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The electronic and optical properties of Cs adsorbed GaAs nanowires via first-principles study

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ABSTRACT

In this study, we investigate the Cs adsorption mechanism on (110) surface of zinc-blende GaAs nanowire. The adsorption energy, work function, dipole moment, geometric structure, Mulliken charge distribution, charge transfer index, band structures, density of state and optical properties of Cs adsorption structures are calculated utilizing first-principles method based on density function theory. Total-energy calculations show that all the adsorption energies are negative, indicating that Cs adsorption process is exothermic and Cs covered GaAs nanowires are stable. The work function of nanowire surface has an obvious decrease after Cs adsorption. Besides, the ionization of nanowire surface is enhanced as well. More importantly, Cs adsorption contributes to a lower side shift of bands near Fermi level, and the corresponding band gap disappears. Additionally, the absorption peak and energy loss function after Cs adsorption are far higher than those before adsorption, implying better light absorption characteristic of nanowire surface after Cs adsorption. These theoretical calculations can directly guide the Cs activation experiment for negative electron affinity GaAs nanowire, and also lay a foundation for the further study of Cs/O co-adsorption on the nanowire surface.

1. Introduction

GaAs as one of commonly semiconductor material has some fascinating properties [1], such as direct band gap, high electrons mobility, etc. Differing from bulk or film materials, one-dimensional GaAs nanowire structure can be employed as building blocks in the field of nanoscale optoelectronic and microelectronic devices because of their small diameters and unique geometries [2–5]. So far, plenty of experimental results have reported that the prepared GaAs nanowires with zinc-blende structure have hexagonal cross sections with six facets orthogonal to the [111] growth direction. In general, the orientations of side facets for zinc-blende structure are (112) or (110).

Negative electron affinity (NEA) can be realized by covering Cs and O on the semiconductor material surface aiming at reducing the surface work function, finally improving the photoemission performance of materials [6–8]. Since the NEA GaAs-Cs photoemitter is reported for the first time [9], much theoretical and experimental effort has been devoted to the exploration of surface activation mechanism on GaAs surfaces. Turnbull et al. [10] described the role played by a surface coating of Cs and O, instead of single Cs, in obtaining high-yield photoemission from GaAs. The spectral distributions of yields indicate that the work function of Cs/O coatings is at least as low as that of GaAs-Cs. Rodway et al. [11] performed an in situ study of the activating layer on GaAs (Cs, O) photocathodes, suggesting that the optimum Cs/O ratio is between 4:1 and 2.7:1 with a typical work function reduction of 275 meV. Yu et al. [12] conducted a comprehensive study on the adsorption of Cs atom on $Ga_{0.5}Al_{0.5}As$ (001) and (011) surfaces utilizing plane-wave ultrasoft pseudopotential method, indicting (001) surface is more beneficial for photoelectric activation. Up to now, the previous works for Cs or Cs/O co-adsorption on GaAs surface are mainly concentrated on the bulk or film crystal material. However, the interaction mechanism between Cs adatom with GaAs nanowire is still unknown. Therefore, a theoretical research for Cs adsorption on zinc-blende GaAs nanowire surface is desperately needed.

In this study, we undergo a detailed first-principles investigation on the electronic and optical properties of Cs on (110) plane of GaAs nanowire grown along [111] direction with zinc-blende structure. We also calculate the adsorption energy, work function, dipole moment of Cs adsorption on different sites of nanowire surface. The calculations can direct the Cs activation experiment of GaAs nanowire surface, and also provide valuable reference for preparing high-quality NEA GaAs nanowire photocathodes.

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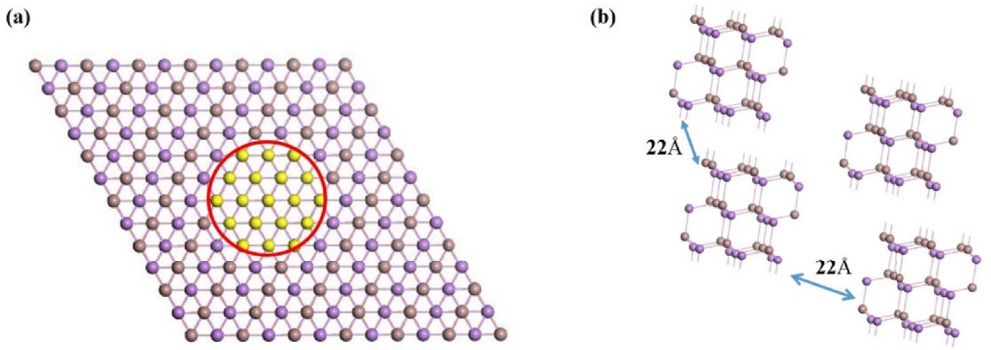

Fig. 1. Top view of (a) a $6 \times 6 \times 1$ GaAs supercell with zinc-blende structure and (b) $Ga_{19}As_{19}$ supercell with a nanowire of infinite length along [111] direction. A vacuum of 22 Å between neighboring nanowires is included in the supercell.

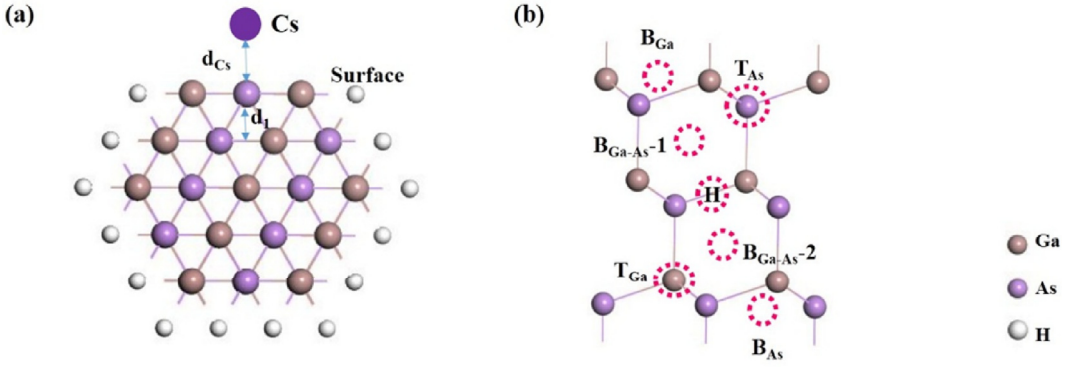

Fig. 2. (a) Top view of Cs adsorption on zinc-blende GaAs nanowire surface and (b) seven possible sites for Cs adsorption on one side facet of GaAs nanowire.

2. Methods of calculation

At room temperature and pressure, the theoretical lattice parameters of zinc-blende GaAs phase are a = b = c = 5.56 Å [13]. All GaAs nanowire models have been generated from the ideal bulk GaAs supercell along (111) crystallographic with zinc-blende structure through cutting the extra atoms outside of the red circle, shown in Fig. 1(a). The obtained GaAs nanowire has a hexagonal cross section enclosed by (110) facets. Along the [111] growth direction, the length of GaAs nanowire can be infinitely extended. In Fig. 1(b), taking into account the unit cell dimension, the thickness of vacuum is set as 22 Å in order to eliminate the interaction among the neighboring nanowires. Fig. 2 depicts the top view and side view of Cs adsorption on GaAs nanowire surface. The model contains 19 Ga atoms and 19 As atoms and the diameter is 9.63 Å. For the sake of simplicity, we only consider the mechanism of one Cs atom adsorbed on the one side surface of GaAs nanowire. Because the surface consist of three Ga atoms and three As atoms, the coverage of Cs is considered as 1/6 Monolayer (ML). In every slab, to avoid the effects of surface states and unnecessary charge transfer, the surface dangling bonds of the other five facets are saturated by four fractional pseudo-hydrogen atoms, which is shown in Fig. 2(a). In the (110) facet, there are many sites for Cs adsorption, so seven possible sites have been selected and discussed in this work, shown in Fig. 2(b), in which B_{Ga} and B_{As} denote the bridge site between two adjacent Ga or As atoms, respectively; $B_{Ga\text{-}As}$-1 and $B_{Ga\text{-}As}$-2 represent the bridge site of Ga atom and As atom; T_{Ga} and T_{As} are the top site of Ga atom and As atom, respectively; H is the hollow site. The distance from the adatom to the nanowire surface is initially set as 1.62 Å.

Geometry optimizations and the total energy calculations for Cs atom on GaAs nanowire surface were performed utilizing first-principles method based on density function theory. The first principles calculations were realized with the ab initio quantum mechanics software of Cambridge Serial Total Energy Package (CASTEP) [14]. We chose the Broyden-Flecher-Goldfarb-Shanno method (BFGS) to carry on geometry optimization for clean and Cs adsorbed surface models. In the self-consistent calculations, the geometry optimization will end up when the convergence tolerance of energy change is below 2×10^{-6} eV/atom, the force is lower than 0.001 eV/nm, the stress is less than 0.05 Gpa and atoms displacement is less than 0.0002 nm. The generalized gradient approximation (GGA) with Perdew, Burke and Ernzerhof (PBE) was employed to deal with the exchange and correlation energy of adsorption systems [15]. The electron wave function was expanded in plane waves up to a cutoff energy of 300 eV. In the Monkhorst-Pack special scheme, a gamma-centered grid of $1 \times 2 \times 1$ k-point was used to sample the irreducible Brillouin zone [16]. All calculations were implemented in reciprocal space with Ga: $3d^{10}4s^24p^1$, As: $4s^24p^3$, Cs: $5s^25p^66s^1$ as the valence-electron configuration. The scissors operator correction was adopted in the calculations for optical properties to improve the accuracy.

3. Results and discussions

3.1. Adsorption energy

The most favorable adsorption site on GaAs nanowire surface for Cs adsorption is measured by evaluating the adsorption energy of different

Table 1
Adsorption energy of Cs covered zinc-blende GaAs nanowire surface with different adsorption sites.

Cs adsorption sites	B_{Ga}	T_{As}	$B_{Ga\text{-}As}$-1	H	$B_{Ga\text{-}As}$-2	T_{Ga}	B_{As}
Adsorption energy (eV)	−2.450	−3.180	−2.879	−2.706	−2.683	−3.027	−3.285