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**FIRST PRINCIPLES CALCULATIONS OF SEMICONDUCTOR ALLOY PHASE DIAGRAMS:
ORDERED TERNARY PHASES**

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ABSTRACT

Combining the self-consistent local density total energy approach with the Cluster Variation Method, we demonstrate that inclusion of both elastic and chemical interactions in the total energy functional leads to new features in the phase diagram of A_xB_{1-x} alloys, including the appearance on the same phase diagram of ordering and phase separation. Strain stabilization of both stable and metastable ordered phases is also predicted.

INTRODUCTION

Mixture of a compound A with another B leads in general to formation of ordered stoichiometric compounds A_nB_m , disordered solid solutions $A_{1-x}B_x$ of composition x, and/or the coexistence of different phases. The study of phase diagrams and their correlation with the microscopic properties of the constituents A and B has been an ongoing challenge in metallurgy [1-4] and semiconductor physics [5-9]. However, many of the features of experimental phase diagrams [10-11] are not understood on the basis of existing theoretical models [4-9]. The limitations of these models are in general related to the unsatisfactory description of one or both of the contributions to the alloy free energy $F=\Delta H-TS$, namely the internal energy (ΔH) or the entropy (S) associated with the alloy state of order. In semiconductor physics, only the high temperature part (near the solidus) of the phase diagrams has been considered in detail, where the simple solid solution concept [4-9] has proven to give a reasonable description of the experimental data. However, recent observations of ordered phases in semiconductor alloys, such as in ternary $Ga_{1-x}Al_xAs$ [12a], $Ga_{1-x}In_xAs$ [12b], and $GaAs_{1-x}Sb_x$ [12c], grown at low temperature cannot be explained by models [13] based on the use of the random disorder approximation, and the neglect of chemical energies responsible for alloy ordering. To study the solid-solid phase diagrams of semiconductor alloys we therefore propose a new approach based on a combination of first principles calculations of the alloy internal energy [14] with the Cluster Variation Method (CVM) [15] which allows an accurate calculation of the state of order (configurational entropy).

THEORETICAL MODEL

Consider the ordered stoichiometric structures $\{A_nB_m\}$ ($n+m=\text{constant}$) formed by distributing A and B on a fixed lattice. Each structure is characterized by its structural parameters $\{a^{(n)}\}$ and the excess total energy (measured with respect to equivalent amounts of the constituents at their equilibrium lattice parameters a_A and a_B):

$$\Delta E^{(n)}(a) = E[A_nB_m; a] - nE[A; a_A] - mE[B; a_B]. \quad (1)$$

The formation enthalpy of each ordered phase is the equilibrium (eq) value of Eq. (1), i.e., $\Delta H^{(n)} \equiv \Delta E^{(n)}[a_{eq}^{(n)}]$. Consider a substitutionally dis-

ordered (D) phase on the same lattice with lattice parameter $a(x)$ and represent its state of order by a superposition with probabilities $P^{(n)}(x,T)$ of all permissible local atomic arrangements [16,17] exhibited by $\{A_n B_m\}$, [where $P^{(n)}(x,T)$ and $a(x)$ are those that minimize the free energy [17]]. Calculation of $\{P^{(n)}(x,T)\}$ from $\{\Delta E^{(n)}(a)\}$ then allows to obtain the phase diagram of the underlying alloy using any of the statistical mechanics techniques available for such Ising problems [16-17]. In the fourfold coordinated face centered cubic (fcc) binary alloys $A_x B_{4-x} C$ treated here, limiting the short range order to nearest neighbors on the fcc lattice results in five $A_n B_{4-n} C_4$ ($0 \leq n \leq 4$) ground state ordered structures [18]. For a given value $a(x)$ of the alloy lattice parameter, the cluster energies $\Delta E^{(n)}(a)$ are obtained from the total energy of the associated ordered structure $A_n B_{4-n} C_4$. In general this energy can be separated into two pieces: the first $\epsilon^{(n)}$ is volume [or $a(x)$] independent, and termed "chemical," while the second $\Delta F(nA, mB, a)$, volume-dependent, is called "elastic". $\epsilon^{(n)}$ is related to the equilibrium charge transfer, polarization relaxation of the C-sublattice and spin-coupling in $A_n B_{4-n} C_4$ [18]. We thus have

$$\Delta E^{(n)}(a) = \epsilon^{(n)} + \Delta F(nA, mB, a). \quad (2)$$

The compound enthalpy of formation is then $\Delta H^{(n)} = \epsilon^{(n)} + \Delta F(a_{eq}^{(n)})$, where $a_{eq}^{(n)}$ is the equilibrium lattice parameter of $A_n B_{4-n} C_4$. From Eq. (2) one can express the mixing enthalpy of the disordered alloy as

$$\Delta H^{(D)}(x,T) = \sum_n P^{(n)}(x,T) \epsilon^{(n)} + G[a(x)], \quad (3)$$

where $G[a(x)] = \sum_n P^{(n)}(x,T) \Delta F[nA, mB, a_{eq}^{(n)}]$ is the average alloy elastic energy and ΔF is the volume deformation energy of AC and BC to $a_{eq}^{(n)}$. The two terms of Eq. (3) reflect the dual coordinates used in phenomenological models of solubility [2,8], compound stability [1,3], and mixing enthalpies [3], e.g., the Darken-Gurry [2] and Miedema [3] models.

Many approximations have been previously adopted in treating the alloy phase diagram problem (Eqs. 2 and 3): the first class of models neglects the chemical energies ($\epsilon^{(n)}=0$) and retains only the elastic part $G[a(x)]$. This includes approaches such as the elastic model of Fedders and Muller [7]. This approximation precludes the existence of ordered structures [12] or order-disorder transformations, despite its reasonable description of the then-available data (miscibility gap, enthalpy of mixing). A second class of models neglects the elastic energy $G[a(x)]$ and reduces the alloy problem to a generalized Ising problem [19]. Ordering [$\epsilon^{(n)} < 0$] and phase separation [$\epsilon^{(n)} > 0$] can be separately described with this framework (but not their appearance on the same phase diagram). Balzarotti and co-workers [19] have treated both chemical and elastic contributions to the free energy, hence, pioneering modern approaches to this problem. However, having chosen positive chemical energies $\epsilon^{(n)}$ (in the absence of a first-principles estimate for them), no ordered phases or order-disorder transformations were considered, in apparent conflict with recent observations [12]. In the present work, we illustrate the consequences of both elastic and chemical (ordering) energies on alloy phase diagrams using an ab-initio quantum mechanical calculation of the total energy of the $A_n B_{4-n} C_4$ which includes on the same basis chemical and elastic energies. This calculation is based on a first principles total energy minimization within the non-local pseudopotential representation of the local density formalism [18].

In the variational approach of Kikuchi [15], the entropy is obtained,

lattice parameter $a(x)$ and n with probabilities $P^{(n)}(x,T)$ [16,17] exhibited by $\{A_n B_m\}$, minimize the free energy [17]]. n allows to obtain the phase of the statistical mechanics [16-17]. In the fourfold alloys $A_x B_{1-x} C$ treated here, neighbors on the fcc lattice ordered structures [18]. For parameter, the cluster energies of the associated ordered $[a(x)]$ independent, and termed volume-dependent, is called charge transfer, polarization $[a(x)]$ in $A_n B_{4-n} C_4$ [18]. We thus

$$3, a) \quad (2)$$

$H(n) = \epsilon^{(n)} + \Delta F(a_{eq}^{(n)})$, where $A_n B_{4-n} C_4$. From Eq. (2) one can alloy as

$$G[a(x)] \quad (3)$$

the average alloy elastic energy of AC and BC to $a_{eq}^{(n)}$. The two sites used in phenomenological [1,3], and mixing enthalpies [3] models.

adopted in treating the alloy first class of models neglects only the elastic part $G[a(x)]$. model of Fedders and Muller of ordered structures [12] reasonable description of the of mixing). A second class and reduces the alloy problem $[\epsilon^{(n)} < 0]$ and phase separation this framework (but not their Grotti and co-workers [19] have ons to the free energy, hence,

However, having chosen position of a first-principles estimate order transformations were observations [12]. In the present elastic and chemical (ordering) initio quantum mechanical C_4 which includes on the same calculation is based on a first the non-local pseudopotential [18]. [15], the entropy is obtained,

within a given cluster approximation, from the associated cluster configuration probabilities $P^{(J)}(x,T)$. The choice of the size of the basic cluster fixes the number and type of the possible ordered structures present at $T=0$ K. In the case of $A_{1-x} B_x C$ alloys, these so-called ground state ordered structures are the multinary compounds $A_n B_m C_{n+m}$. We have used the first non trivial CVM-approximation for the FCC-like, $A_x B_{1-x} C$ alloys i.e., the FCC-tetrahedron approximation ($n+m=4$). The alloy entropy is a function of the point (x_i) , pair (y_{ij}) and quadruplet $[P^{(J)}(x,T)]$; $J = ijkl$, $i,j,k,l = AC$ or BC given as [20]:

$$S = -k [2 \sum_J P_J \ln P_J - 6 \sum_{i,j} y_{ij} \ln y_{ij} + 5 \sum_i x_i \ln x_i] \quad (4)$$

where x_i and y_{ij} are linear sums of the $P^{(J)}$'s [17]. From the configurational variables $P^{(J)}(x,T)$, one defines the probabilities $P^{(n)}(x,T)$ of having n atoms B in the cluster. Minimizing the free energy $F = \Delta H - TS$, of Eqs. (2) and (4), with respect to the $P^{(J)}$'s results in a set of self-consistent equations $\vec{P} = \vec{f}(\vec{P})$ which allow complete determination of the cluster probability distribution (\vec{P}) once the energetics $\{\Delta E^{(n)}(a)\}$ is given. Furthermore, the CVM allows description of preferential ordering on the four sites (i,j,k,l) of the tetrahedron through introduction of different symmetry relations on the $P^{(J)}$'s associated with ordering in the different compounds $A_n B_{4-n} C_4$. It therefore permits the calculation of the free energies of both ordered and disordered phases and hence allows the study of both phase separation (miscibility gaps) and ordering processes.

APPLICATIONS AND DISCUSSIONS

Using $Ga_{1-x} In_x P$ alloys as an example, we calculate $\Delta E^{(n)}(a)$ of Eq. (1) for the structures GaP , $Ga_3 In P_4$, $Ga In P_2$, $Ga In_3 P_4$ and InP ($n=0,1,2,3$ and 4 , respectively), in the Landau-Lifshitz fcc structures [17,18]. These exhibit all nearest-neighbor local atomic arrangements around the common (phosphorus) atom, i.e., for $n=0$ and $n=4$ we use the $P\bar{4}3m$ zincblende structure (clusters of Ga_4 and In_4 , respectively), for $n=1$ and $n=3$ the $P\bar{4}3m$ Luzonite form ($Ga_3 In$ and $Ga In_3$ clusters, respectively), whereas for $n=2$ we use the $P\bar{4}m2$ structure having a $CuAu-I$ cation sublattice (the $Ga_2 In_2$ cluster). The $\Delta E^{(n)}(a)$ are calculated self-consistently in the local density formalism, using the momentum space pseudopotential total energy representation [14] and a plane wave basis set with only atomic numbers and positions as input [18]. While our CVM calculation does not utilize the separation of variables indicated in Eq. (2) [we use directly $\Delta E^{(n)}(a)$ of Eq. (1) shown in Fig. 1a], for purposes of analysis we display this decomposition as follows: we use here $\epsilon^{(n)} = \Delta E_{CE}^{(n)} + \Delta E_{pol}^{(n)} + \Delta E_{VFF}^{(n)}$, all evaluated at $a_{eq}^{(n)}$ (notation of Ref. 18), calculated [18] from first principles total energy method (first two terms) and the VFF method (last term). In Ref. 18 we calculated the elastic energy $\Delta F[a_{eq}^{(n)}] = \Delta E_{VD}^{(n)}$ using the first-principles computed lattice constants $a_{eq}^{(n)}$. This underestimates the lattice mismatch $a_{InP} - a_{GaP}$ (0.213 Å) relative to experiment (0.42 Å), hence the elastic energy of Ref. 18 is underestimated too. Here, and in Ref. 21 we correct this by using the experimental lattice parameters. Note that consequently $\Delta F[a_{eq}^{(2)}] = 3.29$ is larger than the value of Ref. 18 (0.87) in which theoretical lattice constants were used. The values of $\Delta F[a_{eq}^{(n)}]$ are: 2.33, 3.29, and 2.64 Kcal/pair (3rd column of Table I in Ref. 23), and $\Delta E_{VFF}^{(n)} = -1.47, -2.36,$ and -2.03 Kcal/mole for $n = 1, 2,$ and 3 , respectively. The total formation energy is $\Delta H^{(n)} = \epsilon^{(n)} + \Delta F[a_{eq}^{(n)}] = \{\Delta E_{CE}^{(n)} + \Delta E_{pol}^{(n)} + \Delta E_{VFF}^{(n)} + \Delta E_{VD}^{(n)}\}$. Hence, our $\Delta H^{(2)} = -0.29$ is smaller than the value of -1.65 derived in Ref. 18 (for the chalcopyrite structure) using

a smaller Δa . We will see (Fig. 1c below) that the new $\Delta H^{(n)}$ values produce a good agreement with the measured $\Delta H^{(n)}(x)$ without any adjustment¹⁸ of $\Delta H^{(n)}$. Inspection of Table I here shows that the elastic energies are clearly non-negligible even at equilibrium. Furthermore, $\Delta E^{(n)}(a)$ can change sign as a function of a (Fig. 1a), a feature missing from both elastic [5-9] and simple Ising [17,20] models.

The calculated thermodynamic properties (Fig. 1b,c) and the phase diagram (Fig. 2a) indicate that (i) Despite an ever positive mixing enthalpy $\Delta H^{(D)} \equiv \Omega(x,T)x(1-x)$ [Eq. (3)] of the disordered phase evident in Fig. 1c (the calculated Ω at $T=1400$ K and $x=0.5$ is 2.0 Kcal/mole, compared with the value 3 ± 1 Kcal/mole inferred [5,6] from high-temperature data), ordered phases (shaded areas in Fig. 2a) are predicted to be stable at low temperatures [since $\Delta H^{(n)} < 0$], in contradiction with the predictions of all elastic models [5-9] and Ref. [19], but in agreement with recent observations of the A_3BC_4 and AB_3C_4 (in InGaAs [12b]) and ABC_2 (in GaSbAs [12c]) ordered phases and with the early predictions of Srivastava et al. [18]. (ii) The elastic energy tends to favor, at each alloy composition x , those local atomic arrangements which are least strained at the corresponding lattice parameter $a(x)$. This is evidenced by the substantial departure from randomness $\Delta P^{(n)}(x,T)$ of the disordered phase: e.g., Fig. 1b exhibits a ~20% enhancement at $T=600$ K of the $n=1,2,3$ species at $x=1/4, 1/2$, and $3/4$, respectively. This can explain the observed [5,11] growth-temperature-dependent alloy properties (e.g., width of Raman lines, carrier mobilities, and exciton trapping rates). (iii) This (x,T) -dependence of $P^{(n)}(x,T)$ introduces similar dependences in $\Delta H^{(D)}$ through Eq. (3) evident in Fig. 1c. While absent in all regular solution models [5-8], such hitherto unexplained dependences had to be incorporated phenomenologically in detailed fits to measured phase diagrams [9]. (iv) Despite the all-attractive ordering energies $\epsilon^{(n)}$, a miscibility gap for disordered phases (dashed area in Fig. 2a) can exist together with ordering (shaded areas), in contradiction with the predictions of simple Ising models with fixed interactions [16,17].

To analyze the consequences of models which retain in $\Delta E^{(n)}$ only chemical ordering energies [16,17,20], we show in Fig. 2b the phase diagram calculated with the same (attractive) $\{\epsilon^{(n)}\}$ of Table I, but omitting the elastic energy $G(a)$. Comparison of Fig. 2a and 2b illustrates the three main effects of elastic energy on systems with attractive chemical interactions: First, strain leads to stabilization of ordered stoichiometric compounds: narrower single-phase domains (shaded areas) and broader two-phase domains relative to Fig. 2b. Second, the elastic energy is seen to lead to a miscibility gap where two disordered phases exist (D and D' in Fig. 2a). Third, while the overall topological resemblance of the coherent phase diagram of Fig. 2b to many experimental data [10] (or to Fig. 2a) has led many authors to adjust $\{\epsilon^{(n)}\}$ to the observed critical temperatures, this leads to spuriously small values [21] of $\Delta H^{(n)}$ and considerably overestimates solubilities [4].

In order to characterize systems with small repulsive $\Delta H^{(n)}$'s we have recalculated the phase diagram using the same elastic energy of Fig. 2a but with positive $\Delta H^{(n)}$ values. In addition to a broad miscibility gap (Fig. 2c), we find, remarkably, metastable multinary ordered phases inside the miscibility gap at stoichiometric compositions. They disappear, for any value of $\{\Delta H^{(n)}\}$, when the elastic energy is eliminated (i.e., as assumed in simple Ising models). Thus, we conclude that unstable species ($\Delta H^{(n)} > 0$) can be induced metastably at low temperatures by large elastic energies. The large reorientation activation barriers and small atomic diffusion constants at low temperatures characteristic of semiconductors [5] may hence lead to the quenching-in of such phases. It is a distinct possibility that some of the ordered phases reported to occur inside the miscibility gap at low temperatures [12] indeed correspond to such metastably quenched phases.

Table I: Components of Eq. (3) for $Ga_nIn_{4-n}P_4$. Energies in Kcal/atom-pairs, lattice constants in Å.

| System | $\Delta H^{(n)}$ | $\Delta F(a_{eq}^{(n)})$ | $\epsilon^{(n)}$ | $a_{eq}^{(n)}$ |
|-----------------|------------------|--------------------------|------------------|----------------|
| n=0 GaP | 0.0 | 0.0 | 0.0 | 5.450 |
| n=1 Ga_3InP_4 | -0.244 | +2.33 | -2.57 | 5.5545 |
| n=2 $GaInP_2$ | -0.29 | +3.29 | -3.58 | 5.659 |
| n=3 $GaIn_3P_4$ | -0.243 | +2.64 | -2.88 | 5.7635 |
| n=4 InP | 0.0 | 0.0 | 0.0 | 5.868 |

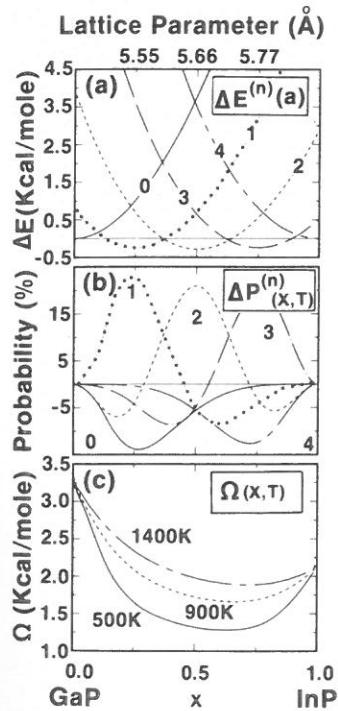


Fig. 1: (a) excess cluster energies; (b) cluster probability differences (actual-random) at 600K; (c) interaction parameter of alloy.

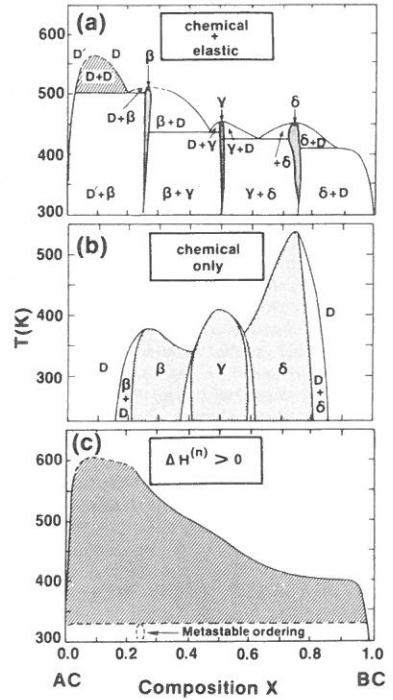


Fig. 2: CVM phase diagram: (a) first principles energies; (b) chemical energies only; (c) elastic-energy dominant. Shaded areas: single ordered phases; dashed: miscibility gap. D=disordered, $\beta=A_3BC_4$, $\gamma=ABC_2$, $\delta=AB_3C_4$, respectively.

t the new $\Delta H^{(n)}$ values produce without any adjustment¹⁸ of what the elastic energies are. Furthermore, $\Delta E^{(n)}(a)$ can capture missing from both elas-

Fig. 1b,c) and the phase diagram over positive mixing enthalpy ordered phase evident in Fig. 1c) 0 Kcal/mole, compared with the high-temperature data), ordered phase to be stable at low temperature. The predictions of all elastic energy with recent observations of the ordered phases in GaSbAs [12c]) ordered phases et al. [18]. (ii) The elastic energy x , those local atomic order corresponding lattice parameter a and departure from randomness ϵ . Fig. 1b exhibits a ~20% enhancement $x=1/4, 1/2$, and $3/4$, respectively] growth-temperature-dependent carrier mobilities, and dependence of $P^{(n)}(x,T)$ introduces $\Omega(x,T)$ evident in Fig. 1c. While such hitherto unexplained deviations in detailed fits to all-attractive ordering energies (dashed area in Fig. 2a) as), in contradiction with the interactions [16,17].

which retain in $\Delta E^{(n)}$ only chemical energy in Fig. 2b the phase diagram of Table I, but omitting the elastic energy and 2b illustrates the three attractive chemical interactions of ordered stoichiometric compounds (dashed areas) and broader two-phase regions. Elastic energy is seen to lead to coexistence (D and D' in Fig. 2a). The presence of the coherent phase diagram (or to Fig. 2a) has led many theoretical temperatures, this leads to metastable and considerably overestimates small repulsive $\Delta H^{(n)}$'s we have elastic energy of Fig. 2a but a broad miscibility gap (Fig. 2a) ordered phases inside the miscibility gap. They disappear, for any $\Delta H^{(n)} > 0$ eliminated (i.e., as assumed in at unstable species ($\Delta H^{(n)} > 0$) phases by large elastic energies. Small atomic diffusion coefficients of semiconductors [5] may hence be a distinct possibility that inside the miscibility gap at which metastably quenched phases.

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