Reactivity to sulphur of clean and pre-oxidised Cu(1 1 1) surfaces

F. Wiame *, V. Maurice, P. Marcus

Laboratoire de Physico-Chimie des Surfaces, CNRS–ENSCP (UMR7045), Ecole Nationale Supérieure de Chimie de Paris,
11 rue Pierre et Marie Curie, F-75231 Paris, Cedex 05, France.

Abstract

The reactivity of clean and pre-oxidised Cu(1 1 1) surfaces exposed to sulphur (H_2S) has been studied at room temperature by Auger electron spectroscopy, low energy electron diffraction and scanning tunneling microscopy. On the clean surface, the sulphur-saturated surface structure is dominated by the $\begin{vmatrix} 4 & 1 \\ 3 & 5 \end{vmatrix}$ or so-called "zigzag" superstructure. It is shown that a single orientation domain is favoured by the slight misorientation ($\sim 2°$) of the surface with respect to the (1 1 1) plane. Scanning tunneling microscopy measurements also revealed two minority structures. Pre-oxidation $\left(\begin{vmatrix} 4 & 1 \\ 3 & 8 \end{vmatrix} - O/Cu(1 1 1)\ \text{structure} \right)$ was performed by exposure to 1.5×10^4 L of O_2 at 300 °C. Under exposure to H_2S (1×10^{-7} mbar) at room temperature, the oxygen is totally substituted by sulphur. Once initiated, sulphur adsorption seems to propagate to cover the whole surface on the O-covered surface faster than on the clean Cu(1 1 1). At saturation by adsorbed sulphur, the surface is completely covered by the $(\sqrt{7} \times \sqrt{7})R19.1$ superstructure of highest coverage. This enhanced uptake of sulphur is assigned to the surface reconstruction of the copper surface induced by the pre-oxidation, causing a stronger reactivity of the Cu atoms released by the decomposition of the oxide.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Scanning tunneling microscopy; Auger electron spectroscopy; Low energy electron diffraction; Chemisorption; Copper; Sulphur; Oxygen

1. Introduction

The sulphuration of copper has been the object of several studies in the past [1–9]. The most stable structure is the $(\sqrt{7} \times \sqrt{7})R19.1°$ formed at saturation and assigned to a coverage of 0.43 monolayer (ML). Another structure, the so-called "zigzag" structure, was also evidenced at near saturation and assigned to a coverage of 0.35 ML. Numerous models, based on several experimental techniques, have been proposed to explain these structures, but no general agreement was found [7–9]. All of them are characterised by a surface reconstruction of the topmost Cu plane promoted by the strong S–Cu bonding.

Several studies of the reactivity to H_2S of pre-oxidised metal surfaces were performed [10–15]. However, very few results have been reported on the reactivity of the oxidised

Cu(1 1 1) surface and only at low temperature ($T < 173$ K) [16]. We report here on the comparison of the sulphuration of clean and pre-oxidised Cu(1 1 1) surfaces studied by means of Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). To our knowledge, the present article provides the first study of the room temperature (RT) reactivity to H_2S of the pre-oxidised Cu(1 1 1) surface.

2. Experimental

The surface of the (1 1 1)-oriented copper single crystal was prepared by mechanical and electrochemical polishing followed by annealing at 700 °C for several hours under a flow of hydrogen at atmospheric pressure.

The experiments were performed in an ultra high vacuum system (base pressure below 10^{-10} mbar) equipped with STM (Omicron, STM1 with SCALA system) and with facilities for AES (Riber, OPC-105), LEED (Riber,

* Corresponding author.
  E-mail address: frederic-wiame@enscp.fr (F. Wiame).

OPD-304) as well as sputtering and annealing of the sample. The Cu(111) surface was prepared by repeated cycles of sputtering ($P_{Ar} = 1.0 \times 10^{-5}$ mbar, 600 V, 1 µA sample current) and annealing (600 °C) until a sharp (1×1) LEED pattern was observed and no contamination was detected in the AES spectrum. STM imaging of the clean surface indicated an average terrace width of ∼6 nm, corresponding to a misorientation of about 2° of the sample.

Oxidation was carried out by exposing the Cu(111) surface to 1.5×10^4 L (1×10^{-6} mbar for 375 min) of O_2 (Alpha Gaz, 99.995% purity) at 300 °C. The $\left| \begin{smallmatrix} 4 & 1 \\ 3 & 8 \end{smallmatrix} \right| - O/Cu(111)$ phase was obtained, which has been assigned in previous studies to the formation of a surface precursor oxide for the growth of Cu_2O [17].

All STM images were recorded at RT in constant current mode (topographic mode). No filtering was applied. Background plane subtraction and linear drift correction were performed when needed.

3. Results and discussion

3.1. Sulphuration of Cu(111)

The sulphuration of the Cu(111) surface was carried out by exposure to H_2S (Alpha Gaz, 99.5% purity) at 1×10^{-7} mbar at RT and followed by measuring the variation of the h_S/h_{Cu} ratio between the peak-to-peak heights of the sulphur signal (150 eV) and Cu signal (920 eV) in the derivative AES spectra as a function of the H_2S exposure. Fig. 1 shows the h_S/h_{Cu} ratio as a function of the exposure to H_2S for the clean and pre-oxidised surface. In the case of the clean surface, the h_S/h_{Cu} ratio saturates at 1.1 for an exposure between 30 and 40 L, in agreement with the value of 40 L obtained by Campbell and Koel [2].

An STM image of the RT sulphur-saturated Cu(111) surface is presented in Fig. 2(a). Different regions, labelled A to C, are identified. Most of the surface was observed to be covered by the structure labelled B. Fig. 2(b) shows the corresponding LEED pattern. It reveals a $\left| \begin{smallmatrix} 4 & 1 \\ 3 & 5 \end{smallmatrix} \right|$ structure, also called the "zigzag" structure in the literature [5], and

corresponding to near saturation coverage. Note that, contrary to previously reported results, the LEED pattern is mainly single-domain. As the substrate has a three-fold symmetry and as the superlattice is oblique (i.e. there is no mirror plane), six equivalent domains should be observed, giving rise to the "complex" LEED pattern usually reported [1–3]. The slight misorientation of the single crystal, by about 2° relatively to the (111) plane, induces rather narrow terraces. This is advanced to explain the observation of essentially one domain [18], corresponding to region B in Fig. 2(a).

Fig. 3 shows at higher resolution the three types of structure observed locally on the S/Cu(111) surface. One of these is the well-known $(\sqrt{7} \times \sqrt{7})R19.1°$ (Fig. 3(a)), hereafter called "$\sqrt{7}$" structure, generally assigned to a surface completely saturated by sulphur [7]. Two mirror domains of this structure are equally present.

The structure imaged in Fig. 3(b) is similar to the "zigzag" structure evidenced by Ruan et al. [5] and corresponds to the main structure, in agreement with the LEED data. The two structures in Fig. 3(b) and (c) have unit cells that are mirror images one of each other, suggesting mirror domains of the "zigzag" structure. However, the inner structures of the unit cells observed by STM are dissimilar. Electronic effects may have to be taken into consideration in order to explain this discrepancy. A more detailed structural analysis of these structures will be fully discussed elsewhere [19].

3.2. Sulphuration of O/Cu(111)

Pre-oxidation of the Cu(111) surface was obtained by exposing the copper surface to O_2 at 1×10^{-6} mbar and 300 °C. The resulting $\left| \begin{smallmatrix} 4 & 1 \\ 3 & 8 \end{smallmatrix} \right| - O/Cu(111)$ structure was exposed to H_2S in the same conditions as for the Cu(111) surface. The AES shows that, under exposure to H_2S, surface oxygen is progressively substituted by sulphur and totally disappears at S-saturation. Oxygen probably desorbs in the form of H_2O after dissociative adsorption of H_2S [16].

Fig. 1 shows that the h_S/h_{Cu} ratio saturates for an exposure similar to the one measured on the Cu(111) surface, but the saturation coverage is higher (h_S/h_{Cu} ratio of 1.3 instead of 1.1). Moreover, one should notice that the growth mode is different. Indeed, the rate of variation of the h_S/h_{Cu} ratio increases until the saturation is reached for the O/Cu(111) surface while it decreases for the Cu(111) surface. As the Auger signal of copper is almost constant during exposure, the derivative of the h_S/h_{Cu} ratio is roughly proportional to the sticking probability. This means that while the sticking probability is decreasing with the amount of sulphur at the surface in the case of Cu(111), the probability for H_2S to react with the surface is increasing with the number of already reacted sites until the surface is fully covered. Once initiated, sulphur adsorption seems to propagate faster to cover the whole surface on pre-oxidised Cu(111).
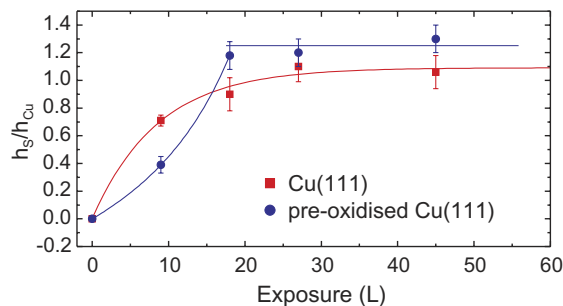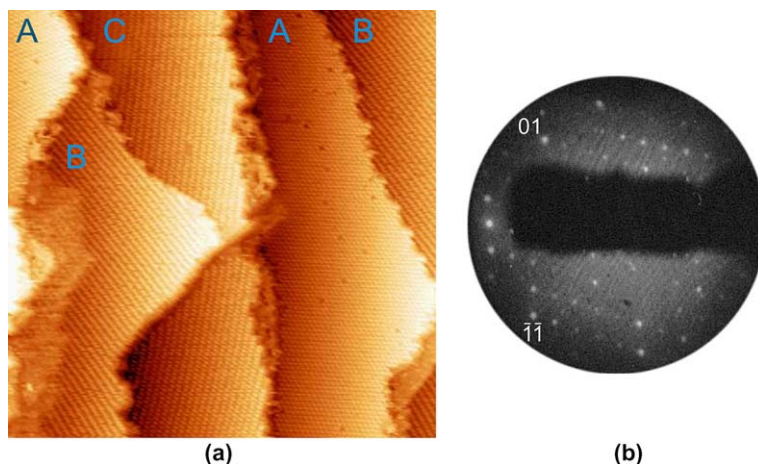
Fig. 1. Variation of the h_S/h_{Cu} AES ratio as a function of the exposure of Cu(111) (clean and pre-oxidised) to H_2S at RT. Lines serve only as guide for the eye.

Fig. 2. (a) STM image (50 nm × 50 nm, $V = 0.2$ V, $I = 1.0$ nA) and (b) LEED pattern ($E_p = 113$ eV) of the RT sulphur-saturated Cu(1 1 1) surface. The A, B and C regions correspond to Fig. 3(a)–(c), respectively.
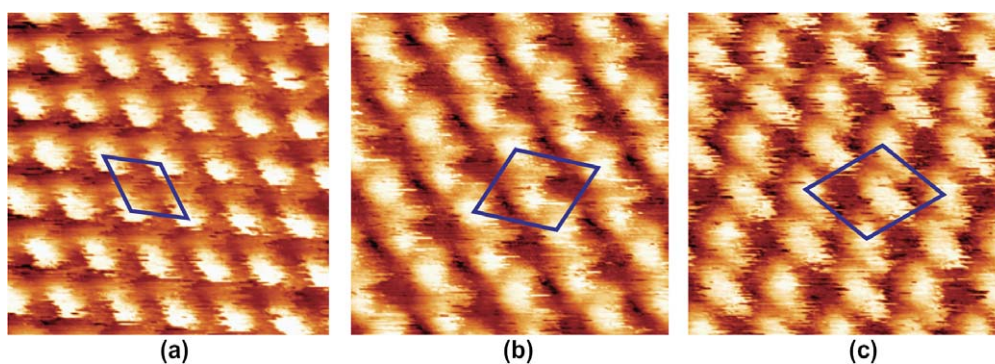

Fig. 3. STM images (4 nm × 4 nm, $V = 0.2$ V, $I = 1.0$ nA) of the three superstructures observed on the RT sulphur-saturated Cu(1 1 1) surface. The unit cell of each structure is drawn. See text for details.

Fig. 4(a) shows an STM image of the pre-oxidised Cu(1 1 1) surface after sulphur saturation at RT. To a much larger extent than for Cu(1 1 1), the step edges are preferentially oriented along the main directions of the superstructure. The effect of the pre-oxidation appears clearly compared to Fig. 2(a). After 27 L, the surface is completely covered by the "$\sqrt{7}$" structure while, in the case of direct sulphuration, contributions from the "zigzag"
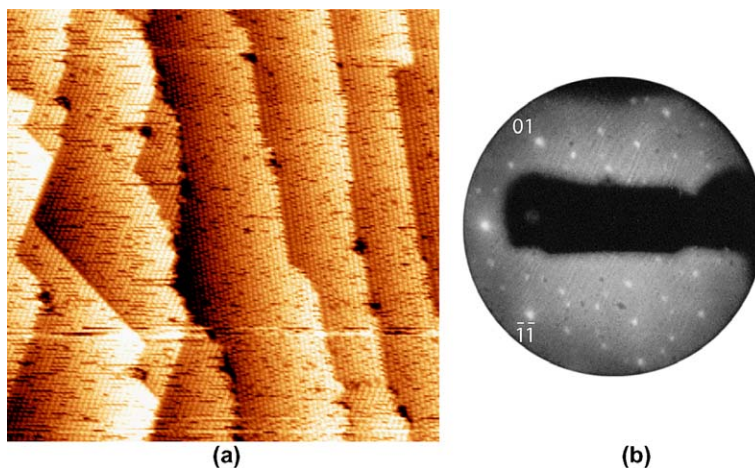

Fig. 4. (a) STM image (50 nm × 50 nm, $V = 0.5$ V, $I = 0.5$ nA) and (b) LEED pattern ($E_p = 113$ eV) after RT saturation by sulphur of the pre-oxidised Cu(1 1 1) surface.

structure were observed for exposures up to almost 150 L. Two mirror domains are evidenced on the STM images.

The LEED pattern associated with the oxidised surface rapidly disappears as the surface is exposed to H_2S. After 18 L, the observed LEED pattern is mainly (1×1) with diffuse intermediate spots. Fig. 4(b) corresponds to the LEED pattern observed for 27 L. No evolution was noticed for further exposure. It corresponds to the "$\sqrt{7}$" structure with two domains, confirming the STM data.

From the STM images and from the LEED intensities, it appears that the two mirror domains are equally present on the surface. In this case, the surface misorientation seems not to be large enough to favour one particular orientation of the "$\sqrt{7}$" superstructure [18].

Thus, besides promoting the propagation of S adsorption, pre-oxidation of the Cu(1 1 1) surface also increases the saturation coverage by the sulphur atoms. Such an enhancement of the reactivity to H_2S compared to the clean surface was also observed for the $(2\sqrt{2} \times \sqrt{2})R45°-$O/Cu(1 0 0) [15]. The number of sulphur atoms for the "$\sqrt{7}$" structure is estimated to 3/7 (0.43) of the number of Cu atoms in a Cu(1 1 1) plane, while the "zigzag" structure is associated with a lower S coverage estimated to 6/17 (0.35) [2,5,7]. This is consistent with the increase of the h_S/h_{Cu} saturation value on the pre-oxidised surface measured in our study. One explanation may reside in the fact that the pre-oxidation is performed at 300 °C and causes a substantial restructuring of the topmost Cu planes to produce the surface oxide phase forming a precursor to the growth of Cu_2O [17,20]. The "$\sqrt{7}$" phase which can be obtained at RT is generally improved by annealing at around 200 °C [7,8]. The pre-oxidation, by restructuring the surface, favours the highly ordered structure of higher coverage on Cu(1 1 1).

4. Conclusion

The effect of pre-oxidising the Cu(1 1 1) surface on the reactivity towards H_2S was studied at RT with AES, LEED and STM. A significant modification of the reactivity was observed. The sulphur adsorption reaction propagates faster on the pre-oxidised surface than on the oxygen-free surface until the full saturation of the surface is reached. An increase of the amount of adsorbed sulphur at saturation is evidenced by AES. This is confirmed by STM and LEED, which show the formation of the "$\sqrt{7}$" S-superstructure (0.43 ML) on the pre-oxidised surface instead of the "zigzag" superstructure (0.35 ML). This enhanced uptake of sulphur is assigned to the surface reconstruction of the copper surface characterising the pre-oxidised surface, and enabling a higher reactivity of the Cu atoms released by the decomposition of the surface oxide phase exposed to H_2S.

References

[1] J.L. Domange, J. Oudar, Surf. Sci. 11 (1968) 124.
[2] C.T. Campbell, B.E. Koel, Surf. Sci. 183 (1987) 100.
[3] K. Motai, T. Hashizume, H. Lu, D. Jeon, T. Sakurai, Appl. Surf. Sci. 67 (1993) 246.
[4] N.P. Prince, D.L. Seymour, M.J. Ashwin, C.F. McConville, D.P. Woodruff, Surf. Sci. 230 (1990) 13.
[5] L. Ruan, I. Stensgaard, F. Besenbacher, E. Lægsgaard, Ultramicroscopy 42–44 (1992) 498.
[6] E. Wahlström, I. Ekvall, H. Olin, S.-A. Lindgren, L. Walldén, Phys. Rev. B 60 (1999) 10699.
[7] M. Foss, R. Feidenhans'l, M. Nielsen, E. Findeisen, T. Buslaps, R.L. Johnson, F. Besenbacher, Surf. Sci. 388 (1997) 5.
[8] M. Saidy, K.A.R. Mitchell, Surf. Sci. 441 (1999) 425.
[9] G.J. Jackson, S.M. Driver, D.P. Woodruff, B.C.C. Cowie, R.G. Jones, Surf. Sci. 453 (2000) 183.
[10] P.S. Uy, J. Bardolle, M. Bujor, Surf. Sci. 134 (1983) 713.
[11] K. Prabhakaran, P. Sen, C.N.R. Rao, Surf. Sci. 169 (1986) L301.
[12] Y. Zhou, J.M. White, Surf. Sci. 183 (1987) 363.
[13] G.E. Mitchell, M.A. Schulz, J.M. White, Surf. Sci. 197 (1988) 379.
[14] D.R. Huntley, Surf. Sci. 240 (1990) 24.
[15] M.L. Colaianni, P. Syhler, I. Chorkendorff, Phys. Rev. B 52 (1995) 2076.
[16] L. Moroney, S. Rassias, M.W. Roberts, Surf. Sci. 105 (1981) L249.
[17] F. Jensen, F. Besenbacher, E. Lægsgaard, I. Stensgaard, Surf. Sci. 259 (1991) L774.
[18] J.M. Moison, J.L. Domange, Surf. Sci. 67 (1977) 336.
[19] F. Wiame, V. Maurice, P. Marcus, in press.
[20] T. Matsumoto, R.A. Bennett, P. Stone, T. Yamada, K. Domen, M. Bowker, Surf. Sci. 471 (2001) 225.