss intensities in the data.
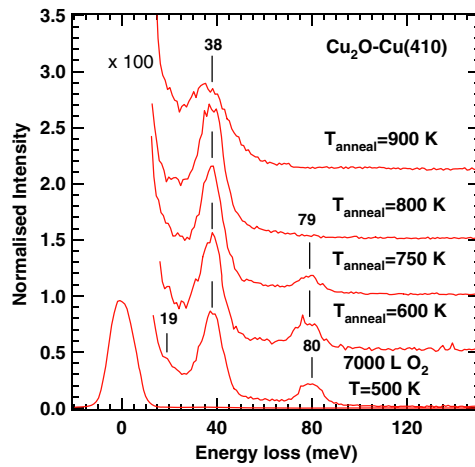
Figure 4. HREEL spectra recorded after annealing the layer obtained by dosing 7000 L O_2 on Cu(410) at $T = 500$ K at different temperatures.

increasing O_2 pressure during the dose. At 700 K, Cu_2O formation still occurs, possibly with a reduced efficiency with respect to the 500 K exposure, at least at intermediate O_2 pressure (5×10^{-4} Pa).

We can rationalize our findings as follows. The step edge of the Cu(410) surface is expected to be an efficient source of mobile Cu atoms and to act as an entrance gate for

subsurface diffusion of O atoms [21]. On clean Cu(410) the step edge has the largest vibrational amplitude and relaxes [22]. Moreover, its atoms are expected to be less strongly bound with respect to terrace atoms because of their lower coordination. O adsorption stabilizes the step edges by forming Cu–O chains, which look straight in STM images recorded at room temperature [14], but it further weakens the Cu–Cu bonds [9]. Thus, step-edge Cu atoms can be detached in thermally activated step roughening, accounting for the initial increase in Cu_2O formation with surface temperature (at fixed O_2 pressure). Their lifetime is short, since migration brings the adatoms back to the step edges. In order for them to act as nucleation centres for Cu_2O, a high O_2 flux is thus necessary. In fact the higher the oxygen flux is, the higher is the chance that such mobile Cu atoms are hit by some oxygen and yield nuclei of Cu_2O before returning to the step edge. The oxygen flux, i.e. a *kinetic factor*, limits the amount of oxide being formed. Moreover, high temperature also enhances the mobility of O atoms at the surface and into the bulk. The maximum of Cu_2O production around 500–600 K for fixed pressure arises thus from the competition between the increasing amount of mobile Cu adatoms being detached and their decreasing lifetime.

The need for a critical O_2 pressure to observe oxide nucleation can be accounted for only by a thermodynamic argument. If Cu_2O formation could occur below a certain O_2 pressure, it should be observed at all possible pressures for long enough O_2 doses, contrary to experimental evidence. This result is consistent with the calculated (p, T) phase diagram [23], showing that at fixed temperature and below a certain oxygen pressure, Cu_2O is not stable, and decomposes. Only by lowering the surface temperature can Cu_2O decomposition be avoided, and Cu_2O be observed in UHV conditions. On the other hand, when the surface temperature is further increased, the total amount of Cu_2O formed for fixed exposure decreases, as is apparent from the series of experiments at $P = 5 \times 10^{-4}$ Pa. Such a decrease can be due either to the onset of Cu_2O decomposition or to the reduced lifetime of mobile Cu atoms. In the former hypothesis the limited Cu_2O production at high T would have a thermodynamic origin (again in agreement with the calculated (p, T) phase diagram [23]), in the latter one a kinetic origin. In both cases, on increasing the O_2 pressure at a fixed T, the stability of bulk Cu_2O increases due to the change in the oxygen chemical potential.

In order to address this last issue we performed post-dose annealing (i.e. in the absence of oxygen atmosphere) at different temperatures (T_{anneal}) of a layer obtained after exposure to 7000 L of O_2 at 500 K. The spectra are reported in figure 4. Since an oxide peak of significant intensity is still present upon heating to 750 K, the reduced efficiency in Cu_2O production at $T > 600$ K (see figures 2(A) and 3) cannot be due to decomposition of Cu_2O (which is even more stable in the presence of oxygen!) and is therefore of kinetic origin. Moreover, since the peak at 38 meV starts decreasing only above 800 K, when cuprous oxide has already decomposed, the assumption that the amount of adatoms present at the surface for a long enough exposure is independent of the dosing condition is confirmed.

4. Summary

Initial nucleation of Cu_2O on Cu(410) has been observed by HREELS for thermal exposure at temperatures higher than 400 K and at O_2 pressure of at least 10^{-4} Pa. Cu_2O formation depends on both the surface temperature *and* the O_2 pressure. Thermal activation of step roughening yielding mobile Cu adatoms, the thermodynamic instability of Cu_2O at high temperature and below a certain O_2 pressure and the limited lifetime of the mobile Cu adatoms, which need to react before returning back to the step edge, account for the observed phenomenology.

Acknowledgments

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