

Thermodynamic states and phase diagrams for bulk-incoherent, bulk-coherent, and epitaxially-coherent semiconductor alloys: Application to cubic (Ga,In)N

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The morphology and microstructure of $A_{1-x}B_xC$ semiconductor alloys depend on the type of thermodynamic states established during growth. We distinguish three main cases: (i) *bulk-incoherent* structures occur when the alloy grows without being coherent with an underlying substrate and when each of the possible alloy species—phase separated AC and BC constituents, random $A_{1-x}B_xC$ alloy, or ordered $(AC)_n/(BC)_m$ structures—maintain their own lattice structures and lattice constants, giving up mutual coherence. Bulk incoherence is common in thick films with sufficient dislocations. For cubic (Ga,In)

itaxial thermodynamics.¹ The purpose of this paper is to describe the constraints characterizing these cases, to provide a first-principles calculation of the relevant energetics, and to provide the corresponding phase diagrams. These ideas will be illustrated for cubic zinc blende (Ga,In)N alloy.

II. CONSTRAINED AND UNCONSTRAINED EXCESS

characterizes the strain energy $U^{\text{coh}}(x)$. The formation enthalpy $H_{\text{bulk}}^{\text{coh}}(\hat{\mathbf{k}})$ [Eq. (4)] can then be expressed as

$$H_{\text{bulk}}^{\text{coh}}(\hat{\mathbf{k}}) = E(\hat{\mathbf{k}}) - E_{CS}^{\text{min}}(x). \quad (6)$$

As we will see below (Sec. IV B), coherent strain energy is minimal at $\hat{\mathbf{k}}=(100)$.

The coherent strain energy $E_{CS}^{\text{min}}(x)$ for a bulk zinc

lowest energy structures at $T=0$ and then how to compute the temperature-composition phase diagrams.

A. Calculations of the configurational energy and phase diagram for bulk-incoherent alloys

Since the configurational excess energy $E(\sigma)$ of Eq. (1) encompasses $O(2^N)$ configurations for a unit cell of N sites, direct first-principles calculations of all of these structures are practically impossible. We calculate, instead, $O(50)$ structures with first-principles local-density approximation (LDA) and project the results on a generalized cluster expansion, allowing us to readily and accurately evaluate $O(2^N)$ structures. The excess energy $E(\sigma)$ [Eq. (1)] of (Ga,In)N pseudobinary zinc blende semiconductor alloy is described here by using a mixed-basis cluster expansion¹⁸ (MBCE) total-energy Hamiltonian. Within the cluster expansion framework, one first chooses an underlying parent lattice (e.g., fcc for pseudobinary zinc blende alloys) and defines a configuration σ as a specific atomic occupation of each of

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phase diagram has richer features than the miscibility-gap. The free energy integration approach described above, for every candidate phase is not feasible any more. The phase boundary tracing algorithm developed by van de Walle *et al.*²⁴ and implemented in the ATAT software package²⁵ is employed here to construct the whole phase diagram. This method is coupled with semigrand-canonical ensemble Monte Carlo simulation. In a semigrand-canonical ensemble, the phase transition occurs when two phases have the same natural thermodynamic potential (free energy). Once we have found a transition point (on phase boundary), it decides the change in chemical potential with respect to the temperature change to preserve the equality of the free energies between those two phases and then calculates the concentrations of the two phases at this updated chemical potential and temperature via the semigrand-canonical Monte Carlo simulations. We obtain the whole phase boundary by scanning temperature T upward or downward.

C. Calculations of configurational energies and phase-diagram

wise one might incorrectly identify a ground state structure. For example, Fig. 3(b) shows that whereas the In-rich $\text{In}_{0.75}\text{Ga}_{0.25}\text{N}$ composition has a stable coherent ground state, the symmetric counterpart $\text{In}_{0.25}\text{Ga}_{0.75}\text{N}$ does not, for it will spontaneously disproportionate into a mixture of 50% $(\text{InN})_2/(\text{GaN})_2$ CH phase plus 50% pure GaN. This mixture has a lower energy than the lowest energy configuration of $(\text{InN})_1/(\text{GaN})_3$. The reason that In-rich $(\text{InN})_3/(\text{GaN})_1$ has systematically lower energy than Ga-rich $(\text{InN})_{1\text{GaN}}$

ing the crystal structures at those compositions shows that all of them are (201) superlattices. We conclude that in In-rich domain, there are quasidegenerate adaptive structures that differ from each other by small structural mutations.

2. Absence of ground state structure of bulk coherent



Our CE predicts no “breaking point” at this composition. The reason is that H

perature $T_{MG}=1870$ K of the bulk-incoherent state but is much higher than the transition temperature $T_c=600$ K of the bulk-coherent state. The transition point at $x=0.80$ is calculated as around 630 K.

The effect of epitaxial strain on the thermodynamics of (Ga,In)N alloys is discussed in Refs. 27, 29, and 50. Teles *et al.*²⁷ used their real space cluster expansion for “averaged energy” (see Sec. IV C) to obtain the “ground states” as chalcopyrite (at $x=0.50$) and the $(\text{InN})_3/(\text{GaN})_1/(\text{InN})_2/(\text{GaN})_2$ (201) superlattice (at $x=0.625$). They qualitatively predicted the substrate-coherence induced ordering in such alloys, but the obtained ground states are not the true ground states as we have discussed in this paper. The composition-temperature phase diagrams for (Ga,In)N epitaxial thin films on substrate were calculated by Karpov *et al.*²⁹ and Teles *et al.*⁵⁰ Both calculations failed to predict substrate-coherent induced ordering because their treatments of epitaxial strain were insufficient. This is because they^{29,50} adopted much simpler energy functionals to take epitaxial strain into account and employed simple statistical models (e.g., regular

- ¹⁶L. G. Ferreira, S.-H. Wei, and A. Zunger, *Phys. Rev. B* **40**, 3197 (1989).
- ¹⁷S.-H. Wei, L. G. Ferreira, and A. Zunger, *Phys. Rev. B* **41**, 8240 (1990).
- ¹⁸David B. Laks, L. G. Ferreira, Sverre Froyen, and Alex Zunger, *Phys. Rev. B* **46**, 12587 (1992).
- ¹⁹J. W. Matthews and A. E. Blakeslee, *J. Cryst. Growth* **27**, 118 (1974).
- ²⁰J. P. Perdew and Alex Zunger, *Phys. Rev. B*, **23**, 5048 (1981).
- ²¹G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 15 (1996).
- ²²The cross-validation score is calculated as the average prediction error for a given number of ordered structures by the cluster expansion that is least-squares fitted from the rest of configurations in a data pool.
- ²³L. G. Ferreira, S.-H. Wei, and A. Zunger, *Int. J. Supercomput. Appl.* **5**, 34 (1991).
- ²⁴A. van de Walle and M. Asta, *Modell. Simul. Mater. Sci. Eng.* **10**, 521 (2002).
- ²⁵A. van de Walle (<http://www.its.caltech.edu/~avdw/atat/>).
- ²⁶J. Z. Liu and A. Zunger (unpublished).
- ²⁷L. K. Teles, L. G. Ferreira, L. M. R. Scolfaro, and J. R. Leite, *Phys. Rev. B* **69**, 245317 (2004).
- ²⁸I. Ho and G. B. Stringfellow, *Appl. Phys. Lett.* **69**, 2701 (1996).
- ²⁹S. Yu. Karpov, *MRS Internet J. Nitride Semicond. Res.* **3**, 1 (1998).
- ³⁰C. K. Gan, Y. P. Feng, and D. J. Srolovitz, *Phys. Rev. B* **73**, 235214 (2006).
- ³¹B. P. Burton, A. van de Walle, and U. Kattner, *J. Appl. Phys.* **100**, 113528 (2006).

- ⁷¹D. Gerthsen, E. Hahn, B. Neubauer, A. Rosenauer, O. Schon, M. Heuken, and A. Rizzi, *Phys. Status Solidi A* **177**, 145 (2000).
- ⁷²T. Li, E. Hahn, D. Gerthsen, A. Rosenauer, A. Strittmatter, L. Reibmann, and D. Bimberg, *Appl. Phys. Lett.* **86**, 241911 (2005).
- ⁷³M. J. Galtrey, R. A. Oliver, M. J. Kappers, C. J. Humphreys, D. J. Stokes, P. H. Clifton, and A. Cerezo, *Appl. Phys. Lett.* **90**, 061903 (2007).
- ⁷⁴T. P. Bartel, P. Specht, J. C. Ho, and C. Kisielowski, *Philos. Mag.* **87**, 1983 (2007).