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A New Slab Model Approach for Electronic Structure Calculation of Polar Semiconductor Surface

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A new slab model approach is examined for the electronic structure calculation of a polar semiconductor surface. Our proposed slab model contains fractionally charged H atoms which completely terminate a noninteresting surface of the slab. We have studied in detail the electronic structure of the polar GaAs(001) surface in order to examine the reliability of our slab model. Calculation is performed by the *ab initio* pseudopotential method. We have found that our slab model can accurately describe a polar semiconductor surface. In addition, this model can greatly reduce the computational time.

[polar semiconductor surface, surface electronic structure, slab model, *ab initio* pseudopotential method, local density functional formalism, fractionally charged H atom, covalent bond, dangling bond]

Polar semiconductor surfaces, especially the GaAs(001) surface, are technologically important. This is because the polar GaAs(001) surface can be conveniently prepared by molecular beam epitaxy (MBE). The GaAs(001) surface has been intensively studied by various experimental techniques, and its electronic and structural properties are gradually being clarified.[1-3] As for theoretical studies, a number of first principle calculations have been reported.[4-6] However, the theoretical studies of the polar semiconductor surface contain, in principle, many more difficulties than those of the nonpolar surface.

The use of a slab model has been the popular method to calculate the surface electronic structure, even though the surface Green function approach was introduced recently.[7] When we used a slab model to study the polar surface, several problems emerged. One problem was a charge transfer from one surface of the slab to the other surface. This charge transfer is crucial because the relative position and dispersion of the surface state bands are changed by the effect of electrostatic potential resulting from the charge transfer. This charge transfer occurs because the surface states of cation dangling bonds are located above those of anion dangling bonds. Another problem was that the two surface states interacted with each other through the slab. These two surface states form bonding and antibonding states and split each other by the interaction. In order to decouple the two surface states, a thick slab calculation was necessary. This calculation required an extremely long computational time.

As for the first problem mentioned above, some attempts at solution have been carried out. For example, Kaxiras *et al.* used the skillful slab model which contained fictitious Ga atoms to calculate the As-terminated surface.[8] In their model, the two central atomic layers of slab contained the same kind of atoms, and these layers were modeled by fractionally charged atoms which were properly chosen to prevent the charge transfer. As a result, both sides of the slab were terminated by the As layers. Their model had inversion symmetry; thus, there were no artificial fields in the vacuum region. Their model accurately described the As-terminated surface. However, it could not decouple the two surface states on either side of the slab. Therefore, the thick slab calculation was inevitable. Actually, they carried out a 16-atomic-layer slab calculation.

In this paper, we will investigate a new slab

model which avoids the simultaneous charge transfer and interaction through the slab. In order to justify our slab model, we will calculate the electronic and structural properties of the GaAs(001) surface.

Our investigated model is based on a simple feature of a covalent bond. Covalent bonds are characterized by the bond charge between two neighboring atoms. The III–V semiconductors are described extremely well by the covalent bond features. In GaAs, 0.75 electrons from Ga atoms and 1.25 electrons from As atoms combine and form covalent bonds between each other. Dangling bonds contain 0.75 electrons and 1.25 electrons on a Ga-terminated ideal surface and an As-terminated ideal surface, respectively. Naturally, when the fractional 0.75 charged atoms are adsorbed to the As dangling bond, perfect covalent bonds are formed. Consequently, all of the dangling bonds at the surface disappear. For the case of Ga dangling bonds, 1.25 charged atoms are required to achieve perfect covalent bonds.

On the basis of the above discussion on dangling bonds, it is natural that we propose a slab model in which irrelevant surface atoms are terminated by fractionally charged H atoms, which are shown in Figs. 1(a) and 1(b), in order to calculate the polar semiconductor surface. Figures 1(a) and 1(b) represent the slab model for describing the As-terminated GaAs(001) surface, and illustrate 5- and 8-atomic-layer configurations, respectively. As shown in Figs. 1(a) and 1(b), the dangling bonds of no interest form perfect covalent bonds with the fractionally charged H atoms. Because of the perfect covalent bonds at the terminated surface, the charge transfer from one side of the slab to the other side does not occur. In addition, the terminated surface states energetically leave the band gap region due to the formation of the covalent bonds. As a result, only the surface state bands of interest remain in the band gap. Here, it is assumed that we can correctly calculate the electronic structure of a polar semiconductor surface using a rather thin slab model with fractionally charged H atoms. Additionally, the computational time is assumed to be significantly reduced.

We calculated the electronic structure of the As-terminated ideal GaAs(001) surface by 11-, 8- and 5-atomic-layer slab models which contained fractionally charged H atoms to investigate the reliability of these slab models. As a comparison, we also calculated the electronic structure of the Kaxiras slab model which contains 12 atomic layers including 2 central fictitious Ga atomic layers. The calculations were performed by the norm-conserving pseudopotential method on the basis of the local density functional formalism (LDF).[9] In this calculation, the exchange-correlation potential is approximated by the Xα method where $\alpha=0.7$. The pseudo wavefunctions are described by the plane-wave basis set whose cut-off value is 7.3Ry in kinetic energy. In Fig.

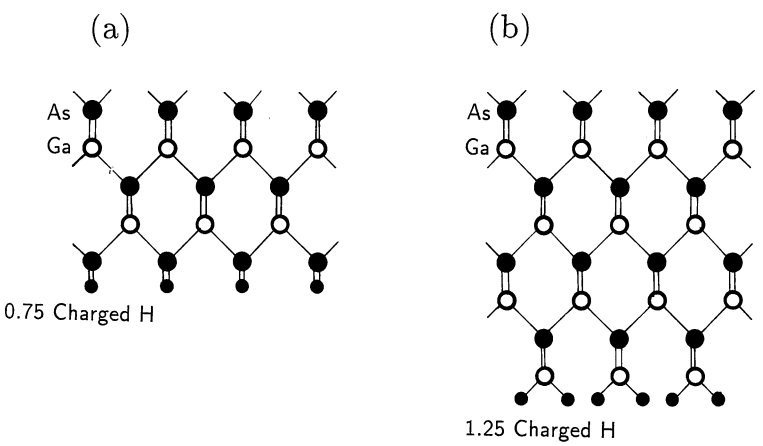

Fig. 1. Our proposed slab models: (a) 5-atomic-layer-thick slab model; (b) 8-atomic-layer-thick slab models.

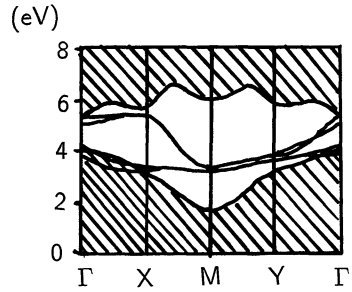

Fig. 2. Calculated energy band structures of As-terminated GaAs(001) (1 × 1) surface by using the Kaxiras slab model. This Kaxiras slab model contains 12 atomic layers, and two central layers are modeled by the 3.5 charged Ga atoms in order to prevent the charge transfer.

2, we give the energy band structure of the Kaxiras slab model. As seen in Fig. 2, there are four bands in the band gap region. These bands are doubly degenerated along the X-M-Y line; however, doubly degenerated bands split each other by the interaction through the slab. By using thinner models, these splits become too large to describe the GaAs(001) surface. Figures 3(a), 3(b), and 3(c) show the energy band structures of 11-, 8-, and 5-atomic layers slab models, respectively. As seen in Figs. 3(a), 3(b), and 3(c), there are only two surface state bands in the band gap region of each figure. The calculated energy band structures are very similar to the energy band structure of the Kaxiras model except that the surface state bands on the other side of the slab disappear due to the adsorption of the fictitious H atoms. In addition, the surface state bands depend only slightly upon the slab thickness. Thus our appoach can describe the polar GaAs(001) surface well by using much thinner slab models than the Kaxiras approach. As for the two surface state bands in the band gap region, the lower band (D) is not dispersive and the upper band (B) is dispersive along the y-direction (dangling bond direction). Figures 4(a) and 4(b) show the charge density contour plots of these two surface state bands at the M point in a surface Brillouin zone. The lower band D is designated as a dangling bond band whose charge density is perpendicular to the surface. This D band charge distribution results in a small overlap of the wave functions parallel to

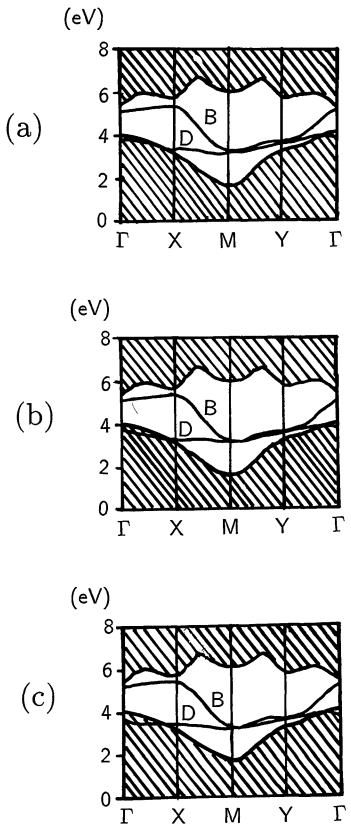

Fig. 3. Calculated energy band structures of As-terminated GaAs(001) (1 × 1) surface using various thicknesses of the slab model: (a) 11-atomic-layer-thick slab model; (b) 8-atomic-layer-thick slab model; (c) 5-atomic-layer-thick slab model.

the surface plane; consequently, it is not dispersive. On the other hand, the upper band B is designated as a bridge band whose charge density is along the surface dangling bond. The overlap of the B band wave functions along the surface dangling bond direction is rather large; as a result, the B band dispersion is large along the y-direction (dangling bond direction). This character does not depend on the thickness of the slab. In Table I, the z component of the Hellmann-Feynmann force of the surface As atoms is given. As seen in Table I, the Hellmann-Feynmann force depends very little on the thickness of the slab model. Actually, we can reproduce the atomic structures of the Ga-terminated GaAs(001) (2 × 1) surface reported by Qian *et al.* by the guide of the Hellmann-Feynmann force.[5] Our slab model does not take into account the artificial

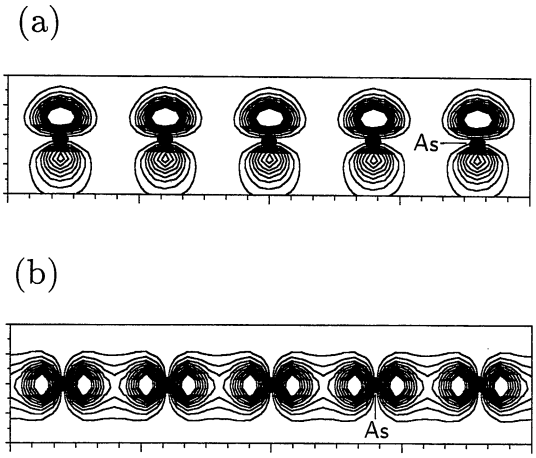

Fig. 4. Calculated band charge density contour plot of two surface state bands at point M: (a) D band charge density; (b) B band charge density.

Table I. The calculated Hellmann-Feynmann force for various thicknesses of slabs.

Thickness	Hellmann-Feynmann force
5 atomic layers	2.66×10^{-2} Ry/a.u.
8 atomic layers	2.71×10^{-2} Ry/a.u.
11 atomic layers	2.72×10^{-2} Ry/a.u.

field in the vacuum region; thus, we must check the effect of this artificial field by imposing the inversion symmetry as described in Fig. 5. We have found that both the energy band and the Hellmann-Feynmann force are unaffected by the artificial field. As discussed above, we can describe the surface electronic and structural properties correctly using a much thinner slab model as compared to the slab model which Kaxiras *et al.* employed. This is because GaAs is a typical covalent bond crystal, and its surface properties reflect a local feature around the surface.

In summary, we have studied a slab model in which a surface of no interest is terminated by fractionally charged H atoms in order to calculate the polar semiconductor surface. In addition, we have investigated the reliability of this model by calculating the polar GaAs(001) surface from the first principles. We have shown that both structural and electronic properties can be well described using a rather thin slab model, which contributes to a large computational time reduction.

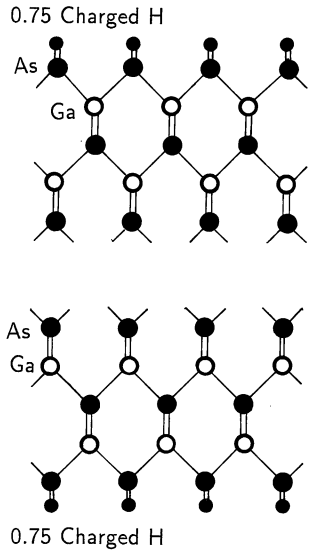

Fig. 5. Our investigated slab model with inversion symmetry.

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