First-principles study of fluorine-doped zinc oxide

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We present first-principles calculations for fluorine-doped zinc oxide (ZnO:F) by using density-functional theory. Under O-poor condition, fluorine substitution for oxygen (F_O) is energetically favorable in ZnO. F_O can effectively diminish oxygen vacancies. With high fluorine concentration, fluorine interstitial (F_i) may appear. The high transition energies of F_O and F_i suggest that F_O and F_i could act as deep donor and acceptor which cannot provide free carriers in ZnO at room temperature. The increase of carriers and mobility in ZnO:F could not contribute from deep donor F_O, but may be due to the surface passivation effect of fluorine. © *2010 American Institute of Physics*. [doi:10.1063/1.3492444]

Zinc oxide (ZnO) is a wide-band-gap semiconductor and has been receiving much attention in recent years due to its optoelectronic applications in ultraviolet lasers,[1,2] solar cells,[3] ultraviolet detection,[4] light-emitting diodes,[5] thin film transistor,[6] and liquid crystal displays as a substitute for indium tin oxide.[7]

Fluorine, the radius of which is close to that of oxygen, could be an appropriate anion doping candidate. A lower lattice distortion could be expected for F doping, compared with Al, Ga, and In doping. Recent investigations reveal that doping fluorine with low concentration in ZnO thin film could significantly improve the transmittance in visible region and the mobility of carries. Therefore, fluorine-doped zinc oxide (ZnO:F) thin films with such advantages could be applied for transparent electrodes in thin film silicon solar cell.[8] A giant linear electro-optics (Pockels) effect (up to 17 pm V^{-1} for wavelength about 435 nm) could been achieved in ZnO:F crystalline films deposited on bare glass.[9] ZnO:F thin films can be deposited by many techniques such as radio frequency magnetron sputtering,[10,11] spray pyrolysis,[12,13] and sol gel.[7,14] ZnO:F nanocrystalline films can also been prepared from thermal oxidation of ZnF_2 films deposited on a silica substrate by electron beam evaporation.[15]

First-principles method is a powerful tool to understand the native point defects in ZnO.[16,17] However, no theoretical investigation of F-doped ZnO has been reported.

In this paper, the first-principles pseudopotential method was used to calculate the defect formation energies and electrical transition levels in ZnO:F. The calculated results were discussed in detail, combining with available experimental phenomenon.

Density functional theory calculations within the local-density approximation (LDA) in the Teter–Pade[18] were performed using plane-wave pseudopotential code ABINIT.[19,20] Norm-conserving Troullier–Martins[21] type pseudopotentials for Zn, O, and F were used. The calculated formation enthalpies of ZnO and ZnF_2, shown in Table I, were highly consistent with the experimental data.[22] The 72-atom supercell with $3\times3\times2$ in the x,y,z directions obtained by repeating the optimized structure of perfect unit cell was used in the defect calculations.

The formation energy $\triangle H_f\ (q)$ is a function of both of the electron Fermi energy E_F and the chemical potentials of the species involved in the defects.[23]

$$\Delta H_f(q) = \Delta E(q) + n\mu_O - \mu_F + qE_F. \quad (1)$$

Where

$$\Delta E(q) = E(\text{defect},q) - E(\text{perfect}) + n\mu_O^0 - \mu_F^0 + qE_{VBM}, \quad (2)$$

and where $E(\text{defect},q)$ is the total energy of the fluorine-doped supercell with charge q. $E(\text{perfect})$ is the total energy of the perfect supercell. n is the number of oxygen atom removed from the supercell. μ_O and μ_F are the chemical potential of O and F relative to their chemical potential μ_O^0 and μ_F^0 in elemental phase. E_{VBM} is the energy of valence-band maximum. E_F is the Fermi energy of the electrons referenced to the VBM of ZnO. The details of calculation could been found in literature.[24]

The defect transition energy level $\varepsilon_\alpha(q/q')$ is defined as the value of the Fermi level where the formation energy of q equals that of q' of the same defect, i.e.,

$$\varepsilon_\alpha(q/q') = [\Delta E(q) - \Delta E(q')]/(q' - q). \quad (3)$$

Taking into account the restriction of the chemical potentials according to the method described in literature,[24] the calculated stability triangle for ZnO:F systems in the μ_O and μ_F plane is constructed and shown in Fig. 1. The dashed zone represents the region of stability of ZnO. The labels A, B, and C represent (O-rich and F-rich) limit, (O-rich and F-poor) limit and (O-poor and F-poor) limit, respectively.

Table II summarizes the formation energies of F_O and F_i at points A, B, and C defined by Fig. 1. In Table II, the Fermi energy E_F is set at valence band maximum (VBM) or con-

TABLE I. Formation enthalpies (in eV) of ZnO and ZnF_2.

Constituents	Calculated data (this work)	Experimental data (Ref. 22)
$Zn+\frac{1}{2}O_2\rightarrow ZnO$	−3.56	−3.63
$Zn+F_2\rightarrow ZnF_2$	−4.22	−4.30

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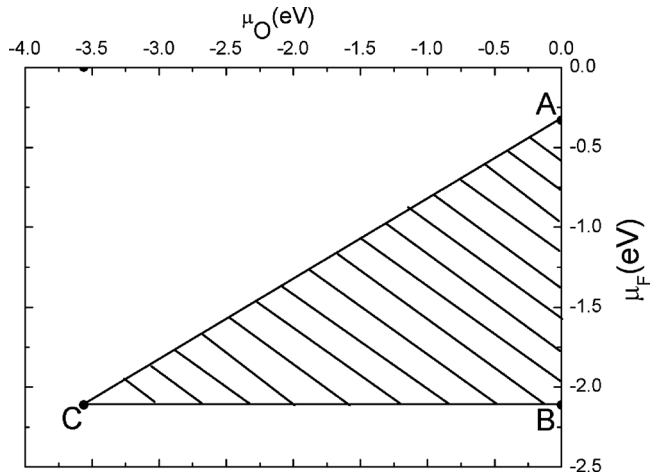

FIG. 1. Calculated stability triangle for ZnO:F systems in the μ_O and μ_F plane.

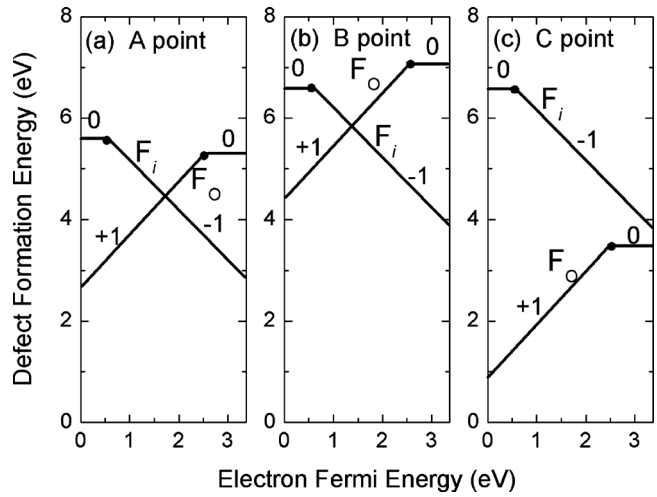

FIG. 2. Formation energies of F_O and F_i in ZnO as a function of the electron Fermi energy E_F at atomic chemical potentials A, B, and C shown in Figs. 1(a)–1(c), respectively. The signed numbers stand for the charge states of defects. Solid dots denote the values of E_F where transition between charge states occurs.

duction band minimum (CBM), which is corresponding to p-type or n-type ZnO, respectively. The defect formation energies, shown in Fig. 2, are strongly dependent on E_F for the charge states. It is evident that F_O has the lowest formation energies under the O-poor condition (C point), compared with those under the O-rich condition (A and B). First-principles calculations by Janotti *et al.*[16] have found that oxygen vacancy has the lowest formation energy and acts as the dominant defect species under Zn-rich (O-poor) condition. Therefore, less energy is required for fluorine atom entering into the site where the oxygen vacancy forms. From Fig. 2(c), it should be noted that the formation energy of F_O is much lower in p-type ZnO than that in n-type ZnO, where F_O is assumed to be 1+ charge state. F_O acts as a deep donor with the transition energy level $\varepsilon(0/+)$ at 0.762 eV below the CBM, shown in Fig. 3.

In the wurzite structure ZnO, the fluorine atom could occupy the tetrahedral interstitial site or octahedral interstitial site. The calculation results indicate that only octahedral interstitial site could be stably occupied. As shown in Fig. 2, the formation energies of F_i are relatively high, even under the F-rich condition. F_i could act as a deep acceptor with the transition energy level $\varepsilon(-/0)$ at 0.672 eV above the VBM, shown in Fig. 3.

The high transition energies indicate that neither F_O nor F_i can provide carries to the continuous band (conduction band or valence band) by thermal excitation in steady state at room temperature. It is suggested that one cannot achieve n-type or p-type ZnO at room temperature through doping fluorine. However, F_O or F_i can be a potential source of compensation in p-type or n-type ZnO, respectively.

TABLE II. Formation energies (in eV) of F_O and F_i at points A, B, and C defined by Fig. 1. The Fermi energy E_F is set at VBM and CBM which is corresponding to n-type and p-type ZnO, respectively.

E_F	Defect	A	B	C
VBM	F_O	2.674	4.454	0.894
	F_i	5.554	6.554	6.554
CBM	F_O	5.282	7.062	3.502
	F_i	2.856	3.856	3.856

It is evident that F_O is energetically favorable and could be dominant in ZnO:F, which has been experimentally supported.[15] Fluorine ions occupied at oxygen sites could result in a diminishing of the oxygen vacancies, which can been confirmed by the decrease in the absorption and emission spectra in the visible region due to oxygen vacancies.[25] Due to the high activation energy of donor F_O (0.762 eV), the increase in carrier concentration and mobility of ZnO:F could not attribute to the electrons from donor F_O. In fact, in nanocrystal thin film of ZnO, a considerable amount of surface dangling bonds can trap free carriers and decrease the mobility of carriers. Fluorine ions at grain boundaries could cause surface passivation effect by saturating these dangling bonds and thus increase carrier concentration and mobility.[15]

With high fluorine doping concentration, F_i could appear and act as deep acceptors. The high concentration fluorine in ZnO films may lead to the change in grain size and increase the scattering process, and therefore the majority carries mobility is decreased.[26]

Both F_O and F_i in ZnO could cause the noncentrosymmetric charge density distribution which may lead to the enhancement of the linear electro-optics effect.[9]

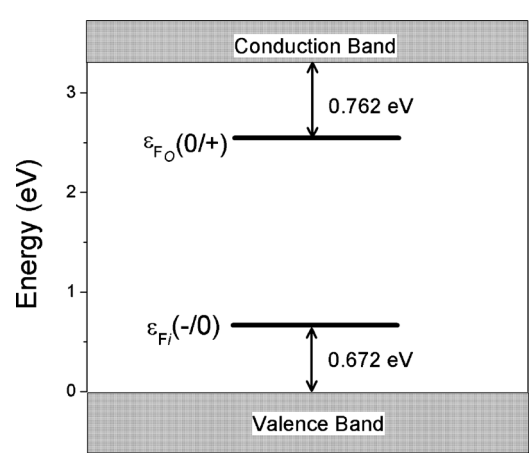

FIG. 3. Calculated transition energy levels of F_O and F_i in ZnO.

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In summary, the calculations of formation energies for fluorine in ZnO indicate that under O-poor condition, F_O has lower formation energy than that of F_i. With high fluorine concentration, fluorine ions may form interstitials. F_O and F_i could act as deep donor and acceptor with high activation energies of 0.762 eV and 0.672 eV, respectively, indicating that neither F_O nor F_i can provide free carriers at room temperature. F_O could play an important role in diminishing oxygen vacancies which is responsible for absorption in visible region. The fact that doping fluorine with low concentration can increase the carriers and mobility could be explained by the surface passivation effect of fluorine.

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[1]H. Cao, J. Y. Xu, E. W. Seeling, and R. P. H. Chang, Appl. Phys. Lett. **76**, 2997 (2000).
[2]Z. K. Tang, G. K. L. Wong, P. Yu, M. Kawasaki, A. Ohtomo, H. Koinuma, and Y. Segawa, Appl. Phys. Lett. **72**, 3270 (1998).
[3]V. Kruefu, E. Peterson, C. Khantha, C. Siriwong, S. Phanichphant, and D. L. Carroll, Appl. Phys. Lett. **97**, 053302 (2010).
[4]S. N. Das, K.-J. Moon, J. P. Kar, J.-H. Choi, J. Xiong, T. I. Lee, and J.-M. Myoung, Appl. Phys. Lett. **97**, 022103 (2010).
[5]T. Aoki, Y. Hatanaka, and D. C. Look, Appl. Phys. Lett. **76**, 3257 (2000).
[6]P. F. Carcia, R. S. McLean, M. H. Reilly, and G. Nunes, Appl. Phys. Lett. **82**, 1117 (2003).
[7]T. Minami, Thin Solid Films **516**, 5822 (2008).
[8]F. Yakuphanoglu, Y. Caglar, S. Ilican, and M. Caglar, Physica B **394**, 86 (2007).
[9]I. V. Kityk, J. Ebothe, A. E. Hichou, M. Addou, A. Bougrine, and B. Sahraoui, J. Phys.: Condens. Matter **14**, 5407 (2002).
[10]Y.-Z. Tsai, N.-F. Wang, and C.-L. Tsai, Thin Solid Films **518**, 4955 (2010).
[11]H. S. Yoon, K. S. Lee, T. S. Lee, B. Cheong, D. K. Choi, D. H. Kim, and W. M. Kim, Sol. Energy Mater. Sol. Cells **92**, 1366 (2008).
[12]P. M. Ratheesh Kumar, C. Sudha Kartha, K. P. Vijayakumar, F. Singh, and D. K. Avasthi, Mater. Sci. Eng., B **117**, 307 (2005).
[13]A. Sanchez-Juarez, A. Tiburcio-Silver, A. Ortiz, E. P. Zironi, and J. Rickards, Thin Solid Films **333**, 196 (1998).
[14]S. Ilican, Y. Caglar, M. Caglar, and F. Yakuphanoglu, Appl. Surf. Sci. **255**, 2353 (2008).
[15]H. Y. Xu, Y. C. Xu, R. Mu, C. L. Shao, Y. M. Lu, D. Z. Shen, and X. W. Fan, Appl. Phys. Lett. **86**, 123107 (2005).
[16]A. Janotti and C. G. V. d. Walle, Phys. Rev. B **76**, 165202 (2007).
[17]A. F. Kohan, G. Ceder, D. Morgan, and C. G. V. d. Walle, Phys. Rev. B **61**, 15019 (2000).
[18]S. Goedecker, M. Teter, and J. Hutter, Phys. Rev. B **54**, 1703 (1996).
[19]The ABINIT code is a common project of the Université Catholique de Louvain, Corning Incorporated, and other contributors. http://www.abinit.org.
[20]X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, P. Ghosez, J.-Y. Raty, and D. C. Allan, Comput. Mater. Sci. **25**, 478 (2002).
[21]N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
[22]J. A. Dean, *Lange's Handbook of Chemistry*, 14th ed. (McGraw-Hill, New York, 1992).
[23]S. B. Zhang and J. E. Northrup, Phys. Rev. Lett. **67**, 2339 (1991).
[24]B. Liu, Z. Qi, and C. Shi, Phys. Rev. B **74**, 174101 (2006).
[25]R. Gonzalez-Hernandez, A. I. Martinez, C. Falcony, A. A. Lopez, M. I. Pech-Canul, and H. M. Hdz-Garcia, Mater. Lett. **64**, 1493 (2010).
[26]A. Sanchez-Juarez, A. Tiburcio-Silver, and A. Ortiz, Sol. Energy Mater. Sol. Cells **52**, 301 (1998).

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