Band structure and stability of zinc-blende-based semiconductor polytypes

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Using a first-principles generalized one-dimensional Ising model we have studied the band structure and stability of two types of zinc-blende-based polytype series: type-a $GaInP_2$ and type-b $CuInSe_2$. The interaction parameters for the formation energy are found to be short range, while the convergence is slower for the band-gap and conduction-band energies of the type-a $GaInP_2$ polytypes. We predict that the CuAu-like phase can coexist in nominally chalcopyrite $CuInSe_2$ and $CuInS_2$, while such coexistence is less likely in $CuGaSe_2$. We also predict that type-II band alignment can exist between different ordered type-a $GaInP_2$ polytypes, despite that the band alignment between ordered and disordered $GaInP_2$ are predicted to be type I. [S0163-1829(99)51804-3]

$A_{1-x}B_xC$ semiconductor alloys grown epitaxially on (001) substrate often exhibit atomic ordering,[1] manifested, e.g., by the CuPt-like structure[2] [Fig. 1(a)] in $A^{III}B^{III}C_2^V$ compounds ($GaInP_2$, $AlInAs_2$, and $GaInAs_2$), and by the chalcopyrite structure[3] [Fig. 1(c)] in the $A^IB^{III}C_2^{VI}$ compounds ($CuInSe_2$, $CuInS_2$, and $CuGaSe_2$). Unlike classic cases of long-range order in metallurgical systems, semiconductors often show surprisingly a coexistence of domains of a few types of ordered structures in the same sample. For example, epitaxial samples of nominally chalcopyrite $CuInS_2$ exhibit electron diffraction evidence[4] of the CuAu-like [Fig. 1(d)] ordered phase. Also, nominally CuPt-like $GaInP_2$ samples have been suggested to contain a Y2-like phase[5] [Fig. 1(b)], antiphase boundaries (APB) on the (001) planes,[6] and ''orientational superlattices''[7] with periodically alternating (111) and (11$\bar{1}$) ordered subvariants.[8,9] Such samples with mixed ordering domains often exhibit interesting optical effects such as localized excitons,[10] spatially indirect interband transitions in magnetic field,[11] and excitation intensity dependent emission energies.[12] However, attempts to identify the microstructure responsible for these highly unusual effects in an *ordered* compound have failed. For example, the suggested[11–13] coexistence of CuPt-ordered domains with random-alloy domains cannot explain the spatially indirect transitions since the offset in this system is type I.[14,15]

In this paper, we provide an easy and systematic way to study theoretically the electronic and structural properties of the mixed-phases ordered semiconductor compounds discussed above. We show that these ordered structures can be formed by different stacking of basic (001) atomic planes, i.e., they are polytypes.[16] The physical properties, such as the formation energies, band gaps, and band offsets of any member of a polytype series can be predicted systematically using a generalized one-dimensional Ising model,[17] where the Ising interaction parameters are obtained from accurate, first-principles electronic structure calculation on a few (small unit cell) polytypes. We find that $CuInSe_2$ polytypes have very similar formation energies (thus, explaining phase coexistence in this system) and that certain $GaInP_2$ polytype pairs manifest a ''type-II'' band alignment, thus holding the potential for explaining the puzzle of exciton localization

and spatially indirect interband transitions in chemically homogeneous and highly ordered compounds.[10–13]

We discuss here two classes of polytypes for the 50%-50% compounds ABC_2. Unlike the well studied case of hexagonal/cubic SiC and ZnS polytypes,[16] here we discuss the case of pure fcc polytypes. Figure 2 shows the basic (001) atomic plane from which the two polytypes are constructed. For both planes, a uniform shift of the plane by $\tau = (1/2, 1/2, 0)a$ is equivalent to the permutation of A to B. In the type-a plane [Fig. 2(a)], the A and B atoms form alternating lines along the [110] direction. The polytypes that can be constructed by stacking the type-a plane on an fcc lattice include the CuPt [Fig. 1(a)] and the Y2 [Fig. 1(b)] structures. All the type-a polytypes ABC_2 contain equal numbers of
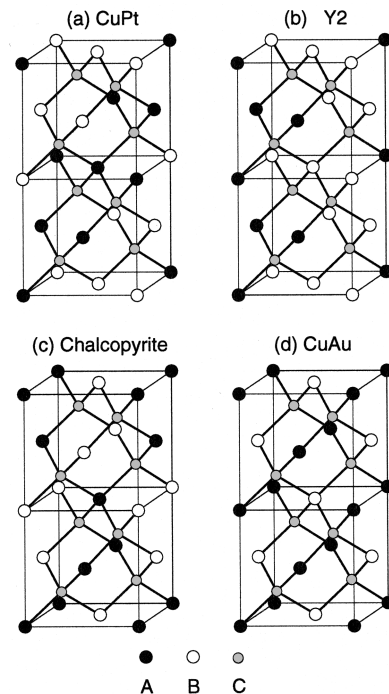

FIG. 1. Crystal structures of (a) CuPt, (b) Y2, (c) chalcopyrite, and (d) CuAu pseudobinary semiconductor compounds. CuPt and Y2 belong to type-a polytypes while chalcopyrite and CuAu belong to type-b polytypes.
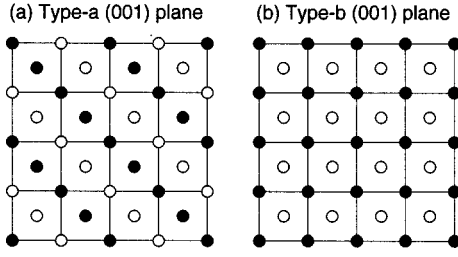
FIG. 2. Planar structures that form the polytypes: (a) type-a (001) plane and (b) type-b (001) plane.

A_3B and AB_3 tetrahedral clusters around the common C atom [Figs. 1(a) and 1(b)]. In the type-b plane [Fig. 2(b)], the A and B atoms form alternating lines along the [100] and [010] directions. The type-b polytypes include the chalcopyrite [Fig. 1(c)] and the CuAu [Fig. 1(d)] structures. All the type-b polytypes contain only the A_2B_2 tetrahedral clusters around the common C atom [Figs. 1(c) and 1(d)].

The two polytype series can be described in a similar way by first projecting the A and B atoms on a (110) plane (Figs. 1 and 3). A spin variable S_i is then assigned to each plane i. A reference structure (CuPt for type a and chalcopyrite for type b) is chosen for which $S_i \equiv 1$ for all i. For other polytypes, if a plane i is shifted by $\tau = (1/2, 1/2, 0)a$ relative to the same plane in the reference structure, then $S_i = -1$. Using this description Fig. 3 shows the schematic diagrams of the atomic arrangements, the spin variables $\{S_i\}$ in a conventional unit cell, and the associated Zhdanov notation[18] for some of the polytypes. In this notation, the CuPt (or the chalcopyrite) structure is denoted as $\langle\infty\rangle$, while Y2 (or CuAu) structure is denoted as $\langle2\rangle$. $\langle nm \rangle$ indicates a periodic (001) APB structure where n unshifted CuPt (111) ordered planes are followed by m shifted CuPt (111) ordered planes [$\langle n\rangle \equiv \langle nm\rangle$]. Notice that $\langle\infty\rangle$ and $\langle1\rangle$ are two subvariants of the same bulk ordered structure with different orientations (Fig. 3). Therefore, a periodic orientational superlattice (OS) with n layer CuPt (111) ordered plane followed by m layer CuPt $(11\bar{1})$ ordered plane is denoted by OSnm and described by n spin 1 and $m/2$ spin $1\bar{1}$ pairs. For example, OS44 $=[11111\bar{1}1\bar{1}]=\langle5111\rangle$ (Fig. 3).

It is possible to determine theoretically the electronic structure of a few polytypes from first principles. However,
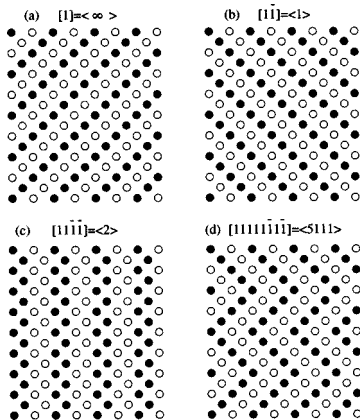

FIG. 3. Schematic diagrams of the atomic arrangement and the notations of nine pseudobinary polytype semiconductors.

TABLE I. Pair correlation functions $\bar{\Pi}_{k=\mathrm{even}}$ [Eq. (2)] for some of the polytype structures. See also Fig. 3 for the spins and notations for some of these structures.

Structure	Notation	$\bar{\Pi}_2$	$\bar{\Pi}_4$	$\bar{\Pi}_6$	$\bar{\Pi}_8$
CuPt; CH	$\langle\infty\rangle$	1	1	1	1
Y2; CuAu	$\langle2\rangle$	0	1	0	1
OS21	$\langle3\rangle$	1/3	1/3	1	1/3
OS31	$\langle4\rangle$	1/2	0	1/2	1
OS22	$\langle31\rangle$	1/2	1	1/2	1
OS33	$\langle411\rangle$	2/3	1/3	0	1/3
OS44	$\langle5111\rangle$	3/4	1/2	3/4	1
OS5111	$\langle62\rangle$	1/2	1/2	1/2	1

to understand the trends in the whole series, one needs to consider also polytypes whose unit cell size is larger than currently amenable to first-principles calculations. We have thus developed an Ising-like one-dimensional expansion that describes the physical property P of any polytype configuration σ in terms of a small set of effective, kth neighbor layer-layer interaction energies $\{J_k\}$. These are determined by mapping first-principles calculated properties $P(\sigma)$ of a few (small cell) polytypes σ onto this formal expansion. Specifically, we define

$$P(\sigma)=J_0+\sum_{k=\mathrm{even}}^{\mathrm{pairs}} \bar{\Pi}_k(\sigma)J_k+O(>\mathrm{pairs}). \quad (1)$$

Here, J_k is the pair interaction between two kth neighbor layers, and $0 \leq \bar{\Pi}_k(\sigma) \leq 1$ is the average of the kth neighbor layer pair correlation function, given by

$$\bar{\Pi}_k(\sigma)=\frac{1}{2N}\sum_{i=1}^{N}[1+S_i(\sigma)S_{i+k}(\sigma)], \quad (2)$$

where N is the layer period of the polytype. $O(>\mathrm{pairs})$ contain high-order (three layer or more) multilayer interactions. Since $P(\langle\infty\rangle)=P(\langle1\rangle)$, only $k=$ even pair interactions are included in the expansion. Table I gives $\bar{\Pi}_{k=\mathrm{even}}$ for some of the polytypes. For APB structure $\langle n\rangle$ we have

$$\bar{\Pi}_k(n)=(n-k)/n \quad \mathrm{for}\ n \geq k,$$

while for orientational superlattices OSmm we have

$$\bar{\Pi}_k(m)=(m-k/2)/m \quad \mathrm{for}\ m \geq k-1.$$

It is interesting to notice that if only the second nearest pair interaction J_2 are included in the expansion, then

$$P(\sigma)=\bar{\Pi}_2(\sigma)P(\langle\infty\rangle)+[1-\bar{\Pi}_2(\sigma)]P(\langle2\rangle). \quad (3)$$

So, in this case, the property of each polytype is the appropriate weighted average of the properties of the $\langle\infty\rangle$ and $\langle2\rangle$ polytypes. In this sense, $\langle\infty\rangle$ and $\langle2\rangle$ are ''end-point'' polytypes.

To test the convergence of Eq. (1) with respect to the range of pair interactions, we have calculated, using the first-principles local-density approximation[19] (LDA) as implemented by the linearized augmented plane wave (LAPW)

TABLE II. Differences $P(\sigma)-P(\text{CuPt})$ of the LDA calculated formation energies ΔH (in meV/4-atom) and band-gap energies ΔE_g, and the valence-band and conduction-band energy alignments ΔE_v and ΔE_c, respectively (in meV), of the type-a GaInP$_2$ poly-types. The predicted results using Eq. (1) with pair interactions up to J_6 are given in parentheses. The fitted interaction parameters are also given. The structures used in the fitting to obtain the interaction parameters are denoted by an asterisk. The others are predictions.

Structure	ΔH	ΔE_g	ΔE_v	ΔE_c
*CuPt $\langle\infty\rangle$	0(0)	0(0)	0(0)	0(0)
*Y2 $\langle 2\rangle$	$-82(-82)$	333(333)	$-75(-75)$	258(258)
*OS21 $\langle 3\rangle$	$-64(-64)$	256(256)	$-63(-63)$	193(193)
*OS31 $\langle 4\rangle$	$-57(-57)$	278(278)	$-59(-59)$	219(219)
OS22 $\langle 31\rangle$	$-41(-41)$	133(167)	$-44(-38)$	89(129)
OS33 $\langle 411\rangle$	$-39(-39)$	215(226)	$-46(-41)$	169(185)
OS44 $\langle 5111\rangle$	$-28(-29)$	115(139)	$-35(-30)$	80(110)
OS5111 $\langle 62\rangle$	$-49(-49)$	201(222)	$-49(-48)$	152(174)
Interaction				
J_0 (meV)	-98	445	-97	347
J_2 (meV)	80	-272	73	-199
J_4 (meV)	16	-112	22	-90
J_6 (meV)	2	-61	2	-58

FIG. 4. Band-gap energies and VBM and CBM energy levels of type-a GaInP$_2$ polytypes as a function of layer thickness n of APB polytypes $\langle n\rangle$.

method,[20] the total-energy, band-gap energy and the energy lineups of the valence-band maximum (VBM) and conduction-band minimum (CBM) of four GaInP$_2$ polytypes: $\langle\infty\rangle$, $\langle 2\rangle$, $\langle 3\rangle$, and $\langle 4\rangle$ belonging to the type-a series. From these four calculated LDA values we then determine four interactions (J_0, J_2, J_4, and J_6) for each physical property. Using this calculated $\{J_{k\le 6}\}$ we then predict from Eq. (1) the properties of other polytypes, not used in the fit. Table II shows the directly calculated LDA results for the GaInP$_2$ polytypes, and in parentheses, the values obtained from the Ising expansion, using the fitted $\{J_{k\le 6}\}$. Figure 4 plots the band-gap energy and the VBM and CBM energies as a function of the layer thickness n of the APB superlattice $\langle n\rangle$. Similar calculations were performed for type-b polytypes CuInSe$_2$ (Table III). We note the following observations.

(i) *Formation energies.* The Ising expansion converges rapidly for the formation energies. Within the accuracy of the underlying LAPW calculation, one needs to retain only J_2 and J_4 for the GaInP$_2$ polytypes. For the CuInSe$_2$ polytypes, only J_2 is needed. The exceedingly small energy difference $E_{\langle\infty\rangle}-E_{\langle 2\rangle}=-8.2$ meV/4-atom found between chalcopyrite and CuAu phases of CuInSe$_2$ suggests the coexistence of CuAu-like phases in nominally chalcopyrite CuInSe$_2$. Similar results are found for CuInS$_2$ where $E_{\langle\infty\rangle}-E_{\langle 2\rangle}=-7.8$ meV/4-atom. In contrast, for CuGaSe$_2$ we find $E_{\langle\infty\rangle}-E_{\langle 2\rangle}=-36.2$ meV/4-atom, so CuAu phase is expected to be less abundant in CuGaSe$_2$. The situation is different for type-a GaInP$_2$ polytypes where $E_{\langle\infty\rangle}-E_{\langle 2\rangle}=82$ meV/4-atom is large: The formation of the type-a polytypes in GaInP$_2$ is attributed to the surface effects that are known[21] to stabilize the type-a planar structure.

(ii) *Electronic properties.* For type-a GaInP$_2$ polytypes, the Ising expansion of the band-gap energies and the conduction-ba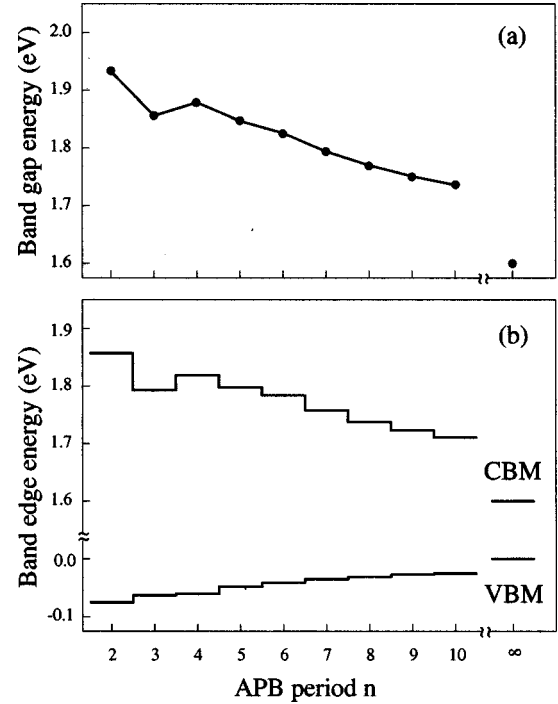nd energies converge slower than for the total energy (Table II). Furthermore, the calculated band-gap energies and the conduction-band energies show an odd-even oscillation as a function of the APB period $\langle n\rangle$ (Fig. 4), especially when n is small. These behaviors are due to different band-folding and resulted level-repulsion and wave-function localization[22] of the CBM in these polytypes: For the type-a polytypes, when n is odd, the zinc-blende L state folds into Γ, while when n is even, the zinc-blende X state folds into Γ. Since Γ-L coupling (and thus level repulsion) is larger than the Γ-X coupling,[23] the band gap and the CBM energies tend to be lower when n is odd. For the type-b CuInSe$_2$ polytypes, the convergence of the band gap is much faster than the type-a polytypes. This is partly due to the fact that X state folds into Γ for all type-b polytypes. We find that it is sufficient to keep only J_2 for this system, i.e., Eq. (3) is valid. This indicates that the properties of type-b CuInSe$_2$ polytypes are a weighted average of those of chalcopyrite $\langle\infty\rangle$ and CuAu $\langle 2\rangle$. The small band-gap difference $E_g(\text{CH})-E_g(\text{CuAu})=46$ meV for CuInSe$_2$ (30 meV for CuInS$_2$) suggest that formation of polytypes in these compounds has

TABLE III. Differences $P(\sigma)-P(\text{chalcopyrite})$ of the LDA calculated formation energies ΔH (in meV/4-atom) and band-gap energies ΔE_g (in meV) for the type-b CuInSe$_2$ polytypes. The predicted values using Eq. (3) with the interactions J_2 only are given in parentheses.

Structure	ΔH	ΔE_g
Chalcopyrite $\langle\infty\rangle$	0(0)	0(0)
CuAu $\langle 2\rangle$	8.2(8.2)	$-32(-32)$
OS22 $\langle 31\rangle$	4.1(4.1)	$-16(-16)$
OS33 $\langle 411\rangle$	2.9(2.7)	$-10(-11)$

little effect on their electrical and optical properties. In contrast, $E_g(\text{CH}) - E_g(\text{CuAu}) = 232$ meV for $CuGaSe_2$. Thus, the effect is larger for $CuGaSe_2$.

(iii) *Band alignment*. Due to the effective long-range layer interactions for the type-a $GaInP_2$ conduction-band states, type-II band alignment is predicted between some polytype pairs, especially for polytypes with small domain sizes. This is the case, e.g., between $\langle 3 \rangle$ and $\langle 4 \rangle$ (Fig. 4) or between $\langle 411 \rangle$ and $\langle 62 \rangle$ (Table II). Thus, if $\langle 3 \rangle$ and $\langle 4 \rangle$ coexist in a sample, Fig. 4 shows that the hole will localize on $\langle 4 \rangle$ and the electron on $\langle 3 \rangle$. This finding provides a natural explanation to the following puzzle: Despite the fact that band alignment between CuPt and Y2 or between ordered and disordered $GaInP_2$ is type I,[14] experimentally, type-II band alignment behavior is observed in some multidomain samples, especially those having small domain sizes.[11–13]

In summary, we have studied the formation energy and electronic structures of type-a $GaInP_2$ polytypes and type-b $CuInSe_2$ polytypes using a first-principles generalized one-dimensional Ising model. We predicted that CuAu-like phase can coexist in nominally chalcopyrite $CuInSe_2$ and $CuInS_2$, while such coexistence is less likely in $CuGaSe_2$. We found that type-II band alignment can exist between different ordered type-a $GaInP_2$ polytypes.

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