New insight into the structure of saturated chlorine layer on Ag(1 1 1): LT-STM and DFT study

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A B S T R A C T

Atomic structures formed on the Ag(1 1 1) surface as a result of molecular chlorine adsorption have been studied with a low-temperature scanning tunneling microscopy (LT-STM) in a combination with DFT calculations. We have found that saturated chlorine coverage on Ag(1 1 1) is a complex system consisting of two different structural phases: small anti-phase domains of a (3×3) reconstruction and nanoclusters Ag_3Cl_7.

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1. Introduction

The interaction of chlorine with Ag surfaces has been a subject of numerous experimental and theoretical investigations since the 1970s. The interest to this system is closely related to the promotional role of chlorine in the important technological reaction of ethylene epoxidation [1,2] on the silver catalyst. Indeed, the presence of small levels of chlorine-containing molecules in the reactor can increase the selectivity of the reaction toward ethylene epoxide to more than 80%.

Experimentally, the structure of chlorinated silver (1 1 1) surface has been studied by LEED [3–8,11], RT-STM [10] and EXAFS [9,11]. The room temperature chlorine adsorption on Ag(1 1 1) gives rise to the appearance of a complex LEED pattern interpreted as distorted (3×3) [4,5], (10×10) [6,11], (17×17) [10], double diffraction from epitaxial AgCl layer [7,3]. In fact, all the authors observed very similar LEED patterns, but interpreted them in a different way.

In the most detailed room-temperature LEED work by Bowker and Waugh [3] 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. At further increase of chlorine coverage pattern C gradually transferred to a 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. [8] for a saturated chlorine coverage.

Recently, we have shown that the application of low-temperature (5 K) scanning tunneling microscopy in a combination with DFT calculations makes possible recognition of atomic structures formed by chlorine on a silver surface [12]. In particular, we have shown that complex pattern C observed by many authors is explained by the diffraction on a system of antiphase (3×3) nanodomains formed in the course of the reconstruction of the upper silver layer.

In this work, we have examined a saturated layer of chlorine formed on Ag(1 1 1) at room temperature. According to the notation made by Bowker and Waugh [3], this coverage corresponds to a LEED pattern marked as D. Although, in the course of the C–D transformation the Cl/Ag AES peak ratio increases only by 15% [3], the structure of the chlorinated surface may exhibit significant modifications. The aim of the present paper is to recognize the atomic structure of the saturated chlorine coverage on Ag(1 1 1) using low temperature scanning tunneling microscopy in a combination with DFT calculations.

2. Experimental and computational methods

All experiments were carried out in a UHV setup containing Omicron LT-STM operating at 5–77 K and LEED optics. The silver (1 1 1) sample was prepared by repetitive circles of Ar⁺ bombardment (1 keV) and annealing up to 800 K. Chlorine inlet on the

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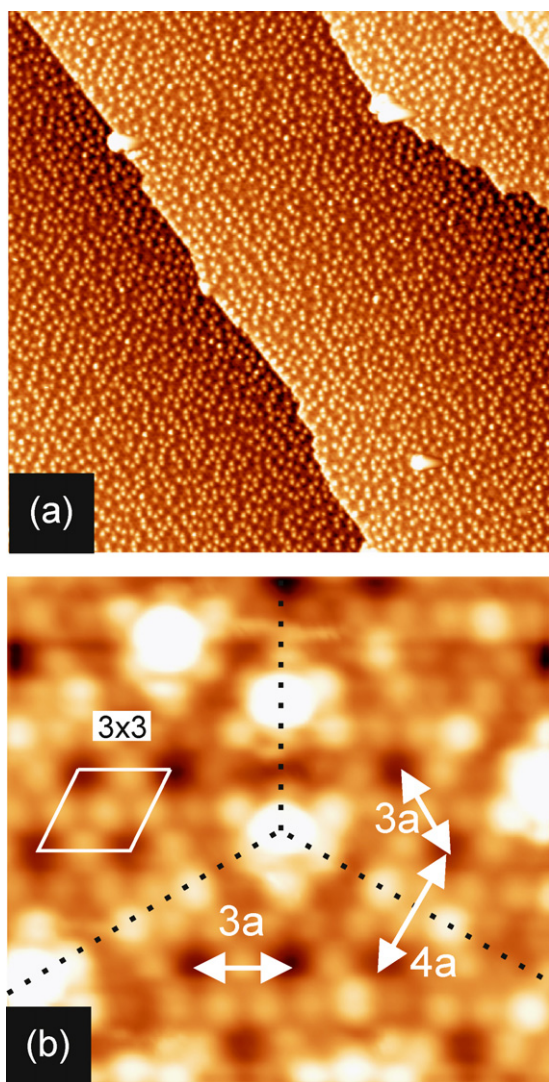
Fig. 1. (a) Panoramic STM image (1000 Å × 1000 Å, $U_s = -856$ mV, $I_t = 0.8$ nA, 5 K) of saturated chlorine coverage on Ag(1 1 1) formed after adsorption of Cl$_2$ at 300 K; (b) an atomic-resolution STM image (68 Å × 68 Å, $U_s = -1.4$ V, $I_t = 0.5$ nA, 5 K) showing the atomic structure of bright clusters.

Ag(1 1 1) surface was done at room temperature using a fine leak piezo-valve.

All DFT calculations were carried out using the Vienna *ab-initio* simulation package (VASP) [13–16] employing the projector augmented wave method [17] and GGA-PBE (Perdew, Burke, Ernzerhof) functional [18]. A plane-wave cut-off energy of 375 eV was applied. The silver substrate was modeled by a four layer slab. During structure optimizations the top layer of Ag atoms as well as the chlorine overlayer atoms were allowed to relax, while the bottom three layers of Ag were held fixed. A vacuum layer with a thickness of 14 Å was inserted between two neighboring slabs. The integration over Brillouin zone was done using a Monkhorst–Pack [19] k-point mesh (14 × 14 × 1) per (1 × 1) of Ag(1 1 1). STM images were simulated from the DFT results using the simple Tersoff–Hamann approximation [20] considering states between E_F and $E_F - 0.5$ eV.

3. Results and discussion

Fig. 1a shows a panoramic STM image of Ag(1 1 1) surface saturated with chlorine at 300 K. According to the STM image, the

surface area is covered by an array of small bright objects occupying approximately one half of the surface. These bright objects are surrounded by a structure with characteristic corner holes (Fig. 1b). This type of reconstruction of the chlorinated Ag(1 1 1) surface has been considered in our recent paper [12] for separate domains with local (3 × 3) periodicity. At saturation coverage, the size of most domains with reconstruction is even less than a (3 × 3) unit cell, as seen from Fig. 1b. For this reason, in further discussion we will call this reconstruction (3 × 3)-like.

The atomic-resolution STM image presented in Fig. 1b indicates that each bright object can be considered as a cluster with a six-atom basement and a bright atom (or group of atoms) in the middle. Clusters play the role of domain boundaries between three adjacent anti-phase domains of (3 × 3)-like reconstruction, as shown in Fig. 1b.

To clarify the process of clusters formation, we looked again at the STM image of the chlorinated Ag(1 1 1) surface acquired at a lower coverage (see Fig. 2a) and focused on the atomic structure of boundaries between the adjacent (3 × 3) domains. According to Fig. 2a, the most interesting objects are formed on the boundary between three adjacent (3 × 3) domains. They have a shape of triangles consisting of six chlorine atoms. The arrangement of atoms in the boundary and in the basement of the clusters appears to be exactly the same, as shown in Fig. 1b. Therefore, we believe that clusters are formed on top of the domain boundaries between (3 × 3) domains.

In this connection, it is of great importance to understand the atomic structure of the domain boundary including the structure of the underlying silver layer.

According to the model of the (3 × 3)-like reconstruction, within a (3 × 3) unit cell six Ag atoms in the top layer are arranged in two triangles with atoms occupying fcc and hcp sites, respectively (see upper right part of Fig. 2b). Chlorine atoms may be placed between four Ag atoms and in the off-center position in the hole [12]. Thus, the building block of the silver layer reconstruction consists of three silver atoms. If we start to span the surface with such building blocks simultaneously for three antiphase domains taking the positions of the corner holes from the experimental STM image, then we will see the formation of boundaries between domains. There are two types of boundaries. The first type arises along the line of contact of two domains. Due to the symmetry of the system one can find three equivalent directions of this type of boundaries shown in Fig. 2b by dashed lines. On these lines new triangles consisting of six silver atoms are formed. It is worth noting that some atoms forming these triangles participate in the (3 × 3)-like reconstruction in two adjacent domains. Due to increase of the size of the silver triangle making domain boundaries there is an additional three-fold adsorption site in the middle also occupied by a bright chlorine atom. The second type of the boundary arises in the place of the intersection of three antiphase domains. According to the drawing presented in Fig. 2b, it also has a triangular shape and contains 21 silver atoms packed in the (1 × 1) lattice. Similar to the case of more simple boundaries, the corners of this big silver triangle participate as building blocks in the (3 × 3)-like reconstruction in the neighboring domains. The (1 × 1) arrangement of the inner atoms in the triangle is necessary to produce three-fold adsorption sites for six "bright" atoms adsorbed on the boundary in accordance with the experimental STM image in Fig. 2a. In our model, six chlorine atoms occupy two different three-fold positions marked in Fig. 2b as "1" and "2" and form a characteristic bright chlorine triangle. Such atom positions perfectly reproduce interatomic distances of 4.4 Å measured in the STM image between neighboring atoms on the sides of the triangles. The difference in adsorption sites explains the different brightness of the three corner atoms and three side atoms.