First principles study of IIIA atoms adsorbed on ZnO (0001) surface and the applications in optoelectronic devices

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Abstract. First principles method is used to study the adsorption behavior, formation energy and electronic structure of IIIA (B, Al, Ga, In) atoms adsorbed on Top, T4 and H3 sites of ZnO (0001) surface. The data shows that the formation energy of B, Al, Ga and In atoms adsorbed on Top site is highest, then followed by T4 site, and H3 is a more stable adsorption site. With the periodic increase of B, Al, Ga and In atoms, the formation energy of corresponding models decreases gradually, and the binding ability with O atoms also decreases gradually. The electronic structure of ZnO (0001) surface is sensitive to the adsorption sites. When these atoms are adsorbed on Top sites, the electronic structures of B-Top, Al-Top, Ga-Top and In-Top models have a little change compared with ZnO (0001) surface. However, when these atoms are adsorbed on T4 and H3 sites, the impurity states appear on the VBM, which narrowing the band gap of the corresponding models.

Keywords: First-principles, ZnO (0001) surface, IIIA atoms, adsorption.

1. Introduction

Transparent conductive oxidized films (TCOs) have important applications in the field of optoelectronic devices, such as flat panel displays, organic light emitting diodes and thin film solar cells [1-4]. ZnO has become another important optoelectronic material after GaN because of its wide bandgap (3.37 eV) and high excitation energy (60 meV) [5-7]. In recent years, TCOs based on ZnO substrate have been extensive studied by researchers [8, 9]. The prepared ZnO films usually exhibit weak n-type conductive behavior. In order to realize the application of ZnO in the field of TCOs, it is necessary to improve its electrical conductivity and optical transmittance significantly. Researchers have found that the modified ZnO by IIIA atoms (B, Al, Ga, In) show high electrical conductivity, high optical transmittance and well n-type conductive behavior [10-14]. At present, the research on the modification of ZnO properties by these atoms mainly focuses on experiments, while the related theoretical research lags behind. Compared with the doping of B, Al, Ga and In atoms into ZnO bulk materials, there are few reports on the adsorption of these atoms on ZnO surface by theoretical calculation. ZnO has four main low-miller-index surfaces: nonpolar (10¯10) and (1120) surfaces as well as polar (0001)-Zn and (000¯1)-O surfaces [15, 16]. Among the four surfaces, (0001)-Zn (also can be expressed as ZnO (0001) surface) is the only one surface with n-type conductive behavior. ZnO (0001) surface has the narrowest band gap, the strongest UV absorption in the low energy region, and the most obvious red-shift of the absorption edge, so ZnO (0001) surface has been widely researched. Due to the n-type conductivity behavior of ZnO
(0001) surface, and improving the n-type conductivity is very important to ZnO application, so in this paper, we will study the adsorption behavior of B, Al, Ga and In atoms on ZnO (0001) surface and their effects on the surface electronic structure by first principles method.

2. Calculation Model and Method

For the study of B, Al, Ga and In atoms adsorbed on ZnO (0001) surface, the surface has been simulated by $2 \times 2$ periodic supercells with eight Zn-O double layers. In order to prevent the interaction of periodic repeated surfaces, a vacuum spacer of 15 Å is introduced by z-direction. In order to prevent unphysical charge transfer between the top and bottom layers, the dangling bonds at the bottom layer are saturated by pseudo-hydrogens. For the adsorption of B, Al, Ga and In atoms, three high-symmetry adsorption sites (T4, H3 and Top) are main considered (see Figure 1) [16]. In this paper, we only consider the adsorption model with single atom on different adsorption sites. On this basis, these models are named as: B-Top, B-T4, B-H3; Al-Top, Al-T4, Al-H3; Ga-Top, Ga-T4, Ga-H3; In-Top, In-T4 and In-H3. The upper four Zn-O bilayers as well as the adatom layer are allowed to relax in structure optimization, and the lower four bilayers and pseudo-hydrogens are fixed to mimic bulk substrate.

All calculations are performed by first principles method. The generalized gradient approximation (GGA) with the Perdew Burke Ernzerhof (PBE) scheme is adopted by exchange-correlation potential. The electron wave functions are described by projector augmented wave (PAW)[17-20]. It is well known that the traditional GGA method usually underestimates the band gap of ZnO and overestimates the energy level of Zn 3d states. To ease the problem, the GGA + U method is used to treat 3d electrons of Zn with the Hubbard on-site Coulomb interaction parameter (U–J) of 7.5 eV, so that the valence band and Zn 3d energy levels are in excellent agreement with the experimental values[16]. The energy cutoff of plane-wave basis is set as 400 eV. Brillouin zones are sampled by k-point meshes of $4 \times 4 \times 1$. A higher cutoff energies and denser k-points also have been tested and the results barely changed.

Figure 1. Side view and top view of ZnO (0001) surface. Top, T4 and H3 are the considered adsorption sites.

3. Results and discussion

3.1. Formation energy analysis

To determine relative stability of adsorption models, the formation energies are calculated by following formula:

$$E_{\text{ads}} = E_{\text{X/slab}} - E_{\text{slab}} - \Delta n_x \mu_x$$  \hspace{1cm} (1)
Where $E_{\text{ad}}$ is formation energy, $E_{X\text{slab}}$ is the total energy of B, Al, Ga and In atoms adsorbed on surface respectively, $E_{\text{slab}}$ is the total energy of clean and relaxed ZnO (0001) surface, $\Delta n_x$ and $\mu_x$ are the adatom number and chemical potential of B, Al, Ga and In atoms. Formation energies of above models are shown in figure 2. It can be seen from the figure that the model stability is affected by adsorbed atoms and adsorption sites. For the adsorption of same atom at different sites, the relationships of formation energy are as follows: $\text{B-Top} > \text{B-T4} > \text{B-H3}$, $\text{Al-Top} > \text{Al-T4} > \text{Al-H3}$, $\text{Ga-Top} > \text{Ga-T4} > \text{Ga-H3}$, and $\text{In-Top} > \text{In-T4} > \text{In-H3}$. The dates show that the formation energies of B, Al, Ga and In atoms adsorbed at different sites have similar changing regular, that is, the value is highest at Top site, then followed by T4 site, and H3 is a more stable adsorption site. Different adsorption sites lead to the formation energy is different for the same adsorbed atom, but the difference value decreases with the periodic increase of B, Al, Ga and In atoms. For example, the difference value between B-Top and B-T4 is large, while that between Al-Top and Al-T4 has obvious decreases, and that between Ga-Top and Ga-T4 is small, and that between In-Top and In-T4 is unobservable. The formation energies of B, Al, Ga and In atoms adsorbed at T4 site are slightly larger than those at H3 site, but the difference values all are small, which indicates that T4 and H3 both are the preferred adsorption sites. Different atoms adsorbed at the same site, the relationships of formation energy are as follows: $\text{B-Top} > \text{Al-Top} > \text{Ga-Top} > \text{In-Top}$, $\text{B-T4} > \text{Al-T4} > \text{Ga-T4} > \text{In-T4}$, and $\text{B-H3} > \text{Al-H3} > \text{Ga-H3} > \text{In-H3}$. The dates show that with the periodic increase of B, Al, Ga and In atoms, they are more easily adsorbed on ZnO (0001) surface.

![Figure 2](image.png)

**Figure 2.** The formation energies of B, Al, Ga and In atoms adsorbed on Top, T4 and H3 sites of ZnO (0001) surface

3.2. Structural optimization analysis

In order to study the effects of B, Al, Ga and In atoms on the structure of ZnO (0001) surface, the optimized structures of those models are shown in figure 3. Figure 3a is the side view of optimized B-Top, B-T4 and B-H3 models. It can be seen from figure 3a that ZnO (0001) surface is sensitive to the B atom with different adsorption sites. For B-Top model, Zn$_2$ atom move upwards obviously and bond with B atom, and the new formed B-Zn$_2$ bond length is 2.16 Å. Influenced by the adsorbed B atom, the bond length of Zn$_1$-O$_2$ and Zn$_1$-O$_2$ changes to 2.11 Å and 2.19 Å from original 1.96 Å. For B-T4 model, the optimized structure is significantly different from initial structure. Because the bonding ability of B-O bond is greater than that of B-Zn bond, B atom approaches to O$_4$ atoms during the structure optimization and forms a B-O$_4$ bond with 1.29 Å. The formed B-O$_4$ bond seriously destroys the
hexagonal wurtzite structure of ZnO (0001) surface, that is, the original Zn$_2$-O$_4$, Zn$_3$-O$_4$ and Zn$_4$-O$_4$ bonds are broken, then form new Zn$_2$-B, Zn$_3$-B and Zn$_4$-B bonds. For B-T4 model, B atom still situates above O$_4$ atom, while Zn$_2$, Zn$_3$ and Zn$_4$ atoms move upwards obviously and almost at the same level with B atoms. For B-H3 model, the adsorbed B atom also seriously destroys the structure of ZnO (0001) surface. B atom approaches to the inclined top of O$_4$ atom from original H3 site during the structure optimization, then bonds with O$_4$ atom. Similar to B-T4 model, the formed B-O$_4$ bond of B-H3 model also leads the breaking of Zn$_2$-O$_4$ and Zn$_3$-O$_4$ bond, and forming of Zn$_2$-B and Zn$_3$-B bond.

Figure 3b is the side view of optimized Al-Top, Al-T4 and Al-H3 models. For Al-Top model, the adsorbed Al atom bonds with Zn$_2$ atom, and the bond length of Al-Zn$_2$ is 2.64 Å. The corresponding Zn$_2$-O$_2$ bond lengthen to 2.11 Å, and Zn$_1$-O$_2$ bond shorten to 1.94 Å. For Al-T4 model, the adsorbed Al atoms not only bond with O$_4$ atom, but also bond with the adjacent Zn$_2$, Zn$_3$ and Zn$_4$ atoms. The bond length of Al-O$_4$ is 1.89 Å, and is 2.46 Å for Zn$_2$-Al, Zn$_3$-Al and Zn$_4$-Al bonds. For Al-H3 model, the adsorbed Al atom also obviously migrates from the original H3 site to O$_4$ atom. Similar to Al-T4 model, Al-O$_4$ and Zn$_2$-Al, Zn$_3$-Al and Zn$_4$-Al bonds also are formed in the Al-H3 model, and the bond lengths are 1.85 Å, 2.42 Å, 2.42 Å and 2.64 Å, respectively. For Al-T4 and Al-H3 models, the adsorbed Al atom doesn’t destroy the original Zn-O bond of ZnO (0001) surface, which indicates that the binding ability of Al-O bond is weaker than that of B-O bond.

Figure 3c is the side view of optimized Ga-Top, Ga-T4 and Ga-H3 models. In the initial Ga-T4 model. The situation indicates that the binding ability of Ga-O bond is weak. For Ga-Top model, the formed Ga-Zn$_2$ bond length is 2.66 Å, and the corresponding Zn$_2$-O$_2$ bond lengthen to 2.11 Å and Zn$_1$-O$_2$ bond shorten to 1.95 Å. For Ga-T4 model, the adsorbed Ga atom doesn’t bond with O atom, but bonds with the adjacent Zn$_2$, Zn$_3$ and Zn$_4$ atoms. The bond lengths of Ga$_2$-Ga, Zn$_3$-Ga and Zn$_4$-Ga all are 2.58 Å. The corresponding Zn$_2$-O$_2$ and Zn$_3$-O$_2$ bond lengthen to 2.10 Å and 2.01 Å, respectively. For Ga-H3 model, the adsorbed Ga atom migrates from original H3 site to the right above of Zn$_2$ and Zn$_3$ atoms. The formed Ga-Zn$_2$ and Ga-Zn$_3$ bond lengths both are 2.47 Å, and the corresponding Zn$_2$-O$_2$ and Zn$_3$-O$_4$ bond lengthen to 2.07 Å and 2.16 Å.

Figure 3d is the side view of optimized In-Top, In-T4 and In-H3 models. It can be seen from the figure that the adsorbed Ga atom bonds with Zn atom, but doesn’t bond with O atom in the three models, even Ga atom situates above O atom in the initial Ga-T4 model. The situation indicates that the binding ability of Ga-O bond is weak. For Ga-Top model, the formed Ga-Zn$_2$ bond length is 2.66 Å, and the corresponding Zn$_2$-O$_2$ bond lengthen to 2.11 Å and Zn$_1$-O$_2$ bond shorten to 1.95 Å. For Ga-T4 model, the adsorbed Ga atom doesn’t bond with O atom, but bonds with the adjacent Zn$_2$, Zn$_3$ and Zn$_4$ atoms. The bond lengths of Ga$_2$-Ga, Zn$_3$-Ga and Zn$_4$-Ga all are 2.58 Å. The corresponding Zn$_2$-O$_2$ and Zn$_3$-O$_2$ bond lengthen to 2.10 Å and 2.01 Å, respectively. For Ga-H3 model, the adsorbed Ga atom migrates from original H3 site to the right above of Zn$_2$ and Zn$_3$ atoms. The formed Ga-Zn$_2$ and Ga-Zn$_3$ bond lengths both are 2.47 Å, and the corresponding Zn$_2$-O$_2$ and Zn$_3$-O$_4$ bond lengthen to 2.07 Å and 2.16 Å.

From above analysis, it can be found that when B, Al, Ga and In atoms adsorbed on Top and T4 sites, they have a little movement in the horizontal direction during the structure optimization, but the movement is obvious when they adsorbed on H3 site. The situation shows that it is unstable when B, Al, Ga and In atoms adsorbed on H3 site. In order to satisfy the principle of minimum energy, they will approach T4 site during the structure optimization, which leads the formation energies of corresponding models gradually decrease, even lower than those at T4 sites.
Figure 3. Optimized structure of III atoms adsorbed on ZnO (0001) surface: (a) B adsorption, (b) Al adsorption, (c) Ga adsorption, (d) In adsorption

3.3. Electronic structure analysis

In order to study the effect of B, Al, Ga and In atom adsorption on the electronic structure of ZnO (0001) surface, based on the above optimized models, the total density of states (TDOS) and partial density of states (PDOS) by GGA+U method are calculated, as shown in Figure 4-7. Figure 4 is the TDOS and PDOS of B-Top, B-T4 and B-H3 models. Compared with the TDOS of ZnO (0001) surface, the change of valence band maximum (VBM) and conduction band minimum (CBM) of B-Top model is slight. This case is also suitable for Al-Top, Ga-Top and In-Top models, which indicates that the electronic structure of ZnO (0001) surface is insensitive to the adsorption of B, Al, Ga and In atoms on Top site. For B-T4 and B-H3 models, the TDOS shows that impurity states appear on VBM and narrow the model band gap. The PDOS shows that the peak patterns and positions of B2p orbitals are similar to those of O2p and Zn4s orbitals, which indicates that B atoms can hybridize well with ZnO (0001) surface when it adsorbed on T4 and H3 sites. The situation also indicates that B-T4 and B-H3 are more stable than B-Top, which is consistent with the formation energy analysis. Figure 5 is the TDOS and PDOS of Al-Top, Al-T4 and Al-H3 models. For Al-Top model, the change of TDOS is similar to that of B-Top model. For Al-T4 and Al-H3 models, Al3p orbitals both appear at the VBM and narrow the model band gap obviously. Under the suitable light source, the electrons will transition from Al3p to Zn4s orbitals, and then the transition from O2p to Zn4s orbitals will occur. So, Al atom adsorbed on T4 and H3 sites can greatly modify the electronic structure of ZnO (0001) surface. Figure 6 is the TDOS and PDOS of
Ga-Top, Ga-T4 and Ga-H3 models. The electronic structure change of Ga-Top model is similar to that of B-Top and Al-Top models. For Ga-T4 and Ga-H3 models, the band gap of Ga-T4 is narrower than that of Ga-H3. Compared with Ga-H3 model, the Ga4p orbitals of Ga-T4 hybridize better with Zn4s and O2p orbitals of ZnO (0001) surface. The phenomenon is consistent with the fact that there are three Ga-Zn bonds for Ga-T4 and only two Ga-Zn bonds for Ga-H3. Figure 7 is the TDOS and PDOS of In-Top, In-T4 and In-H3 models. Through the comparison of figures 6 and 7, the effects of Ga and In adsorption on the electronic structure of ZnO (0001) are very similar, which is related to their similar structural after optimization. For In-Top model, it can be seen from PDOS that In5p orbitals are highly hybridized with Zn4s and O2p orbitals. Combined with B-Top, Al-Top and Ga-Top models, it can be found that Top sites has little effect on the electronic structure of ZnO (0001) surface. However, with the periodic increase of B, Al, Ga and In atoms, their hybridization degree with ZnO (0001) surface becomes higher and higher. It is also confirmed that with the periodic increase of B, Al, Ga and In atoms, the formation energy of B-Top, Al-Top, Ga-Top and In-Top models becomes lower and lower.

Figure 4. The TDOS and PDOS of B-Top, B-T4 and B-H3 models.

Figure 5. The TDOS and PDOS of Al-Top, Al-T4 and Al-H3 models.
4. Conclusion

IIIA (B, Al, Ga, In) atoms adsorbed on Top, T4 and H3 sites of ZnO (0001) surface is studied by first principles method. The formation energy analysis indicates that T4 and H3 both are the preferred adsorption sites than Top site. With the periodic increase of B, Al, Ga and In atoms, they are more easily adsorbed on ZnO (0001) surface. The optimized structures analysis indicates that the binding ability of B, Al, Ga and In atoms with O atoms becomes weaker and weaker. B atom adsorbed on T4 and H3 sites seriously destroys the hexagonal wurtzite structure of ZnO (0001) surface. Electronic structure analysis indicates that B, Al, Ga and In atoms adsorbed on Top sites have a little influence on the electronic structure of ZnO (0001) surface. When these atoms adsorbed on T4 and H3 sites, the hybridization of them with Zn4s and O2p orbitals becomes higher and higher with the atom periodic increase. Al atom adsorbed on T4 and H3 sites shows the most obvious modification effect to the electronic structure of ZnO (0001) surface.
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