

Oxygen adsorption on Cu(110) at low temperature

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(Received 8 May 2007; published 11 December 2007)

The interaction of oxygen on Cu(110) in the temperature range between 10 and 500 K has been investigated by reflectance difference spectroscopy, scanning tunneling microscopy, and low energy electron diffraction. The results show that the dissociation of molecular oxygen is complete below 45 K. Atomic oxygen induces the expulsion of Cu atoms from the terraces in a temperature range between 70 and 200 K, indicating a low energetic barrier for this process. Further annealing to temperature above 250 K leads to the formation and ordering of a $(2 \times 1)\text{O}$ stripe phase.

DOI: [10.1103/PhysRevB.76.245412](https://doi.org/10.1103/PhysRevB.76.245412)

PACS number(s): 68.37.Ef, 68.43.Jk, 68.55.Ac

I. INTRODUCTION

The chemisorption of oxygen on Cu(110) has been investigated extensively in numerous theoretical and experimental studies since the pioneering work of Ertl.¹ It is quite clear nowadays that oxygen adsorbs dissociatively on the Cu(110) surface at room temperature.² The atomic oxygen then forms Cu-O compounds by combining with Cu adatoms which are evaporated from step edges and diffuse across on the surface. These Cu-O compounds grow into long Cu-O strings (the so-called “added rows”³) oriented along the [001] direction of the substrate by connecting with other Cu-O compounds, Cu adatoms, and atomic oxygen. The uniaxial growth is due to the strong attractive interaction between these species along the [001] crystallographic direction.^{4,5} When the density of the added rows increases, they agglomerate into (2×1) reconstructed stripes.⁶ It is believed that the rate-limiting step of this process is the supply of Cu adatoms from step edges rather than the reaction and diffusion of adatoms (O and Cu). Although another supply channel, namely, the expulsion of Cu adatoms on the otherwise flat terraces associated with the formation of monolayer deep vacancy islands, has also been observed, this process is believed to have a much higher activation energy.²

At very low temperature, however, the situation is less clear. For instance, there are questions concerning primarily the existence of molecular oxygen on the surface and the dissociation mechanism that leads to the formation of atomic oxygen. It is also not clear how, after dissociation, the atomic oxygen interacts with the Cu(110) surface at low temperature when Cu adatoms are not readily evaporated from step edges. Recent experimental investigations reveal that the oxygen adsorbs at least partially as a molecule at very low temperatures.^{7,8} This has been confirmed by a first principles study which shows that molecular oxygen prefers to adsorb at the fourfold hollow site on Cu(110). Yet, the dissociation barrier at this site is only 150 meV.⁹ On the other hand, the Cu(110)- $(2 \times 1)\text{O}$ reconstruction is still inhibited for temperatures $T \leq 150$ K.^{10,11} Using low energy electron diffraction (LEED) and high resolution electron energy loss spectroscopy, Sasaki *et al.* have shown that the (2×1) reconstruction starts to form in the temperature range between 200 and 300 K.¹² The same authors have also demonstrated that the oxygen adsorbed on Cu(110) at 100 K is

more reactive by a factor of 25 to CO than the oxygen in the $(2 \times 1)\text{O}$ phase,¹² indicating a different binding configuration of the atomic oxygen at these low temperatures. However, the details of the dissociation and reaction process of oxygen on Cu(110) are still not fully understood and contradicting dissociation temperatures have been reported by different authors.²

In this paper, the interaction of oxygen molecules and atoms with the Cu(110) surface will be discussed based on the results obtained by reflectance difference spectroscopy (RDS), scanning tunneling microscopy (STM), LEED over a wide temperature range. We have explored the mechanisms which eventually lead to the formation of the (2×1) added row phase and to the ordering of the Cu-CuO stripe phase. This includes the dissociation of the oxygen molecules at low temperature, the formation of Cu-O added rows involving mass transport of Cu adatoms from the topmost Cu surface layer, and finally the arrangement of these Cu-O chains into a periodic array of CuO stripes with uniform width and spacing.⁶ Our results demonstrate that RDS is sensitive to the different ordering steps. Combined with the complementary information obtained by STM and LEED, we are able to derive a detailed picture of the underlying atomistic processes.

II. EXPERIMENT

All the experiments reported here have been carried out in a UHV chamber equipped with facilities for Auger electron spectroscopy (AES), LEED, a home-build variable temperature STM,¹³ and temperature programmed desorption. The residual gas pressure is below 10^{-10} mbar. A high-quality single-crystal Cu(110) sample with a miscut angle of 0.1° has been used in this study. The sample is mounted on a manipulator and can be cooled to 10 K by means of a continuous flow liquid He cryostat, to which the sample holder is connected via a copper braid. Using an electron impact heater fixed at the backside, the sample can be heated to above 1000 K. A programmable temperature control unit allows the sample temperature to be set and held at any intermediate temperature, and to accurately control the heating and cooling rate. The sample temperature is measured with a K-type thermocouple clamped to the crystal. The temperature reading has been calibrated at low temperature by ther-

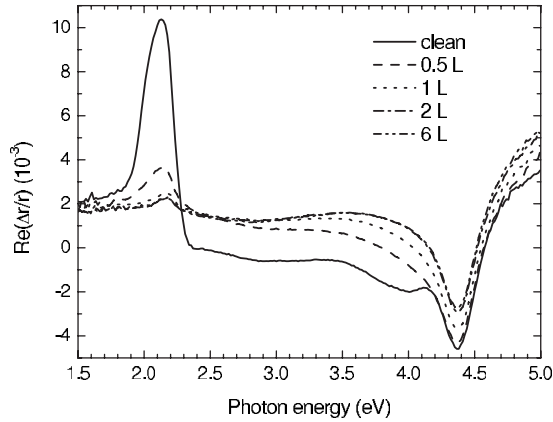


FIG. 1. Real part of the RD spectrum for the clean Cu(110) surface and after exposures of 0.5, 1, 2, and 6 L of oxygen at 12 K.

mal desorption of several kinds of gases, and the error is estimated to be smaller than 1 K. The Cu(110) surface is cleaned by sputtering with 900 eV Ar⁺ ions at room temperature and subsequent annealing to 800 K. After the preparation, the surface impurity is lower than the detection limit of AES and the LEED image reveals a sharp (1 × 1) diffraction pattern.

An RD spectrometer of the Aspnes type¹⁴ is attached to the UHV chamber via a strain-free optical window. The light from a Xe lamp is directed on the sample at normal incidence with the polarization axis oriented at an angle of 45° with respect to the two main crystallographic axes [1 $\bar{1}$ 0] and [001] of the Cu(110) surface. The change of the polarization state of the reflected light is measured using a modulation detection technique. By means of a grating monochromator, the reflected light is further analyzed with respect to the photon energy. As a result, the normalized reflectance difference defined as

$$\frac{\Delta r}{r} = 2 \frac{r_{[1\bar{1}0]} - r_{[001]}}{r_{[1\bar{1}0]} + r_{[001]}} \quad (1)$$

can be recorded as a function of the photon energy in the range between 1.5 and 5.5 eV.

III. RESULTS AND DISCUSSION

A. Molecular adsorption of O₂ on Cu(110) at 12 K

Figure 1 shows the RD spectra recorded from the bare Cu(110) surface and after dosing different amounts of oxygen at 12 K. As reported previously,^{15,16} the RD spectrum of clean Cu(110) shows a pronounced peak at 2.1 eV which contains three different contributions, namely, (i) optical transitions between an occupied and an unoccupied surface state located at the \bar{Y} symmetry point of the surface Brillouin zone, (ii) a modified bulk transition related to the onset of the interband transitions ($\Delta_5 \rightarrow \Delta_1$) in copper in the vicinity of the bulk symmetry point X , and (iii) intraband contributions (Drude term) associated with the anisotropic free-electron-like transport along the [1 $\bar{1}$ 0] and [001] surface directions,

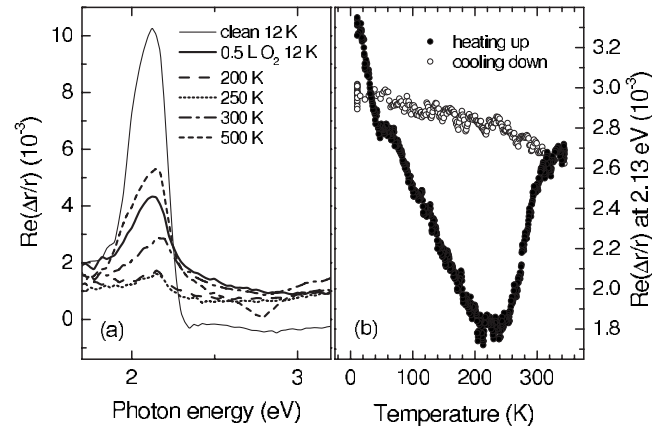


FIG. 2. (a) Real part of the RD spectrum recorded for the clean Cu(110) surface, after adsorption of 0.5 L oxygen at 12 K, and after subsequent annealing of the oxygen covered surface to 200, 250, 300, and 500 K, respectively. All spectra were recorded at 12 K. (b) Intensity of the RDS signal at 2.13 eV during heating up (filled circles) and cooling down (open circles) of the Cu(110) sample exposed to 0.5 L of oxygen at 12 K.

respectively. Among these three contributions, the surface state transition is the dominant one and is extremely sensitive to surface defects and adsorbates.^{16,17} The RD signal at 2.1 eV can thus be used to monitor the presence and ordering of surface defects and adsorbates. Another pronounced feature of RD spectrum of Cu(110) is the negative peak at 4.3 eV originating from a Cu bulk transition ($E_F \rightarrow L_1^u$).¹⁸ This feature is particularly sensitive to atomic displacements due to adsorbate induced surface stress^{19,20} or thermal expansion.¹⁸ At $T=12$ K, the oxygen adsorbates can exist in a molecular state on the Cu(110) surface.^{7,8} The main feature seen in Fig. 1 is the fast quenching of the RD intensity around 2.1 eV and some modification of the signal around 4.3 eV. After an oxygen exposure of 2 L (1 L = 10⁻⁶ Torr s), the RD signal is saturated, indicating that the surface is fully covered by oxygen species. Furthermore, not only the surface state transition at 2 eV is totally quenched but also the $\Delta_5 \rightarrow \Delta_1$ bulk related transition at 2.18 eV (Refs. 15 and 16) is completely removed. Additionally, the simultaneous changes around 4.3 eV indicate the modification of the surface stress induced by the adsorbates.^{19,20} All these observations suggest a rather strong interaction between the adsorbed oxygen species and the Cu(110) surface.

B. Interaction of oxygen with the Cu(110) substrate

RDS has also been applied to study the effect of thermal annealing of the oxygen adlayer on Cu(110). At first, the Cu(110) surface was exposed to 0.5 L of oxygen at 12 K. Then, the sample was heated up to a certain temperature with a heating rate of 1 K/s. After each heating step, the sample was cooled down to 12 K again, and a RD spectrum was recorded. The real part of these spectra are shown in Fig. 2(a). The initial oxygen exposure of 0.5 L at 12 K leads to a decrease of the RD intensity at 2.1 eV by about 60%. Heating the sample to temperature ≤ 200 K results in a further

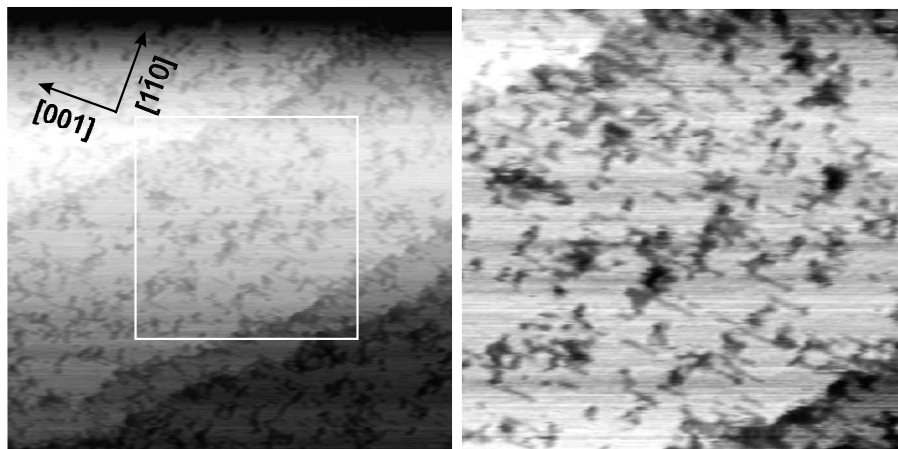


FIG. 3. STM images of the Cu(110) surface exposed to 0.7 L of oxygen at 200 K. Scan size: $1250 \times 1250 \text{ \AA}^2$ (left) and $625 \times 625 \text{ \AA}^2$ (right). The scan area of the right image is marked in the left one by a white frame. Tip bias and tunneling current: $V_t=1 \text{ V}$ and $I=1.1 \text{ nA}$.

monotonous decrease of the intensity. Subsequent annealing to 250 K induces no further change. Heating from 250 to 300 K, however, leads to a steep increase of the RD signal at 2.1 eV. The RD intensity at this energy continues to increase after annealing to still higher temperature, although the effect becomes smaller and saturates at around 500 K. The same behavior can also be inferred from Fig. 2(b) where the RD intensity has been monitored at a fixed photon energy of 2.13 eV during heating the sample at a rate of 1 K/s up to 350 K and subsequent cooling down. The filled circles are the data points recorded during heating and the open circles represent the cooling curve. Obviously, there are several distinct processes occurring in the temperature range between 12 and 350 K. In the following sections, these processes will be discussed in more detail.

1. Dissociation of O_2 and roughening of the Cu(110) surface

The initial decrease of the RD intensity at 2.1 eV after oxygen exposure at 12 K has already been discussed in Sec. III A. Heating the sample to 200 K leads to a further decrease of the RD intensity at 2.1 eV. In addition, the decrease of the intensity between 12 and 200 K can be described by two linear segments with different slopes connected by a small plateau between 45 and 70 K [see Fig. 2(b)]. This indicates that at least two different processes are involved in this temperature range. The first segment ($T \leq 45 \text{ K}$) could be related to the dissociation of the oxygen molecules on the surface. One oxygen molecule dissociates into two oxygen atoms, so that the surface coverage of the adsorbates increases; in addition, the interaction between atomic oxygen and the substrate is stronger than for an oxygen molecule. As a result, the RD intensity at 2.1 eV should be reduced. The second segment ($T \geq 70 \text{ K}$) may be caused by the creation of defects (oxygen induced roughening) on the Cu surface. Indeed, it is well known that oxygen atoms on Cu(110) have the tendency to bind to Cu atoms by forming Cu-O pairs which subsequently grow into elongated Cu-O strings oriented along the [001] direction.² According to room temperature STM studies,^{2,3,21} there are two channels for the supply of the Cu atoms, (i) the detachment and diffusion of Cu atoms from nearby step edges and (ii) expulsion of Cu atoms from the terraces and formation of one layer deep vacancy trenches or islands. It is believed that at

room temperature, where the mobility of the Cu adatoms is high, a finite equilibrium concentration of Cu adatoms exists on the terraces, created mostly by “evaporation” from step edges.^{2,3,21,22} Therefore, at room temperature, process (i) is the dominant source for the Cu adatoms. As a result, the Cu-O “added” rows will be formed on the otherwise flat terraces. For temperatures below 200 K, however, the mobility of the Cu adatoms is quite small, if not negligible.²³ Most importantly, the evaporation of Cu atoms from steps is not sufficiently activated at this temperature. As a result, process (i) is unlikely to occur at this temperature. Then, the Cu-O strings on the terrace, if they can form at all at this low temperature, can only be generated through process (ii) and the formation of vacancies of missing first-layer Cu atoms on the terraces. Again, owing to the low temperature, the vacancies are rather immobile on the surface.²³ As a result, one would expect randomly distributed vacancies or small vacancy islands on the large terraces in addition to small Cu-O strings located in the vicinity of these vacancies. This expectation has been confirmed by STM measurements. Figure 3 shows two STM images of the Cu(110) surface after exposure of 0.7 L of oxygen. The oxygen was exposed at 200 K and then the STM images were recorded at the same temperature. On these two images, dark holes and gray rows can be seen all over the surface—with no apparent preference to either the vicinity of the step edges or the center of the terraces. The gray rows are running along the [001] direction and most of them start either from a step edge or a dark hole. The dark holes are vacancy islands where Cu atoms have been removed from the Cu surface layer to form Cu-O added rows along the [001] direction. These added rows are imaged in gray (rather than as bright protrusions) due to electronic effects as reported previously.^{21,22} Coming back to the decrease of the RD intensity, the vacancies that appear as dark holes in the STM images act as scattering centers for the surface state electrons as discussed in Ref. 17. Consequently, the RD intensity at 2.1 eV is further reduced upon Cu-O row growth by vacancy formation. Therefore, it can be concluded that the decrease of the RDS intensity at 2.1 eV during the annealing of the Cu(110) surface exposed to oxygen at 12 K is due to (a) O_2 dissociation in the temperature range between 12 and 45 K and (b) roughening of the surface due to creation of vacancy islands and Cu-O strings on the surface in the temperature range between 70 and 200 K.

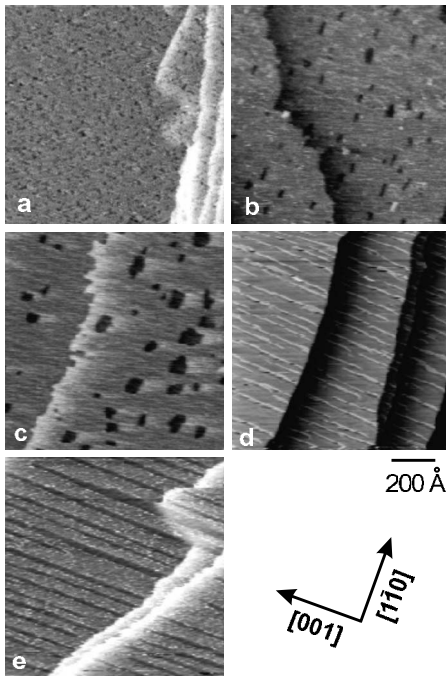


FIG. 4. STM images of the Cu(110) surface after exposure to 0.7 L of oxygen at (a) 200 K and after annealing to (b) 280 K, (c) 300 K, and 300 K and holding the temperature for (d) 2 min and (e) 480 K. All images were recorded at 200 K. Tunneling conditions: $V_t=1$ V and $I=1.7$ nA. The size of the images is $1000 \times 1000 \text{ \AA}^2$.

2. Thermal annealing and ordering of the $(2 \times 1)O$ stripe phase

Between 200 and 250 K, the RDS intensity at 2.1 eV stays almost constant [Fig. 2(b)]. This suggests that no surface reaction occurs in this temperature range. Heating the sample above 250 K, the RD intensity increases steeply. This observation can be associated with two effects: (1) the recovery of a flat surface, i.e., an increase of the average terrace width on the surface and (2) the formation of a well ordered Cu-CuO stripe phase which reduces the diffuse scattering of surface electrons.²⁴ Yet, the dip in the RD spectrum at 2.7 eV, which is a characteristic feature of the well ordered Cu(110)- $(2 \times 1)O$ phase,²⁵ only appears after annealing to 500 K [Fig. 2(a)]. This confirms that the ordering of the well

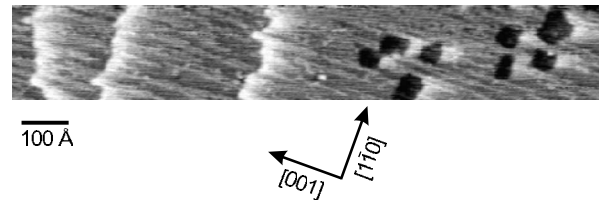


FIG. 6. CuO stripes and vacancy holes obtained after annealing the oxygen covered Cu(110) surface (0.7 L of O_2 exposed at 200 K) to 300 K. Image size: $1250 \times 200 \text{ \AA}^2$.

ordered Cu-CuO stripe phase is only completed at elevated temperature.

The morphology of the Cu(110) surface after exposure to 0.7 L of oxygen at 200 K and subsequent annealing to different temperatures was imaged with the STM at 200 K. A series of characteristic images is shown in Fig. 4. As discussed in the preceding section, at 200 K, the surface is covered with short Cu-O added rows and small vacancy islands on the Cu surface. Heating the sample to 280 K, the Cu-O rows grow longer and, simultaneously, the size of the vacancy islands increases. The vacancy islands have a rectangular shape elongated along the close packed $[1\bar{1}0]$ direction where the mobility of a single vacancy is expected to be larger.

This can be seen more clearly in Fig. 5 where STM images with a smaller scan size are shown. The line scan in Fig. 5(c) shows that the vacancy islands are one atomic layer deep. Besides the large vacancies, some small dark holes are still visible on the terraces; this suggests that the formation of large vacancy islands is in its early stage. After heating to 300 K and immediately cooling down the sample back to 200 K, the vacancy islands have grown even larger [Fig. 4(c)] and the Cu-O rows aggregate along the $[1\bar{1}0]$ direction, forming narrow (2×1) ordered stripes. These stripes are better resolved in Fig. 6 for a different tip condition. The vacancy islands are now mainly located at the center of large terraces and the holes on the small terraces have disappeared. This observation suggests two possible channels for the annealing of the vacancy islands: (1) they can diffuse to the step edges which act as sinks for the vacancy islands and (2)

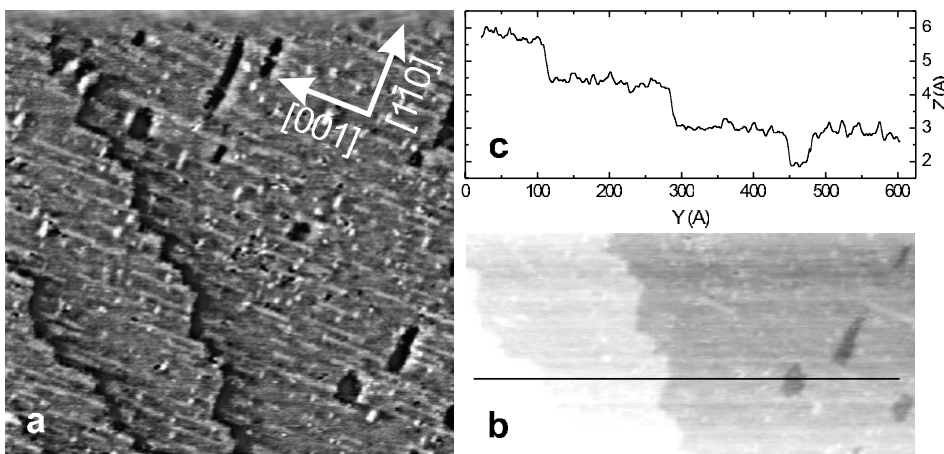


FIG. 5. STM images of the Cu(110) surface after exposure to 0.7 L of oxygen at 200 K and subsequent annealing to 280 K. The image was taken at 200 K. (a) $625 \times 625 \text{ \AA}^2$, (b) gray scale image ($625 \times 330 \text{ \AA}^2$) from the same surface area, and (c) line profile along the dark line marked in (b).

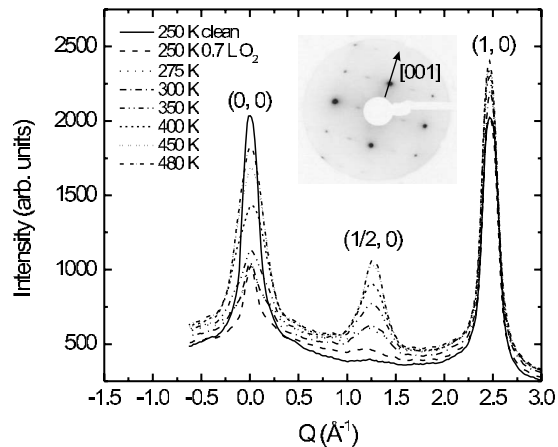


FIG. 7. Line profiles of the LEED intensity between the (0,0) and (1,0) spots along the $[1\bar{1}0]$ direction before and after exposure of 0.7 L oxygen at 250 K on the Cu(110) surface and after subsequent annealing to the indicated temperature. The LEED profiles were recorded at 250 K with a beam energy of $E=145$ eV. The inset shows a complete LEED pattern of the Cu-CuO stripe phase recorded after annealing the O/Cu(110) sample to 480 K (electron beam energy $E=145$ eV).

the Cu adatoms that evaporate from the step edges can diffuse to the vacancy islands and fill them up. Both processes are thermally activated at 300 K. If the sample is held at 300 K for 2 min, the vacancy islands are completely removed from the surface [Fig. 4(d)]. On the other hand, the CuO stripes are still not contiguous and have an irregular shape. The ordering is considerably improved after heating to 480 K, as one can see in Fig. 4(e). The stripes become straight and most of them even extend across the step edges separating neighboring terraces. In addition, the Cu(110)-(2 × 1)O stripes have an almost equal width of 20–30 Å and are regularly spaced. This sequence of alternating CuO and bare Cu stripes is referred to as the Cu-CuO stripe phase.⁶

The ordering of the Cu-CuO stripe phase has also been followed by LEED. Figure 7 presents line profiles of the diffraction intensity across the (0,0) and (1,0) spots along the $[1\bar{1}0]$ direction. After exposing the clean Cu(110) surface to 0.7 L of oxygen at 250 K, the intensity of the (0,0) spot decreases dramatically due to the formation of Cu-O strings and vacancies on the Cu(110) surface. The absence of a (1/2, 0) diffraction peak and the line shape of the (0,0) spot suggest that the Cu-O strings and the vacancies are randomly distributed. Annealing the sample gradually up to 480 K, a peak at the (1/2, 0) position appears and its intensity increases monotonously, indicating the formation and ordering of the oxygen induced (2 × 1) structure. The intensity of the (0,0) spot is also partially recovered. Broad shoulders appear at either side of the (0,0) peak, attributed to the ill-resolved satellite peaks due to the long-range ordering of the Cu-CuO stripe phase with a periodicity of about 80 Å in the $[1\bar{1}0]$ direction. Figure 8 shows the normalized peak intensity of the (0,0) spot and the normalized full width at half maximum (FWHM) of the (1/2, 0) spot as a function of the annealing temperature. The monotonous increase of the (0,0) peak in-

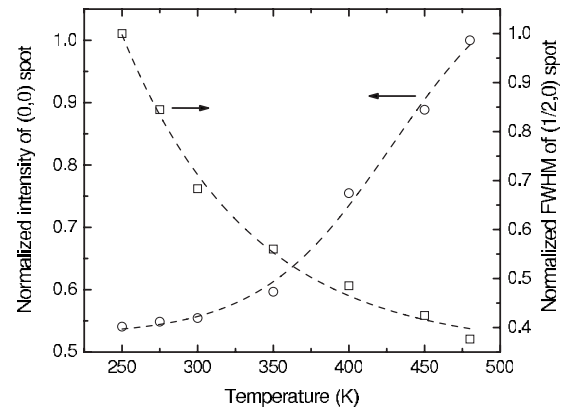


FIG. 8. Normalized peak intensity of the (0,0) spot (open circles) and FWHM of the (1/2, 0) spot (open squares) obtained from Fig. 7. Dashed lines are guides the eye.

tensity indicates the increase of the average terrace width, whereas the decrease of the FWHM of the (1/2, 0) peak is directly related to the growth and ordering of the Cu(110)-(2 × 1)O stripes.

From the above STM and LEED studies, it can be concluded that the smoothing and healing of the O/Cu(110) surface sets in at about 250 K and the average terrace width on the Cu surface starts to increase. This annealing effect can be divided into two steps, namely, (1) the coalescence and removal of the Cu vacancies and (2) the aggregation of short Cu-O strings into well ordered CuO stripes. Both processes lead to the reappearance of the Cu(110) surface state on large portions of the surface and, consequently, an increase of the RD intensity at 2.1 eV, as observed in Fig. 2.

IV. CONCLUSION

By adsorbing molecular oxygen at 12 K and subsequent annealing up to 500 K, the interaction of oxygen adsorbates with the Cu(110) surface has been investigated by RDS, STM, and LEED. Three different interaction regimes have been identified, namely, (1) molecular adsorption and dissociation ($T \leq 45$ K), (2) oxygen induced roughening and Cu-O string formation ($70 \leq T \leq 200$ K), and (3) growth and removal of vacancy islands followed by formation and ordering of (2 × 1) reconstructed CuO stripes ($T \geq 250$ K). Molecular oxygen is not stable at temperatures above 45 K where all oxygen on the surface is thermally dissociated. After dissociation, atomic oxygen interacts strongly with the Cu(110) surface, leading to the formation of short Cu-O strings by expulsion of Cu atoms from the terraces, leaving monolayer deep vacancies on the terraces. The rough O/Cu(110) surface is stable at temperatures below 250 K. Above this temperature, the vacancy islands start to heal out, while Cu-O strings start to coalesce and finally form a well ordered Cu-CuO stripe phase.

Considering the atomic processes involved, forming Cu-O rows by expulsion of Cu atoms from the topmost Cu layer on flat terraces in the presence of adsorbed oxygen atoms requires a surprisingly small activation energy since it can oc-

cur at temperatures lower than 200 K. This observation could be explained by the strong bonding between O and Cu surface atoms. Indeed, first principles calculations based on density functional theory show that the bonding between the O adatoms and the Cu(110) surface is predominantly ionic.⁵ Consequently, a modification of the local surface stress can be expected, which may favor the expulsion of Cu atoms and reduce the related activation energy substantially. It is reasonable to believe that this process is also important at room temperature where most of the previous STM studies have

been performed. The absence of vacancies in most of the STM images recorded at room temperature may be caused by the high density of mobile Cu adatoms which fill in the vacancies immediately after their formation.

ACKNOWLEDGMENT

We are grateful for financial support by the Austrian Science Fund (FWF) through NFN S90 Project No. S9002-N20.

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