

Theoretical Investigations of Au-induced Surface Reconstructions on the GaAs(111)B surface

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ABSTRACT

We have performed a detailed theoretical study of the atomic geometry and electronic structure of Au adsorbed GaAs(111)B surfaces using *ab initio* pseudopotential calculations. Recently, it has been observed that small amounts of Au induce a well-ordered ($\sqrt{3}\times\sqrt{3}$) reconstruction on the GaAs(111)B surface from the Scanning Tunneling Microscopy (STM), replacing the (2×2) As-trimer structure of the clean surface. We investigate the stable adsorption sites and simulate STM images of Au adsorbed on the semiconducting Au/GaAs(111)B- $(\sqrt{3}\times\sqrt{3})$ surface on the basis of the results from the STM observations. Our calculation reveal that the Au-induced surface reconstruction becomes energetically favorable for lower coverages of Au, in agreement with the STM images obtained by Hilner *et al.* of the wetting layer with one Au per unit cell located in a threefold hollow (H_3) site.

Keywords: Adsorption of Au, GaAs surface, STM simulation

1 Introduction

The (111) polar surfaces of III-V compound semiconductors exhibit a considerable number of reconstructions depending on substrate temperatures and surface compositions [1]. For the $\{111\}$ A,B surface of GaAs, while the (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]. In contrast to the clean GaAs(111)B surface a metal covered GaAs(111)B surfaces present a different character. In particular, the Bi- and Sb-covered GaAs(111)B surfaces present very well defined $c(2\times 4)$ and (1×3) reconstructions formed by Bi-trimers[6] and Sb-chains[7], respectively. A microscopic understanding of the substrate modification due to metal would be greatly helped by theoretical investigations on the atomic scale of the metal/semiconductor systems.

Gold atom is the most widely studied metal element in semiconductor technology; e.g., Au is often used as electrodes and wirings for GaAs in the micro-electronics technology [8], [9]. With respect to Au-covered $(\sqrt{3}\times$

$\sqrt{3})$ - $R30^\circ$ reconstructed Si(111) surface, Murayma *et al.* [10] calculated the band structure of various structure models. Restricted to Au-covered GaAs(111)B surfaces, however, little is known about the Au adatom positions, the surface reconstructions, the electronic structures, and their dynamics. Thus the aim of this work is to investigate how Au adsorption on the GaAs(111)B surface affects the surface structure, by theoretical approach based on the *ab initio* pseudopotential method. Especially, we address the Au/GaAs(111)B- $(\sqrt{3}\times\sqrt{3})$ surface with monolayer Au coverage. Since Hilner *et al.* [11] recently succeeded in the identification by Low Energy Electronic Diffraction/Microscopy (LEED, LEEM) and Scanning Tunneling Microscopy (STM) measurements of the Au/GaAs(111)B surface morphology, showing Au-covered surface presents predominantly a $(\sqrt{3}\times\sqrt{3})$ reconstruction at low coverage of Au atoms.

In this work we present an *ab initio* study of the Au-induced GaAs(111)B surface. The equilibrium atomic geometry and the presence of Au wetting layer of the experimentally proposed Au/GaAs(111)B- $(\sqrt{3}\times\sqrt{3})$ reconstruction have been determined. It will be shown that the minimum-energy structure corresponding to the Au atoms chemisorbing 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 has also been calculated and shown to be metallic. Moreover, STM images of occupied and unoccupied states have been simulated.

2 Computational Method

The calculations of the geometric and electronic structure of the GaAs(111)B surface were performed in the framework of the density-functional theory within the generalized gradient approximation combined with ultrasoft pseudopotentials [12] and plane-wave expansions in the VASP (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 modeled using periodic slabs of six GaAs bilayers, separated by a vacuum region 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 atoms were allowed to relax until all the forces were smaller than 0.01 eV/Å. The momentum-space integrations have been done on a Monkhorst-Pack grid of 8×8 \mathbf{k} points per 1×1 surface unit cell, using a smearing of $\sigma = 0.02$ eV. These parameters are found to produce well-converged results for the atomic geometries of the clean GaAs(110). All calculations have been performed using the theoretical equilibrium lattice constants of 5.738 Å.

3 Results and Discussion

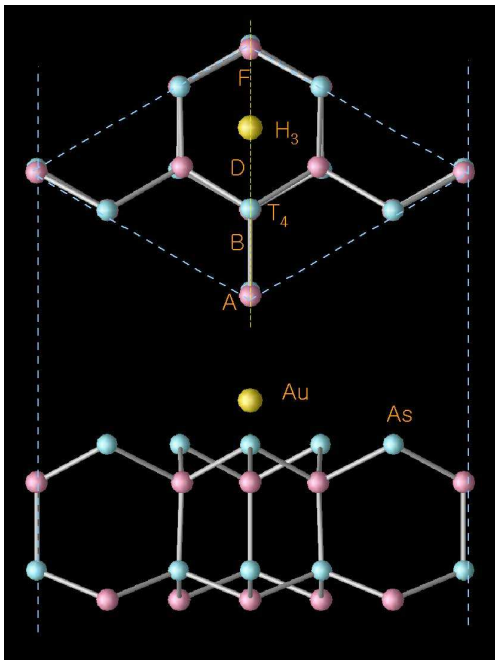


Figure 1: Schematic top and side view of the relaxed Au/GaAs(111)B- $(\sqrt{3} \times \sqrt{3})$ model. Adsorption sites of Au adatom on the surface at different sites : A, B, T_4 , D, H_3 , F. Bond length of Ga-As ~ 2.56 Å.

The first step toward a calculation of the electronic properties of the Au-chemisorbed GaAs surface is the determination of geometric structure of the uppermost surface layer. Motivated from a recent experimental STM observation of Au/GaAs(111)B- $(\sqrt{3} \times \sqrt{3})$ structure [11], in this work we only consider $(\sqrt{3} \times \sqrt{3})$ reconstruction. Assuming, in accordance with the experiments, that the $(\sqrt{3} \times \sqrt{3})$ reconstruction is retained after Au chemisorptions on the Au/GaAs(111)B- $(\sqrt{3} \times \sqrt{3})$ surface, we have performed total-energy geometry optimization calculations for a variety of possible positions for the Au atoms within the Au/GaAs(111)B- $(\sqrt{3} \times \sqrt{3})$ surface unit cell. This surface does not follow the electron counting rule presented by Pashley [15]. The dangling bond of each As surface atom is filled with 5/4

of an electron and thus the surface is metallic. Although the proposed structure for the $(\sqrt{3} \times \sqrt{3})$ - $R30^\circ$ does not obey the electron counting model, this is not sufficient reason for ruling it out. There are several structures in the literature of compound semiconductor surfaces having partially filled dangling bonds. [16], [17] Now, we focus our attention on the Au/GaAs(111)B- $(\sqrt{3} \times \sqrt{3})$ surface with 1/3-monolayer (ML) coverage. Here, the 1×1 surface unit cell with one adatom corresponds 1-ML coverage. The coordinates of the substrates as well as the adatoms are fully relaxed to minimize the total energy. Thus, the structure shown in Fig. 1 is found to be the most energetically stable. In this configuration, the gold atoms chemisorb in the vicinity of the H_3 hollow sites. Indeed, the Au atoms preferably adsorb on every third hcp threefold hollow site of the Ga lattice, giving rise to these smaller triangles. These results give a useful hints for the interpretation of simulated STM images responsible for the metallic phase.

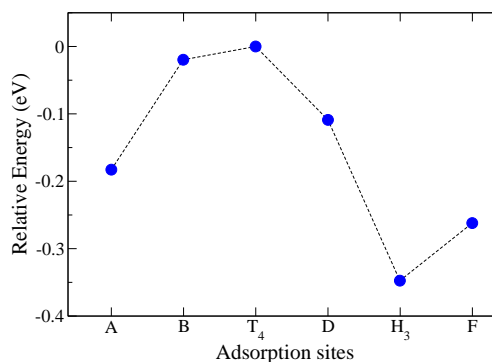


Figure 2: Potential energy curve of Au/GaAs(111)B at different adsorption sites. Au atom is slightly more stable at a H_3 site than at a fourfold top T_4 site.

The chemical binding of an Au adatom on the $(\sqrt{3} \times \sqrt{3})$ surface and Au-surface interaction have been carefully investigated here by estimating the adiabatic potential experienced by an isolated Au adatom interacting with the surface. More specifically, we placed an Au above the reconstructed GaAs(111)B surface on the two dimensional plane. Then the adatom is kept fixed at a given position, while the z -coordinate of it and all the substrate atoms are fully relaxed by minimizing the total-energy of the system. This relaxation procedure is repeated for all positions of a regular grid, thus resulting in a mapping of the potential energy curve as shown in Fig. 2. The Au binding sites and the energy barriers opposing the adatom diffusion have been identified by the local minima and the saddle points of the PES estimated for the Au adatom, respectively. It should be note that there is symmetric-equivalent potential minima at a threefold hollow (H_3) site and the corruga-

tion of the potential energy curve is remarkably small. The maximum variation of the adiabatic potential in the (111)B plane is $\simeq 0.35$ eV and the diffusion barrier height is smaller than 0.2 eV. This results implies a large mobility of Au atoms on the surface compared to the rate of Au detachment from the nanoparticles.

A deep understanding of the electronic structures leading to the metallic state can be accomplished with an accurate theoretical study of the STM images. For the calculation of STM images, the geometry and the total energy corresponding to the most favorable Au sites have been then refined by fully relaxing the geometry of the Au-surface system. After structural relaxation, isocontour of a suitably defined local density of states were extracted within the Tersoff-Hamann approximation [18]. Within this approximation, the tunneling current was proportional to the local density of states at the tip position integrated over the energy range restricted by the applied bias voltage. The isocontour surfaces generated in this way correspond to STM images taken in constant current mode. The simulated STM images of the Au/GaAs(111)B- $(\sqrt{3} \times \sqrt{3})$ for the filled state ($V_b = -2.0$ V) and the empty state ($V_b = +2.0$ V) are shown in Fig. 3(a) and (b), respectively. We find that the structural units of the $(\sqrt{3} \times \sqrt{3})R30^\circ$ are triangular units with bright centers.

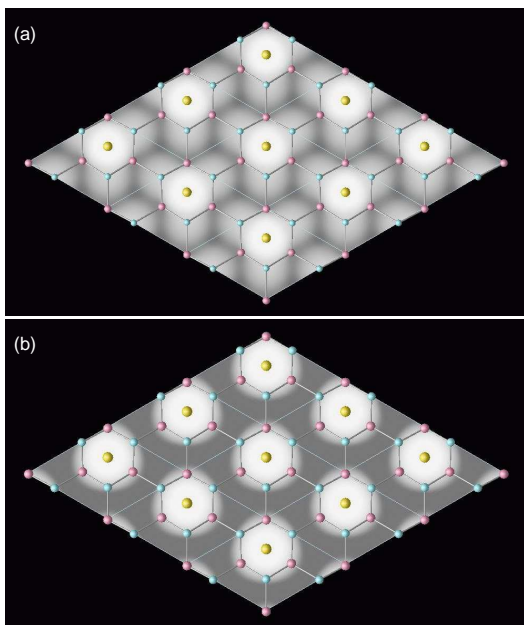


Figure 3: STM image (7×5)nm of triangular structural units on the surface ($V = -0.6$ eV). Gray scale extend over 1 \AA . Inset shows the simulated STM images from DFT calculations.

In this model the Au atoms preferably adsorb on every third hcp threefold hollow site of the Ga lattice. We believe that the Au atoms rather binds to Ga as there exists a number of compounds between Au and Ga, but none between gold and As. The adsorption energy per Au atom on the ideally As-terminated, relaxed GaAs(111)B surface is 2.96 eV for this structure, slightly smaller than the calculated cohesive energy of bulk gold, $E_{coh}^{Au} = 3.01$ eV. However, such a wetting layer may still be thermodynamically stable in equilibrium with Au nanoparticles, since entropic contributions to the free energy favor spreadings out of the gold onto the substrate. By simulating STM images of the clean GaAs(111)B surface, we also verified that the presence of Au is essential for obtaining the correct image. Various assumed structures of the clean surface yield STM images markedly different from the experimentally observed ones. This gives evidence that the restructuring of the surface is really due to the presence of Au atoms, and not just a result of processing conditions.

4 Summary

We have studied the GaAs(111)B surface with Au deposited either homogeneously or as nanoparticles, and found the presence of Au in either form to give rise to a $(\sqrt{3} \times \sqrt{3})$ Au-induced surface reconstruction. In the structural model supported by our DFT calculations for an Au coverage of $1/3$ ML, Au atoms are adsorbed at every third threefold hollow hcp site of the Ga lattice. The proposed structural model is in agreement with experimental data from low-energy electron diffraction and STM. In this model Au atoms are adsorbed at every third threefold hollow hcp site of the Ga lattice on the GaAs(111)B surface at smaller amounts of Au. As the amount of Au gets larger adsorption is also seen on the other similar sites in between the adsorption sites for the first Au atoms.

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