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# Effect on nitrogen acceptor as Mg is alloyed into ZnO

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Our Raman measurement indicates that the intensity of the peaks (510 and 645 $\text{cm}^{-1}$) related to nitrogen concentration is enhanced in MgZnO compared with that in ZnO. Using first-principles band structure methods, we calculated the formation energy and transition energy level for nitrogen acceptor in ZnO and random $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ (with $x=0.25$) alloy. Our calculations show that the incorporation of nitrogen can be enhanced as Mg is alloyed into ZnO, which agrees with our experiments. The acceptor energy level deeper in the alloy ascribes to the downward shift of the valence-band maximum edge in the presence of magnesium. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2857496]

Optoelectronic device applications based on ZnO (Refs. 1–4) and its related alloys require that the materials be doped both *n*- and *p*-type. Recently, MgZnO (Ref. 5) alloy was proposed as the potential barrier material in the fabrication of ZnO-based light-emitting diode (LED) to obtain UV electroluminescence because of its nontoxicity compared with BeZnO.[6] The *n*-type MgZnO with high crystal quality can far more readily be prepared. However, as in most wide-band-gap II-VI semiconductor materials,[7] $\text{Mg}_x\text{Zn}_{1-x}\text{O}$, with wider band gap, as Mg content increases,[8,9] it is difficult to be doped *p*-type. Similar to ZnO, group-V elements, such as N, P, As, and Sb substituting on the anion site have been the promising acceptors[10] and many experimental efforts have been taken to prepare *p*-type MgZnO: Heo *et al.* prepared phosphor doping *p*-type MgZnO;[11] Zhang *et al.* fabricated *p*-type MgZnO by N–Al codoping;[12] and our research group realized N-doped *p*-type MgZnO by postgrowth annealing.[13] However, no UV LED is prepared using the *p*-type MgZnO as barrier material up to now, indicating that the general understanding of the acceptor behavior in MgZnO alloy is still unclear.

In the present paper, we report a theoretical investigation combined with our Raman spectra results on the solubility and ionization energy of acceptor N in ZnO and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloys using the density function theory (DFT) methods. The alloy in this study is represented using the special quasirandom structure[14,15] (SQS) approach, where the cations are distributed in a way that its atomic correlation function is closest to that of random alloys. All the calculations were carried out using the frozen-core projector-augmented-wave[16] method within the DFT, as implemented in the code VASP.[17] The Zn 3*d* electrons are explicitly treaded as valence electrons. The energy cutoff for the plane wave expansion is 400 eV. The summation of charge densities over the Brillouin zone was done using the *k*-point that is equivalent to the $4\times4\times4$ Monkhorst–Pack special *k*-point meshes in the zinc-blende (ZB) Brillouin zone. For charged defects, a homogeneous compensating background charge is added. In all calculations, all the atoms are allowed to relax until the Hellmann–Feynman forces acting on them become less than 0.01 eV/Å. For the convenience of computation and the feasibility of the SQS approach, our simulations are performed using the cubic ZB alloys and we expect that our results from the ZB alloy are also applicable for the wurtzite (WZ) ones because many previous tests have shown that the defect levels in ZB and WZ are quite similar.[18,19]

The formation energy of a defect or impurity *D* in charge state *q* is defined as[20]

$$\Delta H^f(D,q) = E^k(D,q) - E^k(\text{pure}) + \sum_i n_i\mu_i + q\{E^{\Gamma}_{\text{VBM}}(D) - [\varepsilon^{\Gamma}_D(0) - \varepsilon^k_D(0)] + E_F\}, \tag{1}$$

where $E(D,q)$ is the total energy of the supercell with defect *D* in charge state *q*; *E* (pure) is the total energy of the supercell without defect; and $n_i$ indicates the number of atoms of type *i* (O and N) that have been added to ($n_i>0$) or removed ($n_i<0$) from the supercell. $\mu_i$ is chemical potentials of species i referenced to the elemental solid/gas energy. *q* is the number of electrons transferred from the supercell to the reservoirs in forming the defect cells. $E_F$ is the Fermi level with respect to the valence-band maximum (VBM) and $E^{\Gamma}_{\text{VBM}}$ (*D*) is the energy of valence band maximum in the defective supercell and is aligned using the electrostatic potential away from the defect. $\varepsilon^k_D(0)$ and $\varepsilon^{\Gamma}_D(0)$ are the Kohn–Sham levels for neutral defect at special *k*-points (averaged) and at Γ-point, respectively. The ionization energy of acceptor $\text{N}_\text{O}$ $\varepsilon(0/-)$ with respect to the VBM is the Fermi energy in Eq. (1) where the formation energy $\Delta H^f(\text{N}_\text{O},-)$ of $\text{N}_\text{O}$ in charge $-1$ equals to $\Delta H^f(\text{N}_\text{O},0)$.

Formula (1) indicates that for neutral defect $q=0$, its formation energy and, consequently, the solubility of the dopant depend sensitively on the chemical potential $\mu_i$. That

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TABLE I. The formation energy $\Delta H_f(\mathrm{N_O},0)$ and the transition energy level $\varepsilon$ (0/-) for $\mathrm{Mg_{0.25}Zn_{0.75}O:N}$ and ZnO:N.

| | $\Delta H_f(\mathrm{N_O},0)$ | $\varepsilon$ (0/-) |
|---|---|---|
| 3NN | $2.509\text{-}\mu_N+\mu_O$ | 0.385 |
| 2NN | $2.054\text{-}\mu_N+\mu_O$ | 0.404 |
| 1NN | $1.623\text{-}\mu_N+\mu_O$ | 0.436 |
| 0NN | $1.215\text{-}\mu_N+\mu_O$ | 0.468 |
| ZnO | $1.113\text{-}\mu_N+\mu_O$ | 0.420 |

is, for substitutional nitrogen in oxygen site, the formation energy of $N_O$ will decrease if the chemical potential of N increases or if the chemical potential of O decreases. To keep ZnO thermodynamically stable, it is required that $\mu_O+\mu_{Zn} = \Delta H_f(\mathrm{ZnO})$ and to avoid the phase separation, i.e., the formation of MgO, $\mu_O$ is limited by $\mu_O+\mu_{Mg} \leq \Delta H_f(\mathrm{MgO})$, where $\Delta H_f(\mathrm{ZnO})$ and $\Delta H_f(\mathrm{MgO})$ are the formation energy of solid ZnO and MgO. Our calculated $\Delta H_f(\mathrm{MgO}) = -5.946$ eV and $\Delta H_f(\mathrm{ZnO}) = -3.458$ eV is in good agreement with the experimental value of −3.6 eV.

The calculated formation energies for $N_O$ as the function of $(-\mu_N+\mu_O)$ and the ionization energy $\varepsilon(0/-)$ for $N_O$ in ZnO and the random $\mathrm{Mg_8Zn_{24}O_{32}}$ alloys are shown in Table I. For N in the alloy, we have calculated the $N_O$ at different sites. The *n*NN denotes that there are *n* Mg atoms in the tetrahedral nearest neighboring sites centered on the dopant N atom. It can be noticed from these results that the change of formation energy for the $N_O$ defect in $\mathrm{Mg_{0.25}Zn_{0.75}O}$ strongly depends on the number of Mg atoms that are nearest neighbors to nitrogen. For example, the formation energy of $N_O$ increased for nitrogen at an oxygen site with zero, one, two, and three Mg atoms as the nearest neighbors. These results suggested that N is easier to bind with Zn than Mg. This is because the Zn–N bond is stronger than Mg–N and our calculation shows that Mg–N bonds are longer than that of Zn–N. Figure 1 is the Raman spectra for samples ZnO, N doped ZnO, and N doped MgZnO alloy with Mg content at about 20 at. % prepared by plasma-assisted molecular beam epitaxy. Peaks at 510 and 645 $\mathrm{cm^{-1}}$ are attributed to nitrogen related defect.[21] We could see the obvious increase of N incorporation into MgZnO alloy. This might be related to the reduction of chemical potential of oxygen in the presence of Mg. Experimentally, we can obtain the $\mathrm{Zn_{1-x}Mg_xO}$ films with different Mg contents by changing the oxygen flow rate and keeping the other conditions unchanged and the Mg content is decreased with the increase of oxygen flow rate.[22] Therefore, on the contrary, we could control the $\mu_O$ in MgZnO smaller than that in ZnO by controlling the temperature of Mg source. From Table I, the formation energy of $N_O$ in $\mathrm{Mg_8Zn_{24}O_{32}}$ will be lower than that in ZnO if $(-\mu_N+\mu_O)$ in the alloy is about 0.2 eV smaller than that in ZnO, which becomes possible as Mg is alloyed into ZnO for fear of forming MgO.

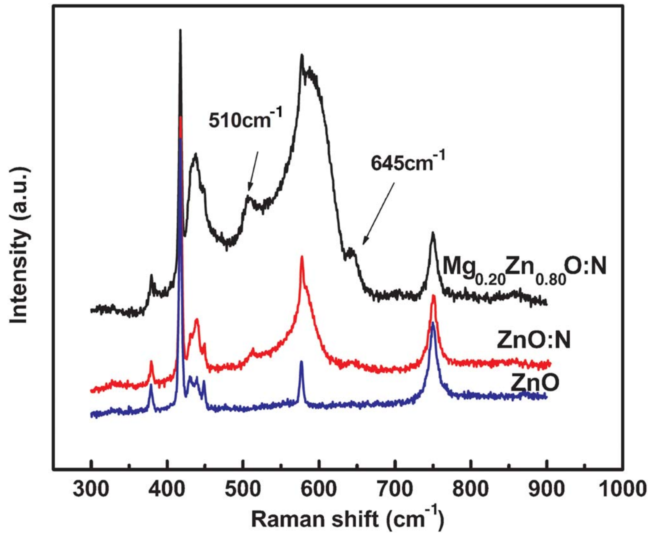

FIG. 1. (Color online) Raman spectra of ZnO, N doped ZnO, and $\mathrm{Mg_xZn_{1-x}O}$ with $x \approx 20$ at. %.

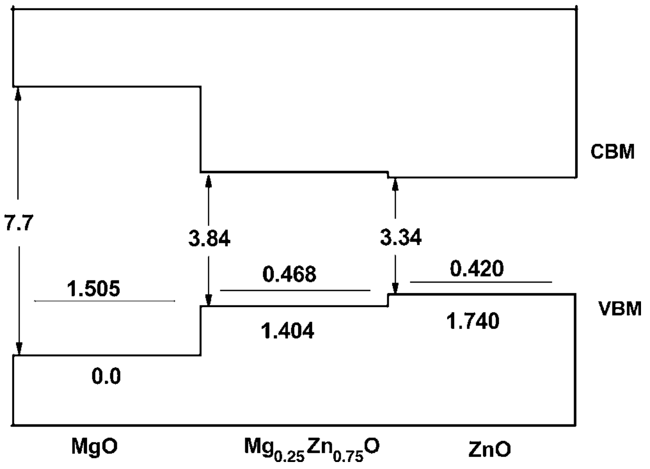

FIG. 2. The absolute defect transition energy level of $N_O$ in MgO, ZnO, and $\mathrm{Mg_{0.25}Zn_{0.75}O}$ alloy, the numbers on the defect levels are the binding energies with respect to the VBM. The band gaps are from experiments.

For the ionization energy of $N_O$ in ZnO, the calculated level $\varepsilon(0/-)$ locates at 0.42 eV. This agrees well with previous first-principles calculations.[23,24] For that in $\mathrm{Mg_8Zn_{24}O_{32}}$ alloy, we find that the relative position of $N_O(0/-)$ depends on the location of nitrogen in the alloy. It decreases from 0.468 eV when N has zero nearest neighboring Mg atoms to 0.385 eV with three Mg nearest neighbors. This is related to the decrease of *p*-*d* coupling that lowered the acceptor level relative to the VBM in the same alloy. Li *et al.*[25] have proposed that the acceptor transition energy could be reduced by replacing the surrounding Zn with isovalent Mg. Combined with the formation energy shown in Table I, which showed that N preferred to locate at the position with no NN Mg surrounding it, we see that the N acceptor is about 50 meV deeper in the random alloy with $x=0.25$, which is consisted in our experimental observation from the study of the photoluminescence of nitrogen-doped MgZnO films.[26] To account for the above observed trends, we have plotted in Fig. 2 the valence-band offsets between MgO, ZnO, and $\mathrm{Mg_{0.25}Zn_{0.75}O}$ alloy and the nitrogen acceptor energy level in them. The conduction-band offsets are obtained from our calculated valence-band offsets by adding the difference of measured gaps $E_g = 3.34+2.0x$.[27] From the calculated results, we see that the valence-band offset for MgO/ZnO is about 1.74 eV, which is in contrast with the "common-anion rule"[28,29] that the valence-band offset between two semiconductors having the same anion will be small. This is because the VBM is composed of the anion *p* states and the interaction between cation *d* states and anion *p* states will strongly effect the position of VBM.[30] Our calculated valence-band offset between $Mg_xZn_{1-x}O$ and ZnO is about 0.134 and 0.336 eV, consequently, the $\Delta E_c/\Delta E_v$ is 0.87/1 and 0.49/1 for $x=12.5\%$ and 25.5%, respectively, suggesting that the band alignment between ZnO and $Mg_xZn_{1-x}O$ depends obviously on the Mg concentration $x$ and the valence-band offset is non-negligible. The experiment from the analyses of exciton binding energy also revealed that the offset of valence band was large enough to be neglected.[31] Using this band alignment, we find that for acceptors, the absolute transition energy level with respect to vacuum increased with the addition of Mg due to the downward shift of the VBM edge as the Mg incorporation.

In summary, our first principles total energy calculations indicate that the formation energy for nitrogen on the O site decreases with the addition of Mg. Our Raman spectra clearly show that the solubility of nitrogen is enhanced as Mg is alloyed into ZnO. The calculated $N_O$ acceptor energy level in $Mg_8Zn_{24}O_{32}$ is significantly deeper than that in ZnO as the result of the downward shift of the VBM edge in the presence of magnesium. Our general understanding of substitutional acceptor N in MgZnO alloys at relative high Mg content is expected to be applicable to other substitutional acceptor, such as P, As, Li, and Na. Qiu *et al.*[32] has proved that the acceptor $Li_{Zn}$ in $Mg_xZn_{1-x}O$ was deepened by the increase of Mg content.

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