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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.
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$A_{1-x}B_xC$ 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 $A^{I}B^{III}C_2^{VI}$ 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 (111) 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

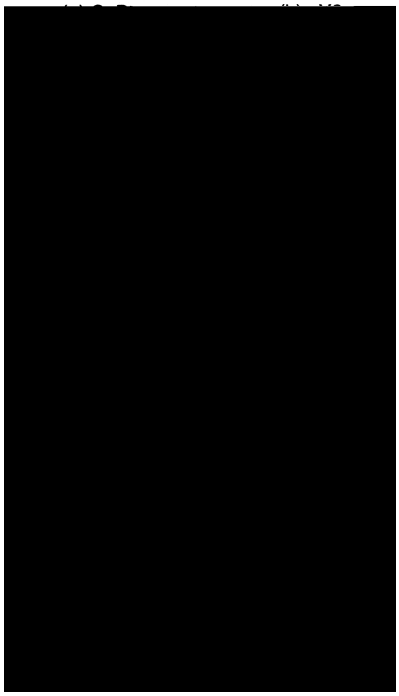

FIG. 1. Crystal structures of (a) CuPt, (b) Y2, (c) chalcopyrite, and (d) CuAu pseudobinary semiconductor compounds. CuPt and Y2 belong to type-a polytypes while chalcopyrite and CuAu belong to type-b polytypes.

A_3B and AB_3 tetrahedral clusters around the common C atom [Figs. 1(a) and 1(b)]. In the type-b plane

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 $\{J_{k\leqslant 6}\}$ 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 $\{J_{k\leqslant 6}\}$. 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

little effect on their electrical and optical properties. In contrast, $E_g(\mathrm{CH})\ 2\ E_g(\mathrm{CuAu})\ 5\ 232$ meV for $CuGaSe_2$. Thus, the effect is larger for $CuGaSe_2$.