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Thermodynamic Stability of GaAs/InAs Heterostructure

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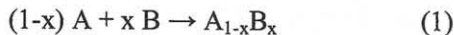
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1. Introduction

Advanced growth techniques have allowed the production of interesting heterostructures such as quantum wells and superlattices. The characteristics of these structures depend on their compositions, which are affected by the intermixing of the materials. The phase diagram is normally referred to when such a problem is concerned. However, most of the thermodynamics studies have focused on the equilibrium of the unstrained bulk, while the materials in the heterostructures are strained due to their lattice mismatch, and the strain alters their equilibrium phase. In this work, we study the equilibrium phase of the layer-by-layer GaAs/InAs heterostructure, by applying first principle methods to calculate their solution energies. By expanding the alloy energy in terms of the concentration and the strain, the strain dependence of the solution energy can be determined, and the equilibrium concentration of the strained layer in the heterostructures can be calculated.

2. Theory

One of the main ingredients for studying phase equilibrium is the solution energy, which can be computed for materials A and B from the energy change in the reaction



The ratio $\Delta E/x$ in the limit of $x \rightarrow 0$ gives the solution energy of B into the matrix of A.

The energy of $A_{1-x}B_x$ alloy can be assumed to be a third degree polynomial in the concentration of B, therefore it can be completely determined by the solution energies of A into B and B into A. The cluster variation method (CVM) [1] provides an expression for the entropy of the alloy. The composition of the phases in equilibrium is found by minimizing the CVM free energy.

For a coherent heterostructure of alternating A and B layers of thicknesses L_A and L_B , at finite temperature intermixing between layers occurs and the structure becomes layers of $A_{1-x}B_x$ and A_yB_{1-y} , as long as the degree of intermixing is small. The solute concentration

in each layer can be determined by minimizing the free energy of the heterostructure.

For simplicity we assume the typical case where the interface is the (001) plane. The lattice coherency leads to a strain field that is uniform and can have 2 independent components, the in-plane and perpendicular components, in each layer. Expanding the energy of each layer as a polynomial in the solute concentration and the strain components and keeping only terms linear in the concentration and the square in the strain, we write the energy per volume of a layer as

$$E(x, \varepsilon_x, \varepsilon_y) = E_o + x[E_s + (2\varepsilon_x + \varepsilon_y)E_{se}] + \frac{C_{11}}{2}(2\varepsilon_x^2 + \varepsilon_y^2) + C_{12}(2\varepsilon_x\varepsilon_y + \varepsilon_y^2) \quad (2)$$

where E_s and E_{se} are the solution energy and its dependence on the strain, respectively. By minimizing the energy with respect to the strain, the composition dependence of the lattice parameter is obtained.

The dependence of the solution energy on the strain can be calculated from the stress caused by the solute atom [2].

As the solute concentration is small the entropy of the alloy is well approximated by the entropy of a random solution, $S(x) = -k_B[x \ln x + (1-x) \ln(1-x)]$. The free energy per area of the heterostructure is

$$F(x, y, \varepsilon_x^A, \varepsilon_x^B, T) = L^A E^A(x, \varepsilon_x^A) + L^B E^B(y, \varepsilon_x^B) - T[L^A S^A(x) + L^B S^B(y)] \quad (3)$$

The perpendicular strain components are independent from each other, and they will assume equilibrium values that depend on the solute concentration and the in-plane strain in each layer only. Therefore we do not write them as the variables for the free energy. The lattice coherency gives a relation between the in-plane strains and because the intermixing occurs by swapping atoms between layers, there is a relationship between x and y . Therefore, at a fixed temperature, the free energy is a function of 2 variables, e.g. x and ε_x^A only.

3. Results

We use a first principle method [3] based on the local density approximation of the density functional theory to compute the solution energies of dissolving GaAs into InAs and dissolving InAs into GaAs. The solution energy of GaAs into InAs matrix was found to be 15 kJ/mol, and the solution energy of InAs into GaAs was 17 kJ/mol. The positive solution energies mean that GaAs-InAs is a phase separating system. The bulk solid solution phase diagram was calculated and the maximum temperature of the miscibility gap was found to be 546°C, which is in excellent agreement with a thermodynamic assessment of As-Ga-In ternary system [4].

It is noticed that the mismatch of the lattice parameter contributes most to the solution energies, therefore the strained structure can be expected to have a rather different phase equilibrium than the unstrained bulk.

The strain dependence of the solution energy was found to be 412 kJ/mol for GaAs into InAs and -572 kJ/mol for InAs into GaAs. The plus (minus) sign indicates that the solution energy is reduced in compressive (expansive) strain. The result shows a strong dependence of the solution energy on the strain, and for a hydrostatic strain of about 4% the solution energy should vanish. However, this should be taken as a guideline only, because as the strain is increased the deviation of the alloy energy from our expansion in eq. (2) also increases.

The equilibrium solute concentration as a function of temperature in GaAs/InAs heterostructure was calculated at various thickness ratios of the GaAs rich- and the InAs rich- layers. Fig. 1 shows the GaAs concentration in the InAs-rich layer. It must be noted that our approximation is valid only in the region where the solute concentration is small. The result where the concentration is high is also shown here for the sake of illustration, only.

As indicated by the GaAs concentration in InAs layer shown in Fig. 1, the intermixing increases rapidly with the temperature. Above 100K, the GaAs concentration approaches 100%, and the layer structures of GaAs/InAs are expected to be unstable. Thicker InAs layers have lower GaAs concentration at a fixed temperature, however, to have a stable heterostructure the thickness of the InAs layer must be less than 5% of the thickness of the GaAs layer. This is in agreement with our earlier calculation that shows that deposition of GaAs on InAs substrate will not form a stable heterostructure. For the three cases shown in Fig. 1, as the thickness of the GaAs layer is much larger than the InAs layer, the InAs layer is strained to match with the GaAs lattice, and GaAs is virtually unstrained.

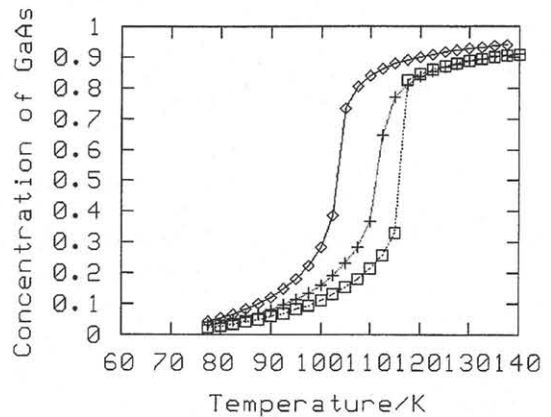


Figure 1. Concentration of GaAs in InAs-rich layer as a function of temperature. The ratios of InAs-rich layer thickness to GaAs-rich layer thickness are 1:200, 1:100 and 1:50 for lines indicated by diamond, cross, and square signs, respectively.

4. Conclusions

In the lattice coherent GaAs/InAs heterostructure, the strain reduces the energy barrier for intermixing and thereby makes the heterostructure structure unstable with respect to intermixing. Therefore the GaAs/InAs heterostructure is not an equilibrium structure, and their existence is due to the slow diffusion rate.

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References

- [1] D. de Fontaine, in *Solid State Physics*, ed. By H. Ehrenreich, F. Seitz and D. Turnbull (Academic Press, New York, 1979).
- [2] S. Vannarat, M Sluiter and Y. Kawazoe, *Mat. Trans. (JIM)*, **42**, 429 (2001).
- [3] G. Kresse and J. Furthmüller, *Comp. Mat. Sci.* **6**, 15 (1996).
- [4] J. Y. Shen, C. Chatillon, I. Ansara, A. Watson, B. Rugg and T. Chart, *Calphad*, **19**, 215 (1995)