Miscibility gaps and spinodal decomposition in III/V quaternary alloys of the type \( A_x B_y C_{1-x-y} D \)

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Thermodynamic concepts have been developed for the calculation of solid-phase miscibility gaps and spinodal decomposition in quaternary alloys of the type \( A_x B_y C_{1-x-y} D \). These concepts have been applied to the analysis of III/V quaternary alloys using the delta-lattice-parameter (DLP) solution model. In addition, the effects of coherency strain energy have been included in the calculation. Results are presented for the systems \( Al_x Ga_{1-x} In_{1-y} P \), \( Al_x Ga_{1-x} In_{1-y} As \), \( InP_{x} As_{y} Sb_{1-x-y} \), and \( GaP_{x} As_{y} Sb_{1-x-y} \). Even though these systems all have miscibility gaps, they are shown to be stable against spinodal decomposition at all temperatures due to the elastic strain energy inherent in coherent decomposition of single crystalline alloys.

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INTRODUCTION

Quaternary III/V alloys of the type \( A_x B_y C_{1-x-y} D \), where three elements share a single sublattice, are interesting for a number of applications. Stringfellow\(^1\) suggested that the system \( Al_x Ga_{1-x} In_{1-y} P \) might be the optimum system for the production of high-efficiency, visible-light-emitting diodes (LEDs) and short-wavelength injection lasers. This system contains the highest direct band gap (2.2 eV) III/V alloy lattice matched to GaAs. These alloys cannot be grown by LPE\(^2\) (liquid phase epitaxy) because of the extremely large Al distribution coefficient. However, they have been grown by MBE (molecular beam epitaxy)\(^2\) and growth may be possible by OMVPE (organometallic vapor phase epitaxy).\(^3\) A similar system is \( Al_x Ga_{1-x} In_{1-y} As \), which may be useful for tandem (or cascade) solar cells\(^4\) and as a confining layer in field transistors.\(^4\) \( Al_x Ga_{1-x} In_{1-y} As \) alloys are difficult to grow by LPE\(^2\), but because of the high Al distribution coefficient, may be grown by MBE\(^3\) and OMVPE.\(^6\) Alloys of the type \( AB_x C_{1-x-y} D \), such as \( InP_{x} As_{y} Sb_{1-x-y} \) (Ref. 7) and \( GaP_{x} As_{y} Sb_{1-x-y} \) (Ref. 8) are also of interest. The former alloys are interesting for superlattice structures and IR light sources and detectors for the wavelength range 3-4 \( \mu \). Some \( InP_{x} As_{y} Sb_{1-x-y} \) alloys have been grown by OMVPE, although the system is found to have a large miscibility gap.\(^7\)

Many pseudobinary III/V alloys have solid phase miscibility gaps, based on experimental evidence and simple thermodynamic calculations.\(^8\) Such miscibility gaps prevent the equilibrium growth of a range of solid compositions when the critical temperature \( T_c \), above which no miscibility, exists is higher than the growth temperature. Even for alloys where \( T_c \) is less than the growth temperature but greater than 300 K, the miscibility gap could cause problems, since spinodal decomposition and clustering would be expected to occur during high temperature processing or even stimulated by recombination enhanced diffusion\(^10\) during laser or LED device operation.

Recent calculations\(^9\) have shown that quaternary alloys of the type \( A_x B_{1-x} C_{1-y} D \) have even larger miscibility gaps and higher values of the critical temperature than the bounding pseudobinary systems. One purpose of this paper is to analyze alloys of the type \( A_x B_{1-x} C_{1-y} D \) (or \( AB_x C_{1-x-y} D \) which is thermodynamically equivalent) to determine whether these alloys are also less stable than the bounding pseudobinary systems.

In addition to considering only chemical driving forces for phase separation, Cahn\(^11\) showed that in metal systems, the coherency strain energy acts to stabilize alloys. Stringfellow\(^12\) extended these calculations to \( A_x B_{1-x} C_{1-y} D \) quaternary alloys and showed that most III/V pseudobinary and \( A_x B_{1-x} C_{1-y} D \) quaternary alloys are stabilized against spinodal decomposition by the coherency strain energy at all temperatures. These calculations will also be extended to \( A_x B_{1-x} C_{1-y} D \) quaternary alloys in the present work.

The purpose of this paper is to develop the thermodynamic concepts necessary to calculate the spinodal and critical temperature for a system of the type \( A_x B_{1-x} C_{1-y} D \) in the conventional way, including only chemical terms, and in addition to include the effects of the coherency strain energy. Results will be presented specifically for the systems \( Al_x Ga_{1-x} In_{1-y} P \), \( Al_x Ga_{1-x} In_{1-y} As \), \( GaP_{x} As_{y} Sb_{1-x-y} \), and \( InP_{x} As_{y} Sb_{1-x-y} \).

CALCULATION OF THE SPINODAL NEGLECTING STRAIN ENERGY

The stability criterion for pseudoternary alloys of the type \( A_x B_{1-x} C_{1-y} D \) (or \( AB_x C_{1-x-y} D \)) may be written\(^12,14\)

\[
\left( \frac{\partial^2 G}{\partial x^2} \right)_{T,P} < 0,
\]

where \( G \) is the Helmholtz free energy per unit volume, which is taken to be equal to the Gibbs free energy per unit volume for a solid phase at one atmosphere pressure.\(^13\) Thus, \( G \) is the product of the Gibbs free energy per mole of the solid \( G' \) and the number of moles per unit volume of the initial, homogeneous solid \( N_r \). The value of \( G' \) is obtained from a simple thermodynamic model of the solid, either the regular solu-
For the regular solution model,
\[ G = x\alpha_1 + x(1-x-y)\alpha_2 + y(1-x-y)\alpha_3 \]
\[ + RT\left[ x \ln x + y \ln y + (1-x-y)\ln(1-x-y) \right] \]
\[ + xG^0_{AD} + yG^0_{BD} + (1-x-y)G^0_{CD}, \]  
(2)

where \( \alpha_1, \alpha_2, \) and \( \alpha_3 \) are the interaction parameters for the three pseudobinary systems bounding the pseudoternary solidus plane, \( \alpha_{AD-CD}, \alpha_{AD-CD}, \) and \( \alpha_{BD-CD}, \) respectively, and \( G^0_{AD}, G^0_{BD}, \) and \( G^0_{CD} \) are the free energies per mole of the three pure binary compounds. For the DLP model,
\[ G_S = -\kappa a_0^{-2.5} + RT\left[ x \ln x + y \ln y + (1-x-y)\ln(1-x-y) \right], \]  
(3)

where \( \kappa \) is a constant equal to \( 1.15 \times 10^{7} \) cal mole\(^{-1} \) A\(^{2.5} \). Unfortunately the empirical regular solution interaction parameters are not known for the systems InP\(_x\)Sb\(_{1-x}\) and GaP\(_x\)Sb\(_{1-x}\), so would have to be estimated from the DLP model. For the other systems under consideration, the regular solution model interaction parameters agree with those predicted from the DLP model. The largest deviation is for the GaAs\(_x\)Sb\(_{1-x}\) system where the DLP interaction parameter (3355 cal/mole) is considerably smaller than the 4000 cal/mole obtained from a regular solution model fit to the pseudobinary phase diagram. Thus, the simplest and most consistent approach is to develop the calculation based on the DLP model.

Relation (1) can now be written, using the DLP model,
\[ G = M\Delta a^2 + RT\left[ \frac{(1-y)}{x(1-x-y)} \right] \]
\[ \times \left\{ -M\Delta a_B + RT\left[ \frac{(1-x)}{y(1-x-y)} \right] \right\} \]
\[ - \left[ -M\Delta a_B \Delta a_A + RT/(1-x-y) \right]^2 > 0, \]  
(4)

where \( M = 8.75 \kappa a_0^{-4.5} \), \( \Delta a_A = a_{AD} - a_{CD} \), and \( \Delta a_B = a_{BD} - a_{CD} \) where the lattice parameter of the compound \( ij \) is denoted \( a_{ij} \). Relation (4) can be manipulated to yield an expression for the spinodal surface,
\[ T = \left( M/R \right) \left[ x\Delta a_A^2 + y\Delta a_B^2 - \left( x\Delta a_A + y\Delta a_B \right)^2 \right]. \]  
(5)

This equation can be solved to yield the values of \( x_c, y_c \), and \( T_c \). It can be shown that in all cases, either \( x_c, y_c \), or \( (1-x_c - y_c) \) is equal to zero, i.e., the critical temperature is equal to that for the boundary pseudobinary having the highest value of \( T_c \). This result is strikingly different than that for quaternary alloys of the type \( Ax_Bx_{1-x}y_{1-x}D_{1-x}y \), where \( T_c \) often falls near \( x_c = y_c = 0.5 \) and is substantially higher than \( T_c \) for any of the bounding pseudobinary systems. The calculated spinodal isotherms for the systems InP\(_x\)As\(_{1-x}Sb_{1-y}\), Al\(_x\)Ga\(_{1-x}\)In\(_{1-y}\), P, Al\(_x\)Ga\(_{1-x}\)In\(_{1-y}\)As, and GaP\(_x\)As\(_{1-x}Sb_{1-y}\) are shown in Figs. 1-4.

For the InP\(_x\)As\(_{1-x}Sb_{1-y}\) system, Fig. 1, \( x_c = 0.56, y_c = 0, \) and \( T_c = 1319 \) K. The value of \( x \) is slightly different than that calculated, assuming \( \Delta a < \bar{a} \) where \( \bar{a} \) is the average value of lattice parameter. This approximation yields \( x_c = 0.5 \) (Refs. 9, 12) and \( T_c = 1303 \) K. This 1% error is negli-
FIG. 2. Calculated spinodal isotherms for the system Al$_x$Ga$_y$In$_{1-x-y}$P. The calculation neglects the coherency strain energy. Including this contribution to the free energy gives $T_c < 0$.

FIG. 3. Calculated spinodal isotherms for the system Al$_x$Ga$_y$In$_{1-x-y}$As. The calculation does not include the coherency strain energy. The strain energy would make the solid stable over the entire composition range.
FIG. 4. Calculated spinodal isotherms for the system GaP, As, Sb, . The calculation neglects the coherency strain energy $T_c > 0$. The calculated spinodal isotherms for the system GaP, As, Sb, . The calculation neglects the coherency strain energy $T_c > 0$.

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energy function containing the effect of coherency strain energy before spinodal decomposition is allowed to begin. Using this free energy function, the stability criterion can be written.

\[
\left\{- (M - S) \Delta a_x^2 + RT \left[ \frac{(1 - y)}{x(1 - x - y)} \right] \right\} \\
\times \left\{- (M - S) \Delta a_y^2 + RT \left[ \frac{(1 - x)}{y(1 - x - y)} \right] \right\} \\
- \frac{[ - (M - S) \Delta a_x \Delta a_y + RT/(1 - x - y)]^2 > 0},
\]

(7)
a duplicate of relation (4) with \( M \) replaced by \( M - S \). Naturally, this yields an equation similar to Eq. (5) (for the critical temperature) with \( M \) replaced by \( M - S \).

The values of \( E/(1 - v) \) were obtained from the data of V. V. Voronkov,16 either directly or by estimation from similar systems. All four quaternary systems considered in this paper are stabilized by the coherency strain energy, i.e., \( T_c < 0 \) K.

**CONCLUSIONS**

The thermodynamics of spinodal decomposition in quaternary alloys of the type \( A_x B_y C_{1-x-y} D \) have been developed. Based on the DLP model of the free energy of mixing of semiconductor alloys, an analysis has been developed for the calculation of the spinodal surface and the critical temperature for solid quaternary III/V alloys where the mixing is restricted to three elements on a single sublattice. It is found that the critical temperature for such alloys always occurs at the edge of the triangular solid phase field, i.e., for either \( x = y \), or \( 1 - x = y \), equal to zero. Thus, the critical temperature is never higher in the quaternary than for the bounding pseudobinary systems. Solid-solid isotherms are presented for the systems \( \text{Al}_x \text{Ga}_{1-x} \text{In}_{1-y} \text{P} \), \( \text{Al}_x \text{Ga}_{1-x} \text{In}_{1-y} \text{As} \), \( \text{Ga}_x \text{As}_{1-x} \text{Sb} \), and \( \text{In}_x \text{P}_{1-x} \text{As}_{1-y} \). The calculations agree quite well with experimental data for the systems \( \text{In}_x \text{P}_{1-x} \text{As}_{1-y} \text{Sb} \) and \( \text{Ga}_x \text{As}_{1-x} \text{Sb} \).

Concepts are also developed for the thermodynamic analysis of spinodal decomposition in these quaternary alloys, including the effect of the coherency strain energy. This addition to the free energy of the inhomogeneous solid is shown to completely stabilize the alloys of interest even at temperatures below room temperature.

\[ E = \frac{1}{2} \sum_{ij} C_{ij} \left( \frac{\partial \gamma}{\partial x_i \partial x_j} \right)^2 \]