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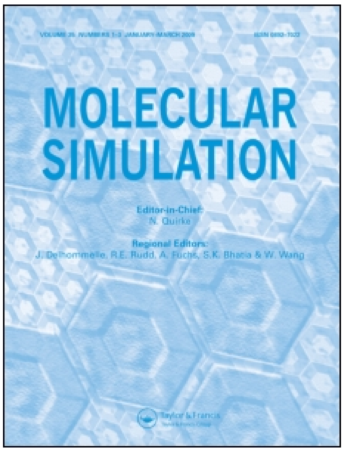

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Gold-induced surface reconstruction on GaAs(111)*B* surface

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We have investigated the atomic structure of the Au/GaAs(111)*B*-($\sqrt{3}\times\sqrt{3}$) surface and have performed scanning tunnelling microscopy (STM) simulations of the surface by using first-principles calculations. The atomic geometry determined with Au adatoms located at every third threefold hollow hcp site of the Ga lattice, agrees well with results reported from STM and low-energy electron diffraction experiments. The simulated STM images support experimental observations of bright centers with triangular spots. The calculated value of the diffusion barrier height of the Au adatom quantitatively explains the experimentally observed reconstruction of the wetting layer of Au on the Au/GaAs(111)*B*-($\sqrt{3}\times\sqrt{3}$) surface.

Keywords: density functional theory; scanning tunnelling microscopy; GaAs(111) surface; gold adatom

1. Introduction

The (111) polar surfaces of III–V compound semiconductors exhibit a considerable number of reconstructions depending on the substrate temperature and surface composition [1]. For the {111}*A*, *B* surface of GaAs, while (2 × 2) and ($\sqrt{19}\times\sqrt{19}$)$R23.4^\circ$ reconstructions are observed on the As-terminated (111)*B* surface [2,3], only a (2 × 2) reconstruction with one Ga vacancy in each unit cell is observed on the Ga-terminated (111)*A* surface [4,5]. The most stable reconstruction of the ideal GaAs(111)*B* surface is the (2 × 2) reconstruction on the (111)*B* surface formed by the As trimers on top of a complete layer of As atoms [3].

With regard to the clean GaAs(111)*B* surface, a metal-covered GaAs(111)*B* surface presents different characteristics. In particular, Bi- and Sb-covered GaAs(111)*B* surfaces present very well defined *c*(2 × 4) and (1 × 3) reconstructions formed by Bi trimers [6] and Sb chains [7], respectively. Au is the most widely studied metal element in semiconductor technology [8,9]. Recently, Hilner et al. [10], using low-energy electron diffraction (LEED) and scanning tunnelling microscopy (STM) images, concluded that a Au-covered GaAs(111)*B* surface predominantly exhibits a ($\sqrt{3}\times\sqrt{3}$) reconstruction at low coverage of Au atoms. This model is formed by one Au adatom per unit cell located in a threefold hollow (H_3) site, but does not satisfy the electron counting rule (ECR) [11]. To our knowledge, little is known about the Au/GaAs(111)*B*-($\sqrt{3}\times\sqrt{3}$) surface reconstructions on the atomic scale. Thus, the aim of this work is to investigate how Au adsorption on the GaAs(111)*B* surface affects the surface structure by employing a theoretical approach.

In this paper, we present an *ab initio* study of the Au-induced GaAs(111)*B* surface. For the proposed Au/GaAs(111)*B*-($\sqrt{3}\times\sqrt{3}$) reconstruction, the most favorable atomic geometry is determined and the presence of a Au wetting layer is confirmed. It will be shown that the minimum-energy structure corresponding to the Au atoms chemisorbs at the high-coordination H_3 hollow sites rather than at the fourfold coordinated T_4 sites. The electronic structure of this minimum-energy structure is also determined and shown to be metallic. The simulated STM images support the Au-induced surface reconstruction model proposed by Hilner et al. [10].

2. Computational method

The determination of the geometric and electronic structures of the GaAs(111)*B* surface was performed in the framework of the density-functional theory within the generalised gradient approximation combined with ultrasoft pseudopotentials [12] and plane-wave expansions in the Vienna *ab initio* simulation package [13,14]. The wave functions were expanded in a plane-wave basis set with a kinetic energy cutoff of 320 eV. The surface was modelled using periodic slabs of six GaAs bilayers, which were separated by vacuum regions of ~ 13 Å. The lowest atoms in the slab had their dangling bonds saturated with hydrogen atoms. The atoms in the bottom two bilayers and the *H* atoms were fixed, while the rest of the atoms were allowed to relax until the forces was smaller than 0.01 eV/Å. The momentum-space integrations were performed on a Monkhorst-Pack grid with 8 × 8 *k* points per 1 × 1 surface unit cell by using a smearing of

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$\sigma = 0.02\,\mathrm{eV}$. These parameters were found to produce well-converged results for the atomic geometries of clean GaAs(110) surface. All calculations were performed using the theoretical equilibrium lattice constant of 5.738 Å.

3. Results

The first step in the determination of the electronic properties of the Au-adsorbed GaAs(111)*B* surface is the determination of the atomic geometry of the uppermost surface layer. Motivated from a recent LEED observation of Au/GaAs(111)*B*-($\sqrt{3} \times \sqrt{3}$) [10], we consider only the ($\sqrt{3} \times \sqrt{3}$) reconstruction. The ($\sqrt{3} \times \sqrt{3}$) reconstruction is retained after Au chemisorptions on the GaAs(111)*B*-($\sqrt{3} \times \sqrt{3}$) surface with a 1/3-monolayer (ML) coverage. Here, the 1 × 1 surface unit cell with one adatom corresponds to 1-ML coverage. Figure 1 shows the most favorable atomic structure for the Au-induced GaAs(111)*B* surface reconstruction. In this configuration, the gold atoms preferably chemisorb in the vicinity of every third hcp threefold hollow site H_3 of the Ga lattice.

It should be noted that this clean GaAs(111)*B*-($\sqrt{3} \times \sqrt{3}$) surface does not follow the ECR presented by Pashley [11] since the dangling bond of each As surface atom is filled with 5/4 of an electron. Thus, each H_3 site containing a Au atom introduces 3/4 electrons into the Au—As bond. Correspondingly, the clean GaAs(111)*B*-($\sqrt{3} \times \sqrt{3}$) surface and the Au/GaAs(111)*B*-($\sqrt{3} \times \sqrt{3}$) surface become metallic. There are a few stable ($\sqrt{3} \times \sqrt{3}$)-*R*30° surface reconstructions of the III–V semiconductors for which the electroneutrality condition is not satisfied. For instance, the observed ($\sqrt{3} \times \sqrt{3}$)-*R*30° surface reconstruction of the S/InSb(111)*A* surface [15] violates the electronic counting requirement. Although the proposed Au/GaAs(111)*B*-($\sqrt{3} \times \sqrt{3}$) surface reconstruction does not obey the ECR, this is not a sufficient reason for ruling it out. Indeed, there are several structures in the literature on compound semiconductor surfaces possessing partially filled dangling bonds [16,17].

In order to determine the diffusion barrier height on the surface, we consider the differences between the binding energies at the adsorption sites and those at the saddle points on the chosen pathways as the diffusion barriers. More specifically, we place a Au adatom above the reconstructed GaAs(111)*B* surface on a two dimensional plane at some symmetric sites indicated by T_4, H_3 and *A*, as shown in Figure 1. The adatom is then kept fixed at a given position, while its *z*-coordinate and all the substrate atoms are fully relaxed by minimising the total energy of the system. Figure 2(a) shows the relaxed height of the Au adatom with respect to that of the outermost As atom. The potential energy profile in the diffusion direction along the curve ($T_4 \rightarrow A \rightarrow H_3 \rightarrow T_4$) is shown in Figure 2(b). We find that the minima of the potential energy curve is at a threefold hollow H_3 site. The diffusion barrier height is $\simeq 0.18\,\mathrm{eV}$, which is very small as compared with other GaAs(001) surfaces. This result indicates the formation of a Au wetting layer which was proposed by Hilner et al. [10].

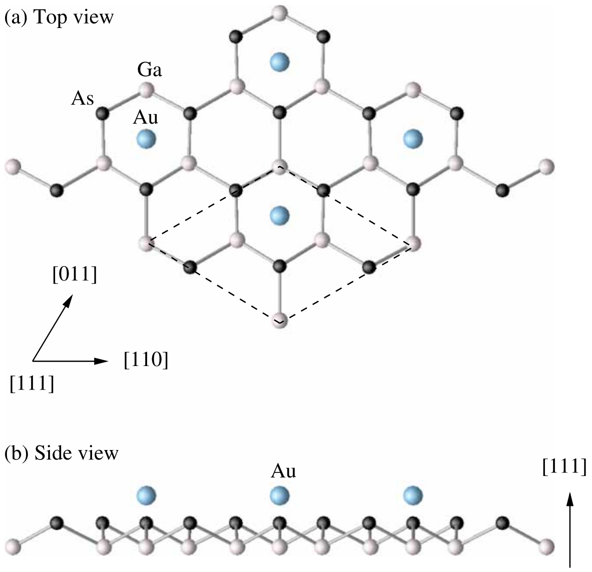

Figure 1. Schematic top and side views of the atomic configuration of the clean Au/GaAs(111)*B*-($\sqrt{3} \times \sqrt{3}$) surface. The small and medium balls and the large balls represent the As, Ga and Au atoms, respectively.

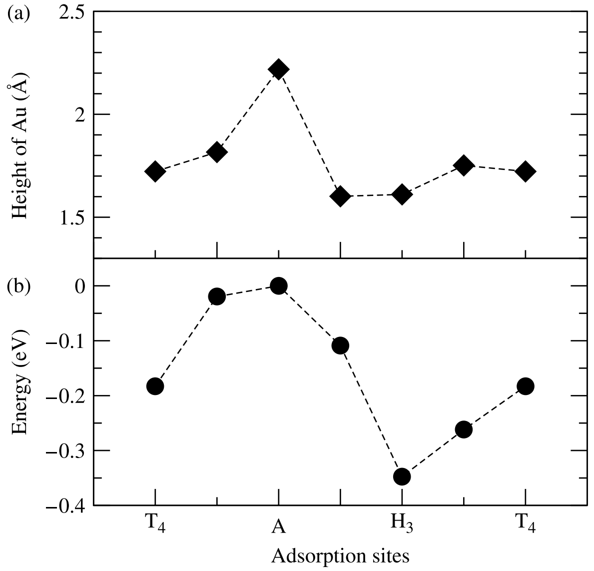

Figure 2. (a) Relative height of a Au atom with respect to the outermost As atom and (b) relative total energies for a Au adatom on the GaAs(111)*B*-($\sqrt{3} \times \sqrt{3}$) surface at the different adsorption sites. Surface unit cell is indicated with dashed lines. The total energy of Au at the top of the As site (A) is taken as the reference.

A deep understanding of the electronic structure can be obtained by an accurate theoretical study of the STM images. For obtaining the STM images, the isocontour of a suitably defined local density of states is extracted within the Tersoff–Hamann approximation [18]. Within this approximation, the tunnelling current is proportional to the local density of states at the tip position integrated over the energy range restricted by the applied bias voltage:

$$I(r, \pm V) \propto \pm \sum_{n\mathbf{k}} \int_{E_F}^{E_F \pm V} |\psi_{n\mathbf{k}}(\mathbf{r})|^2 \delta(E - E_{n\mathbf{k}}) dE,$$

where ψ is the wavefunction of the single electron state in Kohn–Sham state, and $+V$ and $-$ represent the sample bias voltages for the empty- and the filled-state measurements, respectively. To obtain the voltage-dependent simulated images, we vary the bias voltage V in the above formula. Figure 3 shows the simulated STM images of Au/GaAs(111)B-($\sqrt{3} \times \sqrt{3}$) for the filled state ($V = -2$ eV). We observe that the structural units of the ($\sqrt{3} \times \sqrt{3}$)$R30^\circ$ are triangular units with bright centers. Our STM image clearly indicates that the Au adatom is stable at a hollow H_3 site, with the maximum charge density being localised around the H_3 site instead of the fourfold top T_4 site. The peak-to-peak corrugation is found to be ~ 2.0 Å. A similar amplitude of corrugation was observed by Ohtake et al. [5] on the GaAs(111)B-(2 × 2) surface.

In this model, the Au atoms preferably adsorb on every third hcp threefold hollow site of the Ga lattice. Actually, the Au atoms rather bind with Ga as there exist many compounds between Au and Ga but none between gold and As. Furthermore, by simulating the STM images of the clean GaAs(111)B surface, we also verified that the presence of Au is essential for obtaining the correct image of the Au/GaAs(111)B-($\sqrt{3} \times \sqrt{3}$) surface reconstruction. It is worthwhile to note that the various structures assumed for the clean surface yield STM images markedly different from the experimentally observed ones. This indicates that the restructuring of the surface is actually due to the presence of Au atoms and not just a result of the processing conditions.

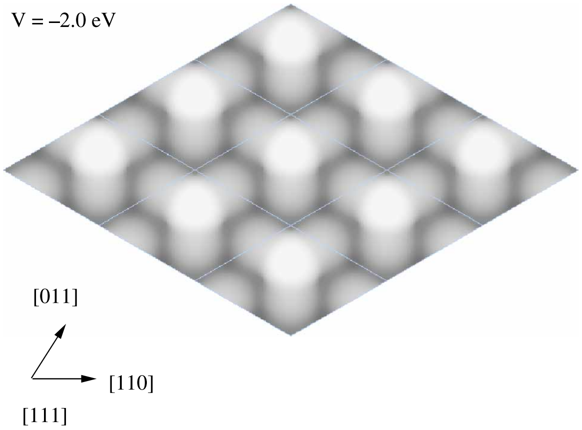

Figure 3. Theoretical STM image of the Au/GaAs(111)B-($\sqrt{3} \times \sqrt{3}$) surface of 21 × 21 Å. The images map the height of constant-current electron density for the electron density integral for an energy interval of -2 eV below the calculated Fermi level.

4. Summary

We have investigated the atomic geometry and electronic structure of the Au/GaAs(111)B-($\sqrt{3} \times \sqrt{3}$) surface using *ab initio* pseudopotential planewave calculations. We found the presence of Au to give rise to the ($\sqrt{3} \times \sqrt{3}$) surface reconstruction. In this model, Au atoms are adsorbed at every third threefold hollow hcp site of the Ga lattice with a Au coverage of 1/3-ML. The proposed structural model is in good agreement with experimental data from LEED and STM.

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