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Thermodynamic modeling of bulk ternary alloy crystal growth: Comparison of experiments and theory for GaInSb alloys

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ABSTRACT

Ternary alloy GaInSb crystals are grown from a melt in the horizontal Bridgman configuration for high (70%) and low (30%) Ga compositions. Each composition is compared to ideal and regular solution model predictions. Good agreement is found between the regular solution model and experimental observations. However, this agreement is quite sensitive to the starting proportions of the constituent elements.

1. Introduction

Tailoring the bandgap of bulk grown III–V ternary semiconductor crystals is a promising concept with many real-world implications. In the case of $Ga_{1-x}In_xSb$, various compositions yield bandgaps from 0.18 eV (InSb) to 0.725 eV (GaSb) [1], an incredibly versatile range. Applications include optical and thermophotovoltaic devices, IR detectors and super high-speed terahertz electronics. A long-term goal for this research is to predict what starting composition and replenishment is required to produce a single crystal with specific bandgap properties, from a bulk melt.

The regular solution model has been widely used to predict the thermodynamic properties of a crystal. This model was proposed for binary systems as early as the 1950s [2], and was adapted to ternary systems in the early 1970s [3]. A recent review of the regular solution model is given by Jacobs [4]. In the present work, the ideal and regular solution models are implemented numerically to predict the final composition distribution of Bridgman grown $Ga_{1-x}In_xSb$ alloys with various compositions. It is confirmed that the regular solution model agrees well with experiments, verifying that the melt remained well-mixed throughout the growth.

Attempts at homogeneous ternary alloy growth have been performed in various configurations. Mitric et al. [5] grew by vertical Bridgman and employed an alternating magnetic field to address segregation and interface destabilization issues, recognized by the numerical modeling performed by Stelian and Duffar [6]. While radial uniformity was achieved, the axial composition was not controlled. Nakamura et al. created a model to predict the composition distribution of $In_xGa_{1-x}As$ crystals grown using a TLZ method [7] and corresponding experiments for InGaAs and GaInSb resulted in a uniform composition distribution for diameters up to 2 mm [8,9].

2. Ideal and regular solution models for growth from a well-mixed melt

If the melt remains well-mixed during growth, then solidification is governed by the Scheil equation and the phase diagram determines the distribution of solute in the crystal. Well-mixed melts can be obtained with strong convective mass transport or with sufficiently slow growth rates to allow for complete diffusion in a stagnant melt. The Bridgman experiments discussed here combine slow growth rates and moderate melt convection. Comparisons with regular solution model predictions confirm the melt remained well-mixed throughout the growth.

2.1. Ideal solution model

The characteristic assumption of the ideal solution model is that the interaction energies between the different constituents are equal. Assuming that $Ga_{1-x}In_xSb$ is a two component melt

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Table 1
Starting masses of Ga, In and Sb for the target $Ga_{0.30}In_{0.70}Sb$, $Ga_{0.50}In_{0.50}Sb$ and $Ga_{0.70}In_{0.30}Sb$ experiments.

Target alloys	mass Ga (g)	mass In (g)	mass Sb (g)
$Ga_{0.30}In_{0.70}Sb$	2.007	7.712	11.683
$Ga_{0.50}In_{0.50}Sb$	3.486	5.741	12.175
$Ga_{0.70}In_{0.30}Sb$	5.090	3.590	12.700

(GaSb and InSb) that is well described by this assumption, the free energy of mixing per mole is $\Delta F^l_{\mathrm{mix}} = RT(x_1 \ln x_1 + x_2 \ln x_2)$ and the heat of mixing is zero. The changes in chemical potentials are $\Delta\mu_1{}^l = RT\ln x_1$ and $\Delta\mu_2{}^l = RT\ln x_2$ [4,10]. The solidus and liquidus lines for the ideal pseudobinary diagram are given by

$$x^s_{\mathrm{InSb}} = x^l_{\mathrm{InSb}} \exp\left(\frac{\Delta H_{\mathrm{InSb}}(1-T/T_{M,\mathrm{InSb}})}{RT}\right) \tag{1a}$$

and

$$x^l_{\mathrm{InSb}} = \frac{1-\exp(\Delta H_{\mathrm{GaSb}}(1-T/T_{\mathrm{M,GaSb}})/RT)}{\exp(\Delta H_{\mathrm{InSb}}(1-T/T_{\mathrm{M,InSb}})/RT)-\exp(\Delta H_{\mathrm{GaSb}}(1-T/T_{\mathrm{M,GaSb}})/RT)} \tag{1b}$$

2.2. Regular solution model

For ternary alloys, the heat of mixing in the melt phase is not zero due to changes in van der Waals forces and the reformation of chemical bonds between neighbors. These non-idealities are expressed as Bx_1x_2 where x_1 and x_2 are the mole fractions of the components and B is an interaction parameter [10]. This interaction parameter contains enthalpy contributions to non-ideality, and for a solid it also includes distortion energy. It is represented as B^l for liquids and B^s for solids. With these non-idealities the free energy of mixing per mole is $\Delta F^l_{mix} = RT(x_1\ln x_1 + x_2\ln x_2) + B^l x_1 x_2$ and the changes in chemical potentials are $\Delta\mu_1{}^l = RT\ln x_1 + B^l x_2^2$ and $\Delta\mu_2{}^l = RT\ln x_2 + B^l x_1^2$. Comparing with the general form $\mu = RT\ln x + RT\ln\gamma$, the activity coefficients in the liquid γ^l are then $\ln(\gamma_1{}^l) = (B^l/RT)x_2^2$ and $\ln(\gamma_2{}^l) = (B^l/RT)x_1^2$.

The free energy for the solid becomes $\Delta F^s_{\mathrm{mix}} = RT(x_1\ln x_1 + x_2\ln x_2) - x_1L_1(1-T/T_1) - x_2L_2(1-T/T_2) + B^s x_1x_2$. Activity coefficients for the solid γ^s are given by $\ln(\gamma^s_1) = (B^s/RT)x_2^2$ and $\ln(\gamma^s_2) = (B^s/RT)x_1^2$. The conditions for equilibrium may be written as

$$RT\ln(1-x^s_{\mathrm{InSb}}) - RT\ln(1-x^l_{\mathrm{InSb}}) + B^s(x^s_{\mathrm{InSb}})^2 - B^l(x^l_{\mathrm{InSb}})^2 + \frac{\Delta H_{f,\mathrm{GaSb}}(T-T_{M,\mathrm{GaSb}})}{T_{M,\mathrm{GaSb}}} = 0 \tag{2a}$$

and

$$RT\ln\left(\frac{x^l_{\mathrm{InSb}}}{1-x^l_{\mathrm{InSb}}}\right) + B^l(1-2x^l_{\mathrm{InSb}}) - RT\ln\left(\frac{x^s_{\mathrm{InSb}}}{1-x^s_{\mathrm{InSb}}}\right) - B^s(1-2x^s_{\mathrm{InSb}}) + \frac{\Delta H_{f,\mathrm{GaSb}}(T-T_{M,\mathrm{Gasb}})}{T_{M,\mathrm{Gasb}}} - \frac{\Delta H_{f,\mathrm{InSb}}(T-T_{M,\mathrm{Insb}})}{T_{M,\mathrm{InSb}}} = 0 \tag{2b}$$

It is shown in Fig. 4 of Foster and Woods that $B^l \approx 0$ and $B^s \approx RT$ for the GaSb–InSb system [10]. These values are substituted into Eq(s). ((2a) and (2b)) to calculate the regular solution pseudobinary phase diagram as in Fig. 6 of Dutta et al. [11].

3. Experimental procedure

Crystals were grown at target proportions $Ga_{0.30}In_{0.70}Sb$, $Ga_{0.70}In_{0.30}Sb$ and $Ga_{0.50}In_{0.50}Sb$. The $Ga_{0.50}In_{0.50}Sb$ crystal was previously compared to a crystal grown by a horizontal traveling heater method [12]. The process used here consisted of a vertical synthesis followed by horizontal growth. In the synthesis, desired proportions of gallium, indium and antimony were melted, mixed and quenched to produce a well-mixed, appropriately shaped charge. The final crystal was then grown by the horizontal Bridgman technique.

3.1. Vertical synthesis and horizontal growth

A quartz tube with diameter 11 mm was used as an ampoule. Table 1 shows the initial masses of each element for the three experiments based on molar masses of 69.723 g/mol for Ga, 114.818 g/mol for In and 121.760 g/mol for Sb. All elemental constituents were combined in the ampoule and sealed under vacuum.

The charge was synthesized in a vertical furnace above the liquidus temperature for 16 h to allow the melt to mix thoroughly by diffusion. After synthesis, the ampoule was cooled quickly to limit differentiation along the length of the crystal. The ampoule was scored and broken to retrieve the now properly shaped charge. The charge was lightly ground and etched with a mixture of HCl, HNO_3 and deionized water to remove oxides. Further experimental details can be found in Houchens et al. [12]. The charge was placed in a new ampoule and sealed under vacuum. The ampoule was then placed inside a large horizontal quartz tube surrounded by a cylindrical furnace. The heating element was approximately 5 cm long and provided the temperature profile shown in Fig. 1, which is closely approximated with a 4th order polynomial fit [12].

The temperature was raised above the liquidus for the particular alloy. Once the entire charge was molten, it was again allowed to mix for a minimum of 12 h. The furnace was then translated horizontally and the crystal solidified as it exited the hot zone at a growth rate of 0.9 mm/hr.

3.2. Characterization

Two axial slices were cut from the center of the crystals using a wire saw. The 2.04 mm thick slice was polished on both sides for analysis via Fourier Transform Infrared (FTIR) and Ultra Violet–Visual (UV–vis) wavelength spectroscopy. The other 1.78 mm thick slice was polished on one side for Electron Microprobe (EMP) analysis. Samples were hand-lapped and polished to a mirror finish using a diamond liquid suspension. EMP analysis was performed by Geller Microanalytical Lab with measurements

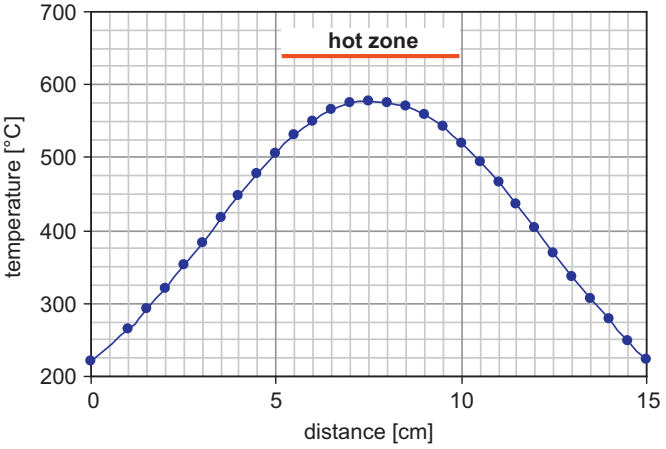

Fig. 1. Temperature profile of the horizontal growth heater for a sample heater set point of 640 °C.