Electronic structures of halogen-doped Cu_2O based on DFT calculations*

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(Received 13 May 2013; revised manuscript received 3 July 2013; published 12 November 2013)

In order to construct p–n homojunction of Cu_2O-based thin film solar cells that may increase its conversion efficiency, to synthesize n-type Cu_2O with high conductivity is extremely crucial, and considered as a challenge in the near future. The doping effects of halogen on electronic structure of Cu_2O have been investigated by density function theory calculations in the present work. Halogen dopants form donor levels below the bottom of conduction band through gaining or losing electrons, suggesting that halogen doping could make Cu_2O have n-type conductivity. The lattice distortion, the impurity formation energy, the position, and the band width of donor level of $Cu_2O_{1-x}H_x$ (H = F, Cl, Br, I) increase with the halogen atomic number. Based on the calculated results, chlorine doping is an effective n-type dopant for Cu_2O, owing to the lower impurity formation energy and suitable donor level.

Keywords: cuprous oxide, halogen doping, DFT calculations, n-type conductivity

PACS: 74.62.Dh, 71.20.−b, 71.20.Nr, 72.20.−i **DOI:** 10.1088/1674-1056/23/1/017401

1. Introduction

Cuprous oxide (Cu_2O) is a very suitable material for solar energy conversion, because it has many advantages, such as simple composition and structure, abundant component elements in the crust of the Earth , nontoxicity, and a direct band gap of 1.9–2.1 eV. Therefore, it has been extensively investigated in the fields of solar cells,[1–4] photocatalytic water splitting,[5–7] CO_2 reduction,[8] or photodegradation of pollution.[9,10] As an absorber material for thin-film solar cells, it was prepared by various experimental approaches,[1,11–18] and its corresponding optoelectronic properties have also been studied in detail. Up to now, the best energy conversion efficiency of Cu_2O-based thin-film solar cells is only 3.83%.[4] In fact, the theoretical limit of the energy conversion efficiency for Cu_2O-based thin-film solar cell is as high as about 20%, according to Shockley–Queisser photo balance calculations.[19]

One reason for its low conversion efficiency is nonexistence of n-type Cu_2O.[20] Cu_2O is a spontaneous p-type semiconductor, owing to the presence of a large amount of copper vacancies, which acts as a shallow and efficient hole producer.[21] The self compensation effects make it difficult to acquire n-type Cu_2O, so it is particularly challenging to prepare p–n homojunction of Cu_2O. However, it is generally accepted that a p–n homojunction of Cu_2O is the best way to increase the efficiency of Cu_2O-based solar cells.[20] Therefore, the development of n-type Cu_2O has become an important research goal and is vital for the realization of high-efficiency Cu_2O-based thin-film solar cells. In the past decades, the p–n homojuction of Cu_2O solar cells has been fabricated by two-step deposition process, but only showed a conversion efficiency of 0.1% under AM1 illumination.[15,22–25] The low efficiency is attributed to the high resistivity of p- and n-type Cu_2O, which needs to reduce the doping.[15,22] On the other hand, the origin of the n-type conductivity in these films is still a matter of debate, with oxygen vacancies or copper antisites being suggested as the source of donors.[22,26,27] For example, Raebiger *et al*. considered that oxygen vacancies could not act as a donor in Cu_2O because it has no ionization levels in the band gap.[21,28]

Doping is a common practice to control the conduction type and resistivity of Cu_2O and the relevant semiconductors.[29–33] In our previous work, we reported nitrogen-doped Cu_2O is a perfect intermediated band material for the novel kind of solar cells.[34] However, the approach of doping Cu_2O to make it n-type semiconductor has received little attention. Recently, Han *et al*. reported n-type doping of Cu_2O films by chlorine during electrodeposition.[35,36] Other groups obtained similar results.[37,38] The authors of these literatures found that Cl-doped Cu_2O has conductivity of about one order of magnitude greater than the undoped material, and chlorine acts as a donor in place of the oxygen. Bai *et al*. adopted first-principles calculations to study the n-type doping in Cu_2O synthesized from an acidic solution environment.[39] They found that F, Cl, and Br in substitution of an atom have low formation energies and present an n-type conduction behavior with donor levels below. Even though the n-type conductivity of Cu_2O has been achieved, there remain some open questions: the doping effects of halogen on the electronic structure of Cu_2O have not been reported in detail; differences of the halogens have not been compared; and the

*Project supported by the National Natural Science Foundation of China (Grant No. 21263006), the Science Research Foundation of Educational Commission of Yunnan Province, China (Grant No. 2012Y542), and the Introduced Talents Foundation of Kunming University of Science and Technology, China.

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intrinsic mechanism for halogen to improve the optoelectronic properties of Cu_2O has not been clearly elucidated yet. Therefore, to solve these issues, the crystal structure and electronic structure of halogen-doped Cu_2O are studied by ultrasoft pseudopotential plane wave method based on density functional theory (DFT) framework in the present work. Based on the calculated results, some previous experimental observations are clarified.

2. Computational methods

The supercell model of halogen-doped Cu_2O considered in the present work is the same as our previous work.[34] In the $2 \times 2 \times 2$ supercell, one oxygen atom is substituted by one halogen atom (F, Cl, Br, or I). Hence, the impurity concentration of halogen is also 2.08% (atomic fraction, equal to 1.6×10^{21} cm^{-3}) in total.

For sake of comparison, we adopt the same computational methods as that in our previous work. The periodic density functional theory package is chosen as the Cambridge serial total energy package (CASTEP) codes.[40] The exchange–correlation effects of valence electrons are described through the generalized gradient approximation (GGA) within the Perdew–Burke–Ernzerhof (PBE) function.[41] The method of GGA+U ($U_{\rm eff} = U - J = 8.5$ eV) is adopted to overcome the well-known shortcoming of GGA.[42] The energy cutoff is set as 440 eV to expand the Kohn–Sham wave functions. The minimization algorithm is chosen as the Broyden–Fletcher–Goldfarb–Shanno (BFGS) scheme.[43] Other details about the computational model and method can be referred to our previous work.[34]

3. Results and discussion

Firstly, the doping effects of halogen on crystal structure of Cu_2O are analyzed, and the calculated results are listed in Table 1. The crystal distortion caused by halogen doping is very small for all models, suggesting that Cu_2O could still keep its original exceptional photoelectric performance. Another critical parameter is the bond length between metal and nonmetal, which is listed in Table 2. From these tables, we find that the lattice distortion and the Cu–H bond length are increasingly augmenting with increasing atomic number. The impurity formation energies at neutral conditions, which were calculated in Ref. [44], indicate that the halogen impurity could be readily incorporated into the crystal lattice of Cu_2O under O-poor condition, i.e., reducing atmosphere. For these four impurities, the impurity formation energy also increases with the increase in atomic number. In the case of iodine doping, the impurity formation energy is positive under both conditions, suggesting that it is relatively difficult to prepare I-doped Cu_2O material.

The calculated band structures of all supercells are illustrated and compared in Fig. 1. The important feature in the cases of halogen doping is that the Fermi energy level shifts upwards to the bottom of conduction band (CB), and across the first energy level of CB. According to the definition of semiconductor conductivity, the first energy level of CB acts as the role of donor. This result indicates that the halogen doping could make Cu_2O have n-type conductivity. In different cases of halogen doping, the position and band width of donor level are different. For fluorine doping, the donor level is an isolated state away from the CB with a gap of 0.05 eV, and its bandwidth is about 0.85 eV. For other three halogen elements doping, the position of donor level moves upwards to the bottom of CB, and completely overlaps with the bottom of CB, resulting in the disappearance of gap between donor level and CB. At the same time, the bandwidth of donor level also broadens with increasing atomic number, as shown in Table 1. The donor level introduced by the halogen doping and the related variation of its position and width, leads to the change in the band gap of Cu_2O host, as shown in Fig. 1 and Table 1. For chlorine and bromine doping, the band gap is slightly narrowed from pure Cu_2O. While for iodine doping, the band gap is almost equal to that of pure Cu_2O. In the present work, we find that the band gap of $Cu_2O_{1-x}H_x$ broadens with increasing atomic number, owing to the donor level shifting and broaden.

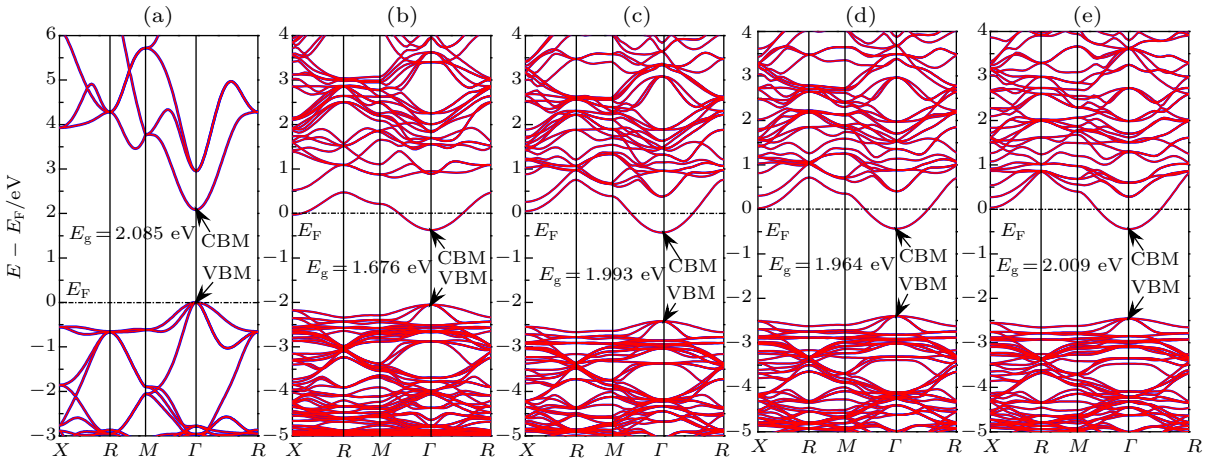


Fig. 1. (color online) The calculated band structure of (a) pure Cu_2O, (b) $Cu_2O_{1-x}F_x$, (c) $Cu_2O_{1-x}Cl_x$, (d) $Cu_2O_{1-x}Br_x$, and (e) $Cu_2O_{1-x}I_x$ along the high symmetry directions of the Brillouin zone. The blue lines represent the spin-up states, while the red lines represent spin-down states.

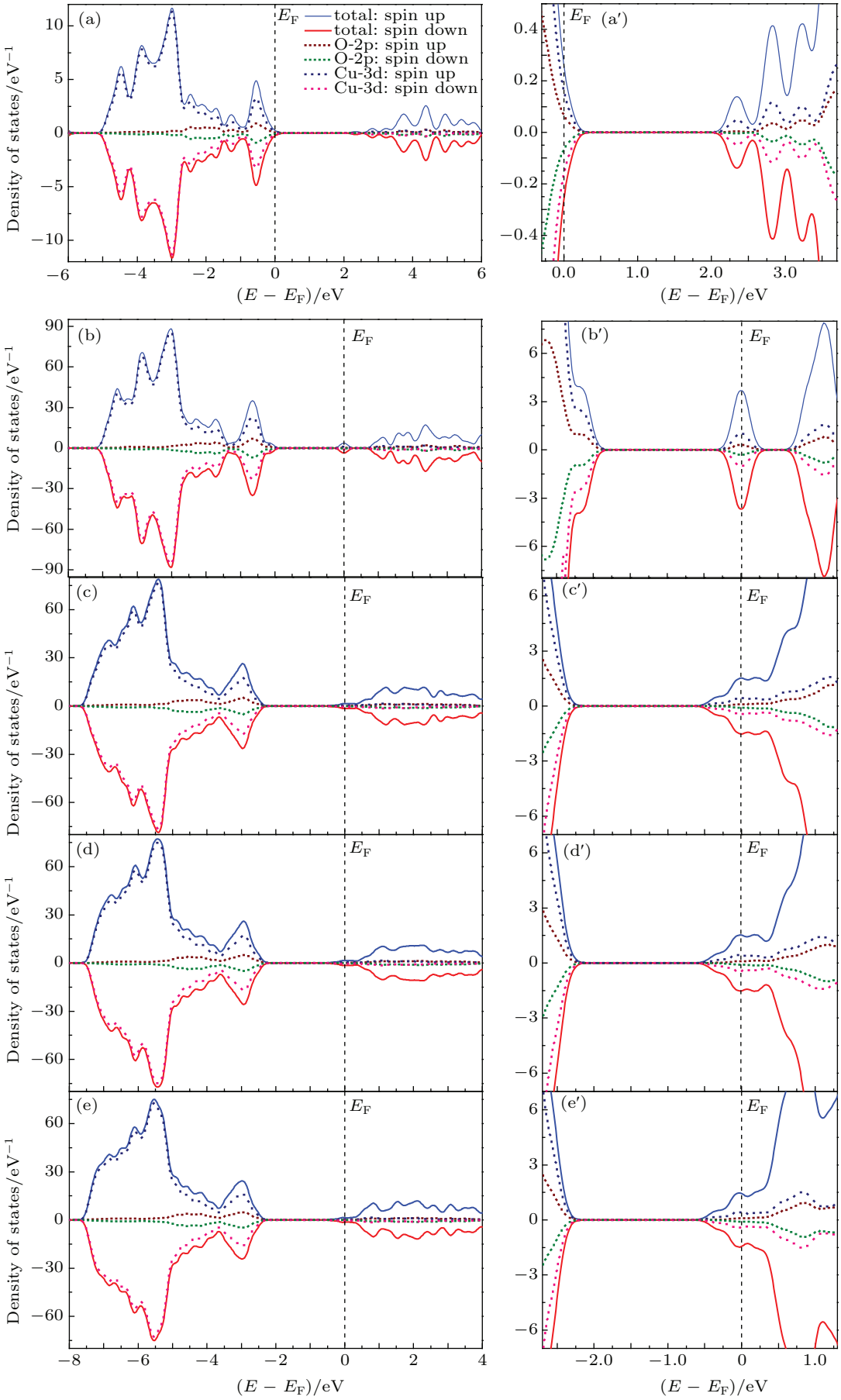


Fig. 2. (color online) The total and local partial density of states of (a) pure Cu_2O, (b) $Cu_2O_{1-x}F_x$, (c) $Cu_2O_{1-x}Cl_x$, (d) $Cu_2O_{1-x}Br_x$, and (e) $Cu_2O_{1-x}I_x$. (a')–(e') The enlarged DOS for each model.

Table 1. Calculated lattice distortion, impurity formation energy, band gap, and band width of donor level of $Cu_2O_{1-x}H_x$ in the present work.

	Δa/Å	ΔV/Å^3	Impurity formation energy/eV		Band gap/eV	Band width/eV
			O rich	O poor		
$Cu_2O_{1-x}F_x$	0.0195	1.0541	2.6783	−2.6831	1.677	0.850
$Cu_2O_{1-x}Cl_x$	0.0477	2.5986	4.1352	−1.2262	1.993	1.188
$Cu_2O_{1-x}Br_x$	0.0654	3.5806	4.8986	−0.4628	1.964	1.154
$Cu_2O_{1-x}I_x$	0.0864	4.7514	5.7315	0.3701	2.009	1.294

Table 2. Calculated Mulliken atomic and bond populations of pure Cu_2O and $Cu_2O_{1-x}H_x$ in the present work. The band length is also listed.

	Species	s	p	Total	Charge/e	Bond	Length/Å	Population/e
Cu_2O[34]	O	1.81	4.83	6.64	−0.64	Cu-O	1.8340	0.33
$Cu_2O_{1-x}F_x$	F	1.95	5.44	7.39	−0.39	Cu-F	1.9675	0.17
$Cu_2O_{1-x}Cl_x$	Cl	1.88	5.07	6.59	0.41	Cu-Cl	2.1027	0.35
$Cu_2O_{1-x}Br_x$	Br	0.09	4.92	4.92	2.08	Cu-Br	2.2314	0.18
$Cu_2O_{1-x}I_x$	I	0.24	4.63	4.87	2.13	Cu-I	2.3763	0.13

In order to clearly analyze the chemical bonding mechanism, the corresponding total density of states (DOS) and local partial DOS are illustrated in Fig. 2. The p states of halogen are mainly concentrated in the energy range from −13.5 V to −12 eV, with a very narrow band width of about 0.4 eV. This calculated result suggests that their valence electron states indirectly contribute to the constitution of band edge near the band gap. In other words, the constitutions of bandedge of $Cu_2O_{1-x}H_x$ near the band gap almost have the same features as pure Cu_2O. The difference is that the first peak of CB of pure Cu_2O becomes the donor level due to halogen doping effects, and the corresponding position and band width vary with the atomic number of dopants. Based on these calculated results, we could draw a conclusion that $Cu_2O_{1-x}H_x$ should have a different optical absorption band above the fundamental absorption band, due to the presence of donor level. In particular, this phenomenon should be more noticeable in the case of fluorine doping. Thus, our calculated results could explain some experimental observations.[24]

The electron localization function (ELF) is an important tool to study electronic structure, especially for chemical bonding states.[45,46] In Fig. 3, the ELF of $Cu_2O_{1-x}H_x$ is plotted and compared. For fluorine doping, the electron localization states around fluorine atoms are only slightly varied, in comparison with oxygen atoms. Thus, the covalent bonding nature of $Cu_2O_{1-x}F_x$ does not change. While in additional three halogen dopings, the electron localization states around dopant (Cl, Br, or I) atoms are more obvious than that of neighboring oxygen atoms, and concentrated on the Cu–H bonds. Thus, in the cases of $Cu_2O_{1-x}H_x$ (H = Cl, Br, I), the ionic bonding nature are more prominent. In order to have a deeper understanding of this phenomenon, we analyze the electron density difference and Mulliken atomic and bond populations, as shown in Fig. 4 and Table 2. In the case of $Cu_2O_{1-x}F_x$, the situation of electron gaining around fluorine atoms is very similar to oxygen atoms, but the magnitude is slightly weaker than that of the latter. However, in the cases of $Cu_2O_{1-x}H_x$ (H = Cl, Br, I), the dopant atoms gain electrons along the direction of Cu–H bond, while they lose electrons on the opposite directions. Furthermore, the magnitude of electron gaining or losing augments with increasing atomic number. Based on the above calculated results, we believe that halogen dopants form the donor levels below the bottom of CB through electron gaining or losing on different directions, although their valence electrons are not directly involved in the constitution of band edge near the band gap. Owing to the lower impurity formation energy and suitable donor level, chlorine doping is an effective n-type dopant for Cu_2O.

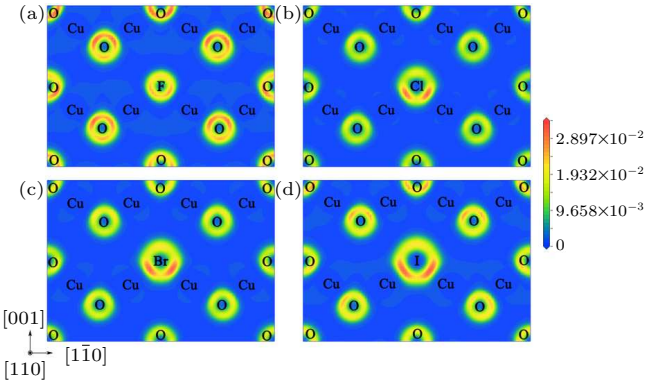


Fig. 3. (color online) The electron localization function of (a) $Cu_2O_{1-x}F_x$, (b) $Cu_2O_{1-x}Cl_x$, (c) $Cu_2O_{1-x}Br_x$, and (d) $Cu_2O_{1-x}I_x$ through the (110) plane.

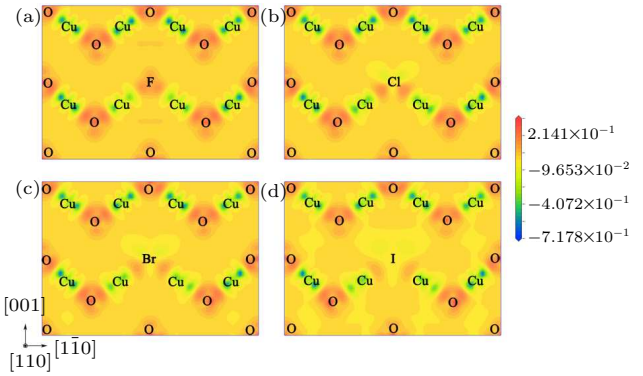


Fig. 4. (color online) The calculated electron density difference of (a) $Cu_2O_{1-x}F_x$, (b) $Cu_2O_{1-x}Cl_x$, (c) $Cu_2O_{1-x}Br_x$, and (d) $Cu_2O_{1-x}I_x$ through the (110) plane.

4. Conclusions

The doping effects of halogen on the electronic structure of Cu_2O have been investigated by density function theory calculations. Halogen dopants form the donor levels below the bottom of CB through electron gaining or losing in different directions, although their valence electrons are not directly involved in the constitution of band edge near the band gap. Thus, halogen doping could make Cu_2O have n-type conductivity. The atomic number of halogen determines the doping effects, such as lattice distortion, impurity formation energy, position, and the band width of donor level. Based on the calculated results, chlorine doping proves to be an effective n-type dopant for Cu_2O. The calculated results in the present work may be useful for future studies on the photovoltaics applications of Cu_2O.

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