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A structured two-dimensional Au–Si alloy

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ABSTRACT

We report the formation of an ordered two-dimensional gold–silicon (Au/Si) alloy by deposition of a sub-monolayer of Si onto Au(1 1 1). Scanning tunneling microscope (STM) images show that at room temperature the Au/Si alloy consists of parallel rows with row-spacing 0.47 nm. These rows appear to float on Au(1 1 1) in bundles. Each bundle of rows can bend quite freely forming arches of arbitrary curvature. By annealing to 300 °C in ultra-high vacuum, the alloy changes its structure by forming straight rows with row spacing 0.35 nm.

1. Introduction

In recent years, there has been a growing interest in the preparation of silicon nanowires using a vapor–liquid–solid method at the eutectic temperature of Au–Si [1,2]. The process involves exposing a nanometer-sized Au particle to a silicon-containing gas which decomposes at the surface and deposits Si onto Au. Eventually a Au–Si eutectic liquid is formed and Si begins to precipitate in solid form if the concentration of Si becomes higher than that of the eutectic composition. The relevance of Au–Si eutectic in nanofabrication of Si wires has sparked a wave of interest in the atomic scale structure of the Au–Si interface [3,4]. In addition to its applications in nanotechnology, the Au–Si system has also drawn a great deal of attention from the research community due to the observation of a two-dimensional crystal of Au–Si alloy floating on top of the eutectic liquid [5–7] and its size effects during phase transition [3]. Gold and silicon do not form any crystalline bulk compounds at any temperature and composition. When cooling from the melted state, phase separation into pure Au and Si phases occurs. However, bonding frustration and geometric confinement lead to remarkable complication in two-dimensional structures, such as gold silicides on silicon surfaces [5,6,8,9] and gold surfaces [10]. Recently it has been found by X-ray diffraction that an ordered two-dimensional layer exists on the liquid surface of eutectic $Au_{82}Si_{18}$ alloy at 359 °C [5]. Based on the diffraction data, a surface unit cell consisting of four gold atoms and eight Si atoms is proposed [5]. We do not find any previous complimentary study of such a system using the STM because of the difficulty in handling a liquid metal. Moreover, from the surface science perspective, there are numerous studies on deposition of gold on silicon surfaces [11], i.e. under silicon rich conditions. In contrast, silicon deposition onto gold is rarely studied. In this paper, we report the observation, by using scanning tunneling microscope, of an ordered two-dimensional Au/Si alloy with a fibre-like structure on the Au(1 1 1) substrate at room temperature. We prepare our sample by depositing silicon atoms onto Au(1 1 1) in ultra-high vacuum.

2. Experimental

The Au(1 1 1) surface was a thin film (∼500 nm) created by thermal deposition of gold onto highly oriented pyrolitic graphite held at 380 °C inside a BOC Edwards Auto 306 evaporator. The graphite substrate was cleaved in air and after transferring to the evaporator it was heated at 380 °C for ∼1 h to degas. The deposition rate is about 5 nm/min. The sample was then transferred into an ultra high vacuum chamber with a base pressure of 2×10^{-10} mbar, and cleaned by eight cycles of ion sputtering with 1 keV Ar^+ ions and 30 minutes' thermal annealing to 1000 K. The sputtering and annealing cycle was repeated several times until the surface was judged clean based on STM images. The sample prepared in this way consists of interconnected crystallites, all with the (1 1 1) plane parallel to the graphite substrate. STM imaging is always performed on a single crystallite, and hence the sample behaves effectively as a (1 1 1)-oriented gold single crystal. Silicon was evaporated onto the sample from a Knudsen cell held at 1240 °C with a calibrated deposition rate of 0.02 ML/min. Imaging was performed at room temperature

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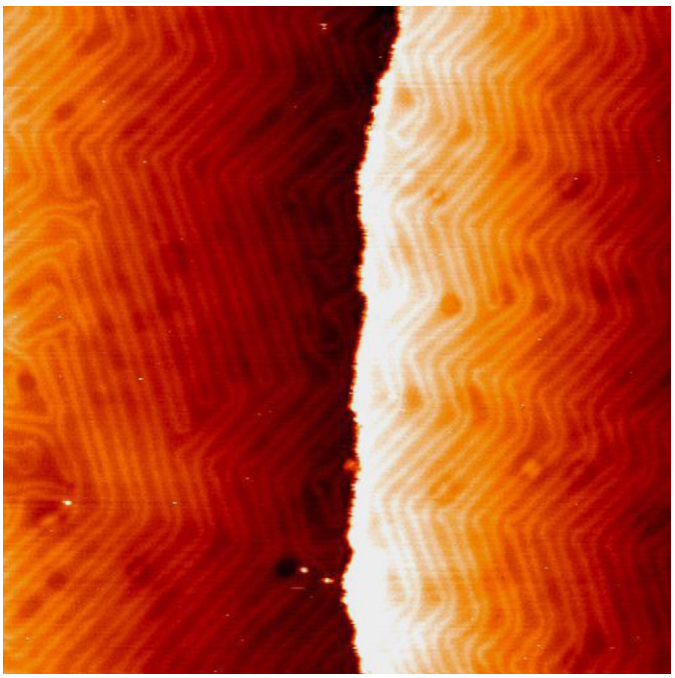

Fig. 1. STM image, 150 nm × 150 nm, showing the structure of the Au(1 1 1) surface before deposition of Si.

(RT) using an Omicron variable temperature scanning tunneling microscope (VT-STM) using electrochemically etched tungsten tips.

3. Results and discussion

Fig. 1 shows a typical STM image from the Au(1 1 1) surface that we used for all of our measurements. The image has all the features of a clean Au(1 1 1) surface with its usual herringbone reconstruction pattern [12–14]. After about 0.2 ML of silicon is deposited onto Au(1 1 1), dark spots appear in STM images as shown in Fig. 2a. One monolayer is defined as 6.78×10^{14} atoms/cm^2. These dark spots, 0.15 nm lower than the Au(1 1 1) substrate, are direct products of silicon deposition. However, the chemical composition of the dark spots is not clearly identified at the present time. Since the physical dimensions of many dark spots are significantly larger than the size of a single atom, what inside the dark spots are probably small silicon clusters embedded in the gold substrate. They appear dark under both bias polarities and this may be due to either a geometric effect or an electronic effect. The latter could arise from weak electronic coupling between the material inside the dark spot and its surrounding gold host. Accompanying the dark spots, growth of irregular structures along step edges is also observed. The grown structure suggests that the incorporation of silicon atoms into the gold surface may have released some gold atoms which subsequently diffuse to the step edges. It is unlikely that the grown structure at step edges is due to the aggregation of silicon atoms because the silicon atoms are immobilized rapidly upon landing. Fig. 2b shows a magnified view where it can be seen that the dark spots are rather randomly distributed. This distribution is in great contrast to the preferential occupation of the elbow site exhibited in the deposition of many metallic elements on Au(1 1 1) [15,16], and it indicates that the mobility of silicon atoms on Au(1 1 1) is rather limited presumably due to a much stronger Si–Au interaction. Most part of the Au(1 1 1) surface shown in Fig. 2 is not covered by silicon, and the herringbone pattern of the surface reconstruction is clearly seen in such areas.

The sample with 0.2 ML of deposited silicon was thermally annealed to 570 K for 10 min. Fig. 3a shows an STM image following such an annealing procedure. The darks spots shown in Fig. 2 disappear, and a reconstructed Au(1 1 1) with a characteristic network of discommensuration lines is observed, Fig. 3b. The discommensuration lines seen in Fig. 3b bend much more frequently than that on the clean Au(1 1 1) surface. Similar changes to the herringbone pattern of Au(1 1 1) has also been observed after depositing a small amount of Gd at 550 K [17], and after depositing 0.23 ML of Na followed by thermal annealing to 500 K [18]. This kind of dislocation network on Au(1 1 1) can be explained through various degrees of surface stress [19]. The clean surface reconstructs due to the presence of excess surface charge. This charge excess can either be suppressed by adsorbing electronegative species or enhanced by putting down electropositive elements. Depositing Na, Gd, and Si onto Au(1 1 1) leads to more enhanced surface charge density due to charge transfer to Au, and hence a more extensive surface reconstruction than that on the clean Au(1 1 1) surface. This is opposite to the situation where electronegative species such as iodine are deposited onto the same surface. Due to electron transfer from gold to iodine, the surface reconstruction is lifted [20]. Some small dark spots can be seen in Fig. 3b, and most of them

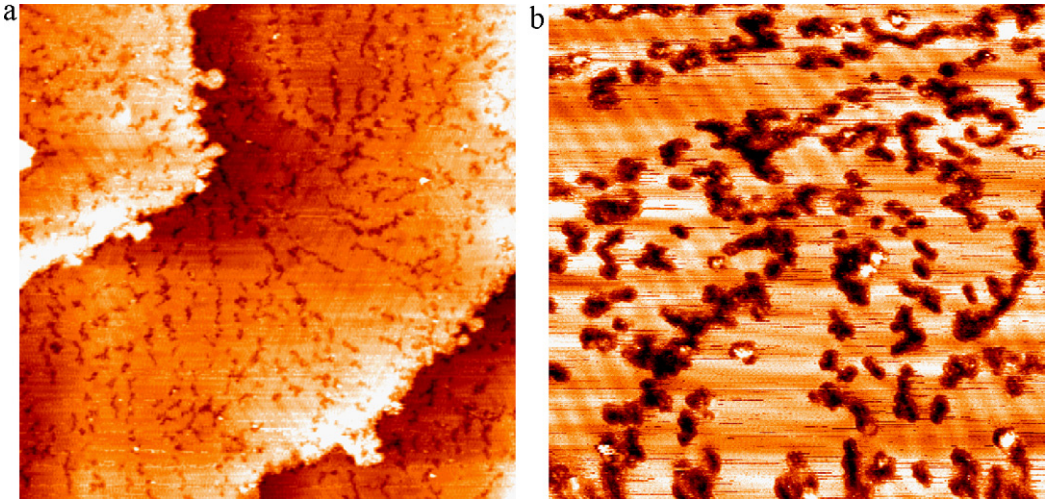

Fig. 2. STM images showing the morphology of Au(1 1 1) after 0.2 ML of Si is deposited at RT. (a) Dark spots on flat atomic terraces and the irregular structures grown at step edges. 175 nm × 175 nm; V_b = 0.456 V; I_t = 0.03 nA. (b) Magnified view, 70 nm × 70 nm, showing random distribution of the dark spots and the remaining discommensuration lines from the herringbone reconstruction. V_b = 1.028 V; I_t = 0.3 nA.