

Oxygen-induced reconstructions on Cu(211)

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The chemisorption of oxygen on the vicinal Cu(211) surface and the subsequent reconstructions have been studied by means of He-atom scattering, spot profile analysis–low-energy electron diffraction, scanning tunneling microscopy, and Auger-electron spectroscopy. At temperatures below 250 K oxygen adsorbs without any pronounced ordering whereas at elevated temperatures above 300 K the surface starts to reconstruct and the formation of double steps occurs. Several ordered superstructures have been identified that depend on the thermal activation. The double steps are thermally stable up to 800 K. Experiments for very low oxygen coverages indicate that the reconstruction starts initially at the step edges and involves later subsurface oxide formation. Preliminary measurements for a regularly kinked surface reveal a similar oxygen-induced reconstruction. [S0163-1829(98)10439-3]

I. INTRODUCTION

Knowledge of the detailed processes of surface oxidation is of key importance for an understanding of corrosion.¹ Moreover, the metal oxidation is of interest for a number of technological processes in the fabrication of metal-insulator interfaces (e.g., metal-oxide-semiconductor technology).² A particular interest in copper oxides has been stimulated by the recent progress in the metal-oxide-based high-temperature superconductors.³

Previous studies of the oxidation of Cu(100) and Cu(111) (Ref. 4) surfaces revealed a small initial sticking coefficient $s(0)$ for oxygen. Considering $s(0)$ as a measure for the reactivity of a substrate with respect to a certain adsorbate the more open surfaces [e.g., Cu(110)] appear to be much more reactive since their sticking coefficient is by two orders of magnitude higher than for the close packed Cu(111) substrate [$s(0)=10^{-3}$ and $s(0)=0.2$ for Cu(111) and Cu(110), respectively⁴]. For all low indexed copper surfaces complex oxide superstructures were observed that are sometimes interpreted in terms of bulk-terminated copper oxide surfaces.⁵ Vicinal surfaces can be used as model systems to study the influence of atomic defects (like vacancies and steps) on the chemisorption and oxidation on “real” surfaces. The step density on such highly ordered regularly stepped surfaces can be controlled by their macroscopic orientation (i.e., by the choice of the angle with respect to the low indexed terrace). However, studies of surface chemical reactions on an atomic scale are further complicated by possible adsorbate-induced reconstructions that have been obtained for a number of adsorbate systems. Especially, for regular stepped metal surfaces with close packed [e.g., fcc(111) oriented] terraces an oxygen-induced transition from monatomic to double-height steps has been obtained for various metals

(Cu,Pt,Rh,Ni).^{6–10} On the other hand, for the more open stepped surfaces [e.g., (100) or (110) oriented terraces] an oxygen-induced faceting appears.^{11–14} These phenomena are attributed to the small difference in the surface free energy between the low indexed surface and the vicinal surface, compared to the relatively large binding energy of the oxygen (i.e., >4 eV), which adsorbs predominantly at the steps.^{5,15}

In the present study we have investigated the oxygen-induced reconstruction of the Cu(211) surface. As shown in Fig. 1(a) the bare Cu(211) surface consists of three-atom-rows-wide (111) terraces separated by monoatomic steps running along the close-packed [011] direction with a distance of 6.25 Å. The chemisorption of oxygen on this particular surface and the subsequent double step reconstruction at room temperature was first observed in a pioneering x-ray photoelectron diffraction (XPD) and low-energy electron diffraction (LEED) study by Thompson and Fadley.⁶ They demonstrated that on the reconstructed surface the oxygen occupies fourfold hollow sites at the bottom of the double height steps.

Here we report on a refined study of the coverage and temperature dependence of the oxygen-induced reconstructions and their activation, which was carried out by means of He-atom scattering (HAS), spot profile analysis LEED (SPA-LEED), scanning tunneling microscopy (STM), and Auger-electron spectroscopy (AES). From the combination of the complimentary diffraction and microscopy techniques information about the periodic and local oxygen superstructure are deduced. The low oxygen coverage STM measurements, especially, reveal information about the initial steps of the oxidation. Additional SPA-LEED measurements for the Cu(532) surface, which is basically a regularly kinked (211) surface, indicate that oxygen-induced double step

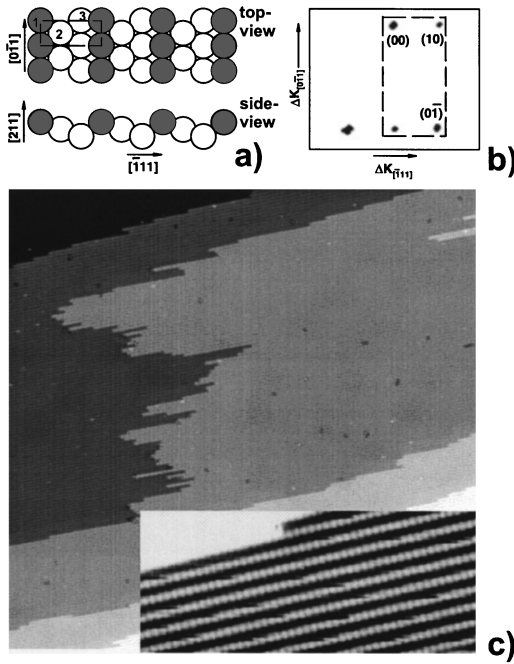


FIG. 1. (a) Hard-sphere model of the Cu(211) surface. The unit cell is marked by a dashed line. (b) SPA-LEED pattern recorded at $T_s = 90$ K from the Cu(211) substrate ($E = 76$ eV). (c) A 1000×1000 Å STM-topograph recorded from the bare Cu(211) surface at $T_s = 80$ K. The inset shows an atomically resolved STM image (55×130 Å) measured at $T_s = 40$ K. In both cases a voltage of 0.2 V was applied, the tunneling current amounted to 0.1 and 1 nA for the large image and the inset, respectively.

formation takes place also for this type of surface.

The paper is organized in the following way. First we describe briefly the various techniques used in this study. In Sec. III we recall first the structural characterization of the bare Cu(211) surface and then report the observed oxygen-induced reconstructions on Cu(211). This section closes with a presentation of results concerning the clean and oxygen covered Cu(532) surface. In Sec. IV we summarize the results and discuss them in the context of the stability of stepped surfaces upon oxygen chemisorption.

II. EXPERIMENTAL SETUP

The present HAS, SPA-LEED, and STM experiments have been carried out in three separate UHV setups. Since all of these machines have been described in connection with various studies on the clean and adsorbate covered Cu(211) surface they are mentioned here only briefly.

Basically, the HAS apparatus¹⁶ allows the angular and time-of-flight resolved detection of thermal energy He atoms scattered from the surface. The energy of the nearly monoenergetic He beam ($\Delta E/E < 2\%$) is determined by the supersonic nozzle temperature and can be varied between $E_i = 10$ – 100 meV. In-plane He-atom diffraction scans are recorded by rotating the sample with respect to the incident He-atom beam. Extensive measurements of the He diffraction intensities for the clean Cu(211) and Cu(511) surfaces were reported in a previous study and have been compared with close-coupling scattering calculations to determine the lateral corrugation of the He-surface interaction potential at

the steps.¹⁷ Moreover, high-resolution inelastic He-atom scattering has been used to study the phonon dynamics of these surfaces and to determine the nature of step-localized phonon modes.¹⁸

The SPA-LEED measurements were carried out in a separate UHV apparatus, which is described in detail in connection with a previous study of cesium adsorption on Cu(211) and Cu(511) surfaces.¹⁹ For the present study LEED patterns for electron energies between 40 and 200 eV have been recorded with a resolution of up to 100 pixels per Å⁻¹ and a beam current of 80 nA. Depending on the gate time and image size the recording of each pattern took 5–30 min. The dynamical range of the LEED system amounts to 10^5 .

The scanning tunneling microscope experiments were performed with a low-temperature STM operated at 30–100 K.²⁰ Its capability to resolve single CO molecules or lead atoms adsorbed on the Cu(211) surface and their controlled manipulation has been demonstrated in several previous studies.^{21–23} The STM images were taken for tunneling currents between 100 pA and 5 nA. The bias voltages given in the paper refer to the sample voltage with respect to the tip.

The copper samples which have been oriented and polished to within $\pm 0.1^\circ$ of the desired orientation were prepared in all three UHV systems by repeated cycles of Ar⁺-ion sputtering (750 eV) and subsequent annealing to 800 K. After several cycles no further narrowing of the He-atom and/or electron diffraction peaks were achieved and contamination levels of less than 1% of a monolayer were found in the recorded Auger-electron spectra.

The oxygen exposure was carried out by backfilling the sample chamber to a pressure of 5×10^{-9} mbar. To distinguish between coverage dependence and thermal activation of the reconstructions the surface was first exposed to oxygen at a crystal temperature of 100 K and afterwards heated. The samples were dosed to oxygen exposures between 0.05 and 100 L ($1 \text{ L} \equiv 1 \times 10^{-6}$ mbar s).

III. RESULTS

A. Bare Cu(211) surface

Before reporting on oxygen experiments we recall briefly the results of the structural characterization of the bare Cu(211) surface to illustrate the various techniques employed in this study. The SPA-LEED pattern [Fig. 1(b)] reflects the rectangular shape of the nonprimitive surface unit cell, which contains three atoms denoted by 1, 2, and 3 in the hard-sphere model in Fig. 1(a). Figure 2(a) shows a typical HAS angular distribution recorded along the direction perpendicular to the step edges ($[\bar{1}11]$ azimuth). As in the SPA-LEED pattern the distance between the diffraction peak maxima reflects substantial features of the surface geometry, in this particular case the distance between adjacent step edges. In contrast to LEED, the large azimuthal anisotropy of the surface corrugation at the steps governs now the scattering process and causes very intense HAS diffraction peaks for scattering perpendicular to the step edges compared to the weak diffraction peak intensities observed for the azimuth direction along the step edges.¹⁷ From a quantitative analysis of both, the SPA-LEED and the HAS experiments the excellent order of the Cu(211) surface up to $T_s = 350$ K has been determined²⁴ and is well corroborated by

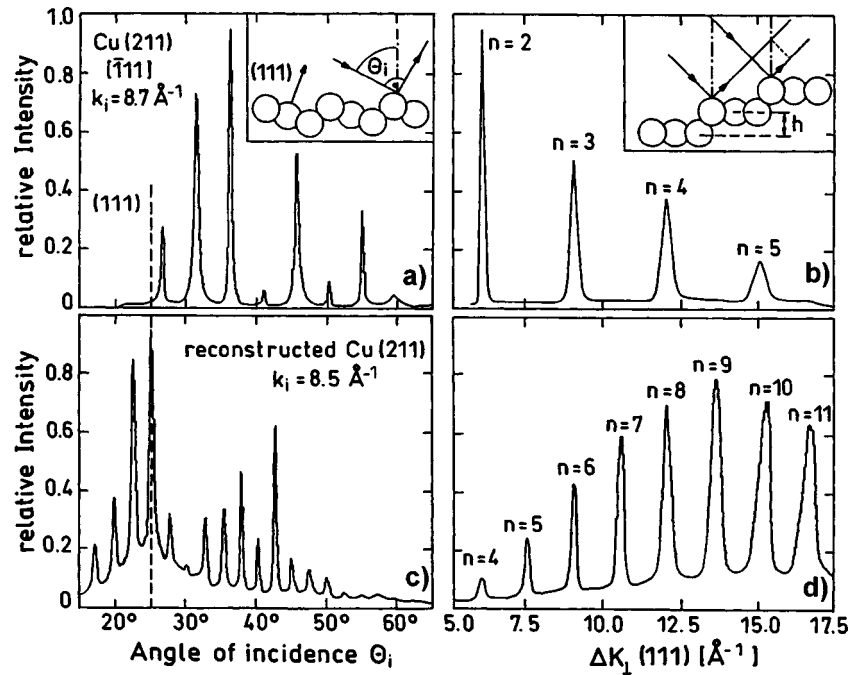


FIG. 2. (a) HAS angular distribution recorded along the $[\bar{1}11]$ direction. The intensity of the scattered He atoms is plotted as a function of the incident angle Θ_i (see inset). The vertically dashed line indicates the “terrace specular condition” ($\Theta_i = 25.75^\circ$, see text). (b) Drift spectrum measured from the bare Cu(211) surface. The variation of the terrace specular intensity is plotted as a function of the scattering vector K_\perp . The latter is parallel to the (111) direction in the geometry of the measurement illustrated in the inset. (c) Same as (a) but for a Cu(211) surface exposed to 1 L O_2 and annealed to $T_s = 750$ K. (d) Same as (b) but for a surface treated by O_2 as described in (c). All scans were recorded at $T_s = 100$ K.

STM measurements. Typical STM topographs recorded at low temperature (< 100 K), as shown in Fig. 1(c), display large, more than 500-Å-wide terraces consisting of nearly perfectly ordered step edges running along the $[0\bar{1}1]$ direction. Closer inspection of the atomically resolved image [shown as inset of Fig. 1(c)] confirms the existence of undisturbed (i.e., kink free) step edges over distances of more than 125 Å as well as the excellent correlation between adjacent step edges. At this point we note that, in contrast to the behavior at low temperatures, at room temperature copper kink atoms are mobile. Enhanced mobility of step edge atoms has been extensively studied for several stepped copper surfaces²⁵ and affects significantly the behavior of adsorbed atoms on this surface.

Moreover, from the He-atom scattering information about the average vertical order of the sample (i.e., the step height distribution) can be deduced. In formal analogy of the LEED $I(V)$ curves the intensity of the HAS specular peak is recorded as a function of the incident wave vector^{16,17} k_i and the resulting intensity variation can be attributed to constructive and destructive interference between He atoms scattered from various height levels of the surface (in contrast to LEED, where these intensity variations are predominantly caused by the bulk layer stacking at the surface). A typical example of such a HAS “drift” measurement is shown as a function of the size of the scattering vector along the (111) direction, $K_\perp(111)$, together with the kinematics of the experiment in Fig. 2(b). The recorded intensity is not corrected for the decrease of the incident He flux with increasing nozzle temperature and thus with increasing $K_\perp(111)$. An incident angle of $\Theta_i = 25.75^\circ$ with respect to the (211) nor-

mal was chosen for recording the spectrum. This assures the scattering vector \mathbf{K} to be parallel to the terrace normal [indicated by a vertically dashed line in the inset of Fig. 2(b)], which is oriented along the (111) direction: $\mathbf{K} = \mathbf{K}_\perp(111)$. From the separation $\Delta K_\perp(111)$ between adjacent intensity maxima, the step height h [see Fig. 2(b)] can be easily calculated using the formula $h = 2\pi/\Delta K_\perp(111)$. The determined value of $h = 2.03(\pm 0.05)$ Å is in very good agreement with the expected interplanar bulk separation of $h_{(111)} = 2.08$ Å. The absence of any intermediate maxima and the low diffraction intensity at the out-of-phase conditions indicates the absence of larger step heights.

The STM line scans perpendicular to the step edges reveal a corrugation amplitude of about 0.3 Å. A similar value of about 0.5 Å was determined from an analysis of extensive He-atom diffraction intensity measurements in the frame of close-coupling scattering calculations.¹⁷ The corrugation amplitudes probed in both techniques are thus significantly smaller than the *geometric* corrugation amplitude of 1.47 Å. This might be explained by the comparable large distance of the He-atom turning point and tip-surface distance of several Å and/or by possible charge redistribution at the steps mainly governed by the Smoluchowski effect.²⁶

B. Oxygen-induced reconstructions of Cu(211)

Figure 2(c) shows a HAS angular distribution for the direction perpendicular to the step edges ($[\bar{1}11]$ azimuth) taken from the Cu(211) surface exposed to 1 L O_2 at $T_s = 100$ K and subsequently annealed to $T_A = 750$ K. Compared to the clean surface [Fig. 2(a)] new, half-order diffraction peaks

appear indicating a doubling of the distance between adjacent step edges. The corresponding drift spectrum for the oxygen exposed surface [Fig. 2(d)] reveals also additional intensity maxima on half-integer positions showing the presence of regularly diatomic step heights on the surface. Whereas the evaluation of the angular scan alone cannot completely rule out alternative structure models, such as, for example, missing-row-type reconstructions, the drift spectrum provides an important and decisive piece of information about the resulting step structure: an O_2 exposure as small as 1 L (even 0.5 L, as it will be demonstrated below) and subsequent annealing to $T_A \geq 500$ K is already sufficient to induce a well-ordered double step reconstruction of the entire Cu(211) surface. The observed doubling of the step heights and the separation between step edges as well, denoted by Cu(211)(2×1) in this paper, is in excellent agreement with the model suggested previously by Thompson and Fadley.⁶ According to their model the Cu(211)(2×1) surface is composed of (111) terraces consisting of five-atom rows wide terraces separated by double steps formed by small (100) facets, as illustrated in Fig. 3(a).

The comparable half-widths of the HAS diffraction peaks in the angular distributions and drift spectra of the single and double stepped surfaces in Fig. 2 suggest the preservation of the excellent long-range order of the Cu(211) surface after the reconstruction. The shape of the background in Fig. 2(c) with a maximum at $\Theta_i \approx 25^\circ$ is interpreted as a rainbow pattern. In contrast to the entirely step-edge dominated diffraction from the clean Cu(211) substrate¹⁷ [Fig. 2(a)] the larger terrace width of the reconstructed surface gives now rise to an additional contribution to the diffraction intensity along the (111) terrace specular direction. This effect was first observed by Lapujoulade and Lejay²⁷ in HAS experiments for a Cu(711) surface which consists of four-atom-rows-wide (100) oriented terraces similar to the present situation. This additional feature provides further evidence for an intact and undisturbed terrace structure of the Cu(211)(2×1) surface and thus supports the proposed structure model that the oxygen preferentially occupies fourfold sites at the step edges and that the terraces are oxygen free⁶ for low oxygen coverages [see Fig. 3(b)].

In view of the very complex oxygen induced faceting observed for several vicinal copper surfaces,^{13,28} the stability and long-range order of the Cu(211)(2×1) reconstruction has motivated us to investigate the aspects of oxygen adsorption on Cu(211) more in detail as a function of temperature and coverage using SPA-LEED, STM, and HAS.

Figure 4 summarizes a series of SPA-LEED patterns from the oxygen covered Cu(211) surface recorded for low (1 L) and high oxygen exposures (15 L), respectively, after different thermal treatments. For the low oxygen coverages a (1×1) SPA-LEED pattern with a gradual increased background due to disordered adsorbed oxygen persists for annealing temperatures below $T_A = 250$ K. Starting from $T_A = 300$ K weak additional peaks on the $(\frac{1}{2}0)$, $(\frac{1}{4}\frac{1}{2})$ and equivalent positions [cf. top of Fig. 4(a)] appear in the SPA-LEED images. After heating up to $T_A = 450$ K a well ordered SPA-LEED pattern emerges as shown in Fig. 4(a). Spots at the $(\frac{1}{2}0)$ or $(\frac{1}{2}1)$ position are in accordance with the double-step reconstruction. The remaining peaks, for

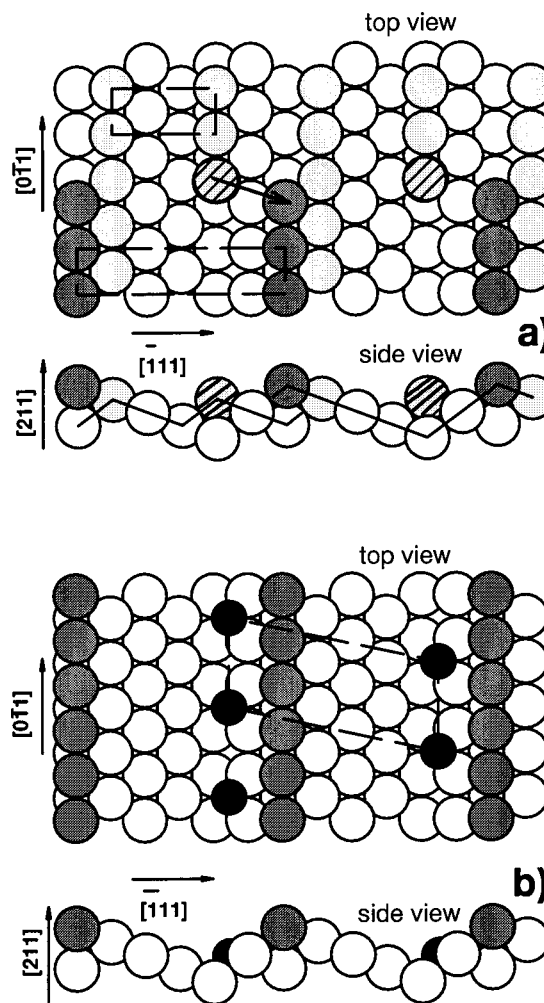


FIG. 3. (a) Top and side view of a hard-sphere model of the morphology of the unreconstructed, single stepped surface (upper part) and the reconstructed Cu(211)(2×1) surface (lower part) together with the corresponding unit cells (dashed lines). The hatched circles illustrate schematically the atoms that are shifted upon the reconstruction. (b) Top and side view of a hard-sphere model of the oxygen $c(2 \times 2)$ super structure. The small, black circles indicate the location of the oxygen atoms at the step sites.

example $(\frac{1}{4}\frac{1}{2})$ and $(\frac{3}{4}\frac{1}{2})$, indicate the existence of an ordered super structure on the surface that can be straightforwardly identified as a $c(2 \times 2)$ structure with respect to the Cu(211)(2×1) substrate. Figure 3 shows an arrangement of oxygen atoms (black circles) that coincides with a $c(2 \times 2)$ structure. According to Ref. 6 the oxygen atoms adsorb in step sites as shown in Fig. 3. This figure suggests, furthermore, an oxygen concentration of $\theta = 0.08$ on Cu(211)(2×1). Further heating at $T_A = 650$ K results in a gradual splitting of the $(\frac{1}{4}\frac{1}{2})$ and equivalent spots [Fig. 4(b)]. These spots vanish after annealing the sample to $T_A = 750$ K as shown in Fig. 4(c). The latter pattern corresponds to the HAS angular distribution and drift spectrum shown in Figs. 2(c) and 2(d). The absence of additional spots along the $[0\bar{1}1]$ direction resulting from the adsorbed oxygen under this condition is attributed to a disordered arrangement of the remaining O atoms along the step edges of the reconstructed Cu(211)(2×1) surface. The analysis of the one-dimensional

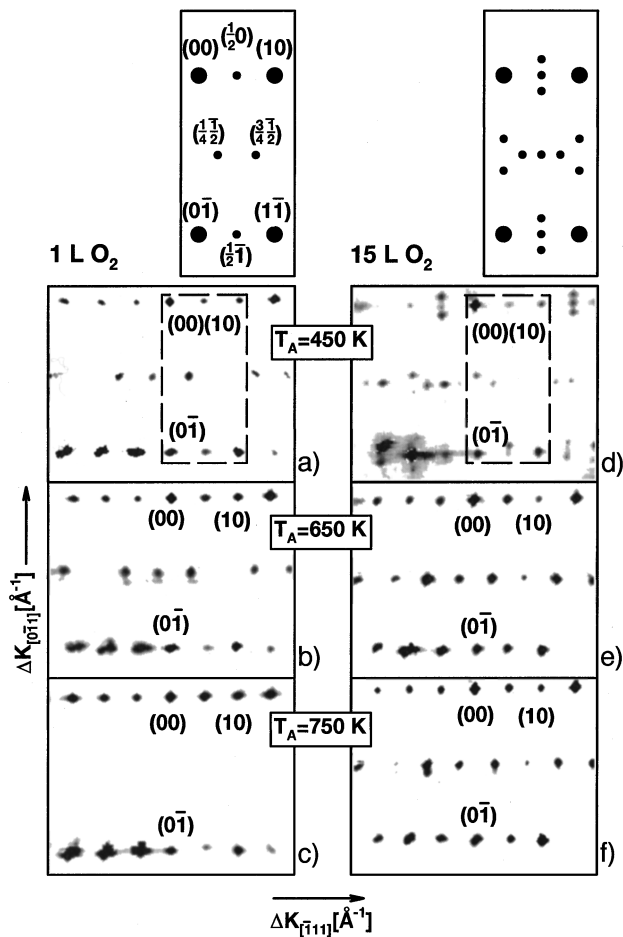


FIG. 4. Sequences of SPA-LEED patterns recorded from oxygen covered Cu(211) surfaces. The images (a)–(c) and (d)–(f) were measured after initial exposure of 1 L O₂ and 15 L O₂, respectively, at $T_s=90$ K and annealing for 5 min at three different temperatures T_A denoted in the figure. All scans were taken at $T_s=90$ K and an electron energy of $E=76$ eV. Schematic and magnified diagrams of the peaks observed in the sections marked in (a) and (d) are presented at the top of the figure. The large circles correspond to peaks observed from the bare substrate. The small circles illustrate additional features in the patterns induced upon oxygen adsorption.

SPA-LEED scans along the $[\bar{1}11]$ direction revealed comparable half-widths for the integer and half-integer peaks. Thus the remarkable long-range order of the step edges demonstrated already in Fig. 1(c) is not significantly disturbed by the reconstruction into diatomic steps.

For oxygen exposures ranging from 0.5 L to 5 L O₂ very similar results were obtained. In contrast, for exposures below 0.5 L O₂ a considerable broadening of the half-integer peaks along the $[\bar{1}11]$ direction and the appearance of streaks in the LEED patterns was observed indicating an uncompleted reconstruction even upon heating to temperatures as high as $T_A=750$ K. Thus the lower exposure limit for the oxygen stabilized Cu(211) double step reconstruction amounts to 0.5 L. Accompanying AES measurements of the peak-to-peak intensities of the oxygen KLL peak at 503 eV (I_O) and copper LMM peak at 920 eV (I_{Cu}) reveal a ratio $I_O/I_{Cu}=0.11$ that corresponds to an oxygen concentration of only 5% on the surface. We note that this oxygen concentra-

tion is in good agreement with the oxygen coverage of $\theta=0.08$ expected for the double step reconstructed Cu(211) surface. Heating the surface after exposing to 0.5–2 L to temperatures above 800 K for several minutes results also in a broadening of the half-order peaks along the $[\bar{1}11]$ direction. The corresponding HAS angular distributions show a reduction of the half-order peak intensities by an order of magnitude compared to the integer peak intensities, which indicates a gradual decay of the double steps and a return to single steps. From the AES measurements after heating a signal ratio of $I_O/I_{Cu}=0.05$ was derived corresponding to an oxygen concentration of 2% on the surface. Thus a minimum oxygen concentration of 3–5% is required to stabilize the double steps. Thompson and Fadley reported a lower exposure limit for the reconstruction of 3 L O₂.⁶ We note, however, that they studied the room-temperature behavior without explicit thermal activation, which might explain the different values. Assuming a constant sticking coefficient for very small oxygen coverages the initial sticking coefficient can be estimated²⁹ from the minimum exposure to achieve an entire double step reconstruction and the corresponding oxygen coverage and values of $s(0)\approx 0.5$ and $s(0)\approx 0.18$ have been determined for adsorption at 100 and 300 K, respectively.

Significant changes in the adsorption behavior occur if the oxygen exposure is increased by about an order of magnitude. This can be inferred from the series of SPA-LEED patterns for 15 L O₂ shown in the right panel of Fig. 4. Whereas at low temperatures only a gradual increase in the background signal with oxygen exposure was observed, new extra spots appear after annealing the sample to $T_A=450$ K which is illustrated schematically in Fig. 4(d). Particularly in the vicinity of the half-integer spots [e.g. $(\frac{1}{2}0)$] additional peaks appear, indicating the existence of a large periodicity along the $[0\bar{1}1]$ direction. By carefully comparing different SPA-LEED images taken from this structure neither shifting nor splitting of single spots as a function of incident electron energy over the range from 50 to 165 eV was observed. Thus, decomposing of the surface into preferred facets as reported for Cu(511) (Ref. 13) can be ruled out. Upon further heating to temperatures $T_A\geq 600$ K again the already known sharp $c(2\times 2)$ patterns appear [see Figs. 4(e) and (f)], which are typical for long-range ordering rather than faceting.

Thompson and Fadley obtained for oxygen exposures above 40 L at room temperature a strong increase in the LEED background intensity, which they interpreted as a gradual faceting of the Cu(211) surface.⁶ In contrast we observed always the same ordered LEED pattern for low-temperature oxygen exposures ranging from 15 to 100 L and subsequent heating. This result suggests that at low temperatures (100 K) the oxygen saturation is reached already for exposures below 100 L and further that at room temperature the reconstruction is already thermally activated and thus the onset of three-dimensional oxide formation is likely.

Accompanying HAS and STM measurements provide further interpretation of the SPA-LEED image in Fig. 4(d). All observed spots can be explained by a coexistence of a structure with a relatively large unit cell³⁰ and the above intro-

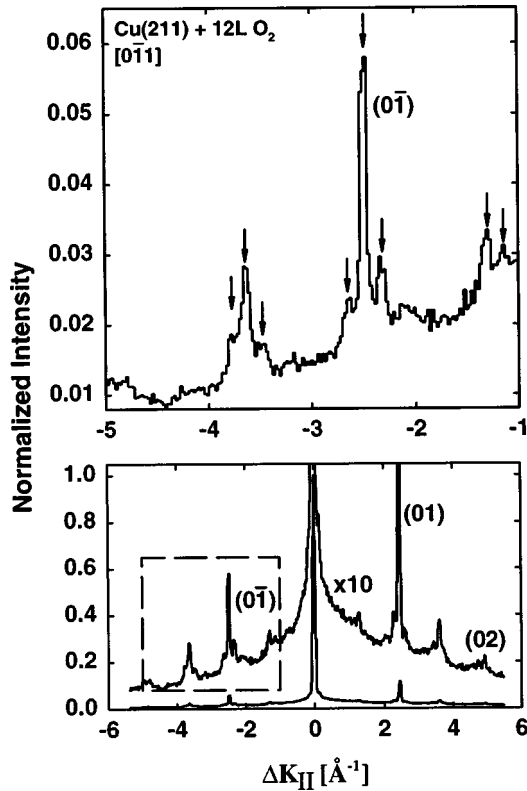


FIG. 5. HAS angular distribution along the $[0\bar{1}1]$ direction. The Cu(211) surface was exposed to 12 L O_2 and annealed to $T_A = 450$ K. The measurement was taken at $T_s = 100$ K for an incident wave vector of $k_i = 9.1 \text{ \AA}^{-1}$. The upper panel shows the section marked by a dashed rectangle in the bottom panel on a different wave-vector scale.

duced $c(2 \times 2)$ structure, which persists upon annealing to higher temperatures [see Fig. 4(e) and 4(f)]. The above mentioned large unit cell implies a periodicity of about 36 \AA (which corresponds to 14 nearest-neighbor Cu-Cu distances along the step edge) on the surface. More instructive is the inspection of the corresponding HAS angular distribution Fig. 5 recorded from a similarly prepared Cu(211) surface along the step edges ($[0\bar{1}1]$ direction). From the separation of adjacent diffraction maxima (see blow up in the upper panel of Fig. 5) again a real space distance of about 35 \AA is determined. In this context we point out the moderate corrugation along the step edges inferred from the small diffraction peak intensity relative to the specular peak. In contrast to that, HAS angular scans taken from several oxygen superstructures on Ru(0001) and Cu(100) surfaces^{31,32} reveal diffraction peak intensities of the same order of magnitude as the specular peak and thus a substantial corrugation of the oxygen-covered surface. Therefore the significant smaller corrugation in the present case favors an incorporation of the adsorbed oxygen in the step edges, e.g., the formation of Cu-Cu-O chains, or the occupation of subsurface adsorption sites, giving rise to a gradual long-range modulation with the observed periodicity. This picture is further corroborated by the STM topograph depicted in Fig. 6(a) which shows a $50 \times 50 \text{ \AA}^2$ section of the Cu(211) surface exposed to about 20 L O_2 and subsequently annealed to $T_A = 500$ K. Again the measured distance of 12.5 \AA between adjacent maxima in the profile recorded perpendicular to the step edges, Fig. 6(c),

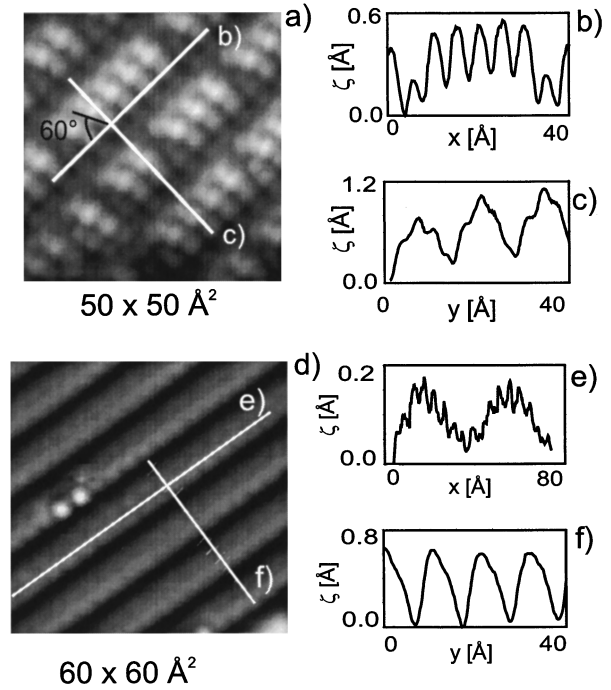


FIG. 6. (a) STM topograph of the Cu(211) surface exposed to 20 L O_2 and annealed to $T_A = 500$ K. (b) Profile recorded along the $[\bar{1}11]$ direction marked in (a). (c) As (b), but along $[0\bar{1}1]$. (d) As (a) but annealed to $T_A = 700$ K. (e) Profile recorded along the $[\bar{1}11]$ direction marked in (d). (f) As (e), but along $[0\bar{1}1]$. Both STM images were measured at $T_s = 40$ K.

reflects the occurrence of diatomic steps (see Fig. 3). The periodicity of 5.1 \AA observed along the step edge direction [Fig. 6(b)] is expected for a twofold superstructure. In addition this structure is clearly modulated by another periodicity of about $33 \pm 3 \text{ \AA}$, which is in good agreement with the diffraction measurements.

Moreover, a comparison of the STM images for the clean [Fig. 1(a)] and oxygen-covered Cu(211) surface [Fig. 6(a)] indicates that due to the oxygen adsorption the corrugation of the terrace is increased. On some terraces in the STM image shown in Fig. 6(a) three bright bumps can be identified, which are aligned at an angle of 60° with respect to the step edges. From previous detailed experiments it has been concluded that such bright spots observed in the STM upon oxygen adsorption are attributed to metal atoms.¹³ Since different oxidation states can also result in different electronic surface configurations the oxygen adsorption on terraces at larger exposures cannot be decisively confirmed by STM. These additional features disappear after annealing at temperatures of $T_A = 700$ K and the terraces appear smoother as shown in Fig. 6(d). The remaining double step structure is extremely well ordered, besides the protrusions in the left part of the image Fig. 6(d), which are probably due to impurity atoms and the terraces. The regular size of the double-step terraces is again confirmed in the STM profile in Fig. 6(f). The comparison of both images in Fig. 6 reveals also a reduction of the corrugation along the step edges by a factor of three upon annealing the oxygen covered surface and thus confirms the ‘‘smoothing’’ obtained already in the He-atom diffraction. In addition to the remaining periodicity of about 5.1 \AA [Fig. 6(e)], which agrees well with the corresponding

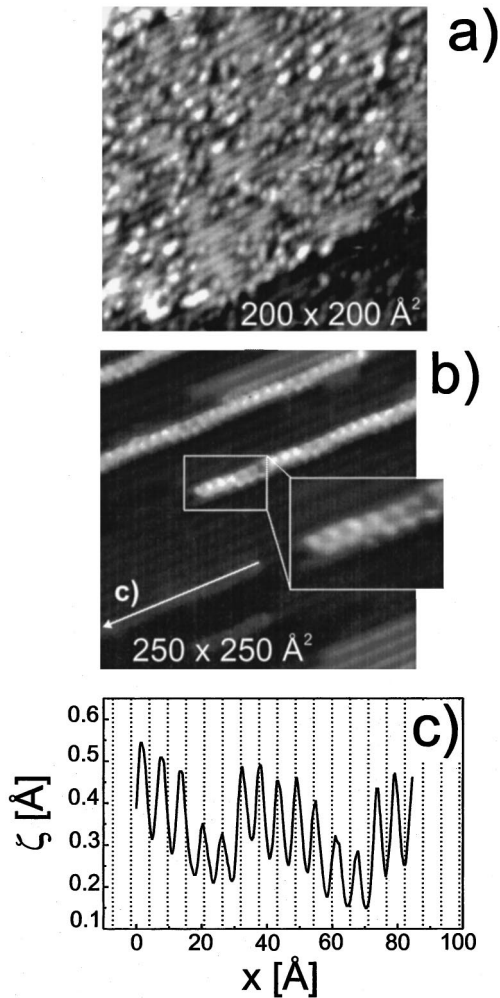


FIG. 7. STM topographs of Cu(211) covered by low amounts of oxygen. (a) 0.05 L O₂, annealed to $T_A=200$ K. (b) 0.4 L O₂, annealed to $T_A=300$ K. (c) Line scan along a double step as indicated in (b).

SPA-LEED patterns [Figs. 4(e) and 4(f)], there is still a modulation along the step edges of about 37 Å.

Further insight in the onset of the reconstruction process is provided by the STM topographs shown in Fig. 7. The image in Fig. 7(a) was measured after exposing the surface to only 0.05 L O₂ at $T_s=200$ K. The surface is rough and disordered. There are no ordered reconstructed areas or double step structures as observed in the other images. The interpretation of the image is that oxygen is randomly incorporated in the Cu(211) surface and single copper atoms are removed from the step edges and appear as the white spots in the image. The situation changes completely when the surface is exposed to oxygen at room temperature. Figure 7(b) shows a topograph of the Cu(211) surface after exposure to 0.4 L oxygen at room temperature. At least four long perfect double step rows protruding from the unreconstructed surface can be identified. The inset shows two adjacent single step edges belonging to the unreconstructed substrate "growing together" to form a double step row.

The line scan taken along an isolated double step [Fig. 7(c)] row clearly shows, apart from a twofold (i.e., 5.1 Å) periodicity, already a long-range periodicity of 15 copper

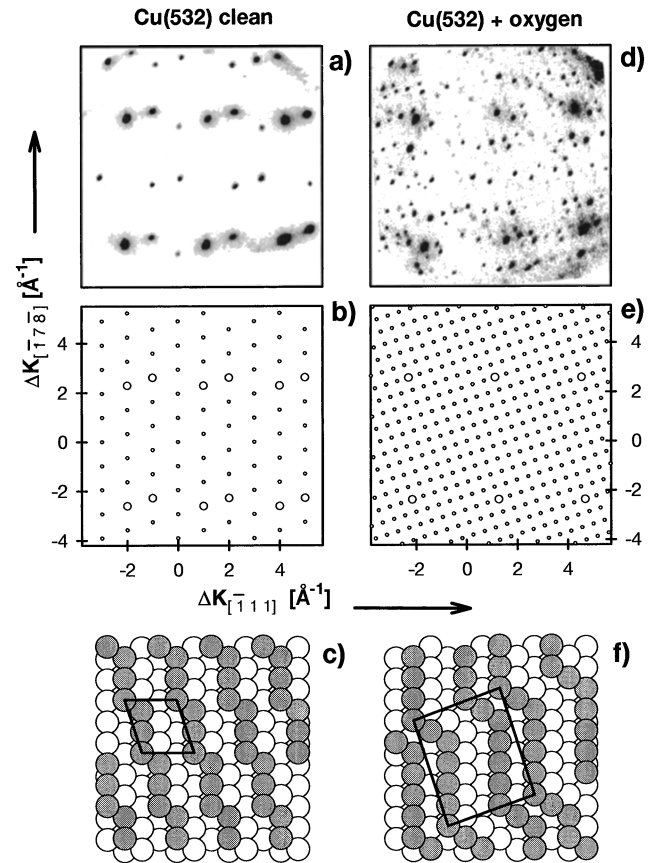


FIG. 8. SPA-LEED pattern of the clean (a) and oxygen-covered (d) Cu(532) surfaces recorded for an electron energy of 163 eV. To illustrate the LEED pattern the schematic diffraction patterns are also shown below. The panels (c) and (f) show a top view hard sphere of the clean Cu(532) surface and a structure model for an oxygen induced double step reconstructed Cu(532) surface.

neighbor distances (i.e., 38 Å). A closer inspection of the line scan identifies this overstructure as a phase skip in registry with respect to the substrate of one copper neighbor distance.

C. Oxygen-induced reconstruction of Cu(532)

To study the influence of surface kinks on the oxygen interaction additional LEED measurements of the oxygen adsorption on a regularly kinked/stepped Cu(532) surface were carried out. The hard sphere model (top view) in Fig. 8(c) illustrates that this surface structure can be derived from Cu(211) [cf. Fig. 1(a)] by periodically introducing kinks in the close-packed step edges of that surface. Whereas the (111) terrace structure of both surfaces is almost identical.

The SPA-LEED pattern recorded from the clean Cu(532) surface presented in Fig. 8(a) reveals sharp LEED spots and a low background signal similar to the patterns of Cu(211) [cf. Fig. 1(b)] confirming a well-ordered substrate at temperatures studied here ($T_s < 350$ K). As it can be inferred from the schematic pattern of the SPA-LEED image [Fig. 8(b)] a considerably greater number of diffraction spots is expected for this surface. Since most of these peaks vanish due to out-of-phase conditions, SPA-LEED patterns measured at about ten different electron energies and results of

calculations based on a kinematical model were carefully compared. This analysis undoubtedly corroborates the (1×1) (i.e., bulk-terminated) structure of the bare Cu(532) surface and confirms the assignment of the crystallographic directions and the spots shown in Fig. 8.

A different SPA-LEED pattern was observed after exposing the surface to 15 L O₂ at $T_s = 100$ K and subsequently annealing to $T_A = 500$ K as it is demonstrated in Fig. 8(d). After comparison with other SPA-LEED images recorded at different electron energies facetting of the surface can be ruled out. Moreover, similar to Cu(211) the bright and sharp LEED spots suggest an astonishingly high order also of this kinked surface after oxygen adsorption. A precise analysis of the SPA-LEED pattern allows the completion of the reciprocal space of the oxygen-induced structure as it is illustrated schematically in Fig. 8(e). Assuming again a double step type of reconstruction a structure model [shown in Fig. 8(f)] is suggested that is consistent with the stacking of the different copper layers and the obtained surface periodicity. Within this model the oxygen induces not only a doubling of the step-edge separation (i.e., the terrace width is enlarged) as for Cu(211) but also a “doubling” of the kinks as it can be easily seen by comparison of the structure models.

IV. DISCUSSION AND CONCLUSIONS

Compared to the rather small initial sticking coefficient of oxygen on the close packed Cu(111) surface [$s(0) = 0.001$ at room temperature^{33,34}] a dramatically larger value of more than two orders of magnitude is observed for the Cu(211) surface [$s(0) \approx 0.2$]. Similar large differences for the initial sticking coefficient were reported for the adsorption of oxygen on the stepped Cu(511) [$s(0) = 0.3 \pm 0.02$ (Ref. 13)] and the corresponding terrace surface Cu(001) [$s(0) = 0.01$ (Ref. 4)]. This demonstrates the initial adsorption of the O atoms on steps and illuminates the importance of such chemically active sites for gas-surface reactions.

After oxygen exposure of as little as 0.5–1 L and subsequent annealing above room temperature the Cu(211) surface undergoes a reconstruction and forms double steps. Heating to 450 K is sufficient to achieve an entire surface reconstruction. Additional annealing to 650 K causes a smoothing of the lateral corrugation along the step edges that is attributed to an oxygen incorporation. At the same time no evidence for remaining oxygen on the doubled terraces was observed in the STM measurements for the induced reconstruction for oxygen exposures below 15 L. The double step structure remains thermally stable up to 800 K. The gradual decay at higher temperatures might be attributed by oxygen diffusion into the bulk and/or thermal Cu-O dissociation and desorption which results in an oxygen dilution at the surface.

Although the Cu(511) and Cu(211) surfaces have a similar step edge distance¹⁹ their oxygen induced restructuring is completely different. For the Cu(511) surface a decomposition into (410) and metastable (311) facets with remaining monatomic steps¹³ has been observed starting above a critical oxygen coverage and at elevated temperatures (i.e., $T_s > 350$ K).¹² The occurrence of this reconstruction coincides with the onset of the $(2\sqrt{2} \times \sqrt{2})R45^\circ$ structure induced by

oxygen on the (001) terrace.³⁵ In strong contrast to these terrace driven types of reconstructions of the vicinal copper (001) surfaces the double step reconstruction of Cu(211) studied in this work seems to be entirely governed by the step edges. This can be confirmed by a comparison of the oxygen coverages required to induce the respective reconstruction: Whereas the facetting of the Cu(511) surface is obtained for critical coverages of 0.34 ML and higher¹² the Cu(211) reconstruction was already found for coverages between 0.05 and 0.1 ML (see also Ref. 6). This behavior can be attributed to the smaller mass transport, which requires only the reorientation of every second step row in order to achieve the double step formation and which is corroborated by the appearance of double steps already at very low oxygen coverages.

For the double step reconstruction of the Cu(211) surface studied here over a wide range of oxygen exposures and annealing treatments the appearance of a super structure with a modulation of about 33–38 Å in addition to the twofold oxygen structure along the step edges was observed, which is interpreted in terms of a stressed Cu-Cu-O chain. Recently, it has been claimed, that oxygen superstructures consisting of O-Cu-O chains are the energetically preferred configuration of the oxygen atoms on several Cu surfaces.^{34–37} Within this general picture it can be speculated that the incorporation of the oxygen atoms in the step edges of the Cu(211) surface as observed in this work leads to the formation of the desired Cu-Cu-O chains rather than a complicated reconstruction of the (111) terrace as reported for the Cu(111) surface where only locally O-Cu-O configurations have been found.³⁴ Thus the terrace is virtually unaffected upon oxygen adsorption and remains intact even after the completion of the reconstruction.

The formation of the observed highly ordered double step structure requires a certain mobility of complete Cu-O complexes. Initially the mobile Cu-atoms are trapped on randomly adsorbed oxygen atoms and this nucleus starts to grow very rapidly by adding other Cu and O atoms and incorporating the underlying steps. Later the entire Cu-O double steps need to be rearranged in order to achieve the long-range double step order. Double steps have shown recently to be considerably more mobile on Cu(511) than single steps.¹³

A possible driving force for the double step reconstruction is the minimization of the surface free energy, which favors the extension of (111) terraces.³⁸ Recently, Hecquet and Salanon obtained in a molecular dynamics calculation of the surface energy an instability for Cu(211) with monatomic steps.³⁹ In contrast to the Cu(511) surface that is rather stabilized by monoatomic steps the Cu(211) surface is energetically stabilized by double steps.

The oxygen induced reconstruction of the Cu(532) surface [which can be regarded as a kinked Cu(211) surface] reveals, besides the double steps, also a very regular kink super structure along the step edges. This is probably stabilized by the repulsive kink interaction that causes also a remarkable regular ordering of the clean surface. The formation of oxygen-induced and thermally stable double steps provides an interesting way to produce well-ordered regular surfaces with terrace widths of more than 10 Å. Usually the preparation of such surfaces is hampered because vicinal sur-

faces become less stable with increasing terrace widths due to the roughening of the step edges. Thus these reconstructed surfaces provide a path to produce nanostructures that might be used as templates for the orientation of large molecules or as nanogratings.

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