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The atomic size mismatch between different binary semiconductors has been long known to limit their mutual solubility, leading instead to phase separation into incoherent phases, forming mixtures that severely limit technological applications that rely on carrier transport. We show here that this atomic size mismatch can lead, under coherent conditions, to the formation of a  $\text{AB}_2$  alloy with characteristic (201) two-monolayer ordering. This occurs because such specific layer arrangement corresponds to a unique strain-minimizing network in tetrahedral systems.

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The atomic configuration in semiconductor alloys combining compounds, such as Si-Ge, InP-GaP, InN-GaN, or ZnO-ZnS, decides much of their electronic, optical, and transport properties [1,2]. For example, the optical band gap and transport effective masses of ordered alloys differ significantly from those of random alloys of the same chemical composition [1], and the carrier mobility in phase-separated alloys can be very different from that of ordered alloys [3]. It is now understood that such atomic arrangements often represent the minimum-strain atomic topologies formed under the constrained conditions present during growth [1,4–7]. For example, in epitaxial growth, the equilibrium  $AC$ - $BC$  solid solubility is enhanced, because phase separation into substrate-coherent constituents  ${}_yAC$  on substrate  ${}_yBC$  on substrate have a higher strain energy than phase  $(A_{1-x}B_x)_yC$  on substrate [4,5] and are suppressed in favor of formation of the latter solid solutions. Another example is the surface-reconstruction-induced long-range ordering [1]: Surface reconstruction creates strain patterning in a few near-surface layers [6,7] and leads, in turn, to an energetic driving force for selective incorporation of the smaller (larger) of two alloy atoms at high (low) strain subsurface sites, leading to the formation of long-range ordered  ${}_yAC$ / ${}_yBC$  CuPt-like phases [8].

In addition to the above atomic configurations that emerge in substrate-coherent, surface-exposed growth, there is an important question about the nature of the lowest energy structures of three-dimensional bulk semiconductor alloys. This question pertains, for example, to either substrate-disengaged (“relaxed”) films or to growth methods lacking exposed surfaces (e.g., traditional liquid or melt approaches). Long-standing tradition [2,5] suggests that the formation enthalpy of such freestanding isovalent semiconductor alloys

algorithm [17] methods, for a set of III-V semiconductor alloys, finding rather surprising minimal strain configurations.

The global view of  $\Delta H_j(x, \sigma)$  for zinc blende alloys spanning  $\sim O_j^0$  configurations [Fig. 1(a)] is obtained by an exhaustive enumeration approach [16], in which each of the  $\sim O_j^0$  lattice configurations is obtained by decorating the cation sublattice by either In or Ga atoms and then minimizing its energy by relaxing all atom positions without swapping atoms. To examine whether the restriction to  $N^0$  alters the identity of the strain-minimizing structures, the search was extended to  $N^+$ , aided by the genetic algorithm [17]. We find that the minimal strain energy configurations are short-period superlattice structures  $\sim j / j$  -



layered chalcopyrite motif as best able to accommodate atomic size-mismatch-induced strain in a tetrahedral network. Thus, under  $\beta$ - $\beta$  growth conditions, chalcopyrite ordering provides lower energy structure than the phase separation. The bulk stable chalcopyritelike long-range ordering in semiconductor alloys is important [23], because it represents a reaction channel that could circumvent the detrimental incoherent phase separation.

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the detection of such (201) ordered phases, we have calculated the Warren-Cowley short-range order (SRO) parameter, i.e., the deviation of pair correlations from the ideal random alloy [22]. Such deviation might be detected in the disordered solid solution  $\beta\gamma$   $\beta$   $\beta$ . Ordering tendency is manifested by peaks in the SRO parameter away from  $\mathbf{k} = \mathbf{0}$  in the reciprocal space, whereas peaks at  $\mathbf{k} = \mathbf{0}$  indicate clustering or phase separation. Figures 4(b) and 4(c) show the calculated SRO for  $\beta\gamma$   $\beta$  in reciprocal space at  $T = 100$  and concentration  $x = 0.0$  and 0.95. The  $x = 0.0$  alloy shows clear peaks at the  $\beta\gamma$  wave vectors, which correspond to the (201) superlattices CH at low temperature [Fig. 4(a)]. In contrast, for the alloy at  $x = 0.95$ , coherent  $\beta$  has lower energy than the ordered structures [Fig. 3(c)]. The SRO peaks at  $\mathbf{k} = \mathbf{0}$  show up. With decreasing temperature in our MC simulation, a phase-separation process is observed.

(201) CH ordering has been seen in bulk samples of InAs-GaAs [10,11] and GaAs-GaSb [12] alloys. The measured size of CH domains was quite small ( $\leq 0$ ), so it is reasonable to expect well-maintained coherence in such small size precipitates. Coherence in bulk samples, therefore, provides a new mechanism to understand the formation of CH.

In summary, a direct search of either the valence-force-field or the LDA-based functional identifies the (201)-

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