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Design of shallow acceptors in ZnO through compensated donor-acceptor complexes: A density functional calculation

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The intrinsic large electronegativity of O 2*p* character of the valence-band maximum (VBM) of ZnO renders it extremely difficult to be doped *p* type. We show from density functional calculation that such VBM characteristic can be altered by compensated donor-acceptor pairs, thus improve the *p*-type dopability. By incorporating (Ti+C) or (Zr+C) into ZnO simultaneously, a fully occupied impurity band that has the C 2*p* character is created above the VBM of host ZnO. Subsequent doping by N in ZnO:(Ti+C) and ZnO:(Zr+C) lead to the acceptor ionization energies of 0.18 and 0.13 eV, respectively, which is about 200 meV lower than it is in pure ZnO.

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Currently, *p*-type doping in ZnO is still a daunting challenge in semiconductor physics.[1] N seems to be one of the best dopants for *p*-type doping in ZnO.[2,3] However, the obtained nominal *p*-type ZnO:N samples tend to exhibit high resistivity and often revert to *n* type after a few days of depositions.[4,5] This has impeded the practical application of ZnO in optoelectronic devices.[4,6] The difficulty in doping *p*-type ZnO is attributed to the high ionization energy and formation energy of the dopant nitrogen in ZnO, which leads to low ionization rate and instability.[7,8] Although the solubility of nitrogen dopants in ZnO could be greatly enhanced by nonequilibrium growth techniques,[9,10] the high ionization energy, which is caused by the very low valence-band maximum (VBM) of ZnO, is difficult to overcome.[11] Figure 1 plots the calculated total and atom-projected partial density of states (DOS) of ZnO. It shows that the VBM state of ZnO composes of mostly the anion oxygen *p*-orbital character. Because oxygen is much more electronegative than any of the attempted group-V acceptor dopants,[3] the ionization energy of the (group-V)$_O$ acceptors are always high. In another words, it is the intrinsic oxygen 2*p* character of the VBM state that renders ZnO extremely hard to be doped *p* type than any other wide-band-gap semiconductors, such as GaN.[12–15] This is indeed the common characteristic for *p*-type doping in post-transition-metal oxides. For example, in the transparent conducting oxides In_2O_3 and SnO_2, *p*-type doping encounters the same obstacles.[7,16] Therefore, to achieve efficient *p*-type doping in ZnO, a key step is to modify the O 2*p* character of the VBM state while sustaining its original integrity. Previously, various theoretical and experimental works have been carried out toward this goal. Based on density functional theory (DFT) calculations, Yan *et al.* proposed that the formation of shallow acceptors in ZnO by (Ga+N) codoping[17–19] is caused by the formation of an impurity (Ga+N) band above the VBM of the host ZnO that lowered the ionization energy of additional N_O acceptors. In this case, the impurity band has changed the composition of the VBM from the 2*p* character of oxygen to that of nitrogen, therefore further doping by the same nitrogen dopant is guaranteed to create shallow levels.[8] Furthermore, the formation of the acceptor-donor pairs also stabilized the defects. Nevertheless, the calculated acceptor level in this system (~0.2 eV) is still too deep to ionize and produce enough holes for device application operated at room temperature. Therefore, better approaches to create more stable and shallow acceptors in ZnO are still a subject of intense research interest.

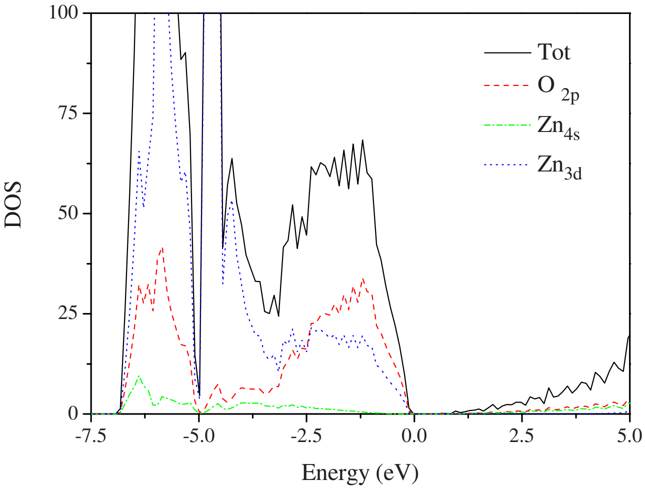

FIG. 1. (Color online) The total and atom-projected DOS ZnO. The highest occupied VBM state is chosen as the Fermi energy and is set to zero.

In this Brief Report, we attempt to upshift the VBM of host ZnO by designing passivated donor-acceptor pairs (DAP) and investigate their effect on the ionization of additional acceptor. As discussed above, the shift of the acceptor energy levels can be approximately estimated by comparing the dopant and the VBM's anion atomic *p* orbital energy levels (Table I). Raising the *p* orbital energy of the VBM and lower the *p* orbital energy of the dopant can lead to lower

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TABLE I. Atomic orbital eigenvalues (in eV) of dopant atoms along with Zn and O atoms are listed to show the general chemical trend.

Atom	s	p	d
$C(2s^2 2p^2)$	−13.64	−5.41	
$N(2s^2 2p^3)$	−18.41	−7.24	
$O(2s^2 2p^4)$	−23.75	−9.19	
$Zn(3d^{10} 4s^2 4p^0)$	−6.23	−1.22	−10.42
$Ga(3d^{10} 4s^2 4p^1)$	−9.17	−1.63	−19.39
$Ge(3d^{10} 4s^2 4p^2)$	−11.94	−4.05	−29.54
$Ti(3d^2 4s^2 4p^0)$	−4.60	−1.54	−4.43
$Zr(4d^2 5s^2 5p^0)$	−4.60	−1.55	−3.70

ionization energies.[20] Because C has shallower $2p$ orbital energy than N, compared with N_O, substitutional carbon on oxygen site, C_O, should lead to larger upward shift of the VBM than N_O. Therefore, by codoping carbon with special compensative donors, we anticipate that it can lead to a semiconducting system with much higher VBM than ZnO. If the system is subsequently doped by N, shallow acceptor energy level and high concentration of carrier at working temperature would be expected. In the following, using first-principles band-structure calculations, we will investigate which compensating dopant is optimal in combining with C to lower the acceptor energy level and minimize the perturbation to the band structure in ZnO.

The total-energy and band-structure calculations in this work are carried out within the framework of DFT, as implemented in the Vienna *ab initio* simulation package.[21] The frozen-core projector-augmented-wave method is used to represent the electron and core interactions.[22] All plane waves with a cutoff energy of 400 eV were used in the basis function. For all the doped systems, a 64 atoms supercell is used for the defect calculations. The lattice constants of the supercells are kept fixed to that of pure ZnO. All the ion positions are allowed to relax until the forces on each of them become less than 0.02 eV/Å. For ion relaxation, a $2 \times 2 \times 2$ Monkhorst-Pack k-point sampling is used and for DOS plots, a more refined $8 \times 8 \times 8$ is employed.[23] The detailed procedures for calculating the formation energy, transition energy level, and the binding energy E_b of defect pairs $A+B$ formed of impurities A and B can be found elsewhere.[3,7,24]

The valence electron configuration for Ga is $3d^{10}4s^2 4p^1$, i.e., Ga has one more electron than $Zn(3d^{10}4s^2)$. Therefore, Ga_{Zn} acts as a single donor. The energy level of this donor inside the band gap relies on the energy difference between Ga $4s$ orbital and Zn $4s$ orbital, as the conduction band of ZnO has predominantly the Zn s and O s characters (Fig. 1). The calculated (0/+) ionization energy of Ga_{Zn} is 0.18 eV below the conduction-band minimum (CBM). This is consistent with the fact that Ga $4s$ orbital is much lower than that of Zn $4s$ orbital (Table I). Accordingly, the calculated transition energy level for single acceptor N_O is 0.37 eV above the VBM of ZnO.[3] When donor Ga and acceptor N are incorporated simultaneously into ZnO, they introduce defect levels above VBM and below CBM, respectively. In the neutral charge states, the donor state is occupied with one electron and the acceptor state has one hole on it. Thus, it is energetically favorable for the electrons on the donor levels to drop and occupy the acceptor levels and recombine with the holes on them. As can be seen from the total DOS (Fig. 2) that the valence band is completely filled. The ionized acceptor and donor will bind with each other strongly through Coulomb interaction with the calculated binding energy for Ga_{Zn}-N_O complex of 1.158 eV.

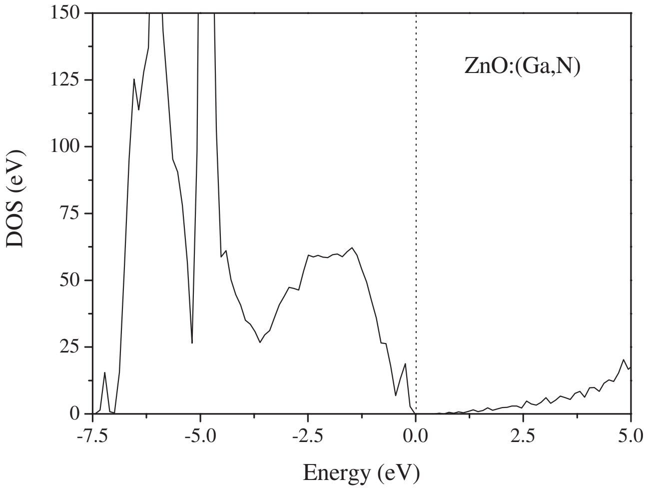

FIG. 2. The total DOS for ZnO:(Ga,N). The highest state is set to zero.

To see the effect of such passivation on the relative shift of VBM, the DOS of pure ZnO is compared with the codoped ZnO containing the passivated DAP Ga_{Zn}-N_O, as shown in Fig. 3. Here, the eigenvalues of different systems are aligned with respect to the core level of the atom away from the defect complexes. The PDOS for N_{2p} are amplified ten times for clarify. As can be seen from Fig. 3, the VBM for system ZnO:(Ga+N), which is mainly composed of N p character now, moved upward by about 0.19 eV relative to

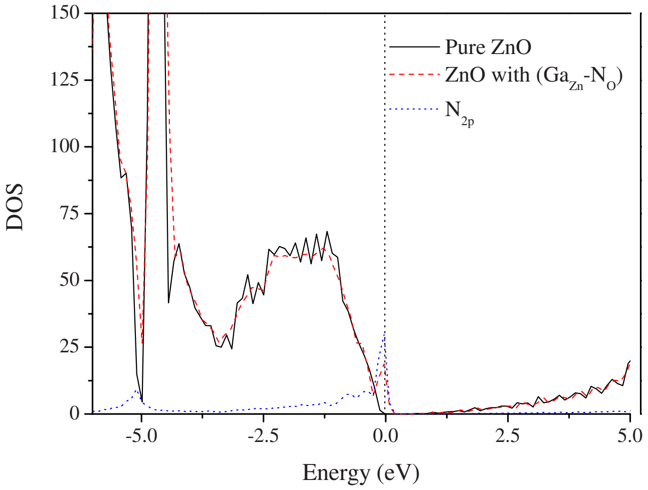

FIG. 3. (Color online) The calculated DOS of undoped ZnO and (Ga+N)-codoped ZnO. The Fermi level of pure ZnO is presented with dashed line. The partial DOS plots are amplified for clarity.

TABLE II. Calculated transition energies for the acceptors and donors referenced to the VBM and CBM of ZnO or the top of the defect bands when ZnO is codoped with (Ga+N), (Ti+C), and (Zr+C), respectively.

Defects	$\varepsilon(2+/0)$	$\varepsilon(+/0)$	$\varepsilon(0/2-)$	$\varepsilon(0/-)$
Zr_{Zn} in ZnO				
Ti_{Zn} in ZnO				
Ga_{Zn} in ZnO		0.18		
N_O in ZnO				0.37
C_O in ZnO			0.95	0.76
N_O in ZnO:(Ga+N)				0.20
N_O in ZnO:(Ti+C)				0.18
N_O in ZnO:(Zr+C)				0.13

the VBM of pure ZnO. As we have expected, the upward shift of the VBM will facilitate the *p*-type dopability of ZnO. The calculated ionization energy for acceptor nitrogen in the formed system ZnO:(Ga+N) is 0.20 eV and about 0.17 eV shallower than it is in pure ZnO. As the ratio of carrier concentration to impurity concentration follows $\exp(-E_A/k_BT)$, the hole concentration can be increased by at least three orders of magnitude. However, the obtained ionization energy as large as 0.2 eV renders that there is only about one percentage of N_O is activated at room temperature. Such carrier concentration is well below that for most device application with moderate dopant density.

C has two less electrons than O, so C_O is a double acceptor. One can see from Table I that the C 2*p* orbital is higher in energy than that of O and N, so the acceptor energy level of C_O in ZnO is much higher than that of N_O. The calculated acceptor levels for C_O with respect to the VBM of pure ZnO are listed in Table II. The high ionization energy of C indicates that C itself is not a desirable acceptor for *p*-type ZnO. However, in this work, the purpose of introducing dopant C is not to accept the thermally excited electrons from the VBM, thus contribute directly to the *p*-type conductivity. Instead, we want to combine C with a donor to create a high lying passivated defect bands, as discussed below. In order to create stable passivated defect bands above the VBM with C, which is a double acceptor, one has to choose a double donor on Zn site to enhance the DAP Coulomb binding. This indicates that the donor should have four valence electrons because Zn has valence of 2. Some of the options are Ge, Ti, and Zr. However, as we can see from Table I, Ge 4*s* orbital energy is rather deep, thus is not a good passivation element because it will create deep donor levels below the CBM. To cause least perturbation to the CBM, we should choose elements that has four valence electrons and high *s* orbital energy. From Table I, we choose Ti and Zr as our attempted donors because they have shallow *s* as well as *d* valence orbital energies than Zn 4*s* orbital energy.

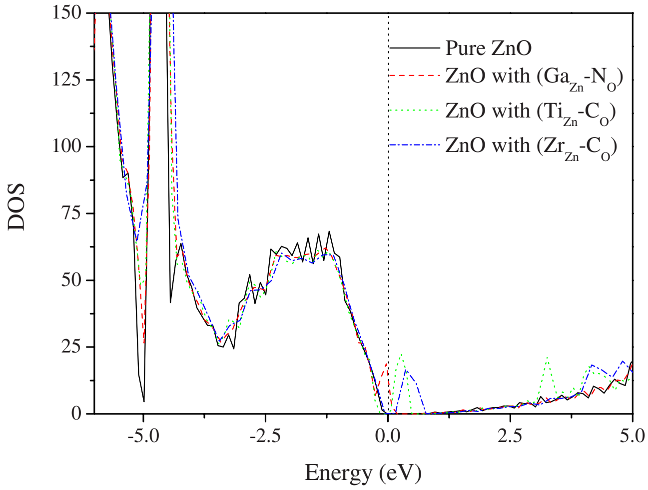

FIG. 4. (Color online) The calculated DOS of undoped ZnO and ZnO codoped with (Ga+N), (Ti+C), and (Zr+C). The Fermi level of pure ZnO is presented with dashed line.

When an isolated Ti atom substitutes on Zn lattice site it creates a double donor state that should have Ti *d* character. Table I shows that the Ti *d* orbital level is above that of Zn *s*, which means that Ti_{Zn} defect level might be a resonant donor state inside the conduction band. Indeed, we find the neutral Ti_{Zn} is unstable, that is, the electrons on the donor state spontaneously drop to the CBM without thermal excitation. When Ti and C are codoped into ZnO, a similar fully occupied impurity band is created above the VBM, just as codoping with Ga and N. The significant difference between ZnO doped with these two defect pairs is the position of the impurity band, i.e., the relative shift of the passivated defect bands with respect to the VBM of ZnO. Our calculations indicated that the VBM of ZnO:(Ti+C) is about 0.48 eV higher than that of bulk ZnO and 0.29 eV higher than that of ZnO:(Ga+N). This is due to the deeper character of C_O acceptor than N_O. Therefore, passivated complexes with acceptor C are more effective to uplift the VBM of ZnO.

Similar results are obtained for ZnO containing C and codoped with Zr (Fig. 4). Just like Ti_{Zn}, Zr_{Zn} is also a resonant donor as its *d* orbital energy is even higher than that of Ti's. However, the calculated energy of the impurity band edge for ZnO:(Zr+C) is 0.78 eV higher than that of pure ZnO or 0.3 eV above that of ZnO:(Ti+C). This is because the Zr 4*d* orbital energy is higher than that of Ti 3*d* orbital energy, Therefore the *p*-*d* coupling between the unoccupied Zr 4*d* and occupied O 2*p* is weaker compared with the *p*-*d* coupling between Ti 3*d* and O 2*p*. This reduced *p*-*d* coupling in ZnO:(Zr+C) accounts for the higher band edge for this system. Consequently, the higher impurity band edge in ZnO:(Zr+C) will favors the creation of even shallower acceptors. For example, when additional acceptor nitrogen is available, electrons are thermally excited from the fully occupied impurity bands, rather than from the original valence band of ZnO, to the N_O acceptor level. The calculated ionization energies of N_O in ZnO:(Ti+C) and ZnO:(Zr+C) with respect to the impurity band edges are 0.18 and 0.13 eV, respectively, which are about 0.2 eV lower than it is in pure ZnO. Moreover, as Ti_{Zn} and Zr_{Zn} are resonant donor states above the CBM, these codopant will not cause much perturbation on the position of CBM, only the position of the VBM was moved upward. This unique feature of band structure also indicates that ZnO:(Zr+C) can also be used to enhance the photoelectrochemical catalytic efficiency of ZnO in producing hydrogen through water splitting.[25]

To study how the formation of the defect band affects the hole transport property, we have calculated the hole effective mass for pure ZnO and ZnO doped with passivated (Zr+C). We find that the effective mass of the ZnO system passivated with (Zr+C) is only 46% larger than that of pure ZnO, suggesting that the deterioration of the transport property is still tolerable, although the defect band is rather deep. Moreover, the reduction in the band gap due to the formation of the defect band can be easily corrected by alloying with other isovalent elements such as Mg or Be without changing the doping properties.[8]

As discussed above, the formation of a passivated donor-acceptor complex is the preassumption in our calculations. To test this, we calculated binding energy E_b for the neutral complexes Ga_{Zn}-N_O, Ti_{Zn}-C_O, and Zr_{Zn}-C_O, and they are 1.158, 2.691, and 2.717 eV, respectively.[26] The larger binding energies for the C-containing defect complexes can be understood by noticing that for instance, Zr_{Zn} donates *two* electrons to C_O, forming the neutral (Zr_{Zn}^{2+}-C_O^{2-}) complex, which results in stronger Coulomb interactions between the doubly charged defects. This indicates that the formation of Zr_{Zn}-C_O and Ti_{Zn}-C_O are more stable than Ga_{Zn}-N_O.

In summary, by examining the characteristic of valence-band edge of ZnO, we proposed a compensated codoping method to alter this character and to make *p*-type ZnO with high hole concentration attainable. We show that it is the intrinsic O *p* character of the valence-band edge of ZnO that poses challenges to *p*-type doping. Such character can be altered via the incorporation of (Zr+C) or (Ti+C) into ZnO simultaneously. As a consequence, the VBM now has the C *p* character and the position of it is shifted upward significantly. The upshifts of the VBM with respect to that of host ZnO are 0.483 and 0.782 eV for ZnO:(Ti+C) and ZnO:(Zr+C), which are determined by the energy levels of the C_O acceptor and the *p*-*d* repulsions between the codoped donor-acceptor pairs. The calculated ionization energies for N doping in ZnO:(Zr+C) is 0.13 eV and is about 0.24 eV lower than that in pure ZnO. The concept discussed in this Brief Report can also be used to overcome doping difficulty in other wide-band-gap semiconductors and can be used for band-structure engineering for materials that can be used, for example, for the photoelectrochemical hydrogen production through water splitting. Further experimental testing is called for to validate our proposal.

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[26] In this calculation the initial state Ti_{Zn} and Zr_{Zn} is actually $Ti_{Zn}^{2+}+2e$ and $Zr_{Zn}^{2+}+2e$, with the two electrons at the CBM.