Growth of Si nanostructures on Ag(001)

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Abstract

The first stages of the growth of silicon on Ag(001) at moderate temperatures start by the formation of a p(3 × 3) superstructure, which continuously evolves with increasing coverage toward a more complex superstructure. In this paper, the atomic arrangement of the p(3 × 3) and of the “complex” superstructure has been investigated using scanning tunnelling microscopy, surface X-ray diffraction and low energy electron diffraction. The atomic model retained for the p(3 × 3) reconstruction consists in four silicon atoms (tetramers) adsorbed near hollow and bridge sites of the top most Ag(001) surface layer. For higher coverages, i.e., when the “complex” superstructure starts to develop, the silicon overlayer forms periodic stripes, most probably bi-layers, with a graphitic like structure.

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1. Introduction

The formation of self organized-nanostructures (nanodots, nanowires or nanostrines) on metallic surfaces has been, for few years, intensively studied [1,2] in relation to their new chemical/physical properties. In this frame, the growth of nanoclusters of semiconductors (Si or Ge) self-organized on metallic surfaces that form unexpected structures is of special interest [3–6]. This peculiar behaviour is probably due to the delicate balance between the tendency to establish metallic bonds for the surface of the substrate and, at variance, covalent bonds for the deposited semiconductor. This is especially true for non-reactive metal-semiconductor systems, i.e., systems which present a strong trend toward phase separation. Instead, when the trend is toward order, one generally observes the formation of surface alloys, silicide or germanide like, even though some times new interesting superstructures are also observed [7–9].

In this context, we have undertaken a study of the Si/Ag system, which shows a pronounced tendency toward phase separation [10]. On the Ag(110) surface, a previous investigation of the silicon deposition at room temperature (RT) has revealed the formation of silicon nanowires (NWs) [11], in a massively parallel arrangement along the [−1 1 0] direction of silver; all these NWs, that differ only in length, have the same width (16 Å) and height (2 Å). In order to clarify the role of the surface orientation on the silicon organization, we carry out here a comparative study of the first stages of growth of silicon on the more symmetric Ag(001) surface.

On this face, the growth at RT studied by Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED) is layer-by-layer like, without formation of any long range ordered structure [12]. However, upon annealing at ~230 °C or during the growth at the same temperature, two ordered surface structures have been evidenced [13]. The first one, a p(3 × 3), appears from the very first stages of growth up to about one monolayer (ML), i.e., up to the first break observed in the Auger growth
curves [12,13]. Beyond that, new spots appear over the $p(3 \times 3)$ LEED pattern, revealing the formation of a novel superstructure that we have called “complex” since the new spots were quite fuzzy, among streaks, and displayed no clear symmetry.

In this paper we report (i) detailed Scanning Tunnelling Microscopy (STM) and Synchrotron Radiation (SR) Surface X-Ray Diffraction (SXRD) investigations of the $p(3 \times 3)$ superstructure, for which we derive a precise atomic model, (ii) thorough STM observations of the “complex” structure, for which we propose a tentative model.

2. Experimental details

The STM experiments were performed at RT in an Ultra High Vacuum (UHV) chamber equipped with a LEED apparatus and a commercial Omicron STM. The Ag(001) sample was cleaned by several cycles of sputtering (600 eV Ar$^+$ ions, $P \sim 10^{-5}$ Torr) followed by annealing at 400 °C until a sharp $p(1 \times 1)$ pattern is obtained. Silicon, evaporated by direct current heating of a piece of Si wafer, was deposited onto the Ag(001) surface held at 230 °C. The silver substrate temperature was controlled by a thermocouple located close to the sample. The SXRD experiments were carried out on the UHV diffractometer installed on the superconducting wiggle beamline DW2 of the DCI storage ring at the LURE (Orsay, France). The surface normal was aligned with the diffractometer azimuthal rotation axis ($\omega$) so as to maintain the incident angle constant. It was kept at the critical angle value ($\alpha_c \approx 0.3^\circ$ for the wavelength of 0.8266 Å) during all scans. The acceptance angle of the detector is defined by $3 \times 3$ mm$^2$ slits in front of the detector, 330 mm away from the sample. As usual, the experimental data are corrected for the Lorentz, polarisation and area factors [14]. A standard tetragonal surface coordinate system (scs) consistent with the conventional LEED notation is used. The basis vectors are $a_{scs} = (a_{bulk} + b_{bulk})/2$, $b_{scs} = (-a_{bulk} + b_{bulk})/2$ and $c_{scs} = c_{bulk}$, with modules and angles: 0.28915 nm, 0.28915 nm, 0.408917 nm, 90°, 90°, 90°. Crystal Truncation Rods (CTRs) from the bare Ag(001) surface were measured prior to silicon deposition. These rods (101, 111 and 201) are well fitted with a model of bulk silver (unrelaxed (001) surface) in agreement with previous works [15], using a surface roughness parameter $\beta = 0.1$ and a Debye–Waller factor of 0.63 Å$^2$.

3. Experimental results and discussion

3.1. The $p(3 \times 3)$ superstructure

After the deposition of about one silicon monolayer on the Ag(001) surface heated at 230 °C, the LEED pattern displays a sharp $p(3 \times 3)$ reconstruction. The sample is then transferred to the STM chamber where topographs are recorded. Fig. 1 displays a filled states STM image showing two orthogonal domains separated by clear border lines. Each domain contains parallel stripes oriented either along the [110] or the [−110] direction of the silver surface. A modulation is apparent along each stripe. One can also notice on top of the structured layer a number of aggregates with different shapes and sizes. The smallest ones appear to straddle two stripes. The detailed appearance of the $p(3 \times 3)$ superstructure is revealed in Fig. 2. In the unit cell, one observes four protrusions forming apparently a rectangle with sides of $\sim$0.41 nm and $\sim$0.28 nm. In order to precise the atomic arrangement, we further performed a detailed SXRD analysis.

The SXRD study of the $p(3 \times 3)$ superstructure comprises in-plane reflections and rod profiles. A series of 70 fractional order in-plane reflections have been measured providing 27 non-equivalent reflections. The structure factor values of these latter reflections are shown by black half circles in Fig. 3. In addition, three fractional order and three integer order rod profiles have been measured; they are shown in Fig. 4. Each experimental datum comes from the integration of rocking curves taking into account the grain misorientation which turns out to be about 0.2° Half Width at Half Maximum (HWHM). Standard deviations of the structure factor values are derived from the counting statistics and from the reproducibility of the symmetry equivalent reflections. Data analysis and structural refinement were performed using the ROD program [16]. A preliminary analysis relied on the in-plane fractional order reflections and the subsequent Patterson map. Several models with various numbers of Si atoms in the unit cell have been investigated. Models with silicon atoms in adatom positions as well as in substitution in the first silver layer have been tested. It turns out that only a model with
four Si atoms on the Ag surface could fit the experimental data. The rather weak oscillations observed in the fractional order rods are a strong indication that the reconstructed overlayer is relatively thin and most probably does not involve much more than the Si layer itself. The observed data are then fitted to a model with four silicon atoms in the p(3 × 3) unit cell on top of a Ag surface layer. The free parameters are the atomic positions, the Debye–Waller factors of the silicon atoms, and two different scale factors for the fractional order and the integer order reflections. The former is slightly larger to account for parts of the surface that could be unreconstructed. No significant improvement of the fit can be gained by changing the Debye–Waller factor of the silver atoms from the bulk value (0.63 Å²) and the surface roughness parameter β from that of the clean Ag(001) surface. The best result is obtained with two tilted silicon dimers, whose coordinates are shown in Table 1. Within these dimers, the silicon atoms are located near the hollow and bridge adsorption sites of the Ag(001) surface. Their Si–Si interatomic distance is 0.234 ± 0.002 nm, which is precisely the Si–Si interatomic spacing in bulk silicon. These dimers, separated by 0.40 ± 0.01 nm within the unit cell, form one-dimensional (1D) stripes (Fig. 5). We can view this particular Si atomic arrangement as a quasi rectangular arrangement of tetramers forming stripes. The surface corrugation given by the height difference between the highest and the lowest silicon atoms amounts to 0.13 nm. The silicon adsorption does not significantly change the interlayer spacing $d_{12}(\text{Ag})$ between the first Ag layer and the second Ag layer, from that of the clean Ag surface (unrelaxed) and of bulk $d_0(\text{Ag})$. On average, there is just a slight expansion of 1.6% with a corrugation within the first Ag layer of about ±0.01 nm.

The top layer arrangement deduced from the SXRD analysis is in fair agreement with the atomically resolved STM images. Indeed, both techniques reveal a p(3 × 3) superstructure made of a silicon tetramer with a quasi rectangular shape. The side distances of the tetramer measured by STM (0.28 nm and 0.41 nm) are quite similar to those found by SXRD (0.234 nm and 0.40 nm). Both techniques reveal the formation of 1D tetramer stripes on the silver surface running along the [110] and [−110] directions of the silver (001) substrate. These stripes are perfectly ordered in their orthogonal directions forming the p(3 × 3) two dimensional array.

The existence of strong Si–Si bonds is confirmed by the Si–Si interatomic distance in the dimers ($d_{12} = 0.236 ± 0.002$ nm, $d_{34} = 0.232 ± 0.002$ nm) close to the Si–Si bond length in bulk silicon and by the height distribution of the silicon atoms, which shows that the tetramers are not planar on the surface. On the other hand, the formation of a silicon monolayer wetting the silver surface (instead of three dimensional (3D) Si clusters) indicates that the interactions with the substrate are probably significant. Nevertheless, compared with the Ge on Ag(001) system (which forms more compact Ge tetramers with a quite strong distortion of the two top Ag atomic layers [5]), the Si–Ag interactions appears to be weaker since only the first plane of silver is just slightly distorted. This difference can be related to the bulk phase diagrams which show a quite large solubility of Ge in Ag while there is no solubility of Si in Ag.

### 3.2. The "complex" superstructure

As already mentioned, beyond one silicon ML deposition, the LEED pattern displays the so-called “complex” superstructure. A filled-state STM image at atomic resolution of the p(3 × 3) superstructure is shown in Fig. 2. The p(3 × 3) unit cell is indicated (6.4 × 6.1 nm², $V = −1.02$ V, $I = 1.14$ nA).

Fig. 2. Filled-state STM image at atomic resolution of the p(3 × 3) superstructure. The p(3 × 3) unit cell is indicated (6.4 × 6.1 nm², $V = −1.02$ V, $I = 1.14$ nA).

The non-equivalent fractional order SXRD reflections of the (3 × 3) superstructure are shown in Fig. 3. The measured and simulated structure factor amplitudes are shown by the area of the black and white half circles respectively. The conventional LEED (1 × 1) reciprocal surface cell is indicated.

Fig. 3. Non-equivalent fractional order SXRD reflections of the (3 × 3) superstructure. The measured and simulated structure factor amplitudes are shown by the area of the black and white half circles respectively. The conventional LEED (1 × 1) reciprocal surface cell is indicated.
superstructure [13]. Fig. 6 presents a filled-state STM image obtained after a deposition of 1.6 silicon ML. One observes the coexistence of two superstructures: the p(3 × 3) and a new one, the “complex” one, in agreement with the LEED observations. This “complex” structure is composed of new stripes running again along the [110] and [\(\bar{1}10\)] directions of the silver (001) surface forming also two equivalent perpendicular domains. Details of the stripes are shown in Fig. 7. Several stripes present structural defects and deviate from being straight. Nevertheless, when the stripes are straight and well ordered they are \(2.0 \text{ nm}\) in width, which corresponds in practice to seven times the surface of Ag parameter (\(7 \times 0.289 = 2.023 \text{ nm}\)).

We can describe the stripe structure by two joined chains of regular hexagons (sides: \(0.35 \text{ nm}\)) indicated in black line in Fig. 7. The periodicity of the hexagons along the stripes, as shown on the line scan below the STM image, is \(1.16 \text{ nm}\), which corresponds to four silver parameters (\(4 \times 0.289 = 1.156 \text{ nm}\)). The unit cell of this complex superstructure composed of two joined hexagons is drawn with a grey rectangle; as a matter of fact it corresponds locally to p(7 × 4) reconstruction, which can explain the new spots superimposed over the former p(3 × 3) LEED pattern [13].

Just from STM images, which only reflect a map of the density of states, it is always risky to deduce an atomic model. Nevertheless, the observation of hexagons on the

Table 1

<table>
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<th>#</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
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<tr>
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<td>0.840</td>
<td>0.467</td>
<td>0.833</td>
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The associated unit cell is \((a = b = 0.867 \text{ nm}, c = 0.409 \text{ nm}, \alpha = \beta = \gamma = 90^\circ)\). The silver surface layer (in average \(Z = 0.5\)) is slightly distorted in comparison with bulk. The upper plane of bulk Ag atoms is located at \(z = 0\).
STM images on the one hand, as well as, on the other hand, the pronounced metallic character of the silicon layers [13] could indicate that the construction of the new silicon stripes of the “complex” structure (local (7 × 4)) originates from a kind of distorted Si(1 1 1) bilayer. Hence, the atomic model that we can tentatively propose relies on such a type of modified Si(1 1 1) bilayer on top of the silver (0 0 1) surface with the [−1 0 1] direction of the silicon (1 1 1) plane aligned with the [1 1 0] direction of the silver surface (see the model of Fig. 8). Let us note the perfect match between four silver parameters and three silicon parameters which can explain the preferential propagation direction of the stripes and, obviously, for symmetry reasons, the two perpendicular domains.

With a rigid bilayer model, the atoms which constitute the hexagon chains would not belong to the same Si(1 1 1) plane. Yet, all protrusions which draw the hexagonal shapes in the STM images appear roughly at the same height. Hence, we can suppose that the stripes are not composed of a rigid silicon (1 1 1) bilayer, but, more likely, to a more “graphite” like silicon layer, which could also explain the strong metallic character of these stripes. Nevertheless,
assuming this model, all the atoms of the silicon “graphitic layer” are not visible on the STM image. In fact, only few corresponding protrusions are clearly observed. In the model of Fig. 8, the black pattern shows the two joined hexagon structure revealed by STM; the silicon atoms that sit directly on top of the silver atoms are drawn in black balls.

The narrow width of the stripes (~2.0 nm, i.e. 7 times the silver parameter) can possibly be justified by the fact that every six silver parameters a silicon atom sits in a hollow site. \textit{Ab initio} calculations are in progress to simulate the STM images of the stripes and, eventually, confirm our model.

4. Conclusion

The behaviour of silicon deposited on silver (001) held at 230 °C is particularly surprising. Up to a coverage of about one silicon ML, a p(3 × 3) superstructure is observed. The atomic model derived from STM observations and a thorough SXRD analysis corresponds to silicon tetramers with a quasi rectangular shape self-organized on the surface. The silicon atoms are in adatom positions near hollow and bridge sites of the silver (001) surface. Upon further silicon deposition, a local p(7 × 4) superstructure develops from the former p(3 × 3) structure. STM images reveal new silicon stripes self-organized along the [−110] and [110] silver directions. These stripes seem to be constituted with a “graphitic” silicon layer.

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