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Diverse growth of Mn, In and Sn islands on thallium-passivated Si(1 1 1) surface

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ABSTRACT

Controlled growth of thin films on highly reactive silicon surfaces has been a challenge for decades. High density of surface dangling bonds, however, hinders the adsorbate diffusion and its self-organization. In our work, we propose a novel use of the Tl-(1 × 1) layer as a passivating agent, which highly enhances diffusion of adsorbates by saturating all dangling bonds of the Si substrate.

We use room-temperature scanning tunneling microscopy to study structures formed on the Si(1 1 1)/Tl – (1 × 1) surface after deposition of submonolayer amounts of three elemental adsorbates: Mn, In and Sn. As a result, three significantly different surface structures are observed. Manganese atoms aggregate to stable dendritic islands nucleated on Si steps. Indium islands are compact and unstable during observation. Unlike Mn and In, Sn atoms intermix with Tl atoms and arrange into an array of triangular objects.

The growth kinetics of the three deposited metals on the Tl – (1 × 1) layer is discussed and compared with the kinetics observed in previously studied systems. The comparison shows that the growth of the layers adsorbed on the Tl-passivated surface is similar to the growth of the adsorbate layers on less reactive metal surfaces.

1. Introduction

Controlled growth of thin films has been for many years a key driver in the surface science and related technological applications like thin film transistors. In order to obtain defect-free flat films on highly reactive (typically silicon or germanium) surfaces, a transformation method called passivation is often used [1]. Among other passivated surfaces, the Si(1 1 1)/Tl – (1 × 1) [2] has been shown to have outstanding properties [3]. Despite the fact that the surface behaves as ideally passivated one (stable, inert and with completely saturated surface dangling bonds [4,5]), it has never been used as a substrate for further growth of adsorbates. The only exception is the study of interaction of the second Tl layer with the Si(1 1 1)/Tl – (1 × 1) surface showing very weak bonding between Tl layers [5].

Thallium exhibits unique properties, which are extraordinary among other chemical elements. First of all, an inert-pair effect results in an opportunity to act monovalently in various reconstructions [4,6,7]. Above that, thallium, as a heavy element (atomic number 81), exhibits large spin-orbit coupling. The coupling in the two-dimensional Tl – (1 × 1) surface layer induces unusually large Rashba spin-splitting of surface bands [3], which is of a great value for a potential use in future spintronic devices [8].

The Si(1 1 1)/Tl – (1 × 1) surface can be prepared by deposition of one monolayer ($1\,\mathrm{ML} = 7.83 \times 10^{14}\,\mathrm{atoms\,cm^{-2}}$) of Tl on the Si(1 1 1) – (7 × 7) surface and annealing at ≈300 °C [4]. The surface is stabilized by electrons that are transferred from Tl 6p orbitals to Si dangling bonds. In the structure, Tl atoms are located in T_4 positions of the bulk-terminated Si surface [4,9–11].

In order to utilize the large spin-splitting in the Tl – (1 × 1) layer, the split surface states are required to be metallic. As it was determined by the scanning tunneling spectroscopy (STS) [5] and photoemission spectroscopy supported by ab-initio calculations [4], the clean Si(1 1 1)/Tl – (1 × 1) surface has a bandgap (≈0.5 eV and 0.34 eV, respectively). Spin-split surface bands do not cross the Fermi level; therefore they cannot be used for generation of spin-polarized electrons. However, as Gruznev et al. [12,13] recently showed, spin-split metallic bands can be created by using a dense 2D alloy layer containing a metal with strong spin-orbit coupling (e.g. Tl) and another metal which modifies the surface reconstruction. Experimentally, it has been shown that metallicity of the Si(1 1 1)/Tl – (1 × 1) surface can be also naturally induced by the presence of defects in the passivating layer [14,15].

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In our work, we use a room-temperature scanning tunneling microscopy (STM) to observe the growth of three elemental adsorbates (Mn, In and Sn) deposited on the Si(1 1 1)/Tl – (1 × 1) surface in submonolayer amounts. Experiments show that the studied adsorbates behave very diversely. By the intra-comparison of the surface morphologies and the comparison with previously studied systems we determine kinetic models of the growth. The models give insight into the substrate–adsorbate and adsorbate–adsorbate interactions on the Si(1 1 1)/Tl – (1 × 1) surface.

2. Experimental

Experiments were carried out in an ultra-high vacuum non-commercial STM apparatus with a base pressure below 8×10^{-9} Pa. Pressure during the experiments was sustained within the order of 10^{-8} Pa. The Si(1 1 1) – (7 × 7) surface was prepared on the Sb-doped Si monocrystal (resistivity 0.005–0.01 Ω cm) by flashing to ≈1200 °C.

The Si(1 1 1)/Tl – (1 × 1) surface was prepared by the thermal deposition of 1 ML of thallium (purity 99.999 %) on the Si(1 1 1) – (7 × 7) surface and annealing at ≈300 °C for 2 min [4]. The samples were resistively heated by passing DC current. Manganese, indium and tin were deposited on the passivated surface after cooling down the sample to room temperature (20–40 °C). Resistively heated tantalum and tungsten evaporators were used for the deposition.

Sample temperature was determined with absolute and relative measurement accuracies of ± 30 °C and ± 10 °C, respectively. The deposition rates and the deposited amounts were measured by a quartz crystal thickness monitor. Coverages and distances were estimated from the STM images with a relative error of 15%. Presented X and Y dimensions of each STM image already account for calibrated piezo and thermal drifts. Hereafter, only mean values without respective errors are stated in cases they agree with the above stated errors.

3. Results and discussion

3.1. Si(1 1 1)/Tl-(1 × 1)

Fig. 1 displays the clean Si(1 1 1)/Tl – (1 × 1) surface before the deposition of metals. Fig. 1(a) shows Tl-covered Si islands evenly distributed over the surface (some of the islands are marked by black arrows). The islands are formed during the post-deposition annealing of the Si(1 1 1)/Tl surface, when the (7 × 7)-reconstructed Si surface transforms into the (1 × 1)-reconstructed one [7]. In this process, excess Si atoms are excluded to the surface and create islands, which are covered by Tl (see the schematic drawing of the cross-section of the surface in Fig. 1(b). The step edges of Tl-covered Si islands are essentially of the same nature as the step edges of Tl-covered Si terraces. Hence, in this work Tl-covered Si terraces and Tl-covered Si islands are referred as “terraces” and “Si islands”, respectively. The density and the size of the Si islands vary and depend on exact experimental conditions during the preparation of the Si(1 1 1)/Tl – (1 × 1) surface.

3.2. Si(1 1 1)/Tl-(1 × 1)/Mn

In order to use the Si(1 1 1)/Tl – (1 × 1) surface as a substrate for further deposition of adsorbates, it is necessary to examine the stability of the passivating layer. In our study we have tested the stability by deposition of Mn, which is known for its high reactivity with bare silicon surfaces [16,17]. We have performed experiments with two different amounts of deposited Mn: (0.18 ± 0.05) ML and (0.35 ± 0.10) ML.

The Si(1 1 1)/Tl – (1 × 1) surface after the deposition of the smaller amount of Mn is presented in Fig. 2(a). The figure shows Tl-covered Si islands surrounded by several bright clusters (some of them are marked by white arrows). Since the clusters are not present on the surface before the deposition of Mn (see Fig. 1), we conclude that they consist of nucleated Mn atoms.

Fig. 2(c) presents the detailed image of the surface. It displays two terraces and one Si island. A few Mn islands are nucleated on the Si island and terrace step edges. For the insight into the vertical topography the figure also includes a height profile which is placed under the image. A contour from which the profile is extracted is marked by a blue dotted line “1”. The line crosses three Mn islands which are assigned to the peaks of the profile by gray dotted arrows. Taking into account the known composition and topography of all objects in the figure, we constructed a simplified explanatory drawing of the cross-section of the surface, which is displayed in the inset of Fig. 2(a).

Fig. 2(b) presents the surface with a higher deposited amount of Mn. Two displayed terraces are separated by a step edge which runs from the top right corner to the bottom left corner of the image. The edge is decorated by Mn islands elongated in a direction perpendicular to the step (two of the islands are marked by white dotted arrows). Si islands (one of them is marked by a black solid arrow), surrounded by highly-branched Mn islands (white solid arrows), are evenly distributed over both terraces. In contrast with the low-coverage case, where no preferred growth orientation is visible, at higher coverage Mn islands grown on Si islands form triangularly enveloped dendritic structures (marked by blue-dotted equilateral triangles). All envelopes are congruently oriented: one side is parallel to the $[1\bar{1}0]$ direction and one apex is pointing in the $[11\bar{2}]$ direction.

Fig. 2(d) displays a detail of a step edge between two terraces. Two height profiles (placed on the right side of the figure) are extracted from the image. Positions of the profiles are marked by the pink and blue dotted lines, which cross Mn islands nucleated next to an Si island and a step edge of a terrace, respectively. As can be seen from Fig. 2(d), Mn islands nucleated on the top of step edges merge with those that are nucleated on the bottom. It is noteworthy that (i) gradually descending profiles of Mn islands are formed at Si steps and (ii) longer parts of the merged Mn islands are located on tops of edges. The latter phenomenon can be explained as follows. The annealing of the Si(1 1 1)/Tl surface at 300 °C causes nucleation of Si islands as well as growth of terraces due to nucleation of Si atoms on step edges. The outer border areas of terraces are newly nucleated, hence much lower concentration of defects and Si islands are observed on them. The shielding effect of Si islands blocks most of the deposited Mn atoms from nucleation on the bottom side of terrace step edges. On the other hand, lower concentration of Si islands in the vicinity of steps on top terraces enables more Mn atoms to diffuse to top sides of step edges and nucleate there.

The average apparent height of Mn islands (measured from the bottom terraces of steps) is determined to be 2.3 times the height of an Si step (i.e. 0.72 nm). However, as it is illustrated by the profile “1” of Fig. 2(c), height of individual Mn islands varies significantly (as much as 25%). These observations of gradually descending profiles and high variance of height of the Mn islands indicate that, although an inner structure of Mn islands has not been resolved, ordering of Mn atoms in the islands is only short-range.

Growth of dendritic islands as those observed in Fig. 2(b) can be found in many metal-on-metal surface systems (e.g. Ir(1 1 1)/Au, Pt(1 1 1)/Au [18] or Pt(1 1 1)/Ag [19]). Monte Carlo simulations of such a growth unveiled that two conditions are necessary for the growth of dendritic islands: (i) high mobility of deposited atoms on the surface and either (ii-a) low diffusivity of nucleated atoms along islands edges [18], (ii-b) a high