Long-Range Spatial Self-Organization in the Adsorbate-Induced Restructuring of Surfaces: Cu{110}-(2 × 1)O

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He diffraction and scanning-tunneling-microscopy investigations on the growth of the Cu{110}-(2×1)O added-row structure reveal a novel phenomenon: the long-range spatial self-organization of two-dimensional islands. In a wide coverage range the anisotropic Cu-O islands arrange themselves in a striped periodic supergrating, with the stripes running along the ⟨001⟩ direction. The spacing of the supergrating depends on oxygen coverage and temperature and varies between 140 and 60 Å.

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The adsorbate-induced restructuring of surfaces, originally proposed by Langmuir in 1916 [1], has been the subject of numerous experimental and theoretical investigations in the past two decades [2,3]. Oxygen on the {110} and {100} surfaces of Cu are among the best studied systems [3]. In his pioneering work Ertl [4] showed that the (2×1) and $c(6\times2)$ LEED patterns of the Cu{110} surface observed upon adsorption of oxygen are due to alternations of the unit cell by displacements of Cu substrate atoms. Nevertheless, it took more than twenty years until a consensus on the structure and the growth mechanism for the oxygen-induced (2×1) reconstruction of Cu{110} was reached.

Detailed scanning-tunneling-microscopy (STM) [5] studies revealed that the (2×1) phase is formed by aggregation of mobile oxygen atoms on terraces with Cu adatoms diffusing in from step edges. Because of strongly attractive Cu-O interactions, long Cu-O strings are formed along the ⟨001⟩ direction on top of the substrate which act as nuclei for the growing reconstructed phase. With increasing oxygen coverage Cu{110}-(2×1)O islands grow by aggregation of Cu-O strings. At full coverage ($\Theta_O = 0.5$) the structure is identical to the earlier inferred missing-row structure [6] with the Cu-O strings 5.12 Å apart. In view of the formation process this structure is now more properly named the added-row structure [5].

With the successful STM work [5] the oxygen-induced restructuring of the Cu{110} surface was generally believed to be a closed matter. In the present Letter we will demonstrate that this assessment was premature; the oxygen-induced reconstruction of Cu surfaces continues to be a challenge for experimentalists and theorists.

The present Letter reports on a novel phenomenon in the spatial organization of two-dimensional Cu-O islands on a Cu{110} substrate. We have found that in a wide coverage range ($0.05 < \Theta_O < 0.45$) the (2×1)-reconstructed Cu-O island stripes consisting of eight to fourteen Cu-O strings arrange themselves in the form of a one-dimensional periodic grating with a spacing varying between 60 and 140 Å. The periodic supergrating forms properly both upon oxygen exposure while keeping the Cu surface at $T > 450$ K or by room-temperature exposure and subsequent annealing at $T > 450$ K.

The results reported here are based on high-resolution He diffraction and scanning-tunneling-microscopy measurements. The experiments have been performed in two separate experimental setups with two different Cu{110} samples cut from different Cu single-crystal rods.

The diffraction data below have been obtained with the UHV high-resolution He-scattering spectrometer described in detail in Ref. [7]. The wavelength of the incident beam in the present experiments was 1.06 Å at a monochromaticity of $\Delta\lambda/\lambda = 0.007$.

The real-space images have been obtained with an UHV version of the "beetle-type" scanning tunneling microscope in the constant-current mode [8]. The He-diffraction patterns and the STM images were recorded at room temperature. The cooling time from the annealing temperature was a few minutes.

Both Cu samples were cut by spark erosion and then carefully polished. The crystal orientation was determined by Laue backreflection to be within 0.2° of {110} for both samples. The Cu{110} surfaces were cleaned by successive cycles of sputtering with Ar ions and heating. The quality of the surface was checked by Auger electron spectroscopy (AES), LEED, and He reflectivity. Oxygen was adsorbed by exposing the Cu{110} surface to an O_2 background pressure of 2×10^{-9} mbar. When the desired coverage was reached the oxygen atmosphere was pumped off.

In Fig. 1 we show a He-diffraction pattern from the Cu{110}-(2×1)O surface at an oxygen coverage of $\Theta_O = 0.28$ [$\Theta_O^{sat} = 0.5$ refers to the full (2×1) coverage] obtained by exposing the clean Cu sample at 640 K to 1.8 L [1 langmuir (L) $= 10^{-6}$ Torr s] oxygen. The plane of incidence of the He beam is along the ⟨1$\bar{1}$0⟩ direction, i.e., normal to the Cu-O strings. The expected parts of the diffraction pattern consist of the specular peak and the weak and broad half-order diffraction peak at $Q = 1.23$ Å^{-1}. The latter originates from the doubled periodicity along the ⟨1$\bar{1}$0⟩ direction of the Cu-O islands with the (2×1) structure. Unexpected are the four additional dif-

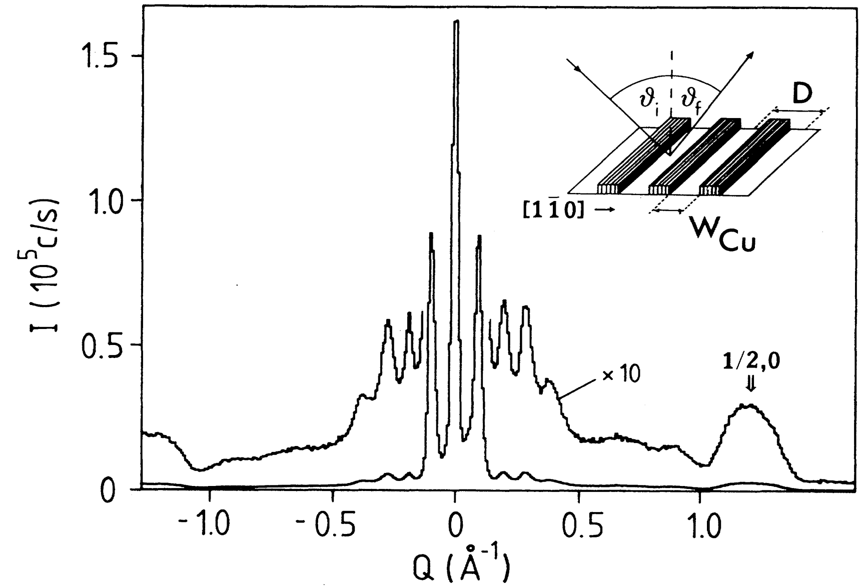

FIG. 1. He-diffraction pattern from a Cu{110}-(2×1)O surface at an oxygen coverage of $\Theta_O = 0.28$. The He wavelength was $\lambda_{He} = 1.06$ Å. Inset: Sketch of the scattering arrangement.

fraction peaks at wave vectors $|Q| = 0.094$, 0.188, 0.283, and 0.377 $Å^{-1}$. Note the sharpness of these peaks and the high intensity of the first one (about half the intensity of the specular beam). The location of the diffraction maxima at each side of the specular peak corresponds to a periodicity of $D = 2\pi n/|Q| = 66.7$ Å in real space.

The diffraction pattern can be explained if we assume that the reconstructed Cu-O islands, consisting of Cu-O strings spaced by 5.12 Å, arrange themselves in stripes of nearly equal width running along the ⟨001⟩ direction, which in turn are regularly spaced. These stripes separated by clean Cu areas form a periodic supergrating with a spacing of 66.7 Å. This is sketched schematically in the inset of Fig. 1.

The He-diffraction pattern from such a surface grating is particularly simple. The clean Cu{110} stripes reflect the helium beam almost mirrorlike, while the Cu-O islands have a 1-order-of-magnitude lower reflectivity. [This results from a comparison of the He reflectivities of the clean Cu{110} and of the saturated Cu{110}-(2×1)O surface.] The diffraction pattern is, therefore, analogous to that of light scattered by a periodic grating with broad slits, as discussed in most elementary textbooks. Here, the highly reflective Cu{110} stripes correspond to the slits, while the poorly reflecting Cu-O island stripes correspond to the opaque bars between slits. In the plane-wave approximation we obtain

$$I(\vartheta_i,\vartheta_f) = \frac{1}{N^2}\left[\frac{\sin\beta}{\beta}\right]^2\left[\frac{\sin N\alpha}{\sin\alpha}\right]^2, \quad (1)$$

with $\beta = (k_{He} w_{Cu}/2)(\sin\vartheta_i - \sin\vartheta_f)$ and $\alpha = (k_{He} D/2) \times (\sin\vartheta_i - \sin\vartheta_f)$. Here, N is the number of Cu(110) stripes, k_{He} is the wave vector of the incident He beam, w_{Cu} is the width of the clean Cu{110} stripes in the [1$\bar{1}$0] direction, and D is the spacing of the grating.

All parameters entering Eq. (1) except for w_{Cu} are inferred either from the peak locations ($2\pi n/D$) or from the features of the instrument itself ($k_{He},\vartheta_i,\vartheta_f$). There are two independent ways to determine the width of clean Cu stripes, $w_{Cu} = D - w_{Cu\text{-}O}$. One is by measuring the oxygen coverage with Auger spectroscopy. The errors can be kept as low as ~10% because only the ratio between the actual coverage Θ_O and the saturation coverage of the Cu{110}-(2×1)O is needed: $w_{Cu\text{-}O}/D = \Theta_O/\Theta_O^{sat}$. Alternatively, and much more sensitive with respect to the magnitude of w_{Cu} and thus of the oxygen coverage, there are the intensities of the peaks relative to the specular peak as given by Eq. (1). To this end Eq. (1) is evaluated at the position of the primary diffraction peaks (at which $\alpha = n\pi$). Simple algebra yields

$$I^n(\Theta_O) = \left[\frac{\sin[n\pi(1-2\Theta_O)]}{n\pi(1-2\Theta_O)}\right]^2, \quad (2)$$

showing that the relative intensity of the nth diffraction maximum is uniquely determined by the oxygen coverage Θ_O. Changes of only a few percent in Θ_O lead to dramatic changes in the relative intensities. Thus, from the best fit of Eq. (2) to the measured intensities from patterns like the one in Fig. 1, accurate values for Θ_O are obtained. In Table I, the measured and calculated relative intensities obtained for various oxygen exposures at 640 K are shown. Up to an oxygen coverage of $\Theta_O = \frac{1}{3}$ (i.e., for $w_{Cu\text{-}O} < 2w_{Cu}$) the agreement is remarkable in view of the crudeness of the model. Also shown are the corre-

TABLE I. Measured and calculated He-diffraction intensities from the Cu{110}-(2×1)O striped island grating as a function of oxygen coverage (see text).

Oxygen coverage		Measured diffraction intensity				Calculated diffraction intensity			
AES	Best fit of Eq. (2)	$n=1$	$n=2$	$n=3$	$n=4$	$n=1$	$n=2$	$n=3$	$n=4$
0.10	0.104	0.060				0.060	0.038	0.015	0.003
0.125	0.136	0.109				0.109	0.047	0.006	0.001
0.14	0.163	0.162				0.162	0.044	0	0.009
0.15	0.190	0.217	0.017	0.007		0.228	0.031	0.005	0.017
0.21	0.226	0.336	0.008	0.016		0.330	0.007	0.030	0.007
0.25	0.287	0.534	0.025	0.028	0.012	0.529	0.028	0.036	0.022
0.25	0.291	0.549	0.030	0.016	0.012	0.542	0.035	0.033	0.027
0.31	0.333	0.714	0.143			0.683	0.169	0	0.043
0.36	0.327	0.662	0.143			0.663	0.144	0.001	0.046

sponding best-fit oxygen coverages which are compared to the coverages as deduced from Auger spectroscopy. The agreement is very good too.

The spacing D of the striped grating, i.e., the average distance between neighboring Cu-O islands, depends on the average oxygen coverage as well as on the annealing temperature. This is shown in Fig. 2. At a given coverage the formation of the grating is kinetically hindered below ~600 K. Thus only weak and broadened first-order superstructure diffraction peaks are observed. With increasing annealing temperature the mobility of the islands increases and the system forms a more perfect grating with the spacing settling at about 65 Å (for $\Theta_O=0.25$). Figure 2(a) shows the dependence of the spacing D on coverage for layers which have all been annealed at a temperature high enough (640 K) to minimize kinetic effects. The spacing D appears to keep a minimum constant value around 65 Å in the range $0.20<\Theta_O<0.35$ and to increase steeply outside this range.

The picture of the spatial self-organization of the Cu-O islands revealed by He diffraction is corroborated in all details by real-space images obtained with a scanning tunneling microscope. Figure 3 shows two STM images of the surface. In the image of Fig. 3(a) the Cu(110) surface was exposed to 2 L of oxygen at ~550 K, resulting in a coverage of $\Theta_O=0.26$. Over more than 1000 Å the Cu-O islands appear as dark regularly spaced stripes of nearly equal width, clearly visualizing the long-range spatial self-organization [9]. The spacing of $D=86$ Å is in good agreement with the values deduced from diffraction measurements in Fig. 2. Most astonishing, the striped grating even extends practically undisturbed across monatomic steps on the Cu substrate.

An STM image with atomic resolution is shown in Fig. 3(b). Here, the Cu sample was dosed with about 5 L of oxygen ($\Theta_O\approx 0.4$) at a temperature of ~600 K. The (2×1) lattice in the reconstructed Cu{110}-(2×1)O is-

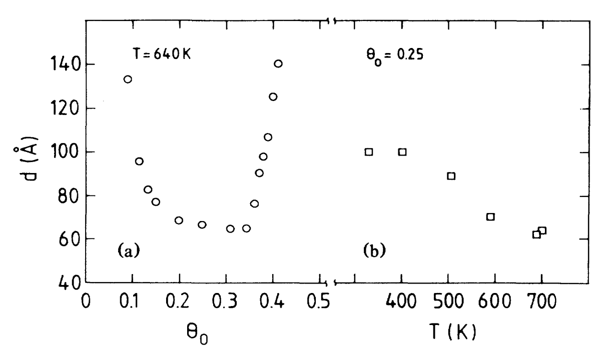

FIG. 2. Spacing of the island supergrating as a function of oxygen coverage and temperature.

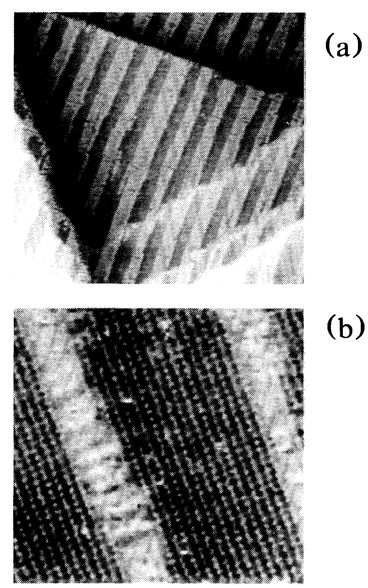

FIG. 3. STM images of the Cu{110}-(2×1)O surface at two coverages. (a) 930×930-Å^2 image at an oxygen coverage of $\Theta_O=0.26$ (annealing temperature ~550 K); tip bias −0.78 V, tunneling current $I=1$ nA. Dark stripes, Cu{110}-(2×1)O islands; bright stripes, clean Cu{110}-(1×1) areas. (b) 154×154-Å^2 image at an oxygen coverage of $\Theta_O=0.38$ (annealing temperature ~600 K); tip bias ±0.06 V, $I=1$ nA.

lands is clearly resolved showing the unit cell of 5.12 Å in the $\langle 1\bar{1}0\rangle$ and 3.6 Å in the $\langle 001\rangle$ direction. Each island consists of about fourteen Cu-O strings and the islands are regularly spaced at $D=100$ Å, again in agreement with the spacings deduced from the corresponding diffraction measurements in Fig. 2.

In addition, STM images taken at low oxygen coverage show that initially Cu-O strings are formed which then tend to aggregate in stripes. The same tendency has also been observed in previous STM measurements in which, however, the oxygen adlayer has not been annealed above room temperature [5]. Annealed layers, such as those investigated in the present experiments, show two additional decisive features which lead to the formation of the periodic supergrating and its particular behavior: The aggregation appears to saturate when the stripes contain eight to twelve strings *and* each stripe as a whole seems to repel its neighbor stripes so that they become more or less equidistant. This explains the steep increase of the supergrating spacing at low coverages [Fig. 2(a)] where the number of stripes consisting of eight to twelve Cu-O strings is simply limited by the lack of oxygen atoms. It seems that at high coverage ($\Theta_O > \frac{1}{3}$), where the repulsion between stripes becomes important, the increase of the individual stripe width by aggregation of Cu-O strings is resumed [e.g., in Fig. 3(b) the stripes consist of about fourteen strings]. This leads to the sharp increase of the spacing towards high coverages. Note that the onset of this increase at $\Theta_O = \frac{1}{3}$ coincides with the breakdown of the good fit of the peak intensities by Eq. (2) in Table I.

In summary, we have shown that at temperatures above 450 K the islands formed during the growth of the Cu{110}-(2×1)O added-row phase arrange themselves into regularly spaced stripes, forming a periodic supergrating. There seem to be three interaction regimes present in this very unique chemisorption system. Along the $\langle 001\rangle$ direction there is a strongly attractive short-range interaction between Cu and O atoms, giving rise to the formation of long and stable Cu-O strings already at very low oxygen coverage. In the island formation process these strings are held together by medium-range attractive forces along $\langle 1\bar{1}0\rangle$ forming long Cu-O stripes. A long-range repulsive interaction orders the anisotropic Cu-O island stripes in a periodic grating. The saturation of the aggregation process of the Cu-O strings and the very long range of the repulsion forces between stripes might point towards substrate-mediated elasticity as an explanation of this novel surface phenomenon. We are anxiously awaiting a founded theoretical explanation.

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[9] As already shown by Coulman *et al.* [5], at low bias voltages (also used in this investigation) the Cu{110}-(2×1)O islands appear as dark areas with an apparent "depth" of up to 0.4 Å. Thus, the relative height of (2×1) to clean Cu-(1×1) areas is not governed by a topographic effect but instead by the oxygen-induced change of the local electronic structure on the Cu sample. New He-interference measurements [P. Zeppenfeld, J. Goerke, K. Kern, and G. Comsa (to be published)] show that the actual height of the Cu{110}-(2×1)O islands above the bare substrate is about 1.4 Å. This indicates that the islands are one monolayer thick (the interlayer spacing of the clean Cu{110} surface is 1.27 Å).

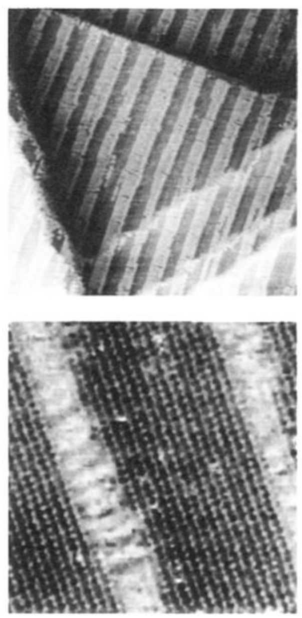
(a)
(b)

FIG. 3. STM images of the Cu{110}-(2×1)O surface at two coverages. (a) 930×930-Å^2 image at an oxygen coverage of Θ_O=0.26 (annealing temperature ~550 K); tip bias −0.78 V, tunneling current I=1 nA. Dark stripes, Cu{110}-(2×1)O islands; bright stripes, clean Cu{110}-(1×1) areas. (b) 154×154-Å^2 image at an oxygen coverage of Θ_O=0.38 (annealing temperature ~600 K); tip bias ±0.06 V, I=1 nA.