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Atomic geometry and electronic structure of $Al_{0.25}Ga_{0.75}N(0\,0\,0\,1)$ surfaces covered with different coverages of cesium: A first-principle research

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ABSTRACT

We investigate cesium adsorption on $Al_{0.25}Ga_{0.75}N(0\,0\,0\,1)$ surface at different coverages using first principle method based on density functional theory. Adsorption energies, atomic structure, Mulliken charge distribution, electron transfer, band structures, and density of states of the adsorption systems corresponding to different Cs coverages were obtained. Total-energy calculations show that cesium adsorption on $Al_{0.25}Ga_{0.75}N(0\,0\,0\,1)$ surface is more and more difficult as the increase of cesium coverage. A single cesium adatom is preferred to locate at the top of Ga atom (T_{Ga}). Meanwhile, it is not the most stable configuration when two cesium atoms were located on the top of two Ga neighbors at the same time. This is mainly because the distance of Cs adatoms is so small that repulsive force between adatoms rises. At low coverage, electrons transfer from Cs adatom to Ga atoms on the topmost and second topmost bilayers. Meanwhile, the efficiency of electron transfer decreases as the increasing of Cs coverage. There appear new bands at −25 to −23 eV and −14 to −10 eV, which were caused by Cs 5s and Cs 5p state electrons. Under the joint effect of Cs 5s and 5p state electrons, density of states at Fermi level increases, and the adsorption surfaces show more metal properties. Electrons transferring from Cs adatoms to $Al_{0.25}Ga_{0.75}N$ substrate induces dipole moment, which is useful to lower work function. What is more, there exists an optimum of cesium coverage to obtain the lowest work function.

1. Introduction

Studies of alkali-metal adsorption on solid surfaces have been reported over the last decade and cesium is the most attractive metal for adsorption on III–V semiconductor surfaces to reduce work function [1]. The AlGaN-based photocathodes are currently attracting great interest due to their potential application in ultraviolet regions [2]. Cs adsorption on (0 0 0 1) surface of AlGaN photocathodes is the most popular method to obtain negative electron affinity (NEA). Many cesium activation experiments show that cesium adsorption on AlGaN surfaces will result in a lower work function, meanwhile there will appear a phenomenon called "Cs-kill" when the surface is over-cesiated [3–5]. Nevertheless, the reason of lower work function and "Cs-kill" phenomenon was not explained based on a thorough knowledge about the microscopic structure and electronic states of Cs adsorbed AlGaN(0 0 0 1) surfaces. The theoretical research of surface morphology, electronic structure, and electron transfer of AlGaN(0 0 0 1) surfaces with different coverages of Cs adatoms was inadequate.

In this paper, we undergo first principle calculations of different atomic configurations corresponding to different coverage of Cs adatoms on $Al_{0.25}Ga_{0.75}N(0\,0\,0\,1)$ surface. Adsorption energies, surface morphology, Mulliken charge distribution and bond population, electron transfer, and density of states were calculated. The work is important for the research of the action mechanism between Cs adatom and $Al_{0.25}Ga_{0.75}N(0\,0\,0\,1)$ surface.

2. Computational details

Geometry optimizations and total energy calculations of Cs adatoms and $Al_{0.25}Ga_{0.75}N(0\,0\,0\,1)$ surface substrate were performed employing first-principles approach. Density-functional-theory general-gradient-approximate (DFT-GGA) [6] framework with the pseudopotential plane wave method was used in the calculations. Ultrasolft pseudopotentials (USP) [7] were used for all atomic species, and nonlinear core corrections (NLCC) [8] were

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Table 1
Adsorption sites of Cs atoms in the adsorption systems with different adatom coverages.

Cs coverage (ML):	0.25			0.5		0.75		1	
Model no.:	1	2	3	4	5	6	7	8	9
Adsorption sites	T_{Ga}	T_N	B_1	T_{Ga}, T_{Ga}	T_{Ga}, T_N	T_{Ga}, T_{Ga}, T_{Ga}	T_{Ga}, T_N, T_{Ga}	T_{Ga}, T_{Ga}, T_{Ga}, T_{Al}	T_{Ga}, T_{Ga}, T_N, T_N

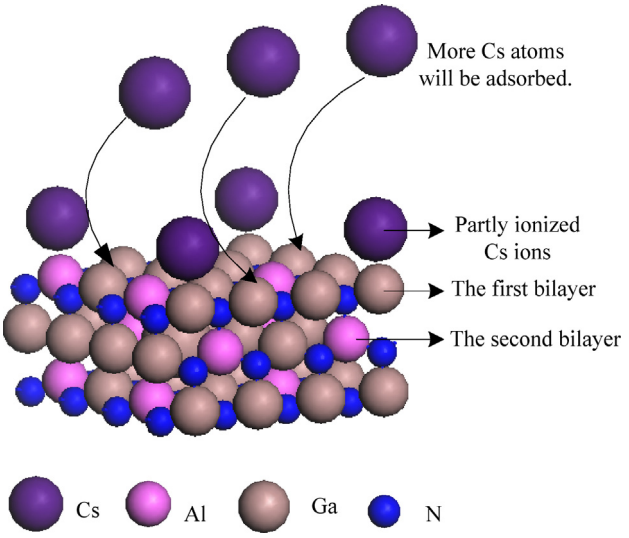

Fig. 1. Adsorption process of Cs adatoms on $Al_{0.25}Ga_{0.75}N(0\,0\,0\,1)$ surface.

adopted for Ga atoms. A plane wave basis set of 400 eV was used for valence electrons. A $4 \times 4 \times 1$ Monkhorst–Pack [9] k point grid was used to sample the Brillouin zone (BZ) of the surface.

The surfaces with different coverage of Cs atoms were modeled by supercell geometry. 2×2 supercells containing eight bilayers of $Al_{0.25}Ga_{0.75}N$ and 15 Å of vacuum were built. In every slab, one side was saturated with four fractional pseudohydrogen atoms, and the other side was adsorbed with Cs atoms. The atoms in the top four bilayers of the slab and the adatoms were relaxed freely. Fig. 1 depicts the adsorption process of Cs adatoms on $Al_{0.25}Ga_{0.75}N(0\,0\,0\,1)$ surface, and Fig. 2 is the top view and side view of clean $Al_{0.25}Ga_{0.75}N(0\,0\,0\,1)$ surface. For different Cs coverage, there are so many configurations with different adsorption sites for Cs atoms. After many calculations, several models with typical adsorption sites were discussed in this paper. Model numbers and the corresponding adsorption sites of Cs adatoms are listed in Table 1, in which T_{Ga}, T_{Al}, and T_N represent the top of Ga, Al, and N atoms respectively; B_1 denotes the bridge site between two adjacent Ga atoms.

3. Analysis

The adsorption energies in the systems of Cs adsorbate and $Al_{0.25}Ga_{0.75}N(0\,0\,0\,1)$ surface substrate, can be obtained as the following relation [10]:

$$E_{ads} = E_{tot}[Cs/surface] - E_{tot}[surface] - n_{Cs}E_{tot}[Cs_{bulk}] \quad (1)$$

where $E_{tot}[Cs/surface]$ is the total energy of the adsorbate–substrate system after enough relaxation, n_{Cs} is the number of Cs adatoms; $E_{tot}[surface]$ is the total energy for the clean surface; $E_{tot}[Cs_{bulk}]$ represents the energy of a Cs atom in bulk bcc, and the calculated value is −548.9 eV in this paper. The adsorption energies for the structures that we have studied are present in Table 2. It can be found that the adsorption energies of adsorption systems with 0.25 ML, 0.50 ML, or 0.75 ML Cs atoms are negative while those of systems with 1.00 ML Cs atoms are positive. So adsorption processes of 0.25 ML, 0.50 ML, or 0.75 ML Cs on $Al_{0.25}Ga_{0.75}N(0\,0\,0\,1)$ surface are exothermic, while adsorption of 1 ML Cs is endothermic. The adsorption energies increase monotonously with the increase of Cs coverage, so the adsorption system is more and more unstable. The adsorption system is dangerous when the coverage of Cs reaches 1 ML. The adsorption site on the top of Ga atom (T_{Ga}) is the favorable site for 0.25 ML Cs atom to locate, while the adsorption system with two Cs atoms at T_{Ga} sites simultaneously (Model 4) is not the most stable one in the systems with 0.50 ML Cs. If there is no correlation between Cs adatoms, the most favorable configuration

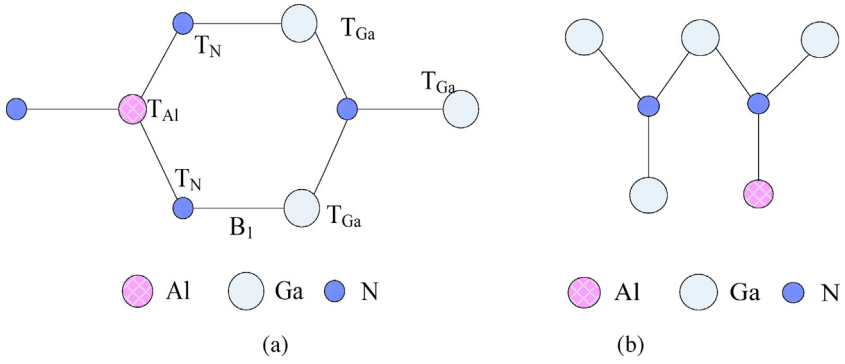

Fig. 2. Schematic representation of $Al_{0.25}Ga_{0.75}N(0\,0\,0\,1)$ surface (a) top view and (b) side view.

Table 2
Adsorption energies of different Cs adsorption systems.

Cs coverage (ML):	0.25			0.5		0.75		1	
Model no.:	1	2	3	4	5	6	7	8	9
Adsorption sites	T_{Ga}	T_N	B_1	T_{Ga}, T_{Ga}	T_{Ga}, T_N	T_{Ga}, T_{Ga}, T_{Ga}	T_{Ga}, T_N, T_{Ga}	T_{Ga}, T_{Ga}, T_{Ga}, T_{Al}	T_{Ga}, T_{Ga}, T_N, T_N
Adsorption energy (eV)	−2.04	−1.98	−1.89	−1.05	−1.13	−0.64	−0.76	1.34	1.21