Dynamics of oxygen-induced reconstruction of Cu(100) studied by scanning tunneling microscopy

F. Jensen, F. Besenbacher, E. Lægsgaard, and I. Stensgaard Institute of Physics, University of Aarhus, DK-8000 Aarhus C, Denmark (Received 2 April 1990)

Scanning-tunneling-microscopy investigations on the nucleation and growth of the Cu(100)- $(2\sqrt{2} \times \sqrt{2})R45^{\circ}$ -O structure revealed that the reconstruction is formed by "squeezing out" every fourth [001] surface row of Cu atoms, resulting in the formation of Cu islands which agglomerate at elevated temperature. This growth mode is opposed to the (2×1)O reconstruction on the Cu(110) surface which involves removal of Cu atoms from step edges. A general picture evolves in which both reconstructions are stabilized by Cu-O-Cu chains directed along the [001] surface direction.

For adsorbates which interact strongly with the substrate, the chemisorption process is often accompanied by the breaking of several nearest-neighbor bonds within the substrate lattice, resulting in a reconstructed surface phase with a substantially altered atomic density in the topmost layer. The microscopic mechanism for nucleation and growth of such adsorbate-induced reconstructions is still open for vigorous dispute. Oxygen chemisorption on Cu surfaces is a prototype of this category of reconstructions which has recently provoked a considerable experimental and theoretical interest.¹⁻⁸

Using scanning-tunneling-microscope (STM) results, we will show in this Communication that the nucleation and growth of the Cu(100)- $(2\sqrt{2} \times \sqrt{2})R45^{\circ}$ -O reconstructed phase proceeds via formation of islands created by "squeezing out" every fourth [001] surface row. These extra Cu atoms form epitaxial islands on top of the Cu surface. This growth mode deviates dramatically from the formation of the oxygen-induced (2×1) reconstruction on the Cu(110) surface.²⁻⁴ A simple picture evolves in which both reconstructions are stabilized by Cu-O-Cu chains directed along the [001] surface direction.

The chemisorption of oxygen on Cu(100) has been studied extensively over the past twenty years.⁶ Molecular oxygen chemisorbs dissociatively on Cu(100), and it has been suggested that two superstructures occur: For low oxygen coverage, a $(\sqrt{2} \times \sqrt{2})R45^\circ$ or, equivalently, a $c(2\times2)$ structure was observed which developed into a $(2\sqrt{2}\times\sqrt{2})R45^\circ$ structure at higher oxygen exposures or at elevated temperature. However, the information obtained by different structural techniques often seemed conflicting. Many studies concentrated on the $c(2\times2)$ structure for which it was assumed and reported that no restructuring occurred,⁹ and models were proposed with the oxygen at several different adsorption sites.¹⁰⁻¹⁴

Very recently, the experimental situation was clarified in the sense that low-energy electron diffraction (LEED) studies proved the $c(2\times2)$ structure to be absent.^{6,15} The $(2\sqrt{2}\times\sqrt{2})R45^{\circ}$ structure, with an oxygen saturation coverage $\Theta = 0.5$ ML (monolayer),⁶ is thus the only well ordered and thermodynamically stable structure, and based on a multiple-scattering analysis of LEED intensities,⁷ it was concluded that this phase is consistent with a missing-row-type reconstruction.

The present experiments were performed with a fully automated STM described earlier.^{16,17} The images shown below, recorded in the constant-current mode, are typically obtained in 3–10 sec. The bias voltage (V_t) is applied to the sample with the tip at virtual ground, and normally electrons are tunneling from filled tip states to empty sample states. The initial calibration of the lateral STM scans was derived from the atomic resolution obtained on the reconstructed Si(111)-(7×7) surface, and the z calibration from a single-layer step on the same surface. The Cu(100) surface was prepared as the Cu(110) surface,³ using standard techniques.

Figure 1(a) shows an STM image of the Cu(100) surface prior to oxygen exposure. As seen, we are indeed able to resolve the single Cu atoms on the (1×1) surface. The corrugation along a (011) surface row is quite small (≈ 0.1 Å). This image serves to determine the orientation of the crystal.

To create a fully developed $(2\sqrt{2} \times \sqrt{2})R45^{\circ}$ -O structure, with a sharp LEED pattern, the Cu(100) surface was exposed to 1000 L oxygen at 300 °C and at a pressure of 2.5×10^{-6} mbar, followed by an anneal at 300 °C for 5 min.^{6.7} [1 langmuir (L)=10⁻⁶ Torrsec.] Figure 1(b) shows a topograph of this surface over an area of 15×15 Å². The [001] and [010] directions are equivalent on the Cu(100) surface, and thus the reconstruction is twinned into two different domain orientations which appear to be randomly distributed [Fig. 3(b) below]. In the following, we shall for simplicity use the orientational notation shown in Fig. 1(b).

The chains of bright spots along the [001] direction have a corrugation and periodicity of ≈ 0.2 and 3.6 Å, respectively, the latter being the interatomic distance along the [001] direction. The chains appear to be grouped in pairs of two, and the distances from A to B and from B to C are 2.9 and 4.3 Å, respectively, implying that the structure in the [010] direction repeats itself for every 7.2 Å. This allows us to superimpose a unit cell on Fig. 1(b). The number of bright spots within the unit cell is equal to the number of oxygen atoms, given that $\Theta = 0.5$ ML. We interpret the chains of bright spots along the [001] direction as Cu-O-Cu chains or bonds, equivalent to the obser-

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FIG. 1. (a) Atomically resolved STM topograph ($V_t \approx 0.8$ V and $I_t \approx 1.4$ nA) of a 15×15 -Å² region of a bare (1×1) Cu(100) surface. (b) STM topograph ($V_t \approx 0.01$ V and $I_t \approx 3.8$ nA) of a 15×15 -Å² region for a fully developed ($2\sqrt{2} \times \sqrt{2}$)R45° structure. The height scale from black to white correspond to 0.3 and 0.45 Å for (a) and (b), respectively; surface protrusions are white, while depressions are black. (c) Atomistic model of the Cu(100)-($2\sqrt{2} \times \sqrt{2}$)R45°-O reconstructed phase. The small and large white circles represent the O atoms and the remaining Cu surface atoms, respectively, whereas the grey and dark circles represent Cu atoms in the second and third layers, respectively. The arrows indicate the missing rows of Cu atoms. In (b) and (c) a unit cell is shown.

vations for the Cu(110)-(2×1)O structure.³ Along the [010] direction, the resulting periodicity of 7.2 Å can be explained by removal of every fourth row of Cu atoms, as will be discussed shortly (Fig. 2). We will return to the details of this image [Fig. 1(b)] and the correlation with an atomistic model of the Cu(100)-($2\sqrt{2} \times \sqrt{2}$)R45°-O reconstructed phase, Fig. 1(c).

An important question, which has not been addressed before, concerns the nucleation and growth mode of this reconstructed phase. Figure 2 shows two terraces separated by a monatomic step. This step was imaged continuously (every ≈ 10 sec) during oxygen exposure at RT at a pressure of 1.5×10^{-5} mbar. When the oxygen is adsorbed at RT a higher exposure is required before saturation $\Theta = 0.5$ ML occurs.⁶ Figures 2(a)-2(d) were recorded prior to [Fig. 2(a)] and after [Figs. 2(b)-2(d)] oxygen exposures of 1.6×10^4 , 2.4×10^4 , and 6.2×10^4 L, respectively. From these three topographs, we immediately conclude that the dramatic change depicted in the topographs reflects the nucleation and growth of small islands on both terraces, whereas the step is essentially intact. The islands grow preferentially along the [010] and [001] directions, at saturation [Fig. 2(d)] they cover 25% of the surface area as determined from a plot of the height distribution, and their height is 1.8 Å [the interatomic-layer distance for Cu(100)].¹⁸ These observations give the first direct proof that oxygen-induced reconstruction of the Cu(100) surface is of the missing-row type, with one quarter of the Cu[001] rows missing, and that these extra atoms nucleate and grow epitaxially in small islands on top of the Cu surface. The LEED pattern after RT oxygen saturation was a diffuse $(2\sqrt{2} \times \sqrt{2})R45^\circ$, but after an anneal to $\approx 300^\circ$ C for ≈ 5 min, the fairly small islands in Fig. 2(d) have agglomerated, as seen in Fig. 3(a), and the LEED pattern has become a bright $(2\sqrt{2} \times \sqrt{2})R45^\circ$.

One might wonder why the Cu islands nucleated at RT did not grow into larger ones. This may be explained by the fact that in between the nucleated Cu islands, the surface is reconstructed to the $(2\sqrt{2} \times \sqrt{2})R45^{\circ}$ structure, consisting of Cu-O-Cu chains, and these chains reduce the surface diffusion of Cu, as observed for the Cu(110)- $(2 \times 1)O$ reconstructed phase.³ When the surface is saturated with oxygen at RT, the nucleated Cu islands also become reconstructed [Fig. 3(b)]. This figure also displays the two different domain orientations of the reconstruction. It is the existence of these two domain orientations which explains the domain structure of the nucleated Cu islands, i.e., why they grow preferentially along the [010] and [001] directions.

In the early stages of the oxygen adsorption at RT or



FIG. 2. Series of STM grey-scale topographs ($I_t \approx 1.2$ nA and $V_t \approx 0.15$ V) over an area of 500×500 Å², showing the dynamic nucleation and growth of the reconstructed phase. The surface was imaged while exposed to O₂ at RT to a pressure of 1.5×10^{-5} mbar. (a)-(d) were recorded (a) prior to and (b)-(d) after oxygen exposures; cf. text. The height scale is 4.5 Å from black to white. A small drift is observed in the STM topographs corresponding to ≈ 1 Å/min.



FIG. 3. For the inclined view STM images [(a) and (b)] ($V_t \approx 0.2$ V and $I_t \approx 2.0$ nA), the surface was saturated with O₂ at RT and (a) annealed at 300 °C for 5 min, showing the agglomeration of the islands in Fig. 2(d) over a 1500×1500-Å² region, and (b) imaged with higher magnification, 100×100-Å² region, showing that the surface is reconstructed in between and on top of the Cu islands. In image (c), recorded after 100 L exposure at 500 K, the disordered regions are shown to coexist with the ordered $(2\sqrt{2} \times \sqrt{2})R45^\circ$ phase, 150×150 Å² and $V_t \approx 0.2$ V and $I_t \approx 0.9$ nA. For all three images the z scale is 1 Å/div.

after a low exposure (≈ 100 L) at 300 °C, i.e., before the Cu islands start to nucleate, we observe [Fig. 3(c)] a disordered structure which coexists with the ordered $(2\sqrt{2}\times\sqrt{2})R45^\circ$ phase, consistent with the fact that the LEED pattern in this case was a very faint $(2\sqrt{2})$ $\times \sqrt{2}$ R45°. One might speculate that in the earlier stages of the chemisorption, the impinging oxygen molecules dissociate and are adsorbed at the Cu surface. It is energetically favorable for the O-Cu surface to reconstruct since the energy cost to break the Cu-Cu bonds (0.3 eV) is smaller than the gain in chemisorption energy of O atoms to the reconstructed relative to that for the unreconstructed surface (1.4 eV).¹ The oxygen adsorbates thus locally break the Cu bonds, causing a local "roughening" of the surface. Initially the disrupted Cu bonds are so far apart that the reconstruction cannot proceed, and only at a higher oxygen coverage will the O-induced Cu-bond breaking be shared in a collective fashion, and the surface restructures to its lowest energy state in a sizable area. From then on, further chemisorption causes the reconstructed area to grow in size at the expense of the disordered phase. This disordered phase was also suggested from LEED studies, but Wuttig, Franchy, and Ibach⁶ concluded that it did not coexist with the ordered $(2\sqrt{2} \times \sqrt{2})R45^{\circ}$ structure, which occurred spontaneously at $\Theta = 0.34$ ML. This is clearly inconsistent with the present direct observations [Fig. 3(c)].

It is natural to compare the reconstruction of the Cu(100) surface with the Cu(110)- $(2 \times 1)O$ reconstructed phase. For both surfaces, we observe the formation of Cu-O-Cu chains oriented along the [001] surface direction, but the nucleation and growth of the two reconstructions deviate significantly. For the Cu(110) surface, it was found that Cu, removed from step edges, reacted with diffusing oxygen species, and formed Cu-O-Cu chains or "added" rows oriented along the [001] direction. $^{2-4}$ In this case no disordered structure was observed. This seems natural since nucleation of "added" rows does not involve the underlying Cu surface. For the Cu(100) surface, we again observe Cu-O-Cu chains directed along the [001] direction, but the surface transformation now proceeds by "squeezing out" 25% of the Cu[001] surface rows which then nucleate into Cu islands. While the

former process can be considered a two-dimensional precipitation and condensation of a solid phase from a mixed fluid phase, the latter process can be regarded as rather a two-dimensional solid-solid transformation, equivalent to the CO-induced structural transformations of Pt(110).¹⁹

The driving force for the oxygen-induced reconstruction on both surfaces might in fact be the formation of these Cu-O-Cu chains. This is supported by recent theoretical calculations based on the effective medium theory¹ which show that if the coordination number of the Cu atoms is decreased in the reconstruction process, this will lead to a rise in the position of the 3d level for these atoms. Consequently the antibonding levels, which result from the hybridization between the oxygen 2p state with the Cu 3dstates, are shifted above the Fermi level and emptied. This enhances the oxygen binding energy to the reconstructed surface by more than it costs to reconstruct the clean surface, thereby stabilizing the oxygen-induced reconstructions.

Finally, we return to the highly resolved STM topograph of the $(2\sqrt{2} \times \sqrt{2})R45^{\circ}$ structure [Fig. 1(b)]. Along the [010] direction, the observed periodicity of 7.2 Å can be explained by removing every fourth row of Cu atoms, consistent with the conclusion drawn from Fig. 2, with theoretical calculations¹ and with both LEED (Ref. 7) and x-ray diffraction⁸ experiments. The apparent height in STM images like, e.g., Fig. 2(b) is a convolution of surface topography and the electronic structure represented as the density of states near the Fermi level. In fact, we obtained only highly resolved images like Fig. 1(b) for very low V_t , and we tentatively interpret the bright spots along the [001] direction as the antibonding states for the Cu-O-Cu bonds. These antibonding states are fairly delocalized along the [001] direction, and thus we cannot associate the white protrusions with either O or Cu atoms but only as a result of the Cu-O-Cu bonds. The pairing of the Cu-O-Cu chains in the [010] direction can be explained by displacing the Cu and/or O atoms next to the missing row ≈ 0.35 Å towards the missing row, consistent with the recent experimen $tal^{7,8}$ and theoretical¹ findings.

In conclusion, the direct imaging by the STM enables us to study the dynamics of the nucleation and growth of the Cu(100)- $(2\sqrt{2} \times \sqrt{2})R45^{\circ}$ -O reconstructed phase by imaging the surface with atomic resolution during oxygen adsorption. Apart from being of utmost interest in itself, the dynamic information gained by the STM investigations appears to be very crucial also for the subsequent understanding of the static surface structure.

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