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

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ABSTRACT

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 Ag₃Cl₇.

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 (5K) 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) nano-domains 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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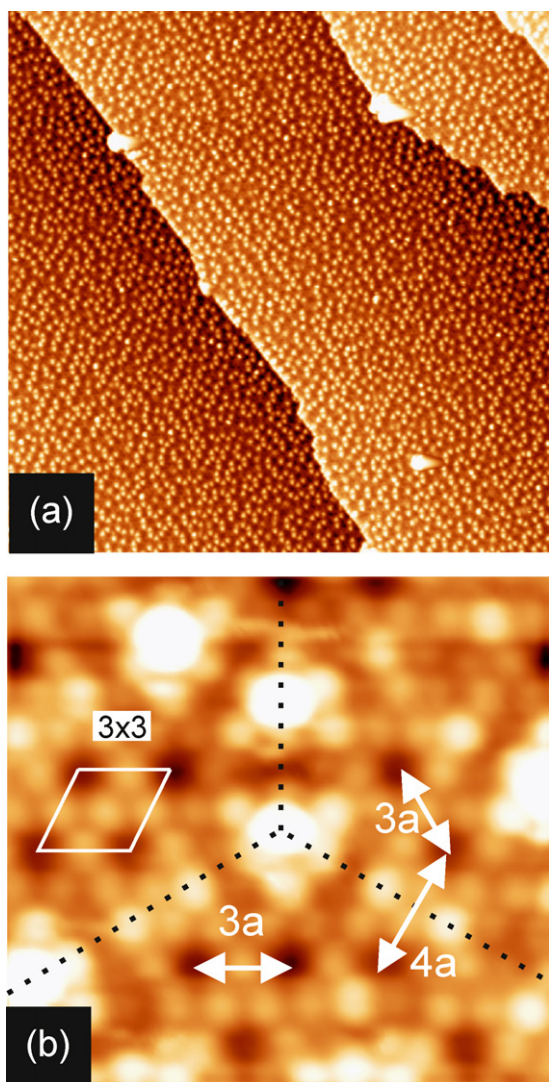


Fig. 1. (a) Panoramic STM image ($1000 \text{ \AA} \times 1000 \text{ \AA}$, $U_s = -856 \text{ mV}$, $I_t = 0.8 \text{ nA}$, 5 K) of saturated chlorine coverage on Ag(111) formed after adsorption of Cl_2 at 300 K ; (b) an atomic-resolution STM image ($68 \text{ \AA} \times 68 \text{ \AA}$, $U_s = -1.4 \text{ V}$, $I_t = 0.5 \text{ nA}$, 5 K) showing the atomic structure of bright clusters.

Ag(111) 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 \AA was inserted between two neighboring slabs. The integration over Brillouin zone was done using a Monkhorst–Pack [19] k-point mesh ($14 \times 14 \times 1$) per (1×1) of Ag(111). STM images were simulated from the DFT results using the simple Tersoff–Hamann approximation [20] considering states between E_F and $E_F - 0.5 \text{ eV}$.

3. Results and discussion

Fig. 1a shows a panoramic STM image of Ag(111) 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(111) 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(111) 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 \AA 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.

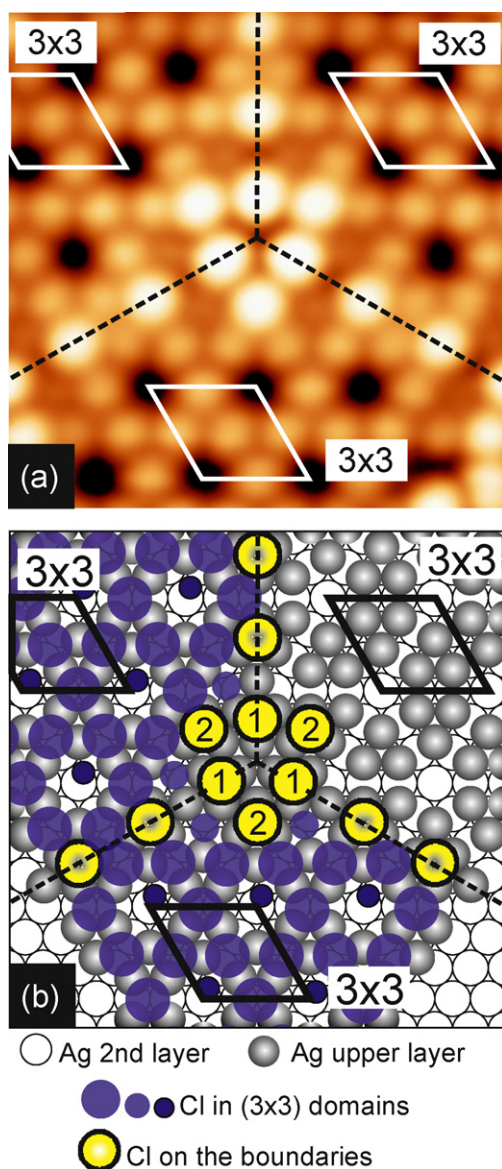


Fig. 2. (a) The fragment of the experimental STM image ($40 \text{ \AA} \times 40 \text{ \AA}$, $U_s = -1.2 \text{ V}$, $I_t = 1.6 \text{ nA}$, 5 K) of the boundary between three 3×3 islands. (b) Hard ball model demonstrating arrangement of silver and chlorine atoms in 3×3 domains and in the domain boundary. In the upper right part of the drawing chlorine atoms are not shown.

As it follows from the STM image in Fig. 1b, there are two different orientations of 6-atom chlorine triangles on the surface (“corner up” and “corner down”). If we assume that silver atoms in the (1×1) triangle lying in the basement of the domain boundary in Fig. 2b occupy fcc positions, then silver atoms in the basement of the domain boundary with opposite orientation should occupy hcp sites.

To determine the atomic structure of the clusters, we used DFT calculations with the VASP code. In general case, clusters do not form a periodic lattice. However, in some places clusters form a new “rosette-like” superstructure described by a (7×7) unit cell as shown in Fig. 3a,b. Taking into account that the basement of each cluster is formed by a triangle of 21 silver atoms with (1×1) periodicity (Fig. 2b), we present in Fig. 3c a model showing arrangement of silver atoms in the basement of the (7×7) reconstruction. Within (7×7) unit cell there are two oppositely oriented triangles of silver atoms. In the first triangle, atoms occupy fcc sites, whereas in

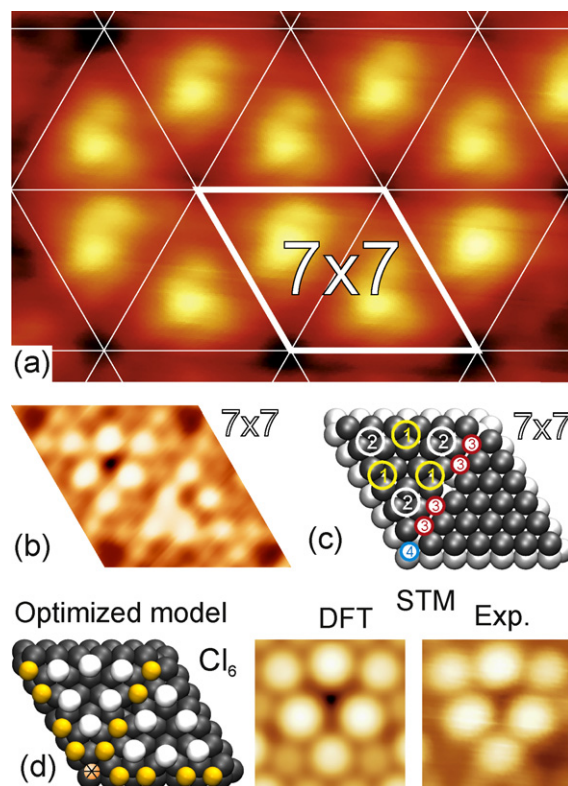


Fig. 3. (a) The fragment of the experimental STM image ($81 \text{ \AA} \times 41 \text{ \AA}$, $U_s = -0.8 \text{ V}$, $I_t = 0.8 \text{ nA}$, 5 K) demonstrating partial ordering of clusters in a (7×7) superstructure; (b) and (c) STM image ($U_s = -1.2 \text{ V}$, $I_t = 1.6 \text{ nA}$) and hard ball model of the (7×7) reconstruction. Different adsorption sites for chlorine atoms are indicated. Threefold positions marked as “1” and “2” correspond to atoms in the basement of clusters. Chlorine atoms also occupy the site “3” with nearly four-fold symmetry and the corner-hole site “4” as in original (3×3) -like reconstruction; (d) optimized structural model and corresponding theoretical and experimental STM images of cluster Cl_6 .

the second one – hcp. Chlorine atoms may occupy threefold hollow adsorption sites on silver triangles marked as “1” and “2” forming a characteristic chlorine triangle, as shown in Fig. 3c. Between silver triangles there are nearly fourfold hollow adsorption sites marked as “3” similar to the case of the original (3×3) -like reconstruction. Similar to the case of the (3×3) -like reconstruction, the holes in the corners of the (7×7) unit cell are occupied by chlorine atoms in positions “4”.

Note that a complete (7×7) reconstruction is not realized in a real experiment even at saturation coverage. However, from the theoretical point of view it appears to be very convenient for DFT modeling of the clusters due to minimum size of the unit cell. That is why all model calculations performed for clusters were made using the (7×7) unit cell.

In our DFT calculations we considered all the stages of clusters formation. First a simple model of the six chlorine atom triangle was considered (see Fig. 3d). Using a Tersoff–Hamann approach [20], we have calculated a theoretical STM image for this structure. The result of the calculations obviously reproduces all features of the experimental STM image including a difference of the brightness between chlorine atoms in different types of the threefold positions (marked in Fig. 2b as “1” and “2”).

On the next stage, we have tested two simple structures with an additional chlorine or silver atom placed in the middle of a 6-atoms chlorine triangle. However, the correspondence of both theoretical images with the experiment appeared to be rather poor.

To look for a correct model, we considered an STM image corresponding to the case of incompletely formed clusters, as shown

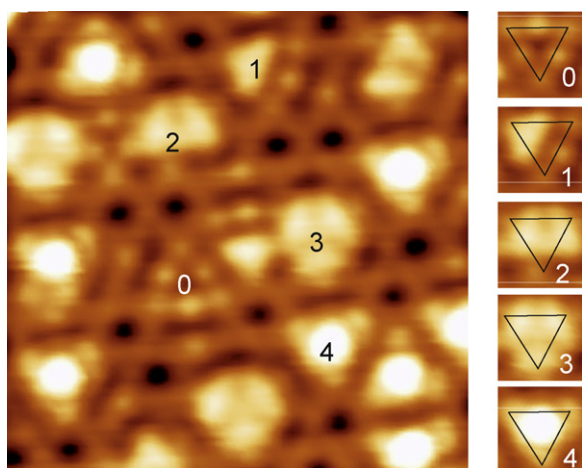


Fig. 4. Experimental STM image ($70 \text{ \AA} \times 70 \text{ \AA}$, $I_t = 1.5 \text{ nA}$, $U_s = +536 \text{ mV}$, 5 K) of the intermediate chlorine coverage on $\text{Ag}(1\ 1\ 1)$ demonstrating different stages of clusters formation. 0 – unfilled initial triangles, 1 – one additional object in the corner, 2 – two objects in the corners, 3 – three objects in each corner, 4 – complete cluster.

in Fig. 4. One can find five different types of objects on the surface. A simple triangle containing six chlorine atoms is marked as 0. In all objects marked as 1 we detect a light spot in one of the corners of a triangle. In the objects 2 already two corners are occupied, and in the objects 3 there is a light spot in each corner of a triangle. Note also, the presence of the distinct minimum in the center of the object 3. Finally, we marked as 4 the complete clusters with characteristic bright spots in the center of triangle. We believe that objects 1–4 represent the stages of cluster formation. In this process the initial basement 0 accumulates step-by-step four additional atoms (chlorine and/or silver).

Fig. 5 presents optimized models and corresponding theoretical and experimental STM images ($U_s = -500 \text{ mV}$) describing the stages of Ag_3Cl_7 formation on the basement of a six atom triangle. According to our calculations, an additional silver atom in a corner of a triangle gives rise to the appearance of a bright feature in good correspondence with the experimental observation (Fig. 5a). This kind of objects (cluster AgCl_6) appears in the STM images rather early simultaneously with islands of the (3×3) -like reconstruction. Further DFT calculations were performed for cluster Ag_2Cl_6 corresponding to occupancy of two corners of triangles with silver atoms. Excellent agreement of the theoretical STM image and experimental images is obvious from Fig. 5b. A cluster Ag_3Cl_6 with three silver atoms in the corners of a triangle was also considered with DFT. However, it is not shown in Fig. 5, since we were not able to acquire a high-resolution STM image of such objects at negative bias voltage required for the correct comparison with the theoretical image. At positive voltages (see Fig. 4), the resolution appeared to be much worse.

On the final step of the cluster design we have tested silver (Fig. 5c) and chlorine atoms (Fig. 5d) placed above the center of Ag_3Cl_6 cluster. We see that the model with four silver atoms does not correspond to the experimental observation, whereas the theoretical STM image of the Ag_3Cl_7 pyramid with a chlorine atom on top and the experimental STM image of a cluster observed at saturation are very similar.

Thus, we have shown that a 2D array of clusters Ag_3Cl_7 is formed on the $\text{Ag}(1\ 1\ 1)$ surface at saturation of the chlorine coverage. The sequence of atomic layers in Ag_3Cl_7 corresponds well to the sequence of layers in a silver chloride bulk crystal in the direction $(1\ 1\ 1)$. It is of interest to analyze the atomic structure of the Ag_3Cl_7 pyramid in comparison with the AgCl lattice. In the case of bulk AgCl the interplane distances in a $(1\ 1\ 1)$ direction are equal to 1.60 \AA [21]. In the case of Ag_3Cl_7 , the calculated distance between

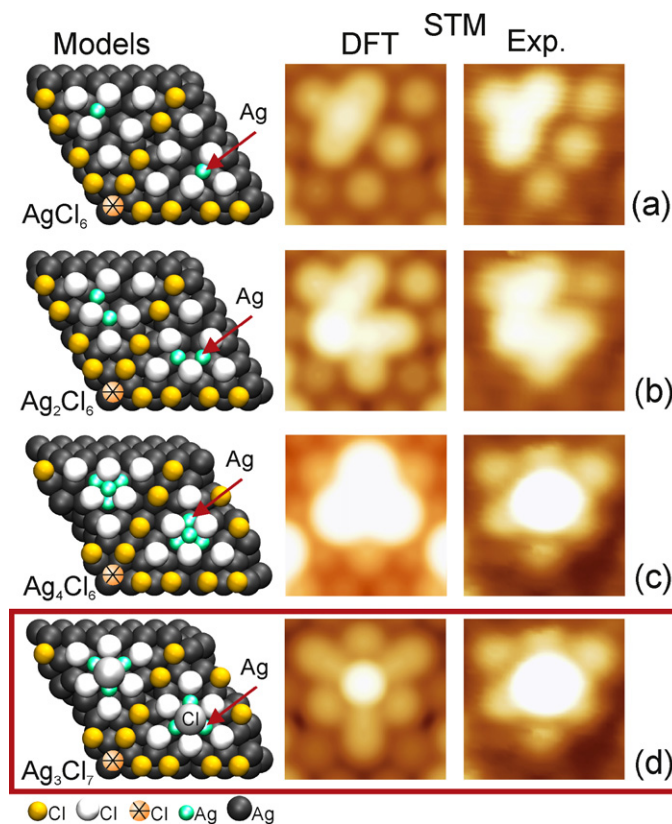


Fig. 5. Structural models describing the formation of clusters and corresponding theoretical STM images shown in comparison with experimental observations. (a) Cluster AgCl_6 , (b) cluster Ag_2Cl_6 , (c) cluster Ag_4Cl_6 , (d) cluster Ag_3Cl_7 . Theoretical STM images for (a) and (b) are shown in comparison with appropriate experimental STM frames acquired at intermediate coverages. For (c) and (d) comparison was made with STM image of cluster obtained at saturation.

the upper chlorine atom and the plane consisting of the three silver atoms is equal to 1.468 \AA which deviates by $\approx 8\%$ from the bulk value. In our model, pairs of atoms $\text{Ag}_1\text{--Ag}_2$, $\text{Ag}_2\text{--Ag}_3$ and $\text{Ag}_3\text{--Ag}_1$ are separated by the distance of 3.636 \AA that is slightly less than the nearest neighbor distances in a $(1\ 1\ 1)$ plane of bulk AgCl crystal, *i.e.* 3.93 \AA [21]. Our calculations show that silver atoms (Ag_1 , Ag_2 , Ag_3) occupy approximately threefold hollow adsorption sites above the upper silver layer. Analogous threefold hollow positions are also occupied by six chlorine atoms from the basement of the cluster. That is why the short distance ($\approx 0.39 \text{ \AA}$) between the silver plane in Ag_3Cl_7 and an average basal chlorine plane is not surprising. Note, that we also obtained a little contraction of the nearest-neighbor chlorine distances in a basal chlorine plane ($\approx 4.13 \text{ \AA}$) in comparison with Cl--Cl distances in a 6-atom domain boundary from Fig. 2a ($\approx 4.4 \text{ \AA}$).

Thus, according to our analysis, the upper chlorine atom and three silver atoms occupy positions in a slightly distorted AgCl lattice. The basement of the Ag_3Cl_7 cluster could be considered in some sense as an interface between the $\text{Ag}(1\ 1\ 1)$ substrate and an Ag_3Cl cluster.

4. Conclusions

In conclusion, using LT-STM and DFT we have determined the morphology and the atomic structure of the saturated chlorine coverage on $\text{Ag}(1\ 1\ 1)$ formed as a result of the room temperature adsorption. According to our findings, two different phases coexist on the surface: islands with a (3×3) -like reconstruction and Ag_3Cl_7 clusters. The process of the final structure formation is

self-consistent. In other words, silver atoms extracted from the substrate in the process of the (3×3) -like reconstruction participate in the formation of clusters on the boundaries between adjacent (3×3) domains. We have discovered a new type of surface objects – Ag_3Cl_7 clusters never discussed previously in the literature for the Cl/Ag system.

An interesting point concerns the promotional effect of chlorine in a reaction of ethylene epoxidation. According to Campbell [22] the selectivity of the reaction increases with chlorine coverage, however the reaction rate goes to zero at saturation of chlorine coverage. In our work, at coverage slightly below the saturation we observed incomplete clusters Ag_3Cl_6 , Ag_2Cl_6 , AgCl_6 . The chemical state of the silver atoms in these structures could be different from that of atoms from the bulk. Therefore, the system can be interesting from the point of view of oxygen adsorption into these new adsorption sites that could be important in further studies of the mechanism of the epoxidation reaction.

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