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Electronic structure of ZnO:GaN compounds: Asymmetric bandgap engineering

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ZnO and GaN have a type-II band offset. The incorporation of one compound into the other would lead to a reduced bandgap as compared to that of either ZnO or GaN. Our density-functional theory calculation reveals an asymmetric bandgap reduction in this nonisovalent system; i.e., incorporating GaN in a ZnO host results in a much more effective bandgap reduction than incorporating ZnO in a GaN host. We further find that the random-alloy system is more favorable than the superlattice system in terms of light absorption in the longer-wavelength regions. Our results suggest that the wave-function localization at the band edges plays an important role in how to choose the host material and dopant for effective bandgap engineering through semiconductor compound alloying.

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I. INTRODUCTION

Bandgap engineering is an important step in designing novel functional semiconductor materials. For example, efficient photoelectrochemical (PEC) splitting of water to hydrogen usually requires photoelectrodes that: (i) are highly stable, (ii) have band-edge positions that match the H_2/H_2O and H_2O/O_2 levels, and (iii) can absorb most of the photons from the solar spectrum.[1–3] For optimal use of solar energy, the optically visible range of the spectra must be used, and in order to achieve this, the desired photoelectrode must be a semiconductor with bandgap of around 2.0 eV. Unfortunately, at present, most semiconductors cannot meet all the criteria. TiO_2 meets almost all the criteria,[2] but its bandgap is too large to absorb sunlight efficiently. Thus, bandgap reduction in TiO_2 has been studied extensively. The most common method used for bandgap reduction is the incorporation of impurities, such as C and N.[4,5] However, it has been argued that although impurities can reduce the bandgap, their incorporation also leads to poor photoresponse because the partially occupied impurity band can act as a killer for photogenerated carriers. It has been demonstrated that passive donor-acceptor co-doping may suppress the recombination and yet maintain a reduced bandgap, revealing that nonisovalent compound alloying could be an excellent choice for bandgap engineering due to the large band offsets between the compounds.[6–8] Compound alloying poses several critical problems, including choosing the appropriate host and alloying semiconductors, the alloying approach, and the alloying concentration. A thorough understanding of the nonisovalent alloying physics is necessary to prescreen the potential alloying materials for a given purpose and, hence, to avoid the expense of the trial-and-error method.

In this paper, we have studied the electronic structure of the ZnO:GaN nonisovalent compound-alloy system by density-functional theory (DFT). We choose the ZnO:GaN compound system as a case study for two reasons: First, recent experimental results have revealed dramatically improved PEC performance on the ZnO:GaN system;[7] second, ZnO and GaN have the same structure (wurtzite) and similar bandgaps. The lattices of ZnO and GaN match very well (ZnO: $a=3.245$ Å and $c=5.232$ Å; GaN: $a=3.195$ Å and $c=5.202$ Å). We find that incorporating one compound into the other indeed leads to reduced bandgap as compared to that of either ZnO or GaN. A recent theoretical study has also shown bandgap reductions in these mixed materials.[9] Interestingly, we find that the bandgap reduction is not symmetric; i.e., incorporating GaN in ZnO host results in much more effective bandgap reduction than incorporating ZnO in a GaN host. We find that this phenomenon can be understood qualitatively by electron and hole wave-function localizations, as reflected by their respective effective masses; it can also provide general rules on how to choose host materials for more effective bandgap engineering. We further find that both the ZnO:GaN superlattice and random-alloying systems can result in bandgap reduction. However, optical absorption at longer-wavelength regions (near visible range) is more efficient in the random-alloy system than in the superlattice system. These results are applicable to other semiconductor compound materials.

II. COMPUTATIONAL METHODS

For our calculation, we use the generalized gradient approximation (GGA) (Ref. 10) to DFT and the projected augmented wave (PAW) basis[10,11] as implemented in the Vienna *ab initio* simulation package (VASP 4.6.21).[12,13] A plane-wave cutoff energy of 400 eV was used, and the ion positions were always relaxed until the force on each of them was 0.01 eV/Å or less. For the alloy system we took a $3\times3\times3$ supercell, containing 108 atoms. To achieve energy convergence, a dense $5\times5\times3$ K-point mesh was used for the final energy calculations. It is known that within the GGA, the Zn d orbital lies too high in energy. GGA+U can partially correct this problem. A value of $U_{\mathrm{eff}}=7$ eV has been used for the Zn and Ga d bands throughout our calculations. The calculated bandgap for ZnO with GGA+U is 1.60 eV, which is still much lower than the measured bandgap of 3.37 eV. On the other hand, for GaN, the calculated bandgap is 2.44 eV, in contrast to an experimental bandgap of 3.44 eV. The optical properties were calculated by the OPTIC code[14] as implemented in the all-electron WIEN2K code.[15] For the optical plots in this paper, only the diagonal components of the momentum matrix were calculated, because the off-diagonal elements would not contribute significantly.

Previous calculations have shown that the calculated bowing of semiconductor alloys is close to the experimental value, even for systems with very large bowing parameters,[16] where the bowing parameter b for a ZnO:GaN alloy can be defined by the following equation:

$$E_g(x) = (1-x)E_g(\text{ZnO}) + xE_g(\text{GaN}) - bx(1-x), \tag{1}$$

where $E_g(x)$, $E_g(\text{ZnO})$, and $E_g(\text{GaN})$ are the bandgaps for the ZnO:GaN alloy, ZnO, and GaN, respectively. This indicates that to the first-order approximation, the DFT bandgap correction can be linear to the concentration x as the nonlinear term with bowing parameter can be cancelled out. Hence, a linear interpolation can be used to correct the calculated bandgap; i.e., a value

$$\Delta E_g = x\Delta E_g(\text{ZnO}) + (1-x)\Delta E_g(\text{GaN}) \tag{2}$$

was added to the calculated bandgap, where $\Delta E_g(\text{ZnO})$ and $\Delta E_g(\text{GaN})$ are the bandgap differences between the GGA $+U$ and the corresponding experimental bandgaps. For example, a recent experimental study found that the bandgap of 6% Zn-O concentration in GaN is of 2.77 eV,[17] whereas our interpolated bandgap at 5.6% Zn-O in GaN is 2.83 eV, which is in quite good agreement.

ZnO and GaN have a type-II band alignment. Here, we consider two representative cases for the compound-alloy system: (i) $(\text{ZnO})_n(\text{GaN})_n$ superlattices and (ii) a random-$(\text{ZnO})_{1-x}(\text{GaN})_x$ alloy system, i.e., random distribution of one compound into another that serves as the host. Case (i) can be obtained by epitaxial growth, whereas case (ii) is likely to be found in sintered mixed compound powders.[7] We simulate the "random alloy" by taking the minimum-energy configuration of the "dopant" in the host system out of several possible configurations in our supercell. Because of the symmetrical nature and finite size of the supercell, the number of possible configurations is limited. For example, for Ga and N "codoping" (termed as "Ga-N doping") in a ZnO supercell, where Ga substituted the cation site and N substituted the anion site, the possible number of combinations are very limited. In fact, Ga and N tend to bond together in ZnO host to compensate for the charge imbalance caused by N doping alone. N atom far from Ga atom in ZnO matrix would create local defects centers, which may result in charge recombination centers. This is because the effect of Ga would be screened by surrounding ZnO network. So only two possibilities exist, either Ga-N reside on the same layer together, or they are on tow adjacent layer along c axis. It was found that, even for larger number of Ga-N (Zn-O) dimers, they tend to cluster together in the host ZnO (GaN). Strictly speaking, this may not correspond to the actual thermodynamic random system, but it is sufficient for the present purpose. Most of the following discussion for alloy system would be centered on one pair of dopant in the host supercell.

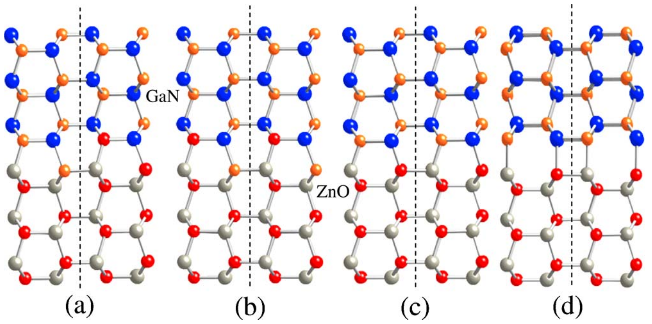

FIG. 1. (Color online) Possible $(1\bar{1}00)$ GaN:ZnO interfaces. (c) was found to be the energetically most favorable interface. Red, gray, blue, and orange spheres represent O, Zn, Ga, and N atoms, respectively. The dashed vertical lines show the $[1\bar{1}00]$ directions.

III. RESULTS AND DISCUSSIONS

A. Superlattice system

We first discuss the electronic properties of the superlattice that also allow us to calculate the band offsets between ZnO and GaN. Both ZnO and GaN have strong polarities along their c axis. Their polar surfaces, $\pm(0001)$, are usually unstable and can lead to large carrier separation. Thus, in our study, the ZnO:GaN superstructures are constructed on the nonpolar surfaces, e.g., $(1\bar{1}00)$. We have considered a series of possible interfacial structures on the $(1\bar{1}00)$ surface. Figure 1 shows some representative structures projected along the $[1\bar{1}20]$ direction. The upper part is GaN and the lower part is ZnO. In Fig. 1, the red balls are O atoms, orange balls are N atoms, gray balls are Zn atoms, and blue balls are Ga atoms. Figures 1(a)–1(c) have lattice-matched interfacial structures. Figures 1(a) and 1(b) have two different degrees of chemical intermixing, i.e., O and N atoms exchange their location at the interface. Figure 1(c) has no such chemical mixing. Figure 1(d) is an inversion domain boundary. We find that chemical mixing on the nonpolar surface is not energetically preferred. Figure 1(c) has the lowest energy among these structures because it contains a minimum number of "wrong bonds" (i.e., Ga-O and Zn-N bonds) at the interface.

We have considered superlattices with different thicknesses of the $(\text{ZnO})_n(\text{GaN})_n$ layer. Figure 2 shows the GGA$+U$ corrected bandgap variations with respect to the layer thickness. The bandgap opening with thinner layers is a direct consequence of the quantum confinement. This shows that the bandgap—and, hence, the absorption properties—can be tuned by the superlattice thickness n. For $(\text{ZnO})_n(\text{GaN})_n$ superlattices, the top of the valence band is mainly composed by the N p orbitals located at the GaN side with large weight near the interface. On the other hand, the bottom of the conduction band is mainly composed by the O $2s$ and cation $4s$ orbitals. These results indicate that only the regions around the interface, where the bonding between Ga-O and Zn-N occurs, would absorb photons with energies corresponding to the reduced bandgap.

We have also calculated the band offsets between ZnO and GaN. We use the supercell, as described above, to cal-

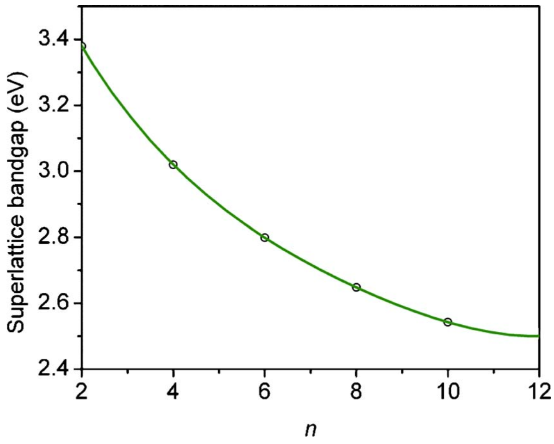

FIG. 2. (Color online) Calculated GGA+U corrected bandgaps as a function of the layer thickness n of superlattice $(ZnO)_n(GaN)_n$.

culate the relative energy positions between O 1*s* and N 1*s* states. Two separate calculations for pure ZnO and GaN cells were also performed to find the energy position of the valence band maximum (VBM) with respect to O 1*s* and N 1*s*, respectively. The VBM offset between ZnO and GaN was then derived by comparing the relative positions of these core bands.[18] Our calculated GGA+U VBM offset between ZnO and GaN is 0.7 eV, with higher GaN VBM. As GaN and ZnO have similar bandgaps, the band offset between their conduction-band minima (CBM) is almost the same. It should be noted that the experimentally measured band offset depends on the interfacial structure and chemical compositions. It has been shown that, depending on the cation- or anion-rich interface, the band offset can vary from 0.5 to 1.0 eV.[19,20] Therefore, our calculated band offsets are in the range of experimentally reported values.[19]

B. Random-alloy systems

We now discuss the electronic structures of $(ZnO)_{1-x}(GaN)_x$ random-alloy systems. We have considered both randomly distributed Ga-N pairs in a ZnO host and randomly distributed Zn-O pairs in a GaN host. Figure 3(a) shows the calculated band structure for a 108-atom ZnO supercell containing one Ga-N pair ($x=0.0185$). The introduction of Ga-N in ZnO does not alter the basic band structure

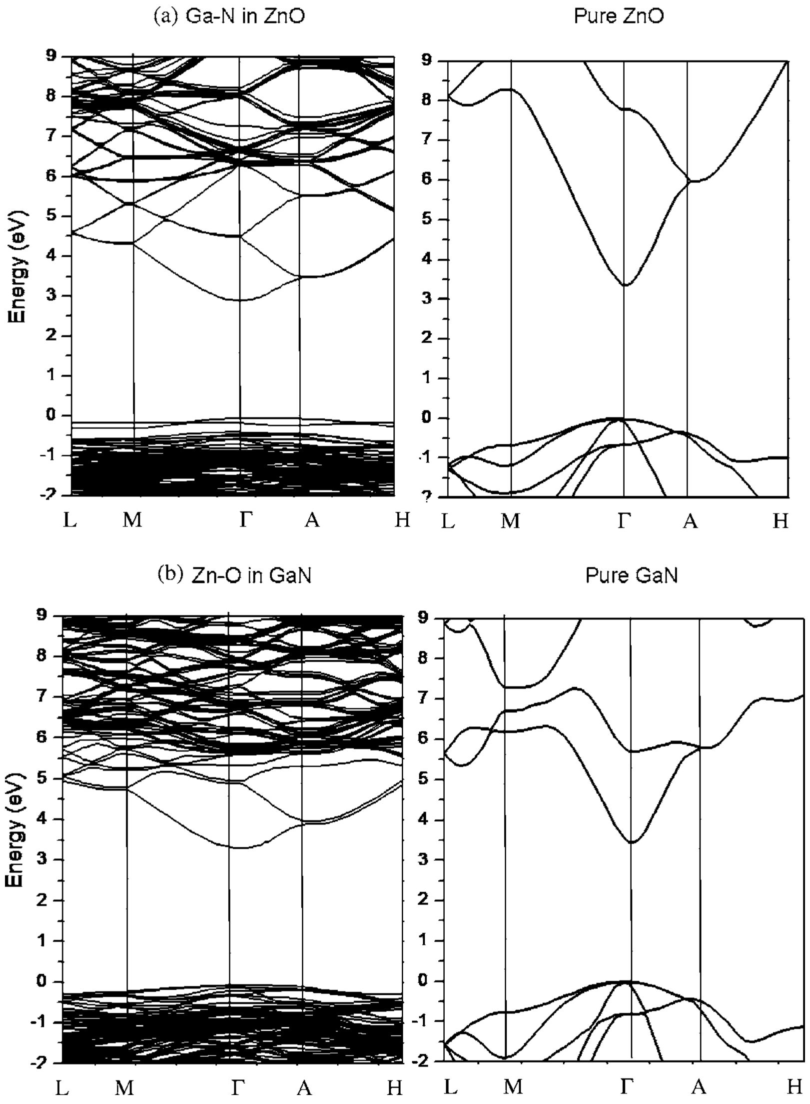

FIG. 3. Band structures of (a) Ga-N-doped ZnO and (b) Zn-O-doped Ga-N ($x=0.0185$). The corresponding pure host's band structures are also shown. It should be noted that in the doped alloy's band structure, multiple band foldings are seen due to bigger supercell, compared to the pure host. As a $3 \times 3 \times 3$ supercell was used threefold band foldings are seen in all the three directions. Also bandgaps are corrected according to the formula discussed in the paper.

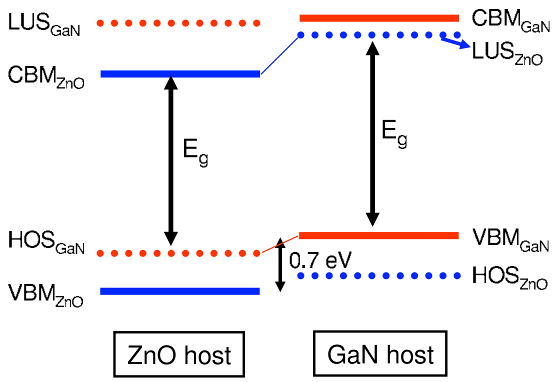

FIG. 4. (Color online) Possible band-edge positions for (left) Ga-N pair in ZnO host and (right) Zn-O pair in GaN host.

of ZnO, except at the VBM.[21] Because N is less electronegative than O, the top of the VBM now consists mainly of N *p* orbitals and is raised about 0.43 eV compared to the VBM of the host ZnO, whereas the shift of the CBM is only 0.02 eV upward, giving a net bandgap reduction of 0.41 eV. The calculated GGA+U corrected bandgap is 2.93 eV. Increasing the N concentration leads to broadening of the N *p* bands and further reduction in the bandgap.

For Zn-O pairs distributed in a GaN host, a different picture emerged. The calculated band structure [Fig. 3(b)] indicates that the substitution of Ga-N with ZnO causes only a small change to the basic bandgap of GaN. As O is more electronegative than N, one would not expect that substitution of N by an O will raise the VBM of GaN. However, we found that at $y=1-x=0.0185$, the VBM is raised by 0.04 eV. This is because the Zn *d* bands are shallower than the Ga *d* bands. The coupling between N *p* and Zn *d* causes the upshift of VBM. The total bandgap reduction is found to be only 0.10 eV, which is much smaller than that of a Ga-N pair in a ZnO host, 0.41 eV. Our results thus suggest that clearly the bandgap reduction for the ZnO:GaN system is asymmetric; i.e., bandgap reduction is much more effective for Ga-N in a ZnO host than for Zn-O in a GaN host. Thus, it is important to choose the right host material to achieve effective bandgap reduction.

We find that this asymmetric phenomenon can be understood by the VBM and CBM effective masses of these semiconductor compounds. As shown above, ZnO and GaN have a type-II band offset of about 0.7 eV for both CBM and VBM, as depicted by the solid lines in Fig. 4. Therefore, one may expect a similar bandgap reduction for both ZnO host and GaN host. However, in the case of incorporating pairs of one compound into another host compound, the actual situation would be different. The lowest unoccupied state (LUS) and the highest occupied state (HOS) of the pairs are not at the same positions as of CBM and VBM of their corresponding bulk state due to quantum confinement from the host. For example, when a Ga-N pair is incorporated into a ZnO host, the HOS of Ga-N will shift downward due to the confinement from the ZnO host. However, this downward shift is small because of the heavy VBM effective mass. Thus, the position of HOS of the Ga-N pair is close to that of the VBM of GaN in the calculated band offset, as indicated qualitatively in the left panel of Fig. 4. The LUS of Ga-N has virtually no effect on the CBM of ZnO. As a result, the bandgap is reduced significantly even when a small number of Ga-N pairs is incorporated. On the other hand, when a Zn-O pair is incorporated into a GaN host, the confinement occurs on the unoccupied states of the Zn-O pair due to the type-II band offset. Because of the light CBM effective mass, the upshift of the LUS of the Zn-O pair is large. Therefore, the position of the LUS of the Zn-O pair is much higher than that of the CBM of the ZnO bulk, close to the CBM of GaN, as shown in the right panel of Fig. 4. Thus, the bandgap reduction caused by a Zn-O pair in a GaN host is much smaller than that caused by a Ga-N pair in a ZnO host. Because the nominal concentration of impurity pairs is always limited due to their thermodynamic solubilities, our analysis suggests that ZnO should be a better host than GaN for effective bandgap reduction in the random-compound-alloy system because the localized wave function gives a large effective dopant concentration around the N atoms. The same principle can be applied to other semiconductor compound systems.

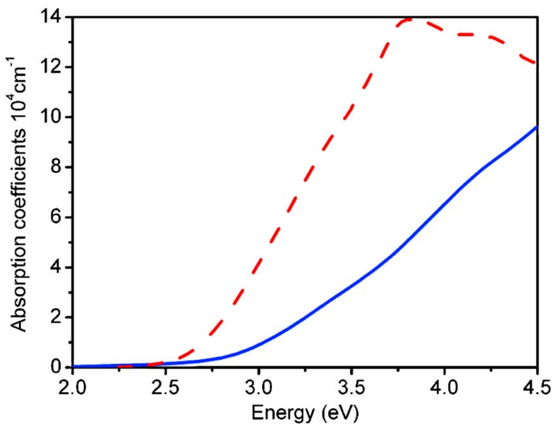

FIG. 5. (Color online) Calculated total absorption coefficient spectra of superlattice of $(ZnO)_8(GaN)_8$ (solid blue curve) and $(ZnO)_{1-x}(GaN)_x$ (red dashed curve) random alloys ($x=0.0740$).

C. Optical absorptions of superlattice and random-alloy systems

Finally, we compare the superlattice and the random-alloy systems as discussed above. Our calculations reveal that both systems can result in reduced bandgaps. To achieve a bandgap of around 2.6 eV using the superlattice system, we need an eight-layer superlattice. To achieve the same bandgap using the random-alloy system, we need an alloy with a Ga-N concentration of 7.4%. Figure 5 shows the calculated total absorption coefficients for the superlattice system for $(ZnO)_8(GaN)_8$ (solid blue curve) and the random-alloy system $(ZnO)_{1-x}(GaN)_x$ with $x=0.0740$ (dashed red curve). Both systems have a similar bandgap of 2.6 eV. However, the random-alloy system exhibits much larger absorption coefficients than the superlattice system in the longer-wavelength regions as can be seen in Fig. 5. The main reason for this difference is that in the superlattice system, the VBM is localized at the GaN side, and the CBM is localized at the ZnO side. The overlap of the CBM and VBM wave functions occurs only in the interface regions; therefore, the transition matrix elements and the absorption of light in the long-wavelength regions are small. On the other hand, in the random-alloy system, all the incorporated Ga-N pairs would participate in the absorption. A recent experiment did show that random-alloy ZnO:GaN has increased photoresponse under visible light[6] compared to pure ZnO or N-doped ZnO. However, for superlattice system such experimental results are not available as far as we know. Thus, in general, the random-alloy system is more efficient than the superlattice and core-shell[21] systems in light absorption in the longer-wavelength regions. We also want to point out that the bandgap reduction for the random-alloy system could be limited by achievable alloy solubility, but the superlattice system may not have such a limitation.

IV. CONCLUSIONS

In conclusion, we have studied the electronic structure of nonisovalent ZnO:GaN compound-alloy systems by DFT. We found that the alloying of ZnO and GaN can result in bandgap reduction as compared to that of ZnO or GaN, and thus, light absorption in longer-wavelength regions. We found that the bandgap reduction in the ZnO:GaN system is not symmetric, i.e., incorporating of GaN in a ZnO host results in much more effective bandgap reduction than incorporating ZnO in a GaN host. We explained this phenomenon by CBM and VBM effective masses. We further found that, in general, the random-alloy system should be better than the superlattice system for efficient light absorption in the longer-wavelength regions. Our study, therefore, provides important insights and guidelines for designing bandgap reduction using nonisovalent semiconductor compound systems.

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