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STM study of the S chemisorption on a vicinal Cu surface: evidence for an interaction between overlayer structures and steps

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Résumé. — Nous avons étudié par microscopie à effet tunnel (STM) la structure d'une face vicinale (1,1,17) de cuivre en présence de soufre chimisorbé. A bas taux de couverture en soufre, des îlots formés de 4 atomes de soufre s'établissent sur le bord supérieur des marches de cuivre. A plus haut taux de couverture en soufre, la couche superficielle due à la présence de soufre présente une structure désordonnée sauf quelques domaines qui possèdent une structure cristalline. Ces domaines germent sur un bord de marche et se développent sur la terrasse supérieure en imposant à la marche d'être parallèle à une rangée dense du nouveau réseau. Ces images STM à haute résolution montrent qu'il existe une interaction entre les marches et la structure de la couche superficielle due au soufre.

Abstract. — The structure of a stepped (1,1,17) Cu surface under S chemisorption has been investigated by scanning tunneling microscopy. At low S coverage, islands formed by 4 S atoms are found. They are mainly located on top of the step edge. At higher S coverage, the S-induced overlayer is disordered except crystalline domains which grow from step edges and force these step edges to be parallel to a dense row of their lattice. These atomically resolved images give evidence for an interaction between S-induced overlayers and the step edges.

1. Introduction.

Adsorbate induced structures on metal surfaces were extensively studied in the last decades. For example, Domange and Oudar [1] have studied in detail the sulfur adsorption on copper surfaces. They have shown that several structures grow on these surfaces. On Cu (001), upon increasing S coverage, a (2 × 2) superstructure, a diffuse structure and a two-domain complex structure were identified by LEED. After this work, several studies of the overlayer structures induced by S chemisorption on vicinal surfaces around the (001) face have been reported [2-4]. In particular, Bouillard and Sotto have observed a new structure indexed as c (4 × 2) on vicinal surfaces with <110> steps [4]. To explain the origin of this structure, they have proposed that the sulfur overlayer induces changes in the orientation of the steps, a structural transition termed two-dimensional faceting (2D faceting). For higher coverage, S chemisorption was shown to induce

strong structural changes in surface topography since facets with new orientations (3D-faceting) were detected [4].

In contrast to LEED which is an averaging technique, scanning tunneling microscopy (STM) provides direct information on the topography of surface defects [5]. For S segregation on Cu (1,1,11) surface, Rousset *et al.* [6] have shown that there is a strong structural relationship between the local orientation of the step edge and the presence of the (2×2) or $c(4 \times 2)$ superstructures on the terrace. Their STM images clearly exhibit steps with 2D faceting related to the overlayer lattice. However, the mechanism of this 2D faceting is not established.

Here, we present the first results we obtain by STM on a (1,1,17) copper surface covered by sulfur. These observations demonstrate that the steps play a major role in the growth on the overlayer structure.

2. Experimental.

This study has been performed in a UHV chamber equipped with a commercial STM (Omicron) and facilities for cleaning and heating the sample. The base pressure is below 1×10^{-10} mbar. As Auger electron spectroscopy (AES) was not available in the STM chamber, the chemical composition has been checked in a separate chamber. The Cu single crystal is a cylinder (diameter = 12 mm thickness = 2 mm). It was oriented by X-Ray diffraction so that its surface is parallel to the (1,1,17) plane. The ideal surface can be described as steps parallel to dense packed rows ($\langle 110 \rangle$ direction) and (001) terraces. The terrace width is 21.6 Å and the step height 1.8 Å.

After orientation, the sample was electropolished in H_3PO_4 and then rigidly fixed on a Mo plate by two thin Ta stripes. A chromel-alumel thermocouple was spot-welded on the support of the Mo plate. So there is small difference between the measured temperature and the sample temperature.

In UHV, the sample was first sputtered for 30 mn (600 eV Ar+) and annealed for 2 mn at 750 K. Several cycles were required to obtain a clean copper surface as checked by AES. The chemisorbed sulfur results from the segregation of the residual sulfur in the Cu bulk with various conditions as reported below. Tips made by a standard electrochemical method from tungsten wire (0.25 mm) were used after an ion sputtering (30 mn, 600 eV Ar+). All the images presented here were recorded in the constant-current mode and obtained at room temperature. They are rough data.

3. Results and discussion.

Before we present the data obtained on S-covered surface, the description of some STM images of the clean Cu surface is required.

1) Clean surface

The morphology of the clean surface depends on the observed areas along the surface. On some parts, some white dots (high around 10-15 Å, diameter 30-50 Å) are found. Their density is roughly homogeneous (one dot for about $600 \times 600 \text{ \AA}^2$). Clearly some of these dots modify both the density and the local orientation of monoatomic steps of the copper surface. The nature of these defects remains unknown. The existence of such big defects on Cu surfaces has been previously reported [7]. The other parts of the surface exhibit a regular arrangement of steps as seen in the STM image reproduced in figure 1. The mean density of step is equal to 20 \AA which is in good

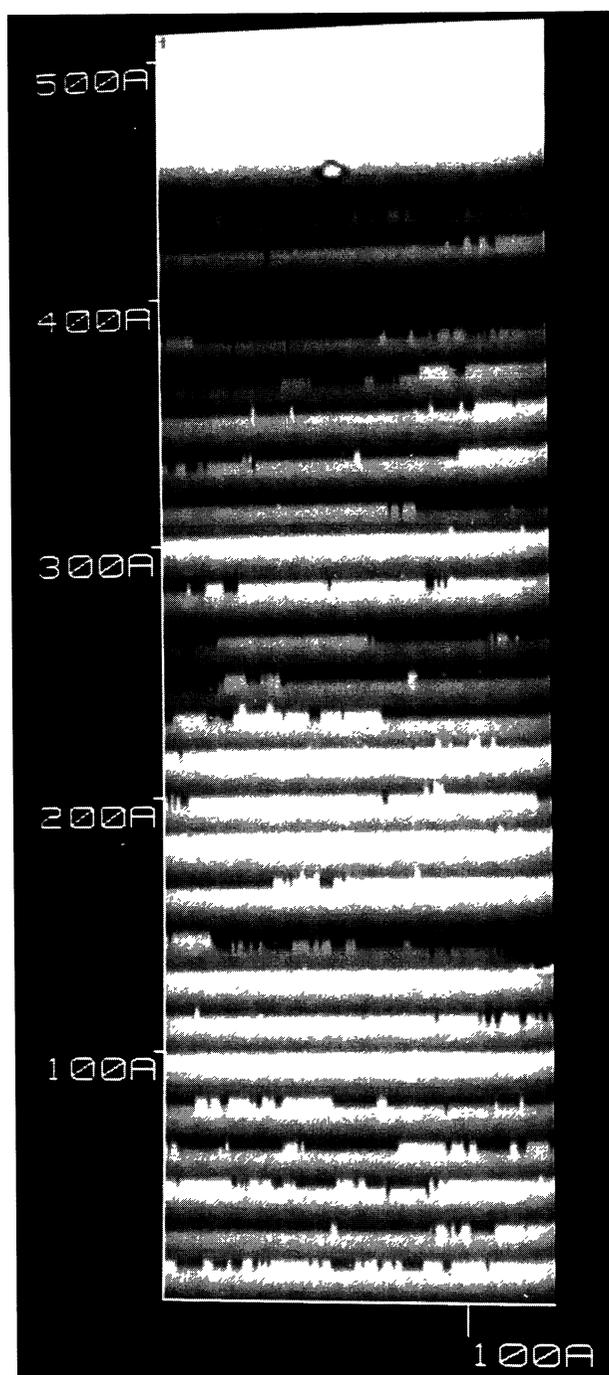


Fig. 1. — STM image of a (1,1,17) Cu surface at room temperature. The straight part of the step edges are parallel to dense rows of the Cu crystal ($\langle 110 \rangle$ direction). The scan area is $512 \times 128 \text{ \AA}$. ($V = -0.8 \text{ V}$, $I = 0.3 \text{ nA}$).

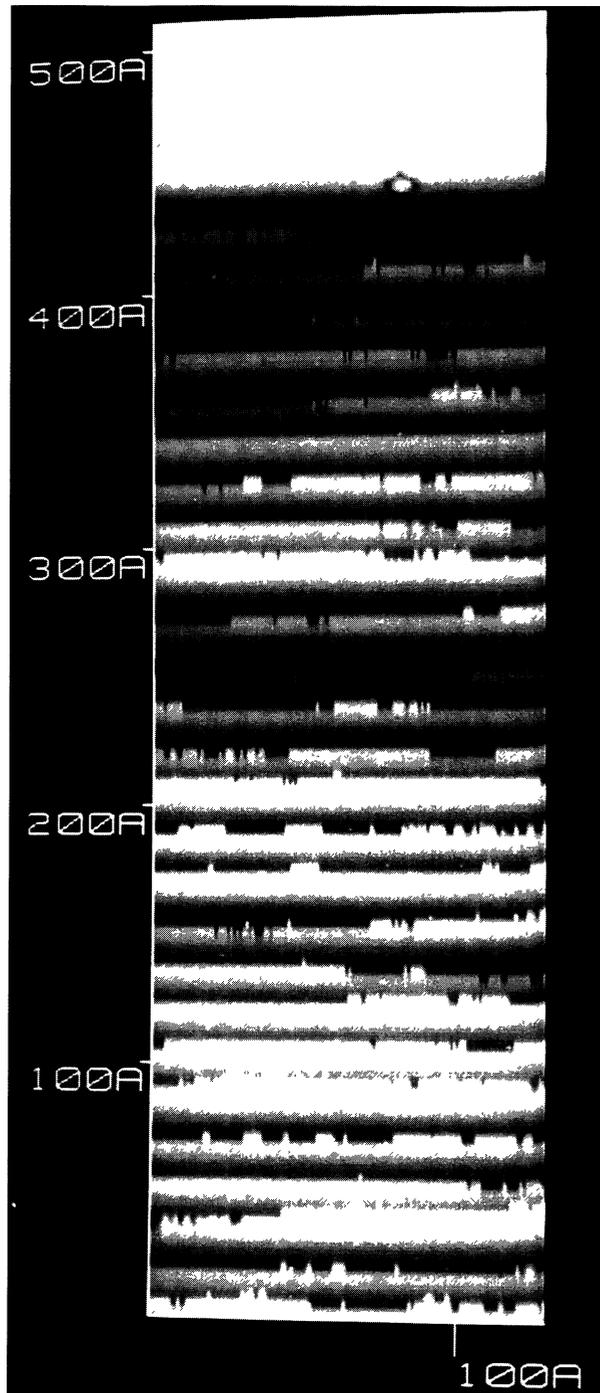


Fig. 2. — STM image recorded just after the image shown in figure 1 on the same area. The square defect in the upper part of the image gives a mark to locate each step edge in both images. Comparison between the step shapes demonstrates the fluctuations in the step position (Same tunneling conditions than in Fig. 1).

agreement with the macroscopic orientation of the surface. The measured height associated with the step is 1.9 \AA . Some step edges are perfectly straight while others exhibit kinks the width of which corresponds to an atom diameter (2.5 \AA). Therefore, these monoatomic steps are parallel to the dense packed rows of Cu atoms ($\langle 110 \rangle$ direction) with monoatomic kinks. Most of the step edges exhibit teeth parallel to the scanning direction. In order to understand the origin of these teeth, we compare two images obtained in sequence on the same area (Figs. 1 and 2). The time elapsed between the first line scan of these images is 2 mn. With the defect in the upper part of the images considered as a landmark, we are able to identify each individual step in a both images. The comparison between these two images reveals clearly that the shape of steps changes in the meantime. This demonstrates that the mobility of copper atoms along the step edge remains important at room temperature. Then the teeth parallel to the scan direction correspond to step or atoms displacements between two consecutive scans of the STM tip. Such an appearance of monoatomic steps in STM images of Cu surface has been already discussed [8-11].

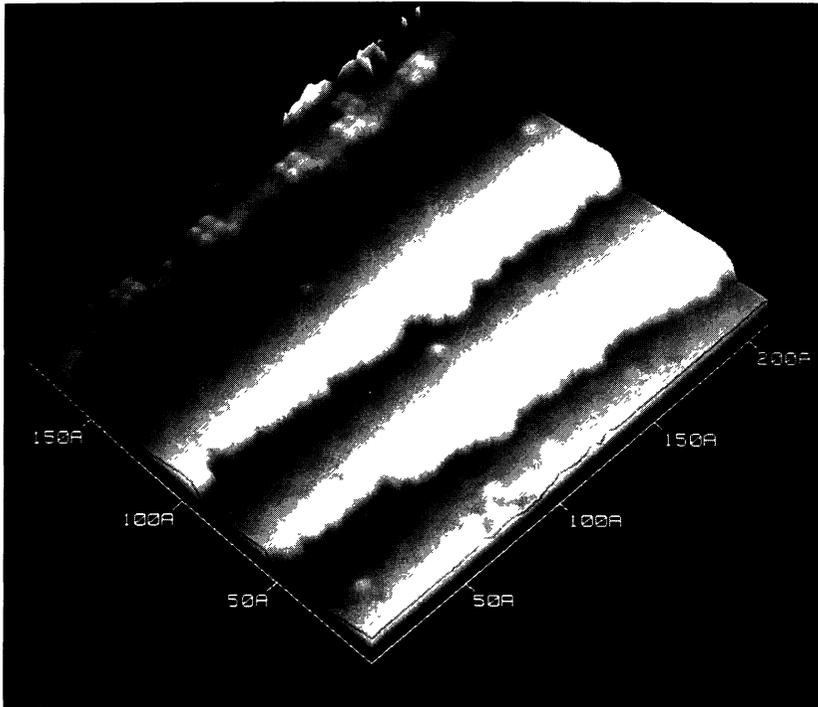


Fig. 3. — STM image of a $210 \times 180 \text{ \AA}$ region of a vicinal Cu surface partially S covered. Each bump is identified with one S atom. Square islands formed by 4 S atoms are mainly situated on top of the step edge. ($V = -1.2 \text{ V}$, $I = 0.4 \text{ nA}$).

2) S chemisorption

In this part, we will concentrate on the influence of the step edge in the overlayer structure. A short annealing (10 mn) at 820 K of the sample modifies the surface structure as shown in the

STM image (Fig. 3). Monoatomic steps of copper surface are clearly visible but small bumps are now detected on the terraces. As AES has shown that S segregates to the surface, we identify these bumps with S atoms. In this case, the S coverage is around 0.03 with respect to the copper atoms. Remarkably, most of S atoms gather by 4 to form islands with a square shape. In fact,

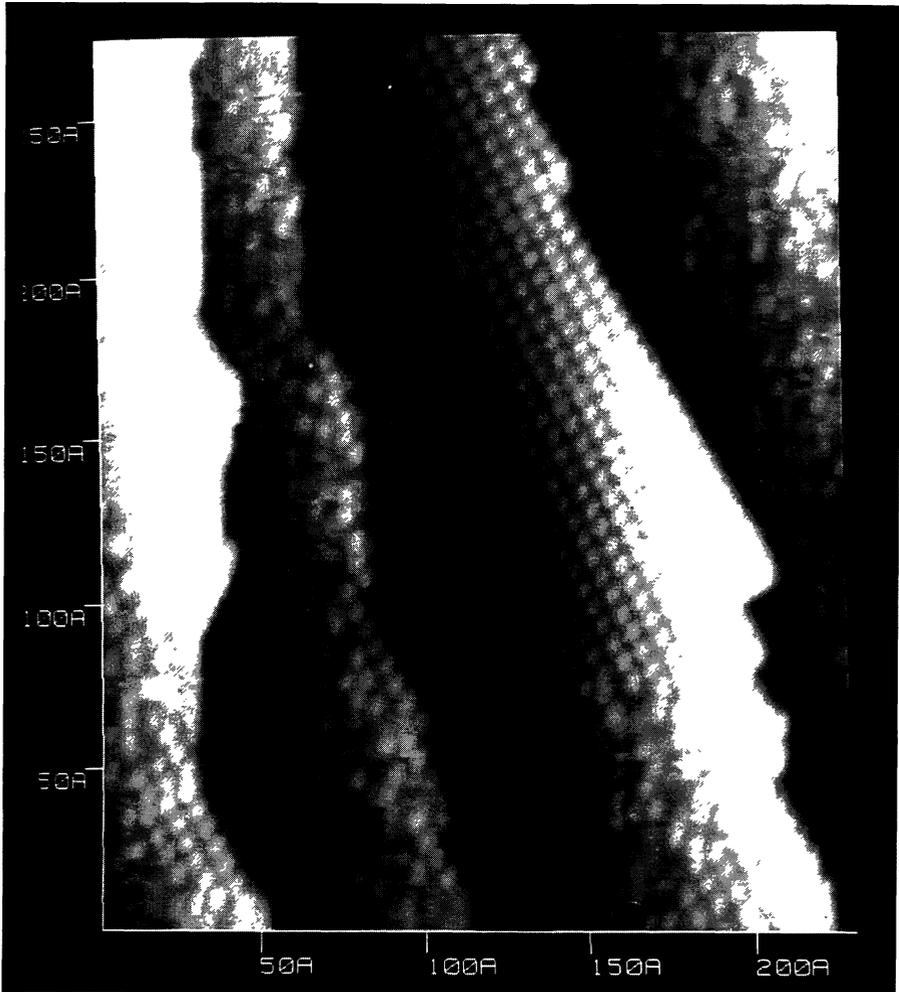


Fig. 4. — STM image of a $220 \times 275 \text{ \AA}$ area of a S induced-overlayer on a vicinal Cu surface. The vertical is parallel to the Cu $\langle 110 \rangle$ direction. As soon as the ordered domains grow on the terrace, the step edge becomes parallel to the $\langle 100 \rangle$ direction of the superstructure lattice. ($V = -1 \text{ V}$, $I = 0.2 \text{ nA}$).

85% of S atoms are involved in the island formation. The distribution of these islands appears inhomogeneous over the surface. Surprisingly, they are mainly situated on top of the step edges while the terraces are almost bare. Furthermore these square islands exhibit the same orientation: their sides are parallel to the $\langle 110 \rangle$ directions of the copper surface. The distance between S atoms is equal to 5.2 \AA which corresponds well to a 2×2 superstructure. The orientation and the

relative arrangement of these islands on the surface give evidence that they are in registry with the copper lattice. Therefore, these square islands appear as nucleates of the (2×2) S superstructure developping on Cu(001) [2 – 4]. A corrugation amplitude of about 0.5 Å is measured for each atom in the island. We point out that the centre of the islands appears higher (0.3 Å) than the Cu terrace. We also notice that the step edge shape is modified in the vicinity of the S island. Furthermore, a strong decrease of the mobility along step edge is inferred from the absence of tooth in the step edges.

After a longer annealing (90 mn) at 900 K, both the structure and the overall topography of the surface change drastically. As seen in the STM image reproduced in figure 4, the regular arrangement of monoatomic steps has disappeared. Now the surface can be described as covered by an overlayer with disordered atoms with some islands characterized by an ordered structure. The areas of the surface which are covered with disordered atoms show large terraces and steps roughly parallel to the $\langle 110 \rangle$ of copper crystal. For the crystalline domains, the steps present a new orientation. In fact, the step direction is parallel to the $\langle 100 \rangle$ direction of this new structure which exhibits a square lattice. Interestingly all the ordered domains which spread on a single terrace are localized on top of the step edge. As a very small domain formed by 5 atoms is detected in the bottom middle of figure 4, we deduce that this ordered structure requires a step edge to nucleate and then grows only on the upper terrace of the step from the step edge. During its growth, this superstructure forces the step edge to be parallel to the $\langle 100 \rangle$ direction of its lattice. A careful observation reveals some defects in the lattice of the ordered domains. In particular in the right bottom part, a stacking fault in the lattices of two adjacent ordered domains is detected. Remarkably, the shape of the associated step edge reflects this defect. This well illustrates the interaction between the ordered domains and the step edge. We notice also that both the domain size and the shape of the ordered domains do not change with time on a time scale of 30 mn. This means that the mobility in the overlayer is drastically reduced to that observed on the clean surface. This decrease is consistent with previous measurements [13]. The identification of the overlayer structure deserves further measurements and will be reported elsewhere [12].

These data are consistent with the first STM study of S-induced 2D faceting of steps on Cu (1,1,1) surface [6]. They make this study complete on two points: i) the interaction between S atoms or S-induced superstructures and the Cu step edges occurs at several S coverages ii) the mechanism of the 2D-faceting can be identified. After the nucleation of the S-induced superstructure at the step edge on top of the step from the disordered overlayer, its growth on the terrace forces the step edge to undergo a 2D faceting. Such a mechanism occurs at high temperature since no mobility can be detected in the STM images.

4. Summary and conclusion.

We have presented STM data obtained at room temperature on a (1,1,17) Cu surface. On the clean surface, we have brought clear evidence that mobility along the $\langle 110 \rangle$ step edge is high enough at 300 K to modify the step shape during a tip scan.

At very low S coverage, most of S atoms gather to form square islands which are mainly situated on top of the step edge. The arrangement of S atoms in these islands corresponds to a 2×2 superstructure. At higher S coverage, high resolution STM images show that the surface is covered by a disordered overlayer in which some crystalline domains grow. Nucleation and growth of these ordered domains are related to the presence of step edge. Indeed the nucleation of the ordered domain requires the step edge which is forced to be parallel to the dense packed row of the growing superstructure (2D faceting).

These high resolution STM images demonstrate that the step edges play a major role in nucleation and growth of the overlayer structures induced by S chemisorption.

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