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Structural transformations of Cu(110) surface induced by adsorption of molecular chlorine

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ABSTRACT

The adsorption of molecular chlorine on Cu(110) has been studied by scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) in the combination with density functional theory (DFT) calculations. We have found that at early stage of chlorine adsorption the reconstruction of the Cu(110) surface takes place. At coverages $0.4<\theta<0.5$ ML (monolayer), an array of the striped light domain walls separating the c(2×2) domains forms on the surface. According to DFT calculations, each light domain wall contains an additional row of copper atoms in the middle. As the coverage increases to 0.5 ML, all the light domain walls disappear from the adlayer and a simple c(2×2) structure forms. Further chlorine dosing results in the uniaxial splitting of the overlayer spots in LEED indicating the compression of the chlorine layer in the $\langle 110\rangle$ direction. At coverages close to the saturation level, the adsorption of chlorine leads to formation of 1D facets consisting of two {210} planes and running along the [001] direction.

1. Introduction

Adsorption of chlorine on the low-index copper surfaces has been a subject of numerous investigations since the 1970s [1,2]. In the case of the close-packed hexagonal (111) plane, chlorine forms a simple $(\sqrt{3}\times\sqrt{3})$ R30° structure at 0.33 ML [3–7]. Increase of the coverage above 0.33 ML leads to an uniaxial compression of the adsorbate lattice via a domain-wall mechanism [5,7]. For chlorine adsorption on the Cu(100) surface characterized by a square symmetry, only one c(2×2) structure at 0.5 ML was observed [8]. Further compression of the chlorine lattice on Cu(100) is unfavorable since the nearest neighbor distance in the c(2×2) structure (3.61 Å) corresponds well to the van der Waals diameter of chlorine (3.6 Å). The more opened Cu(110) surface is potentially more active, therefore, the formation of complex structures and chlorine-induced reconstructions can be expected.

There are no published results on Cl^2 adsorption on Cu(110) in ultra-high vacuum (UHV). However, the adsorption of HCl on Cu(110) was studied by various techniques: AES (Auger electron spectroscopy) [10], LEED [10] and STM [11,12]. In Ref. [10], the formation of the c(2×2) structure at the coverage of 0.5 ML was reported. Further HCl exposure gave rise to the uniaxial compression of the chlorine lattice in the $[1\bar{1}0]$ direction and to the formation of the quasihexagonal structure (3×2).

In the recent work by Carley et al. [11], the adsorption of HCl on Cu(110) was examined with a room temperature STM. At $\theta\approx 0.41$ ML, authors observed the appearance of chlorine double stripes parallel to the [001] direction. Chlorine atoms on the both sides of the double stripe occupy positions in the c(2×2) lattice. A little increase of the coverage resulted in the formation of the periodic array of the double stripes separating antiphase domains with the c(2×2) structure. At $\theta=0.5$ ML, all the stripes disappear and the system comes to the uniform c(2×2) lattice. Increase of chlorine coverage above 0.5 ML leads to appearance of a new striped structure.

Wan and Itaya [13] and Li et al. [14] investigated the HCl adsorption on Cu(110) from a solution with STM. They observed similar structures (4×1) and (5×1), respectively. Authors, however, suggested mutually exclusive structural models.

It is noteworthy, that all the authors reported the increase of the surface mobility induced by adsorption of chlorine.

Recently, the Cl/Cu(110) system was studied theoretically with DFT [15]. The c(2×2) structure was found to be preferable for $\theta<0.5$ ML. According to the calculations, the short bridge adsorption site is the most favorable site for the Cl adsorption.

The present work was aimed at the atomic-scale investigation of the surface structures formed as a result of adsorption of molecular chlorine on Cu(110) at room temperature. The main instruments were scanning tunneling microscopy and low energy electron diffraction supported by DFT calculations.

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2. Experimental and computational details

All the experiments were carried out in a UHV system consisting of two connected chambers, one used for spectral analysis, the other for structural measurements. The analytical chamber was equipped with a quadrupole mass-spectrometer and a cylindrical mirror analyzer for Auger electron spectroscopy. The structural chamber included a room-temperature STM GPI-300 (SigmaScan Ltd.) and 3-grid optics for LEED. The copper sample was cut parallel to (110) plane to an accuracy better than 0.5°. To clean the surface, we used repetitive cycles of argon ion bombardment (1 keV) and annealing at 950 K. Chlorine adsorption and all measurements were carried out at room temperature. The base pressure in the chamber during experiments was better than 1×10^{-10} Torr. The STM image processing was done with the WSxM software [16].

All DFT calculations were carried out using the Vienna ab-initio simulation package (VASP) [17–20] employing the projector augmented wave method [21] and GGA-PBE (Perdew, Burke, Ernzerhof) functional [22]. The plane-wave cut-off energy of 400 eV was applied. The Brillouin zones of the (1×1) unit cells of Cu(110) with the chlorine coverage $\theta\leq0.5$ ML, Cu(110) with $\theta>0.5$ ML and Cu(210) were sampled with 2×3×1, 1×6×1 and 6×6×1 Monkhorst–Pack k-point meshes [23], respectively.

The equilibrium bulk lattice parameter was calculated to be 3.64 Å.

The Cu(110) surface was represented by five-layer slab separated by vacuum region of 14.5 Å. The bottom three layers were fixed, while the geometries of the remaining layers and the adsorbates were allowed to relax.

The Cu(210) surface was represented by a 10-layer slab separated by 12 Å of vacuum. The bottom five layers for Cu(210) were fixed at the calculated bulk structures, while the geometries of the remaining layers and the adsorbates were allowed to fully optimize.

STM images were simulated from the DFT results using the simple Tersoff–Hamann approximation [24].

3. Results

3.1. AES and LEED data

Fig. 1 demonstrates the Cl/Cu AES peak ratio (η) shown as a function of the chlorine dosing time on Cu(110) at 300 K. According to the plot, the first stage of adsorption ($\eta<1.0$) is characterized by a fast linear growth of η. At further dosing, the increase of the Cl/Cu AES peak ratio slows down and the system comes to the saturation at $\eta\approx1.4$. It is noteworthy that chlorine remains in the chemisorbed state up to exposures of 650 s, since no changes in the shape and in the energy position of the chlorine line $L2{,}3VV$ (182 eV) were detected.

To characterize the ordered chlorine structures on Cu(110), a series of LEED patterns was acquired in the course of the continuous Cl_2 adsorption (see Fig. 2). Fig. 2a shows a LEED pattern from the clean Cu(110) surface. The diffraction pattern in Fig. 2b corresponds to the first ordered chlorine structure developed at $\eta=0.4$ (see Fig. 1).

The numerous overlayer spots that appeared between substrate spots form lines parallel to the vector (1,0). This observation means the doubling of the surface periodicity in the direction [001] and the appreciable increase of the periodicity in the $[1\bar{1}0]$ direction. As chlorine adsorbs, the distance a between neighboring spots in the direction of the (1,0) vector continuously decreases. To characterize this type of the LEED pattern existing in the range of $0.4<\eta<0.9$, we introduce a splitting parameter S equal to the ratio a/b (b — the distance between (0,1) and (1,1) spots of the substrate). For the first ordered structure $S\approx0.13\pm0.01$. At $\eta=0.9$, the value of S comes to zero and the split LEED pattern transforms into a c(2×2) LEED pattern (see Figs. 1 and 2c).

Further chlorine adsorption leads to the uniaxial splitting of the c(2×2) spots, as seen from Fig. 2d. We determine another splitting parameter Q as the ratio c/b (c is the distance between overlayer spots). As the coverage increases, the Q value continuously grows up to its maximum at $Q\approx0.4$.

At $Q\gtrsim0.3$ ($\eta\gtrsim1.1$), new lines of the spots parallel to the (1,0) vector appear in the diffraction pattern. According to the LEED pattern in Fig. 2e, the distance between new spots is less than the value of the splitting c. A different nature of new spots and the split c(2×2) pattern becomes evident with increasing of the energy of the primary beam. The split c(2×2) spots emerge more towards the center of the screen, while groups of new spots appear to move in an opposite direction along the vector (1,0). In the LEED pattern shown in Fig. 2e, the splitting parameter Q is equal to 0.37.

After reaching of the maximum level of the splitting at $Q\approx0.4$, the intensity of the spot doublets around the c(2×2) positions starts to diminish up to the complete disappearance of the spots, as seen from Fig. 2f. Further chlorine dosing does not lead to any changes in the LEED pattern.

As a result of our measurements, the characteristic LEED patterns were indicated on the adsorption curve shown in Fig. 1. Thus, we can distinguish three coverage ranges corresponding to the different η and the different types of the LEED pattern:

I. $\eta<0.4$. No ordered structures.
II. $0.4<\eta<0.9$. Appearance of the first LEED pattern (Fig. 2b) and its continuous transformation into the c(2×2) one.
III. $0.9<\eta<1.4$. Splitting of the c(2×2) spots and appearance of the new spots at saturation.

3.2. Low-coverage range I ($\eta<0.4$)

At low coverage ($\eta<0.4$), chlorine does not form ordered structures on the Cu(110) surface at 300 K. In Fig. 3, we present a series of the panoramic STM images obtained in the course of the continuous adsorption of Cl_2 into the STMchamber. According to STM data, the adsorption of chlorine induces advancing of the step edges. The increase of the mass transport on the surface under the chlorine action can be explained by the onset of the missing row reconstruction recently detected in our low-temperature STM experiments [25]. The structural elements of this reconstruction are 'fingers' parallel to the $[1\bar{1}0]$ direction. At low temperature all 'fingers' are perfectly ordered, while at room temperature they become mobile and the ordering disappears. In the present paper, we concentrate exclusively on room temperature STM data.

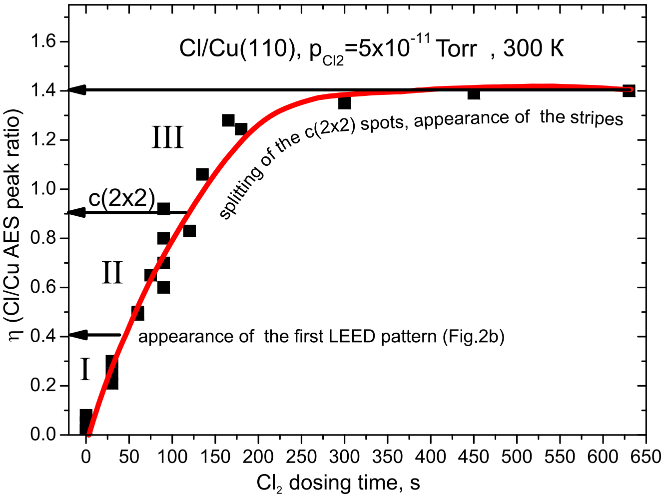

Fig. 1. Cl($L_{2,3}VV$)/Cu($M_{2,3}VV$) AES peak ratio shown as a function of the Cl_2 dosing time at 300 K. Three coverage ranges (I, II, and III) corresponding to the different adsorbate structures in LEED are indicated.