PHYSICAL REVIEW B **66**, 073202 (2002)

Origin of *p*-type doping difficulty in ZnO: The impurity perspective

C. H. Park,[1,2] S. B. Zhang,[1] and Su-Huai Wei[1]

[1]*National Renewable Energy Laboratory, Golden, Colorado 80401*

[2]*Research Center for Dielectric and Advanced Matter Physics, Pusan National University, Pusan 609-735, Korea*

(Received 27 November 2001; published 5 August 2002)

We investigate the *p*-type doping difficulty in ZnO by first-principles total-energy calculations. The dopants being considered are group-I elements Li, Na, and K and group-V elements N, P, and As. We find that substitutional group-I elements are shallow acceptors, while substitutional group-V elements such as P and As are deep acceptors. The *AX* centers that convert acceptors into deep donors are found to be unstable except for P and As. Without compensation by intrinsic defects, the most likely cause for doping difficulty is the formation of interstitials for group-I elements and antisites for group-V elements. Among all the dopants studied here, N is a relatively better candidate for *p*-type ZnO.

DOI: 10.1103/PhysRevB.66.073202 PACS number(s): 61.72.Bb, 61.72.Vv, 71.55.Gs

In wide-band-gap optoelectronics, zinc oxide (ZnO) is conventionally used as a substrate for GaN. Recently, however, ZnO itself became the focus for new optoelectronic applications. ZnO has a 3.4-eV direct band gap, and it can be easily doped *n*-type.[1] While *n*-type ZnO is available even without any intentional doping, it is very difficult to dope ZnO *p* type,[2] although it was recently reported that high densities of holes could be achieved with N or As as the dopant along with novel doping techniques.[3–5] Several mechanisms leading to doping difficulty are known: low solubility, compensation by low-energy native defects, deep impurity level, and structural bistability known as *AX* and *DX* centers. Recent first-principles total-energy calculations showed[6] that the oxygen vacancy V_O and zinc interstitial Zn_i in ZnO have low formation energies, and that Zn_i has a shallow donor level, thus, could be the possible sources for the unintentional *n*-type conductivity. On the other hand, these low-energy intrinsic defects could be responsible for the equilibrium *p*-type doping difficulties of ZnO. However, the role of the individual dopants are not addressed. In this paper, we study the various compensation mechanisms associated with the specific extrinsic *p*-type dopants,[7,8] and identify the best *p*-type dopants for ZnO.

We first examine the substitutional impurities M^I_{Zn} (M^I = Li, Na, and K) and A^V_O (A^V = N, P, and As). We find that group-I elements are better dopants than group V elements in terms of the shallowness of the acceptor levels. Among the group-V elements, N_O has the shallowest acceptor level. P_O and As_O substitutional defects levels are very deep. Because the formation of the *AX* center has been the bottleneck for *p*-type doping in a number of II-VI semiconductors,[7,8] we then study the stability of the *AX* centers for these impurities. It appears that *AX* center is not a problem for ZnO except for P and As. We also investigated other low-energy compensation mechanisms such as dopant interstitial M^I_i, the Zn interstitial-acceptor pair, and the group-V antisite such as As_{Zn}. We find that group-I elements tend to occupy the interstitial site, thereby acting as a donor not acceptor. In this regard, large size impurities such as K are relatively better *p*-type dopants. However, K is unstable against the formation of $(\mathrm{K}_{Zn}+\mathrm{V}_O)^+$ complex. On the other hand, P and As are found to be amphoteric, thus, having the tendency to form P_{Zn} and As_{Zn} antisites.

Our calculations are performed using the first-principles pseudopotential method[9,10] based on the local density approximation (LDA).[11] Norm-conserving nonlocal pseudopotentials[12] were generated by the scheme of Troullier and Martins.[13] A Kleinman-Bylander type of fully separable pseudopotentials was constructed.[14] An energy cutoff of 45 Ry for the plane-wave expansion was used. We include the effects of 3-d electrons of Zn using nonlinear partial core correction (NPC).[15] The direct inclusion of the Zn-3d states as valence electrons would give a rather small band gap of 0.96 eV. The NPC calculation gives, instead, a 1.84 eV gap that is still about 1.56 eV too small compared to the experimental gap of 3.4 eV.[16] The underestimation of the band gap is a well-known LDA error. The crystal structure of ZnO is wurtzite. The calculate lattice constant is $a = 3.14$ Å and the bulk moduli is 1.08 Mbar.[16,17] The calculated heat of formation of ZnO is 2.89 eV compared with the experimental value of 3.6 eV.[18] To simulate isolated defects, we used a supercell with 72 atoms.

Strain effect and energy levels of substitutional impurity: Table I lists the bond lengths between the substitutional impurities and the nearest-neighbor atoms for the (−) charge state, a^-, and the defect levels of the impurities. For the Na, K, P, and As impurities, the bond lengths are significantly larger than the ideal Zn-O bond length of 1.93 Å. These induce large lattice strains around these impurities. In this regard, the N and Li impurities emerge as the best candidates for *p*-type ZnO, because strain increases the impurity formation energy and makes the formation of other compensating defects such as vacancies around the impurity easier. We have calculated the positions of the defect energy levels of the impurities *relatively* to the valence-band maximum (VBM). The results are listed in Table I. They are 0.09 eV for substitutional Li_{Zn}, 0.17 eV for Na_{Zn}, and 0.32 eV for K_{Zn}. On the same energy scale, the levels are 0.40 eV for N_O, 0.93 eV for P_O, and 1.15 eV for As_O. Interestingly, the group-I impurities give rise to shallower acceptor level compared to the group-V impurities, especially to P and As. The reason that group-I impurities have shallow levels is because the VBM state mainly consists of the anion p orbitals with small mixing of the cation p and d orbitals. Thus, replacing Zn by group-I impurities only leads to small perturbations at the VBM. Furthermore, because group-I impurities do not

TABLE I. Calculated nearest-neighbor bond lengths and the defect energy levels for negatively charged substitutional impurities.

Group I	R (Å)	ϵ_i (eV)	Group V	R (Å)	ϵ_i (eV)
Li	2.03	0.09	N	1.88	0.40
Na	2.10	0.17	P	2.18	0.93
K	2.42	0.32	As	2.23	1.15

TABLE II. The energy required to form the positively charged AX centers from the substitutional acceptors.

Group I	ΔE	Group V	ΔE
Li	0.21	N	0.13
Na	1.04	P	-0.46
K	1.38	As	-0.18

have active d orbital, the reduced p-d coupling also lowers the defects levels. For group-V impurities, however, replacing O produces defect levels deep inside the gap. The depth increases as the impurity p-orbital energy levels increase from N to P to As. Consequently, As has the deepest energy level at 1.15 eV above the VBM. Therefore, recent experimental result[4] showing p-type doping using As has to be explained differently other than the substitutional As_O defect.[19]

The stability of the AX centers: The AX center is a deep defect complex which compensates for acceptors. In binary semiconductors it forms through a double broken bond (DBB) mechanism,[20] as shown in Fig. 1. In this defect complex, two neighboring bonds are broken, releasing four electrons. However, two of the electrons are recaptured by the two anions to form a strong anion-anion bond. The net result is the formation of an AX center accompanied by the release of two electrons (equivalent to the capture of two holes). The DBB-like lattice distortion is stabilized only in the presence of holes (preferentially by two holes) near the acceptors. It gains electronic energy by pushing up the empty hole states, and lowers the energy of the occupied states in addition to forming a strong anion-anion bond. The competing mechanism that will destabilize the AX center is the elastic energy induced by the large lattice distortion. This AX model successfully explained the compensation mechanism of N, P, and As, and the persistent photoconductivity in ZnSe and ZnMgSSe.[7,20]

In the wurtzite structure, the lattice relaxation in Fig. 1 takes place in the (0001) plane. For group-I impurities, the DBB structure is relatively simple, as shown in Fig. 1(a). Here two Zn-O bonds are broken and one O-O bond is formed. The calculated O-O bond length is about 1.68 Å. For group-V impurities, the atomic structures of the low-energy AX centers are described in Fig. 1(b). Here instead of forming the O-O bond, an impurity-oxygen bond forms that gives lower energy. The anion-anion bond lengths between the impurity and the oxygen atom are 1.74 Å for N, 1.76 Å for P, and 1.98 Å for As.

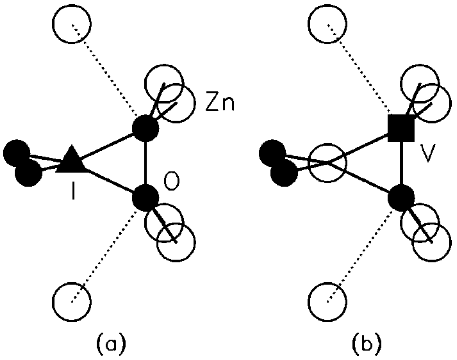

FIG. 1. Schematic atomic structure of the DBB state of (a) the group-I impurities and (b) the group-V impurities in wurtzite ZnO.

The calculated AX stabilization energies, which are the energy differences between the AX centers and the positively charged substitutional defects, are given in Table II. We have tested the effects of the Zn-$3d$ electrons on the formation of the AX centers by treating Zn $3d$ states as valence states. We find that the stabilization energy is increased by a modest 0.08 eV. We have corrected the results for group-V impurities by this value in Table I. We find that the stabilization energy is positive for group-I impurities, indicating that they are only metastable in ZnO. For group-V impurities, we find that P and As AX centers are more stable than the substitutional state. Therefore, P and As are not immune to the formation of AX centers.

The doping difficulty in p-type ZnO can also arise from other compensation mechanisms e.g., the impurity may assume ''wrong'' sites or may form complexes with intrinsic defects. Here we calculate the formation energies of these defects. Because the oxygen vacancy and zinc interstitial in ZnO have low formation energies, and the Zn_i^{2+} defect and V_O^{2+} can even spontaneously form under the Zn-rich condition when the Fermi energy is close to the VBM,[6] we will focus our study of p-type ZnO under the O-rich condition.

Self-compensation of group-I impurities: Substitutional group-I impurities M_{Zn}^{I} are acceptors, but group-I impurities at the interstitial site are electron donors. The formation energies of the positively charged interstitial defects increase with the Fermi energy while those of the negatively charged substitutional impurities decrease with the Fermi energy. Table III shows the calculated formation energies under the O-rich condition as a function of the electron Fermi energy (referenced to the VBM). We assume that the chemical potentials of the impurities are at their elemental ground states $(\mu_i=0)$, except for N where N_2 molecule is used. We find that group-I impurities ''prefer'' interstitial sites over substitutional sites when the Fermi energy is close to the VBM. This is especially true for Li and Na, because the interstitial site is 1.58 and 0.87 eV, respectively, more stable than the substitutional site for Fermi energy at the VBM. (The differences are 4.47 and 3.76 eV, respectively, under Zn-rich condition.) For K, the interstitial is *less* stable due to its large atomic size. Our results suggest that for Li and Na the Li_i and Na_i interstitials are the leading killer defects which prevent p-type doping in ZnO. On the other hand, K has a deeper acceptor level. The large atomic size of K can also lead to the formation of V_O around K. We have calculated the formation energy of the positively charged defect complex $(K_{Zn}+V_O)$. We find that under the O-rich condition, the

TABLE III. The formation energies of the negatively charged substitutional and positively charged interstitial group-I impurities and that of the negatively charged substitutional group-V impurities, and their positively charged defect complexes with a Zn interstitial. The reference energy for ϵ_F is at the VBM. The atomic chemical potentials of the impurities are referenced to their elemental ground states ($\mu_i = 0$) except for N, where the N_2 molecule is used. The results are given under the O-rich condition because it is the most relevant to *p*-type doping in ZnO.

	Sub.	Int.		Sub.	With Zn_i
Li	$-2.69-\epsilon_F$	$-4.27+\epsilon_F$	N	$6.14-\epsilon_F$	$6.58+\epsilon_F$
Na	$-2.03-\epsilon_F$	$-2.90+\epsilon_F$	P	$8.90-\epsilon_F$	$12.13+\epsilon_F$
K	$-0.86-\epsilon_F$	$-0.40+\epsilon_F$	As	$9.19-\epsilon_F$	$13.95+\epsilon_F$

complex is about 1.0 eV lower in energy than that of the substitutional state for ϵ_F at the VBM. Therefore, even under the O-rich condition, O vacancy can easily form in the presence of K, thus, limiting *p*-type doping with K.

Zn self-interstitial and group-V impurity complexes: The formation of the complexes between the Zn self-interstitial and substitutional impurities ($Zn_i + A_O^V$) are important due to the high mobility of the interstitials, the attractive Coulomb interaction between the positively charged interstitials and the negatively charged acceptors, and the fact that the two defects can form first nearest neighbor pairs. Table III compares the calculated formation energy of positively charged ($Zn_i + A_O^V$) with that of negatively charged substitutional group V impurities. We see that the formation energy for ($Zn_i + N_O$) at the O-rich condition is 6.58 eV, but can be as low as of only about 0.80 eV at the Zn-rich limit. Relative to the substitutional N_O defect, the ($Zn_i + N_O$) defect complexes is 2.45 eV more stable under the Zn-rich condition but less stable by 0.44 eV under the O-rich condition, when ϵ_F is the VBM.

Group-V-on-Zn antisites: The antisites A_{Zn}^V are donor-like which provides another mechanism for compensating acceptors. Group-V elements like P and As which are size mismatched to O, are more likely to form such antisites to avoid the build-up of local strains near the O site. Indeed, we find that under the O-rich condition, and where ϵ_F is the VBM, P_{Zn}^{3+} and As_{Zn}^{3+} can form spontaneously.[19]

In summary, a systematic study of the doping properties of group-I and V acceptors in ZnO was carried out. An overall picture emerges from the above calculations:

(1) The formation of the *AX* centers is generally not the reason for *p*-type doping difficulties in ZnO, except for P and As. This is important because if the *AX* is more stable, the formation of the *AX* centers will be difficult to avoid since it typically has small activation barriers. Therefore, one *could* in principle dope ZnO *p* type if a large amount of the dopant (e.g., N) can be incorporated into ZnO through low-temperature non-equilibrium growth conditions.

(2) In terms of the acceptor ionization energy, group-I elements are far better than group-V elements. However, for group-I element doping, the efficiency is generally limited by the formation of compensating interstitials. For group V-dopants, N has the smallest ionization energy, however, only a small percentage of the N dopant will be ionized, consistent with available experimental observations.[21]

(3) Taking into account all the compensating mechanisms studied here, we conclude that the best elemental dopant source for *p*-type ZnO is N because N will not form the N_{Zn} antisite, and the N *AX* center is only metastable.

The work at NREL was supported by the U.S. DOE-SC-BES under Contract No. DE-AC36-99GO10337. C.H. Park also acknowledges support from the Korea Research Foundation, Grant No. KRF-2000-005-D00001.

---

[1] R. G. Gordon, in *NREL/SNL Photovoltaics Program Review*, edited by Stephen S. Holt and Lee G. Muray, AIP Conf. Proc. No. **394** (AIP, Woodbury, NY, 1997), p. 39.

[2] S. B. Zhang, S.-H. Wei, and A. Zunger, J. Appl. Phys. **83**, 3192 (1998), and references therein.

[3] M. Joseph, H. Tabata, and T. Kawai, Jpn. J. Appl. Phys. **38**, L1205 (1999).

[4] Y. R. Ryu *et al.*, J. Cryst. Growth **216**, 330 (2000).

[5] Y. Yan, S. B. Zhang, and S. T. Pantelides, Phys. Rev. Lett. **86**, 5723 (2001).

[6] S. B. Zhang, S.-H. Wei, and A. Zunger, Phys. Rev. B **63**, 075205 (2001).

[7] C. H. Park and D. J. Chadi, Phys. Rev. Lett. **75**, 1134 (1995); Phys. Rev. B **55**, 12 995 (1997).

[8] D. J. Chadi, Phys. Rev. B **59**, 15 181 (1999).

[9] M. L. Cohen, Phys. Scr. **T1**, 5 (1982).

[10] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).

[11] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[12] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979).

[13] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[14] L. Kleinman and D. M. Bylander, Phys. Rev. Lett. **48**, 1424 (1982).

[15] S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).

[16] *Semiconductors, Physics of Group IV Elements and III–V Compounds*, edited by O. Madelung, M. Schulz, and H. Weiss, Landolt-Börnstein, New Series, Group III, Vol. 17, Pt (a) (Springer-Verlag, Berlin, 1984), and references therein.

[17] By treating Zn 3*d* as valence states, the calculate lattice constant is $a = 3.27$ Å, in good agreement with experimental data of 3.25 Å. The calculated bulk modulus is 1.98 Mbar, which is also consistent with the experimental value of 1.43 Mbar.

[18] *Handbook of Chemistry and Physics*, 73 ed., edited by D. R. Lide (CRC, Boca Raton, FL, 1992).

[19] S. B. Zhang, S.-H. Wei, and C. H. Park (unpublished).

[20] C. H. Park and D. J. Chadi, Phys. Rev. Lett. **75**, 1134 (1995).

[21] X. Li *et al.* (private communication).