Structural and Electronic Properties of Sulfur-Passivated InAs(001) (2×6) Surface *

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(Received 6 March 2011)

The structural and electronic properties of S-passivated InAs(001)-(2×6) and InAs(001)-(2×1) surfaces are studied by first-principles total-energy calculations. Based on the calculated adsorption energies and electronic properties, we propose that the reconstruction of a S-treated InAs(001) surface should be InAs(001)*–(2×6)S rather than InAs(001)-(2×1)S. This is similar to the adsorption behavior of S on a GaAs(001) surface. The Fermi level of an InAs(001)-(2×6)S surface exists above the conduction band minimum by 371 meV and the energy gap becomes 0.145 eV smaller than the clean surface. A strong surface electron accumulation layer is formed and downward band bending is increased, which is in good agreement with recent experiments.*

PACS: 68.35.−p, 71.15.Mb, 73.20.At, 73.61.Ey DOI:10.1088/0256-307X/28/8/086802

Indium arsenide is a typical direct transition and a narrow band-gap semiconductor with unique properties, such as Ⅲ alignment at heterojunctions, formation of a native charge accumulation layer, high electron mobility and high carrier densities.[1−4] As a result, it has been widely used to fabricate optoelectronic devices such as infrared lasers, photodiodes, infrared detectors and chemical and biological sensing equipment.[5−9] It is well known that device quality mainly depends on the surface properties of materials. In order to decrease the Schottky barrier and to improve device characteristics, Ⅲ–V compound semiconductor surfaces are often passivated by chalcogen atoms.[10,11] A number of experimental and theoretical investigations have shown that GaAs, GaP and InP can be effectively passivated by sulfur adsorption.[12−20] This makes the surface inert against oxidation in the atmosphere and the surface density states considerably decrease.

So far, a few studies have been performed on the sulfur passivation of narrow band-gap semiconductors such as InAs,[21,22] InN,[23] and InSb.[24,25] In particular, the passivation effects of sulfur adsorption on an InAs (001) surface have been extensively studied by several experimental scientists.[7,21,22,26−32] In those work, low-energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS) or high resolution electron energy loss spectroscopy (HREELS), with the treatment of $(NH_4)_2S_x$ or Na_2S solutions and sulfur exposure, has been employed to characterize the surface structure and atomic composition. It has been revealed that treatment with $(NH_4)_2S_x$ solution makes it possible to remove a natural oxide layer from the InAs surface, with a (2×1) reconstruction formed on the surface. The (2×1) structure is due to the formation of sulfur dimers bonded to In atoms and is oriented along the [110] direction. This is different from the structures of GaP(001)–(2×1) S and InP(001)–(2×1)S,[15,16,19,33] in which sulfur adsorbates prefer to occupy bridge sites without S-S dimers. Based on the results that the sulfur atoms are bonded to In and the sulfur coverage is almost 1 ML, Fukuda *et al.*[27] speculated that the InAs(2×1) model contains one missing sulfur dimer. Subsequently, the presence of missing sulfur dimers was confirmed by Lower *et al.*[29] Meanwhile, they pointed out that it is possible to observe a (2×6) reconstruction using high-energy electron diffraction (RHEED) when the S-InAs(001) samples are annealed *in situ* in the MBE chamber, similar to the GaAs (001)–(2×6)S structure obtained from scanning tunneling microscopy (STM) results.[34−37]

Another interesting research topic is the electronic property of the sulfur passivated InAs(001) surface, since it exhibits unusual and different surface states from other Ⅲ–V materials. However, whether the S-adsorbed InAs(001) surface achieves the electronic passivation effect or does not still remains controversial. Earlier research work suggested that the downward band bending of the adsorbed surface is decreased and the surface state density is lowered,[38,39] as compared with a clean surface. However, recent investigations have drawn incompatible conclusions.[7,29−31] It was found that a S-treated InAs(001) surface induces the increase in downward

*Supported by the Special Funds of the National Natural Science Foundation of China under Grant No 10947102, Foundation of Education Committees of Chongqing (No KJ090503), the Doctoral Foundation of Chongqing University of Posts and Telecommunications (A2008-64).

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band bending and the formation of an electron accumulation layer. Also, the surface Fermi level is located above the conduction band minimum (CBM), indicating that no electrical passivation is achieved. It is obvious that the structural and electronic properties of a S-treated InAs (001) surface demands further study in order to resolve these discrepancies.

To the best of our knowledge, no theoretical studies of the S passivation of an InAs (001) surface by first-principles calculations have been reported until now. In this study, we present an *abinitio* investigation of the structural and electronic properties of S adsorption on the InAs (001) surface. Based on the experimental results, we consider two structural models: InAs(001)–(2 × 1)S and InAs(001)–(2 × 6)S, as shown in Fig. 1. By comparing the adsorption energies between the structural models and the consistency of electronic properties with the experiments, we have determined an optimal structure. The electrical passivation effects for the S-treated InAs (001) surfaces have been elucidated.

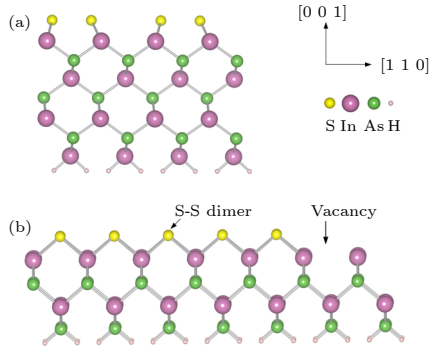

Fig. 1. (Color online) Side views of the InAs(001) surface adsorbed with sulfur. (a) InAs(001)–(2 × 1)S; (b) InAs(001)-(2 × 6)S.

We present first-principles calculations based on the density functional theory using the VASP code.[40,41] The ion-electron interaction is described by the projector augment wave (PAW) method.[42] The local density approximation (LDA) approach is used to deal with the exchange correlation energy.[43] The 4*d* electrons are included for the In atom. The electronic ground state is calculated with residuum minimization techniques. The geometric structure is optimized with the conjugate gradient technique. The wave functions are expanded in plane waves with a cutoff energy of 500 eV. Integration over an irreducible Brillouin zone is carried out using a Monkhorst–Pack grid of $5\times5\times1$. The unit supercell for the InAs(001)–(2×1) surface consists of 4 InAs layers (corresponding to 8 atomic layers) plus a vacuum region equivalent to 11 atomic layers in thickness. For the InAs(001)–$0(2\times6)$ surface, the unit supercell consists of 5 atomic layers and 10 atomic vacuum layers. The sulfur adatoms are adsorbed on only one surface of the slab. In our simulation, to avoid charge transfer between the two sides of the slab, hydrogen-like pseudoatoms with 0.75 (1.25) charges are used to saturate the surface As (In) dangling bonds at the bottom of slab. The optimized lattice constant for bulk InAs is 6.031 Å, consistent with the experimental value of 6.058 Å.[44]

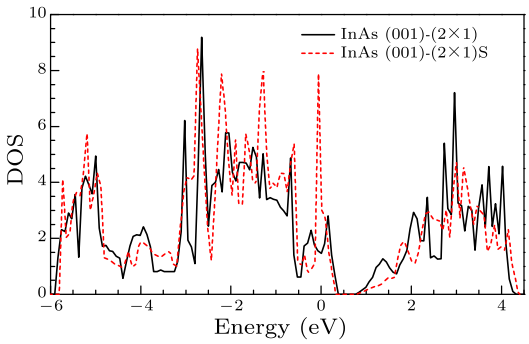

Fig. 2. (Color online) DOS of the InAs(001)-(2 × 1) surface with and without sulfur adsorption.

To obtain the optimized structure of sulfur adsorption on InAs(001)–(2 × 1) surface, we consider several possible adsorption sites: the bridge (HB), pedestal (HH), valley bridge (T3, on top of a third-layer atom), cave (T4, on top of a fourth-layer atom) sites and the surface substitute site, as illustrated in Ref. [33]. These structures have been optimized and the adsorption energies have been calculated. The adsorption energy is defined by the formula shown in Ref. [45]. The results show that the sulfur atoms prefer to occupy substitution sites. The most stable InAs(001)–(2 × 1)S structure consists of a S-S dimer bonded to In atoms, in good agreement with the experimental results.[26–28,31] The InAs(001)–(2 × 1)S structure is shown to be different from the structures of GaP(001)–(2 × 1)S and InP(001)–(2 × 1)S.[15,16,19,33] For the optimized configuration, the S-S dimer bond length is 3.201 Å, and the S-In bond length is 2.507 Å.

The structural model of the S-adsorbed InAs(001)–(2×6) surface, as suggested by the experiments,[29,30] is also studied for comparison. This structure is similar to the S-adsorbed GaAs(001)–(2×6) surface.[34–37] It is composed of five S-S dimers bonded to the second layer of the In atoms, with one missing sulfur dimer along the [110] direction to obey the electron counting rules. The geometrical structure of the S-adsorbed InAs(001)–(2 × 6) structure is optimized. The results show that the bond length is 4.05 Å for the center sulfur dimer and 2.10 Å for the other four sulfur dimers, respectively. The rumpling amplitude of the five sulfur dimers is 0.28 Å. To determine the energetically favorable structures, the adsorption energies of sulfur adsorption on the InAs(001)–(2 × 1) and InAs(001)–(2×6) surfaces are compared. We find that the InAs(001)–(2 × 6)S structure is more stable, with an adsorption energy difference of 0.325 eV.

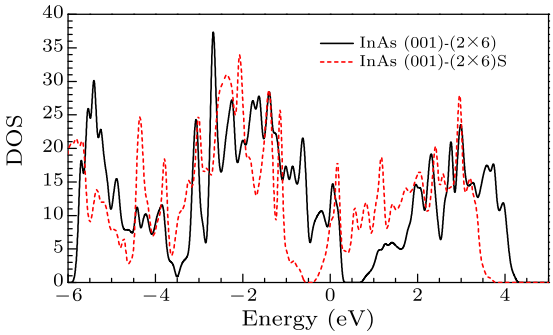

Fig. 3. (Color online) DOS of InAs(001)–(2×6) with and without sulfur adsorption.

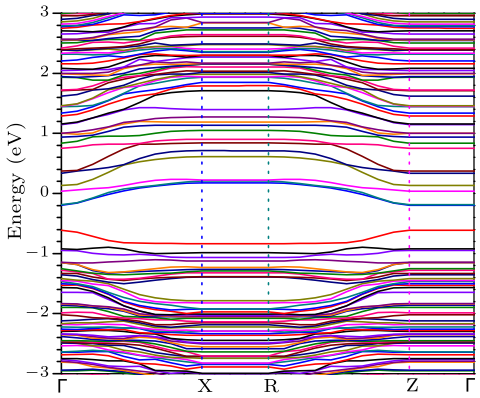

Fig. 4. (Color online) Energy-band structure of InAs(001)–(2 × 6)S.

In order to explain the electronic passivation effect of sulfur adsorption on InAs(001) surface, we perform density of states (DOS) analysis for InAs(001)–(2×6)S and InAs(001)–(2×1)S structures. Figure 2 shows the total DOS distribution of the InAs(001)-(2 × 1) surface with and without sulfur adsorption. The Fermi level (E_f) of the considered system is set to 0 eV. We find that the density of states for the S-treated surface at E_f position is much larger than clean InAs(001)–(2 × 1) surface. This probably results from the fact that sulfur has one excessive valence electron than arsenic, leading to the formation of surface states at E_f. However, the Fermi level is still located below the valence band maximum (VBM) and the surface electron accumulation layer is not formed, which is different from the experiments.[28,30,31]

In the case of InAs(001)–(2 × 6)S, the total DOS and band structure are presented in Figs. 3 and 4, respectively. It can be seen that both the VBM and the conduction band minimum (CBM) for the S-treated surface shift to a lower energy and the Fermi level is located above the CBM by 371 meV, which is smaller than the experimental value of 600 meV.[29–31] Figure 4 shows that the Fermi level arises from two almost degenerated bands. The energy gap of the InAs(001)–(2×6)S is determined to be 0.233 eV, which is 0.145 eV smaller than the clean surface. The LDOS of InAs(001)–(2 × 6)S is also presented in Fig. 5. We find that the VBM is mainly derived from the S p and As p orbitals while the CBM is ascribed to As p and In s orbitals. The surface state at E_f is composed of As-p, In-s, In-p and S-p orbitals. These electronic structures indicate that sulfur adsorption on the InAs(001)–(2 × 6) surface results in the formation of a strong surface electron accumulation layer and that downward band bending is increased. Thus, no electrical passivation is achieved for sulfur adsorption on the InAs(001)–(2 × 6) surface, agreeing well with recent experiments.[29,30] The electron accumulation on the S-adsorbed InAs(001)–(2 × 6) surface is beneficial to ohmic contact and can be used to fabricate high speed transistors.[46]

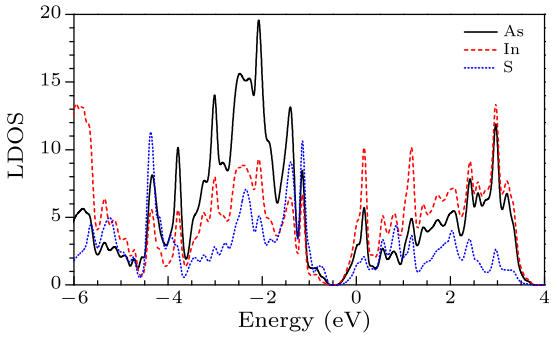

Fig. 5. (Color online) LDOS of InAs(001)–(2 × 6)S.

We propose that the structure of a S-treated InAs(001) surface observed experimentally should be InAs(001)–(2×6)S rather than InAs(001)–(2×1)S, not only because the (2×6) structure is more stable thermodynamically, but also because its electronic structure is consistent with experiments whereas the (2×1) structure exhibits very different electronic characteristics. The stability of the (2 × 6) structure may be explained by the electron counting model. In order to form the dimer and occupy the dangling bonds on the In-terminated InAs(001) surface, each dimer requires 11 electrons in total.[47] The S-S dimer has 12 valence electrons, resulting in one extra electron on the InAs(001)–(2 × 1)S surface. This indicates that this structure is not completely stable based on the electron counting model. However, for InAs(001)–(2 × 6)S configuration, five S-S dimers have five excess electrons, which exactly compensates for the four In dangling bonds due to a vacancy. Therefore, the InAs(001)–(2×6)S surface satisfies the electron counting rule. The InAs(001)–(2 × 1)S is observed in the LEED experiment probably due to the fact that the missing S dimers show no better ordering in the [110] direction when the samples are studied *ex situ* and the sensitivity of LEED is not achieved. For S adsorption on GaAs(001) surface, the (2×6) reconstruction is more stable based on the STM and RHEED observations.[34,48]

It is noted that the electronic property of InAs(001)–(2 × 6)S is different from that for GaAs(001)–(2 × 6)S despite their similar structures. The S-treated GaAs surface has good electrical passivation effects and decreases upwards band bending. This can be explained by the following reasons.[30] The surface states on the clean and S-treated GaAs(001) surfaces act as acceptor-like and donor-like, respectively, which tends to reduce the total surface charge density upon sulfur adsorption. For the clean and S-treated InAs surfaces, however, all the surface states act as donor-like, resulting in the formation of an electron accumulation layer on the surface.

In conclusion, we have investigated the structural and electronic properties of InAs(001)–(2 × 1) and InAs(001)–(2 × 6) surfaces adsorbed with sulfur by the DFT-LDA method. The optimal structure of InAs(001)–(2 × 6)S consists of five S-S dimers bonded to the second layer of In atoms, with one missing sulfur dimer. This structure is similar to that of GaAs(001)-(2×6)S. The calculated adsorption energy shows that the structure of InAs(001)–(2 × 6)S is 0.325 eV more stable than the InAs(001)–(2 × 1)S structure.

For the InAs(001)–(2 × 6)S surface structure, the Fermi level of the S-treated surface is above the CBM by 371 meV. This indicates that a strong surface electron accumulation layer is formed and that downward band bending is increased. Hence, no electrical passivation is achieved for sulfur adsorption on the InAs(001)–(2 × 6) surface. As we know, the DFT-LDA method generally underestimates the band-gap of semiconductors by about 30–40% because the excited states of the electrons are not generated correctly. Therefore, LDA+U is used to test our main results. We find that it does not influence our above discussion. The electronic structure of InAs(001)–(2×6)S is shown to be consistent with the experiments. For an InAs(001)–(2 × 1)S structure, the (2 × 1) structure does not exhibit any increase in the downward band bending observed experimentally. Considering this and that InAs(001)–(2 × 6)S is more stable thermodynamically, we hence propose that the reconstruction of the S-treated InAs(001) surface should be an InAs(001)–(2 × 6)S rather than a (2 × 1) structure. This is similar to the S adsorption on a GaAs(001) surface, in which it is also the (2 × 6) structure that is more stable.

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