

# Surface atomic structure upon Cu(100) chlorination observed by scanning tunneling microscopy

K. N. Eltsov,<sup>1)</sup> A. N. Klimov, V. Yu. Yurov, V. M. Shevlyuga,  
and A. M. Prokhorov

*General Physics Institute, Russian Academy of Sciences, 117942 Moscow, Russia*

U. Bardi<sup>2)</sup> and M. Galeotti

*Dipartimento di Chimica Università di Firenze 50121 Firenze, Italy*

(Submitted 1 August 1995)

*Pis'ma Zh. Éksp. Teor. Fiz.* **62**, No. 5, 431–437 (10 September 1995)

The surface structure of Cu(100) after chlorine adsorption and thermal desorption in ultrahigh vacuum is studied by STM. In both adsorption and desorption regimes the presence of adsorbed chlorine is not detectable by STM at coverages smaller than a full monolayer. We report for the first time atomic-resolution STM images of the Cu(100)-*c*(2×2)-Cl phase, and we show that the growth of a thicker chloride phase at room temperature occurs through the formation of multiatomic layer islands. © 1995 American Institute of Physics.

The reaction of copper with chlorine at low pressures is a convenient model to study the action of halogens on solid surfaces. As a result of the interaction of copper and chlorine, nanometer-size objects with novel properties can be formed. For instance, this surface shows an enhancement of Raman scattering up to six orders of magnitude.<sup>1</sup> Furthermore, it has been found that the chemical state of the surface is reversible and depends only on the coverage.<sup>2</sup> The local structure of the phases formed by chlorine interaction with the Cu(100) surface can be observed using scanning tunneling microscopy (STM), which is the probe able to attain atomic resolution in real space for such a system. The capability of STM to provide data for chlorinated surfaces has been demonstrated by Sakurai *et al.*<sup>3</sup> for the case of a chlorine monolayer on Cu(111).

Early investigations of chlorine adsorption on Cu(100) carried out with LEED (low energy electron diffraction)<sup>4</sup> and EXAFS (extended x-ray adsorption fine structure)<sup>5</sup> revealed the formation of a *c*(2×2)-Cl surface phase at monolayer coverage. In this phase, each chlorine atom occupies a fourfold site with a Cu–Cl bond length of 2.37 Å. The examination of this phase by various techniques<sup>2,4–6</sup> shows that chemisorbed chlorine forms a flat, single-atomic-layer phase, and that no chloride is formed until the completion of the chemisorption process. Our STM results show for the first time atomic-resolution images in real space of the *c*(2×2)-Cl phase, confirming the results of the earlier structural studies. Our data have also permitted imaging of the CuCl multilayer islands that form on the surface at higher exposures to chlorine.

The experiments were carried out in a ultrahigh-vacuum setup consisting of a Riber analysis chamber connected to a second chamber housing the STM apparatus. Both chambers had a base pressure of  $2 \times 10^{-10}$  Torr. The design and main features of the STM

are described in Ref. 7. With this setup it is possible to introduce samples and tips through a vacuum-lock chamber and transfer them between the main chambers by means of a specially designed transfer system. The analysis chamber was equipped with a quadrupole mass spectrometer (MS), single-pass cylindrical mirror analyzer for Auger electron spectroscopy (AES), ion gun, and chlorine inlet system. Sample and tip preparation, chlorination, and thermal desorption were carried out in the analysis chamber while the STM chamber was isolated by means of a gate valve and kept under ultrahigh vacuum. A special algorithm for the recording and processing of STM images<sup>8</sup> was used to calibrate the STM piezoceramics for all coordinates. The calibration can subsequently be used in connection with a method based on the recording of two successive frames<sup>8</sup> in order to correct image distortion for an unknown sample. When this algorithm is used, the accuracy of interatomic measurements is better than 5%.<sup>8</sup> Pt–Rh tips simply cut in air were used, as well as specially prepared W tips with 20 Å end radius and 20° tip angle.<sup>9</sup> The final step of tip preparation was performed in the analysis chamber in order to remove the oxygen and carbon contamination brought from the atmosphere. This contamination could be detected by microfocus AES out to distances of up to 50 μm from the end of the tip. Ar<sup>+</sup> ion bombardment at an angle of 30°–40° to the end face of the tip could completely remove this contamination.

The sample was a 6×10×1 mm copper single crystal with both surfaces oriented along the (100) plane with 1° accuracy. The surface was mechanically polished with diamond powder before being placed in the vacuum system. The layer damaged by the polishing was removed by electrochemical etching. The treatment in ultrahigh vacuum consisted of several cycles of Ar<sup>+</sup> ion bombardment (500 eV, 1 μA/cm<sup>2</sup>) and heating to 870 K. After this treatment the intensities of the O, C and S Auger lines did not exceed 0.5% of the magnitude of the Cu L<sub>2,3</sub>VV line.

Molecular chlorine was introduced in the vacuum chamber by means a capillary line with inner diameter of 2 mm, ending at a distance of 20 mm from the sample surface. The pressure on the copper surface was calibrated according to the procedure described in Ref. 2 and was found to be 250 times higher than in other parts of the chamber. The chlorine beam pressure and the dose was varied by means of a piezoceramic fine valve, and the Cl<sub>2</sub> signal intensity at the mass spectrometer was used as feedback for computer control. The accuracy of dosing in the range of 10<sup>-2</sup>–10<sup>5</sup> L was better than 3%. The chemical state and coverage of chlorine on the surface was checked with AES in the way described in Refs. 2 and 10.

A typical STM image of the clean copper surface is presented in Fig. 1a. Large terraces separated by monatomic steps can be clearly seen. The height of the steps can be determined by STM, which is capable of distinguishing steps of monatomic, diatomic, and multiatomic height. It is important to note here that we observed only stable atomic steps on the clean copper surface in the recording regimes used. In these regimes we did not observe the step fluctuations often reported for copper surfaces.<sup>11</sup>

The STM image of an atomically resolved small area of a copper terrace is presented in Fig. 1b. Although the corrugation of the electron density of the surface is not larger than 0.2 Å, each atom is clearly detectable. We obtained atomic resolution for clean copper for both constant-current and constant-height regimes. The measured interatomic

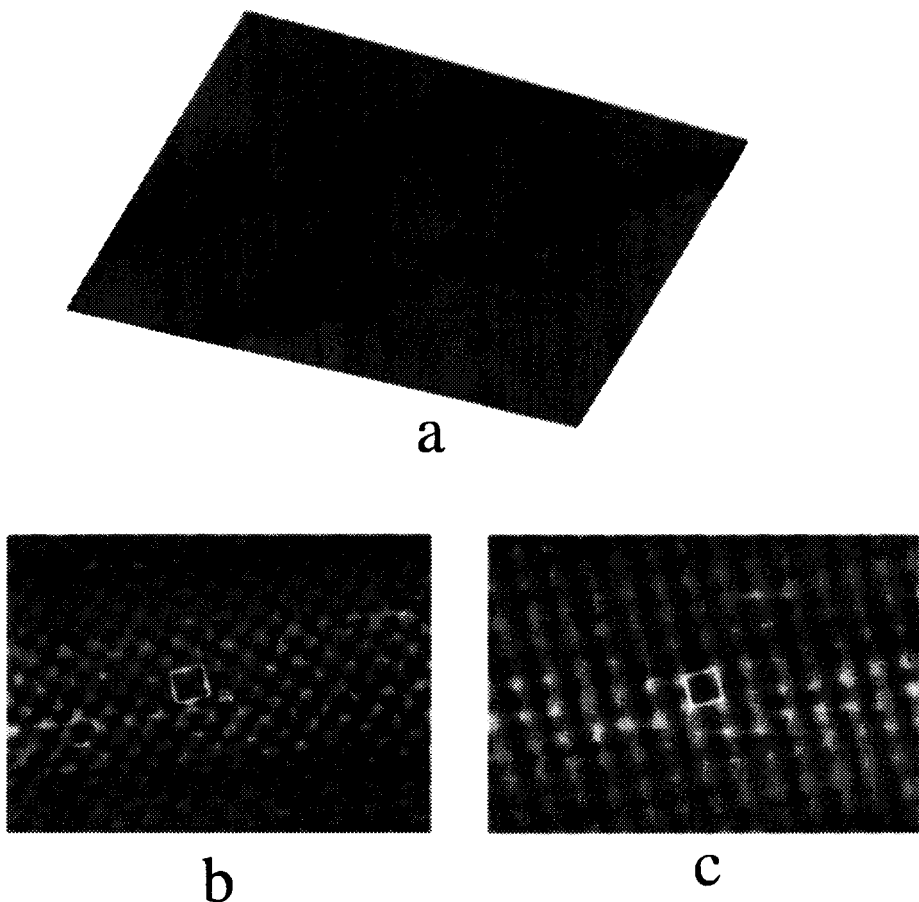


FIG. 1. a)  $165 \times 160 \text{ \AA}$  STM image of Cu(100) surface. Tunnel current  $I=0.7 \text{ nA}$  and bias of sample  $V=-1000 \text{ mV}$ , tip is at virtual ground. b)  $33 \times 46 \text{ \AA}^2$  STM image of Cu(100)-(1 $\times$ 1) surface ( $I=0.8 \text{ nA}$ ,  $V=+700 \text{ mV}$ ). Surface corrugation is  $0.2 \text{ \AA}$ . The unit mesh  $c(2 \times 2)\text{-Cl}$  devised from chlorine fourfold sites is shown; c)  $33 \times 46 \text{ \AA}^2$  STM image of Cu(100)- $c(2 \times 2)\text{-Cl}$  surface at chlorine monolayer coverage ( $I=1.0 \text{ nA}$ ,  $V=-700 \text{ mV}$ ). Surface corrugation is  $0.6 \text{ \AA}$ . The unit mesh  $c(2 \times 2)\text{-Cl}$  is marked out.

distance was  $2.5 \pm 0.1 \text{ \AA}$ , in good agreement with the shortest interatomic distance in the copper lattice ( $2.55 \text{ \AA}$ ).

Exposure to chlorine was carried out at room temperature. To determine the coverage in the submonolayer range we used the intensity of the  $\text{ClL}_{2,3}\text{VV}$  Auger line, which is directly proportional to the chlorine-covered area. The saturation of its intensity at room temperature corresponded to the completion of the chlorine monolayer, due to the sharp decrease of the sticking coefficient.<sup>2,4,5</sup> For doses of 0.1; 0.5; and  $3.0 \text{ L}$  ( $1 \text{ L} = 10^{-6} \text{ Torr}\cdot\text{s}$ ) we observed the formation of monatomic chlorine layers with coverages of

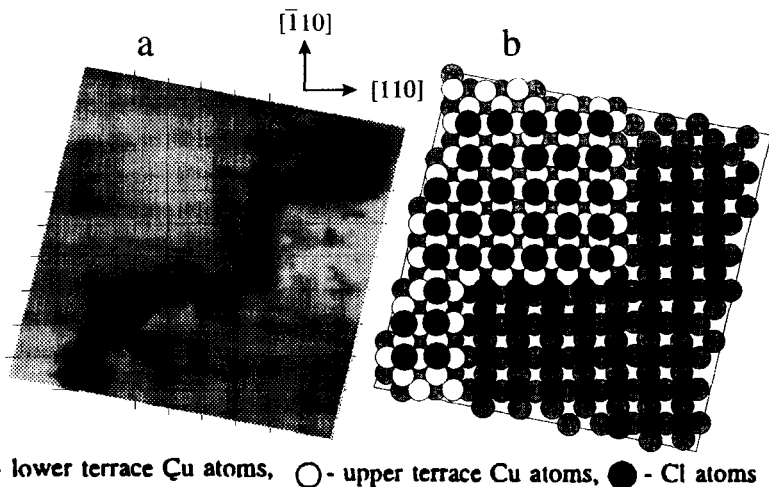
$\Theta=0.2$ ; 0.6; and 1.0 (we assume here that  $\Theta=1$  corresponds to the full  $c(2\times 2)$ -Cl monolayer).

At coverages of 0.2 and 0.6 we could not observe by STM any of the features typical of adsorbate phases, such as islands, deepening, fractional atomic steps, or other effects. The atomic-resolution images at these coverages show only the lattice parameters of clean Cu(100) (Fig. 1b) but not the parameters of chemisorbed chlorine. The insensitivity of STM to chemisorbed chlorine at coverages lower than a full monolayer can be attributed to the effect of the tip on the adsorbate. It is known that chemisorbed chlorine interacts strongly with the topmost layer copper atoms.<sup>2,12</sup> The appearance of characteristic peaks in the electron density distribution of the copper valence band below the Fermi level<sup>12</sup> at submonolayer coverage permits to interpret this state as a "surface molecule," in which the valence electrons of each chlorine atom interact with the electrons in the conduction band of copper. For this reason, the adsorbed chlorine atoms have a high surface mobility and can easily move along the surface under the influence of the STM tip, and therefore could not be detected. We also note that AES showed the remarkable presence of adsorbed chlorine on the tip end, even though the STM chamber was isolated from the chlorine gas during chlorine adsorption on the sample surface and the STM measurements were performed at a residual pressure of chlorine species not larger than  $5 \cdot 10^{-12}$  Torr. Therefore, it appears likely that the origin of chlorine on the tip is transfer from the copper surface during scanning. To estimate the influence of the tip material on the chlorine layer we also used Pt-Rh tips. We found no significant difference in the results.

At  $\Theta=1$  the atomic-resolution STM images show a square lattice rotated by  $45^\circ$  with respect to the  $(1\times 1)$  substrate (Fig. 1b,c). Analysis of the frames, corrected for image distortion,<sup>8</sup> gave the nearest interatomic distances as  $d=3.50\pm 0.15$  Å. This result shows the formation of the Cu(100)- $c(2\times 2)$ -Cl phase (also equivalently indexed as a  $(\sqrt{2}\times\sqrt{2})R45^\circ$ -Cl phase) with interatomic distance Cl-Cl equal to 3.61 Å, as reported in<sup>4</sup> on the basis of LEED observations. The unit mesh of the Cl-covered surface shown in Fig. 1c can be superimposed on the image of the clean copper lattice (Fig. 1b), giving a good fit with the expected  $c(2\times 2)$  periodicity. Apparently, the possibility of getting STM images of the chlorine lattice for full monolayer coverage is due to the absence of empty sites that would allow chlorine atoms to move under the influence of the tip.

The capability of STM to detect the atomic structure in real space is especially effective for the study of more-complex objects in this system, such as atomic steps (Fig. 2). It is clearly seen that the step edges lie parallel to chlorine rows but not to copper rows. The model of the Cu(100)- $c(2\times 2)$ -Cl step edge shown in Fig. 2b fully corresponds to the STM image. The surface lattices of the upper and lower terraces is shifted by half a period in one of two symmetrical  $[110]$  directions for the copper crystal.

Due to the small sticking probability of chlorine adsorption at room temperature, after completion of the monolayer very large doses of chlorine are necessary in order to form higher-coverage phases.<sup>2</sup> In the present experimental conditions we observed the formation of CuCl at room temperature, as evidenced by AES, after a dose of 400 L. We know from the results reported in Refs. 2 and 6 that at substrate temperatures higher than 280–290 K only multiatomic-layer CuCl islands exist on the copper surface. The AES factor analysis approach reported<sup>2,10</sup> was applied here, permitting us to separate each



● - lower terrace Cu atoms, ○ - upper terrace Cu atoms, ● - Cl atoms  
 FIG. 2. a) STM image of a monatomic step on the Cu(100)-c(2×2)-Cl surface. The size of the image is 34×34 Å ( $I=1.44$  nA,  $V=-500$  mV). Thin straight lines are drawn along the chlorine atom rows of upper terrace. b) Model of the atomic structure of a monatomic step on the chlorine-covered Cu(100) surface.

chemical compound resulting from chlorine adsorption on Cu(100) and to estimate that for this exposure the area covered with CuCl islands is 6–8% of the whole surface.

A complete confirmation of the AES analysis was obtained from the STM images. The average area covered by the islands was estimated from the analysis of several STM frames to be approximately 5–10%. In Fig. 3a an image showing 17 islands is presented. A single island is shown in Fig. 3b. In view of the fact that we used sharp W tips, the shape and size of the island are only slightly distorted by the tip. The typical size of the

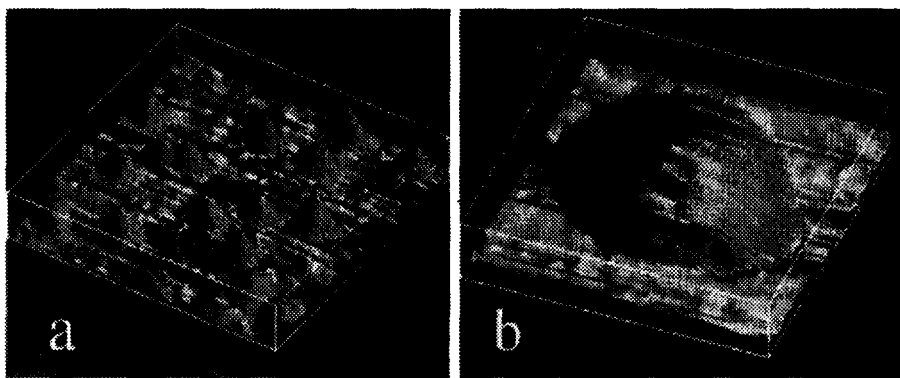


FIG. 3. a) 6100×6000 Å STM image of the Cu(100) surface after exposure to a chlorine dose of 400 L at room temperature ( $I=0.8$  nA,  $V=+2000$  mV). b) STM image of a single CuCl island. The size of the image is 870×900 Å ( $I=0.5$  nA,  $V=+1400$  mV). Island height is 65 Å.

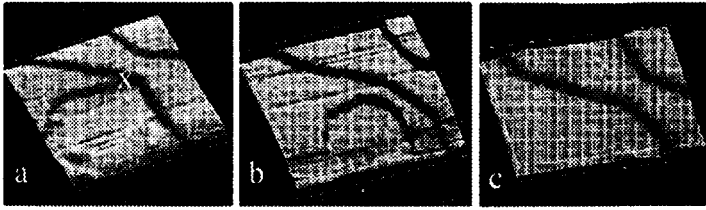


FIG. 4. Step motion and separation observed on Cu(100) covered with a chlorine submonolayer ( $\Theta=0.6$ ) under the influence of the STM tip. The size of STM image is a  $950 \times 950 \text{ \AA}$  ( $I=1 \text{ nA}$ ,  $V=+700 \text{ mV}$ ). a—0 min; b—20 min; c—2 hours.

islands at this dose is about  $600\text{--}750 \text{ \AA}$  in diameter at the base and  $60\text{--}80 \text{ \AA}$  in height. The detailed study of CuCl islands formation will be discussed in a forthcoming paper.

The possibility of removing the chlorination products from the copper surface by heating the sample at moderate temperatures (not higher than  $900 \text{ K}$ <sup>2,13</sup>) opens up a second controllable path for changing the chlorine coverage. The CuCl film sublimates at  $420\text{--}480 \text{ K}$  in the form of trimers  $\text{Cu}_3\text{Cl}_3$ , resulting in the restoration of the chlorine monolayer.<sup>2</sup> At  $T=770\text{--}900 \text{ K}$  chemisorbed chlorine is removed along with the copper atoms of the topmost atomic layer in the form of CuCl molecules. After such a treatment, it is interesting to compare the surface topography of the corresponding coverage obtained by chlorine adsorption or by heating of the chlorinated surface and to determine the surface topography resulting from the removal of the topmost copper layer.

We carried out the thermal desorption of chlorinated copper using of AES and MS as probes to determine the chlorine coverage and the surface composition. The thermal desorption procedure and the data collection were fully computer controlled. The rate of heating was  $2 \text{ K}$  per second. After the desired coverage was reached, the heating was switched off and the sample was allowed to cool down. The STM study of the chlorine monolayer obtained after removal of the copper chloride at  $T=480 \text{ K}$  did not show any traces of CuCl islands, nor surface defects attributable to island sublimation: all the atomic-resolution images showed only the Cu(100)- $c(2 \times 2)$ -Cl phase. It may be possible that the high surface mobility of copper atoms at  $480 \text{ K}$  is enough to smooth away the defects resulting from sublimation. If a coverage of  $0.6$  is created by heating up to  $T=820 \text{ K}$ , only the Cu(100)- $(1 \times 1)$  phase was observed in the STM images.

In both adsorption and desorption regimes the presence of adsorbed chlorine was not detectable by STM at  $\Theta < 1$ . But step motion and separation was observed during repeated scans of a  $1000 \text{ \AA}$  region at  $\Theta=0.6$ . Figure 4 shows the transformation of the surface topography over the course of 2 hours. At the beginning, both monatomic and diatomic steps are detectable (Fig. 4a). At the point marked "X" two monatomic steps unite and then form a diatomic step. After 20 min (Fig. 4b) only monatomic steps are visible on the surface. The diatomic step in Fig. 4a changes into two monatomic steps, forming a cascade of three monatomic steps. The lowest atomic step forms a monoatomic "hole" (Fig. 4b) which disappears at the end of the process (Fig. 4c). The final image is stable and does not show further changes after several hours. Since similar processes were not observed on the clean copper surface, this phenomenon must be due to the

presence of chlorine atoms. Taking into account the strong interaction of the uppermost copper layer with chemisorbed chlorine, as evidenced by the distortion of the  $\text{CuM}_{2,3}\text{VV}$  and  $\text{CuL}_3\text{VV}$  Auger lines and its thermal desorption in the form of  $\text{CuCl}$  molecules,<sup>2,13</sup> we suggest that the presence of chlorine can cause a weakening of the bonding between the second and the topmost copper-atom layers and increase the surface mobility of copper atoms covered by chlorine. The observed motion and step separation could then be initiated by the influence of the STM tip on such a mobile atomic layer.

We would like to thank Drs. V. V. Dremov and S. Y. Shapoval for the tungsten tips specially prepared for the experiments. This work was supported by NATO under the Linkage Program (Grant LG930499), the International Science Foundation (Grant M68300), the Russian Fund for Fundamental Research, Consiglio Nazionale delle Ricerche (CNR, Italy), and the Ministry of Science and Technological Policy of Russia.

<sup>1</sup>)e-mail: eltsov@lc.jpi.msk.su

<sup>2</sup>)e-mail: bardi@lcfs.chim.unifi.it

---

<sup>1</sup>K. N. Eltsov, G. Ya. Zueva, A. N. Klimov *et al.*, *Chem. Phys. Lett.* **158**, 271 (1989).

<sup>2</sup>K. N. Eltsov, G. Ya. Zueva, A. N. Klimov *et al.*, *Surf. Sci.* **251/252**, 753 (1991)

<sup>3</sup>K. Motai, T. Hashizume, D.-R. Jeon *et al.*, *Jap. J. Appl. Phys.* **31**, L874 (1992).

<sup>4</sup>F. Jona, D. Westphal, A. Goldmann, and P. M. Marcus, *J. Phys. C* **16**, 3001 (1983).

<sup>5</sup>P. H. Citrin, D. R. Hamann, L. F. Mattheiss, and J. E. Rowe, *Phys. Rev. Lett.* **49**, 1712 (1982).

<sup>6</sup>M. Galeotti, U. Bardi, B. V. Andryushechkin *et al.*, *J. Electron Spectrosc. Relat. Phenom.* [in press].

<sup>7</sup>S. L. Pryadkin, V. Yu. Yurov, A. N. Klimov *et al.*, *Rev. Sci. Instr.* [to be submitted].

<sup>8</sup>A. N. Klimov and V. Yu. Yurov, *Rev. Sci. Instr.* **65**, 1551 (1994).

<sup>9</sup>V. V. Dremov, V. A. Makarenko, S. Y. Shapoval *et al.*, *Nanobiology* **3**, 83 (1994).

<sup>10</sup>B. V. Andryushechkin, K. N. Eltsov, and V. V. Martynov, *Phys. Low-Dim. Struct.* **6**, 1 (1995).

<sup>11</sup>S. Rousset, S. Gauthier, O. Siboulet *et al.*, *Ultramicroscopy* **42–44**, 515 (1992); J. Winterlin, R. Schuster, D. J. Coulman *et al.*, *J. Vac. Sci. Technol. B* **9**, 902 (1991).

<sup>12</sup>D. Westphal and A. Goldmann, *Solid St. Commun.* **35**, 437 (1980).

<sup>13</sup>H. F. Winters, *J. Vac. Sci. Technol. A* **3**, 786 (1985).

Published in English in the original Russian journal. Edited by Steve Torstveit.