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First-principles study of Si(111)$\sqrt{31} \times \sqrt{31}$-In reconstruction

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ABSTRACT

Using first-principles total-energy calculations, structural properties of the Si(111)$\sqrt{31} \times \sqrt{31}$-In reconstruction have been studied. New refined structural model of the reconstruction has been proposed which adopts 17 In atoms and 31 Si atoms. The model is characterized by the reasonably low surface energy and demonstrates good correspondence between simulated and experimental scanning tunneling microscopy images. Calculations reveal semiconducting nature of the model structure in agreement with experiment.

1. Introduction

Due to variety of forming surface reconstructions [1,2], submonolayer In/Si(111) system has attracted a great attention starting from the very early ages of surface science [3,4]. Interest to the In/Si(111) reconstructions is preserved nowadays stimulated by a set of recent fascinating discoveries as follows. The Si(111)4×1-In reconstruction has been found to exhibit a metal–insulator transition at 120 K [5,6]. Unusual structural transitions have been also detected upon cooling Si(111) $\sqrt{7} \times \sqrt{3}$-In surface [7]. Moreover, the Si(111) $\sqrt{7} \times \sqrt{3}$-In surface reconstruction (which resembles one-atomic-layer In film and nearly free two-dimensional electronic gas system [8]) has been proved to be a suitable object for studying electron transport properties in low dimensions, including discovery of metallic-type conductivity without carrier localization down to 10 K [9] and observing superconducting transition around 3.0 K [10,11]. Several new In/Si(111) reconstructions have been found as a result of specific preparation conditions [12,13]. Using the difference in atomic structure and properties of the template In/Si(111) reconstructions (e.g., Si(111) 4×1-In and Si(111)$\sqrt{31} \times \sqrt{31}$-In), control of metal film growth has been demonstrated [14–16]. However, in spite of pronounced progress in this field, an exact atomic structure of many In/Si(111) reconstructions (e.g., Si(111)$\sqrt{31} \times \sqrt{31}$-In, Si(111)$\sqrt{7} \times \sqrt{3}$-In, Si(111)2×2-In, etc.) remains an open question. Filling these gaps seems to be a demanded timely task for researchers.

In the present work, we have revisited atomic arrangement of the Si(111)$\sqrt{31} \times \sqrt{31}R \pm 9^{\circ}$-In (hereafter, $\sqrt{31}$-In) reconstruction. Using first-principles calculations, we have reconsidered the available background experimental information and reported structural models. As a result, we have proposed a new model, which is characterized by the lower formation energy and better coincidence between simulated and experimental scanning tunneling microscopy (STM) images.

2. Calculation details

The plane-waves total-energy calculations reported here were performed by using the Vienna Ab Initio Simulation Package (VASP) [17–20] based on density functional theory (DFT) [21] with projector-augmented wave (PAW) pseudopotentials [22]. The local density approximation (LDA) after Ceperley–Alder [23] in the Perdew–Zunger parametrization [24] for the exchange and correlation functional has been employed. The electronic wave functions were expanded in a plane-wave basis set with an energy cutoff of 20 Ry. The calculations were performed using slabs of crystal with parallel outer faces of the same type. The supercell geometry used in this study was simulated by a repeating slab of eight double layers with atoms of given reconstruction ($\sqrt{3} \times \sqrt{3}$-In, $\sqrt{31} \times \sqrt{31}$-In, 4×1) on each of the faces and a vacuum region of 15 Å. The central two layers in a slab were kept fixed to simulate the bulk crystal termination of

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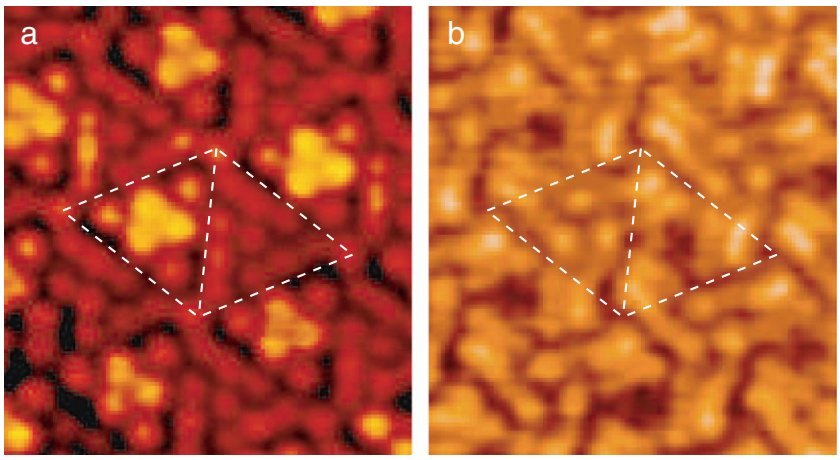

Fig. 1. (a) Empty-state (+1.8 V) and (b) filled-state (−1.8 V) STM images of the Si(111)$\sqrt{31}\times\sqrt{31}$-In reconstruction. Unit cell with two triangular subunits is outlined by the dotted line.

the surface. The geometry was optimized until the total energy is converged to 10^{-4} eV and the total force is converged to 10^{-3} eV/Å. The sensitivity of formation energies on kinetic energy cutoff, k-points setup, and the total energy/force numerical accuracy has been tested and found to have a negligible effect on the total energy differences. To compare the structures having different number of Si and In atoms in the different proposed models, we have used the surface energy per unit cell defined as:

$$E_{surf} = (E_{slab} - N_{Si}\mu_{Si} - N_{In}\mu_{In})/2A,$$

where E_{slab} is the total energy of the system, N_{Si} and N_{In} are the number of Si and In atoms in the supercell, μ_{Si} and μ_{In} are the energies per atom (chemical potentials) in bulk Si and In, respectively, and A is the surface area of the Si(111) substrate expressed in the 1×1 unit cells. The factor of 1/2 accounts for the two surfaces of the slab.

3. Results and discussion

Let us summarize first the available data on the $\sqrt{31}$-In reconstruction. It was first characterized with reflection high-energy diffraction [1,25], but the most essential information on its structural properties has been gained with STM [2,26–30]. In particular, empty-state STM images (Fig. 1a) clearly show that $\sqrt{31}\times\sqrt{31}$ unit cell consists of two inequivalent triangular subunits, one of which contains six and the other ten round protrusions. One more protrusion resides in the unit cell corner. It is typically suggested that these protrusions are due to In atoms, that gives In coverage of 17/31 ~ 0.55 ML in a general agreement with experimental coverage evaluations [1,2,28]. The top atomic Si substrate layer in $\sqrt{31}$-In has been recognized to contain ~0.9–1.0 ML of Si [28,30]. To our knowledge, there have been only two attempts to build the structural model of the $\sqrt{31}$-In reconstruction. The first model (hereafter, old model 1) was proposed in Ref. [27] for Ge(111)$\sqrt{31}$-In surface which has quit similar

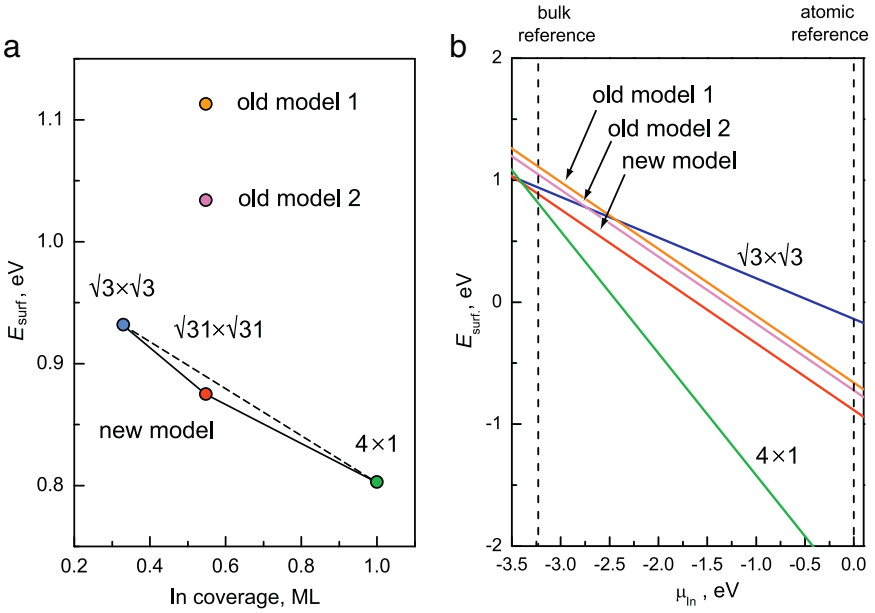

Fig. 2. (a) Surface energies calculated for the structural models of the reconstructions forming in In/Si(111) system in a course of In coverage growth, $\sqrt{3}\times\sqrt{3}$-In [31], $\sqrt{31}\times\sqrt{31}$-In (old model 1 [27], old model 2 [28], and new model), and 4×1-In [32]. The indium chemical potential μ_{In} is taken equal to its bulk value. (b) Surface energies as a function of the In chemical potential μ_{In} (a surface phase diagram) for $\sqrt{3}\times\sqrt{3}$-In (blue line), $\sqrt{31}\times\sqrt{31}$-In, including old model 1 (orange line), old model 2 (pink line), and new model (red line), and 4×1-In (green line).