Surface Science 677 (2018) 8–11

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Anisotropic alloying: Formation of atomic scale trellis on the Si(100)-(2 × 1) surface

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ARTICLE INFO

Keywords:
Scanning tunneling microscopy
Bimetallic structures
Silicon
Silver
Indium
Nanostructures

ABSTRACT

Early stages of growth of two-dimensional bimetallic Ag–In islands on the Si(100)-(2 × 1) surface were studied by means of scanning tunneling microscopy. Mixing the two different metals, one forms 1D chains on the Si(100)-(2 × 1) surface and the other one creates 2D islands, results in anisotropic 2D lattice structures formed of indium chains connected by perpendicular silver chains. Growth at elevated temperatures results in more ordered structures. A model of the observed bimetallic structures and a growth scenario based on experimental data are proposed.

1. Introduction

It is generally accepted that a formation of nanostructured surface alloys is of particular interest in many areas of physics and chemistry, such as clean energy production [1] , magnetic storage devices [2] and others. Control of formation of 3D bimetallic nanoclusters, 2D alloys or 1D bimetallic nanostructures is a challenging task. The way in which particular metal components interact with the surface influences miscibility, dimensionality, structure and consequently properties of resulting bimetallic nanostructures. Especially, mixing of two different metals, which individually exhibit quite distinctive behaviour at the same growth condition, could produce unusual binary nanostructures. Previously, 1D bimetallic atomic chains were created, using metals which form 1D atomic chains on the Si(100)-(2 × 1) surface [3]. Here we are interested in combination of a metal which forms 1D structures with a metal which exhibits 2D growth on the Si(100)-(2 × 1) surface.

The technologically important surface Si(100)-(2 × 1) attracts attention as a natural template for self-assembled growth of truly one-dimensional structures – dimer chains of group III and IV metals, which grow perpendicularly to silicon dimer rows (SDRs) [4–7]. The chain growth has been already explained by a surface polymerization reaction [8]. The structure of the 1D metal chains is known as a parallel adatom dimer model [6] (see Fig. 1a).

Silver, contrary to the aforementioned metals, forms at sub-monolayer coverage on the Si(100)-(2 × 1) surface 2D islands rather than single separated chains [9,10]. The islands are considerably unstable at RT and pinned by surface defects and steps [11]. Reported explanations of the nature of the 2D layer at RT and saturation coverage have remained controversal. It has been stated that Ag adsorption geometry at low and high coverage is different [9]. At very low coverage, adsorption of Ag atoms at cave site positions in trenches between SDRs was proposed [9,12–15] (see Fig. 1b). At higher coverages, the islands exhibit mixture of (2 × 1) and (2 × 2) structures. Several concepts of their atomic arrangement were published [9,13,16–19]. In general, the previous works are consensual in the fact that Ag atoms have a strong tendency to form dimers. However, they propose different adsorption positions as well as orientations of the dimers with respect to the SDR. According to [13], Ag atoms adsorbed at cave site positions form dimers parallel to the SDR which results in the (2 × 2) periodicity and the saturation coverage 0.5 ML (Fig. 1c) (1 ML corresponds to the number of atoms in the first layer of the Si(100)-(2 × 1) surface, i.e. 6.78 × 10^{14} cm^{-2}). Alternatively, the adsorption scenario without dimerization could result in the (2 × 1) periodicity (Fig. 1b). In our previous experiments we observed both of them [10,11] (see Fig. 2). In the presented work, with Ag coverages of order 0.01ML, we assume the simplest adsorption configuration with Ag atoms adsorbed at the cave site positions.

We can summarize, that silver and indium form 2D islands and separate chains, respectively (see Fig. 2). On the other hand, a common feature of both In and Ag is a preferential nucleation at step edges or C-type defects, as well as formation of unstable structures at RT [10,11,20,21]. However, it has to be noted, that stability of In chains is significantly higher in comparison with Ag islands.

In this paper we present results of competitive growth of co-deposited In and Ag on the Si(100)-(2 × 1) surface and propose an interpretation of the observed structures. We will show that the

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https://doi.org/10.1016/j.susc.2018.05.010
Received 23 April 2018; Accepted 17 May 2018

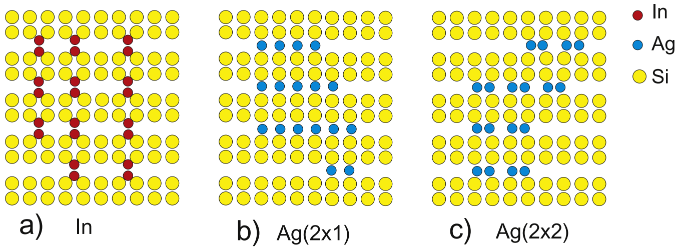

Fig. 1. Simplified model structures of the Si(100)2 × 1 surface with low coverages of a) indium, b) silver (2 × 1) and c) silver (2 × 2).

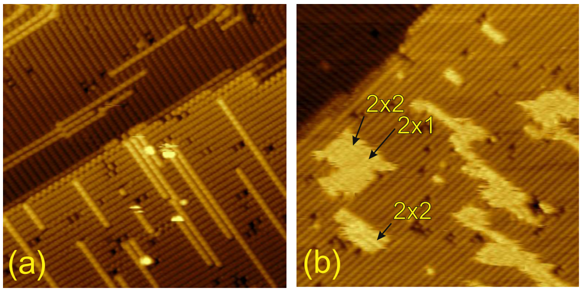

Fig. 2. Morphology of a) In and b) Ag layer on the Si(100)-(2 × 1) surface (coverage 0.1 ML, area size 30 × 30 nm). Fuzzy appearance of Ag islands reflects structural instability at RT.

competition between these two metals results in unusual trellis-like self-organized structures partially stabilized by surface defects.

2. Experiment

Sample preparation and subsequent STM measurements at room temperature (RT) were performed in a non-commercial ultra-high vacuum STM system. The pressure in the system did not exceed 1×10^{-8} Pa during experiments. Si(100) substrates (Sb doped, n-type, resistivity $\leq 0.014\ \Omega$ cm) were used. To obtain the (2 × 1) reconstructed surface, a sample was several times flashed by passing dc current for ≈ 20 s to 1200 °C. In and Ag were deposited from tungsten wire evaporators and evaporation rate was controlled by a quartz crystal thickness monitor. The total coverage was about $\sim$ 0.1 ML . The Si substrate was resistively heated during the deposition by passing dc current and the sample temperature was determined from calibrated heating power. STM tips were prepared by electrochemical etching from a polycrystalline tungsten wire and treated *in situ* by an electron bombardment and on a Pt single crystal.

3. Results and discussion

Morphology of as-deposited Ag–In bimetallic layers depends strongly on the order of deposited metals and on substrate temperature. Due to the instability of both In and Ag structures on the Si(100)-(2 × 1) surface, any further thermal treatment or long time relaxation results in formation of multichain-like structures. The formation of these structures can be facilitated also by simultaneous co-deposition of both metals. A result of the co-deposition at RT is shown in Fig. 3a. Images of the multichain structures show chains with a number of bright dots (BDs) (see Fig. 3a,b). The chains are perpendicular to silicon dimer rows and their minimum spacing is twice of the distance of silicon dimers in the dimer rows. The bright dots are often organized into lines perpendicular to the chains. Co-deposition at elevated substrate temperature results in more ordered structures as shown in Fig. 3b. At 100°C, a tendency to create pronounced elongated clusters of chains is evident. It is worth to note that such behavior at elevated temperatures was observed after deposition of sole In as well [3].

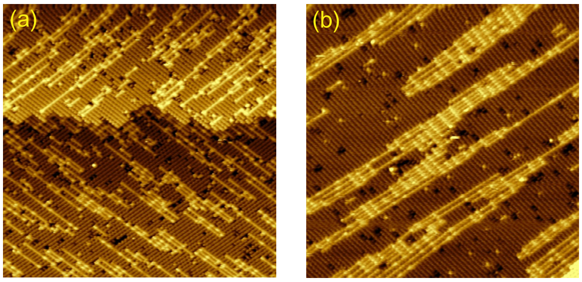

Fig. 3. Dependence of AgIn layer morphology on the deposition temperature: a) Ag and In co-deposition at RT, b) Ag–In co-deposition at 100°C. (Coverage is 0.1 ML, Ag:In ratio is 1:1, area size 50 × 50 nm) .

Let us now discuss in detail the growing AgIn structures. Examples of filled- and empty-state STM images are shown in Fig. 4a-b). Indium and silver on the Si(100) surface exhibit an inverse contrast: In (Ag) appears very bright on empty-state (filled-state) images and somewhat darker on filled-state (empty-state) images. We can therefore estimate which structures correspond to indium chains (details "In"), and which could be related to known silver objects (details "Ag"). In chains at minimal mutual separation appear brighter, other In chains appear a bit darker. We have observed this (probably electronic) effect before, in populations of In chains, without co-deposited silver. The structure "Ag" was also observed previously, after deposition of silver onto the Si (100)-(2 × 1) surface, and represents an Ag dimer captured at the C-type defects. The dimer is parallel with the Si dimer rows [13,21]. The dimers are frequently observed at low Ag coverage, they are rather unstable and induce buckling of the neighboring Si dimers (see also Fig. 4c,f). Fig. 4c shows a highly resolved filled state STM image of the AgIn layer co-deposited at room temperature. Beside known "In" and "Ag" structures, further typical structures can be distinguished in the image:

1) unusual fuzzy parts of the "In" chains (detail "A"),
2) transversal linear segments running parallel to SDRs accompanied with a visible buckling of Si dimers in their vicinity (detail "B")
3) bright dots (detail "BD") visible very often on the crossing of mutually perpendicular linear segments "In" and "B", and appearing also on "In" linear segments itself.

3.1. "A" structure

Parts of In chains denoted as "A" in Fig. 4d,e, which appear a bit darker and have a fuzzy appearance, were never observed in the In/Si (100)-(2 × 1) system. We suppose that these structures are formed from silver, probably single Ag atom captured in a position among activated Si atoms where an In dimer is normally located (see Fig. 5). Possibility that they represent In-Ag dimers cannot be ruled out.

3.2. "B" structure

The observed "B" structures can be explained as chains of Ag atoms running parallel with SDRs. The Ag atoms sit in cave positions. The model is able to explain all observed geometrical structures. The chains could be stabilized by the C-type defects (where small two atom clusters or even longer segments were already observed [13]), by other Ag chains (as in the case of 2D Ag islands – see Fig. 1b), or by the neighboring In dimers (see Fig. 5). We propose that Ag atomic chain "B" acts as a nucleation center for In chains. Conversely, an In chain end acts as a nucleation center for Ag atoms, since a single In dimer activates on each side two neighboring Si dimers (by breaking their π bond). It influences Ag adatoms in neighborhood in a similar way as a C-type defect. Consequently, mutually perpendicular In and Ag chains stabilize each other, which results in formation of the observed trellis structures