Theoretical Scanning Tunneling Microscopy Images of the Ga-rich GaAs(001)-(4×2) Surface(STM-GaAs)

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Theoretical Scanning Tunneling Microscopy Images of the Ga-rich GaAs(001)-(4×2) Surface

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Total energy calculations have been performed for the Ga-rich GaAs(001)-(4×2) surface using first-principles plane-wave pseudopotential techniques. There are two distinctly different structural models proposed for the Ga-rich (4×2) surface. The Ga-model proposed by Biegelsen *et al.* consists of two Ga dimers on the top layer and another Ga dimer at the third layer, whereas the As-model by Skala *et al.* consists of two As dimers on the top layer and two Ga dimers in the second layer. Calculated results show that the As-model can be safely ruled out since the As-model is energetically unstable with respect to the Ga-model. The Ga-model, on the other hand, has a problem that there is apparent discrepancy between the STM image and the surface geometry of the Ga-model. It is found that the local density of states near the Fermi level are significantly affected by the existence of the third layer Ga dimers and that the Ga-dimer atoms on the top layer asymmetrically contribute to the STM image. The calculated charge distributions for the Ga-model can explain the observed STM image quite well.

KEYWORDS: GaAs(001) surface, STM image, LDF calculation

1. Introduction

The GaAs(001) surface exhibits a sequence of reconstructions dependent on surface stoichiometry, starting with the most As-rich c(4×4) phase, through the (2×4), (2×6), (4×6), ending with the Ga-stabilized (4×2) phase. Among them, the As-rich (2×4) reconstruction was extensively investigated in the past since molecular beam epitaxy (MBE) growth of GaAs(001) usually begins with this surface under As-rich growth conditions. Little attention has been directed toward the Ga-rich surface reconstructions such as the (4×2) and (4×6) phases, which is mainly due to the difficulty in preparing these Ga-rich surfaces using the conventional MBE. The study on the structures of the Ga-rich surfaces is of increasing importance in order to comprehensively understand the growth mechanism of the GaAs(001) surface, since the growing front must be terminated alternately with the As-rich (2×4) and the Ga-rich (4×2) surfaces.

Scanning tunneling microscopy (STM) has been utilized for the study of the reconstruction structures of the GaAs(001) surfaces. It is generally accepted from STM observations that the As-rich (2×4) surface consists of As dimers and As-dimer vacancies on the top surface layer [1-5]. As for the Ga-rich (4×2) surface, there are two distinctly different models: one with Ga dimers and the other with As dimers at the outermost surface layer. Biegelsen *et al.* [2] obtained the first STM images of the MBE grown (4×2) phase and proposed that the (4×2) surface consists of two Ga dimers and two Ga-dimer vacancies on the top layer and another Ga dimer at the third layer as shown in Fig. 1(a), which is referred to as Ga-model hereafter. Skala *et al.* [6] proposed a radically different model (referred to as As-model), which has two As dimers in the top layer and two Ga dimers in the second layer in an unit cell, as shown in Fig. 1(b). The faint features assigned to the Ga dimers in their STM image are positioned in between the brighter features identified as the As atoms along the [-110] direction. They claim that their STM image cannot be explained readily by the Ga-model since Ga and As atoms should line up in the Ga-model. Xue *et al.* [7] carried out the first successful *in situ* STM investigation of the Ga-rich (4×2) and (4×6) phases by utilizing migration enhanced epitaxy (MEE). Although their STM image of the (4×2) phase is basically the same as that obtained by Skala *et al.*, they supported the Ga-model instead of the As-model. They claimed that there are ample justification for the Ga-model in interpreting their STM images, for example, the surface preparation process employed favors the Ga-rich surface, not the As-rich surface. They further proposed that the (4×6) phase accommodates the periodic array of Ga clusters at the (4×6) unit corner on top of the (4×2) phase.

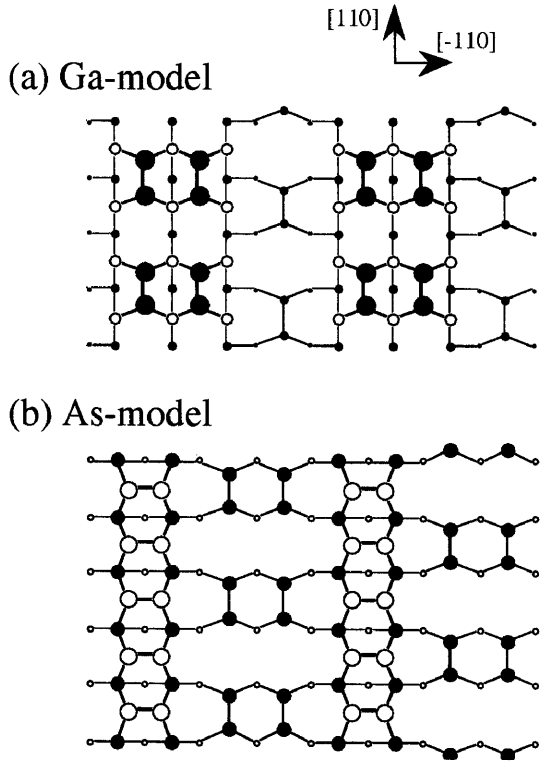

Figure 1. Schematic atomic structures of the Ga-rich GaAs(001)-(4×2) surface: (a) the Ga-model proposed by Biegelsen *et al.* [2] and (b) the As-model proposed by Skala *et al.* [6]. Filled and open circles denote Ga and As atoms, respectively.

If STM simply map the surface atomic geometry, the STM image of the (4×2) surface could not be explained in terms of the Ga-model, as pointed out by Skala *et al.* [6]. However, STM maps not merely the atomic geometry of the surface but the local density of states near the Fermi level. The correct interpretation of the STM image requires the knowledge of surface local density of states near the Fermi level. In order to resolve the discrepancy in the Ga- and As-models, we have performed a first-principles total-energy calculation in this paper. It is found that the calculated local density of states for the Ga-model can explain the observed STM image quite well.

2. Calculation methods

We perform total-energy calculations by using the local density functional (LDF) approach. The total energy functional is minimized with respect to both the plane-wave coefficients of the occupied orbitals and the ionic degrees of freedom by using the conjugate-gradient technique [8]. In computing the total energy, we use the Wigner form of the exchange-correlation energy and *ab initio* norm-conserving pseudopotentials of the Kleinman-Bylander type [9]. The pseudo wavefunctions are expanded in terms of a plane-wave basis set corresponding to a kinetic-energy cutoff of 7.29 Ry. Four special k points are employed to sample the primitive surface Brillouin zone. The surface is modeled using supercells containing six layers of GaAs and one layer of hypothetical hydrogen used for the surface termination [10]. It is found that an energy cutoff of 7.29 Ry and a supercell containing six atomic layers are sufficient to achieve the convergence of energy differences within 0.1 eV.

3. Results and discussions

The formation energies of the Ga-model and the As-model for the Ga-rich GaAs(001)-(4×2) surface are plotted in Fig. 2 as a function of the As chemical potential [4]. In order to determine the upper limit for the As chemical potential which stabilizes the Ga-rich surfaces, two stable As-rich phases are also considered; the (2×4) phase with two As dimers on the top layer and another As dimer at the third layer, which is a mirror image of the (4×2) Ga-model, and the c(4×4) phase with three As ad-dimers on top of a complete As monolayer. The As-model for the (4×2) surface is found to be energetically unstable with respect to the Ga-model for almost all the allowed range of the As chemical potential. Thus, the As-model can be safely ruled out. The (4×2) Ga-model is stable in the range $-0.74 \leq \mu_{As} \leq -0.54$ eV. When μ_{As} exceeds −0.54 eV, the Ga-model surface becomes unstable with respect to the As-rich (2×4) surface.

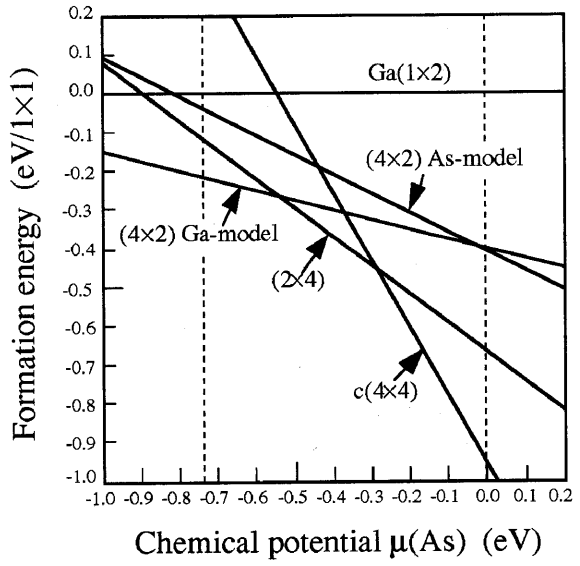

Figure 2. Formation energy per (1×1) unit cell for GaAs(001) surfaces as a function of the As chemical potential. The vertical dashed lines indicate the thermodynamically allowed range of the As chemical potential.

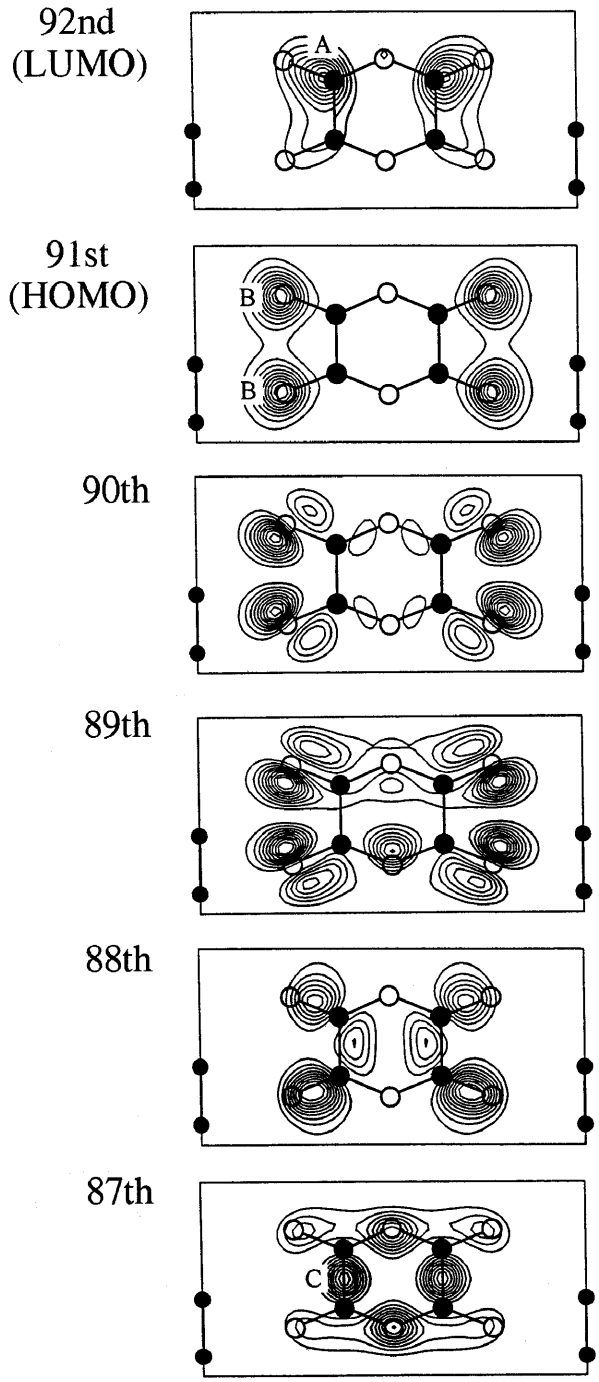

Figure 3. Calculated charge density from the (4×2) Ga-model structure at 0.9 A above the top layer Ga dimer position for the 92nd (LUMO), 91st (HOMO), 90th, 89th, 88th, and 87th bands.

The calculated level charge densities for the (4×2) Ga-model structure are shown in Fig. 3. The 91st band is the HOMO (highest occupied molecular orbital) band and has a charge localized at the As atoms in the second layer (peak B in the figure). The contribution from the Ga dimer on the top layer becomes noticeable only at the deep 87th band, whose charge distribution peaks at the middle of the Ga dimer (peak C in the figure). As the energy level increases from the 87th band to the 91st band, the contribution from the Ga dimer gradually disappears and the charge derived from the As atoms becomes more dominant. The charge distributions of the 90th, 89th, and 88th bands basically overlap with that of the 91st HOMO band. The 92nd band is the LUMO (lowest unoccupied molecular orbital) band derived from the Ga dangling bonds and should be basically empty for the ideal semiconducting (4×2) surface.

By comparing the calculated surface energy levels and the filled-state STM imaging condition at about −2 V [6,7], it is determined that all local density of states between the 87th and 92nd bands contribute to the tunneling current to form the STM image of the (4×2) surface. The 91st HOMO band makes the most significant contribution to the tunneling current because of the lower potential barrier for tunneling, compared with the 90th, 89th, 88th, and 87th bands. Thus, the As atoms in the second layer are imaged as individual brighter protrusions (peak B), whereas the Ga dimer on the top layer is observed as single faint hump (peak C) instead of pair-like feature.

Since there are significant amount of surface defects such as adsorbates and vacancies on the MEE grown (4×2) surface [7], the 92nd LUMO band is partially filled due to the charge transfer from these surface defects and contributes to the tunneling current. The charge distribution of the 92nd band is localized at one of the Ga dangling bond positions (peak A in Fig. 3). The charge localization at the A site is due to the existence of the Ga dimer at the third layer, which is explained as follows [11]. Since the Ga-model satisfies the electron counting rule, each Ga-dimer atom is positively charged and each threefold-coordinated As atom is negatively charged. Fig. 4 presents the calculated total charge density of the Ga-model structure. The total charge density at the D2 position close to the third-layer Ga dimer is higher than that at the D1 position away from the Ga dimer. This is because the positively charged Ga dimer at the third layer attracts electrons. The higher total charge density at the D2 position repels the electron of the 92nd LUMO state and localizes it at the A position. Thus, the Ga-dimer atoms on the top layer asymmetrically contribute to the STM image.

The integrated local density of states from the 87th band to the 92nd band, which is proportional to the tunneling current density, is presented in Fig. 5(a). It is clearly shown that the local density of states (the STM image) does not simply correspond to the atomic geometry of the Ga-model. The extent of the LUMO band contribution to the filled-state STM image depends on the amount of the charge transfer to the Ga dimers. Since the calculated density of states shown in Fig. 5(a) is the mapping of the charge distribution at only 0.9 A away from the surface while the STM image reflects the charge distribution approximately 10 A away, peaks A and B may shift away from the atomic position to some extent. Realizing these effects, the STM image reported [6,7] can be explained well in terms of the (4×2) Ga-model.

The STM image of the MEE grown (4×6) phase is uniquely characterized by the array of large bright oval protrusions regularly located at each corner of the (4×6) unit cell [7]. Xue *et al.* assigned the oval features to Ga cluster adsorbates regularly arranged on the (4×2) Ga-model surface, and also assigned a pair of bright rows running in the [110] direction to the first layer Ga dimers. Since there is a large amount of charge transfer from the Ga clusters to the (4×2) subunits, high LUMO states of the (4×2) Ga-model surface are expected to be filled and contribute to the STM image. Fig. 5(b) presents the integrated local density of states from the 87th HOMO band to the 96th LUMO band. The charge distribution is shown to be highly localized at the top-layer Ga dimers, which is in good agreement with the STM image [7]. Consequently, the differences of the (4×2) and (4×6) STM images can be interpreted in terms of the charge transfer among the second-layer As atoms, top-layer Ga dimers, and Ga adsorbates on the (4×2) Ga-model surface.

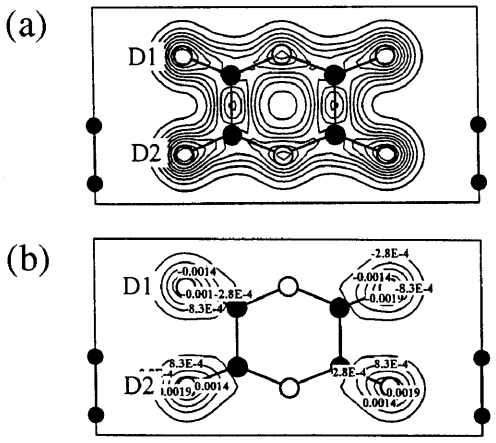

Figure 4. (a) Calculated total charge density for the (4×2) Ga-model. (b) The difference of the charge density between the upper and lower halves of the (4×2) unit cell. The upper half has a negative value while the lower has a positive value.

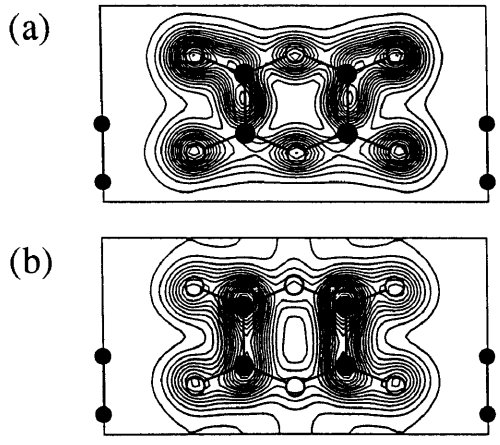

Figure 5. (a) Integrated local density of states from the 87th band to the 92nd band of the (4×2) Ga-model. (b) Integrated local density of states from the 87th band to 96th band.

4. Conclusions

We have performed total energy calculations for the Ga-rich GaAs(001)-(4×2) surface using first-principles plane-

wave pseudopotential techniques. Calculated results show that the As-model can be safely ruled out since the As-model is energetically unstable with respect to the Ga-model. The apparent discrepancy between the STM image and the surface geometry of the Ga-model is well resolved. It is found for the Ga-model that the local density of states near the Fermi level are significantly affected by the existence of the third layer Ga dimers and that the Ga-dimer atoms on the top layer asymmetrically contribute to the STM image. The calculated charge distributions for the Ga-model can explain the observed STM image quite well.

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11) It is noted that the charge localization of the 92nd level is not due to the buckling of the Ga dimer on the top layer. Actually, the Ga dimer is not buckled even when the Ga-model surface has one excess electron per (4×2) unit cell which is transferred from the surface defects.