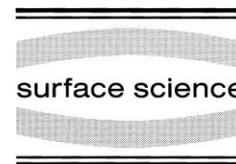




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Atomic structure of saturated chlorine monolayer on Ag(111) surface

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Abstract

STM and LEED techniques were applied to study the structure of saturated chlorine monolayer formed on Ag(111) as a result of Cl₂ adsorption at room temperature. We present for the first time atomic resolution STM images of chlorinated Ag(111) surface obtained in ultra-high vacuum conditions. The structure of chlorine layer was identified by means of a Fourier analysis of the STM images as Ag(111)–(17 × 17)–Cl. The structure of saturated chlorine monolayer remains unchanged for Cl₂ exposures up to 100 000 L and coexists with AgCl islands on Ag(111) surface. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Chemisorption; Chlorine; Fourier transformation; Low energy electron diffraction (LEED); Scanning tunneling microscopy (STM); Silver; Surface chemical reactions; Surface structure

The adsorption of molecular chlorine on Ag(111) has been a subject of intensive investigations since the 1970s. The interest in this problem was stimulated in many respects by the important role of chlorine in the reaction of partial epoxidation of ethylene to ethylene oxide held in the presence of a silver catalyst.

A number of structural studies [1–7] have been made of a chlorine monolayer on Ag(111). At initial chlorine coverage, the weak and diffuse ($\sqrt{3} \times \sqrt{3}$)–R30° LEED pattern was observed [1–3,5]. In Ref. [7] the structure of this coverage was investigated by SEXAFS and a honeycomb structure model was suggested. A more complex LEED pattern was observed for a saturated layer of

chlorine. Roviida et al. [1,2] described partially distorted (3 × 3) structure. Goddard and Lambert [3] reported (10 × 10) structure. Tu and Blakely [4] observed double diffraction pattern from epitaxial layer of AgCl(111) on Ag(111). In the work of Bowker and Waugh [5] two diffraction patterns were observed at coverage close to saturation. One of them (pattern “C”) contains fractional order beams at 0.28 and 0.72 reciprocal substrate lattice units. This pattern is in good agreement with data from Ref. [4], and is interpreted in a similar way. At further increase of chlorine coverage pattern “C” gradually transferred to the more simple pattern “D”, with fractional order beams remaining only at 0.72 reciprocal lattice units. Note that pattern “D” was also observed by Wu et al. [6] for a saturated chlorine coverage.

Due to the complexity of reviewed LEED pat-

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terns, the construction of an appropriate structural model for chlorine coverage on Ag(111) seems to be difficult. Scanning probe microscopy, being a key instrument for surface topography study on atomic scale, could be employed even for this complicated adsorbate system. Early STM investigations have been performed for Ag(111) surface chlorinated in water solution [8–11]. In Refs. [8–10] the samples were studied in ambient STM, while in Ref. [11] both the chlorination and STM measurements were carried out in an electrochemical cell. The STM images obtained in these species of works (ambient and electrochemical cell) are rather different: $\text{Cl}(\sqrt{3} \times \sqrt{3})$ [10], parallel double rows structure of chlorine [8,9] and more complicated structure $\text{Cl}(1.38 \times 1.38)$ [11]. It seems that data presented in Refs. [8–11] cannot be compared directly with data of the electron spectroscopies obtained in UHV conditions due to possible influence of water and ambient adsorbates on a silver surface.

In this paper we present results of the structural study of saturated chlorine coverage on Ag(111) surface obtained by STM as a major tool under UHV conditions. For additional characterization of adsorbate layer LEED, AES and TDS methods were also used.

All experiments were carried out in an ultra-high vacuum setup described in detail in Ref. [12]. It was equipped with a home-made STM [12], quadrupole mass spectrometer, cylindrical mirror analyzer for AES, three-grid analyzer for LEED, ion gun, and gas inlet system. The tips for STM (apex angle $\sim 20^\circ$ and radius $\sim 30\text{--}50 \text{ \AA}$) were prepared finally in the same setup [13]. The base pressure was 2×10^{-10} Torr.

The clean surface of Ag(111) was achieved with repeating cycles of argon ion bombarding (1 keV) and subsequent annealing at a temperature of 850 K. The concentrations of O, S, and C contaminations estimated by the ratio of corresponding Auger peaks and Ag $M_{4,5}$ VV intensities did not exceed 1%. A sharp (1×1) LEED pattern and atomic resolution STM images (Fig. 1) were used as the main criteria of Ag(111) surface quality.

The adsorption of molecular chlorine and STM measurements was carried out at room temper-

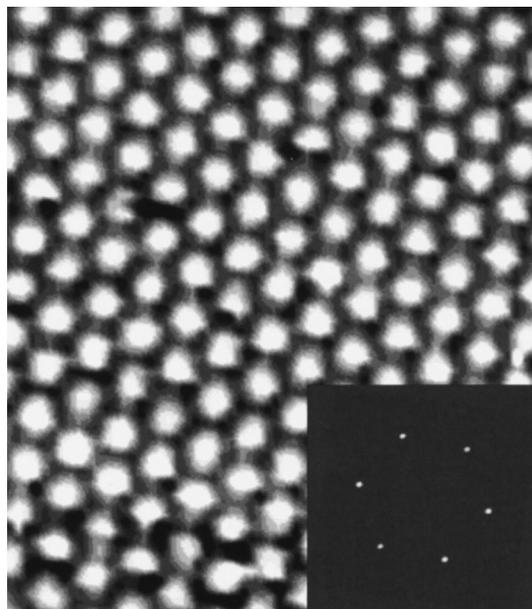


Fig. 1. The atomic resolution $32 \times 36 \text{ \AA}^2$ STM image of clean Ag(111)-(1 \times 1) surface ($I_t = 1.7 \text{ nA}$; $U_s = -5 \text{ mV}$) and its Fourier transform pattern.

ature. To measure the amount of Cl_2 exposure with high reproducibility, and to maintain the pressure of Cl_2 over the surface to be constant, we used a calibrated back-loop of Cl_2^+ signal from the mass spectrometer upon gas inlet.

To eliminate distortions caused by drift and slope of a sample, the special algorithm of image acquisition and processing [14] was used for all STM images presented. Based on this algorithm [14], the STM scanner calibration was carried out for both HOPG and Ag(111) surfaces. As a result we were able to determine interatomic distances on the STM image within an accuracy of 5%.

For the estimation of chlorine coverage on Ag(111) surface at early stages of chlorination, we used Cl $L_{2,3}$ VV/Ag $M_{4,5}$ VV Auger signal ratio. Its increase with chlorine adsorption at exposures less than 3 L and further saturation at a value ~ 0.6 are in good agreement with results published in Refs. [5,6]. TDS measurements showed one peak in the spectrum at exposure $D < 5 \text{ L}$, in accordance with Ref. [5]. This peak contains only AgCl molecules and corresponds to desorption of chemisorbed chlorine. The additional narrow

sharp TD peak of zero order evidently appears after $D \sim 20$ L. It was established in Refs. [15,16] that the origin of this TDS peak was the sublimation process of AgCl islands formed on silver surface by chlorine action.

Unfortunately, we were not able to observe the $(\sqrt{3} \times \sqrt{3})\text{-R}30^\circ$ LEED pattern, probably due to its low intensity marked by other authors [1,2,5,7]. Note also that the atomic resolution STM images at low chlorine coverage show only the lattice parameters of clean Ag(111) but not the parameters of chemisorbed chlorine layer. This insensitivity of STM to chemisorbed chlorine at submonolayer coverage was also mentioned by us in the case of chlorine adsorption on Cu(100) [17]. The possible origin of this phenomenon was explained [17] in terms of extremely high mobility of chlorine atoms on metal surface caused by the STM tip movement. For saturated monolayer the motion of chlorine atoms along the surface is impeded.

The LEED pattern (with fractional spots at 0.3 and 0.7 reciprocal lattice units) similar to "C" of Bowker and Waugh [5] appeared at $D \sim 2$ L and could be observed up to rather large exposures (1000 L). The gradual transformation (spots at 0.28 units disappeared) from the pattern "C" to "D" took place at further increase of chlorine exposure.

Atomic resolution $90 \times 90 \text{ \AA}^2$ STM image of saturated chlorine layer on Ag(111) surface corresponding to pattern "C" is shown in Fig. 2a. The hexagonal symmetry of chlorinated surface reproduces the symmetry of the (111) plane of substrate. The clearly seen modulation of a surface with period about 10 \AA could be caused by atoms with a strong displacement of electron density or lying higher than the main structure. The nearest neighbor distance taken from the STM image is about 4 \AA . A similar STM image was published by Aloisi et al. [11] for chlorination of Ag(111) in an electrochemical cell. We suggest the surface lattice of chlorine to be incommensurate with Ag(111) lattice. In this case different chlorine atoms appear to be placed in non-equivalent positions with respect to the substrate atoms, and look slightly different in the STM image.

The problem of accurate surface periodicity

determination could be solved by an application of Fourier analysis of the STM images. It permits us to get reciprocal lattice vectors (and interatomic distances correspondingly) for a large amount of surface atoms. In this sense the Fourier transform (FT) pattern of the STM image is similar to the LEED pattern. However, the LEED pattern is a result of averaging for a large surface area ($\sim 1 \text{ mm}^2$) exposed by an electron beam. The presence of a large number of surface defects (or domains) placed in this large area can cause strong background, missing and splitting of spots. As a first stage we have applied FT to analyze the STM image of clean Ag(111) surface. The result is shown in the inset to Fig. 1. This pattern seems to be identical with the (1×1) LEED pattern obtained for Ag(111). It consists of bright contrast spots characteristic of a structure with high expressed periodicity. The contrast of the FT pattern was chosen so that the noise was not appreciable.

Fig. 2b shows the FT pattern for chlorinated silver (111) surface. After thorough analysis, spots responsible for Ag(111) lattice were found. These substrate spots cannot appear for all symmetry directions. Their presence in the pattern depends on the conditions of the STM image acquisition and the tip apex state. The radial positions of substrate spots (measured for 15 images) coincide within 5% with data for clean Ag(111) surface. The observation of substrate spots in the FT pattern could be explained in terms of the modulation of chlorine electron density by underlying Ag(111) lattice. To determine adsorbate spot positions on the FT pattern, we used substrate spots as an internal reference. There are two more intensive rings of spots located at distances about 0.3 and 0.7 relative to the substrate. These two distances are also observed in LEED [1–6]. Fig. 3 shows a cross-section of the FT pattern from Fig. 2b along the direction A–A. It was found that the peak positions with good accuracy are multiples of $1/17$ (see also Table 1).

On the basis of these data we offer an interpretation of the investigated structure as (17×17) . The sharp high intensive peak $12/17$ ($=0.706$) is assigned to chlorine lattice, with the interatomic

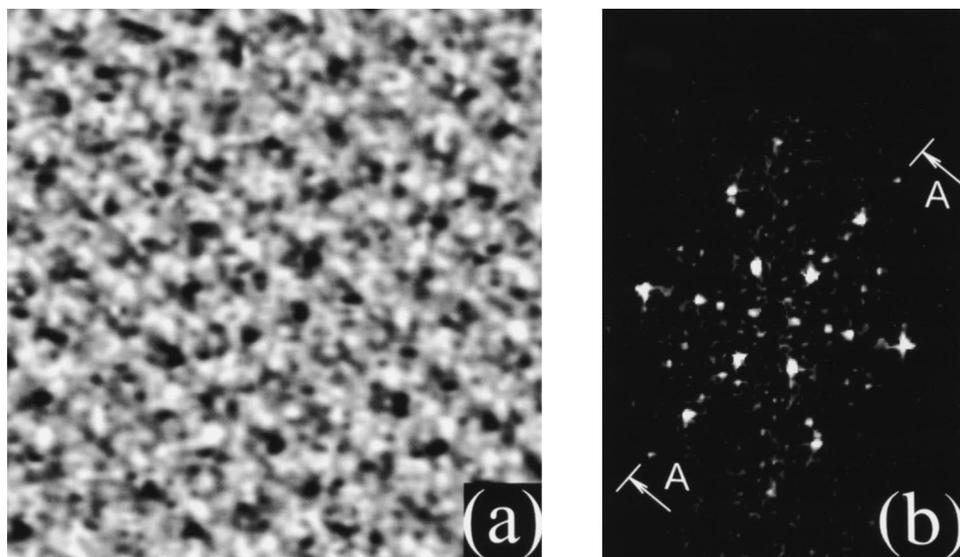


Fig. 2. The atomic resolution $90 \times 90 \text{ \AA}^2$ STM image of Ag(111) surface covered by chlorine layer ($I_t = 0.2 \text{ nA}$; $U_s = -500 \text{ mV}$; no STM images were obtained at positive U_s) (a) and its Fourier transform pattern (b).

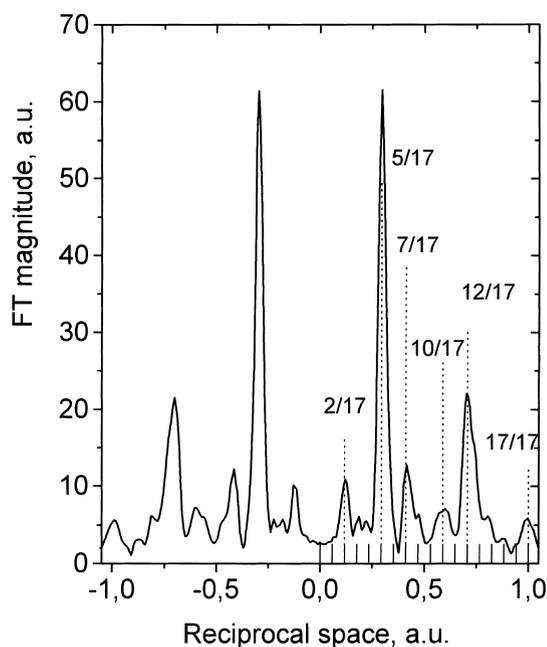


Fig. 3. A cross-section of the STM image taken from Fig. 2b along the A-A direction.

distances being equal to 4.09 \AA . Fig. 4 presents a model of adsorbed chlorine layer on the Ag(111) lattice (unit mesh containing 12×12 atoms is

shown) (Fig. 4a) and atomic resolution STM image of chlorinated silver (111) surface of $48 \times 40 \text{ \AA}^2$ (Fig. 4b). It is seen that even the simple drawing of a chlorine layer on a silver substrate exhibits some features similar to the real STM image. According to the model drawing, positions of different chlorine atoms could be classified as approximately top, bridge or three-fold. Taking into account the covalent radii for chlorine and silver to be 0.99 \AA [18] and 1.445 \AA we can estimate the difference in vertical positions of chlorine atoms occupying top or three-fold positions. This value appears to be appreciable (0.76 \AA). Based on the estimation above, we believe the brightness of each atom on the STM image to be determined by the chlorine atom position with respect to the silver lattice: the three-fold position corresponds to minimum brightness while the top position corresponds to maximum brightness.

Another intensive peak $5/17$ ($=0.294$) of FT (or 9.83 \AA in real space) we assign to visible modulation of a surface on the STM image (Fig. 2a). However, it is easy to obtain from Figs. 2a and 4b that the period of this modulation is not a constant value. It varies from 8.7 to 11.5 \AA and approximately corresponds to coincidence of chlorine

Table 1

FT peak positions obtained for the STM image of Ag(111) surface covered by a saturated chlorine layer (averaged for the five FT STM images)

Value	Notation						
	2/17	3/17	5/17	7/17	10/17	12/17	17/17
Precise	0.118	0.177	0.294	0.412	0.588	0.70	1.00
Measured	0.118	0.175	0.295	0.413	0.590	0.70	1.00

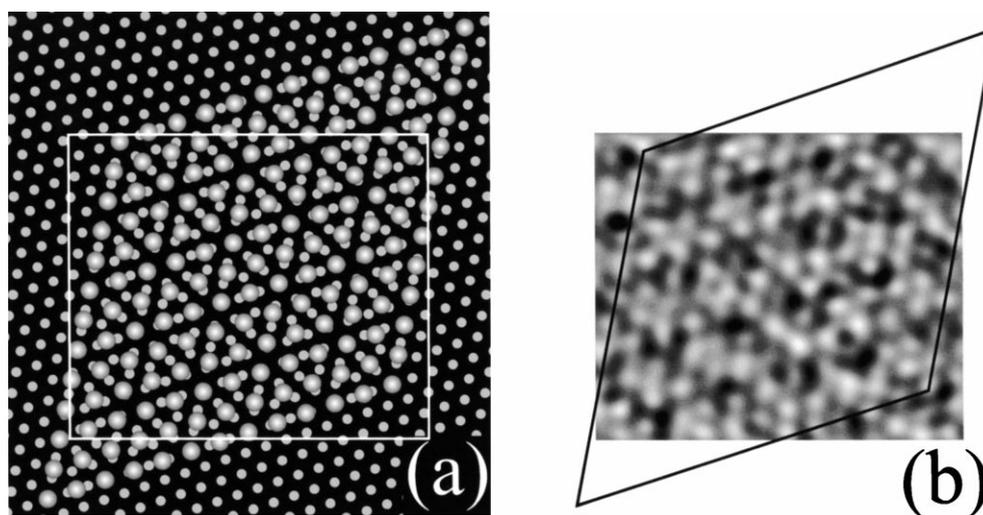


Fig. 4. (a) The model of saturated chlorine monolayer on Ag(111). The unit mesh containing 144 chlorine atoms (large balls) is shown together with underlying silver atoms (small gray circles). The white frame corresponds to the real STM image presented in (b). (b) The atomic resolution $48 \times 40 \text{ \AA}^2$ STM image of Cl saturated Ag(111) surface ($I_t = 0.2 \text{ nA}$; $U_s = -500 \text{ mV}$). The unit mesh of chlorine lattice is shown by a black frame.

atoms to equivalent positions in 3 and 4 silver interatomic distances. This periodicity can also be seen on the model drawing. Note that this modulation is clearly detected even on the large STM images (more than 200 \AA) without atomic resolution.

A concept of double diffraction is known [19] to be introduced for the interpretation of diffraction pattern for incommensurate structure of adsorbate. In our case vectors of real surface lattices for chlorine and silver are related to each other by the ratio $17a_{\text{Ag}} = 12a_{\text{Cl}}$. Basically a full set of spots of the order of $1/17$ can be observed on the diffraction pattern [19]. However, it was shown [20] that only the multiple diffraction spots corresponding to a combination of low-order overlayer and substrate reciprocal lattice vectors have appreciable intensity.

In the present case they should be $5/17$ and $12/17$. Bowker and Waugh [5] determined the spot positions on pattern "C" with high accuracy: 0.28 ± 0.02 and 0.72 ± 0.02 corresponding in our interpretation to $5/17 (=0.294)$ and $12/17 (=0.706)$ accordingly.

It is interesting to show that all previous LEED data [1–6] could be described within our model. A schematic picture of the FT pattern from Fig. 2b is redrawn in Fig. 5 together with data of Refs. [1,5]. Rovida et al. [1] observed the (3×3) LEED pattern for chlorinated Ag(111) surface. However, each bright spot was found to be composed of weak neighboring spots. Carrying out a careful consideration of Rovida's pattern [1], we found the main spots to be located in non-equidistant positions. It was likely that the spot $5/17 (=0.294)$

was described by the authors as $1/3$ and the spot $12/17$ ($=0.706$) as $2/3$. Moreover, in our model the distances between additional weak spots explained by Rovida et al. [1,2] to be due to “imperfect registry between the surface layer and the silver surface” are a multiple of 17. Goddard and Lambert [3] reported the structure of saturated chlorine layer on Ag(111) to be (10×10) . Analyzing the LEED photo [3] we found the most intensive spots corresponding to a lattice of chlorine to be at a distance about 0.7 relative to substrate spots. This size coincides well with $12/17$. Tu and Blakely [4] reported the lattice constant ratio of chlorine layer and silver (111) to be 1.39, that is close to our value of $17/12$ ($=1.416$).

The range of larger chlorine exposures was also studied with STM. It turned out that the formation and growth of chloride islands on Ag(111) surface occurred [16]. The silver surface between AgCl islands remained covered by saturated chemisorbed chlorine layer. The structure of chemisorbed chlorine layer corresponds to (17×17) , described in detail above. In the course of our STM investigations, series of atomic resolution images of (17×17) structure were obtained at chlorine exposures of 1000, 5000, 20 000,

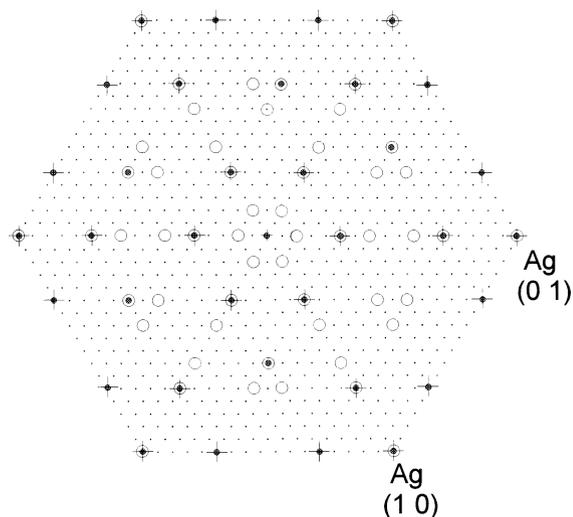


Fig. 5. Schematic diagram of FT pattern for the STM image of chlorinated Ag(111) surface (large open circles). The LEED data of Bowker and Waugh [5] and Rovida et al. [1] are shown as crosses and small gray circles, correspondingly.

100 000 L, with the LEED pattern being practically unchanged up to exposures of 20 000 L and very similar to pattern “D”. According to Ref. [5], only the most intensive spots (0.72 and 1.0 of units) for pattern “D” remained from pattern “C” at larger coverage. Indeed, chloride island growth with corresponding reduction of the surface area occupied by chemisorbed chlorine layer could cause an increase of background and fading of low intensive spots in the LEED pattern.

In conclusion, we can note:

- (1) For the first time atomic resolution STM images for chlorine layer on Ag(111) were obtained under UHV conditions.
- (2) The structure of saturated chlorine layer was identified as (17×17) -Cl with chlorine interatomic distance 4.09 \AA . The strong modulation of a surface with period $\sim 10 \text{ \AA}$ was explained in terms of influence of underlying silver lattice. The structural model proposed coincides well with published LEED data and atomic resolution STM images.
- (3) Both “C” and “D” LEED patterns correspond to saturated chlorine monolayer coverage with Ag(111)- (17×17) -Cl structure. At large coverage saturated chlorine monolayer coexists with AgCl islands.
- (4) The substrate Ag(111) spots were found to appear in FT pattern of STM images. Simultaneous observation of substrate and adsorbate lattice in reciprocal space opens an opportunity to determine precisely structural parameters of adsorbate lattice.

Acknowledgements

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