Solidification of InSb-GaSb alloy and InSb with Vibration

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Abstract Summary

The objective of this project is to determine the influence of vibration on the composition homogeneity and microstructure of alloy semiconductors solidified with the **V**ertical **B**ridgman-**S**tockbarger (VBS) technique. InSb-GaSb and InSb were directionally solidified in a VBS apparatus with axial vibration of the ampoule.

$In_xGa_{1-x}Sb$ with $x = 0.2$ ingots were solidified. **E**nergy **D**ispersive X-ray **S**pectroscopy (EDS) measurements of the In concentration showed that there were no significant radial composition variations in the ingots grown both with and without vibration. The axial composition profiles corresponded to complete mixing of the melt. The quenched interface demarcation technique was used to reveal the interface shape and to measure the variation in growth rate down the ingots. Axial vibration of the ampoule did not seem to affect the average growth rate, but did increase the interface depth during the last-to-freeze parts of the ingots. Vibration appeared to decrease the number of curved boundaries, and to increase the number of straight boundaries.

InSb also was solidified in a VBS furnace with vibration. Again the number of grain boundaries was decreased by the application of vibration and the number of twins was increased, especially at the first-to-freeze part of the ingots. The **C**urrent **I**nduced **D**emarcation (CID) technique was used to reveal the interface during the solidification of InSb. Because of the increased number of twins in the resulting ingots, striations caused by CID were hard to see. The details of the microstructure of InSb ingots is under investigation.

Introduction

Since GaSb and InSb are totally miscible in both liquid and solid phases, the physical properties of InSb-GaSb alloys vary continuously with composition. The InSb-GaSb system is a convenient model for all semiconductor alloy systems because of its low melting temperature and low volatility.

Due to the compositional inhomogeneity and polycrystallinity associated with bulk alloy growth, directionally solidified $In_xGa_{1-x}Sb$ generally has not been suitable for device fabrication. Many efforts have been made to understand and improve the microstructure and composition uniformity resulting from bulk crystal growth by using various techniques and growth conditions [1-5]. Because of the unavoidable thermal and composition gradients, buoyancy-induced convection is always present in the melt during solidification on Earth. It is believed that buoyancy-induced convection can result in the formation of defects in crystal grown from the melt. Therefore, there is interest in growing crystal in space and in using forced convection to eliminate the effects of free convection.

The application of forced convection to the growth of InSb-GaSb reduced the number of twins and increased its grain size [4-6]. A magnetic field was applied to the melt growth of InSb-GaSb by Sen [4]. (A magnetic field reduces natural convection and thereby may eliminate temperature fluctuations in the melt.) Use of a transverse magnetic field decreased the number of grain boundaries [4]. ACRT was used to solidify InSb-GaSb alloy in the thermally stable VBS configuration by Gray [5]. His axial composition profiles correspond to complete mixing and there were no radial composition variations with or without ACRT. The number of grain boundaries and twins in the $In_{0.2}Ga_{0.8}Sb$ ingots decreased when ACRT was applied during growth.

Application of vibration to crystal growth is another approach to enhance convection in the melt during directional solidification. Vibration has been used in melt crystal growth by many researchers [3,6-9] with a wide range of frequencies and amplitudes. For example, ultrasonic vibration at 10 KHz and vibration at the low frequency of 60 Hz and amplitudes up to 1.5 mm were used in the Czochralski growth of Te-doped InSb [6,7]. Vibration at 10-100 Hz and 0.05-1.5 mm increased the grain size and the number of twins in CdTe grown by VBS [3] and $In_xGa_{1-x}Sb$ grown by zone melting [8]. The temperature field in the melt was also affected by the application of ultrasonic vibration during the growth of $In_xGa_{1-x}Sb$ [10]. However, the mechanism by which vibration affects crystal growth from the melt is unclear.

Experiment and results

Figure 1 shows the experimental setup. The growth furnace consists of a 30 cm long hot zone and a 15 cm long cold zone separated by a 6 cm long insulated zone. A Bruel Kjaer vibrator, connected to a power amplifier and a HP function generator, allowed the ampoule to be vibrated axially at a frequency of 1 to 100 Hz at an amplitude up to 1.5 mm.

The growth material was prepared by weighing the proper amount of 6N purity of In, Ga and Sb to give the exact starting composition of $In_xGa_{1-x}Sb$ with x=0.2 or In and Sb for InSb. Materials were prealloyed before solidified. Table 1 shown the conditions for the growth experiments. The temperature profile of the furnace was measured using a K-type thermalcouple in an empty ampoule. Figure 2 shows the temperature profile used for $In_xGa_{1-x}Sb$. The grown ingots were 5 to 8 cm long and 0.9 cm in diameter. After finishing a run, the temperature in the furnace was lowered to that of the cold zone, then lowered to room temperature at 20°C/hr. Table 2 lists the $In_{0.2}Ga_{0.8}Sb$ ingots grown with vibration.

The quenched interface demarcation technique was used to reveal the interface shape in directional solidification of InSb-GaSb. Figure 3 shown the schedule for demarcation. First, the heater temperature was lowered quickly from 800°C to 750°C and maintained at 750°C for 5 minutes. Then the ampoule was rapidly moved down 1 mm in the furnace, followed by raising the heater temperature to 800°C. The combination of temperature lowering and the rapid movement of the ampoule resulted in fast freezing and hence caused a compositional striation in the resulting ingot.

After removing it from the growth ampoule, a grown ingot was sectioned longitudinally and cut into 2 or 3 pieces. The samples were mounted in a resin mold and mechanically polished with 320 and 600 mesh SiC disk paper and then with 5, 0.3 and 0.05 μm alumina polishing powder, respectively. The average growth rate was calculated from the distance between striations. The interface depth was measured as defined by Figure 4.

EDS was used to measure the composition of the polished samples. The electron beam voltage was 15 KeV. The spectra data were collected for 60 seconds over an area of about 2 μm^2 using a Tracor Northern Model TN-2000 attached to an ISI scanning electron microscope. The energy range was from 0 to 10 KeV with an internal potential of 10 eV. A least-squares analysis was used to get the concentration of InSb from the spectra of pure InSb, pure GaSb and InSb-GaSb samples. Both axial and radial composition profile were measured.

In order to reveal the microstructure, the mechanically polished samples were chemically etched. For InSb-GaSb samples, a solution of HNO_3+HF+H_2O (1:1:1) was used for 10 seconds at room temperature. For InSb, the sample was first etched in NHO_3/HF/AcH/Br_2 (100:75:60:2) for 10 seconds, then HNO_3/0.5M $KMnO_4$/AcH (1:1:1) for 6 to 10 minutes. The microstructure of the samples was examined by optical microscopy.

Vibration of the ampoule did not noticably affect the composition profile in the resulting ingots for the growth of $In_{0.2}Ga_{0.8}Sb$. Figure 5 and Figure 6 shown axial and radial composition profiles for some $In_{0.2}Ga_{0.8}Sb$ ingots. The axial compositional profiles all corresponded to complete mixing of the melt. No composition variation in the radial direction was observed for ingots grown with vibration or not. For the solidification of InSb-GaSb alloys, in order to overcome the constitutional supercooling, a high temperature gradient and a low growth rate had to be used. However, it has been shown that a high temperature gradient for the solidification of InSb-GaSb could produce a fine grain structure in the resulting ingots [2]. In our experiments, a low growth rate was used. Because of the very low freezing rate, the buildup of solute ahead of the solid/melt interface might have been avoided by diffusion alone.

With the application of axial vibration of the ampoule in the VBS growth of $In_xGa_{1-x}Sb$, the number of twins was increased and the number of grain boundaries was decreased, especially in the first half of the ingot. Figure 7 shown the microstructure of $In_{0.2}Ga_{0.8}Sb$ ingots grown with and without vibration.

Figure 8 shows the variation in growth rate for $In_{0.2}Ga_{0.8}Sb$ ingots grown with and without vibration. In the first half of the ingots, the freezing rate was greater than the ampoule lowering rate. As the growth proceeded, the freezing rate decreased and was lower than the ampoule lowering rate. Near the ends of the ingots, the growth rate increased a little for ingots grown both with and without vibration. The growth rate for $In_xGa_{1-x}Sb$ seems not to be affected by axial vibration of the ampoule. Figure 9 shows the interface shape for InSb-GaSb ingots grown with vibration. Figure 10 shows how the interface changes with the fraction solidified. In the first half of an ingot, the interface seems not to have been affected by the vibration, but in the second half, vibration increased the depth of the interface. When the frequency was increased and the amplitude was decreased, the interface depth of ingots grown with vibration became close to those grown without vibration.

In order to understand the effect of vibration on solidification using VBS techniques, some InSb ingots were solidified in a VBS furnace with vibration and CID or with periodically stopping the vibration. Figure 11 is the ampoule used for this experiment. With vibration, the number of grain boundaries decreased, but the

number of twins increased. Because many twins existed in the resulting ingots, the striations caused by turning on or off the vibration or the passage of a current pulse were difficult to see. The microstructure for these InSb ingots is under examination.

Plans

1. Directionally solidify InSb with vibration to determine the details of the effect of vibration on the microstructure and interface.

2. Measure the temperature change near the interface caused by vibration.

3. Use a transparent liquid to reveal the flow pattern induced by vibration in a vertical Bridgman configuration.

References

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1, p 23 .

Table 1 Experimental conditions for the growth of $In^xGa^{1-x}Sb$ and InSb

	$In_xGa_{1-x}Sb$	InSb
Hot zone temperature ℃	800	600
Cold zone temperature ℃	480	450
Initial InSb molar fraction	0.2	
Ampoule lowering rate mm/hr.		8

Table 2 $In_{0.2}Ga_{0.8}Sb$ ingots grown with vibration

Ingot No.	Frequency (Hz)	Amplitude(mm)
GA1	no vibration	
GV1	20	0.5
GV4	20	0.1
GV5	40	0.1
GV6	60	0.05

Note: Ampoule lowering rate: 8 mm/day

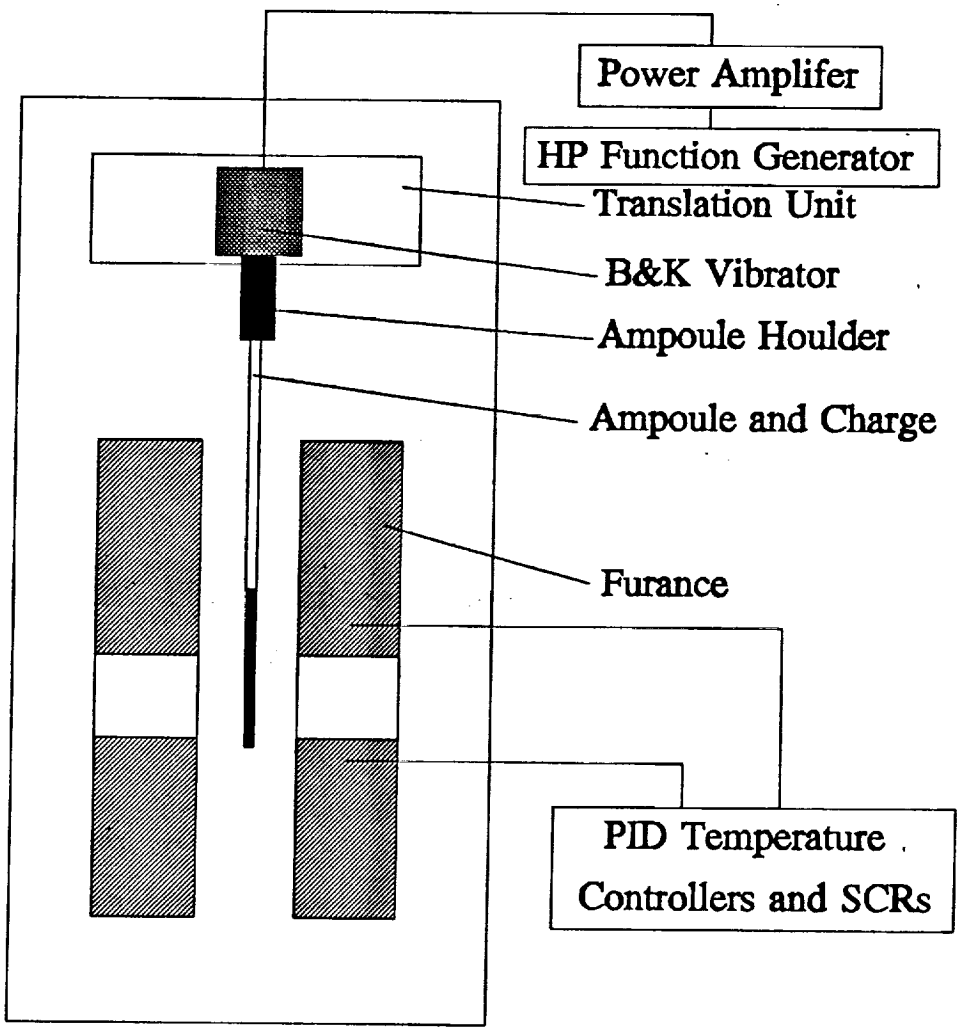


Figure 1. Experiment Setup.

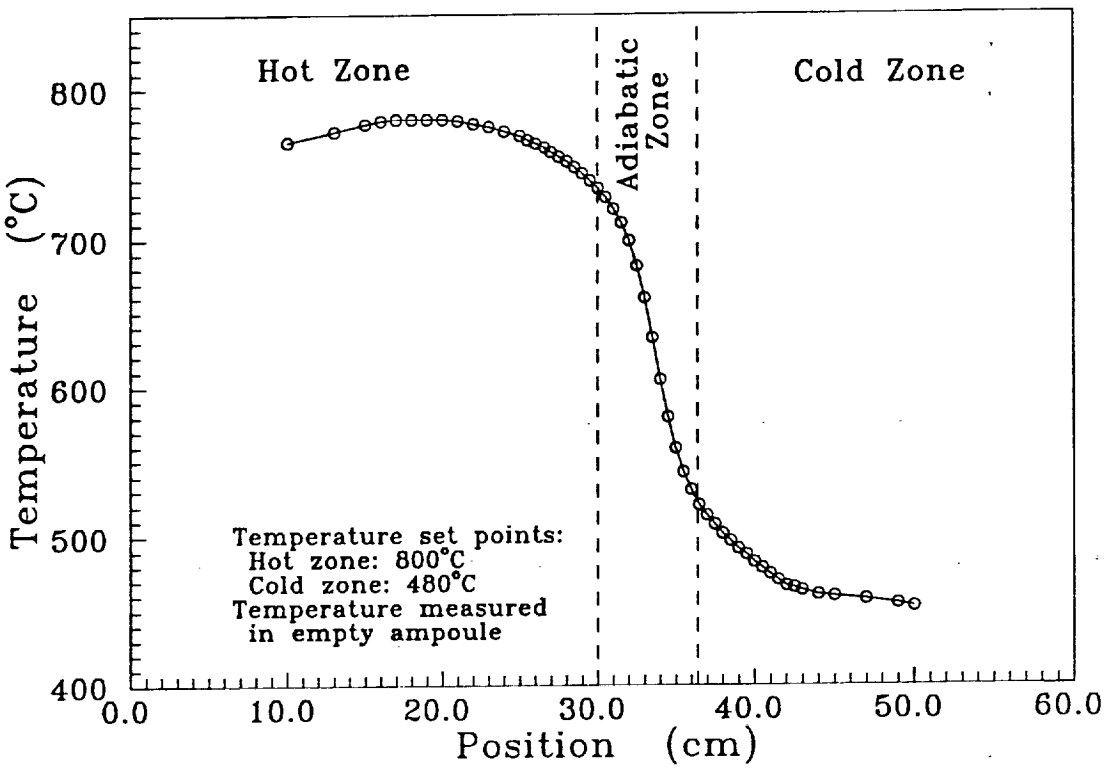


Figure 2. Temperature profile for growth of InSb-GaSb.

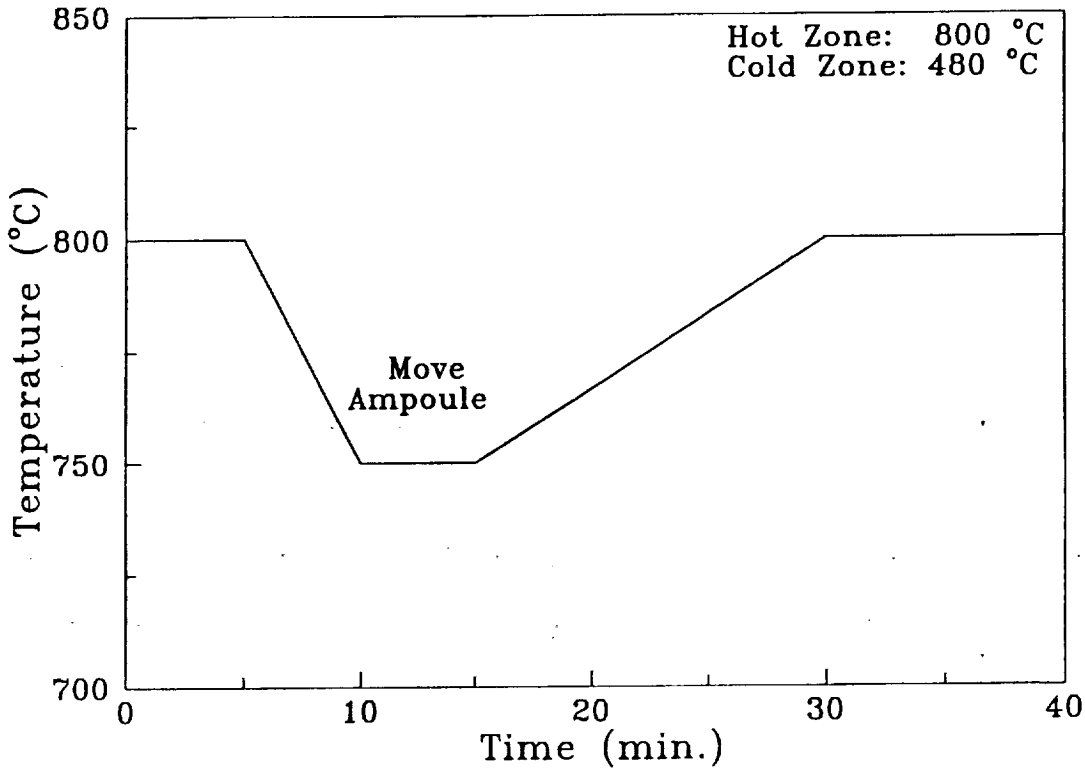
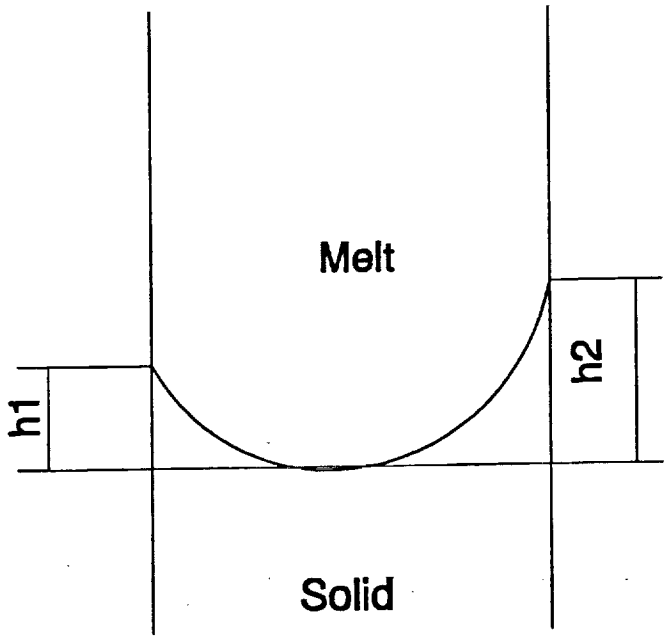


Figure 3. Quenched interface demarcation schedule.



$$h = \frac{h1 + h2}{2}$$

Figure 4. Interface depth definition.

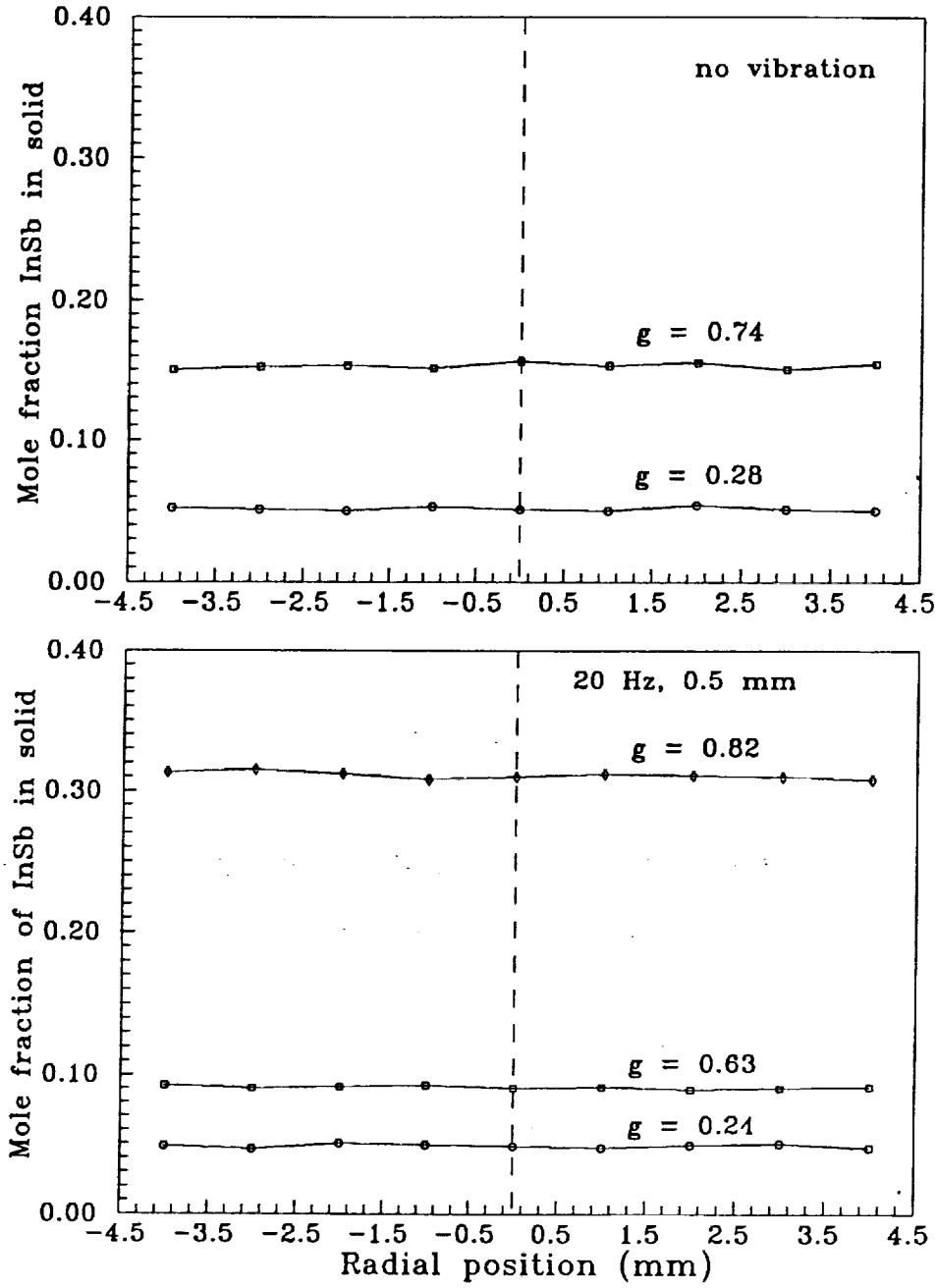


Figure 5. Radial composition profile for $In_{0.2}Ga_{0.8}Sb$.

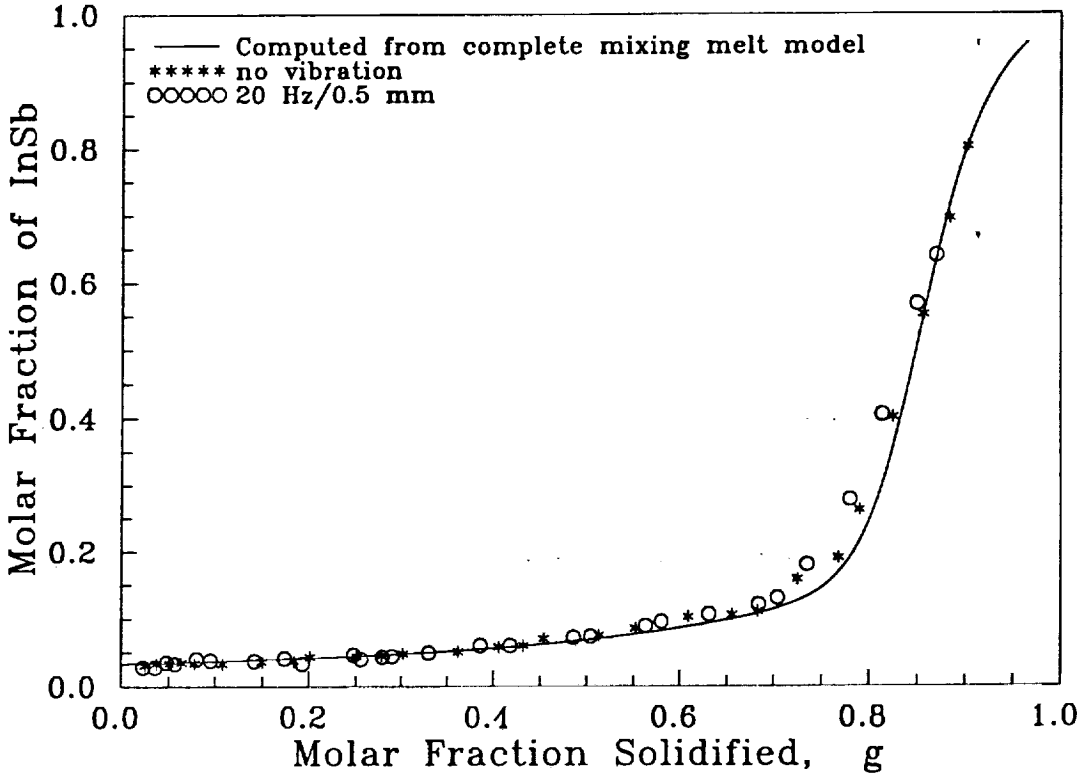


Figure 6. Axial composition profile for $In_{0.2}Ga_{0.8}Sb$.

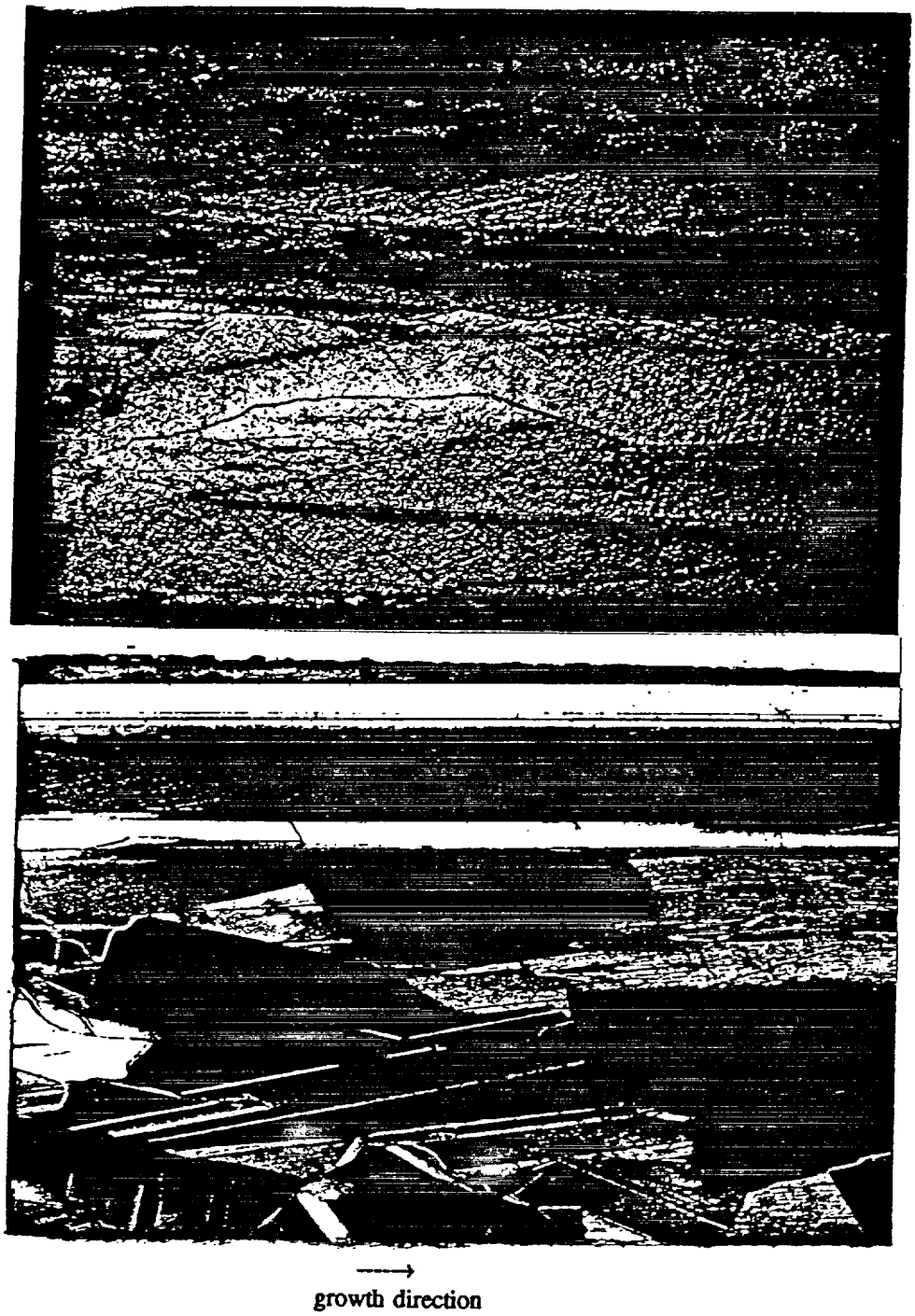


Figure 7. Microstructure for $In_{0.2}Ga_{0.8}Sb$.

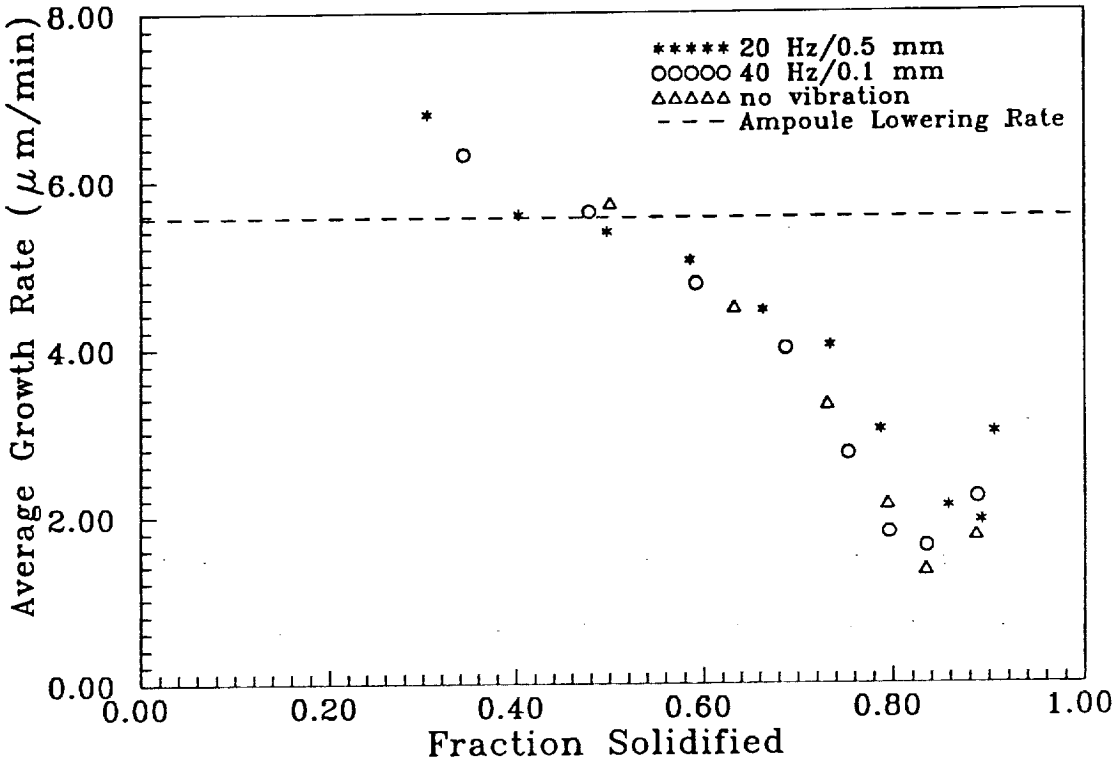
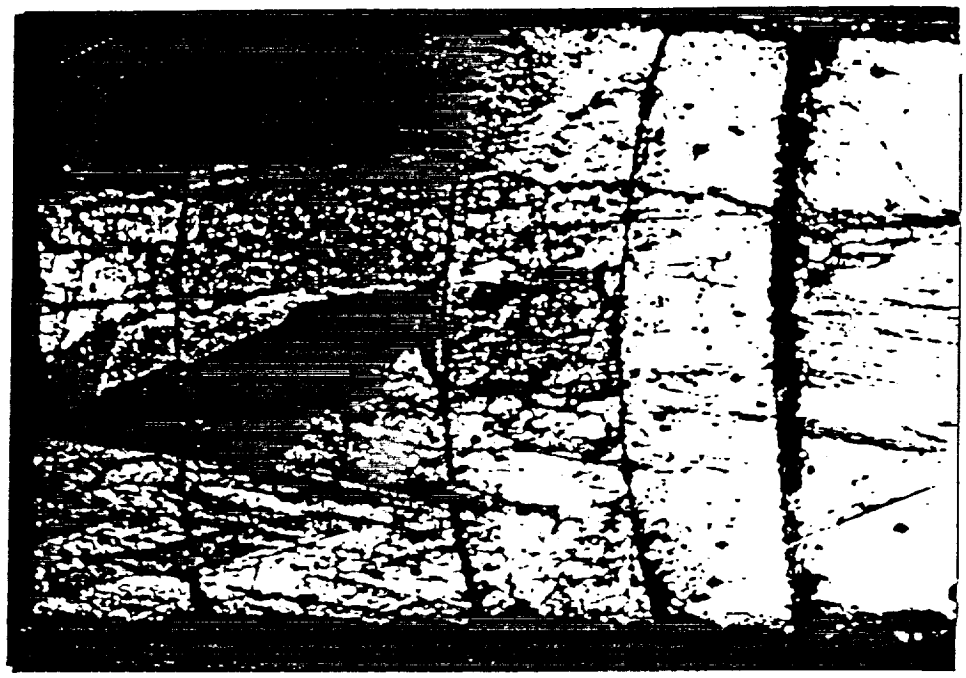


Figure 8. Freezing rate for $In_{0.2}Ga_{0.8}Sb$.



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growth direction

Figure 9. Interface shape for $In_{0.2}Ga_{0.8}Sb$.

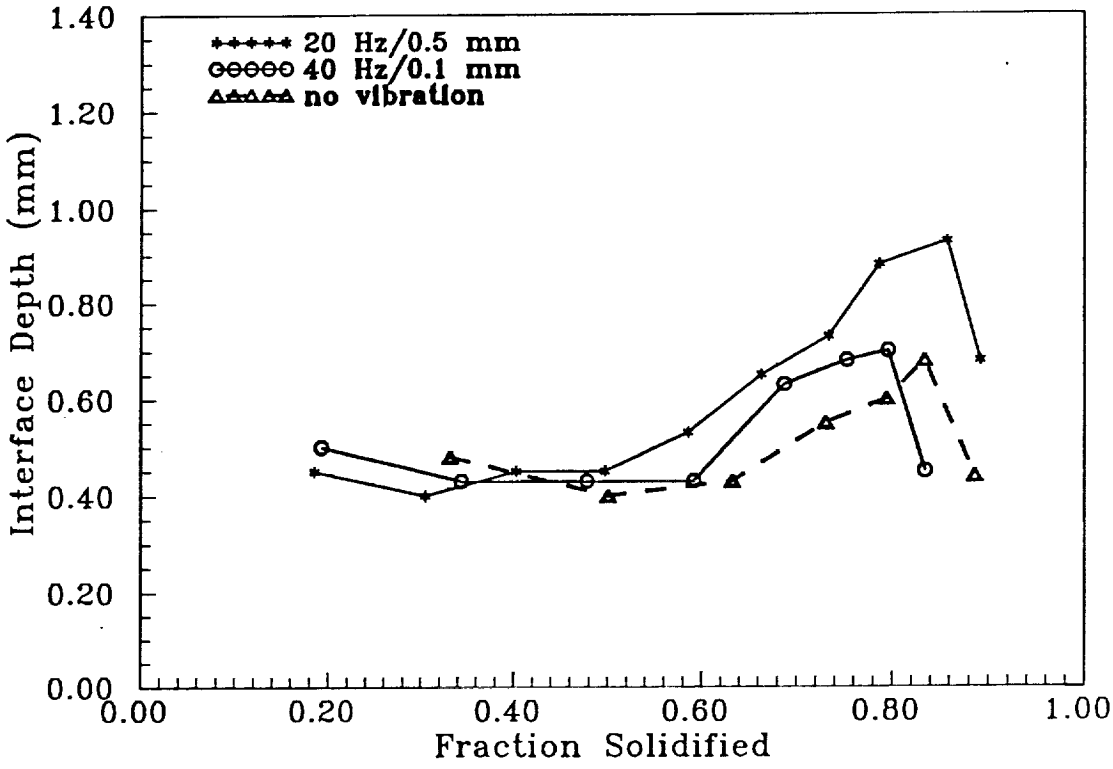

Figure 10. Interface depth variation for $In_{0.2}Ga_{0.8}Sb$.