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Scanning tunneling microscopy of 'commensurate – incommensurate' structural phase transitions in the chemisorbed layers of halogens

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The process of chemical interaction of halogens with the surface of metals generally proceeds in two steps: the formation of a monatomic chemisorbed layer in the first stage of the reaction and then, on filling this chemisorbed layer, the formation of a chemical compound proper — metal halogenide. During the formation of a monolayer coating, substrate atoms remain in their crystal lattice, though a strong perturbation of the electron subsystem of the metal takes place, with the resulting occurrence of additional peaks in the local density of electron states in the valence band both below and above the Fermi level [1]. In the second stage of the reaction, metal atoms escape from the substrate lattice and combine with the halogen to form a new chemical compound with its own crystal structure and corresponding spectral features.

Under controlled ultrahigh vacuum conditions, surface chemical reactions have been studied experimentally since the 1970s, that is, since the invention of the first surface analysis methods, i.e., low-energy electron diffraction (LEED) and Auger electron spectroscopy (AES) [1-3]. The first stage of the reaction under discussion, the formation of a surface lattice by adsorbate, is a process that has been studied comprehensively from the viewpoint of surface crystallography. It was found that the commensurate structures $(\sqrt{3} \times \sqrt{3})$ R30° and c(2×2)-Hal formed on the (111) and (110) faces, respectively, and the commensurate structures $p(2 \times 2)$ -Hal or $c(2 \times 2)$ -Hal formed on the (100) face are transformed in a rather complex way as the degree of coating is increased, with all the changes occurring within one monolayer. The complex diffraction pattern obtained for different 'adsorbate/substrate' combinations showed marked distinctions even for the same orientation of the surface. To interpret LEED data, along with the homogeneous isotropic compression model [1-4], a model of regular domain walls separating commensurate structure domains

was also discussed in the literature [1, 5-8]. In the first case all the adsorbate atoms are arranged in an incommensurate uniform lattice, whereas in the second case the only incommensurate atoms are those which are arranged in domain walls. Both surface structures produce the same diffraction patterns [1, 4, 8, 9], which gives no way of determining the actual atomic structure of a surface using diffraction methods only.

In most work on halogen adsorption on metals performed by the LEED method, the first model was taken to be correct. The main argument against the second model is that the interatomic distances in domain walls are too small for the average density of adsorbate atoms observed in experiments. Simple estimates of the interatomic distances gave values which were much less than the van der Waals diameter of a halogen atom, which was believed to be physically impossible [1, 3, 4]. In the case of homogeneous compression, the interatomic distance in the halogen lattice was approximately equal to the van der Waals diameter [1, 3]. Nevertheless, extended X-ray absorption fine structure (EXAFS) measurements show that in some cases the interatomic spacing for halogen atoms within the layer is much less than the van der Waals diameter. For example, in a chromium layer ($R_{vdW} = 3.60$ A) on the (111) or (110) Ag surfaces [10, 11] they were found to be equal to 2.95 A and 3.14 A, respectively. However, to this day no proper explanation has been provided for these data.

The development of local probing microscopy methods with high resolution (up to the atomic level) and their wide use in surface physics and chemistry in the 90s made possible the direct observation of the actual structure of a surface and, hence, allowed one to gain a correct understanding of structural transformations taking place on this surface.

In this report we present images of the actual structure of the Cu(111) surface obtained with atomic resolution at different stages of the formation of chemisorbed chlorine and iodine layers. These images uniquely show that the 'commensurate-incommensurate' structure transition of the $(\sqrt{3} \times \sqrt{3}) R 30^\circ \rightarrow (n\sqrt{3} \times n\sqrt{3}) R 30^\circ$ type takes place through the formation and evolution of linear domain walls.

All experiments were conducted with the use of an ultrahigh-vacuum four-chamber setup described in detail in Ref. [12]. The setup was equipped with a GPI-300¹ scanning tunneling microscope, a quadrupole mass spectrometer, an analyzer of the 'cylindrical mirror' type for Auger electron spectroscopy, a three-grid analyzer of electrons for LEED, an ion gun, and a gas-filling system. The base pressure in the setup did not exceed 2×10^{-10} Torr. For preparation of Cu(111) and Ag(111) samples measuring $6 \times 10 \times 2$ mm with a surface plane misalignment not worse than 0.5° in ultrahigh vacuum, repetitive cycles of ion etching (Ar⁺, 1 keV) and annealing at temperatures of 950 K (Cu) and 850 K (Ag) were used. The concentration of contaminations on a prepared surface did not exceed 1%, as was estimated from AES data. As a result of such preparation, the surfaces obtained provided high-quality (1×1) LEED patterns and STM images with an atomically smooth surface. The adsorption of halogens (chlorine and iodine in molecular form) and STM measurements were carried out at room temperature. To determine the degree of coverage, AES, LEED, thermodesorption mass spectrometry (TDMS), and STM data were

¹The GPI-300 ultrahigh-vacuum scanning tunneling microscopes are currently manufactured in the Institute of General Physics of RAS.



Figure 1. (a, b, c) STM images obtained for a monatomic layer of chlorine chemisorbed on the Cu(111) surface: (a) $\theta \approx 1/3$, (b) $\theta \approx 0.35$, and (c) $\theta \approx 0.41$. Recording parameters: $I_t = 0.5$ nA, $U_t = 400$ mV. The corresponding Fourier transforms of the STM images and LEED patterns are shown in the insets. (d) Diagram of correlation between Fourier transforms and LEED patterns.

used. The structural analysis of a surface and the identification of LEED patterns were performed on the basis of STM images and their Fourier transforms.

Cu(111)/Cl₂. In the first stage of the adsorption of chlorine, well-defined patterns of LEED corresponding to a Cu(111) – $(\sqrt{3} \times \sqrt{3})$ R30° – Cl structure were observed (see the inset in Fig. 1a). The STM image for this coverage $(\theta = 1/3)$ is a hexagonal symmetry structure with interatomic distances of about 4.4 A turned through 30° relative to the substrate structure. This surface lattice is uniquely interpreted as the $(\sqrt{3} \times \sqrt{3})$ R30° – Cl structure with one adsorbate atom in an atomic cell. The Fourier transform (FT)² of the STM image has the form identical to that of the LEED patterns in Fig. 1a. Further adsorbate reciprocal lattice in LEED patterns into triangles consisting of six spots.

Analysis of successively recorded LEED patterns has shown that this splitting goes on continuously. The righthand insets in Figs 1b and 1c show the initial and final LEED patterns obtained in the process of compression of the adsorbate lattice. The corresponding STM images are shown in Figs 1b and 1c. Both shots are the images of a surface with atomic resolution and exhibit strong modulation of the intensity in the form of bright and dark stripes. In the first case, the modulation period is about 20 A; in the second one, it is about 10 A. The measured interatomic distances remain unchanged only along the stripes (4.4 A), while they vary periodically in a perpendicular direction. The corresponding Fourier transforms (the left insets in Figs 1b and 1c) demonstrates the splitting of reflections for the $(\sqrt{3} \times \sqrt{3})$ R30° – Cl lattice in the direction perpendicular to the stripes.

It should be noted that on the STM images (Fig. 1) only one of the three possible equivalent directions of compression $(0^{\circ}, 120^{\circ}, 240^{\circ})$ is presented, whereas on the LEED patterns by virtue of the low lateral resolution all directions of compression are seen. In order to compare the Fourier transform of the STM image of a surface with the corresponding LEED patterns, the sum of Fourier transforms for all equivalent directions of compression should be used, as shown in Fig. 1d.

As is known from theory [9], within the framework of the uniaxial-compression model such LEED patterns (splitting of the $(\sqrt{3} \times \sqrt{3})$ R30° – Cl structure in the reciprocal space, see the right insets in Figs 1b and 1c) correspond to the formation of either super heavy or light domain walls. To determine the type of domain walls and the exact positions of atoms in a domain wall, we used the fragments of the STM images taken from Figs 1b and 1c, bringing them into coincidence with the atomic grid of Cu(111) substrate (intersections correspond to the positions of copper atoms). This superimposition of the adsorbate and substrate lattices was made taking into account the following facts: (a) chlorine atoms in the $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ – Cl structure occupy the fcc adsorption sites [1, 4]; (b) the phase shift between domains separated by domain walls is constant, that is, each third domain is phased [8]. It turned out that the bright spots (atoms) in the STM image correspond to the positions of atoms in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ – Cl structure and form an ideal hexagon (Fig. 2a), whereas dark spots take nonsymmetric adsorption sites and form a distorted compressed hexagon (Fig. 2a). Thus, spots of lesser brightness in the STM image are those that correspond to atoms in a domain wall. Since the distances between atomic rows in a domain wall turn out to be less than the corresponding distances in a domain, we classified these domain walls as highly relaxed super heavy domain walls. It was found that at $1/3 < \theta < 0.38$ domain walls consist of three or four atomic rows (Fig. 2a), and at $\theta > 0.4$, we observed two or three atomic rows in a domain wall (Fig. 2b).

² Because of the high mobility of chlorine atoms at the coverage $\theta = 1/3$, attempts to obtain an image of a reasonably large portion of the surface with atomic resolution are unsuccessful. The image presented in Fig. 1a was recorded on a narrow terrace where the confined area prevented chlorine atoms from moving under the action of an STM tip. The corresponding Fourier transform consists of very broad reflections, and we do not give it in this figure. High-quality STM images were obtained for higher degrees of coverage, beginning with $\theta \approx 0.35$.



Figure 2. Fragments of STM images for (a) weakly compressed and (b) strongly compressed structures taken from Figs 1b and 1c and super-imposed on the structural grid of the Cu(111) substrate.

Intersections in the structural grid correspond to the positions of copper atoms in the upper atomic layer.

It was established that the process of densification of the layer ceases at a coverage $\theta \approx 0.41$, when only one atomic row remains in the $(\sqrt{3} \times \sqrt{3})R30^\circ$ -Cl domain. The smallest interatomic distance is 3.5 A, which is slightly less than the van der Waals diameter of a chlorine atom (3.60 A).

Cu(111)/I2. For the chemisorbed layer of iodine on the Cu(111) surface, we observed the same uniaxial inhomogeneous compression with the formation of domain walls. Fig. 3 shows the STM image of the Cu(111) surface for two different coverages by iodine: $\theta \approx 1/3$, $(\sqrt{3} \times \sqrt{3}) R 30^\circ - I$ structure (Fig. 3a) and a saturated layer, $\theta \approx 0.36$ (Fig. 3b). Stripes of width three or four atomic rows each with a repetition period of about 36 A are clearly seen in Fig. 3a. Using the procedure described for Fig. 2, we established that the distances between the rows in a stripe turn out to be less than the interatomic distances in domains of the $(\sqrt{3} \times \sqrt{3})R30^\circ - I$ structure (between stripes). This means that domain walls may be either heavy or super heavy. The corresponding Fourier transforms and LEED patterns are presented in the insets in Fig. 3. The observed uniaxial splitting in the Fourier transforms (Fig. 3b) supports the mechanism of compression through domain walls.

For a saturated layer, we succeeded in observing the splitting of reflections from the surface iodine lattice (usually, only a small broadening is observed [13]). In a split reflection, three spots (Fig. 3) are seen instead of six, according to Ref. [9]. Only careful analysis of the STM images described in detail in Ref. [14] allowed us to determine that the compression of an iodine layer takes place through the formation of heavy domain walls. As in the case of chlorine adsorption, these domain walls are highly relaxed, and adjacent atoms in the center of a domain wall are separated by a distance of about 3.3 A.

Ag(111)/Cl₂. As we established in Ref. [15], at room temperature the saturated layer of chlorine on the Ag(111) surface is a uniformly compressed isotropic incommensurate



Figure 3. STM images (132×132 A) obtained for a monatomic layer of iodine chemisorbed on the Cu(111) surface: (a) $\theta = 1/3$, and (b) $\theta \approx 0.36$. Recording parameters: $I_t = 0.3$ nA, $U_t = 500$ mV. The corresponding Fourier transforms of the STM images and LEED patterns are shown in the insets.



Figure 4. (a) STM image $(48 \times 40 \text{ A})$ $(I_t = 0.2 \text{ nA}, U_t = 500 \text{ mV});$ (b) structural model of the adsorbtion lattice; (c) Fourier transform [15]; (d) LEED pattern [2] for a saturated layer of chlorine on the Ag(111) surface. Coverage $\theta \approx 0.50$.

lattice $Ag(111) - (17 \times 17) - Cl$ in which the unit cell of chlorine involving 144 (12×12) atoms occupies a region on the Ag surface comprising 289 (17×17) atoms (Figs 4a, b). The measured Cl-Cl interatomic distance was found to be 4.1 A, and the Fourier transform of this structure (Fig. 4c) agrees well with the LEED patterns (Fig. 4d) obtained by other authors [2, 16]. All our attempts to obtain images of this surface with atomic resolution for lesser coverages failed because of the high mobility of adsorbed chlorine atoms in the loose surface lattice. The fact that chlorine atoms at coverages less than the saturated one are mobile is confirmed by LEED data. At $\theta \sim 0.35 - 0.4$, reflections from the adsorption lattice obtained at temperatures above 240 K had the form of diffuse spots in $(\sqrt{3} \times \sqrt{3})$ R30° positions [2, 16].

Unfortunately, no structural data for the adsorption of chlorine were obtained at lower temperatures. Nevertheless, some assumptions about the process of formation of incommensurate structures $M(111) - (n \times n) - Hal$ can be made on the basis of the temperature dependence of LEED data for the adsorption of bromine on the Ag(111) surface [17]. Bromine, as chlorine, at $T \sim 300$ K form an incommensurate $Ag(111)-(4\times4)-Br$ structure [17]. At a bromine coverage $\theta > 1/3$, variations in temperature in the vicinity of ~ 250 K lead to a structural 'order-disorder' transition. On cooling, each diffuse spot in the $(\sqrt{3} \times \sqrt{3})$ R30° structure splits into six spots forming a regular triangle. The LEED patterns obtained turn out to be close to those for the adsorption of chlorine on the Cu(111) surface (see Fig. 1).

In Ref. [17], the homogeneous-isotropic-compression model was used to explain these results. Taking into consideration the results presented in this work, we believe that there exists a critical temperature below which the kinetic energy of adsorbed atoms is less than the depth of the

potential profile of the substrate and the process of compression of the layer occurs uniaxially through the formation of domain walls.

Diffuse LEED patterns with a $(\sqrt{3} \times \sqrt{3})$ R30° structure observed at room temperature for chlorine and bromine layers adsorbed on the Ag(111) surface can be explained by strong fluctuations in the domain walls or, possibly, even by their disruption. It seems likely that above the critical temperature the adsorbate is not very sensitive to the potential profile of the substrate, and the compression of the layer may be homogeneous. The effect of the crystal structure of the substrate manifests itself in the orientation of an incommensurate adsorbate lattice, which coincides with the substrate orientation. We believe that the critical temperature for a chlorine layer on an Ag(111) surface must be below 240 K. By analogy, it can be assumed that for chlorine and iodine layers on a Cu(111) surface the critical temperature must be above room temperature.

Thus, we were the first to show that the M(111)- $(n\sqrt{3} \times n\sqrt{3})$ R30° – Hal structures observed in electron diffraction patterns are uniaxially compressed inhomogeneous lattices consisting of domains with the $(\sqrt{3} \times \sqrt{3})$ R30° – Hal structure which are separated by linear domain walls. Within the domain walls halogen atoms are arranged more closely together and occupy adsorption centers of a lesser depth compared to those in the domain. It has been found that the compression of the $M(111) - (\sqrt{3} \times \sqrt{3}) R30^\circ - Hal$ structure can occur both through the formation of super heavy domain walls (in the case of $Cu(111)/Cl_2$) and through the formation of heavy domain walls (in the case of $Cu(111)/I_2$). The suggestion has been made that the incommensurate $M(111) - (n \times n)$ - Hal structures may be formed at surface temperatures above a critical temperature, that is, when the kinetic energy of adsorbate atoms becomes greater than the depth of the potential profile of the substrate, and the compression of the layer is homogeneous and isotropic, without formation of domain walls. It is assumed that for Ag(111)/Br₂ such a temperature is T = 250 K, for Ag(111)/ Cl₂ the transition temperature must be below 240 K, and for $Cu(111)/Cl_2$ and $Cu(111)/I_2$ it must be above 300 K.

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