

## Band-Gap Design of Quaternary (In,Ga)(As,Sb) Semiconductors via the Inverse-Band-Structure Approach

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Quaternary systems illustrated by (Ga,In)(As,Sb) manifest a huge configurational space, offering in principle the possibility of designing structures that are lattice matched to a given substrate and have given electronic properties (e.g., band gap) at more than one composition. Such specific configurations were however, hitherto, unidentified. We show here that using a genetic-algorithm search with a pseudo-potential “Inverse-band-structure (IBS) approach it is possible to identify those configurations that are naturally lattice matching (to GaSb) and have a specific band gap (310 meV) at more than one composition. This is done by deviating from randomness, allowing the IBS to find a partial atomic ordering. This illustrates multitarget design of the electronic structure of multinary systems.

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Whereas conventional electronic structure theory proceeds by first specifying the structure-type (for solids) or atomic configuration (for molecules) of the system, and then calculating the ensuing electronic properties, the inverse-band-structure (IBS) approach [1–3] searches from the outset for the atomic configuration that has a given, target material property. Such strategies are potentially important for multinary compounds, manifesting a very large number of possible atomic configurations.

Quaternary systems composed of two cations and two anions, such as  $\text{Ga}_{1-x}\text{In}_x\text{As}_y\text{Sb}_{1-y}$ , represent a high level of complexity, but also opportunities for materials design. Variable- $x$  films can be grown with unlimited thicknesses on a *given substrate*. For example,  $\text{Ga}_{0.75}\text{In}_{0.25}\text{As}_{0.18}\text{Sb}_{0.82}$ ,  $\text{Ga}_{0.50}\text{In}_{0.50}\text{As}_{0.38}\text{Sb}_{0.62}$ , and  $\text{Ga}_{0.25}\text{In}_{0.75}\text{As}_{0.62}\text{Sb}_{0.38}$  are all lattice matched to the same GaSb substrate. As the chemical formulas show, such configurations do not manifest “molecularity”, i.e., they do not have well-defined integer units of In-As and Ga-Sb “molecules.” The ability of lattice-matching to one substrate by variable- $x$  films is afforded by the fact that increasing the concentration  $x$  of the larger of the two cations (In vs Ga) can be compensated by increasing the concentration  $y$  of the smaller of the two anions (As vs Sb). However, having different compositions, each of these quaternary random alloys has distinct electronic properties, e.g., band-gap values. This is illustrated in Fig. 1, which shows the different calculated band gaps [Fig. 1(a)] and the band edges [Fig. 1(b)] of random  $\text{Ga}_{1-x}\text{In}_x\text{As}_y\text{Sb}_{1-y}$  alloys lattice matched to GaSb.

It is interesting to enquire if the huge configurational space afforded by quaternary systems could manifest structures that are lattice matched to a given substrate and have a fixed specified electronic structure (e.g., band gap) at more than one composition. Specific target band-gap values were previously sought by one of two compromises: (i) Abandon molecularity but retain lattice matching, i.e., via random alloys, lattice-matched to a given substrate.

This is illustrated for (Ga,In)(As,Sb) lattice-matched to GaSb in Fig. 1. It shows that to achieve the target band gap of, for example, 310 meV (needed for infrared detectors in the midinfrared wavelength region [4,5]) one needs the In-rich  $\text{Ga}_{0.18}\text{In}_{0.82}\text{As}_{0.69}\text{Sb}_{0.31}$  alloy. Such In-rich alloys are difficult to grow (In segregates), and low-In systems meeting the target gap would be much more desirable. (ii) Retain molecularity but abandon lattice-matching, i.e., select *ordered*  $(\text{InAs})_n/(\text{GaSb})_m$  superlattices (on GaSb) with a target band gap. There are two problems. First, any stoichiometric  $(\text{AC})_n/(\text{BD})_m$  superstructure with binary constituents AC/BD that differ in their equilibrium lattice constants will automatically be mismatched with respect to a substrate made of one of the two constituents. Second, the absorption may be weak. The oscillator strength for the valence-band maximum

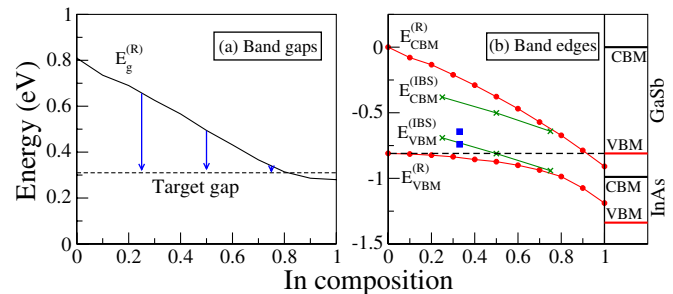


FIG. 1 (color online). Lattice-matched  $\text{Ga}_{1-x}\text{In}_x\text{As}_y\text{Sb}_{1-y}$  random alloys calculated using a 512 atoms unit cell and averaged over four independent random realizations for each composition: (a) Band gaps. Vertical arrows denote the difference between the random alloy and the target band gaps. (b) Band edges energies for the random alloy,  $E_{\text{CBM}}^{(R)}$  and  $E_{\text{VBM}}^{(R)}$ , the IBS final structures with band gap of 310 meV,  $E_{\text{CBM}}^{(\text{IBS})}$  and  $E_{\text{VBM}}^{(\text{IBS})}$ , and the case (showed by squares) in which the (111) As(In, Ga) and Sb(In, Ga) planes are exclusively occupied by As and Sb atoms, respectively. The right-hand side bars denote the band edges of bulk GaSb and InAs.

(VBM)  $\rightarrow$  conduction-band minimum (CBM) transition of  $(\text{InAs})_n/(\text{GaSb})_m$ , calculated using the plane-wave empirical pseudopotential method (as described below), is strong ( $\approx 40\%$  of the bulk GaAs) for  $n < 4$  but drops fast as  $n$  increases. This is because for periods  $n \geq 10$  of the InAs/GaSb superlattices the overall VBM resides on the GaSb segment and the overall CBM resides on the InAs segment, leading to weak spatially-indirect transitions.

In this Letter we show that by using a genetic-algorithm search within a pseudopotential, inverse band structure approach, it is possible to identify among an astronomical number of quaternary alloy configurations, those that exhibit lattice-matching to a given substrate (e.g., GaSb) and a specific target band gap (e.g., 310 meV), at more than one composition, and have strong absorption. The dramatic reduction [vertical arrows in Fig. 1(a)] required in the band gaps, relative to the lattice-matched random alloy, is accomplished by allowing the IBS to explore partial atomic ordering. The IBS search identifies an universal pattern for all compositions: a partial ordering on the anion sublattice in the (111) planes. We explain the effectiveness of this atomic pattern in reducing the band gap of quaternary alloys via a  $L$ -band folding mechanism, familiar from spontaneously ordered pseudobinary  $\text{In}_{0.5}\text{Ga}_{0.5}\text{P}$  alloys [6]. The optical transitions of the designed structures are strong and spatially direct. Whereas the method we used to identify the configuration with the target properties is completely general, allowing ordering on any sublattice and being applicable to widely different systems (described by their appropriate pseudopotentials), the method used *ex-post-facto* to analyze the properties of the selected configuration naturally depends on the type of structure found, but the folding reasoning is identical. Generally speaking, band-gap reduction and alloy bowing are expected to be relatively small for common-anion (mixed cation) alloys and larger for common-cation (mixed anion) alloys [7], because in common-cation direct band-gap semiconductors the level repulsion due to intraband coupling generally occurs in both the valence and conduction band edges, while for common-anion direct gap semiconductors most of the level repulsion occurs in the conduction band [7].

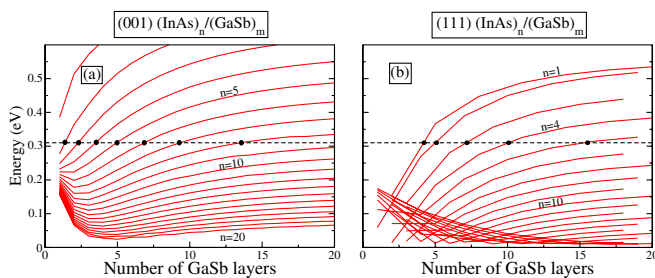


FIG. 2 (color online). Lattice-mismatched ordered superlattices calculated via the present pseudopotential method: Band gaps of (a) (001), and (b) (111)  $(\text{InAs})_n/(\text{GaSb})_m$  superlattices. The horizontal dashed line indicate a target band gap of 310 meV.

*Retaining lattice matching and achieving target band gap at more than one composition.*—We search the atomic configurations that will be lattice-matched to a GaSb substrate and will have a band gap of 310 meV, i.e., reduced from the random alloy gap [Fig. 1(a)] by 346, 182, and 27 meV for  $x = 25\%$ ,  $50\%$ , and  $75\%$ , respectively. We attempt this by allowing the IBS to explore configurational degrees of freedom (by atomic configurations we mean specific assignment of atomic types to lattice sites). The pertinent configurational space consists of a supercell containing  $N_c$  cations (Ga/In) and  $N_a$  anions (As/Sb). It contains

$$M = \frac{N_c!}{[N_c(1-x)]![N_c(x)]!} \times \frac{N_a!}{[N_a(1-y)]![N_a(y)]!} \quad (1)$$

possible configurations, where  $x$  and  $y$  are the cation and anion compositions. For  $N_c = N_a = 216$  used here, this gives  $10^{127}$  possible configurations for  $x = 50\%$ . The goal of the IBS search is to sample but a small fraction of this space (in practice, we require only  $\approx O(10^3)$  band calculations), finding the desired target.

The IBS approach we use is based on a combination of the genetic-algorithm (GA) method [8] and atomistic electronic structure calculations [9,10]. Genetic algorithms are global optimization methods based on the Darwinian rules of survival of the fittest [11]. They have been successfully applied in materials science as a way to determine the global minimum configuration of nanostructures [12,13] and crystal systems [14–16], to find band structure parameters for empirical tight-binding models [17] as well as to select interactions for Ising models [18]. Each alloy configuration (= “individual” in a population) is represented by a “genome”, comprising a string of zeros and ones, representing the specific distribution of the atom types (Ga/In or As/Sb) on lattice sites. Our initial configuration is purely random. Each individual has a “fitness”, measured by the departure of the electronic structure from the target gap. Once an initial population is given, new individuals are generated by “crossover” and “mutation” operations. In the crossover operation, the new individuals are formed by taking complementary parts of the genomes representing two individuals in the population. In the mutation operation, a new individual is created by changing the value of random bits of an individual in the population. The population evolves by replacing a certain percentage (“replacement rate”) of the least fit individuals in the current population [19]. The average numbers of band structure evaluations necessary to reach convergence were 6000, 1800, and 750 for  $x = 25\%$ ,  $50\%$ , and  $75\%$ , respectively. We performed at least five independent IBS runs for each composition, finding that the final results do not show any significant difference, leading to similar qualitative and quantitative conclusions.

The supercell used consists of  $3 \times 3 \times 6$  conventional cubic cells, comprising a total of 432 atoms. Atomic positions and the out-of-plane lattice constant of the super-

cell are relaxed (keeping the in-plane lattice fixed to the substrate), using the valence force field method [20]. The electronic structure is calculated by using the plane-wave empirical pseudopotential method [10] and the folded spectrum method [21]. The empirical pseudopotential is a superposition of screened atomic pseudopotentials, adjusted to reproduce calculated and/or measured band gaps (at  $\Gamma$ ,  $X$  and  $L$ ), effective mass tensors and deformation potentials of the all *bulk* binaries as well as the band-gap and band-edge bowing of all possible ternary alloys. The Schrödinger equation includes the spin-orbit interaction and is diagonalized once (not iteratively). The accuracy on the gap values is within 10 meV.

*Emerging structures—partial atomic ordering.*—The first column of Fig. 3 shows the distribution of the As atoms in the best IBS final configurations for  $x = 25\%$ , 50%, and 75%. For  $x = 25\%$ , one notes that the IBS found clear anion ordering along the (111) direction, which is reduced at  $x = 50\%$  and 75%. The atomic distribution in the cation sublattice, not shown in Fig. 3, on the other hand, shows no evidence of ordering for all compositions  $x$ . The ordering on the anion sublattice follows an  $\text{As}\langle\text{In, Ga}\rangle_1/\text{Sb}\langle\text{In, Ga}\rangle_2$  pattern, where  $\langle\text{In, Ga}\rangle$  denotes that the In and Ga cations are randomly distributed in the cation sublattice. Although the As atoms are all on the (111) planes of the  $\text{As}\langle\text{In, Ga}\rangle$  layers, these planes are not completely filled by As atoms. When the planes are *fully* ordered, occupied exclusively by As and Sb, respectively, the band gap drops to 96 meV. The squares in Fig. 1(b) show the  $E_{\text{CBM}}$  and  $E_{\text{VBM}}$  for this case.

The degree of (111) ordering on the anion sublattice of the IBS results can be quantified by looking at the structure factor for the anion sublattice,  $S_\alpha(\mathbf{k}) = \frac{1}{N_a} \sum_i \exp(-i\mathbf{k} \cdot \mathbf{r}_{ai})$ , where  $\alpha$  identifies the atomic type,  $\mathbf{k}$  represents a vector in the reciprocal space and  $\mathbf{r}_i$  is the position vector of atom  $i$ . Given a certain unit cell,  $S(\mathbf{k})$  can be different from zero only for  $\mathbf{k} = \mathbf{0}$  and for the reciprocal lattice vectors of that unit cell. The calculated  $S(\mathbf{k})$  of the final IBS structures are depicted in the fcc Brillouin zone in the center column of Fig. 3. One can see that, apart from the contributions of the  $\Gamma$  point ( $\mathbf{k} = \mathbf{0}$ ), the structure factor for  $x = 25\%$  clearly exhibits a (111)  $L$  ordering (solid dot in Fig. 3). This ordering is still apparent for  $x = 50\%$ , which also presents contributions in the (001) direction, but it is mostly lost for the  $x = 75\%$  case. The *degree* of ordering along the (111) direction is directly related to the magnitude of the difference, 346, 182, and 27 meV, for  $x = 25\%$ , 50% and 75%, respectively, between the band gap of the random alloy and the target one: The greater the reduction needed to go from the band gap of the random alloy to the target gap, the higher the degree of ordering along the (111) direction on the anion sublattice.

*Electronic consequences.*—The majority representation [22] of wave functions  $\Psi$  for systems lacking translational symmetry (e.g., alloys) identifies the contribution from each allowed  $k$ -vector in the parent ordered solid,  $P_i(\mathbf{k})$ .

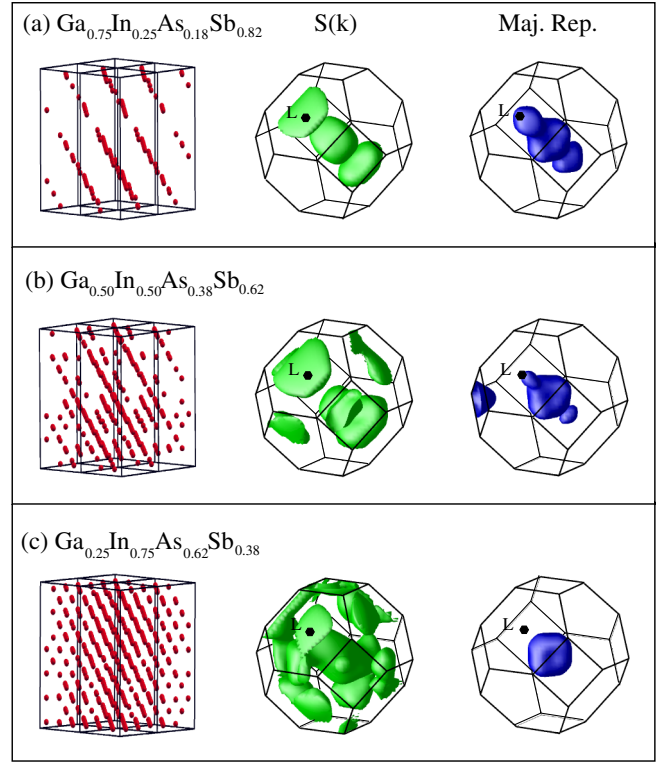


FIG. 3 (color online). Illustration of the As atomic positions (left column), structure factors,  $S(k)$ , for the anion sublattice (center column), and majority representation of the CBM wave function, Eq. (2), (right column) for the structures found by the IBS searches with target 310 meV gap for (a)  $x = 0.25\%$ , (b)  $x = 0.50\%$  and (c)  $x = 0.75\%$  in  $\text{Ga}_{1-x}\text{In}_x\text{As}_y\text{Sb}_{1-y}$  lattice-matched to GaSb.

It is calculated as a sum over  $n$  (the band index) of the projection of the complete set of Bloch functions  $u_{n\mathbf{k}}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$  onto  $\Psi_i(r)$ ,

$$P_i(\mathbf{k}) = \sum_{n=1}^{\infty} |\langle \Psi_i(\mathbf{r}) | u_{n\mathbf{k}}(\mathbf{r}) e^{i\mathbf{k}\cdot\mathbf{r}} \rangle|^2 \quad (2)$$

It is evident from Fig. 3 that for the cases of  $x = 25\%$  and 50% the major contributions to the CBM come from  $\vec{k} = 2\pi/a(1,1,1)$ , while for  $x = 75\%$ , the contribution comes from  $\vec{k} = 2\pi/a(0,0,0)$ .

The (111) ordering in  $S(\vec{k})$  and the analysis of the CBM wave function majority representation show that the  $L$  character of the electronic structures provide the clues to the dramatic reduction in the band gap upon ordering into narrow monolayers. This might be surprising at first, because ordering into narrow layers (Fig. 3) implies formation of quantum confinement, which always raises the CBM and lowers the VBM levels of the material being confined. The opposite we find is explained by noting that in a *bulk* random (Ga,In)(As,Sb) alloy, the energetic order of the conduction levels is  $\Gamma_c < L_c < X_c$ . In *quantum wells* made of random alloys, quantum confinement *raises* the CBM levels, opening the gap. However, for (111) ordered

quantum wells,  $L_c$  folds into  $\bar{\Gamma}(L_c)$ , which repels and pushes the lower energy  $\bar{\Gamma}(\Gamma_c)$  further *down*, making it a low energy CBM. Thus, (111) ordering is very effective in reducing the gap of the random alloy. This was known [6] in the context of common-atom pseudobinary systems. However, although quaternary systems such as (Ga,In)(As,Sb) have been studied for more than a decade, the use of this band folding mechanism as an effective way to reduce their band gaps was previously unsuspected.

*The lattice-matched IBS structures have a strong allowed VBM  $\rightarrow$  CBM transition.*—The previously studied [9,23] (001)  $(\text{InAs})_n/(\text{GaSb})_m$  superlattices with not too short periods present spatially indirect band gaps, with the electrons localized on the InAs wells and the holes localized on the GaSb layers, as seen by the horizontal lines in Fig. 1(b). The crosses in Fig. 1(b) show the band-edge energies,  $E_{\text{VBM}}^{\text{IBS}}$  and  $E_{\text{CBM}}^{\text{IBS}}$ , of our designed structures. We see that for  $x < 50\%$ , the VBM of the IBS structures is higher in energy than the VBM of the GaSb substrate. Thus, the optical transitions will be spatially direct, involving electrons and holes states localized on the quaternary layers. Our calculated oscillator strengths for the VBM  $\rightarrow$  CBM optical transitions at the  $\Gamma$  point, relative to the same transitions in the bulk GaAs, are 0.422, 0.460, and 0.602 for  $x = 25\%$ , 50%, and 75%, respectively, showing rather strong absorption within a factor of 2 relative to those in pure bulk GaAs.

It is interesting to enquire if the VBM and CBM of the designed structures are extended Block-like states or localized impurity states. Direct analysis of the pertinent wave functions (not shown) reveals that both the VBM and the CBM are extended bulklike states on the anion atoms. Further, the CBM states are mainly extended on the  $\text{As}(\text{In, Ga})_1$  layers, while the VBM states present greater contributions from the  $\text{Sb}(\text{In, Ga})_2$  layers of the samples.

Our designed structures require a partial (111) ordering on the anion sublattice for samples grown in the (001) orientation. It might be difficult to realize such designed structures in the laboratory. Our analysis identifies, however, the structural motif that is most responsible for the required band-gap lowering. Thus, growing a low band-gap structure need not position all atoms in the right place, but it could be attempted the much easier task of copying the correct local motifs. Also, atoms can in principle be positioned by scanning tunneling tips [24,25], allowing one to build the IBS atomic configurations shown here. Further, by using a (111) oriented GaSb substrate and intentionally pursuing a  $\text{As}(\text{In, Ga})_1/\text{Sb}(\text{In, Ga})_2$  stacking pattern, it is possible to arrive at band gaps in the mid- to long-infrared wavelength region, while keeping the samples lattice matched to the substrate, as shown by our direct calculations in Fig. 2(b).

Generally, the genetic-algorithm-aided IBS can survey a huge configurational space, finding the target by “visiting” only  $\approx 10^3$  specific cases. In contrast, “direct” search approaches: (i) only search for layer sequences stacked

along well-known, intuitive orientations, (ii) do not generally allow partial ordering, and (iii) search only a very small part of the configurational space. Thus, the IBS promises to be an effective guide to material discovery in complex multinary systems, illustrated here by quaternary systems.

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