Suppression of the formation of interstitial Li through (F, Li) codoping ZnO

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Abstract. Based on the first-principles calculations with density functional theory, the formation energy and electronic structure of (F, Li) codoping ZnO has been investigated, where the configurations including related defects for the ratio of 1:1 of (F, Li) codoping ZnO, and the ratio of 1:2 of (F, Li) codoping ZnO are studied. The calculated results show that the formation energy of F\textsubscript{O}\textsubscript{-}Li\textsubscript{Zn} is lower than that of F\textsubscript{O}\textsubscript{-}Li\textsubscript{i} when the Fermi level approaches the valence band under the O-rich condition, which indicates that the (F, Li) codoping can suppress the Li interstitial. Furthermore, it is found the formation energy of F\textsubscript{O}\textsubscript{-}2Li\textsubscript{Zn} reduces more dramatically than that of F\textsubscript{O}\textsubscript{-}Li\textsubscript{i}. Moreover, the ionization energy of F\textsubscript{O}\textsubscript{-}2Li\textsubscript{Zn} is also lower than that of F\textsubscript{O}\textsubscript{-}Li\textsubscript{i}. It is found, for F\textsubscript{O}\textsubscript{-}2Li\textsubscript{Zn} complex, an occupied state at the top of valence band is formed, meaning that the presence of F, not only enhances the acceptor concentration, but also leads to shallower acceptor level. Therefore, we draw a conclusion that the presence of F atom could suppress the formation of interstitial Li, and F\textsubscript{O}\textsubscript{-}2Li\textsubscript{Zn} may form good p-type tendency in ZnO. Our results are in good agreement with the experiment results.

1. Introduction

Because of wider band gap (3.4 eV) and larger binding energy (60 meV) [1], ZnO is suitable for short wavelength device applications, such as blue and ultraviolet lasers, light-emitting diodes, and solar cells. To realize ZnO-based optoelectronic devices, n-type and p-type are essential. However, it is difficult to dope p-type in ZnO, because of a low solubility of the dopants and high defect ionization energy, and intrinsic defects, such as Zn interstitial, O vacancy, which may act as acceptor compensation centers, make it even more difficult to achieve p-type ZnO [2]. The doping asymmetry problems have hindered potential applications of ZnO materials. So, many groups have employed monodoping ways to realize p-type conductivity ZnO, such as N [3], Li [4], and Ag [5]. C.H. Park et al. [6] pointed out: although N is considered as a good p-type dopant, because of the smallest atomic size and lowest p-orbital energy, it is difficult to obtain better quality p-type ZnO due to the deep acceptor level of 0.4 eV relative to the valence band maximum (VBM). For Li doping ZnO, despite shallow Li acceptor levels, the hole density of these compounds was fairly low. The reason is that interstitial Li acting as donors compensate Li acceptors. So the compensation of Li acceptors by interstitial Li is a serious problem to realize p-type ZnO by Li-doping [7]. Later, Tetsuya Yamamoto et al. [8] have reported p-type doping using Li, N or As species causes an increase in Madelung energy,
n-type doping using B, Al, Ga, In or F species gives rise to a decrease in Madelung energy. Simultaneously, Tetsuya Yamamoto et al. have found that codoping using reactive codopants, Al, Ga, or In, enhances the incorporation of N acceptors in p-type codoped ZnO, and found the delocalized states of N for p-type ZnO codoped with N and Al [9]. So many groups have managed to gain p-type ZnO by codoped ZnO, such as N-Li [10], N-Ag [11], N-Mg [12], N-Zr [13], N-Al [14], and N-P [15]. Lately, Young et al. [16] have reported that the effects of co-doping with fluorine on properties of ZnO thin films grown by pulsed-laser deposition. They have pointed that an ambiguous carrier type was observed in Li-F codoped ZnO films grown at a temperature of 500°C with the oxygen pressures of 20 and 200 mTorr. K.Kobayashi et al. [17] have proposed that Li, F-codoped ZnO films have been prepared by simultaneous evaporation of LiF at 780°C during ZnO growth. They found that the codoped ZnO film has the resistivity of 79 $\Omega$ cm and the electron density of $6.8 \times 10^{16}$ cm$^{-3}$. However, there are few reports about the mechanism of (F, Li) codoping ZnO from theoretical calculations based on the first principles.

In this paper, we proposed codoping method for fabricating low resistivity p-type ZnO with F and Li, based on first-principles calculations, where the formation energy, electronic structure have been investigated. The formation energy of F$_o$-Li$_{Zn}$ is lower than that of F$_o$-Li, under O-rich condition, which indicates that F$_o$-Li$_{Zn}$ can suppress the formation of F$_o$-Li. It is also found that F$_o$-Li$_{Zn}$ form the passivated complex, which demonstrates as an intrinsic state, and could not realize p-type ZnO. So we proposed a new method of one F atom and two Li atoms codoping in ZnO, which can promote good p-type ZnO. The calculated results support and help recent experiment results [16, 17].

2. Calculation models and methods

2.1. Calculation models
In order to investigate the possibility of achieving p-type ZnO using F and Li codoping, we have constructed the configuration with a 2x2x2 supercell of ZnO. The F atom prefers to occupy the O site. The Li atom can choose two sites: one is occupying the Zn site, and the other is occupying the interstitial. The interstitial coordinate is (0.5, 0.5, 0.625). So, the models can be listed: model a: pure-ZnO (32 atoms), model b: one F atom substitutes O site and Li substitutes Zn site (F$_o$-Li$_{Zn}$), model c: F substitutes O site and Li is located in interstitial (F$_o$-Li$_i$), model d: F substitutes O site and two Li substitutes Zn sites (F$_o$-2Li$_{Zn}$). All models can be seen in Fig.1c-1d.
2.2. Calculation methods

All calculations were carried out using the density functional theory with the generalized gradient approximation (GGA) and the projector augmented wave (PAW) pseudo-potentials, as implemented in the VASP codes [18][19]. A gamma centred 5x5x3 k-point mesh for the Brillouin zone was employed. The energy cutoff is 450 eV. We determined the crystal structure of the models by minimizing the total energy. The total energy calculations show that the formation of the F and Li atoms occupied the nearest neighbour sites is favourable. All atoms have been fully relaxed until the force on each atom was below 0.01 eV/Å. By optimizing the geometry of the pure-ZnO, we got the lattice parameters as follows: a= 3.281 Å, b= 3.281 Å, c= 5.277 Å, c/a= 1.608. They are in good agreement with the experimental results [20], which imply that our calculation methods are reasonable, and our calculated results should be authentic.

The formation energy \( E_f(D,q) \), with a defect D at charge state q, can be calculated as [21]

\[
E_f(D,q) = [E_{\text{tot}}(D,q) - E_{\text{tot}}(ZnO)] + \sum_i n_i \mu_i + q(E_F + E_{VBM})
\]

where \( E_f(D,q) \) is the defect formation energy for the studied complex. \( E_{\text{tot}}(D,q) \) is the total energy of a supercell containing the defect D at the charge state q. \( E_{\text{tot}}(ZnO) \) is the energy of the pure ZnO in the same supercell. \( E_F \) is the Fermi energy level with respect to the valence band maximum (VBM) of the host, which varies up to the experimental value of 3.4 eV. \( E_{VBM} \) is the VBM of the pure ZnO. \( \mu_i \) is the chemical potential of the elements. \( \mu_i \) (bulk) is the energy of the bulk material. From the equation: \( 2\mu_L + \mu_F = \Delta H_f(ZnO) \), we can get: The formation energy \( (H_f(ZnO)) \) of ZnO is calculated to be -3.449 eV, as compared to the other calculated value of -3.525 eV [22]. To calculate the formation energies, we use Li, O, LiF as the Li and F sources, respectively. The maximum chemical potentials of Li and F satisfy the following two relations:

\[
2\mu_L + \mu_O = \Delta \mu_{Li,O}
\]

\[
\mu_L + \mu_F = \Delta \mu_{Li,F}
\]

3. Results and discussion
3.1. Formation energy of F-Li codoping ZnO
Fig. 2 shows the formation energies of various dopant systems. Under Zn-rich condition (as shown in Fig. 2a), the formation energy of $F_0{\cdot}2Li_{zn}$ is higher than that of $F_0{\cdot}Li_{zi}$ when the Fermi level is close to the VBM, indicating that it is not available for p-type for F-2Li codoping ZnO under this condition. Simultaneously, when $E_F < 0.6$ eV, the formation energy of $F_0{\cdot}Li_{zi}$ is lower than that of $F_0{\cdot}Li_{zs}$. However, when $E_F > 0.6$ eV, the formation energy of $F_0{\cdot}Li_{zi}$ is higher than that of $F_0{\cdot}Li_{zs}$. There is a crossing point between the formation energies of $F_0{\cdot}Li_{zs}$ and $F_0{\cdot}Li_{zi}$, thus it is unlikely to play an important role in p-type conductivity. So, Zn-rich condition is not suitable for the p-type doping. These results are also consistent with the experiment results [17].

On the contrary, under O-rich condition (as shown in Fig. 2b), the formation energy of $F_0{\cdot}2Li_{zs}$ is lower than that of others when the Fermi level is close to the VBM. That is to say, $F_0{\cdot}2Li_{zs}$ is easy to form, and it could be effective to incorporate the donors and acceptors into the system. Furthermore, $F_0{\cdot}2Li_{zs}$ bring about the lowering the acceptor level, which indicates that the acceptor could be activated easily. Simultaneously, it also indicates that O-rich condition is better for p-type doping than Zn-rich condition. Therefore, we can conclude that codoping with F atom and two Li atoms is more favorable to realize good p-type ZnO under O-rich condition, which suppresses the formation of interstitial Li.

![Figure 2. Formation energies of various dopants systems.](image)

3.2. Electronic structure
Firstly, we performed a calculation on the total density of states (TDOS), partial density of states (PDOS), and band structure of $F_0{\cdot}2Li_{zs}$ complex, as shown in Fig. 3. All energies are relative to the respective Fermi energies. It is found that the conduction bands are mainly introduced by Zn-s, F-p and O-p states. The valence bands are divided into two parts: the lower valence bands are mainly determined by the F-s and O-s states, and the upper valence bands are mainly introduced by the F-p, O-p and Zn-d states. The hybridization between Zn-d, Li-p and F-p, O-p states, which are near the top of the valence band, leads to the shallower acceptor level. We can see that the Fermi level is located on the valence band (as shown in Fig. 3a). It can be observed that some additional peaks appear near the VBM. F atom and Li atoms introduced in ZnO can contribute to the additional peak near the Fermi level. So, $F_0{\cdot}2Li_{zs}$ complex could generate a fully occupied impurity band above the VBM, which can increase the hole concentration, implying the characteristic of p-type ZnO. In Fig. 3b, a new occupied impurity band is generated at the top of the valence band. The acceptor level is expected to decrease when additional Li atoms are introduced into the system for (F, 2Li) codoping ZnO, since electrons may transit from the impurity band. So it indicates that $F_0{\cdot}2Li_{zs}$ complex is favorable for fabricating p-type ZnO.
Then, we have a detail comparison of TDOSs between the pure-ZnO and F$_2$Li codoping ZnO complex as shown in Fig.4a. Compared with the TDOS of the pure-ZnO, it is found that there is an additional peak near the Fermi level for F-2Li codoping ZnO. It demonstrates that F$_2$Li codoping does not change the basic electronic structure, which is similar to the pure-ZnO, but generates an additional fully occupied impurity band above the VBM, which is consistent with the cases of N-Zr [13] and N-Ga [23]. From Fig.3b and Fig.4b, we also can see that the basic structures have not been changed, but a new occupied band generates at the top of valence band, indicating that F-2Li codoping could obtain p-type conductivity ZnO.

Next, we investigated the influence of F-Li codoping related defect upon the p-type ZnO. The PDOSs of F$_2$Li$_{in}$ complex and F$_{2s}$Li$_{in}$ complex are shown in Fig.5a. It is observed that F$_{2s}$Li$_{in}$ demonstrates as an intrinsic state, because F-Li codoping forms the passive complex. So, there is no peak value at the top of the valence band, which is similar to that of pure-ZnO. That indicates F-Li codoping could not promote p-type ZnO. Fig.5b shows that the Fermi level enters the conduction band, which forms the donor level. The donor level is mainly introduced by Zn-s and O-p states. Therefore, self-compensation would be expected to generate, if the two complexes are coexisting in the system under Zn-rich condition. However, has been discussed earlier, the formation energy of F$_2$Li$_{in}$ is lower
than that of F\textsubscript{O}\textsubscript{2}-Li under O-rich condition. So, if we can control the growth condition available, F\textsubscript{O}\textsubscript{2}-Li\textsubscript{2z} complex could suppress the formation of Li interstitial.

![Figure 5a. PDOS of F\textsubscript{O}\textsubscript{2}-Li\textsubscript{2z}.](image1)

![Figure 5b. PDOS of F\textsubscript{O}\textsubscript{2}-Li\textsubscript{i}.](image2)

![Figure 6a. TDOSs of various dopants systems.](image3)

![Figure 6b. Amplified curve near the band gap.](image4)

In order to compare with the electronic structures of the system about the related defects in F-Li codoping ZnO, the TDOSs have been plotted (as shown in Fig.6). In the graphs, the Fermi levels have been set as zero. For F\textsubscript{O}\textsubscript{2}-Li\textsubscript{2z}, it demonstrates as an intrinsic state, because F-Li forms the fully passive complex. However, for F\textsubscript{O}\textsubscript{2}-Li\textsubscript{i}, the Fermi level is located at the conduction band minimum, indicating that behave as a donor. By contrast, for (F, 2Li) codoping in ZnO, it can be seen that the Fermi level is moved into the valence band, which implies good transfer characteristics of charge carriers. And the impurity peak is generated, which possibly demonstrate the characteristic of p-type ZnO. Therefore, we have proposed a new method of F-2Li codoping ZnO. It could be concluded that p-type conductivity is easier to achieve under O-rich condition for F\textsubscript{O}\textsubscript{2}-2Li\textsubscript{2z} complex when we control the growth condition availably.

4. Conclusions

The calculations, including the structure, formation energy and electronic structure of F-Li codoping in ZnO, have been performed. The calculated results indicate: F\textsubscript{O}\textsubscript{2}-Li\textsubscript{2z} complex and F\textsubscript{O}\textsubscript{2}-Li\textsubscript{i} complex have the effect of compensation under Zn-rich condition, while the formation energy of F\textsubscript{O}\textsubscript{2}-Li\textsubscript{2z}
complex is lower than that of \( \text{F}_0\text{-Li} \) complex under O-rich condition. Interestingly, it was found that the presence of F atom could suppress the formation of interstitial Li and \( \text{F}_0\text{-2Li}_\text{Zn} \) forms as a shallower acceptor, which is benefit for gaining good p-type ZnO.

Acknowledgments

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