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Preferential adsorption of gallium on GaAs(111)B surfaces during the initial growth of Au-assisted GaAs nanowires

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ABSTRACT

The mechanism of the preferential adsorption of Ga on GaAs(111)B surfaces during the initial growth of Au-assisted GaAs nanowires is studied by using first-principles calculations within density functional theory. The calculated results show that Au preadsorption on GaAs(111)B surface significantly enhances the stability of the Ga adatom in comparison with the adsorption of Ga on clean GaAs(111)B surface. The stabilization of the Ga adatom is due to charge transfers from the Ga 4*p* and 4*s* states to the Au 6*s* and As 4*p* states. The number of Ga adatoms stabilized on GaAs(111)B surfaces depends on the size of surface Au cluster. The reason is that Au acted as an electron acceptor on GaAs(111)B surface assists the charge transfer of Ga adatoms for filling the partial unoccupied bands of GaAs(111)B surface. Our results are helpful to understand the growth of Au-assisted GaAs nanowires.

1. Introduction

Semiconductor nanowires (NWs) are currently receiving much attention due to their potential applications in nanoscale electronic and photonic devices [1,2], biosensors, and chemical sensors [3]. These nanowires, such as Si and GaAs, are generally grown by the vapor–liquid–solid (VLS) mechanism [4] using the gold (Au) nanoparticles as the catalyst. The Au nanoparticle offers the flexibility to control the growth of single-crystalline nanowires in terms of its location, size, and shape [5–7]. Moreover, Au catalyst can mediate the growth of the axial and radial nanowire heterostructures by varying the vapor chemistry [8,9]. Therefore, the understanding of nanowire growth mechanism, in particular the role and behavior of Au catalyst during the growth period, is of great importance for the development of reliable nanofabrication techniques.

For the growth of Au-assisted nanowires, a key issue is that the region with Au catalysts grows much faster than the surrounding surface. In the typical VLS growth, the reason of the rapid growth of nanowires is assumed the adsorption of vapor atoms on the droplet surface and their transfer to the crystal phase at Au/substrate interface [4]. Recently, Wacaser et al. [10] improved the VLS model and clarified why the nanowires grow faster than the surrounding surfaces. They concluded that the growth of nanowires is based on preferential nucleation at the interface between a mediating material called the collector and a crystalline solid. All these theoretical models are based on a precondition that vapor atoms are more easily adsorbed at the surfaces with Au nanoparticles than the surfaces without Au. Thus, one asks easily why the adsorption of vapor atoms on the surfaces with Au is more favorable than the surfaces without Au catalyst? Although the importance of the issue, works on it are still lacking. A possible reason is that the previous theoretical models based on a macroscopic layer are thus difficult to insight into the adsorption process of vapor atoms in atomic scales.

GaAs nanowires are one of the most extensively investigated semiconductor nano-materials because of their importance in the industry of microelectronic and optoelectronic devices. The growth of GaAs nanowires has been demonstrated by various growth techniques on GaAs(111)B substrate, such as molecular beam epitaxy (MBE) [7,11], chemical beam epitaxy (CBE) [12], and metal organic vapor phase epitaxy (MOVPE) [13]. In the growth process, vapor Ga atoms are considered to fall firstly on the surface of Au droplets, then diffuse into the Au/substrate interface, and finally incorporate into solid wire. However, we must answer the question why the vapor Ga atoms prefer to adsorb on the surface with the pre-deposition Au during the growth of GaAs nanowires. It is of great importance to understand the stabilization mechanism of Ga adatoms on GaAs(111)B surfaces with the Au catalyst.

In this work, we present density functional (DFT) calculations to investigate the stabilization mechanism of Ga on Au-preadsorbed GaAs(111)B surfaces. In order to answer why the adsorption of Ga on the surfaces with Au particles is more favorable than that of the surface without Au, we make a comparative study of Ga adsorption on GaAs(111)B surfaces with and without Au. Our DFT

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results demonstrate the effect of Au catalyst on the stability of Ga on GaAs(111)B surfaces. The results from our work give valuable information on the initial growth of Au-assisted GaAs nanowires.

2. Computational methods

The total energy calculations of density-functional theory (DFT) are carried out using the VIENNA *ab initio* simulation package [14] with the projector-augmented-wave (PAW) pseudopotentials method [15]. A plane-wave basis set with energy cutoff of 320 eV and the generalized-gradient approximation (GGA) of Perdew and Wang [16] for the exchange-correlation energy are employed. Spin-polarized calculations are performed for the entire adsorption systems, but there is no substantial effect on the results. The Ga($3d, 4s, 4p$), As($4s, 4p$), and Au($5d, 6s$) electrons are considered as valence states, while the remaining electrons are kept frozen as core states.

We apply the theoretical lattice parameters of zinc-blende GaAs to construct the surface models. The calculated lattice parameter of zinc-blende GaAs is 5.667 Å, consistent with the corresponding experimental value [17] and the other theoretical values [18]. The GaAs(111)B surface is modeled using a slab geometry consisting of six Ga–As bilayers and a vacuum layer of 12.5 Å separating the slab. The dangling bonds at the bottom layer are satutated with pseudohydrogens of a fractional charge of $1.25e$ in order to prevent unphysical charge transfer between the top and bottom slab surfaces [19]. The surface Brillouin-zone sampling is performed with Gamma centered grid of 6×6 for the (2×2) unit cell, whereas for the (3×3) surfaces, a mesh of 4×4 points is employed. For geometry optimization, all atoms except for the bottommost Ga–As bilayer and pseudohydrogen atoms have been relaxed until the force acting on each atom is less than 0.01 eV/Å.

In order to discuss the relative stability among various surface reconstructions, we calculate the surface formation energy as a function of the chemical potentials of As. For a surface in thermodynamic equilibrium, the surface formation energy γ_s can be obtained by [20]

$$\gamma_s = E_{\text{tot}} - E_{\text{ref}} - \Delta n_{\text{Ga}}\mu_{\text{Ga}} - \Delta n_{\text{As}}\mu_{\text{As}} \tag{1}$$

where E_{tot} and E_{ref} are the total energy of the given surface configuration and reference system, and Δn_{Ga} and Δn_{As} are the excess (or deficit) of Ga and As atoms with respect to reference, respectively. μ_{Ga} and μ_{As} are the chemical potentials of Ga and As, respectively. We can assume the condition that the surfaces under study are in equilibrium with the bulk substrate, so that the allowable value for μ_{As} in this study is $\mu_{\text{As(bulk)}} - \Delta H_f < \mu_{\text{As}} < \mu_{\text{As(bulk)}}$. The upper (lower) limit corresponds to As-rich (Ga-rich) conditions and ΔH_f is the heat of formation of zinc-blende GaAs. The computed heat of formation is 0.749 eV, in good agreement with experimental value (0.736 eV) [17].

The adsorption energies of Ga adatoms at different adsorption sites are determined by the following formula

$$E_{\text{ad}} = (E_{\text{tot}} - E_{\text{ref}} - \Delta n_{\text{Ga}} E_{\text{Ga}})/\Delta n_{\text{Ga}} \tag{2}$$

where Δn_{Ga} is the number of Ga adatoms in the surface unit cell, E_{Ga} is the total energy of Ga atom, and E_{tot} and E_{ref} are the total energies of the adsorbed substrate with and without the Ga adatom on the surfaces, respectively.

To analyze the charge transfer among surface atoms due to their bonding interactions, it is useful to consider the charge density difference. The charge density difference $\Delta\rho(\mathbf{r})$ between Au/GaAs(111)B system and its constituents is obtained as [21]

$$\Delta\rho(\mathbf{r}) = \rho_{\text{Au/GaAs}}(\mathbf{r}) - \left[\rho_{\text{Au}}(\mathbf{r}) + \rho_{\text{GaAs}}(\mathbf{r})\right] \tag{3}$$

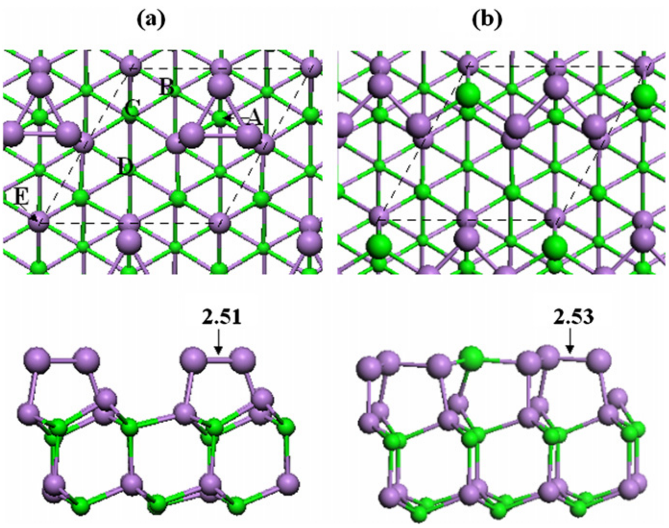

Fig. 1. Top and side views of As trimer adsorbed GaAs(111)B-(2×2) surfaces (a) before and (b) after Ga adsorption. Adsorption sites of Ga adatom are indicated by A, B, C, D, and E. Green and purple spheres represent Ga and As atoms, respectively. The numbers show the Ga–As bond length (in Å). The unit cell is enclosed by dash lines.

where $\rho_{\text{Au/GaAs}}(\mathbf{r})$ is total charge density of Au/GaAs(111)B system, and the latter two components represent the charge density of preadsorbed Au and bare GaAs(111)B substrate in the corresponding Au/GaAs(111)B system, respectively. For Ga adsorption on Au/GaAs(111)B surfaces, the charge density difference $\Delta\rho(\mathbf{r})$ is thus described as

$$\Delta\rho(\mathbf{r}) = \rho_{\text{Ga/Au/GaAs}}(\mathbf{r}) - \left[\rho_{\text{Ga}}(\mathbf{r}) + \rho_{\text{Au}}(\mathbf{r}) + \rho_{\text{GaAs}}(\mathbf{r})\right] \tag{4}$$

where $\rho_{\text{Ga/Au/GaAs}}(\mathbf{r})$ is charge density of Ga-adsorbed Au/GaAs(111)B system, and other three components are the charge density of the Ga adatom, preadsorbed Au, and bare GaAs(111)B substrate in the configuration corresponding to that the relaxed Ga-adsorbed Au/GaAs(111)B system, respectively.

3. Results and discussion

3.1. Ga adsorption on GaAs(111)B surfaces

We first address Ga adsorption on GaAs(111)B surface without Au catalyst. It is useful to provide a reference for subsequent calculations on Ga adsorption on GaAs(111) surfaces with the preadsorbed Au. For the GaAs(111)B surface in the thermodynamics equilibrium, it is not a ideal surface due to high density of unpaired dangling bonds. A large numbers of experimental and theoretical studies have found that GaAs(111)B surfaces exhibit several surface reconstructions such as (2×2), $(\sqrt{19} \times \sqrt{19})R23.4°$, and (1×1) surfaces [22–26]. The atomic resolution scanning tunneling microscopy (STM) observations have shown that the (2×2) reconstruction is found during and after molecular beam epitaxy (MBE) growth under the As-rich condition, and a transition to the $(\sqrt{19} \times \sqrt{19})R23.4°$ surface occurs above 580 °C [26]. Generally, the growth temperature of GaAs nanowires is lower than 580 °C, thus the (2×2) structure is widely accepted as the reconstruction of GaAs(111)B surface under the growth condition. This structure consists of an adsorbed layer of As-timers bonded to a complete As layer with a surface As coverage of 1.75 monolayer, as shown in Fig. 1a. In our investigation on Ga adsorption on GaAs(111)B, we put the Ga adatom on various possible adsorption sites of GaAs(111)B-(2×2) surface, as shown in Fig. 1. Then, the stable structure can be obtained by the fully structural relaxations.