Atomic scale study of CuI film nucleation on copper under molecular iodine action

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Halide nucleation and growth on monocrystalline copper substrates under molecular halogens action was studied by means of Auger Electron Spectroscopy (AES) and Scanning Tunnelling Microscopy (STM). It was found that copper iodide grows on Cu(100) and Cu(111) in a layer-by-layer mode with its outer hexagonal plane parallel to the substrate surface. The STM images of copper iodide demonstrate Moiré-like superstructures. The nature of these superstructures is explained in terms of superposition of the copper iodide layer and the underlying interface monolayer. It was found that the interface layer preserves geometrical and electronic structure of the saturated chemisorbed iodine monolayer for both copper planes. Moreover, we have found out that orientation of copper iodide nuclei on a surface strongly depends on the step edges orientation, which, in turn, is determined by the direction of close-packed atomic rows in the saturated iodine monolayer. [DOI: 10.1390/ejssnt.2004.234]

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I. INTRODUCTION

The nucleation stage in processes of thin semiconductor film growth is unclear up to now and requires a careful experimental study on atomic scale. The only approach able to give adequate atomic scale information about nucleus evolution is use of scanning tunneling microscopy (STM) directly in the technological process. Ultrahigh vacuum technologies of semiconductor film growth are of great interest from this point of view due to their ability to carry out the process on the well-characterized atomically clean surfaces. Among these technologies a special attention should be paid to molecular beam epitaxy mainly owing to its industrial importance for creation of micro- and optoelectronics devices. For near future applications this method looks as the most promising one because it allows creation of lateral nanostructures with predicted electronic and optical properties. Although, for the industrially important systems (Ge/Si, A3B5/A3B5) such investigations have been already started [1, 2], they faced with difficulties due to rather complex initial semiconductor surface (usually reconstructed), and all the more baffling complexity of interface layers (typically solid solutions) strongly limit observation and understanding of atomic scale nucleation process. In such situation the carrying out of the model experiments for more simple surface process is strongly required. A good candidate for this purpose is the interaction of molecular halogens with noble metals (Cu and Ag) because it results in formation of the epitaxial film of metal halide (as a rule, wide gap semiconductor) on metal surface [3]. Perhaps the industrial applications of this reaction are not so important as compared with Ge/Si, A3B5/A3B5 systems, however, it reflects peculiarities of binary semiconductor film growth systems rather correctly.

The realization of such a process in ultrahigh vacuum is rather simple since the ability to vary the partial gas pressure and substrate temperature is enough for the full control of the reaction processes on a surface. The above mentioned process is a specific type of epitaxial film growth including one component feed (halogen) from the gaseous medium and another one (metal) – from the bulk of a substrate. Note that molecular beam epitaxy of germanium on silicon substrate occurs by the similar mechanism because it resulted in formation of the Si1-xGe1-x film [1, 2]. The growth of semiconductor film on metal surface upon the halogenation reaction looks less complicated than the growth of semiconductor on semiconductor upon deposition process due to the relative simplicity of the structure of initial unreconstructed metal surface.

A specific feature of interaction between halogens and metals is formation of monolayer of chemisorbed halogen at the first stage of reaction, whereas nucleation and growth of halide occurs on the second stage. Depending on the system and the temperature halide may form either the 2D crystalline film or 3D islands, i.e. different types of the growth mode are realized. In particular this characteristic property gives an opportunity to model the processes of Stranski-Krastanov growth mode which is typical for Ge/Si, A3B5/A3B5 systems demonstrating self-organization phenomena [1, 2].

The own interest to halogen-metal interactions has been initiated in the 1970’s mainly due to the importance of their technological applications in catalysis, microelectronics and photography. Historically the monolayer stage of reaction has been studied in detail by electron diffraction techniques in ‘70-’80 and a large variety of well-ordered 2D phases of chemisorbed halogens was reported [3]. Recent applications of STM have shown that halogen monolayers on monocrystalline metal surfaces can be considered as useful model systems for the studying 2D phase transitions in chemisorbed layers. In particular, the domain walls driven commensurate-incommensurate phase transition was reported for Cl- and I-layers on Cu(111) [4, 5]. In iodine layer on Cu(100) besides the rich picture of 2D solid-solid structural transitions the phenomenon of 2D melting was also observed [6].

In the paper we present the results of STM study of nucleation and growth of two-dimensional CuI film on Cu(100) and Cu(111) under molecular iodine action. Previous intensive study on atomic scale of process of iodine monolayer formation [5, 6] permits us to decode unknown

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atomic structure of CuI nuclei by use of specific atomic structure of saturated iodine monolayer as a reference. We also give reasonable explanation of unusual orientation of grown atomic rows of CuI film along the Cu substrate.

II. EXPERIMENTAL

All experiments were carried out in a UHV setup consisting of analytical and STM chambers and described in detail elsewhere [7]. The base pressure in both chambers did not exceed $2 \times 10^{-10}$ Torr. To clean the surface of copper (100) and (111) samples we used repeating cycles of argon ion bombardment (1 keV) and subsequent annealing at 900-950 K. As a result of such a treatment a sharp (1 × 1) LEED pattern and perfect STM images with wide terraces were achieved. Adsorption of molecular iodine and all STM measurements were carried out at room temperature. Tungsten tips in situ sharpened by Ar$^+$ bombardment [8] were used for STM measurements.

III. AES DATA TREATMENT

To identify chemical states on a surface during iodine dosing, we employ factor analysis treatment of Auger spectra [9]. Historically, factor analysis is a well-known statistical method applied with success in the analytical chemistry [9]. It was introduced into Auger electron spectroscopy in the works of Gaarenstroom [10].

Application of the factor analysis appeared to be useful when the total spectrum of the investigated system could be considered as a linear combination of the spectra of its components, with their concentrations being varied in the course of a process. It is important that the spectrum of the particular component be unique and independent of the component concentration in the system. Factor analysis allows both the number of independent components in the system to be determined and the behaviour of each component to be determined separately. AES is considered to satisfy the requirements mentioned above. The detailed formalism of factor analysis could be found in the book [9]. Here we briefly outline the main steps of this procedure.

On the first stage of factor analysis, the so-called Principal Component Analysis (PCA), the number of relevant factors (components) is obtained. The measured Auger spectra are written to the data matrix ($[D]$) as rows. Each of the rows of $[D](m, n)$ consisted of the signal intensities for the $n$ points on the energy scale for the array of $n$
spectra. The aim of factor analysis is to decompose the data matrix in a product of two matrices $[R]$ and $[C]$: 

$$[D] = [R] \cdot [C],$$

where the matrix $[R](m,c)$ contains Auger spectra of core components in the system, and the matrix $[C](c,n)$ contains the concentrations of each of $c$ components in the array of $n$ spectra.

According to Ref.[9], the number of the independent components in the system is equal to the number of the non-zero eigenvalues of a covariant matrix $[Z] = [D]^{T} \cdot [D]$. Indicator function (IND) [9] and the standard error in the eigenvalues (SE) [9] are used to determine the number of the eigenvalues statistically different from zero.

On the stage of PCA the pair of matrices $(|[R]|$ and $|\tilde{C}|)$ could be obtained, satisfying to the condition (1). As a rule the pair of matrices $|\tilde{R}|$ and $|\tilde{C}|$ is an abstract solution of Eq. (1) without any direct physical meaning. However, using target transformation procedure it is possible to obtain the required matrices $|\tilde{R}|$ and $|\tilde{C}|$. Formally, target transformation is a procedure for finding an appropriate matrix $[T]$ which will transform $|\tilde{C}|$ into $[C]$ and $|\tilde{R}|$ into $[\tilde{R}]$ [12]:

$$[C] = [T][\tilde{C}],$$

$$[R] = [\tilde{R}]\cdot [T]^{-1}. \tag{2}$$

To find the transformation matrix $[T]$ one should know the information on physical and chemical properties of the investigated system. The matrix $[T]$ can principally be obtained by two different test procedures ("target testing"). The one used more often is based on knowledge of the components in the system and their standard spectra. The spectra of pure components form standard matrix $[R^\ast]$, which also must satisfy to Eq. (3). Mathematically the least square fitting of the matrix $[R^\ast]$ by the product $[\tilde{R}]\cdot [T]^{-1}$ has to be performed for the calculation of the matrix $[T]$. Then using Eq. (2) the matrix $[C]$, containing the concentration dependencies of the components, can be easily calculated. The second way to calculate $[T]$ is based on the knowledge or assumption of concentration dependencies. In this case they form the matrix $[C^\ast]$ which should be fitted by the product $[T][\tilde{C}]$ according to Eq. (2). And finally the calculation of the matrix $[R]$ is straightforward from Eq. (3).

IV. RESULTS

A. CuI/Cu(100)

Figure 1 shows Auger lines intensities obtained for the step-by-step adsorption of molecular iodine on Cu(100). Auger spectra for 1 M$_{2,3}$VV (495-540 eV) and Cu M$_{2,3}$VV (45-75 eV) were collected in a first derivative mode. In Fig. 1(a) the I/Cu AES peak ratio ($\eta$) is shown as a function of dosing time.

Figures 1(b)(c) demonstrate the behaviour of different chemical components obtained as a result of Factor Analysis application to arrays of experimental Auger spectra.

The presence of two components for iodine M$_{4,5}$VV line and three components for copper M$_{2,3}$VV line were detected (see Fig. 2). At the beginning of I$_2$ adsorption (see Figs. 1(b)(c)) up to 300 s ($\eta < 0.31$) only one component of iodine is detected. It corresponds to chemisorbed iodine ($I_{ads}$) which forms a saturated overlayer at the coverage of 0.4 ML [6]. At the same time Cu M$_{2,3}$VV Auger line is superposition of two components. First component ($Cu_{trans}$) describes the electronic structure of upper copper layer disturbed by iodine chemisorption. It is not surprising that intensity of $Cu_{trans}$ follows intensity of $I_{ads}$ as shown in Figs. 1(b)(c). Other component (Cu$_{met}$) preserves the line shape of clean copper and corresponds to lower copper layers. At the higher coverage range ($\eta > 0.31$) the nucleation and growth of copper iodide (CuI component in Figs. 1(b)(c)) starts. After 800 s of I$_2$ adsorption ($\eta \sim 1.0$) the signal from clean copper (Cu$_{met}$) disappears. Note that both components $I_{ads}$ and $Cu(I_{ads})$ remain nonzero even for dosing time exceeding 800 s ($\eta = 1.0$). Further iodine dosing up to 3000 s ($\eta = 1.65$) gives rise to saturation of Cu component and disappearance of $I_{ads}$ and $Cu_{trans}$. Such behavior indicates formation of unbroken film with a thickness exceeding the escape depth of Auger electrons (25-30 Å).

Figure 3 shows the steps of copper iodide growth on Cu(100) followed by STM. Copper iodide nucleation occurs preferably near the step edges. The size and the number of islands increase with iodine exposure as shown in Fig. 3(b). At $\eta \sim 1.0$ copper iodide forms an unbroken film (Fig. 3(c)). Dark depressions in STM image in Fig. 3(c) correspond to the surface area still covered with chemisorbed iodine. We found that dosing of molecular iodine above this coverage leads to the multilayer growth of copper iodide film.

Further attention is concentrated on the coverage at $\eta = 0.35$ (Fig. 3(b)), since in this case islands are large enough to be studied with STM and there is a surface area still covered with chemisorbed iodine. In such a case there is a possibility to decode the atomic structure of copper iodide basing on the knowledge of c(5x2) structure of chemisorbed iodine [6]. The copper iodide islands are seen in the STM images as polygons, with the angles 60° and 120°. The preferable triangular shape of the island is typical for the growth of (111)-oriented fcc or zinc blend crystals. The island sides in the STM images in Fig. 3(b) are not identically oriented on a surface: we have detected 12 different types of CuI islands.

Figures 3(d), (e), and (f) show atomic structures of different types of CuI islands, which all have outer planes of hexagonal symmetry, but different types of the superstructures. The sides of the CuI islands appear to be parallel to close-packed atomic rows. That is why for further analysis we can consider orientations of atomic rows (or atomic lattice) instead of the "orientation of islands".

Copper iodide islands can be classified on the base of superstructures as striped structures ('A1'and 'A2' (Figs. 3(d)(e)), 'screw-like' structure 'B' (Fig. 3(e)) and structure 'C' without visible modulation (Fig. 3(f)). We observed that each structure ('A', 'B', 'C') has four different orientations with respect to the Cu(100) lattice. The structures marked as 'A1' and 'A2' are combined in one group (denoted as 'A') because the directions of the
atomic rows along the stripes (d1 and d2) appear to be equivalent. The distances between the dark stripes in 'A1' image were measured to be 18 Å or 29 Å without any periodicity. The structure 'A2' with a period $\sim 47$ Å was observed only at the corners of some triangular islands with structure 'A1' inside the islands. 'A2' is characterized by wide stripes.

To explain the observed structures we have used the $c(5 \times 2)$ structure as a reference to determine the structural parameters of each island type on atomic level. In Fig. 4 the island of type 'A1' is presented together with the $c(5 \times 2)$ monolayer. The remarkable feature is a full coincidence of the X direction of the monolayer structure with one of the close-packed rows of the copper iodide. It means that orientation of copper iodide lattice is related to the monolayer lattice, since the X and Y directions can not be explained by any crystallographic direction in copper substrate lattice. We have measured the average interatomic distances in the CuI lattice along three basic close-packed atomic rows. They are equal to 4.18 Å, 4.28 Å, and 4.28 Å, respectively. We were able to achieve such accuracy by measuring 50 interatomic distances along atomic rows in Fig. 4(a). The difference in the interatomic distances indicates the compression of the copper iodide lattice (Fig. 4(a)). To characterize the orientation of the CuI lattice we have introduced the angle $\gamma$ between the [100] direction of the substrate and the close-packed atomic row of copper iodide. It is indicated

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FIG. 4: (a) STM image (250 × 298 Å²; $I_t = 0.45$ nA, $U_s = -1.25$ V) showing atomic structures of the copper iodide island and saturated monolayer $c(5 \times 2)$ ($\eta = 0.35$). STM image is shown as a projection on a plane, so the height difference between copper iodide island and terrace with $c(5 \times 2)$ structure is eliminated. (b) The scheme of the $c(5 \times 2)$ structure. Different presentations of the unit cell '1' and '2' are shown. (c) The mutual orientation of copper iodide (111) and the $c(5 \times 2)$ structures in real space. The lattice parameters are denoted as $a_1$, $a_2$, and $a_3$ for CuI(111) structure, and $b_1$, $b_2$, and $b_3$ for $c(5 \times 2)$ lattice. The diagonals of the both hexagons are parallel to the direction $X$.

TABLE I: Parameters of the different types of copper iodide structures on Cu(100). $\gamma$: angle of rotation with respect to [100] direction.

<table>
<thead>
<tr>
<th>Type of structure</th>
<th>Compression</th>
<th>$a_1$ (Å)</th>
<th>$a_2$ (Å)</th>
<th>$a_3$ (Å)</th>
<th>$\gamma$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>Yes</td>
<td>4.28</td>
<td>4.28</td>
<td>4.18</td>
<td>±9.2</td>
</tr>
<tr>
<td>A2</td>
<td>No</td>
<td>4.28</td>
<td>4.28</td>
<td>4.28</td>
<td>±8.6</td>
</tr>
<tr>
<td>B, C</td>
<td>No</td>
<td>4.28</td>
<td>4.28</td>
<td>4.28</td>
<td>±5.8</td>
</tr>
</tbody>
</table>

in Fig. 4 for the compressed structure 'A1' ($\gamma = 9.2°$).

The same approach was used to analyze the islands with 'A2', 'B' and 'C' superstructure. We found that for all these cases the hexagonal copper iodide lattice is not compressed and the interatomic distances appear to be close to bulk CuI(111) values (4.28 Å[11]). The only difference between these structures is the orientation of their lattices on a surface (see Table 1). Note that from the geometrical point of view the structure 'A1' can be described as the slightly distorted structure 'A2'. Indeed, they both have close-packed atomic rows parallel to the direction X in the $c(5 \times 2)$ monolayer lattice. The angular deviation of other two close-packed atomic rows in 'A1' and 'A2' (forming the sides of CuI island) is equal to 0.6° (see Table 1). Therefore, it is not surprising that islands containing the structures 'A1' and 'A2' simultaneously and the islands demonstrating the only structure 'A1' are not distinguished in panoramic STM images. Taking into account the lattice rotation with respect to both [010] and [100] directions of copper it is possible to explain all twelve types of the island orientation.

To clarify the nature of the superstructures formation on top of CuI(111) islands and the mechanism of copper iodide growth on Cu(100) we have performed a simple computer modelling of the superstructures considering them as Moiré-like patterns formed as a result of the superposition of the upper CuI(111) lattice and the underlying layer.

To find an appropriate candidate to the interface layer we consider Auger factor analysis data once more (see Fig. 1). One can note that metal copper state (clean copper) disappears at $\eta \sim 1.0$. This effect is easily explained as a substrate screening by the unbroken CuI film. Panoramic STM image obtained for this coverage (Fig. 3(c)) vali-
FIG. 5: Computer modelling for the explanation of the nature of the Moiré patterns observed in the STM images for CuI layers on Cu(100).

dates this fact as well. However the chemisorbed iodine state remains non zero above this critical coverage (see Fig. 1). To explain this fact we have to assume the existence of the iodine interface layer between substrate and copper iodide, which has electronic structure rather close to saturated monolayer (because we are not able to distinguish them by AES). It could also mean that the atomic structure of the interface layer is close to the structure of the saturated iodine monolayer, i.e. c(5 × 2). To simulate the situation we have chosen the iodine c(5 × 2) structure as the underlying layer for upper CuI(111) lattice. Results of modelling are shown in Fig. 5. For 'A2' the model drawing shows the stripes with a period ∼ 47 Å. This picture is very close to the real STM image shown in Fig. 3(d). The excellent agreement was also achieved for the 'screw-like' structure 'B' (Fig. 3(e)). For the 'C'-type (island without modulation) the modelling resulted in a soft Moiré-like pattern (Fig. 3(f)). We think that such modulation for 'C' is too weak to be seen in the STM images.

Thus, we can conclude that the Moiré-like superstructures on copper iodide islands may be explained by the superposition of the Cu lattice and the iodine interface preserving the structure and electronic spectrum of the saturated iodine monolayer.

B. CuI/Cu(111)

In case of CuI growth on Cu(111) we have found the same behaviour as for CuI formation on Cu(100). Hereafter the situation with CuI growth on the Cu(111) face will be briefly outlined. The evolution of the chemical states on the surface is exactly the same as in the case of (100) surface (see Fig. 1). The peculiarities of present system are related to the different symmetry of surface plane. Therefore, a difference in the atomic structure of the iodine monolayer is expected. The saturated chemisorbed monolayer of iodine forms a striped domain-wall structure, with a period of about 35 Å[4, 5]. This structure is preserved under the growing copper iodide lattice as an interface layer.

Figure 6(a) demonstrates an atomic resolution STM image of a CuI unbroken film on Cu(111) surface. The quasi-hexagonal Moiré-like superstructure is visible. The same scheme of data treatment already described for Cu(100) shows that copper iodide lattice parameters are close to the bulk values of the (111) plane of CuI. Moreover the iodide lattice is rotated with respect to the < 112 > direction of copper by different angles varied in the range of 1.5 – 3.5°. Figure 6(b) demonstrates the result of mod-
FIG. 6: (a) STM image (232 × 232 Å², Iₜ = 0.45 nA, Uₛ = −300 mV) of Cu(111) surface covered with unbroken copper iodide film. It demonstrates a Moiré-like superstructure with a period 30-60 Å superimposed with atomic modulation of CuI(111) lattice. (b) Computer modelling (angle between close-packed rows of CuI(111) and <112> direction is taken as 2°) of the Moiré-like patterns.

delling of the Moiré-pattern which is in agreement with the experimental STM image shown in Fig. 6(a).

V. FINAL REMARKS

Thus, depending on the substrate symmetry and orientation of CuI lattice on a surface, STM images of copper iodide film demonstrate Moiré-like superstructures initiated by the interaction of the undistorted hexagonal lattice of CuI (∼ 4.3 Å) and the lattice of the underlying interface layer. The structure of interface layer for both Cu(100) and Cu(111) was found to be close to the structure of the saturated iodine monolayer on the corresponding plane. Moreover, we have found out [12] that orientation of copper iodide nuclei on a surface strongly depends on the step edges orientation, which, in turn, is determined by the direction of close-packed atomic rows in the saturated iodine monolayer.

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