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# Structures of the O/Cu top layer in O-mediated film growth of Cu on Ru(0001)

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**Abstract**

In order to characterize the disordered O/Cu surfactant layer causing layer-by-layer growth of Cu on O-precovered Ru(0001), an ordered $(3\times 2\sqrt{3})$ O/Cu structure is used as substrate to study further Cu growth. The $(3\times 2\sqrt{3})$ O/Cu structure develops during Cu deposition on O-saturated Ru(0001) at growth temperatures of ca 520 K. It was recently interpreted as being composed of separated wave-like O–Cu–O chains forming a disrupted '$Cu_2O$' surface layer. Scanning tunneling microscopy (STM) is used to characterize domains and defects of the $(3\times 2\sqrt{3})$ O/Cu structure and the morphology of the Cu film growing on-top. For temperatures ca 400 K, again an O-mediated layer-by-layer growth of Cu is observed. The post-deposited Cu films display a similar island shape and island density as found for the Cu film growth on O-saturated Ru(0001) where a disordered O/Cu surfactant layer is present. Initially, domains of the ordered O/Cu structure are revealed on-top of the growing Cu film which are rotated by 120° to each other and separated by boundaries where the $(3\times 2\sqrt{3})$ ordering is disturbed. The domain size drastically decreases with film thickness. As a result, the $(3\times 2\sqrt{3})$ ordering of the O/Cu top-layer is extinguished already after the deposition of a few Cu monolayers. Finally, the surface displays the same disordered corrugation pattern as the O/Cu surfactant layer. The STM investigations indicate a strong correlation between the $(3\times 2\sqrt{3})$ O/Cu structure and the disordered O/Cu surfactant layer. This leads to the conclusion that the O/Cu surfactant layer is composed of a random-like arrangement of O–Cu–O strings which locally form disrupted '$Cu_2O$' fragments. 

*Keywords:* Copper; Epitaxy; Growth; Oxygen; Ruthenium; Surface structure; Surfactant mediated growth; Scanning tunneling microscopy

## 1. Introduction

Epitaxial film systems with defined interfaces are of growing interest in basic research and industrial applications because of their unusual and promising properties. Their preparation presupposes the controlled fabrication of perfect films. In particular, a layer-wise film growth must be achieved to get smooth interfaces. In several publications, it has been demonstrated that small amounts of foreign materials floating on-top of the growing film may induce a layer-by-layer growth [1,2]. Such materials called surfactants are very desirable as they allow manipulation of film growth in an inexpensive and easy way.

In metal epitaxy, O has been identified as a very effective surfactant for the film/substrate systems Cu/Ru(0001) [3], Pt/Pt(111) [4], Cu/Pt(111) [5], Cu/Cu(111) [6] and Co/Cu(110) [7]. However,

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the O-mediated film growth is a complex phenomenon. Different mechanisms of the surfactant action may be involved as has been recently revealed for the Cu/Ru(0001) system by means of scanning tunneling microscopy (STM) [8]. Two different types of the O/Cu surfactant layer (A- and B-type) were observed in dependence of O-precoverage of the Ru(0001) substrate which are different in their surfactant action. The A-Type structure [O-precoverage 0.1–0.4 monolayer (ML)] incompletely covers the Cu film surface and induces a large density of small triangular Cu islands. Here the surfactant effect is explained by the concept of the two mobilities [9]. The high mobility of Cu adatoms on-top of the clean Cu islands implies a high attempt rate for overcoming the so-called Ehrlich–Schwoebel barrier [10,11] at the steps. The probability of step descent of Cu adatoms is therefore enhanced which strongly increases the interlayer diffusion causing a layer-by-layer growth. The B-type structure (O-precoverage 0.4–0.5 ML) completely covers the Cu film. Cu adatoms moving on-top are influenced by its specific diffusion barriers. At step sites, a smaller Ehrlich–Schwoebel barrier is effective in comparison to clean Cu films which also increases interlayer diffusion.

A more detailed understanding of the surfactant action certainly presupposes a better knowledge of the structure of the surfactant and its interaction with the film material. Unfortunately, little is known up to now about the composition and atomic configurations within the surfactant layer. For the O-mediated Cu film growth, low-energy ion scattering [12] and X-ray photoelectron diffraction [13] only show that the surfactant is either rather disordered or highly mobile. STM studies, on the other hand, indicated that the O/Cu surfactant layer displays some order on a local scale composed of distorted hexagons [8,14].

Recently, a $(3\times2\sqrt{3})$ O/Cu surface structure was found by low-energy electron diffraction (LEED) displaying clear long range order. The $(3\times2\sqrt{3})$ O/Cu structure develops during Cu deposition on O-saturated Ru(0001) at temperatures ca 520 K [15] and can be described by a disrupted sandwich-like '$Cu_2O$' layer formed by wave-like O–Cu–O chains [16]. This indicates an O-induced reconstruction of the Cu film top layers and the formation of a strong ionic bonding of Cu and O. In the present investigations, the $(3\times2\sqrt{3})$ O/Cu surface is used as substrate for further Cu growth in order to understand the structural nature of the O/Cu surfactant layer. The Cu deposition onto the $(3\times2\sqrt{3})$ O/Cu substrate was performed at 400 K, that is, at the same temperature where the surfactant effect was observed for Cu deposition on the O-precovered Ru(0001). The investigations were carried out by STM operating at room temperature. First, we characterize the corrugation patterns of the $(3\times2\sqrt{3})$ O/Cu structure found by STM and describe characteristic domain configurations and defects. In the second part, the growth of Cu films on this structure is investigated. The experiments reveal again O-mediated layer-by-layer growth. The island shapes and island densities correspond to those observed for Cu film growth on the O-saturated Ru(0001) substrate where the B-type structure is present [8]. The growing Cu film is completely covered by an O/Cu surfactant layer which is initially composed of domains of the ordered O/Cu structure. The domain size is drastically reduced with the thickness of the Cu film and the areas of a disturbed $(3\times2\sqrt{3})$ order between the domains are increased. After the deposition of a few monolayers of Cu, the $(3\times2\sqrt{3})$ ordering has been already vanished and the O/Cu top layer shows almost the same corrugation pattern as the disordered O/Cu surfactant layer observed in prior investigations [8,14]. This leads to the conclusion that the O/Cu surfactant layer in O-mediated Cu film growth on Ru(0001) is closely related to the ordered O/Cu structure and also composed of ionic O–Cu–O links. A model of the surfactant layer is presented where short O–Cu–O strings are arranged in a random-like manner which occasionally form small and disrupted '$Cu_2O$' fragments.

## 2. Experimental

The experiments were performed in an ultra-high vacuum system (base pressure of ca

$5 \times 10^{-11}$ mbar) equipped with a room-temperature STM, spot profile analyzing LEED, and facilities for a well-defined $O_2$ dosage and Cu evaporation. The Cu films were deposited by molecular beam epitaxy on the ordered O/Cu structure prepared on Ru(0001). For the general outline of the experimental setup and sample preparation, we refer to previous papers [8,16]. The ordered O/Cu structure was prepared in two steps. First, a saturated p(2 × 1) O adsorption layer with an O coverage of 0.5 ML was prepared by exposing the Ru(0001) crystal in an $O_2$ atmosphere of $1 \times 10^{-7}$ mbar ($O_2$ dosage of ca 10 L, $1\ \mathrm{L} = 10^{-6}$ Torr s). In a second step, a Cu film with a thickness between 5 and 10 ML was deposited at 520 K. The morphology of the Cu film indicates a beginning transition to Stranski–Krastanov growth displaying large three-dimensional islands possessing smooth plateaus. The height of the islands only slightly exceeds the mean film thickness. On-top of the extended and flat plateaus of the islands, the ordered O/Cu structure is present as was observed in prior LEED and STM investigations [16]. The Cu films were deposited on these film substrates at a temperature of 400 K. The evaporation rate was ca 0.2 ML $\mathrm{min}^{-1}$. At the beginning of the STM investigations, the sample was imaged on a large scale in order to identify the three-dimensional islands. After positioning of the STM, the Cu films grown on-top of the islands were examined in detail. The STM measurements were performed with a tungsten tip in constant current mode. Usually, a tunneling current of 1–2 nA and a negative sample voltage of 50–100 mV were applied.

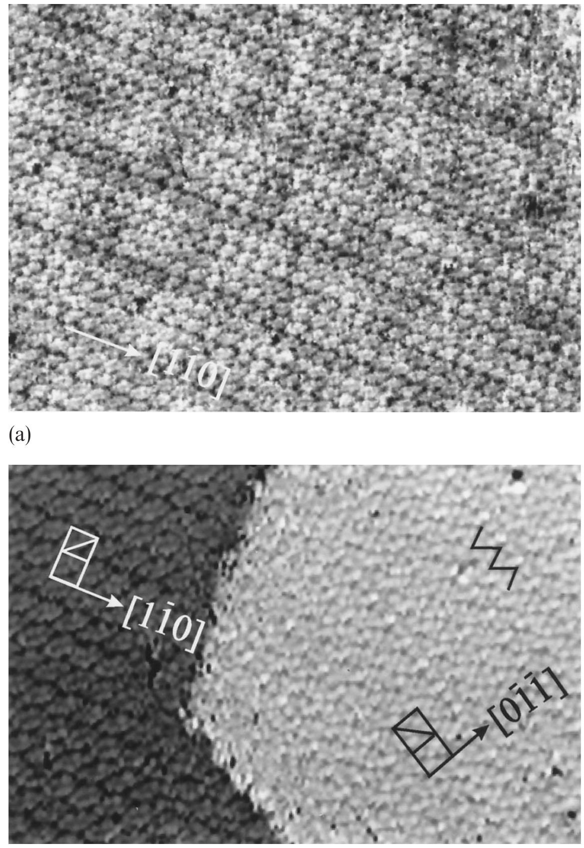



Fig. 1. STM images (a and b) of a Cu film covered with the ordered $(3 \times 2\sqrt{3})$ O/Cu structure used as substrate for further Cu growth. The film was prepared by deposition of 7 ML Cu on O-saturated Ru(0001) at 520 K. The local film thickness is ca 10 ML owing to the transition to Stranski–Krastanov growth. A sample voltage of −90 mV and a tunneling current of 1.5 nA are used. The image size in (a) is 160 Å × 250 Å and in (b) 100 Å × 150 Å.

## 3. Results

Fig. 1 displays STM images of the surface which is used in our experiments as substrate for Cu film growth. They show plateaus of three-dimensional islands which develop during Cu film deposition on O-precovered Ru(0001) at 520 K. The typical plateaus extend ca 3000 Å. The local film thickness or island height, respectively, is ca 10 ML. Usually, the plateaus are atomically smooth as shown in Fig. 1a. Occasionally, monatomic steps were observed as depicted in Fig. 1b. The plateaus are completely covered by the ordered O/Cu top-layer. The latter is revealed in the STM images by a characteristic corrugation pattern. The measured corrugation height of 0.6 Å is by a factor of about five larger than that of clean Cu(111) films [8]. LEED revealed that the O/Cu layer is of long range order giving rise to a $(3 \times 2\sqrt{3})$ superstructure [16]. Fig. 1b shows two different domains of that structure. Two pairs of corresponding rectangular unit meshes are indicated. The depressions are deliberately used as the corner points of the unit meshes. Within the unit meshes, diagonally arranged depression dots are obvious and marked by lines. They indicate that the filling of the unit mesh is asymmetric. The domains imaged in Fig. 1b are rotated by 120° to each other and mirror symmetric. The latter is revealed by the diagonal depression lines of the unit meshes. For the left domain, these lines run from the left bottom corner to the right top corner of the unit mesh. For the right domain, they run from the left top corner to the right bottom corner of the unit mesh. Consequently, six different domains exist, that is, two pairs of mirror symmetric domains which are rotated to each other by 120°. However, the smooth terraces of the plateaus of the Cu islands usually display only one domain type.

The STM imaging strongly depends on tunneling parameters, tip conditions and orientation of the domains with respect to the scanning direction. However, there was no clear systematic behaviour of these dependencies. In some measurements, characteristic zigzag-like corrugation patterns running parallel to [112]-like directions are observed as indicated in the right domain of Fig. 1b by a zigzag line.

Fig. 2 shows an atomic model of the $(3\times2\sqrt{3})$ structure which was previously developed for pseudomorphic Cu layers on Ru(0001) [16]. The model is composed of wave-like O–Cu–O chains in [112]-like directions forming a superstructure with glide plane symmetry. A disrupted '$Cu_2O$' top layer is defined where layers of $O^{2-}$ anions enclose a layer of $Cu^+$ cations forming a sandwich-like (O/Cu/O) structure having an O content of 0.33 ML. In addition, an (O/Cu) composite layer beneath the sandwich is assumed which preserves the initial saturation coverage of O on Ru(0001). As a result, an (O/Cu/O/O/Cu) five plane system is obtained possessing an O content of 0.50 ML.

The ordering of the $(3\times2\sqrt{3})$ structure is not perfect. Different defect types are found. First, a moiré-like reconstruction is induced within the Cu islands because of the misfit to the Ru(0001) substrate which modulates the $(3\times2\sqrt{3})$ structure [16–18]. In Fig. 1a, the moiré-like reconstruction is just perceivable. The size of its unit mesh is ca

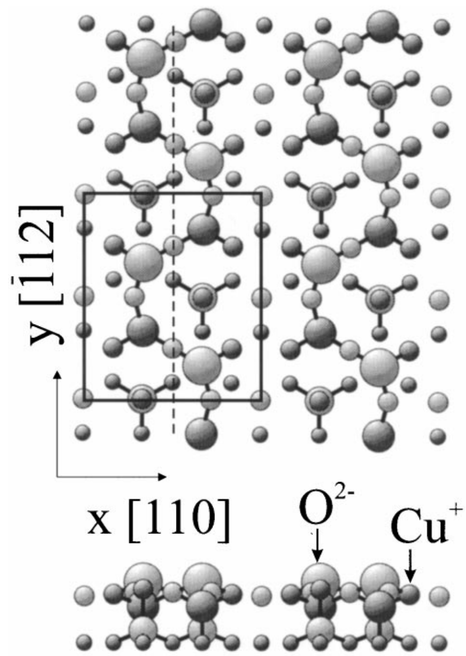



Fig. 2. Model of the $(3\times2\sqrt{3})$ O/Cu structure displayed in top view (above) and side view (below). Wave-like O–Cu–O chains are assumed along [112]-like directions forming a sandwich-like structure with glide plane symmetry where planes of $O^{2-}$ anions enclose $Cu^+$ cations. A rectangular unit mesh is indicated where the dashed line denotes the glide plane.

50 Å. Note that the hexagonal moiré pattern is aligned parallel to [110]-like directions. This is different from the moiré structure previously described by Günther et al. [17] for clean Cu films grown at temperatures $>520$ K. At these growth conditions, a slight rotation of the Cu film lattice is involved inducing a moiré pattern rotated by 12° with respect to [110]-like directions [17,18]. In addition, LEED displayed weak satellite spots indicating a tendency to order in a $(28\times4\sqrt{3})$ superstructure [16] which, however, was not clearly identified by means of STM. Moreover, we frequently observed stripes of a disturbed $(3\times2\sqrt{3})$ pattern. The stripes are about 20 Å in width and run parallel to [110]-like directions. Occasionally, these stripes fluctuate and follow a staircase course as shown in Fig. 3a where they appear as dark lines. The part marked by the arrows is imaged in Fig. 3b in higher resolution. Two pairs of unit meshes are indicated for the

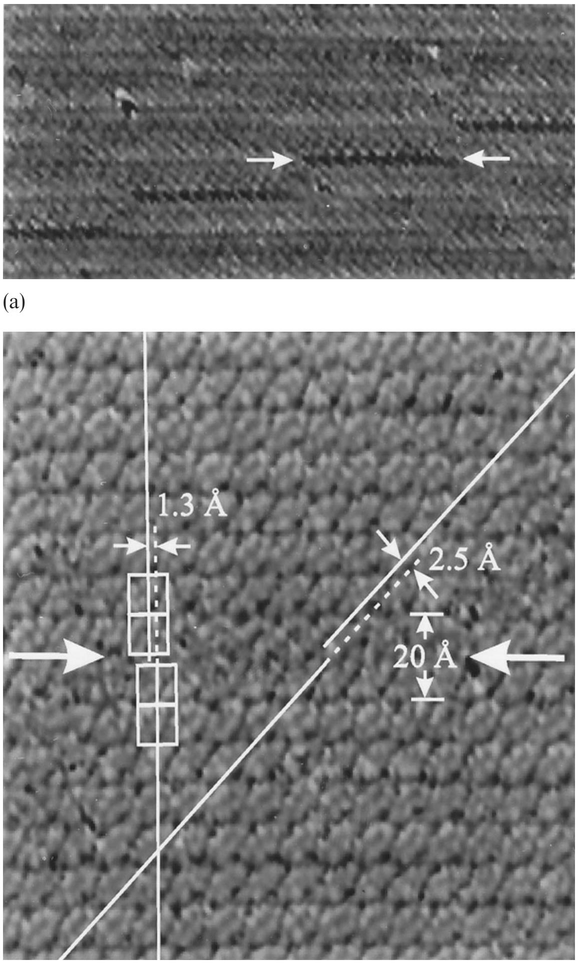



Fig. 3. STM images of the $(3\times2\sqrt{3})$ O/Cu structure revealing in antiphase boundary emerging in the survey (a) as dark fluctuating line. The area between the arrows is imaged in (b) in higher resolution. Same film as displayed in Fig. 1. A sample voltage of −90 mV and a tunneling current of 1.5 nA were applied. The image sizes are 140 Å × 300 Å and 140 Å × 114 Å, respectively.

upper and the lower image area. Inspecting the rows of unit meshes along [112]- and [514]-like directions (see lines) reveals that both areas are slightly displaced forming an antiphase boundary. In Fig. 4a–d possible configurations of the antiphase boundaries of a $(3\times2\sqrt{3})$ domain are displayed and marked by dotted lines. The antiphase boundaries were obtained by cutting the $(3\times2\sqrt{3})$ structure along [110]-like directions. Afterwards, one half of the structure was shifted by $\boldsymbol{b}$ (Fig. 4a), $-\boldsymbol{a}+\boldsymbol{b}$ (Fig. 4b), $2\boldsymbol{a}+2\boldsymbol{b}$ (Fig. 4c) and $2\boldsymbol{b}$ (Fig. 4d) where $\boldsymbol{a}$ and $\boldsymbol{b}$ are the typical lattice vectors of the Cu(111) surface including an angle of 120°. The free areas obtained were filled again with O ions if the O–O distances were larger than $2\boldsymbol{a}$. Note that the boundaries visible in the Fig. 4c and d separate two domains displaying mirror symmetry as indicated by the unit meshes drawn by hatched lines. The configuration shown in Fig. 4a is quite consistent with the structure observed in the STM image of Fig. 3.

We now turn to the Cu films grown on-top of the ordered O/Cu structure. Fig. 5a shows the initial stages of Cu film growth for a temperature of 400 K. About 0.2 ML of Cu were deposited. Two-dimensional islands of rounded shape are observed with a density of ca $1\times10^{11}\,cm^{-2}$. In Fig. 5b, the island (i) of Fig. 5a is imaged in higher resolution. The image reveals that the island is completely covered by the ordered O/Cu structure. However, on-top of the island we observe three different domains of this structure denoted A, B and C which are rotated to each other by 120°. Between the domains, boundaries of disturbed $(3\times2\sqrt{3})$ order are developed. Similar relations are found for the other islands. Generally, the domain size on the islands is relatively small typically extending ca 100 Å.

The STM images of Figs. 6 and 7a show the surface after the additional deposition of ca 5 ML Cu. Again the film morphology is characterized by two-dimensional islands, that is, the layer-by-layer mode of growth is preserved. The surface is completely covered by a strongly corrugated O/Cu structure which holds also for small islands. However, the ordering of the O/Cu structure almost disappeared. Only small domains of the ordered O/Cu structure ca 50 Å in size are occasionally perceptible (see arrows in Fig. 6). In general, the film surface gets an appearance which is very similar to that observed for O-mediated layer-by-layer growth of Cu on O-saturated Ru(0001) at 400 K as the high resolution image of Fig. 7a demonstrates. For comparison, an STM image of the surfactant layer developed for those conditions is presented in Fig. 7b. The corrugation height in

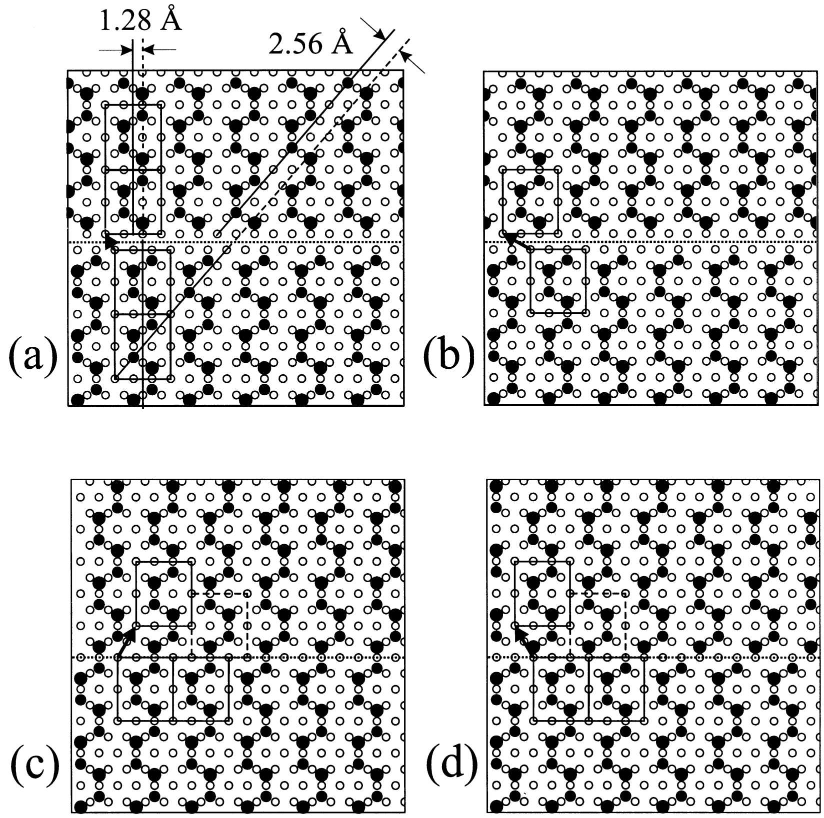
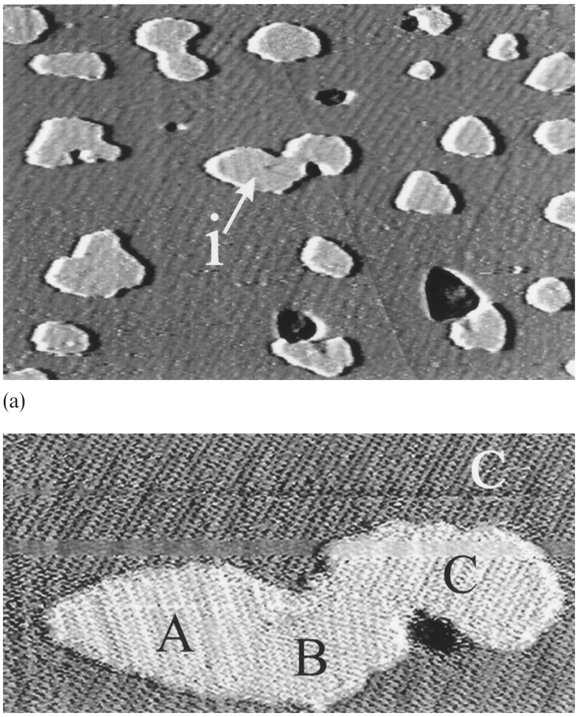



Fig. 4. Possible configurations of antiphase boundaries of a $(3\times2\sqrt{3})$ domain. The three top-planes of the $(3\times2\sqrt{3})$ structure are displayed. (●) and (•) symbolize $O^{2-}$ anions of the upper and lower plane, respectively; enclosing the $Cu^{+}$ cations (○). For explanations see text.

both images is similar and measures ca 0.6 Å. In Fig. 7c, a model of both structures is displayed and will be explained below.

## 4. Discussion

First, we concentrate on the ordered $(3\times2\sqrt{3})$ O/Cu layer present on-top of the Cu plateaux on Ru(0001). Its structure is different from those of oxidized surfaces of Cu(111) crystals found by Jensen et al. [19] after annealing at temperatures ca 700 K. These distorted hexagonal elements are arranged in commensurate superstructure. The corresponding unit cells are 29 or 44 times larger than that of the substrate. The model shown in Fig. 2 was developed from our LEED result by using structural elements of the $Cu_2O(111)$ surface [16]. In the modeling, the hexagonal meshes of the $p(2\times2)$-O structure of the $Cu_2O(111)$ surface are disrupted parallel to [112]-like directions and displaced along [110]-like directions by one lattice distance. Of course, STM is unable to prove the model in detail. In general, a clear interpretation of the STM contrasts obtained from the $(3\times2\sqrt{3})$ structure is problematic. Unfortunately, the images drastically depend on tip conditions which yields strongly differing features of the same structure. We assume that fluctuating O, Cu and/or O/Cu contaminations of the tip were involved. Most conspicuous were zigzag-like contrasts superimposed on the $(3\times2\sqrt{3})$ O/Cu structure similar to those of Fig. 1b. In prior investigations [16], these zigzag-like contrasts even dominated the




(a)

(b)

Fig. 5. Two-dimensional islands (a) grown during the deposition of ca 0.2 ML Cu on the $(3\times2\sqrt{3})$ O/Cu structure at a growth temperature of 400 K as imaged by STM. Sample voltage −50 mV, tunneling current 1 nA. The image size is 1200 Å × 1800 Å. The island (i) of (a) is imaged in (b) in higher resolution which reveals that three domains A, B and C of the ordered O/Cu structure are present on-top. In (b) the sample voltage and the tunneling current were −100 mV and 1.5 nA, respectively. The image size is 300 Å × 600 Å.

$(3\times2\sqrt{3})$ pattern which prevented a clear identification of the unit mesh. In addition, we expect that the STM imaging of the O/Cu layer topography is strongly influenced by the chemical bonding within. As the $(3\times2\sqrt{3})$ O/Cu structure is attributed to a disrupted $Cu_2O$' surface layer, we assume that Cu and O form ionic bondings. The latter implies a significant charge transfer between the Cu and O atoms which makes it more difficult to clearly discriminate between the Cu and the O ions in the images. A further problem of image interpretation concerns the fact that little is known about whether topographic or chemical contrasts dominate the STM imaging. The depressions of the STM image, for example, can be interpreted

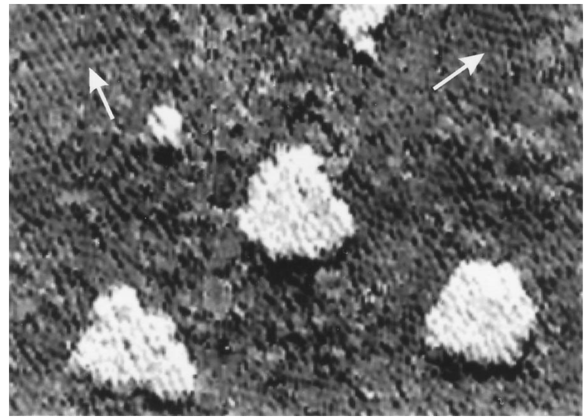


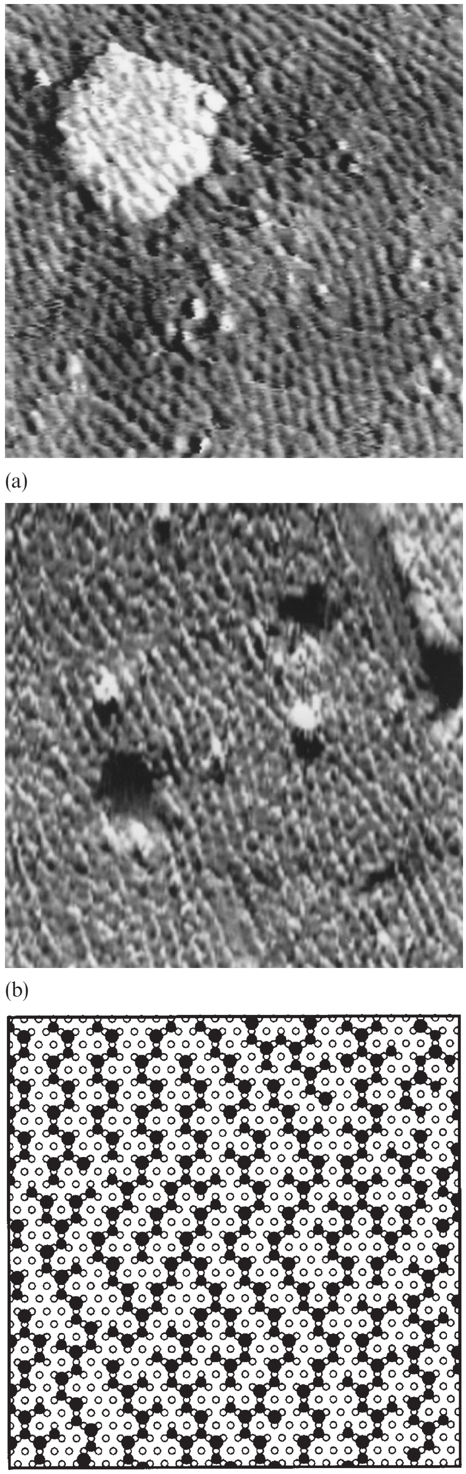
Fig. 6. Two-dimensional islands of a 5.2 ML thick Cu film grown at 400 K on-top of the $(3\times2\sqrt{3})$ O/Cu structure imaged by STM with a sample voltage of −100 mV and a tunneling current of 1.5 nA. The arrows indicate remnants of the ordered O/Cu structure. The image size is 300 Å × 400 Å.

as holes owing to missing Cu atoms as was done for the oxidized top layer of Cu(111) crystals [19]. On the other hand, they can be also attributed to the O ions. Adsorbed O atoms on metals are frequently observed as depressions of the surface [20].

Another problem concerns the O content within the $(3\times2\sqrt{3})$ structure. Considering the different lattice constants of Cu and Ru for a relaxed Cu film (film thickness >3 ML), the five plane (O/Cu/O/O/Cu) model shown in Fig. 2 implies an ideal O content of 0.56 ML with respect to the Ru(0001) substrate if completely covering the surface. Previously, an O content of ca 0.4 ML was assumed to be present on the surface. Investigations performed by Auger electron spectroscopy [21] and ion surface scattering [12] lead to the conclusion that ca 0.1 ML of the precovered O remains at the Cu/Ru(0001) interface. This result suggests that the $(3\times2\sqrt{3})$ structure is probably formed only by three top planes (O/Cu/O) (i.e. one sandwich layer) which corresponds to an ideal O content of 0.37 ML. Ruebush et al., however, recently concluded from X-ray photoelectron diffraction [13] that all preadsorbed O migrates to the surface. Correspondingly, a maximum O content of 0.5 ML has to be presupposed for the O/Cu layer. The latter conclusion promotes the five plane model if one takes into consideration that its actual O content would be clearly $<0.56$ ML because of the relatively large density of O-depleted zones at antiphase boundaries (see Figs. 3 and 4a).

$(3\times2\sqrt{3})$ O/Cu superstructures with long-range order were also observed by $O_2$ postadsorption on strained monolayers and bilayers of Cu on clean Ru(0001) at a temperature of 520 K [16]. However, the $(3\times2\sqrt{3})$ long-range ordering could not be induced by postexposition of $O_2$ on Cu films with a local thickness exceeding 3 ML where the strain is already considerably released [16]. Hence, we assume that the formation of the $(3\times2\sqrt{3})$ structure presupposes a Cu lattice which is strained by the Ru(0001) substrate as it is the case for the monolayer and partly for the bilayer of Cu [16–18]. For the strained Cu films on Ru(0001), the misfit to the $Cu_2O$ lattice is smaller than for compact Cu which may facilitate the formation of the O–Cu–O chains and the disrupted '$Cu_2O$' sandwich layer, respectively, forming the $(3\times2\sqrt{3})$ O/Cu structure. In order to understand the $(3\times2\sqrt{3})$ O/Cu structure on-top of thicker Cu layers grown on O-precovered Ru(0001), we assume that this structure develops at the beginning of the Cu film growth on the strained Cu mono- and/or bi-layer, respectively. There, the strained Cu layers may act like a catalyst. Once the $(3\times2\sqrt{3})$ O/Cu structure is formed, it (or structural elements there from) remains stable during further Cu growth and floats on-top of the growing Cu film [16].

We now turn to the growth experiments where we deposited Cu on-top of the ordered O/Cu structure (Fig. 5). For growth temperatures ca 400 K, the morphological characteristics of the Cu film growth on the ordered O/Cu structure almost perfectly corresponds to those of the Cu film grown on the O-saturated Ru(0001) substrate [8]. In both cases, a perfect layer-by-layer growth is



(a) (b) (c)

Fig. 7. The surfaces of 5.2 ML thick Cu films grown at 400 K on the ordered O/Cu structure (a) and on the O-saturated Ru(0001) substrate (b) displaying the disordered O/Cu surfactant structure. Both images were taken with a sample voltage of −100 mV and a tunneling current of 1.5 nA. The image sizes are 200 Å × 200 Å. In (c) a stochastic model of both structures is displayed. For explanations see text.

induced. For an island coverage of ca 0.2 ML where the maximum island density was observed, we measure a similar island density of ca $1 \times 10^{11}$ $cm^{-2}$ as in the previous experiments [8,14]. The islands are of irregular shape with a rounded contour which is a signature of the Cu growth on O-saturated Ru(0001) substrate (precoverage between 0.4 and 0.5 ML) where the B-type surfactant structure is present. In addition, in both cases the surface is completely covered by an O/Cu structure which is also a characteristic for Cu growth on O-saturated Ru(0001). On the other hand, for precoverages $<0.4$ ML where the A-type surfactant is formed, small islands and island edges remain free of O and the islands display a triangular shape. In the initial stage of the Cu film growth on the $(3\times2\sqrt{3})$ O/Cu surface, small $(3\times2\sqrt{3})$ domains are also observed on-top of the two-dimensional islands (Fig. 5b). However, these domains are much smaller than on the terraces. Typically, we observe more than one domain on individual Cu islands. Between the domains, boundaries originate where the $(3\times2\sqrt{3})$ order is disturbed. Such boundaries are formed also during coalescence of islands covered by different $(3\times2\sqrt{3})$ domains. The long island (i) imaged in Fig. 5 may contain such a boundary as it is most probably developed by coalescence of two islands possessing different $(3\times2\sqrt{3})$ domains. The domains become smaller during Cu film growth which may reflect complications occurring during the swimming up of the O/Cu structure. With the domain size decreasing, the areas of disturbed $(3\times2\sqrt{3})$ order of the domain boundaries increase which induces a strong ordering of the O/Cu top-layer. Beside domain boundaries, one has also to consider a possible increase of the formation of antiphase boundaries within the domains as shown in Fig. 4. A random-like formation of antiphase boundaries would drastically decrease the long range order of the domains. The disordering may be additionally promoted by increased fluctuations of the antiphase boundaries. Unfortunately, the resolution of the STM measurements was insufficient for studying the details of such processes.

After a Cu deposition of ca 5 ML, only few and small $(3\times2\sqrt{3})$ domains survive (Fig. 6). The O/Cu layer displays almost the same degree of disorder as observed for the O/Cu surfactant layer in O-mediated Cu film growth on Ru(0001) at 400 K, that is, the STM images of the O/Cu layers measured in both growth experiments are almost identical for comparable amounts of deposited Cu (cf Fig. 7a and b). Correspondingly, the $(3\times2\sqrt{3})$ LEED spots completely disappeared. In the final state of this disordering, we assume that the O/Cu layer mainly consists of bent and interrupted O–Cu–O strings, which locally may form small and disrupted '$Cu_2O$' fragments. A model of such an O/Cu layer is shown in Fig. 7c. An almost stochastic structure is obtained by a random combination of short O–Cu–O strings and structural elements of the antiphase boundaries displayed in Fig. 4.

The clear similarities in the growth morphology and the final structure of the O/Cu top layers indicate that the film growth on the ordered $(3\times2\sqrt{3})$ O/Cu structure corresponds to the surfactant-induced layer-by-layer growth previously observed on the O-saturated Ru(0001) where the disordered B-type surfactant is present. Obviously, the $(3\times2\sqrt{3})$ O/Cu top layer has gradually changed during the Cu film growth at 400 K into the B-type surfactant structure by the process of domain size reduction and $(3\times2\sqrt{3})$ disordering. Consequently, we conclude that the composition and local structure of the O/Cu top layers are in principle the same in both preparations after growth of ca 5 ML Cu. Hence, the B-type surfactant layer in O-mediated Cu film growth on Ru(0001) should also consist of randomly arranged O–Cu–O strings which occasionally form disrupted '$Cu_2O$' fragments similar as shown in Fig. 7c.

In a similar manner, we interpret the A-type surfactant structure. It is observed for O-precoverages between 0.1 and 0.4 ML and displays some order on a local scale. In the STM images, a distorted hexagonal pattern of depressions is observed [8,14]. It can be considered as being composed of O–Cu–O strings which arrange in a more hexagonal geometry [8,14,16]. An O content of ca 0.3 ML has been estimated from the STM images by deliberately attributing the depressions to the O atoms. It has been demonstrated that the A-type structure forms isolated patches containing small Cu islands [8,14]. During Cu film growth, the areas of the A-type O/Cu structure are laterally displaced over the O-free Cu surface by the spreading Cu islands. The lateral displacement indicates that the binding of the A-type structure to the Cu surface is relatively weak. The effect can be explained by assuming that the A-type O/Cu surfactant consists of sandwich-like '$Cu_2O$' fragments with only three layers (O/Cu/O) involved corresponding to an O content of 0.37 ML with respect to the Ru(0001) substrate. For such a system, most of the O bonds are saturated by the Cu layer in between which implies a correspondingly weak bonding of the surfactant layer to the underlying Cu atoms. For the B-type layer, on the other hand, five layers (O/Cu/O/O/Cu) are more convincing because of the higher O content. The B-type O/Cu structure is supposed to be laterally immobile. It completely covers the Cu film like a carpet. During Cu film growth, we assume that the Cu adatoms migrate on-top of the O/Cu layer. Occasionally, the Cu atoms may penetrate it in order to form Cu nuclei on the underlying Cu interface or to be incorporated at Cu step sites as discussed elsewhere [8]. With the incorporation of new Cu atoms into the Cu film lattice, the O/Cu top layer is locally pushed upwards. Hence, with the Cu film growing, the B-type O/Cu top layer automatically remains at the surface.

## 5. Summary

Cu films with an ordered $(3\times2\sqrt{3})$ O/Cu surface structure were used as substrates to study further Cu film growth by means of STM. The $(3\times2\sqrt{3})$ O/Cu structure develops during Cu film deposition on O-saturated Ru(0001) at 520 K growth temperature. It can be interpreted as an arrangement of ionically bounded O–Cu–O chains forming a disrupted '$Cu_2O$' top layer. The ordering of the $(3\times2\sqrt{3})$ structure is not perfect. In particular, domain and antiphase boundaries are observed by STM. Depositing Cu on-top of the ordered O/Cu structure at 400 K yields almost the same growth morphology as observed for the Cu growth on O-saturated Ru(0001) where a disordered O/Cu surfactant layer is present. Similar as in the latter case, an O/Cu layer swims on-top of the Cu film which completely covers the Cu surface and induces a layer-by-layer growth mode characterized by the same island density and island shape. Initially, small $(3\times2\sqrt{3})$ domains are observed on-top of the Cu film. With increasing film thickness, the size of these domains is drastically reduced and the boundary areas of disturbed $(3\times2\sqrt{3})$ order are increased. As a result, a similar disordered O/Cu surfactant layer develops as in the O-mediated Cu film growth on O-saturated Ru(0001). The similarity of the Cu film morphology and final surface structure found for both O/Cu layers indicates a close correlation between the $(3\times2\sqrt{3})$ O/Cu structure and the disordered surfactant structure. This leads to the conclusion that the disordered O/Cu surfactant layer is composed of ionically bonded and randomly arranged O–Cu–O strings occasionally forming disrupted '$Cu_2O$' fragments.

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