Electronic structure of \((\text{ZnO})_{1−x} (\text{InN})_x\) alloys calculated by interacting quasi-band theory

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We calculated the electronic structure of \((\text{ZnO})_{1−x} (\text{InN})_x\) \((=\text{ZION})\), which belongs to a novel category of hybrid \((\text{II}−\text{VI})_{1−x} (\text{III}−\text{V})_x\) alloys, by the interacting quasi-band theory aided by the sp³ tight-binding model of the wurzite structure. The tight-binding parameters of the irregular bonds \((\text{Zn}−\text{N} \text{ and In}−\text{O})\) were estimated by iterating the relevant normal bonds and the absolute atomic levels were corrected by the electron affinities of \text{ZnO} and \text{InN}. We thus obtained the quasi-band structure of ZION at various concentrations. Across the entire range of concentrations, ZION exhibited a direct energy gap at \(\Gamma\) and the band-gap energy continuously changes from 0.7 to 3.3 eV with a large band-gap bowing. A particularly, large shift was observed around \(x = 0.5\). The obtained theoretical results imply that ZION \((x = 0.1−0.3)\) is a suitable material for visible-light devices.

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1. Introduction

Semiconducting materials have usually been developed under the octet rule, which stipulates that the number of valence electrons in a unit cell is a multiple of eight.\(^1\) Initial investigations of \text{Si} and \text{Ge} were followed by investigations of \text{III}−\text{V} and \text{II}−\text{VI} compounds with multiple combinations of elements. Another important technique in semiconductor technology is alloying, in which the alloy composition dictates the physical properties of alloyed material. Most of the investigated alloy systems fall into the \text{III}−\text{V} or \text{II}−\text{VI} categories. Among the well-known combinations are three \((\text{II}1−\text{VI}x)\) alloys formed by cation substitution and \((\text{II}1−\text{II}x)\) alloys, by the interacting quasi-band theory aided by the sp³ tight-binding model of the wurzite structure. The tight-binding parameters of the irregular bonds \((\text{Zn}−\text{N} \text{ and In}−\text{O})\) were estimated by iterating the relevant normal bonds and the absolute atomic levels were corrected by the electron affinities of \text{ZnO} and \text{InN}. We thus obtained the quasi-band structure of ZION at various concentrations. Across the entire range of concentrations, ZION exhibited a direct energy gap at \(\Gamma\) and the band-gap energy continuously changes from 0.7 to 3.3 eV with a large band-gap bowing. A particularly, large shift was observed around \(x = 0.5\). The obtained theoretical results imply that ZION \((x = 0.1−0.3)\) is a suitable material for visible-light devices.

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the constituent III–V and III–V semiconductors. The calculation procedures are detailed elsewhere.\(^\text{12-14}\) In this study, we further extend the IQB theory to investigate the electronic structure of \((\text{ZnO})_{1-x}(\text{InN})_x\), a typical novel hybrid of the alloy systems (II–VI–VI)\(_{1-x}(\text{III–V})_x\). As stated above, we must properly account for the randomness due to the statistical occupation of atoms. We must also determine the tight-binding parameters of the irregular bonds and the correct off-sets of the potential energies.

2. Theory and calculation model

According to Ref. 7 an appropriate mixture of ZnO and InN generates a pseudo-binary system \((\text{ZnO})_{1-x}(\text{InN})_x\) with neutral average charge. In other words, there may be a charge mismatch in some unit cells, but statistically the whole alloy satisfies the octet rule. Based on the experimental results, we assume a wurzite structure with a regular lattice as shown in Fig. 2. The cation sites 1 and 2 are occupied by a cation (C=Zn or In) atom with respective probabilities \(1-x\) and \(x\). Meanwhile, the anion sites 3 and 4 are occupied either by an anion (A=O or N) atom with respective probabilities \(1-x\) and \(x\).

Reference 15 applied the tight-binding model with the sp\(^3\) model to crystal compound semiconductors with wurzite structure. They successfully reproduced the band structures near the valence and conduction bands in several III–V semiconductors. The cation sites 1 and 2 are occupied by a cation (Zn or In) atom with respective probabilities 1–\(x\) and \(x\). Meanwhile, the anion sites 3 and 4 are occupied either by an anion (O or N) atom with respective probabilities 1–\(x\) and \(x\).

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We first construct the quasi-Bloch wave function for a wave vector \(\mathbf{k} = (k_1, k_2, k_3)\) as

\[
\psi(\mathbf{k}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} \sum_i \sum_\sigma \exp[i \mathbf{k} \cdot (\mathbf{R} + \mathbf{\tau}_i)] \beta_{\sigma}^i \phi_{\sigma}^i(\mathbf{R} + \mathbf{\tau}_i). \tag{1}
\]

Here, \(\phi_{\sigma}^i(\mathbf{R} + \mathbf{\tau}_i)\) denotes the atomic orbital \(\sigma=\text{s}, \text{p}_x, \text{p}_y, \text{p}_z\) at the \(i\)th site at the inner position \(\mathbf{\tau}_i (i = 1, 2, 3, 4)\) in a unit cell located at \(\mathbf{R}\), and \(N\) is the number of unit cells. The atomic orbitals are assumed to be orthogonal with each other: \(\langle \phi_{\sigma}^i(\mathbf{R} + \mathbf{\tau}_i) | \phi_{\sigma'}^j(\mathbf{R'} + \mathbf{\tau}_j) \rangle = \delta_{\mathbf{RR'}} \delta_{\mathbf{\tau}_i \mathbf{\tau}_j} \delta_{\sigma \sigma'}\). It should be reminded that because of randomness the wave vector \(\mathbf{k}\) in alloys is no more a good quantum number, but remains a suitable index in statistical sense. The local amplitude \(\beta_{\sigma}^i\) is assumed as a variational parameter dependent on the occupation at the \(i\)th site. In the case of \((\text{ZnO})_{1-x}(\text{InN})_x\), there are following 32 parameters, each corresponding to the atomic orbital \(\phi_{\sigma}^i\):

\[
\begin{align*}
\beta_{\text{Zn}}^{1Zn} &= (\beta_{\text{s}}^{\text{Zn}}, \beta_{\text{p}_x}^{\text{Zn}}, \beta_{\text{p}_y}^{\text{Zn}}, \beta_{\text{p}_z}^{\text{Zn}}), \\
\beta_{\text{Zn}}^{2Zn} &= (\beta_{\text{s}}^{\text{Zn}}, \beta_{\text{p}_x}^{\text{Zn}}, \beta_{\text{p}_y}^{\text{Zn}}, \beta_{\text{p}_z}^{\text{Zn}}), \\
\beta_{\text{In}}^{1In} &= (\beta_{\text{s}}^{\text{In}}, \beta_{\text{p}_x}^{\text{In}}, \beta_{\text{p}_y}^{\text{In}}, \beta_{\text{p}_z}^{\text{In}}), \\
\beta_{\text{In}}^{2In} &= (\beta_{\text{s}}^{\text{In}}, \beta_{\text{p}_x}^{\text{In}}, \beta_{\text{p}_y}^{\text{In}}, \beta_{\text{p}_z}^{\text{In}}), \\
\beta_{\text{O}}^{1O} &= (\beta_{\text{s}}^{\text{O}}, \beta_{\text{p}_x}^{\text{O}}, \beta_{\text{p}_y}^{\text{O}}, \beta_{\text{p}_z}^{\text{O}}), \\
\beta_{\text{O}}^{2O} &= (\beta_{\text{s}}^{\text{O}}, \beta_{\text{p}_x}^{\text{O}}, \beta_{\text{p}_y}^{\text{O}}, \beta_{\text{p}_z}^{\text{O}}), \\
\beta_{\text{N}}^{1N} &= (\beta_{\text{s}}^{\text{N}}, \beta_{\text{p}_x}^{\text{N}}, \beta_{\text{p}_y}^{\text{N}}, \beta_{\text{p}_z}^{\text{N}}), \\
\beta_{\text{N}}^{2N} &= (\beta_{\text{s}}^{\text{N}}, \beta_{\text{p}_x}^{\text{N}}, \beta_{\text{p}_y}^{\text{N}}, \beta_{\text{p}_z}^{\text{N}}), \\
\end{align*}
\tag{2}
\]

We first consider the expectation value of the Hamiltonian for the wave function (1). We then obtain, for example, the factor

\[
\begin{align*}
&\beta_{\text{Zn}}^{2Zn} \times U_{\text{Zn}}^{\sigma} x \beta_{\sigma}^{3O} + \beta_{\text{In}}^{2In} \times U_{\text{In}}^{\sigma} x (1-x) \beta_{\sigma}^{3N} \\
&+ \beta_{\text{O}}^{2O} (1-x) U_{\text{O}}^{\sigma} x \beta_{\sigma}^{3O} + \beta_{\text{N}}^{2N} (1-x) U_{\text{N}}^{\sigma} (1-x) \beta_{\sigma}^{3N},
\end{align*}
\tag{3}
\]

for a vertical bond between sites 2 and 3. Here \(U_{\text{Zn}}^{\sigma}, \ldots\) for example, denotes the transfer energy between Zn-\(\sigma\) orbital and O-\(\sigma'\) orbital. It should be noted that the above obtained factor contains \(U_{\text{Zn}}^{\sigma}, \ldots\) for irregular bonds in addition to \(U_{\text{Zn}}^{\sigma}, \ldots\) for normal bonds.

We next take the ensemble average over the statistical occupation of each site, neglecting the correlation among different sites. The result is then extremized with respect to \(\beta_{\sigma}^\star\), under the constraint condition, \(\langle \psi^\star(k) | \psi^\star(k) \rangle = 1\). We thus obtain a secular equation for \(\beta_{\sigma}^\star\)’s with \(32 \times 32\) non-Hermitian matrix.
\[
\begin{pmatrix}
H^{1Zn,1Zn} & 0 & 0 & 0 \\
0 & H^{1In,1In} & 0 & 0 \\
0 & 0 & H^{2Zn,2Zn} & 0 \\
0 & 0 & 0 & H^{2In,2In}
\end{pmatrix}
\begin{pmatrix}
(1 - x)H^{1Zn,3O} & xH^{1Zn,3N} & (1 - x)H^{1Zn,4O} & xH^{1Zn,4N} \\
(1 - x)H^{1In,3O} & xH^{1In,3N} & (1 - x)H^{1In,4O} & xH^{1In,4N} \\
(1 - x)H^{2Zn,3O} & xH^{2Zn,3N} & (1 - x)H^{2Zn,4O} & xH^{2Zn,4N} \\
(1 - x)H^{2In,3O} & xH^{2In,3N} & (1 - x)H^{2In,4O} & xH^{2In,4N}
\end{pmatrix}
\begin{pmatrix}
\beta^{1Zn} \\
\beta^{1In} \\
\beta^{2Zn} \\
\beta^{2In} \\
\beta^{3O} \\
\beta^{3N} \\
\beta^{4O} \\
\beta^{4N}
\end{pmatrix}
= E
\]

(4)

where each matrix element is a 4 × 4 matrix itself, which has a form:

\[
H^{1Zn,1Zn} = H^{2Zn,2Zn} =
\begin{pmatrix}
\varepsilon^{Zn} & 0 & 0 & 0 \\
0 & \varepsilon^{Zn} & 0 & 0 \\
0 & 0 & \varepsilon^{Zn} & 0 \\
0 & 0 & 0 & \varepsilon^{Zn}
\end{pmatrix},
\]

\[
H^{3O,3O} = H^{4O,4O} =
\begin{pmatrix}
\varepsilon^{O} & 0 & 0 & 0 \\
0 & \varepsilon^{O} & 0 & 0 \\
0 & 0 & \varepsilon^{O} & 0 \\
0 & 0 & 0 & \varepsilon^{O}
\end{pmatrix},
\]

\[
H^{1C,4A} = H^{2C,3A} = g_3(k)
\]

(5)
Here, suffix stands for C=Zn or In for cation, and A=O or N for anion: $\varepsilon^C_\sigma (\varepsilon^A_\sigma)$ denotes the atomic energy of C-\sigma (A-\sigma) orbital, and $U^{\text{ZnO}}_\text{CA} (U^{\text{InN}}_\text{CA})$ stands for the transfer energy between nearest neighbour C-\sigma and A-\sigma orbitals with vertical (oblique) position. The structure factors are given by

$$
\begin{align*}
g_1(k) &= \exp\left[\left(-\frac{k_1}{3} + \frac{k_2}{3} + \frac{k_3}{8}\right)\right], \\
g_2(k) &= \exp\left[\left(\frac{k_1}{3} - \frac{k_2}{3} + \frac{k_3}{8}\right)\right], \\
g_3(k) &= \exp\left[\left(-\frac{3k_3}{8}\right)\right], \\
f_0(k) &= \exp(i k_3) + 1 + \exp(-i k_3), \\
f_1(k) &= \exp(i k_3) - \frac{1}{2} + \frac{1}{2} \exp(-i k_3), \\
f_2(k) &= 1 \pm \exp(-i k_3).
\end{align*}
$$

The matrix in Eq. (4) contains the tight-binding parameters of pure ZnO and InN crystals (Table I), the concentration $x$, and the structural factors for the $k$-vectors in the Brillouin zone of a wurzite structure (Fig. 3).

It would be informative to show here the relation between the VCA and IQB theory. If we apply the following constraint to the amplitude $\beta_\sigma z$'s in the trial wave function (1)

$$
\beta^Zn = \beta^\text{In}, \beta^Zn = \beta^\text{In}, \beta^\text{O} = \beta^\text{N}, \beta^\text{O} = \beta^\text{N},
$$

it reproduces a typical VCA scheme. After a similar procedure as above we obtain a reduced $16 \times 16$ Hamiltonian matrix which contains only averaged values of the relevant tight-binding parameters, for example

$$
\begin{align*}
\varepsilon^1_x &= \varepsilon^3_x = x \varepsilon^Zn + (1 - x) \varepsilon^\text{In}, \\
U^{\text{ZnO}}_n &= x U^{\text{ZnO}}_n + x U^{\text{ZnN}}_n (1 - x) \\
&+ (1 - x) U^{\text{ZnN}}_n (1 - x).
\end{align*}
$$

Thus the VCA lacks effects of fluctuation in potentials and transfers. In other words, the VCA first takes the average of random Hamiltonian $H_{\text{random}}$ and then solve the Schrödinger equation of $\langle H_{\text{random}} \rangle_x$. While the IQB takes care of the fluctuations in $H_{\text{random}}$ to some extent.

To calculate the electronic structure of compound ZION alloys, we must additionally consider the following points.

1. The transfer energy $U^{\text{ZnO}}_\text{CA}$ and $U^{\text{InN}}_\text{CA}$ appearing in the off-diagonal term of the quasi-Hamiltonian matrix depends on the lattice constants $a$ and $c$ (Fig. 2). As ZnO and InN have different lattice constants, even $U^{\text{ZnO}}_{a\sigma}$ in alloy (ZnO)$_x$ (InN)$_{1-x}$ for example, should differ from that in pure ZnO. It is shown to be satisfactory that the transfer energy depends on the inverse-square of the bond length.

2. Therefore, we corrected them by the following equations.

$$
\begin{align*}
U^{\text{ZnO}}_{a\sigma} (\text{alloy}) &= U^{\text{ZnO}}_{a\sigma} \times \left[ \frac{1}{\sqrt{a_{\text{ZnO}}}} c_{\text{ZnO}} / (a_{\text{alloy}})^2 c_{\text{alloy}} \right]^2, \\
U^{\text{InN}}_{a\sigma} (\text{alloy}) &= U^{\text{InN}}_{a\sigma} \times \left[ \frac{1}{\sqrt{a_{\text{InN}}}} c_{\text{InN}} / (a_{\text{alloy}})^2 c_{\text{alloy}} \right]^2, \\
U^{\text{alloy}}_{a\sigma} (\text{alloy}) &= U^{\text{alloy}}_{a\sigma} \times \left[ c_{\text{alloy}} \right]^2, \\
&= (1 - x) a_{\text{ZnO}} + x a_{\text{InN}}, \\
c_{\text{alloy}} &= (1 - x) c_{\text{ZnO}} + x c_{\text{InN}}.
\end{align*}
$$

Here, $U^{\text{CA}}_{a\sigma}$ (alloy), the transfer energies in the vertical position depends only on the lattice constant $c$ along the $c$-axis, whereas and $U^{\text{CA}}_{a\sigma}$ (alloy) in the oblique position depends on

Table I. Tight-binding sp$^3$ parameters used for crystal ZnO and InN in eV$^{15, 16}$.

| parameter     | ZnO     | InN     |
|---------------|---------|---------|
| $\varepsilon^Zn$ | -19.05  | -11.92  |
| $\varepsilon^\text{In}$ | 4.14    | 0.49    |
| $\varepsilon^\text{O}$ | 4.14    | 0.46    |
| $\varepsilon^\text{N}$ | 1.67    | 0.48    |
| $U^{\text{ZnO}}_n$ | 12.37   | 6.53    |
| $U^{\text{ZnN}}_n$ | 12.37   | 6.53    |
| $U^{\text{O}}_n$  | -1.51   | -0.40   |
| $U^{\text{N}}_n$  | -0.86   | -0.76   |
| $U^{\text{ZnO}}_{a\sigma}$ | 7.08    | 2.86    |
| $U^{\text{ZnN}}_{a\sigma}$ | -1.25   | -0.27   |
| $U^{\text{O}}_{a\sigma}$  | 1.92    | 2.51    |
| $U^{\text{N}}_{a\sigma}$  | -3.52   | -0.77   |
| $U^{\text{alloy}}_{a\sigma}$ | 6.20    | 2.46    |
| $U^{\text{alloy}}_{\sigma}$  | -0.86   | -0.76   |
| $U^{\text{alloy}}_{\sigma}$  | 0.03    | -0.36   |
| $U^{\text{alloy}}_{\sigma}$  | 2.49    | 1.14    |
| $U^{\text{alloy}}_{\sigma}$  | 4.3    | 5.8    |
| electron affinity | 5.21    | 5.71    |
| lattice const. $c$ [Å] | 3.25    | 3.45    |
In our previous study on alloys, such as InGaN, the absolute positions of the site energies are crucial. In the IQB theory, the absolute positions of the site energies are corrected by the correction along Eqs. (10–11). A similar relation is assumed for $U_{ZnN}$ and $U_{InN}$ in the IQB theory. Another choice of the transfer energies of the irregular bonds will be discussed later.

Third, we usually adjust the site energy in the sp³ model so that the resulting valence band maximum is to be located at 0 eV (=Fermi level) in each semiconductor. The relative values $e_{x}^{A}$, $e_{p}^{A}$, $e_{x}^{C}$, and $e_{p}^{C}$ are then meaningful within the same material, but not among two different materials. In the IQB theory, the absolute positions of the site energies are crucial. In our previous study on alloys, such as InGaN, the N atom was common to both InN and GaN. In this scenario, the site energies $e_{N}$ and $e_{p}$ can be shifted to coincide in GaN and InN. However, the present novel hybrid alloy (ZnO)$_{1−x}$(InN)$_{x}$ has no common element, so the site energies are corrected by the electron affinities that is, the difference between the vacuum level and the bottom of the conduction band.

Figure 4 schematizes the present correction for ZION, which sets the absolute origin of the energy level to be the vacuum level. Here, we use the electron affinities listed in Table I. Note that the Fermi level is not 0 eV after this correction.

3. Results and discussion

Figure 5 presents the calculated electronic energy band structures of several ZION compositions. Table I shows the tight-binding parameters used in this study, based on the values in Refs. 15 and 16 with relations given in Table 3 in Ref. 15. A set of these parameters quantitatively reproduces the electronic band structure of pure ZnO and InN crystals.

In the present study, the origin of the energy has been chosen as the vacuum level = 0 eV, we illustrate here those energy levels <0 eV, since those above the vacuum level are inaccurate in the tight-binding model. In these plots, the present results computed by IQB theory (blue solid lines) are compared with those of VCA (green dashed lines) using Eqs. (8) and (12). In both sets of results, ZION exhibits a direct band gap at the Γ point over the entire range of composition ratios. This suggests that ZION is applicable to optical devices.

As stated in our previous papers, the electronic structures obtained by IQB theory are governed by mixing between the quasi-extend states which are approximately reproduced in VCA, and the quasi-localized state (QLS) which represents the effective fluctuation. Thus, the IQB theory gives quasi-Bloch states modulated by randomness in alloys. For (ZnO)$_{1−x}$(InN)$_{x}$ case, QLS’s are located at

$$x_{e}^{Zn} + (1 − x) e_{p}^{In}$$

for cation QLS (Zn,In: $\sigma$ = s, p , (13a)

$$x_{e}^{Q} + (1 − x) e_{p}^{N}$$

for anion QLS (O,N:$\sigma$) $\sigma$ = s, p . (13b)

In the limit $x = 0$ (ZnO), each QLS is nothing but In and Na atomic orbital. In the opposite limit $x = 1$ (InN), each QLS is nothing but Zn and O atomic orbital. Thus, the QLS represents the effect of impurity in the limits $x = 0$ and 1. While in the intermediate concentrations, it represents effective potential fluctuation. As the composition changes, the QLS position shifts and modifies the VCA states. As stated in Refs. 11–14, the obtained 32 electronic levels for each quasi- $k$ vector do not equally contribute to the density of states: contribution is proportional to $|\partial E/\partial k|$. Thus, the QLS contributes null density of states in the crystal limits ($x = 0$ and $x = 1$), and little in the ZnO-rich and InN-rich regions. The flat regions appeared in the calculated band energies in the intermediate concentrations (Figs. 5–8), which are mainly constructed from QLS’s, can be considered as artefact in the IQB theory. (Around $x = 0.3$, flat bands from QLS(O, N,p) appear within the band gap having a finite width. Whether these flat bands are merely
artefact or real mid gap states should be investigated in future work.)

Around \( x = 0.5 \), the QLS(O, N: \( p \)) and the conduction band minimum (CBM) of VCA-like band are mixed remarkably. In ZnO-rich regions (\( x = 0.1 - 0.5 \)) we observe a parallel high-energy shift of the valence band. This shift can be explained as a result of the effect of QLS(O, N: \( p \)). Due to strong potential fluctuation in anion sites (\( i = 3, 4 \) (larger amplitude in higher potential N-sites)), the QLS(O,N: \( p \)) lifts the top of VCA-like valence bands so as to \( \beta_{pp}^{ON} > |\beta_{pp}^{O}| \) for \( i = 3, 4 \). Consequently, the band gap computed by the IQB is narrower than that computed by VCA where \( \beta_{pp}^{IN} = \beta_{pp}^{O} \). In InN-rich regions (\( x = 0.6 - 1 \)), the effect of QLS(O, N: \( p \)) is weakened, then the IQB results are similar to those in VCA.

Fig. 5. (Color online) Calculated electron energy diagrams of \((\text{ZnO})_{1-x}(\text{InN})_x\): blue solid lines (IQB) and green dashed lines (VCA). Flat regions are originated from QLS(cation, \( s \)) and QLS(anion, \( p \)). At \( x = 0 \) and 1 the levels from QLS’s have zero dispersion, then no contribution to the density of states.
As stated before, the transfer energy of the irregular bonds influences the band gap. We have tried several choices of the transfer energy for the irregular bonds, and compared with the experiments on $x = 0.3$ (ZnO-rich) samples, where most accurate and reproducible experimental results are obtained.\(^7\) Figure 6 shows the calculated results assuming that $U_{\text{irr}}$ and $ZnN_{\text{ss}}$ are (a) geometrical mean of the regular bond as shown in Eq. (12), and (b) arithmetic mean, which is larger than a geometrical mean, and (c) zero. It is readily seen that the geometrical mean gives satisfactory results with experimental values. Case (b) does not show high-energy shift of the valence band resulting a similar result in VCA. Case (c) shows simple superpositions of reduced pure ZnO bands and reduced pure InN bands, which do not mix with each other. Thus, we have concluded that the choice of the geometrical mean for the irregular bonds, which is consistent with theoretical investigation Eq. (12), is appropriate.

Figure 7 shows the concentration dependence of the band-gap energy at the $\Gamma$ point, determined by IQB theory and in previous experiments.\(^7\) The VCA results are also shown to guide the eye, by dotted line. The present result shows a continuous change of the band gap energy from 0.7 to 3.3 eV, with a large band-gap bowing and a particularly large shift around $x = 0.5$. This bowing may be derived from randomness in the ZION alloy. The bowing tendency is consistent with the experimental results in ZnO-rich regions ($x = 0.1–0.3$). In InN-rich regions, the present results largely differ from the experimental values. This discrepancy may arise from the reported difficulty of forming InN films by sputtering methods.\(^7\) In particular, an InN film tends to incorporate O as an impurity.\(^20\) Reference 7 reported that in ZION samples with InN-rich composition, peaks of In$_2$O$_3$ and Zn$_3$N$_4$ appear in XRD measurements. These presence might affect the band gap energy. While we assume the wurzite structure in calculation with all composition. This would be a reason for the discrepancy appeared in InN-rich region. From the present results, we conclude that the visible-light region of the band gap energy occurs around $x = 0.1–0.3$, narrower than those estimated by VCA.

In the present study, we used the lattice constant of ZION computed by Eq. (10) and adjusted the tight-binding transfer energies in each alloy composition. Let us now discuss how the deviation of the lattice constant from these ideal values influences the electronic structure. Itagaki’s group fabricated ZION by coherent growth on a ZnO substrate,\(^21\) thereby inducing a shift in the lattice constant (see Table II). When the film is thin, the ZION lattice matches that of the ZnO substrate. On a thick film, the lattice relaxes to stabilize the lattice distortion. The electronic structure differences among ZnO, (ZnO)$_{0.7}$(InN)$_{0.3}$ (coherent growth), and (ZnO)$_{0.7}$(InN)$_{0.3}$ (after relaxation) are shown in Fig. 8. Although relaxation does not remarkably change the conduction band, it removes the degeneracy in the valence band at the $\Gamma$ point, thereby reducing the band gap.

### Table II. Lattice constants and band gap energies of (ZnO)$_{0.7}$(InN)$_{0.3}$.

| Composition | c-axis (Å) | a-axis (Å) | $E_g$ (eV) |
|-------------|-----------|-----------|-----------|
| ZnO         | 5.21      | 3.25      | 3.30      |
| (ZnO)$_{0.7}$(InN)$_{0.3}$ after relaxation | 5.31 | 3.34 | 1.96 |
| (ZnO)$_{0.7}$(InN)$_{0.3}$ coherent growth | 5.46 | 3.21 | 1.79 |

---

Fig. 6. (Color online) Comparison among electron energy diagrams of (ZnO)$_{0.7}$(InN)$_{0.3}$ with different forms of the transfer energy for irregular bonds (a) geometrical mean of the regular bond, (b) arithmetic mean, and (c) zero.

Fig. 7. (Color online) Concentration dependence of the band gap energy in ZION: blue points (IQB), red points (experimental results)\(^7\) and black dotted line (derived from VCA).
4. Conclusions

We calculated the electronic structure of a novel compound semiconductor alloy $(\text{ZnO})_{1-x}(\text{InN})_x (\text{ZION})$ by the IQB theory. To handle such novel systems compromising mixtures of atomic valences, we have assumed statistical charge neutrality in the unit cell, estimated the tight-binding parameters of the irregular bonds, and shifted the site potentials corrected by the electron affinities. The secular Eq. (4) is applicable to various (II–VI)$_{1-x}$(III–V)$_x$ alloy systems of wurzite structure.

The quasi-band structures of the electronic states in ZION were obtained at various composition ratios. ZION exhibited a direct-gap energy across the range of compositions. The concentration dependence of the band-gap energy was nonlinear, showing a large band gap-bowing. The theoretical value of the band gap can be improved by accounting for lattice relaxation under the substrate constraint. The obtained theoretical results suggest that ZION is a suitable candidate for tunable visible-light devices. The likely concentration region is $x = 0.1$–0.3, with higher ZnO enrichment than predicted by Vegard’s rule (VCA).

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