

**SURFACE ATOMIC STRUCTURE AT Cu(100) CHLORINATION
OBSERVED WITH SCANNING TUNNELING MICROSCOPY**

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The surface structure of Cu(100) after chlorine adsorption and thermal desorption in ultra high vacuum was studied with STM. In both adsorption and desorption regimes the presence of adsorbed chlorine was not detectable by STM at coverages smaller than 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 by the formation of multiatomic layer islands.

The reaction of copper with chlorine at low pressure 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 [1]. Furthermore, it was found that the chemical state of the surface is reversible and depends only on coverage [2]. The local structure of the phases formed by chlorine interaction with the Cu(100) surface can be observed using Scanning Tunnelling 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 was demonstrated by Sakurai et al. [3] 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) [4] and EXAFS (extended X-ray adsorption fine structure) [5] showed the formation of a c(2 × 2)-Cl surface phase at monolayer coverage. In this phase, each chlorine atom occupies the fourfold site with a Cu-Cl bond length of 2.37 Å. The examination of this phase by various techniques [2,4-6] 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 also permitted to image the CuCl multilayer islands that form on the surface for larger exposures to chlorine.

The experiments were carried out in a ultrahigh vacuum set-up consisting of a Riber analysis chamber connected to a second chamber housing the STM apparatus. Both chambers had a base pressure of 2×10^{-10} Torr. The STM design and main features are described in Ref. [7]. With this set-up it is possible to introduce samples and tips through a vacuum lock chamber and transfer them

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between the main chambers by means of a specially designed transfer system. The analysis chamber was equipped with quadrupole mass-spectrometer (MS), single-pass cylindrical mirror analyser for Auger electron spectroscopy (AES), ion gun, and chlorine inlet system. Sample and tips 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 ultra-high vacuum. A special algorithm for the recording and treatment of STM images [8] 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 subsequent frames [8] in order to correct image distortion for an unknown sample. Using this algorithm, the accuracy of interatomic measurements is better than 5% [8]. Pt-Rh tips simply cut in air were used, as well as specially prepared W tips with 20Å end radius and 20° tip angle [9]. 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 to extend up to 50 μm distance from the end of the tip. Ar⁺ ion bombardment at an angle of 30° ÷ 40° from the end side of the tip could completely remove this contamination.

The sample was a 6×10×1mm copper single crystal with both surfaces oriented along the (100) plane with 1° accuracy. The surface was mechanically polished with diamond powder before introduction in the vacuum system. The layer damaged by the polishing powder was removed by electrochemical etching. The treatment in ultra high vacuum consisted in several cycles of Ar⁺ ion bombardment (500 eV, 1 μA/cm²) and heating at 870 K. After this treatment the intensities of O, C and S Auger lines did not exceed 0.5% of the magnitude of the Cu L_{2,3}VV line.

Molecular chlorine was introduced in the vacuum chamber by means a capillary line with inner diameter of 2mm, ending at a distance of 20mm from the sample surface. The pressure on the copper surface was calibrated according to the procedure described in Ref. [2] and resulted 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 Cl₂-signal intensity at the mass-spectrometer was used as a back loop for computer control. The accuracy of dosing in the range of 10⁻² ÷ 10⁵ 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, 10].

A typical STM image of the clean copper surface is presented in fig.1a. Large terraces separated by monoatomic steps can be clearly seen. The height of the steps can be determined by STM, that permits to distinguish steps of single-, double- and multiatomic height. It is important to note here that we observed only stable atomic steps on the clean copper surface at the recording regimes used. In these regimes we did not observe the step fluctuations often reported for copper surfaces [11].

The STM image of an atomically resolved small area of a copper terrace is presented in fig.1b. The corrugation of the electron density of the surface is not larger than 0.2Å, nevertheless each atom is clearly detectable. We obtained atomic resolution for clean copper both for constant current and for constant height regimes. The measured interatomic distance was 2.5 ± 0.1Å in good agreement with nearest interatomic distance in the copper lattice (2.55Å).

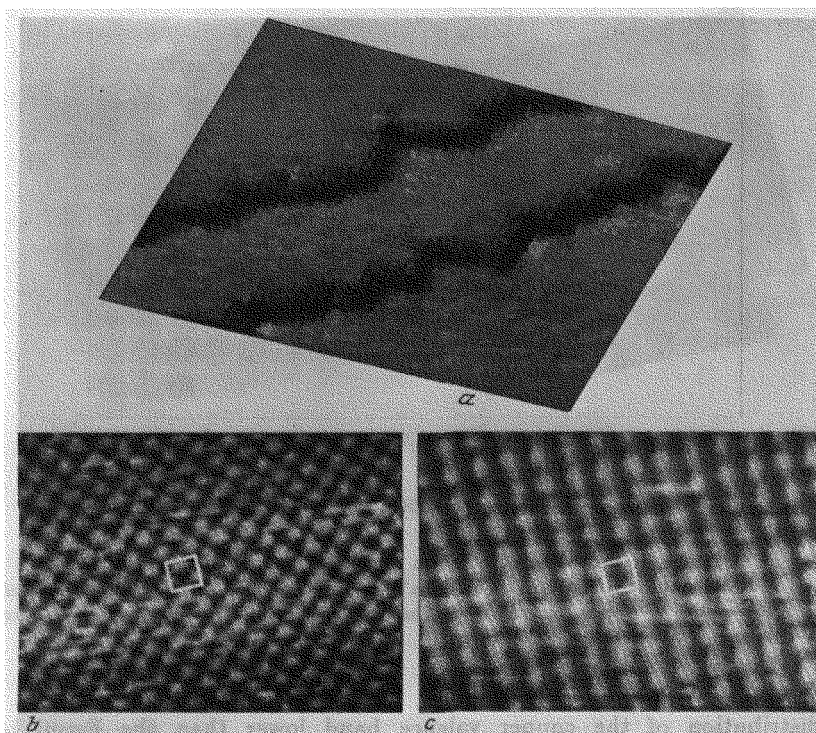


Fig.1. a) $165 \times 160 \text{ \AA}$ STM image of Cu(100) surface. Tunnel current $I = 0.7 \text{ nA}$ and bias of sample $V = -1000 \text{ mV}$, tip is at virtual ground. b) $33 \times 46 \text{ \AA}^2$ STM image of Cu(100)- (1×1) surface ($I = 0.8 \text{ nA}$, $V = +700 \text{ mV}$). Surface corrugation is 0.2 \AA . The unit mesh $c(2 \times 2)\text{-Cl}$ designed 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 \AA . The unit mesh $c(2 \times 2)\text{-Cl}$ is marked out

Exposure to chlorine was carried out at room temperature. To determine the coverage in the submonolayer range we used the intensity of $\text{ClL}_{2,3}\text{VV}$ 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 [2,4,5]. For doses of 0.1; 0.5; and 3.0 L ($1\text{L} = 10^{-6} \text{ Torr}\cdot\text{s}$) we observed the formation of monoatomic chlorine layers of coverages of $\Theta = 0.2$; 0.6; and 1.0 (we assume here that $\Theta = 1$ corresponds to the full $c(2 \times 2)\text{-Cl}$ 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 [2,12]. The appearance of characteristic peaks in the electron

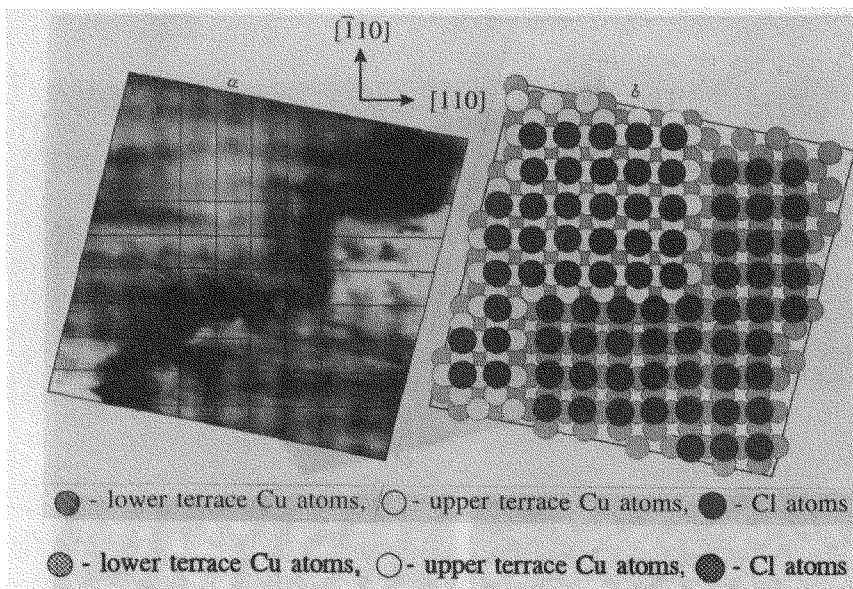


Fig.2. a) STM image of monoatomic step on Cu(100)-c(2 × 2)-Cl surface. The size of the image is $34 \times 34 \text{ \AA}^2$ ($I = 1.44 \text{ nA}$, $V = -500 \text{ mV}$). Thin straight lines are drawn along the chlorine atom rows of upper terrace. b) The model of atomic structure of monoatomic step on chlorine covered Cu(100) surface

density distribution of the copper valence band lower than the Fermi level [12] at submonolayer coverage permits to interpret this state as "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 effect 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 during chlorine adsorption on the sample surface the STM chamber was isolated from the chlorine gas 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 the transfer from the copper surface during scanning. To estimate the material tip influence on chlorine layer we also used Pt-Rh tips. We found no significant difference in the results.

At $\Theta = 1$, atomic resolution STM images show a square lattice rotated of 45° with respect to the (1×1) substrate (fig.1b,c). The analysis of the frames, corrected for image distortion [8], gave the nearest interatomic distances as $d = 3.50 \pm 0.15 \text{ \AA}$. This result shows the formation of the Cu(100)-c(2 × 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 \AA as reported in [4] 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) obtaining a good fit with the expected c(2 × 2) periodicity. Apparently, the possibility to get STM images of the chlorine lattice for full monolayer coverage is due to the absence of empty sites allowing chlorine atoms to move under the effect 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

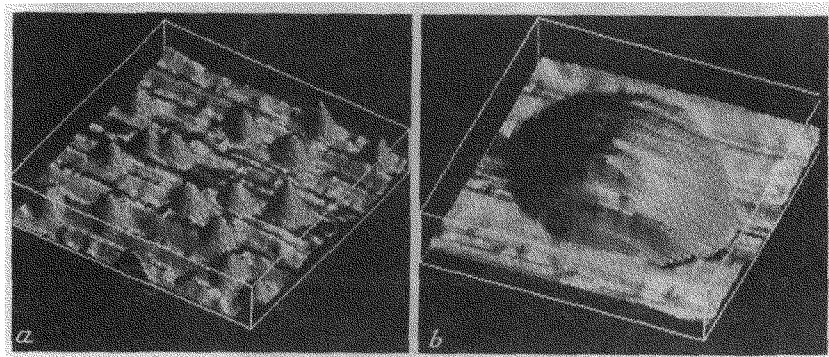


Fig.3. a) $6100 \times 6000 \text{Å}^2$ STM image of Cu(100) surface after a chlorine dose of 400 L at room temperature ($I = 0.8 \text{ nA}$, $V = +2000 \text{ mV}$). b). STM image of single CuCl island. The size of the image is $870 \times 900 \text{Å}^2$ ($I = 0.5 \text{ nA}$, $V = +1400 \text{ mV}$). Island height is 65Å

steps (fig.2). It is clearly seen that the step edges lie parallel to chlorine rows but not to copper rows. The model of Cu(100)- $c(2 \times 2)$ -Cl step edge shown in fig.2b fully corresponds to STM image. The surface lattices of upper and lower terraces is shifted of 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 the completion of the monolayer very large doses of chlorine are necessary in order to cause the formation of higher coverage phases [2]. 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, 6] that at substrate temperatures higher than 280-290 K only multiautomic layer CuCl islands exist on the copper surface. The AES factor analysis approach reported [2,10] was applied here, permitting us to separate each chemical compound resulting from chlorine adsorption on Cu(100) and to estimate that for this exposure the area covered with CuCl islands is $6 \div 8\%$ 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 $5 \div 10\%$. In fig.3a an image showing 17 islands is presented. A single island is shown in fig.3b. Taking into account that we used sharp W-tips, the shape and the size of the island is only slightly distorted by the tip. The typical size of the islands at this dose is about $600 \div 750 \text{Å}$ in diameter of the base and $60 \div 80 \text{Å}$ in height. The detailed study of CuCl islands formation will be discussed in a forthcoming paper.

The possibility to remove the chlorination products from the copper surface by the heating of the sample at moderate temperatures (not higher than 900 K [2,13]) opens a second controllable path to change the chlorine coverage. The CuCl film sublimates at $420 \div 480 \text{ K}$ in the form of trimers Cu_3Cl_3 , resulting in the restoring of the chlorine monolayer [2]. At $T = 770 \div 900 \text{ K}$ 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 the chlorine adsorption or

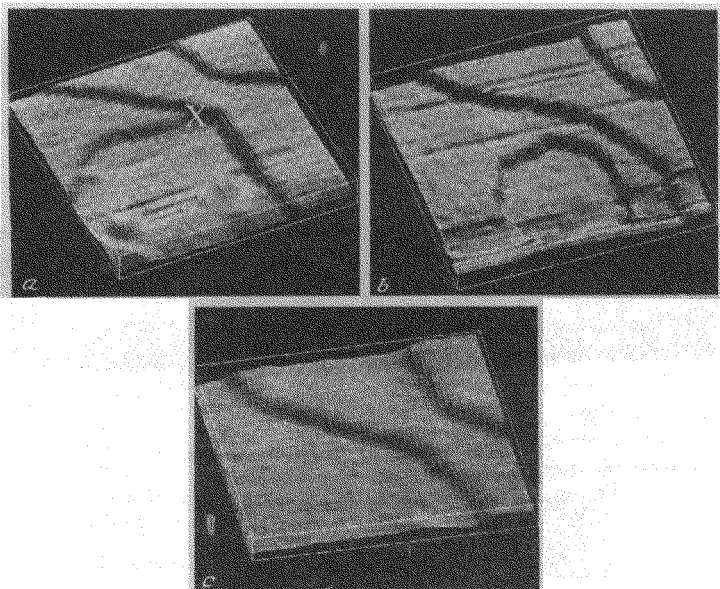


Fig.4. The step motion and separation observed on Cu(100) covered with chlorine submonolayer ($\Theta = 0.6$) under influence of STM tip. The size of STM image is $950 \times 950 \text{ \AA}^2$ ($I = 1 \text{ nA}$, $V = +700 \text{ mV}$): a - 0min; b - 20min; c - 2 hours

the 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 was fully computer controlled. The rate of heating was 2K per second. After the desired coverage was reached, the heating was switched off and the sample allowed to cool down. The STM study of the chlorine monolayer obtained after removing the copper chloride at $T = 480 \text{ K}$ did not show any traces of CuCl islands, nor surface defects attributable to the 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 for copper atoms at 480K is enough to smooth away the defects resulting from sublimation. If the coverage of 0.6 is created heating up to $T = 820 \text{ K}$, only the Cu(100)- (1×1) 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 \AA region at $\Theta = 0.6$. In fig.4 the surface topography transformation during 2 hours is presented. At the beginning, both mono- and diatomic steps are detectable (fig.4a). In the point marked as "X" two monoatomic steps unite and then form a diatomic step. After 20 min (fig.4b) only monoatomic steps are visible on the surface. The diatomic step in fig.4a changes into two monoatomic steps, forming a cascade of three monoatomic 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. Similar processes were not observed on the clean copper surface, hence this phenomenon is related to the presence of chlorine atoms. Taking into account the strong interaction of uppermost copper layer with chemisorbed chlorine, as evidenced by the distortion of $\text{CuM}_{2,3}\text{VV}$ and $\text{Cu L}_{3}\text{VV}$ Auger lines and its thermal desorption in the form of CuCl molecules [2,13], we suggest that the presence of chlorine can cause the 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 STM tip influence on such mobile atomic layer.

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