# Doping by Large-Size-Mismatched Impurities: The Microscopic Origin of Arsenic- or Antimony-Doped *p*-Type Zinc Oxide

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Based on first-principles calculations, a model for large-size-mismatched group-V dopants in ZnO is proposed. The dopants do not occupy the O sites as is widely perceived, but rather the Zn sites: each forms a complex with two spontaneously induced Zn vacancies in a process that involves fivefold As coordination. Moreover, an $As_{Zn}$-$2V_{Zn}$ complex may have lower formation energy than any of the parent defects. Our model agrees with the recent observations that both As and Sb have low acceptor-ionization energies and that to obtain *p*-type ZnO requires O-rich growth or annealing conditions.

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Chemical and size proximities are among the top considerations for choosing a "good" semiconductor dopant with low formation energy, and thus high solubility. For *p*-type doping, it is also desirable to have a dopant with high electronegativity [1]. For materials involving first-row anions such as ZnO, however, choices meeting these criteria are often lacking, because no *p*-type dopant has a size similar to the first-row anion and is also more electronegative. This lack of dopant candidates often constitutes a major hurdle for turning first-row wide-gap materials into useful electronic materials: *p*-type zinc oxide is one such example, for which cation substitution produces only deep acceptor levels [2]. Until recently, it was virtually impossible to dope ZnO *p* type even with nitrogen, the element that is most similar to O in terms of atomic size. ZnO is the II-VI analogy of gallium nitride, having a direct band gap of about 3.4 eV and an exceptionally large exciton binding energy of 60 meV [3]. Were it not for the *p*-doping bottleneck, ZnO would be an ideal material for blue and ultraviolet laser and light-emitting diode applications [4,5].

Recently, codoping was suggested as a possible means to enhance nitrogen solubility in ZnO and to lower its ionization energy, thereby obtaining *p*-type ZnO [6,7]. More recent studies [1,8,9], however, questioned the basic principles of codoping. The results in Ref. [6] are, instead, attributed to the use of metastable dopants and growth kinetics [9]. It is now clear that the level of the nitrogen atom on the oxygen site, $N_O$, is relatively deep, making acceptor ionization difficult [2,10], and N-doped ZnO could be unstable. To further pursue *p*-type ZnO, other group-V dopants have been tried. Interestingly, several research groups have recently reported *p*-type conductivity in ZnO with exceptionally large-size-mismatched dopants such as P [11], As [12,13], and Sb [14] (atomic radius = 1.06, 1.20, and 1.40 Å vs 0.73 Å for O). This is quite puzzling because not only have the basic principles regarding dopant size been violated, but also recent first-principles total energy calculations show that $P_O$, $As_O$, or $Sb_O$ all have very high acceptor-ionization energies. For example, the calculated $As_O$ acceptor level is deep, about 930 meV [15] above the valence band maximum (VBM). Thus, the probability for acceptor ionization at room temperature is less than one in $10^{19}$, making it impossible for $As_O$ to dope ZnO efficiently *p* type.

In this Letter we present a theory for large-size-mismatched impurities by first-principles calculations. Isolated As may form donor ($As_{Zn}$), deep acceptor ($As_O$), or amphoteric interstitial ($As_i$), but none of these could result in *p* typeness, so one must consider As-related defect complexes. Guided by strain relief and Coulomb interaction, we find that among the complexes an $As_{Zn}$-$2V_{Zn}$ complex represents a new class of low-energy defects with shallow acceptor levels. In this complex, the core As occupies the Zn antisite, which is energetic enough to spontaneously induce two Zn vacancies. The resulting $As_{Zn}$-$2V_{Zn}$ complex is an *acceptor* with both low formation energy, $\Delta H_f(q = 0) = 1.59$ eV, and low ionization energy, $\varepsilon(0/-) = 0.15$ eV, in agreement with experiments, 0.12 [13] to 0.18 eV [12]. Because the As atom has *fivefold* coordination, the complex has its own identity that is qualitatively different from either $As_{Zn}$ or $V_{Zn}$. The same is true for Sb with $\Delta H_f(0) = 2.00$ eV and $\varepsilon(0/-) = 0.16$ eV. Our finding could explain the puzzling experimental observations that oxygen-rich growth/annealing conditions, which would severely suppress the formation of $As_O$ and $Sb_O$, are required for successful *p*-type doping.

We used the density functional theory, as implemented in the VASP codes [16], with local density approximation and ultrasoft pseudopotentials [17]. Zinc 3*d* states were included in the valence. The cutoff energy for the plane wave expansion is 300 eV, with additional tests carried out at 400 eV. We used a supercell approach and Monkhorst-Pack *k*-point mesh for Brillouin zone integration. For

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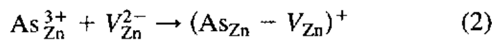
charged defects, a jellium background was used. In the case of As, we calculated for each defect the energy with 36-, 64-, and 96-atom cells. Good linearity with inverse cell volume was observed, which allows for an extrapolation of the defect energies to their dilute limits [18]. In the case of Sb, we used a 64-atom supercell, with cell corrections taken from the corresponding As complex.

The defect formation energy is defined [19] as

$$\Delta H_f = E_{\rm tot}(D, q) - E_{\rm tot}(0) + \Delta n_{\rm Zn}\mu_{\rm Zn} + \Delta n_{\rm O}\mu_{\rm O} + \Delta n_X \mu_X + qE_F, \quad (1)$$

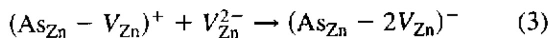
where $E_{\rm tot}(D, q)$ and $E_{\rm tot}(0)$ are the total energies of the supercell with and without the defect, $D$, and $X$ = As and Sb. Quantities $\Delta n_A$ and $\mu_A$ are the number of species $A$ (=Zn, O, As, Sb) removed from a defect-free cell to its respective reservoir to form the defect cell and the corresponding reservoir chemical potential, respectively. The upper limits for $\mu_{\rm Zn}$, $\mu_{\rm O}$, $\mu_{\rm As}$, and $\mu_{\rm Sb}$ are the energies of metallic Zn, gaseous $O_2$, and solid state As and Sb, which are offset to zero in the present study. To keep the ZnO thermodynamically stable, it also requires that $\mu_{\rm Zn} + \mu_{\rm O} = \mu_{\rm ZnO,calc} = -3.58$ eV. This further imposes $\mu_{\rm O}$ to be in the range $-3.58 \text{ eV} \leq \mu_{\rm O} \leq 0$ and redefines $\mu_{\rm Zn} = -3.58 \text{ eV} - \mu_{\rm O}$. Because both As and Sb prefer to bind with O more strongly than among themselves, the precipitation of $As_2O_3$ or $Sb_2O_3$ thus redefines at the oxygen-rich limit ($\mu_{\rm O} = 0$), $\mu^{\rm max}_{\rm As(or\ Sb)} = [\mu_{\rm As_2O_3(or\ Sb_2O_3)} - 3\mu_{\rm O}]/2 = -3.63$ eV (or $-4.05$ eV for Sb). In Eq. (1), $q$ and $E_F$ are the defect charge state and Fermi level with respect to the VBM. For shallow defects, the procedure in Ref. [20] is used to calculate the ionization energy.

Figure 1 shows the defect formation energy calculated under the oxygen- and arsenic-rich conditions, i.e., $\mu_{\rm O} = 0$ and $\mu_{\rm As} = -3.63$ eV. Formation energy under other growth conditions can be readily obtained by using Eq. (1) and Table I, where $\Delta H_f$ at a specific set of $E_F$, $\mu_{\rm O}$, $\mu_{\rm As}$, or $\mu_{\rm Sb}$ is given. Consider isolated As defects: The formation energies of $As_{\rm O}$ are greater than 6.0 eV for all charge states in the band gap. These energies are high because of the very large size mismatch between As and O. Thus, the relevant isolated defects in Fig. 1 are the zinc vacancy ($V_{\rm Zn}$) and arsenic antisite ($As_{\rm Zn}$). Two or more such isolated defects can form complexes. We find that the reaction



$$As^{3+}_{\rm Zn} + V^{2-}_{\rm Zn} \rightarrow (As_{\rm Zn} - V_{\rm Zn})^{+} \quad (2)$$

is exothermic with a binding energy of 1.14 eV. The resulting $As_{\rm Zn}$-$V_{\rm Zn}$ is, however, still energetic. It combines with another $V_{\rm Zn}$ to form $As_{\rm Zn}$-$2V_{\rm Zn}$,



$$(As_{\rm Zn} - V_{\rm Zn})^{+} + V^{2-}_{\rm Zn} \rightarrow (As_{\rm Zn} - 2V_{\rm Zn})^{-} \quad (3)$$

with another 1.70 eV binding energy. The overall reaction can be written as

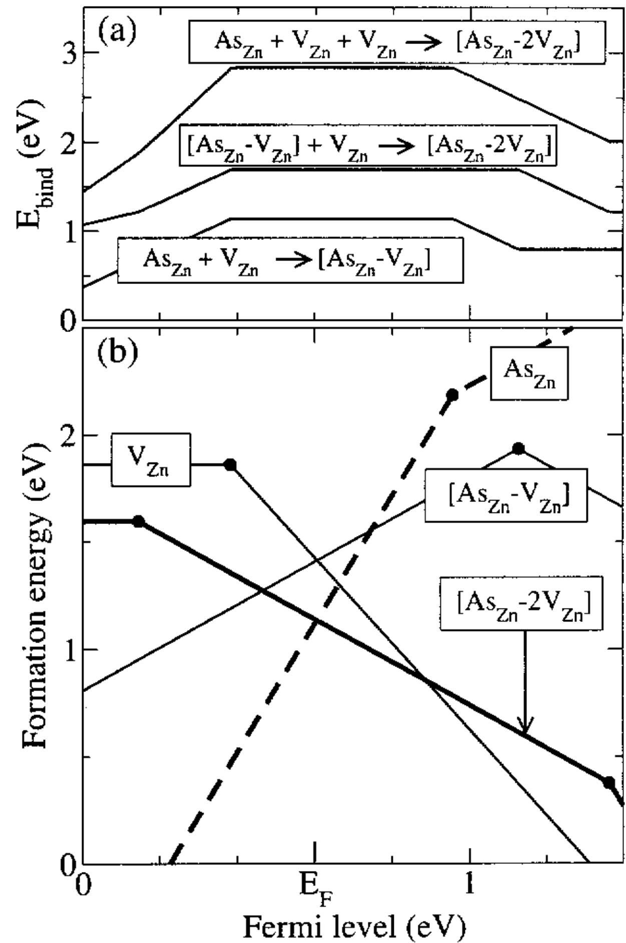
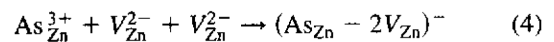



FIG. 1. (a) Calculated binding energy and (b) defect formation energy, as a function of the Fermi level for various As-related defect complexes in ZnO, under the O- and As-rich conditions ($\mu_{\rm O} = 0$ and $\mu_{\rm As} = -3.63$ eV). In (b) the slope of the curves reflects the charge state of the defects and the solid dots denote the energy positions at which transition from one charge state to another takes place.



$$As^{3+}_{\rm Zn} + V^{2-}_{\rm Zn} + V^{2-}_{\rm Zn} \rightarrow (As_{\rm Zn} - 2V_{\rm Zn})^{-} \quad (4)$$

with the total binding energy = 2.84 eV.

The formation of the $As_{\rm Zn}$-$V_{\rm Zn}$ complex is a result of Coulomb binding between two oppositely charged defects. The subsequent formation of the $As_{\rm Zn}$-$2V_{\rm Zn}$ complex is, however, more complicated, involving both the optimization of the Madelung energy and, for certain charge states, the transformation of the As atom into a new fivefold coordination. Figures 2(a) and 2(b) show two characteristic atomic structures for the complexes for $q = 0$ and $3-$. For $q = 0$ and $-$, the As atom is a triple donor, donating all of its three electrons to the two $V_{\rm Zn}$ (each can accept up to two electrons). This high 3+ charge leaves the As atom highly electropositive while sitting in an environment that is highly electronegative with negatively charged oxygen ions. The unique

TABLE I. Calculated defect formation energy (in eV) at $E_F = 0$, $\mu_O = 0$, $\mu_{As} = -3.63$, and $\mu_{Sb} = -4.05$ eV. The energy of $H^+$ is with respect to H in a free $H_2$ molecule. Under the O-rich limit, however, it increases by 1.45 eV due to the precipitation of $H_2O$.

| Defect | Charge | $X =$ As | $X =$ Sb |
|---|---|---|---|
| $X_{Zn}$ | 3+ | −0.68 | −0.80 |
| | + | 1.23 | 0.74 |
| $X_{Zn}$-$V_{Zn}$ | + | 0.81 | 1.08 |
| | − | 3.06 | 3.04 |
| $X_{Zn}$-$2V_{Zn}$ | 0 | 1.59 | 2.00 |
| | − | 1.74 | 2.16 |
| | 3− | 4.47 | 5.33 |
| $X_O$ | 0 | 9.87 | 11.20 |
| | − | 10.80 | 12.82 |
| $V_{Zn}$ | 0 | 1.86 | |
| | 2− | 2.63 | |
| H | + | −0.84 | |

geometry of the wurtzite structure allows for the fifth oxygen (which ideally would be $1\frac{2}{3}$ bond length away along the [0001] direction) and the As to approach each other. The presence of the two neighboring vacancies further assists such displacements by locally softening the lattice. These result in, as indicated in the inset in Fig. 2(a), a strong As-O bond that is 5% shorter than a nominal Zn-O bond. The energy gain is 0.61 eV, in comparison with a configuration of the same charge state but without fivefold coordination, similar to the one in Fig. 2(b). It is interesting to note that for larger impurities such as Sb, the fourfold structure in Fig. 2(b) spontaneously transforms into the fivefold structure without any energy barrier. For the 3− charged complex, however, while both $V_{Zn}$ are doubly negatively charged, the (1+)-charged $As_{Zn}$ is not electropositive enough to induce such fivefold-coordinated As configuration.

The solid dots in Fig. 1(b) show the transition energy level positions for these defects. In particular, $V_{Zn}$ is a moderately deep double acceptor with the transition energy at $\varepsilon(0/2-) = 0.39$ eV(measured from the VBM). On the other hand, $As_{Zn}$ is a multicharge donor with the transition energy at $\varepsilon(3+/+) = 0.95$ eV. The $As_{Zn}$-$V_{Zn}$ complex is an amphoteric defect with the donor/acceptor transition energy at $\varepsilon(+/-) = 1.13$ eV. In contrast, the $As_{Zn}$-$2V_{Zn}$ complex is a multicharge acceptor with two calculated ionization energies at $\varepsilon(0/-) = 0.15$ eV (0.16 eV for $Sb_{Zn}$-$2V_{Zn}$) and $\varepsilon(-/3-) = 1.37$ eV, respectively. In addition, the metastable $As_{Zn}$-$2V_{Zn}$, with fourfold-coordinated As atom, has the $\varepsilon(0/-)$ level at 0.25 eV. The reason that the $As_{Zn}$-$2V_{Zn}$ complexes could have shallower (0/−) acceptor levels than $V_{Zn}$ can be understood as follows: The (0/−) level of $As_{Zn}$-$2V_{Zn}$ is derived mainly from the low-lying $t_2$-like acceptor level of $V_{Zn}$, which could couple to a high-lying $t_2$-like (+/0) level of $As_{Zn}$. The level repulsion between the two, upon the complex formation, pushes the low-lying $t_2$-like level down, therefore leading to shallower $\varepsilon(0/-)$ levels for the $As_{Zn}$-$2V_{Zn}$ complexes. Moreover, the formation of the fifth As-O bond lowers the energy of the $q = -$ state slightly more than that of the $q = 0$ state, hence further lowering the $\varepsilon(0/-)$ level.

Recent experiments showed that ZnO could be doped $p$ type using P [11], As [12,13], or Sb [14] as the dopant to a hole concentration higher than $10^{17}$ cm$^{-3}$. The doping techniques may vary, e.g., radio frequency sputtering for P, hybrid beam deposition for As, and excimer laser doping for Sb, but all have one thing in common: One needs to apply an oxygen-rich ambient, either during growth or during postgrowth thermal treatment. Within the framework of the previous As-on-O acceptor model, this is quite difficult to reconcile. (i) The $As_O$ has high

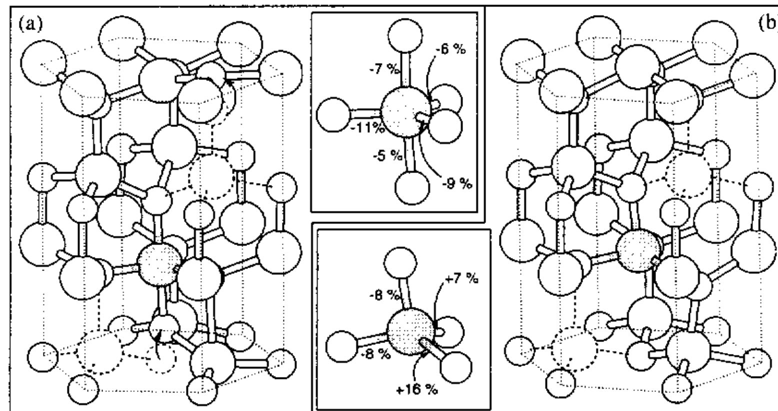



FIG. 2. Atomic structures of the $As_{Zn}$-$2V_{Zn}$ complexes, (a) $q = 0$ and (b) $q = 3-$. The small white spheres are the O, the large white spheres are the Zn, the large shaded spheres are the As, and the large dashed spheres are the missing Zn atoms. The arrows in (a) indicate selectively the displacements of the O atoms with large atomic relaxations. The insets in the middle show bond lengths between the As and neighboring O atoms with respect to that of ideal Zn-O bond (in terms of the percentage difference).

formation energy, therefore it is unlikely to form in any appreciable concentrations. (ii) Even if they do form, the acceptor level of $As_O$ is too deep to provide sufficient holes. (iii) Moreover, the use of the O-rich growth/annealing condition is expected to suppress the formation of $As_O$ to a level at which $As_{Zn}$ (a donor) should be more abundant than $As_O$.

Within the framework of the present $As_{Zn}$-$2V_{Zn}$ complex model, however, all the three major difficulties of the As-on-O model are removed. (i) The formation energy is reasonably low. Figure 1(b) shows that during equilibrium growth the $As_{Zn}$-$2V_{Zn}$ complex would act as the leading acceptor while $As_{Zn}$ would act as the leading donor. This results in a Fermi level, $E_F = 0.61 - \frac{1}{4}kT_G \ln(6/3) = 0.60$ eV, at a typical growth temperature of $T_G = 430\,^\circ\mathrm{C}$. The equilibrium concentration of $As_{Zn}$-$2V_{Zn}$ would be on the order of $10^{15}\ \mathrm{cm}^{-3}$. The actual concentration could, however, be higher, either by high-temperature growth followed by rapid cooling that results in supersaturation of $As_{Zn}$ and $V_{Zn}$, or by nonequilibrium growth in which the As chemical potential exceeds that of $As_2O_3$. In addition, Table I suggests that a large amount of H could be incorporated, which shifts the Fermi level higher. This suppresses isolated $As_{Zn}$ and $As_{Zn}$-$V_{Zn}$ donors, while enhancing $As_{Zn}$-$2V_{Zn}$ acceptors. It is known that H could be annealed out relatively easily. (ii) The ionization energy is low. The calculated ionization energy of 0.15 eV is in fact in reasonable agreement with experiments, 0.12 eV [13] or 0.18 eV [12]. (iii) Low formation energy is achieved and is only achieved under the oxygen-rich condition, also in line with experiments.

There are other ways to construct complexes between $As_{Zn}$ and native defects. However, most of them could be readily ruled out based on their expected electrical behaviors and on their dependence on the growth condition [21]. For example, $As_{Zn}$-$V_O$ would not form because of the high energy of $V_O$ at the O-rich condition. Moreover, both $As_{Zn}$ and $V_O$ are donors. The resulting complex is also a donor that cannot explain $p$-type ZnO. Among the complexes that may compete with $As_{Zn}$-$2V_{Zn}$, we have calculated the following: (a) $As_O$-$V_{Zn}$. While this complex serves to release the large $As_O$ strain and could, in principle, be a triple acceptor, it spontaneously transforms into $As_{Zn}$-$V_O$, which is a donor. (b) Off-center $As_O$ (also known as $As_i$-$V_O$ pair). Despite the high formation energy of $As_O$, the displaced $As_i$ still spontaneously moves back into the vacant oxygen site ($V_O$). (c) $As_{Zn}$-$2O_i$. This is the most probable competing acceptor that works the same way as $As_{Zn}$-$2V_{Zn}$. It deserves attention because, while the formation energy of $O_i$ is considerably larger than $V_{Zn}$, the distance to $As_{Zn}$ can be substantially smaller. However, we find that $O_i$ prefers to form split interstitial with oxygen (e.g., with about 1.4 eV binding energy for $O_i^0$). This not only increases the $O_i$ diffusion barrier by an even larger amount, but also pushes the $(0/2-)$ transition level 1.5 eV above the VBM. This makes the $O_i$ unattractive to $As_{Zn}$ unless $E_F > 1.5$ eV.

In summary, our $As_{Zn}$-$2V_{Zn}$ (and $Sb_{Zn}$-$2V_{Zn}$) model provides a possible answer to a number of mysterious key experimental observations in As- (and Sb)-doped ZnO. The significance of the model could go beyond $p$-type ZnO: It reveals that one could in fact maximize the formation energies of the compensating native defects such as $V_O$ and $Zn_i$, while minimizing that of the dopant by adequate chemical potentials. This is in contrast to currently used doping schemes in which the formation energies of the compensating defects are often minimized along with that of the dopant. So far, complex formation by codoping has been largely discredited because a mechanism in which Coulomb binding could compensate the cost of creating extra defects in the complex is still lacking. Our model here provides a mechanism through which complexes could become more important than their parent defects.

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