

Composition correlations in ternary semiconductor alloys

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Spatial composition fluctuations in semiconductor alloys $A_xB_{1-x}C$ involve elastic energy when the lattice parameters of AC and BC differ. Therefore, the fluctuations are expected to be reduced below those exhibited by a purely random distribution of the constituent ions. We estimate the extent of the reduction, and relate it to recent observations of Raman linewidths and line shapes in $Ga_xIn_{1-x}As$ and $Ga_xAl_{1-x}As$.

Ternary tetrahedrally coordinated semiconductor alloys $A_xB_{1-x}C$ or AC_xD_{1-x} , where A and B are group III (or II) elements, and C and D group V (or VI) elements can for many purposes be described as binary mixtures whose component particles reside (approximately) on the sites of an fcc lattice. Specifically, thermodynamic parameters such as mixing enthalpy¹ and spinodal curves² conform fairly well to the rules describing regular solutions.

The key quantity of regular solution theory is the interaction parameter Ω , which can be interpreted in terms of pair interaction energies; thus

$$\Omega = \frac{1}{2} N_0 Z (2E_{AB} - E_{AA} - E_{BB}) ,$$

where N_0 is Avogadro's number, Z the coordination number (12 for fcc), and E_{ij} are the (negative) pair interaction energies. A negative value of Ω indicates a tendency to ordering (compound formation), a positive value a tendency to decomposition. All the observed interaction parameters of the alloy group with $A, B = Al, Ga, In; (Zn, Cd, Hg)$ $C, D = P, As, Sb; (Se, Te)$ are positive or zero. Thus, one expects—and observes—miscibility gaps and spinodal decomposition below a critical mixing temperature characteristic of each alloy.

The observed interaction parameters are found to be proportional to the square of the lattice parameter difference between the pure compounds that constitute the alloy. This dependence has been interpreted, in the so-called delta-lattice-parameter (DLP) model in terms of the lattice parameter dependence of the average band gap,³ and more recently, especially after details of the composition dependence of bond lengths in $Ga_{1-x}In_xAs$ were revealed by extended x-ray absorption fine structure (EXAFS) measurements,⁴ in terms of the bond distortions associated with the formation of the alloy. By relating the bond distortion energies to the macroscopic elastic constants of the crystals, a good case could be made for ascribing most or all of the observed mixing enthalpy to this cause.^{5,6}

A positive mixing enthalpy would normally produce clustering of like particles above the critical mixing temperature, and an estimate of the degree of clustering to be expected was published recently.⁷ For the model that was used in this calculation, the origin of the positive interaction parameter is irrelevant. It has been pointed out, however, that in the type of "lattice gas" that represents these alloys, with a composition-dependent lattice parameter, if an alloy crystal is formed at all, elastic interactions will suppress the clustering.⁵ It was also suggested that these elastic interactions were likely to produce an ordering tendency, that is to say,

that local composition fluctuations might be reduced below the level to be expected of a purely random distribution of the constituents. What follows is a simple thermodynamic model for the composition correlations induced by the elastic energy.

The lattice parameters of these alloys follow Vegard's law quite accurately. Any deviation from a linear dependence of lattice parameter on composition (bowing) is small enough to be quite negligible for the purpose of this argument. Consider a region of the alloy large enough to be regarded as macroscopic. If the composition of this region deviates from the average composition of the alloy, but must be accommodated in the volume of the virtual lattice that "belongs to it," it will suffer compression or dilatation.

The energy associated with the strain is readily computed.⁵ Let the average composition of the alloy be $A_{x_0}B_{1-x_0}C$ and the local composition $A_xB_{1-x}C$. Then the lattice parameter is

$$d_0 = x_0 a + (1 - x_0) b , \quad (1)$$

where a is the lattice parameter of AC and b the lattice parameter of BC . If the crystal were permitted to relax everywhere, the local lattice parameter would be

$$d = xa + (1 - x) b ; \quad (2)$$

however, the compatibility constraint imposes a local strain

$$\delta = d - d_0 = (x - x_0)(a - b) \equiv \Delta x (a - b) , \quad (3)$$

with an associated energy density (per unit volume)

$$W(\Delta x)^2 = 18B \left[\frac{a - b}{a + b} \right]^2 (\Delta x)^2 , \quad (4)$$

where B is the bulk modulus of the crystal.

Equation (4) is based on isotropic compression or dilatation; an analogous expression can be obtained for a planar strain. In that form the elastic energy is thought to be responsible for the "lattice latching" observed in heteroepitaxy,⁸ the growth of a single lattice-matched alloy composition over a range of melt compositions. It also accounts for the successful heteroepitaxial growth of alloy compositions unstable in the bulk at the growth temperature.

It has been shown⁵ that a reasonable fit to the interaction parameters of the III-V alloys considered here is given by the semiempirical formula

$$W' = 0.226 \times 18B \left[\frac{a - b}{a + b} \right]^2 \quad (5)$$

making a contribution to the mixing enthalpy per mole of

$$\Delta H = W'x(1-x)V, \quad (6)$$

where V is the molar volume of the alloy.

The entropy of mixing is approximately

$$S = \ln \left[\frac{N_A!N_B!}{N_{AA}!N_{BB}!(N_{AB}!)^2} \right], \quad (7)$$

where the N_i are numbers of ions and the N_{ij} numbers of second neighbor pairs. Per mole this is

$$S \approx R [x \ln x + (1-x) \ln(1-x) - x^2 \ln(x^2) - (1-x)^2 \ln(1-x)^2 - 2x(1-x) \ln x(1-x)]. \quad (8)$$

Using Eqs. (4), (6), and (8) in the thermodynamic formula⁹ for macroscopic fluctuations of concentration on an assembly of N sites with total Gibbs free energy G

$$\langle (\Delta x)^2 \rangle = \frac{kT}{(\partial^2 G / \partial x^2)_{T,P,N}}, \quad (9)$$

we find

$$\langle (\Delta x)^2 \rangle = \frac{1}{N} x(1-x) \left[1 + \frac{2(W-W')V}{RT} x(1-x) \right]^{-1}, \quad (10a)$$

or, in terms of the critical mixing temperature T_c given by $2RT_c = W'V = 0.226WV$

$$\langle (\Delta x)^2 \rangle = \frac{1}{N} \left[\frac{x(1-x)}{1 + 13.7(T_c/T)x(1-x)} \right]. \quad (10b)$$

One may guess conservatively that the disorder grown into a crystal corresponds roughly to a value frozen in at the growth temperature. Thus, if we compare a lattice-matched alloy such as $\text{Ga}_{0.5}\text{Al}_{0.5}\text{As}$ with $T_c \approx 0$ with the mismatched alloy $\text{In}_{0.5}\text{Ga}_{0.5}\text{As}$ with $T_c \sim 600$ K grown epitaxially at $T \sim 900$ K, we expect, from Eq. (10a) or (10b) to find a relative reduction of the mean-square concentration fluctuations in the mismatched alloy by a factor ~ 0.3 . The reduction would be expected to be more significant, depending on cooling rate and on the growth parameters, if appreciable solid-state diffusion takes place after growth.

Some qualitative experimental support for this prediction is to be found in linewidths and line shapes observed by Parayanthal and Pollak¹⁰ in Raman scattering from $\text{Al}_x\text{Ga}_{1-x}\text{As}$ and $\text{In}_x\text{Ga}_{1-x}\text{As}$. In this work it was found that the broadening and asymmetry of the Raman line was more pronounced in the lattice-matched alloy $\text{Al}_x\text{Ga}_{1-x}\text{As}$ than in the mismatched $\text{In}_x\text{Ga}_{1-x}\text{As}$.

A "spatial correlation" model has been successfully used to interpret the effect of microcrystalline,¹¹ and implantation damage¹² disorder on Raman linewidths and line shapes. This model replaces the phonons of the infinite ordered crystal with phonons localized within "correlation regions" whose size is a measure of the partial ordering in the imperfect crystal. As a result, the $q=0$ momentum selection rule of the perfect crystal is relaxed, and phonons in a region of the Brillouin zone corresponding to the correlation length participate in the scattering. Experimental values of the correlation length are deduced by fitting the observed

linewidths and line shapes, assuming a Gaussian size distribution of the correlation regions, generally in reasonable agreement with the estimated sizes of crystallites¹¹ or undamaged regions.¹²

Substitutional disorder in an alloy similarly breaks the crystal's translational symmetry and, hence, the $q=0$ selection rule for Raman scattering. Since the perturbation is the phonon modulation of the dielectric tensor, the effective size of the scattering regions is given by the correlation length of this tensor's spatial fluctuations.¹³ No theoretical prediction has so far been made for this quantity, but Parayanthal and Pollack¹⁰ were able to fit their observed Raman lines with a spatial correlation model in which the correlation length is simply a phenomenological parameter determined from the experimental data. For their epitaxially grown alloys, this parameter ranges from about 8 to above 30 lattice parameters.

Of the two alloy series for which results are given, $\text{Ga}_x\text{Al}_{1-x}\text{As}$ has, within experimental accuracy, zero mixing enthalpy, and the cations should constitute a perfect lattice gas on their fcc sublattice. Their concentration fluctuations, which may be taken as measure of the disorder, then are given by Eqs. (10) with $T_c=0$. The Raman lines bear this out qualitatively, in the sense that the linewidths and asymmetries are greatest for samples with x near 0.5.

The broadening of the Raman lines even in the completely random alloy $\text{Ga}_x\text{Al}_{1-x}\text{As}$ is modest as compared with the spectrum of amorphous materials, and the spatial correlation model is successful in the interpretation of the line shapes. This suggests that one might assign the role of the defects that disrupt the phonon modes to fairly large fluctuations from the average composition. The correlation or coherence length can then be related to the statistics of large fluctuations.

In a random binary alloy, the probability distribution of ions is binomial. With a coordination number $Z=12$, the distribution of even the nearest-neighbor shell is fairly well represented by a Gaussian, and the probability of occurrence of a deviation $\geq \xi$ is approximated by

$$P(\xi) = \text{erfc}(\zeta), \quad (11)$$

where $\zeta = \xi / [2\langle (\Delta x)^2 \rangle]^{1/2}$.

In order to arrive at an order of magnitude estimate of the correlation length, we take the size of the defect to comprise one cation shell of Z ions. If a deviation of relative magnitude ξ is to occur in a region containing NZ cations, we should have $NZP(\xi)=1$, and, therefore, the average distance between such defects, which we take to be the correlation length, is

$$L = N^{1/3}a = [Z \text{erfc}(\xi)]^{-1/3}a, \quad (12)$$

where a is the lattice parameter. Equation (12) yields values consistent with the estimates based on the Raman spectra if ξ is about two standard deviations. Using the average value of L for the GaAs-like mode in $\text{Ga}_x\text{Al}_{1-x}\text{As}$ for the four samples with x near 0.5, we find $\xi = 1.88$.

Equations (10) and (12) also provide a comparison of the correlation lengths in $\text{Ga}_x\text{In}_{1-x}\text{As}$ and $\text{Ga}_x\text{Al}_{1-x}\text{As}$. Because of the suppression of concentration fluctuations, we expect the scattering centers associated with wide fluctuations to be rarer, increasing the correlation length. Using the factor 0.3 estimated from Eq. (10) for the reduction in

the mean square fluctuation in Eq. (12), we find

$$\frac{L_{\text{Ga}_{0.5}\text{In}_{0.5}\text{As}}}{L_{\text{Ga}_{0.5}\text{Al}_{0.5}\text{As}}} \approx 12 \quad (13)$$

This factor is larger than the numbers deduced from the Raman spectra by Parayanthal and Pollak, suggesting that additional phonon scattering processes are active.

The reduction in randomness discussed here is expected

to have other experimentally testable consequences, which will be considered elsewhere.

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