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Thermodynamic stability of bulk and epitaxial $\text{Ge}_{1-x}\text{Sn}_x$ semiconductor alloys

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Using molecular-dynamics simulation we have calculated the total energy for unconstrained and biaxially confined model of $\text{Ge}_{1-x}\text{Sn}_x$ alloys. It allows us to study the thermodynamic stability of both disordered and ordered phases of semiconductor alloys. We have found a remarkable suppression of the phase separation in $\text{Ge}_{1-x}\text{Sn}_x$ due to biaxial strain.

1. Introduction

The search for optoelectronic direct-gap materials on the basis group IV semiconductors has been stimulated in the past years by new crystal-growing technologies such as molecular-beam epitaxy and laser crystallization. The research efforts follow several basic lines. One of them consists in growing metastable alloys with a diamond structure and fundamental energy gap at the Γ -point (for example, Ge–Sn and Si–Sn alloys) [1,2]. Under equilibrium growing conditions Ge and Sn, as a rule, normally are not soluble components, however, alloys on their basis can be obtained using nonequilibrium growing techniques. $\text{Ge}_{1-x}\text{Sn}_x$ ($x < 0.3$) metastable semiconductor alloys was synthesised by pulsed UV laser crystallization [3].

Soma *et al* [4] studied the effect of stress on the phase diagrams Ge–Sn and Si–Sn alloys. They predicted the enlargement of stability region of the Ge–Sn solid solution under an external pressure. A common feature of the alloy epitaxies is the strain due to lattice mismatch and different thermal expansion coefficients. The epitaxial layer of binary alloy grown pseudomorphically on the substrate becomes highly strained. The strain and compositional fluctuations influence all types of properties of the alloys including the miscibility.

In this paper we present a theoretical study of thermodynamic properties of strained bulk as well as epitaxial Ge–Sn alloys. We investigate the influence of a biaxial strain of the miscibility of these alloys using molecular-dynamics simulation.

While the basic physical properties of semiconductor alloys are obtained by first-principles self-consistent calculations, a computational simulation by use of molecular dynamics (MD) is helpful for understanding of the stability of semiconductor alloys [5].

2. Molecular-dynamics simulation

For the calculation of thermodynamic stability by the use of molecular dynamics, we have to determine the potential model first. Among many empirical model potentials, which

have been suggested for tetrahedral semiconductors, the Tersoff three-particle potential turned out to be the most successful for investigating many properties of semiconductor compounds [6].

Interatomic potential interaction energy of two neighbour atoms i and j has the form:

$$V_{ij} = f_C(r_{ij})[a_{ij}f_R(r_{ij}) + b_{ij}f_A(r_{ij})], \quad (1)$$

where

$$f_R(r) = A \cdot \exp(-\lambda r), \quad (2)$$

$$f_A(r) = -B \cdot \exp(-\mu r), \quad (3)$$

$$f_C(r) = \begin{cases} 1, & r < R, \\ \frac{1}{2} + \frac{1}{2} \cos\left[\frac{\pi}{2} \frac{(r-R)}{(S-R)}\right], & R < r < S, \\ 0, & r > S, \end{cases} \quad (4)$$

b_{ij} — is many-body-order parameter describing how the bond-formation energy is affected by the local atomic arrangement due to the presence of other neighbouring atoms (the k -atoms). This many-body function of atomic positions i, j, k has the form:

$$b_{ij} = \chi_{ij}(1 + \beta^n \xi_{ij}^n)^{-1/2n}, \quad (5)$$

where

$$\xi_{ij} = \sum_{k(\neq i,j)} f_C(r_{ik})g(\theta_{ijk}) \exp(\lambda_3^3(r_{ij} - r_{ik})^3), \quad (6)$$

$$g(\theta) = 1 + \frac{c^2}{d^2} - \frac{c^2}{d^2 + (h - \cos\theta)^2}, \quad (7)$$

$$a_{ij} = (1 + \alpha^n \eta_{ij}^n)^{-1/2n}, \quad (8)$$

$$n_{ij} = \sum_{k(\neq i,j)} f_C(r_{ik}) \exp(\lambda_3^3(r_{ij} - r_{ik})^3), \quad (9)$$

ξ_{ij} — effective coordination number, $g(\theta)$ is a function of the angle between r_{ij} and r_{ik} , that has been fitted to stabilize the tetrahedral structure.

Parameters for Ge were taken from [6], and for Sn were derived from gray-tin cohesion energy adjustment, equal to 3.12 eV per atom [7], and presented in our previous

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article [8]. Simulation have been done for systems with $N = 216$ particles, the initial positions of which were taken in tetrahedral sites of cell, formed by $3 \times 3 \times 3$ unit cells of the diamond type. The periodic boundary conditions were used. This method was based on solving the Newton equation set using the fast from of Verlet algorithm [9], which being the self-starting, doesn't lead to roundoff errors accumulation. Simulation is started from an initial structure, in which two kinds of atoms are randomly placed on a diamond lattice. After the system passed to the equilibrium state with time step $\Delta t = 0.15 \cdot 10^{-15}$ s we calculated the pair distribution function $g(r)$ for Ge, Sn and $\text{Ge}_{0.74}\text{Sn}_{0.26}$ at various temperatures [8]. When the $\text{Ge}_{1-x}\text{Sn}_x$ substitutional solid solutions are formed, the first peak of pair distribution function splits into three peaks corresponding to the Ge-Ge, Ge-Sn and Sn-Sn bonds. At the same time with temperature growth the pair distribution function peaks becomes something broader and displace a little, that means the conservation of the tetrahedral crystal structure. Besides the coordination number corresponding to the number of nearest neighbours was controlled in modeling process. Such a behavior of the system is confirmed by the total energy as function of the temperature.

3. Bulk semiconductor alloys

The lattice constant of the reference random alloy ($x = 0.5$) and the four ordered structures Ge, α -Sn, ZB-GeSn (zinc blende) and RH-GeSe (rhombohedral) was determined from the condition of minimal total energy as a function of volume (fig. 1). So at 300 K for Ge from our calculation $a = 5.659 \text{ \AA}$ (experimental value 5.657 \AA [7]), for Sn $a = 6.490 \text{ \AA}$ (experimental value 6.489 \AA [7]). To check the stability of the investigating structures against segregation of the two constituents we compare the total energy of the equilibrium ZB-GeSn, RH-GeSn and disordered GeSn with the arithmetic mean of total energies of Ge and Sn. Figure 1 shows that the ordered phases are stabler than the disorder phase, $\Delta E^{(D)} > \Delta E^{(O)}$. The random alloys have two tendencies toward phase transformations at once, i.e. a tendency to decomposition and a tendency to superstructure formation.

For a disordered (D) binary alloys $\text{Ge}_{1-x}\text{Sn}_x$ a Helmholtz mixing free energy ΔF as a function of x and T at a fixed pressure

$$\Delta F(x, T) = F_{\text{GeSn}}(x, T) - (1-x)F_{\text{Ge}}(T) - xF_{\text{Sn}}(T). \quad (10)$$

Than ΔF can be written as

$$\Delta F = \Delta E - T\Delta S, \quad (11)$$

where ΔE is the mixing energy and ΔS is the mixing entropy defined similarly to ΔF . Because the magnitude of $\Delta(PV)$ is small at the normal pressure of about 1 atmosphere, ΔE and mixing enthalpy ΔH are interchangeable. Calculated mixing energy ΔE as a function of composition at $T = 0 \text{ K}$ is represented in Fig. 2 in comparison with pseudopotential calculations of Soma *et al* [4]. The approximation $\Delta E = \Omega x(1-x)$

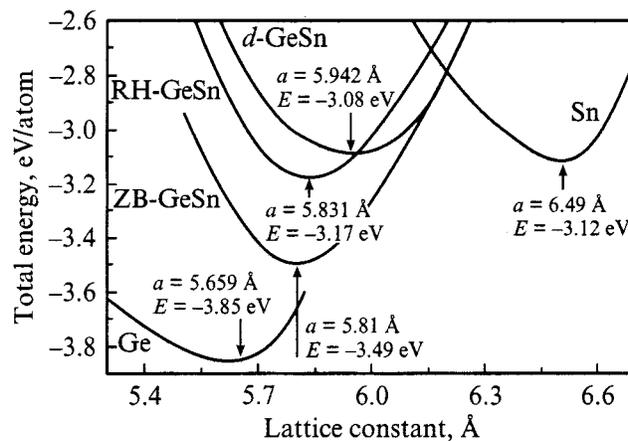


Figure 1. Total energy of Ge, Sn, disordered (d -GeSn), rhombohedral (RH-GeSn) and zinc blende (ZB-GeSn) alloys at $x = 0.5$ as a function of volume.

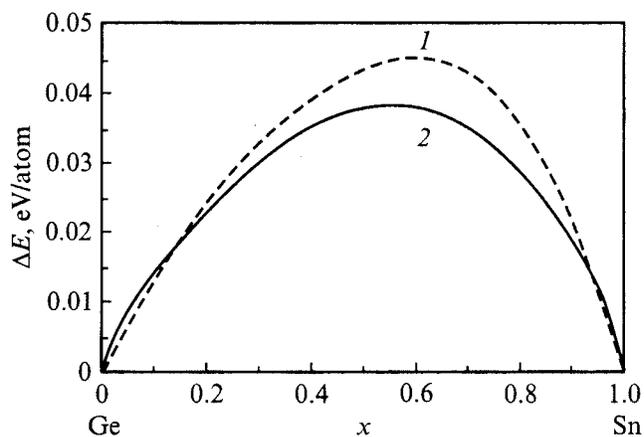


Figure 2. The mixing energy ΔE as a function of composition x of $\text{Ge}_{1-x}\text{Sn}_x$ alloy at $T = 0 \text{ K}$ (1 — pseudopotential calculation of Soma *et al* [4], 2 — our calculation).

should introduce some error in the free energy calculation because our case extends beyond pair interactions. We obtain interaction parameter $\Omega_{\text{Ge-Sn}} = 11.86 \text{ kcal/mole}$ compared with indirect calculated value from the experimental phase diagram $\Omega_{\text{Ge-Sn}} = 7.55 \text{ kcal/mole}$ [10] and theoretical estimation $\Omega_{\text{Ge-Sn}} = 15.3 \text{ kcal/mole}$ [11]. The entropy of mixing is supposed to be equal to the configurational entropy in regular-solution model, given by

$$\Delta S = -R[(1-x)\ln(1-x) + x\ln x]. \quad (12)$$

Fig. 3 shows the mixing free energy of $\text{Ge}_{1-x}\text{Sn}_x$ as a function of x at four temperatures. These curves show that these alloys have miscibility gap (MG). Below the critical temperature $T_C = 830 \text{ K}$ at $x_C = 0.62$ the excess free energy shows a common tangent line at two different x values indicating the tendency for phase decomposition, i.e. the occurrence of miscibility gap. The knowledge of the free energies allows the construction of a phase

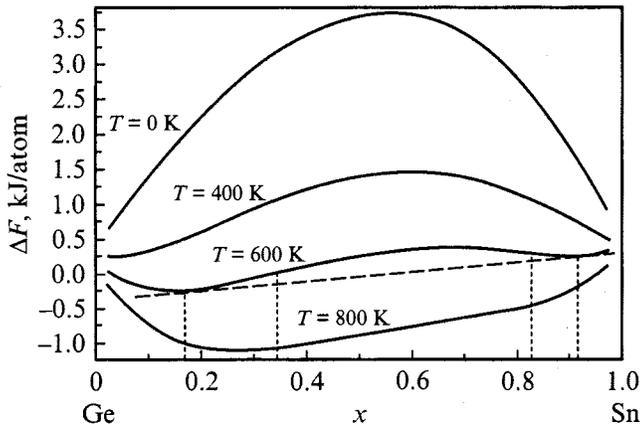


Figure 3. The mixing free energy ΔF of $\text{Ge}_{1-x}\text{Sn}_x$ as a function of x at $T = 0, 400, 600, 800$ K.

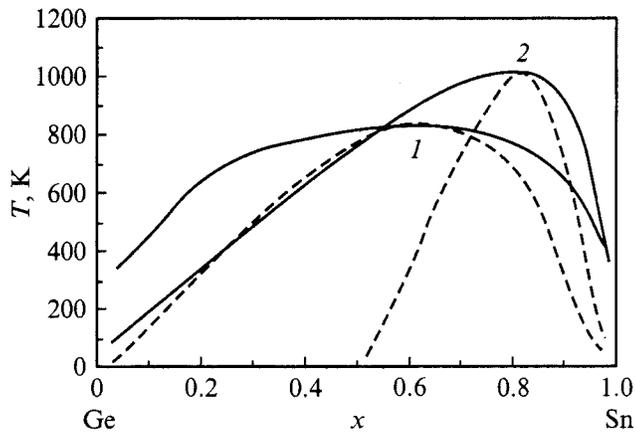


Figure 4. T - x diagram for $\text{Ge}_{1-x}\text{Sn}_x$ alloy. 1 — without deformation, 2 — with biaxial deformation $\varepsilon = 0.03$. Solid lines — binodals, dashed lines — spinodals.

diagram. The T - x phase diagram resulting for $\text{Ge}_{1-x}\text{Sn}_x$ is represented in Fig. 4. The binodal is the line in the (x, T) plane where the Ge- and Sn-rich disordered phase have equal chemical potentials μ . The spinodal line describes the limit of metastability of the disordered phase when $d^2F/dx^2 = d\mu/dx = 0$, F being the free energy. For $T = 300$ K the solubility limit of Sn(Ge) in Ge(Sn) is less than 2%(0%). The phase diagram also indicates that in a wide range between spinodal and binodal curves the random alloy may exist as a metastable phase. We find that the thermodynamically stable ground state corresponds to phase separation. We calculated the temperature limit of stability for ordered ZB and RH phases. Ordering temperatures are $T_0 = 848$ K (for ZB-GeSn) and $T_0 = 365$ K (for RH-GeSn).

At thermodynamic equilibrium the system phase separates below T_C into Ge- and Sn-rich mixtures. If, however, phase separation is kinetically inhibited, metastable long-range ordering will persist below T_0 .

4. Epitaxial semiconductor alloys

We model a thin pseudomorphic epitaxial semiconductor alloy grown on a substrate (s) with lattice constant a_s , by restricting the alloy lattice constant a_{\parallel} parallel to the substrate to be equal to a_s and optimizing the MD calculated total energy through variation of the lattice constant a_{\perp} in the direction perpendicular to the substrate. The excess free energy is decreased by the elastic energy due to the build-up strain. Generally the miscibility gap decreases. In the corresponding T - x diagram (Fig. 4) such a trend is indeed observed. For a biaxial of 3% the critical temperature is about 1010 K at $x_C = 0.8$. The phase diagram becomes more asymmetric, simultaneously the miscibility gap as well as the region of spontaneous decomposition reduce. One can indeed speak about a tendency for suppression of the phase separation in $\text{Ge}_{1-x}\text{Sn}_x$ due to elastic strain. This result explains why in $\text{Ge}_{1-x}\text{Sn}_x$ epilayers with Sn content up to $x = 0.3$ no evidence for phase separation has been observed [3]. The enthalpy of formation ΔH of epitaxial form of phase α is analogous to that of the bulk form. Than substrate strain (ss) energy [12]

$$\Delta E_{ss}^{(\alpha)} = H^{(E_p, \alpha)}[A_m B_n, a_{\parallel} = a_s] - H^{(\alpha)}[A_m B_n]. \quad (13)$$

Fig. 5 shows our calculated enthalpies of the GeSn lattices matched to Ge. The effective enthalpy of formation of an epitaxial film (relative to lattice-matched products)

$$\begin{aligned} \delta H^{(E_p, \alpha)} = & H^{(E_p, \alpha)}[A_m B_n, a_{\parallel} = a_s] - mH^{(\alpha)}[A, a_{\parallel} = a_s] \\ & - nH^{(\alpha)}[B, a_{\parallel} = a_s]. \end{aligned} \quad (14)$$

Note that the stability of the ZB phase of GeSn is increased under epitaxial strain in compare to RH-GeSn, i. e., $\Delta E_{ss}^{(ZB)} < \Delta E_{ss}^{(RH)}$. If phase separation is slow, metastable long-range ordering may occur. These special arrangements have a lower enthalpy than the disordered alloy of the same composition.

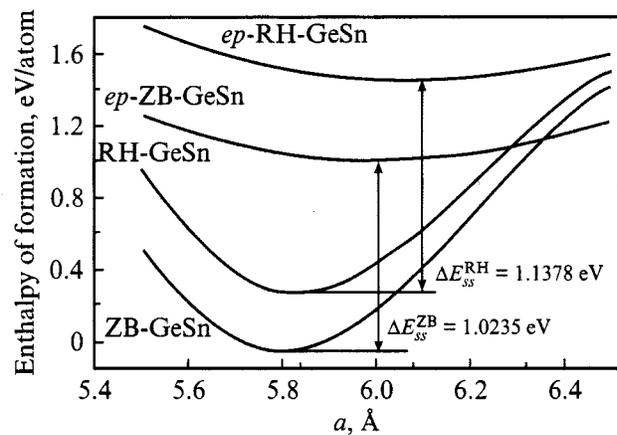


Figure 5. The enthalpies of the formation of zinc-blende (ZB-) GeSn, rhombohedral (RH-) GeSn as a function of lattice constant a , and for epitaxially (ep -) confined (to $a_{\text{Ge}} = 5.645$ Å) ZB- and RH-GeSn.

This work represents one of a few contributions which will surely lead to a better understanding of the physical properties of Sn–Ge alloys.

5. Summary

In conclusion, we have presented a molecular dynamics method to study unstrained and biaxially strained binary $\text{Ge}_{1-x}\text{Sn}_x$ alloys. Biaxial strain has been taken into account by fixing in-plane lattice constant. We observe a broad miscibility gap for unstrained $\text{Ge}_{1-x}\text{Sn}_x$. The critical temperature is about 830 K. However, these is also wide range of compositions where a random $\text{Ge}_{1-x}\text{Sn}_x$ alloy may exist as a metastable phase.

A biaxial strain is extremely important for the miscibility behavior of the alloys. The miscibility gap as well as the region of spontaneous decomposition are reduced. In this case the critical temperature is remarkably enlarged. Strongly ordered zinc-blende or rhombohedral phases are more stable to the spinodal decomposition than the same random alloys. The analysis of the effective enthalpy of formation of an epitaxial films shows that the stability of ZB-phase is increased under epitaxial strain in compare to RH–GeSn and long-range ordering may occur.

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Термодинамическая стабильность объемных и эпитаксиальных полупроводниковых сплавов $\text{Ge}_{1-x}\text{Sn}_x$

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Аннотация Используя молекулярно-динамическое моделирование, мы вычислили полную энергию для нестесненной и двусоно ограниченной модели сплавов $\text{Ge}_{1-x}\text{Sn}_x$. Это позволило изучить термодинамическую стабильность как неупорядоченной, так и упорядоченной фаз полупроводниковых сплавов. Мы обнаружили значительное подавление фазового разделения в $\text{Ge}_{1-x}\text{Sn}_x$ вследствие двусононого напряжения.