Effect of Ag Doping on the Electronic Structure and Optical Properties of ZnO(0001) Surface

Qian Xiang[1 *], *Shutao* Zhao[1] , *Yanning* Wu[1], and *Guangdong* Liu[1]

[1]School of Physics and Electronic Engineering, Fuyang Normal College, Fuyang 236037, China

Abstract. Using first-principle calculations, the geometrical structure, the electronic and optical properties of Ag-doped ZnO(0001) surface have been investigated. We found that Ag-doped ZnO(0001) surface is more easily formed on the first layer. On the other hand, the doped surface has gradually become an equipotential body, showing obvious metallic characteristics. We found that a new peak appeared in the low energy region after Ag doping, which was mainly due to the electron transition between the two orbital levels of Ag-4d and O-2p.

1 Introduction

ZnO is a direct wide band gap(3.37eV) semiconductor with a large excitation binding energy of 60 meV at room temperature[1]. Thanks to these properties, ZnO is used as a photoelectronic material for solar cells, gas sensors, transistors[2-3]. In order to change its electronic and optical properties, the doping of ZnO surface has been a popular technique, such as F-B[4], Cu[5], Al[6]. Due to the ZnO crystal has a spontaneous polarization direction along the c axis,different polar surfaces exhibit different growth characteristics.[7-9]. Lately, from the experiment, Suat Pat[10] found the ZnO and AZO thin films have high transparency using RF sputtering technique. Long xing Su[11] has reported Be doping lead to ZnO surface gap widening. From the theory, Jianping Xiao[12] has proposed that Cu-doped ZnO(0001) surface promote efficient formation of oxygen vacancies. Haifeng Zhang[13] indicated that Si atoms adsorbed on ZnO (0001) surface lead to a slightly blue shift phenomenon. Mohammed Ali Lahmer[14] has reported that hydrogen adsorption is more favored on Mg doping ZnO($000\bar{1}$) surface. So far, Ag-doped ZnO(0001) surface has few reports on theoretical studies.

In this paper, geometrical structure, electrical properties, and optical properties of Ag-doped ZnO(0001) surface are systematically studied by first principles calculations.

2 Computational methods

All calculations are performed by the first-principles method based on the density functional theory with the generalized gradient approximation (GGA)[15], and the projector augmented wave (PAW)[16]pseudo-potentials, as implemented in the VASP codes[17, 18].

* Corresponding author: xiangqian8702@163.com

The gamma centred $8 \times 8 \times 1$ k-points is used for the Brillouin zone. The computational model contains five bilayers in which the two bottom ZnO bilayers are fixed while the top three ZnO bilayers and adatoms are allowed to relax. We carry out calculation with 10Å thick vacuum layers. To prevent unphysical charge transfer between the bottom and top slabs, pseudohydrogens are used on the bottom layer[19]. $Zn^3d^{10}4s^2$, $O2s^22p^4$and $Ag4d^{10}5s^1$ are chosen as valence electrons. The computational model is shown in Fig.1.

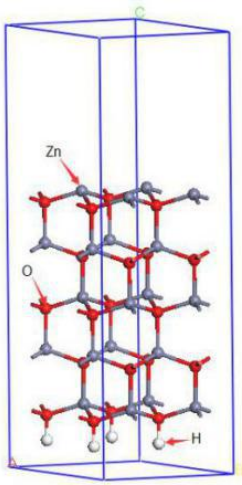

Fig. 1. Configurations of ZnO(0001)surface. Four pseudohydrogen atoms (white ball) are attached to the bottom of the cell

3 Results and discussion

3.1 Geometry structure.

By optimizing the geometry structure of the pure ZnO(0001) surface, The Zn-O bilayer spacings are 0.493Å, 0.591Å and 0.601Å for the first three pairs (counted from the surface), which are slightly smaller than the value in bulk(0.634Å). On the other hand, The Zn-Zn bilayer spacings are 2.711Å, 2.678Å, 2.663Å for the first three pairs (counted from the surface), which are slightly bigger than the value in bulk(2.638Å). This result shows that relaxation only affects the bilayer near the surface, but the relaxation of the deep bilayer is negligible. This result agrees with previous study[20].

3.2 Electrical properties.

The total density of states and projected density of states of Ag-doped ZnO (0001) surface at three layers are presented in Fig.2, respectively. From Fig. 2. We find that the Fermi levels are already in the conduction band, and the Fermi energy gradually moves into the deep conduction band as the doping layer deepened. The surface states near the conduction band minimum(CBM) are mainly contributed by the first layer of the Zn-O bilayer, and the contribution of the second and third layer Zn-O bilayers is less. Therefore, we chose projected density of states (PDOS) of Ag-doped ZnO(0001) surface at first layers to make further analysis. As shown in Fig.2.(b), The valence band maximum(VBM) of Ag-doped

ZnO(0001) surface at first layers is mainly contributed by Ag-4d and O-2p, and the conduction band minimum is mainly contributed by Zn-4s and Ag-5s.

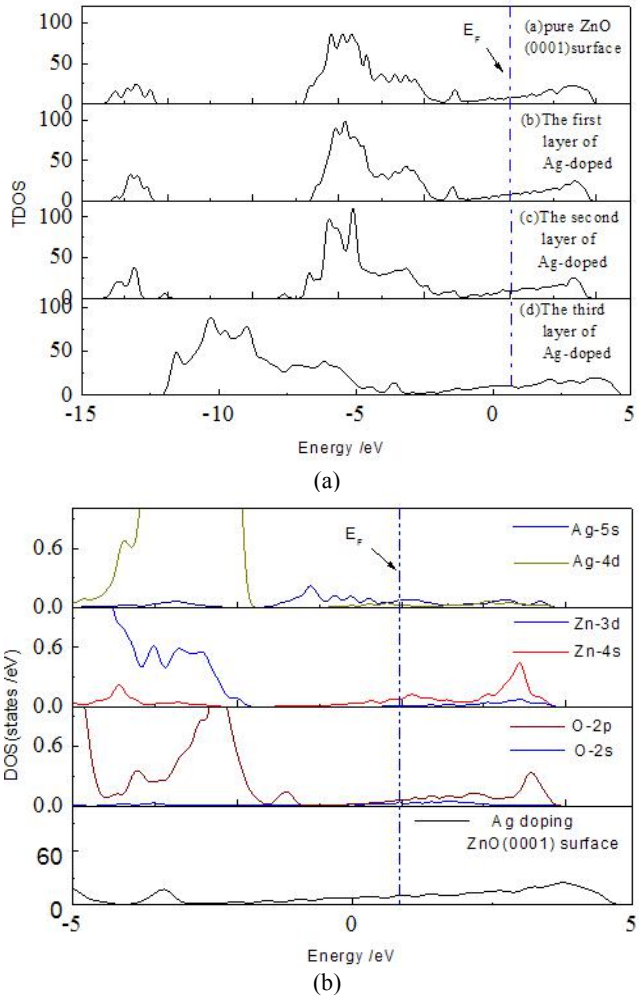

Fig. 2. (a): the total density of states (TDOS) of pure ZnO (0001) surface and the total density of states (TDOS) of Ag-doped ZnO(0001) surface. (b): projected density of states (PDOS) of Ag-doped ZnO(0001) surface at first layers.

In order to study the stability of doped surfaces, the formation energies and electrostatic potential of Ag doped with three layers on ZnO (0001) surface were calculated respectively. The formation energies are as follows: the first layer is -1.65ev; the second layer is -1.39ev; the third layer is -1.29ev. From the change of formation energy, it can be seen that the formation energy of Ag atom doped at the third layer position is highest, and the formation energy decreases gradually as the doping atom position moves to the surface. Therefore, we believe that Ag atoms are more likely to be doped on the first layer of ZnO (0001) surface.

In addition, we calculated the electrostatic potential energy of the pure ZnO (0001) surface and the electrostatic potential energy of the first layer doped Ag on the ZnO (0001) surface along the vertical surface (Z axis), as shown in Fig. 3. The electrostatic potential energy is obtained by the static calculation of the surface model after relaxation. In the calculated surface model, the work function is calculated from the electrostatic potential energy and Fermi energy. The work function is calculated as follows:

$$\phi = x - \varepsilon_F \quad (1)$$

where ϕ is work function. x is electrostatic potential energy. ε_F is Fermi energy.

From the diagram, it is found that the electrostatic potential of each layer decreases as gradually enters the surface, especially at the first layer of the surface. The electrostatic potential fluctuates greatly, and the electrostatic potential energy is lower at the position near the center of the atom, and between the two atomic layers the value is the maximum. Especially after the first layer on the Ag doped ZnO (0001) surface, the electrostatic potential energy increases obviously. The main reason is that the surface structure changes greatly after surface relaxation. Through calculation, we can get that the work function of ZnO (0001) surface is 2.212ev, and the experimental value is 2.8ev[21].

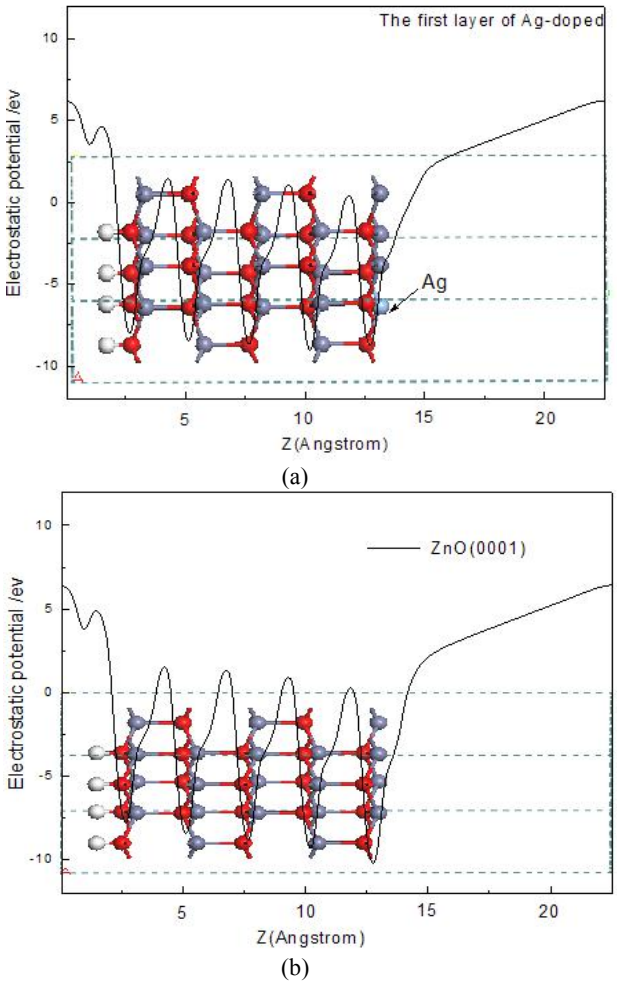

Fig. 3. (a)the electrostatic potential energy of the first layer doped Ag on the ZnO (0001)surface, (b)The electrostatic potential energy of the pure ZnO(0001) surface

3.3 Optical properties.

Sequentially, in order to reveal the relationship between the electronic structure and optical properties, it is necessary to study the imaginary part of the dielectric function. Fig.4 shows the dielectric function of pure ZnO(0001) surface and the first layer doped Ag on the ZnO

(0001) surface. As we can see from the diagram, the imaginary part of their dielectric function is basically the same. However, the peak value is higher compared to the pure surface at 1.25eV. Since each dielectric function peak corresponds to an absorption maximum, the corresponding absorption photon energy at the 1.25eVenergy is 4.23eV. This is mainly due to the electronic transitions between the two orbital levels of Ag-4d and O-2p.

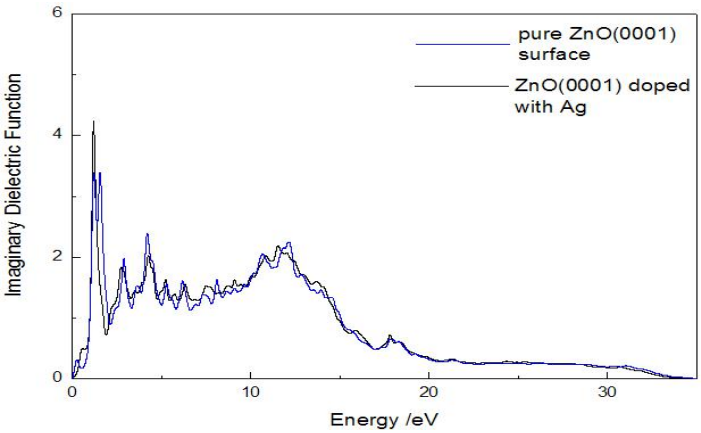

Fig. 4. the dielectric function of pure ZnO(0001) surface and the first layer doped Ag on the ZnO (0001) surface

4 Conclusions

In summary, geometrical structure, electrical properties, and optical properties of Ag-doped ZnO(0001) surface are investigated through the first-principle calculations. The calculated results show that the Fermi energy has entered into the conduction band after doping Ag, and the Fermi energy gradually move into the deep conduction band as the doping layer deepened. At the same time, we found that Ag preferred doping on the first layer of ZnO (0001) surface. From the overall point of view, the doped surface has gradually become an equipotential, showing obvious metallic characteristics. Simultaneity, A new peak is observed at 1.25eV, which is mainly due to the electronic transitions between the two orbital levels of Ag-4d and O-2p. We hope these results could provide useful information about metal atoms doped on ZnO surfaces.

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