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Effect of Surface Dangling Bonds and Molecular Passivation on Doped GaAs Nanowires

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We have investigated the effect of surface dangling bonds and molecular passivation on the doping of GaAs nanowires by first-principles calculations. Results show that the positively charged surface dangling bond on Ga atom is the most stable defect for both ultrathin and large size GaAs nanowires. It can form the trap centers of holes and then prefer to capture the holes from p-type doping. Thus it could obviously reduce the efficiency of the p-type doping. We also found that the NO₂ molecule is electronegative enough to capture the unpaired electrons of surface dangling bonds, which is an ideal passivation material for the Zn-doped GaAs nanowires.

Key words: GaAs nanowire, First-principles calculation, Surface dangling bonds

I. INTRODUCTION

III-V semiconductor nanowires have attracted much attention in recent years due to their possibility for building blocks of the nanoelectronic and nanophotonic devices such as solar cells, light-emitting diodes (LED) and lasers [1–3]. In the past few years, group-III-V semiconductor nanowires have been synthesized by molecular beam epitaxy (MBE) or metal-organic chemical vapor deposition (MOCVD) using metal-catalysts or self-catalysts vapor-liquid-solid (VLS) methods [4–7]. Gallium arsenide nanowires (GaAs NWs) is one of the most important candidates for nanodevices due to its direct gap, high carrier mobility and possible integration with silicon technology [8, 9]. Generally, GaAs NWs grow along [111] direction with zinc-blende (ZB) structures or [0001] direction with wurtzite (WZ) structures. And the WZ-structured GaAs NWs are more stable than ZB-structured GaAs NWs in the limit of small diameters. There are many experimental and theoretical studies on the growth and the electronic structures of GaAs NWs [10–13].

Potential applications of III-V semiconductor nanowires partially depended on their doping because doping is a basic way to provide free carries. Both n- and p-doped GaAs NWs have been synthesized [14, 15]. Zn and Si are usually used as p- and n-type dopant, respectively. And it is well known that, owing to the small diameter and the large surface-to-volume ratio, the quantum size effect and the surface effect

are two important effects in nanostructures. So the surface passivation has been introduced to nanowires to improve the intensity of photoluminescence [16]. Moreover, the surface dangling bonds also could result in the pinning of the Fermi level in semiconductor [17]. It could influence the doping efficiency [18–20]. However, there is no information on the effect of surface dangling bonds (SDBs) on the doping of GaAs NWs.

In this work, we study the results of first-principles calculations on the effect of surface dangling bonds and molecular passivation on the doping of GaAs NWs. The stability of various SDBs on both ZB- and WZ-structured GaAs NWs is studied. Then two different types of molecules, NH₃ and NO₂, adsorbed at the surface dangling bonds of GaAs NWs are also studied. The SDBs can obviously reduce the efficiency of p-type doping and the NO₂ molecule adsorbed at SDBs could eliminate the effect of SDBs. Our results give valuable insight into the realization of doped GaAs NWs.

II. MODELS

Our calculations in this work are performed by using first-principles plane-wave ultrasoft pseudopotential method as implemented in the cambridge sequential total energy package (CASTEP) based on the density functional theory (DFT) [21]. We adopt local-density approximation (LDA) to describe the exchange-correlation interaction and also assume Ga 3d electrons in valence [22]. The plane-wave energy cutoff is chosen as 330 eV and the the Brillouin zone (BZ) is sampled in the *k* space within Monkhorst-Pack scheme by 1×1×4 mesh points [23]. For geometry optimization, all atoms are fully relaxed until the force acting on each

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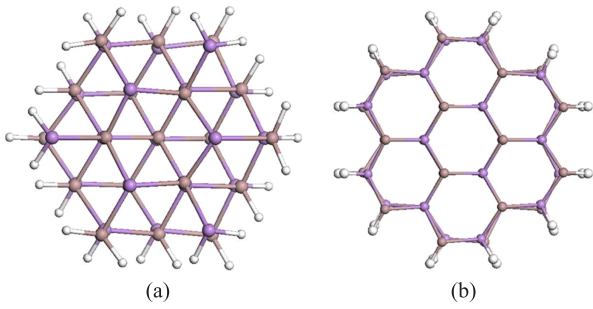


FIG. 1 Atomic structures of (a) ZB- and (b) WZ-structured GaAs NWs after being fully relaxed. The brown, purple and white spheres denote Ga, As, and H atoms, respectively.

other is less than $0.03 \text{ eV}/\text{\AA}$ and the energy between two ionic steps is less than 10^{-5} eV .

The nanowires are created from the optimized GaAs bulk structures. Our calculations are based on the models as shown in Fig.1. The diameters of ZB- and WZ-structured nanowires are 1.1 and 1.3 nm, respectively. Here we consider both ZB- and WZ-structured GaAs NWs in which SDBs are saturated by hydrogen (pseudo-H) atoms. ZB- and WZ-structured GaAs NWs oriented along [111] and [0001] direction, respectively. To avoid the interaction between adjacent nanowires, the distance between the neighboring nanowires is set to 10 \AA . Surface dangling bonds are created by removing H atoms from the surface of GaAs NWs. Three different types of SDBs, surface dangling bond on Ga atom (DB_{Ga}), surface dangling bond on As atom (DB_{As}), and surface dangling bonds on Ga-As pair (DB_{pair}), are obtained during the removing of H atom from corresponding surface atoms. The Zn dopant is introduced into nanowires by substituting one Ga atom.

III. RESULTS AND DISCUSSION

A. Effect of dangling bonds on the doping of GaAs nanowires

To study the stability of the above different types of SDBs, we calculated the defect formation energy $\Delta H_f(q)$ as [24]

$$\Delta H_f(q) = E_{\text{DB}}(q) - E_{\text{T}}(0) + \mu_{\text{H}} + q(E_{\text{VBM}} + E_{\text{f}} + \Delta V) \quad (1)$$

where $E_{\text{DB}}(q)$ and $E_{\text{T}}(0)$ are the energy of q -charged and uncharged GaAs NWs with and without SDBs, respectively. μ_{H} is the chemical potential of H atom. E_{VBM} is the energy of the top of valance band maximum (VBM). E_{f} is the Fermi level referenced to the VBM. ΔV is the difference between average electrostatic potential of GaAs NWs with and without SDBs.

To verify the effectiveness of our calculations, we calculate the lattice parameter of ZB-structured GaAs

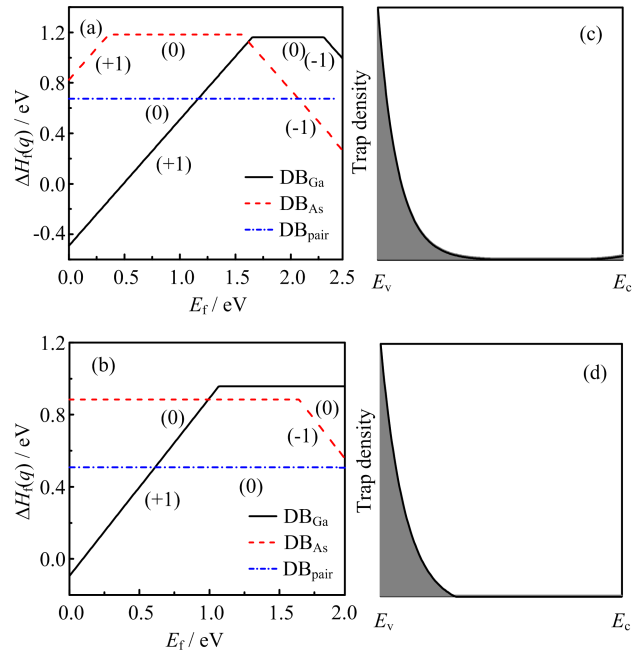


FIG. 2 The defect formation energies of surface dangling bonds on (a) ZB- and (b) WZ-structured GaAs NWs. The trap density of charged SDBs for (c) ZB- and (d) WZ-structured GaAs NWs. The (+1), (-1), and (0) represent the SDBs with the positively, negatively and neutral charged, respectively.

bulk. The calculated value of lattice parameter is 5.59 \AA , which agrees with experimental value (5.65 \AA) and other LDA calculated value (5.61 \AA) [25].

In order to understand the effect of SDBs on the doping of GaAs NWs, three types of SDBs are calculated. The DB_{Ga} , DB_{As} , and DB_{pair} are created by deleting the H atom from Ga, As, and Ga-As atoms of nanowires surface, respectively. These ZB- and WZ-structured nanowires with different charged SDBs are fully relaxed to achieve stable states. Then, we obtain the defect formation energy from Eq.(1) as shown in Fig.2 (a) and (b). The calculated band gap of ZB-structured GaAs NWs without SDBs (2.4 eV) corresponds to other DFT calculation (2.38 eV) [26]. The positively charged dangling bond on Ga atom (DB_{Ga^+}), DB_{pair} and negatively charged dangling bond on As atom (DB_{As^-}) are the most stable defects for ZB-structured nanowires, while the DB_{Ga^+} and DB_{pair} are the most stable defects for WZ-structured nanowires. The charged SDBs with the high stability could form the trap centers of carriers.

Generally, the defect density (D) follows the Boltzmann statistics as [27]

$$D \propto \exp\left(-\frac{\Delta H_f}{k_{\text{B}}T}\right) \quad (2)$$

where k_{B} is the Boltzmann constant, and T is the temperature. The results from Eq.(2) are plotted in Fig.2 (c) and (d). We can find that the density of DB_{Ga^+}

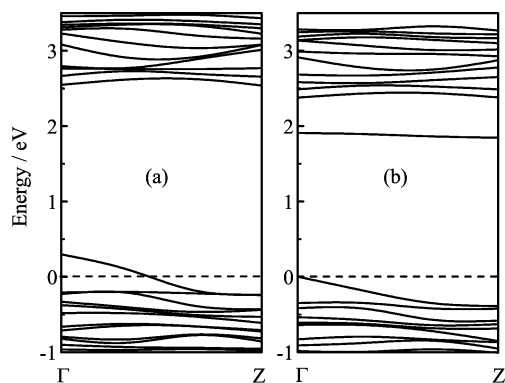


FIG. 3 The band structures of the ZB-structured Zn-doped GaAs NWs (a) without SDBs and (b) with DB_{Ga^+} . The dashed lines represent the Fermi level.

is the most primary trap density in both ZB- and WZ-structured GaAs NWs, while the trap density of DB_{Ga^+} is far larger than DB_{As^-} in ZB-structured GaAs NWs. In other words, the holes from p-type dopant could be captured by the SDBs, and then result that the doped nanowires suppressed its acceptor characteristic. Thus the SDBs may reduce the doping efficiency of p-doped GaAs NWs, but they have less influence on the n-doped GaAs NWs than on p-doped. This result is different from that of Si NWs in which SDBs prefer to asymmetrically deactivate both p- and n-type doped Si NWs [18].

To prove the above results, we calculate the band structures of Zn-doped GaAs NWs with and without SDBs. The results are shown in Fig.3. Figure 3(a) shows the band structure of Zn-doped GaAs NWs without SDBs. It is shown that this is a p-type character. Figure 3(b) shows the band structure of Zn-doped GaAs NWs with DB_{Ga^+} . This band structure shows an intrinsic character because the SDBs capture the holes from Zn dopant. The WZ-structured Zn-doped GaAs NWs has the similar phenomenon (not shown in figures). This result indicates that the SDBs would reduce the efficiency of p-type doping of GaAs NWs. So we should introduce surface passivation to eliminate the effect of SDBs in the p-type doped GaAs NWs. Recently, Casadei *et al.* reported that the p-type doped (C-doped) GaAs NWs with surface passivation offered the better characteristics than that of unpassivation [28].

B. Molecular passivation on the doping of GaAs nanowire

There are several different ways to passivate the semiconductor surface, for instance, using a wider band gap semiconductor such as AlGaAs or using molecules [19, 28]. We use two different types of molecules, NH_3 and NO_2 , to passivate the SDBs on ZB-structured GaAs NWs to choose the appropriate passivation materials.

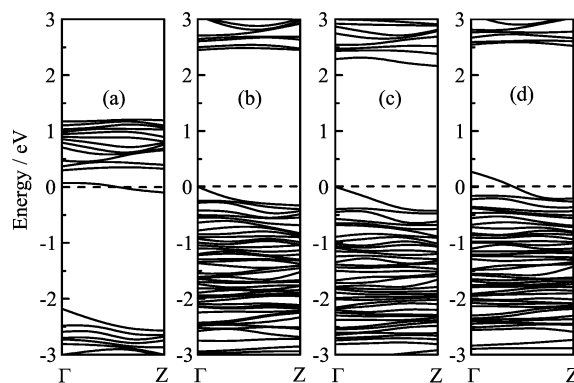


FIG. 4 The band structures of GaAs NWs with (a) NH_3 and (b) NO_2 adsorption and Zn-doped GaAs NWs with (c) NH_3 and (d) NO_2 adsorption. The dashed lines represent the Fermi level.

We prove the mechanism of molecular passivation of SDBs by comparing two types of molecular passivation. In our calculation, the two molecules are adsorbed on the SDBs of the GaAs NWs.

To provide reference for calculations on the adsorption process on the doped GaAs NWs, we first study the adsorption of NO_2 and NH_3 molecules at DB_{Ga^+} on GaAs NWs respectively. The energy decreases are 3.08 and 0.67 eV after NO_2 and NH_3 adsorption on GaAs NWs, respectively. This means the two adsorption processes are energetically favored. Figure 4 (a) and (b) show the band structures of NH_3 and NO_2 adsorption at DB_{Ga^+} on GaAs NWs, respectively. Figure 4(a) shows the band structure with adsorption of NH_3 remains an n-type doping character. In contrast, Fig.4(b) shows the adsorption of NO_2 results in an intrinsic character. The two results suggest that the NH_3 is not electronegative enough to accept the unpaired electrons of DB_{Ga^+} to reach the charge balance, while the unpaired electrons could transfer from DB_{Ga^+} to NO_2 when NO_2 is adsorbed on the DB_{Ga^+} . These results could be proved by charge transfer analysis. The Hirshfeld charge analysis shows the charge transfer from SDBs to the NO_2 molecule is 0.1 e more than to NH_3 . Thus, the adsorption of NH_3 has less influence on the GaAs NWs with SDBs.

In the following step, we investigate the adsorption of NH_3 and NO_2 at DB_{Ga^+} on Zn-doped GaAs NWs respectively. The results are shown in Fig.4 (c) and (d). Figure 4(c) shows the band structure with adsorption of NH_3 remains an intrinsic character. Figure 4(d) shows the NO_2 adsorption recovers the p-type doping character. We can find that the NH_3 can not increase the doping efficiency of Zn-doped GaAs NWs, but the NO_2 can compensate the unpaired electrons of DB_{Ga^+} completely. Moreover, we can deduce that the adsorption of NH_3 is physisorption, but the adsorption of NO_2 is chemisorption. This result is contrast to that of Si NWs in which the adsorption of NH_3 is chemisorption [19].

Finally, we also consider several other different substituting sites of the Zn dopant, and the calculations suggest that the adsorption effect of NH_3 or NO_2 do not depend on the Zn-doped position. The result suggests that the NO_2 -passivation can be used to eliminate the SDBs effect on the doped GaAs NWs.

C. Effect of dangling bonds and molecular passivation on the large size doped GaAs nanowires

It should be mentioned that the diameters of GaAs NWs in the above calculations are smaller than 1.5 nm, but they are about 50–500 nm in experiments and the WZ-structured GaAs NWs only are stable for diameters smaller than 50 nm. As we know, calculating the real size of GaAs NWs exceeds the computational capacity of DFT. But as is well known, the quantum confinement effect decreases with increase of size, thus GaAs(110) thin film can be considered as the large size GaAs NWs. To investigate whether the results as mentioned above are available for large size GaAs NWs or not, we also calculate the formation energies of SDBs on ZB-structured GaAs(110) thin film. The calculated results are shown in Fig.5(a). The band gap of thin film (1.29 eV) is larger than that of GaAs bulk based on the DFT calculation in other work (0.63 eV) [29] but smaller than that of GaAs NWs in our above calculation (2.4 eV). This phenomenon results from the quantum confinement effect. It is also found that the DB_{Ga^+} and DB_{pair} keep their stability for GaAs NWs with larger diameter, while DB_{As^-} lost stability for the whole allowed range of Fermi level. In other words, the doping efficiency of p-type doped GaAs NWs could also be reduced by the SDBs effect for larger size.

We similarly study the electronic properties of NH_3 or NO_2 adsorption at DB_{Ga} of GaAs(110) thin film to prove that the effect of molecular passivation is not dependent on the size of nanowires. The band structures of Zn-doped GaAs(110) thin film with NO_2 adsorption are shown in Fig.5(b) (the band structure of NH_3 adsorption on Zn-doped GaAs(110) thin film are not shown in figure). It is found that its band structure is similar to that on ultrathin GaAs NWs. This result suggests that the effect of NO_2 or NH_3 adsorption on GaAs NWs is not dependent on the size.

IV. CONCLUSION

We have explored the effect of surface dangling bonds and molecular passivation on the doping of GaAs NWs by first-principles calculations. It is found that the DB_{Ga^+} is the most stable SDBs in GaAs NWs for both ultrathin and larger size, while the DB_{As^-} is only stable in the ultrathin ZB-structured GaAs NWs and its trap density is very smaller than that of DB_{Ga^+} . Thus SDBs prefer to mainly reduce the doping efficiency of p-type

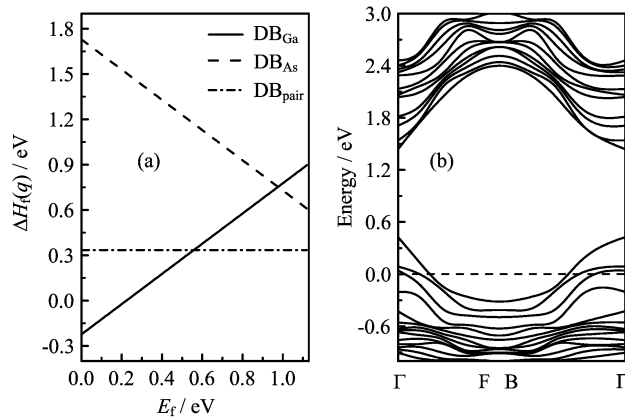


FIG. 5 (a) The defect formation energies of surface dangling bonds on GaAs(110) thin film. (b) The band structure of Zn-doped GaAs(110) thin film with NO_2 adsorptions at SDBs, the dashed line represents the Fermi level.

doped GaAs NWs but have less effect on n-type doping. In other words, surface passivation can improve the efficiency of p-type doped GaAs NWs. Then we have investigated NH_3 and NO_2 molecular passivation on the doping of GaAs NWs to eliminate the SDBs effect. It is found that the two types of molecules have different roles in adsorption process. In contrast to NH_3 , the NO_2 is electronegative enough to compensate the unpaired electrons on SDBs. Thus NO_2 could be used as an appropriate passivation material to improve the p-type doping efficiency of GaAs NWs. We expect that our conclusions can contribute to the research of doping GaAs NWs and designing nanodevices.

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