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DESIGN OF SHALLOW P-TYPE DOPANTS IN ZNO

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ABSTRACT

   Due to the large electronegativity of the oxygen, the ionization energies of acceptors in metal oxides such as ZnO is quite high, making p-type doping a great challenge for the full utilization of ZnO as optoelectronic materials. By analyzing the defect wavefunction characters, we propose several approaches to lower the acceptor ionization energy in ZnO by codoping acceptors with donor or isovalent atoms. We also proposed a universal approach to overcome the doping polarity problem for wide-band-gap semiconductors. This approach can reduce the ionization energies of dopants and the spontaneous compensation from intrinsic defects by effective doping of impurity bands, which can be achieved by introducing passive donor-acceptor complexes or isovalent impurities. The approaches described here for ZnO can be easily extended to other transparent conducting oxides used for solar cell applications.

INTRODUCTION

   ZnO is a wide-bandgap semiconductor that has been used as transparent conducting material in solar cells. However, similar to most oxide materials, ZnO can be easily doped n-type but is difficult to be doped p-type because oxygen is strongly electronegative, so ZnO has a lower valence band maximum (VBM). Consequently, acceptor levels are deep in ZnO and p-type doping in ZnO is difficult [1]. This p-type doping bottleneck has so far hindered the full utilization of ZnO as a novel optoelectronic material such as solar cells. In this work, we propose several approaches [2,3] to lower the acceptor ionization energy in ZnO by codoping acceptors with donor or isovalent atoms. We show that by manipulating the wavefunction character of the defect states, we can design defect complexes that can significantly lower the acceptor ionization energy levels. We will also describe a universal approach to overcome the long-standing doping asymmetry problem for ZnO. This approach is based on the reduction of the ionization energies of dopants through introduction and effective doping of mutually passivated impurity bands, which can be realized by doping the host with passive donor-acceptor complexes or isovalent impurities [4]. These proposed approaches can be applied, in principle, to any wide-band-gap (WBG) semiconductor to overcome the doping asymmetry problem found in these materials and therefore will open a broad vista for the application of WBG materials. It also provides a new opportunity to make p-type ZnO and future-generation solar cells.

METHOD OF CALCULATIONS

   We performed the calculations using the density-functional theory, as implemented in the VASP or LAPW codes [1]. The defect structures were modelled by putting defects or defect complexes in a large periodic supercells. All the internal structural parameters of the supercell are optimized by minimizing the total energy and quantum mechanical forces. For charged defects, a uniform background charge is added to keep the global charge neutrality of the supercells.

   To determine the defect formation energy and defect transition energy levels, one needs to calculate the total energy $E(\alpha,q)$ for a supercell containing defect α in charge state q, the total energy E(host) of the pure host, and the total energies of the involved elemental solids or gases at their stable phases. The defect formation energy also depends on the atomic chemical potentials μ_i and the electron Fermi energy E_F. From these quantities, the defect formation energy, $\Delta H_f(\alpha, q)$, can be obtained by:

$$\Delta H_f(\alpha, q) = \Delta E(\alpha, q) + \Sigma\, n_i\mu_i + qE_F \ , \qquad (1)$$

where $\Delta E(\alpha, q) = E(\alpha, q) - E(host) + \Sigma\, n_iE(i) + q\varepsilon_{VBM}(host)$. E_F is referenced to the VBM of the host with energy ε_{VBM}. μ_i is the chemical potential of constituent i referenced to elemental solid/gas with energy E(i). n_i is the number of elements, and q is the number of electrons transferred from the supercell to the reservoirs in forming the defect cell. The transition energy for the defect α from q charge state to q' charge state, $\varepsilon_\alpha(q/q')$, can be obtained by:

$$\varepsilon_\alpha(q/q') = [\Delta E(\alpha, q) - \Delta E(\alpha, q')] / (q' - q). \qquad (2)$$

CHOICE OF THE ISOLATED DOPANTS

   The difficulty of doping a wide-gap semiconductor such as ZnO is often related to high defect ionization energy in this material, so the defect is not ionized at normal operating temperature. This difficulty can be understood as follows: The acceptor level has a wave function character similar to that of the VBM state, which consists of mostly anion p and cation p and d orbitals. Therefore, to have a shallow acceptor level, the dopant should be as electronegative as possible, that is, it should have low p orbital energy relative to the replaced host elements. For example, simple electron counting suggests that group-V elements, such as N, P, As, and Sb, substituting on the

anion site of a II-VI semiconductors are single acceptors [1]. Because the atomic p orbital energy level of N is the lowest, i.e., most electronegative, among the group V elements (Fig. 1), N_O has been the preferred acceptor dopant for ZnO because it produces the lowest acceptor level compared to the other group-V dopants. However, due to the low VBM of the oxides, the level of N_O in ZnO is still relatively deep, at about 0.35 eV above the VBM, making acceptor ionization difficult [2]. No other group-V elements are more electronegative than the N atom, which explains why it is difficult to have anion-site shallow acceptors for the oxides.
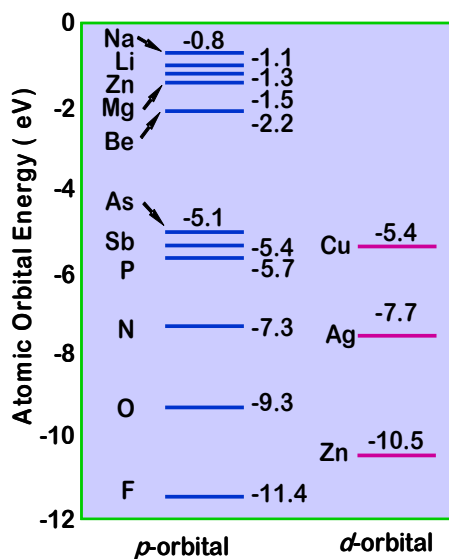

Fig. 1. LDA-calculated valence p and d energy levels of neutral atom to show the general chemical trends.

Cation vacancy is usually the most important intrinsic double acceptor for II-VI semiconductors. However, due to the small bond length, and thus large cation p and anion p coupling, removing Zn and its p orbital causes a large perturbation at the VBM, so V_{Zn} is also deep in ZnO. Because the VBM contains mostly anion p orbitals, replacing Zn by Group-Ia (Li, Na) and Group-Ib (Cu, Ag) elements may be better choices for producing p-type ZnO. However, very few p-type ZnO films have been achieved using Group-Ia elements as dopant. Theoretical studies have revealed the possible reasons for the difficulty. Substitutional Group-Ia elements (Li and Na) at T_d sites are indeed shallow acceptors [1,2]. However, when the Fermi energy is close to the VBM, Group-Ia elements prefer to occupy the interstitial sites in ZnO, which are electron donors. As a result, Group-Ia elements fail to dope ZnO p-type. The reason why Li and Na prefer the interstitial sites rather than substitutional sites is largely due to the low ionization energies of the valence s electron and large size mismatch of ions of the Group-Ia elements. Such mismatches are much less for Group-Ib elements. Thus, Group-Ib elements are expected to be better candidates than Group-Ia elements for p-type ZnO doping.

Our electronic structure calculations [3] have revealed that Cu, Ag, or Au occupying a Zn site creates a single-acceptor state above the VBM of ZnO. Our calculated transition energies $\varepsilon(0/-)$ are at about 0.7, 0.4, and 0.5 eV above the VBM for Cu_{Zn}, Ag_{Zn}, and Au_{Zn}, respectively (Fig. 2). These results indicate that (i) the acceptor level created by Ag_{Zn} is shallower than the acceptor levels created by Cu and Au; and (ii) the transition energies for the substitutional Group-Ib elements are much deeper than that of the substitutional Group-Ia elements. The reason for (ii) can be understood as the following: The substitutional elements induced acceptor level is derived mostly from the VBM state, which has the anion p and cation d characters. For Group-Ib elements, their occupied d orbital energies are near the oxygen p level. Because both the O, p and the Group-Ib d orbitals have the same t_2 symmetry in the tetrahedral environment, there is strong p-d repulsion between the two levels, pushing the acceptor levels higher. On the other hand, Group-Ia elements have no active valence d orbitals, so their defect levels are shallower than the Group-Ib substitutional defects. Among the three Group-Ib elements, Ag has the largest size and lowest atomic d orbital energy, so the p-d repulsion is the weakest. This explains why Ag_{Zn} has the lowest transition energy level among the three Group-Ib elements.
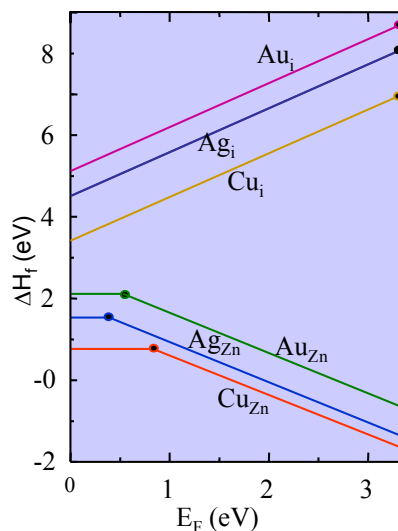

Fig. 2. Calculated formation energies as a function of Fermi level for Group-Ib elements in ZnO.

DESIGN OF SHALLOW DOPANTS

To reduce the acceptor transition energy level in ZnO, in this study we propose some new approaches. The proposals are based on the following considerations: (1) As discussed above, to lower the ionization level, one should find a dopant with low valence p orbital energy (more electronegative), preferably at the anion site. Because the wave function of the V_{Zn} is more localized on the O sites next to the vacancy (Fig. 3a), replacing one of

the neighboring O atoms by the more electronegative F (the F 2p level is 2.1 eV lower in energy than the O 2*p* level, Fig. 1) is expected to reduce the energy level of V_{Zn}. The binding energy between the F_O single donor and the V_{Zn} double acceptor is also expected to be large. Furthermore, this defect complex pair $V_{Zn}+F_O$ contains only one acceptor, so there will be no acceptor-acceptor repulsion that can raise the ionization level. (2) We notice that one of the reasons that the N_O defect level is deep in ZnO is because the N 2p level strongly couples to the nearest-neighbor Zn 3d orbitals (Fig. 3c); both have t_2 symmetry in this tetrahedron environment. If we can replace the Zn atom by an isovalent Mg atom that has no occupied d orbital, the defect transition energy levels of N_O+nMg_{Zn} should be lower than those of N_O in ZnO. The effect should be most efficient for n=4 when the tetrahedral environment around N_O is preserved and no level splitting occurs.
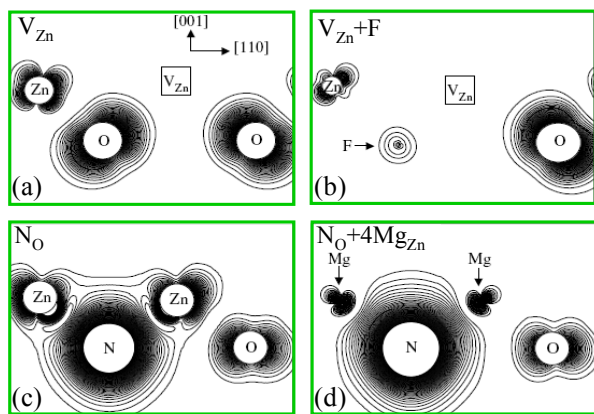
Fig. 3. Charge density plot of defect levels in ZnO: (a) V_{Zn}, (b) $V_{Zn}+F_O$, (c) N_O, and (d) N_O+4Mg_{Zn}.

Our calculations show that, indeed, the single-electron energy level of neutral $V_{Zn}+F_O$ is 0.10 eV lower than that of V_{Zn}. Figure 3b shows the charge density plot of the $V_{Zn}+F_O$ defect level. When F is introduced, it creates defect levels inside the valence band, which removes one of the oxygen dangling bond contribution to the acceptor level and makes the transition energy lower. The calculated (0/-) transition energy level of $V_{Zn}+F_O$ is 0.16 eV, which is much smaller than the corresponding (-/2-) transition energy level of V_{Zn} at 0.34eV. It is also lower in energy than the (0/-) transition energy level of V_{Zn} at 0.18 eV. The calculated $V_{Zn}+F_O$ binding energy is -2.3 eV, indicating that the defect pair is very stable with respect to the isolated defects. Based on this study, we believe that adding a small amount of F in ZnO is beneficial to p-type doping in ZnO. However, we also want to point out that F_O itself is a donor, so too much F_O in the sample can over compensate the acceptors, which is not good for p-type doping.

Our calculations also show that replacing Zn by Mg next to N_O lowers the single electron level by about 0.05 eV per Mg atom. Figure 3d shows the defect level charge density of N_O+4Mg_{Zn}. Compared with N_O+4Zn_{Zn}, we see that the cation *d* character is removed and the defect level is more localized on the N atomic site. The calculated (0/-) transition energies are 0.29 eV for N_O+Mg_{Zn} and 0.23 eV for N_O+4Mg_{Zn}, shallower than that for N_O at 0.35 eV. However, the calculated binding energy for N_O+Mg_{Zn} is positive, indicating that N does not like to bind with Mg in ZnO. This is because the N-Zn bond is stronger than the N-Mg bond. Our calculations show that both N-Zn and Mg-O bonds are shorter than the Zn-O bond, but the N-Mg bond length is longer than the Zn-O bond length. However, for ZnMgO alloys with relatively high Mg concentrations, the opportunity to form N_O+nMg_{Zn} is reasonably high due to the entropy contribution.

Further lowering of the acceptor transition energy level is expected if we replace Mg by Be, because the Be 2p orbital energy is much lower than the 3p orbital of Mg. Indeed, we find that the (0/-) transition energy levels of N_O+Be_{Zn} and N_O+4Be_{Zn} are at 0.18 and 0.12 eV, respectively.

PASSIVATED IMPURITY BAND DOPING

Recently, we also proposed a universal approach [4] to overcome the doping difficulty for wide band gap semiconductors such as ZnO. Our approach is based on the reduction of the ionization energies of dopants through the introduction and effective doping of mutually passivated impurity bands, which can be realized by doping the host with passive donor-acceptor complexes or isovalent impurities (Fig. 4). In this case, the ionization energy is reduced through the impurity band, which is higher than the VBM or lower than the CBM, rather than through the reduction of defect energy levels. Because the dopant and the defect band have similar atomic character, the ionization energy is always small. Furthermore, due to a smaller Fermi level shift, charge compensation is also reduced.
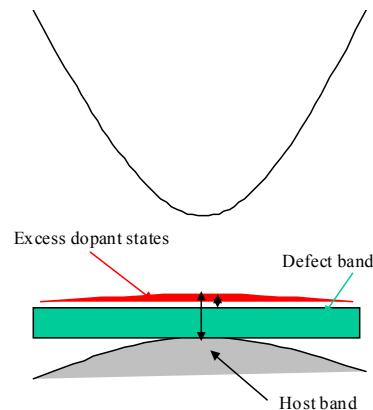

Fig. 4. Schematic plot of the universal doping model. First, through effective doping of mutually passivated defect pairs, a fully compensated defect band near the band edge of the host is introduced. Second, excess dopants are introduced to dope the passivated system by ionizing the defect band.
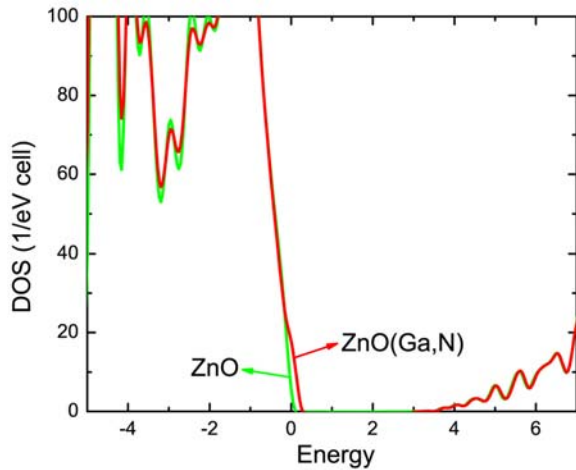
Fig. 5. Calculated total density of states (DOS) of pure ZnO (green curve) and ZnO containing one passive (Ga+N) complex (red curve). It shows that the (Ga+N) defect band raises the valence band maximum, therefore reducing the ionization energy of N acceptor in ZnO.

To obtain p-type ZnO, we show that the first step is to form passive stoichiometric (Ga+N) complexes [5,6], and create a fully occupied impurity band above the VBM of ZnO. Ga and N bind together strongly in ZnO because they passivate each other. Figure 5 shows the calculated total DOS for pure ZnO host (green curve) and a supercell containing a (Ga+N) complex (red curve). It reveals clearly that the formation of a passive (Ga+N) complex does not change the basic electronic structure, but only generates an additional fully occupied band above the VBM. When excess N atoms are introduced, they will dope the passivated system. The transition will occur between the N defect levels and the fully occupied impurity bands, rather than the original valence bands. The calculated acceptor ionization energies in this case are 0.2 and 0.1 eV for N at different sites (Fig, 6), which is significantly smaller than isolated N_O at about 0.35 eV above the VBM, but consistent with experimental observations [7,8].

The physical principle behind this new concept is clear; that is, we can first create a fully passivated impurity band and then dope the impurity band. This approach can be applied, in principle, to any WBG semiconductors to overcome the doping polarity problems found in these materials. It should be pointed out that to be successful, the concentration of the defects inducing the impurity band must exceed a certain percolation limit, so that reasonable transport properties can be achieved. The small bandgap reduction caused by forming an impurity band can also be easily adjusted by alloying with other elements. For example, adding a small amount of Mg or Be in ZnO can easily open the bandgap without changing the doping property [9,10].
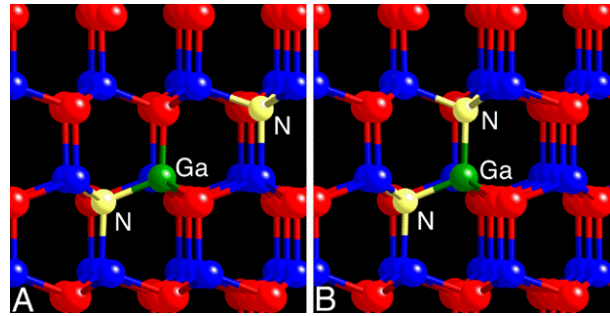
Fig. 6. Relaxed structures for N-Ga-N complexes in ZnO. The blue balls are Zn atoms, red balls are O atoms, green balls are Ga atoms, and yellow balls are N atoms. (A) Neutral state for complex (N-Ga–N) and (B) neutral state for complex (N-Ga-N).

CONCLUSIONS

In summary, we analyzed the chemical trend of defect levels in ZnO and proposed several approaches to lower the acceptor ionization energy in ZnO by codoping. These approaches can also be applied to other metal oxides and provide new avenues for develop p-type transparent conducting oxides for the future generation of solar cells.

ACKNOWLEDGEMENTS

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