Growth of Homogeneous $In_{1-x}Ga_xSb$ Crystals by the Graded Solute Concentration Method

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We propose a new crystal growth method for obtaining homogeneous mixed crystals from their melts in the presence of residual acceleration of the order of $10^{-3} \sim 10^{-4}$ G in microgravity. Our preliminary ground-based experiments using and capillary tubes show the validity of this method.

1. Introduction

Since the successful experiments on InSb undertaken by Walter [1] and Witt et al. [2] in the Skylab project, many researchers have attempted to grow homogeneous semiconductor crystals with low defect densities from a melt in space. However, very few satisfactory results have been obtained. This may be because insufficient consideration has been given to the residual acceleration and g-jitter in a melt, and purely diffusion-controlled mass and heat transport growth may not have been realized in these experiments.

One of the authors designed a $Pb_{1-x}Sn_xTe$ crystal growth experiment [3, 4] which was performed aboard a space shuttle as a part of the First Materials Processing Test of Japan (FMPT) and the compositional profile suggested partial mixing of the melt during crystal growth. This result agreed well with a computer simulation on convective flow due to residual acceleration. In the space shuttle, effective residual acceleration of the order of 10^{-4} G are achieved, but residual acceleration less than 10^{-5} G, preferably less than 10^{-6} G, is required for diffusion limited growth [3, 4] if we wish to obtain crystals larger than 15 mm in diameter.

Naumann reported that extreme care must be exercised in controlling transverse acceleration and gravity levels of less than 10^{-7} G are required to ensure diffusion limited growth [5]. Recently, Lehoczky and co-workers designed microgravity experiments on $Hg_{1-x}Cd_xTe$ which were undertaken during the second United States Microgravity Payload (USMP-2) mission, where special care was taken as regards residual acceleration [6, 7]. Their results also showed that transverse residual acceleration of the order of 10^{-6} G affected the liquid column and caused compositional variations. More recently, Fripp and his co-workers designed experiments on the directional solidification of a $Pb_{1-x}Sn_xTe$ melt which were carried out during the USMP-3 mission to detect the effects of residual acceleration on three different orientations with respect to growth axis [8, 9]. Their results also indicate the existence of convective mixing in the melt. Narayanan et al. reported the effect of an orientation change in residual acceleration on the compositional profile of grown crystals and the importance of controlling the orientation of residual acceleration [10].

Unmanned platforms such as EURECA offer good microgravity environments. Duffar *et al.* have reported on diffusion limited growth experiments undertaken aboard the EURECA [11]. However, in the international space station which is currently being constructed, the microgravity environment may be similar to that of a space shuttle and its order will be 10^{-4} - 10^{-5} G range because several crews always stay there and their activities combined with facility operations will generate g-jitter. Therefore, effective ways must be developed to avoid the effect of residual acceleration and g-jitter during crystal growth to obtain homogeneous high-quality crystals via experiments aboard the international space station [12, 13].

In this paper, we propose a method for growing homogeneous crystals from a melt. This method compensates for the solute loss at the growth interface due to convective mixing by a preinstalled solute profile in the feed and has a possible benefit of suppressing compositional variations due to residual acceleration in the space station. We report some preliminary results of ground-based experiments.

2. Graded solute concentration method

During the growth of such mixed crystals as $In_{1-x}Ga_xSb$, $Pb_{1-x}Sn_xTe$, and $Hg_{1-x}Cd_xTe$, the solute concentration at the solid-liquid (S/L) interface should reach C_0/k to enable homogeneous crystals to grow by the diffusion limited process, where C_0 is the original concentration of the solute in the melt and k is the segregation coefficient. If there is convective flow in the melt, the piled-up solute at the S/L interface will be transported to the remaining melt by convection and the solute concentration at the interface will be reduced. This will result in a non-uniform solute concentration along the crystal growth axis. However, if the convective flow is slow, the amount of solute transported away from the S/L interface will be small, and the solute loss caused by the convective mixing can be compensated by preinstalled solute concentration profile in the feed.

Figure 1 shows the principle of this method. When partial mixing occurs in a melt, a feed with a graded solute concentration rather than a uniform solute concentration will produce more homogeneous crystals by supplying a richer solute at the beginning of the crystal growth and a poorer solute at the end. A similar method has already been proposed by W. Weber, T. Duffar and J. J. Favier [14] for the growth of $In_{1-x}Ga_xSb$, but our method is different in one important respect. They did not try to compensate for the effect of residual acceleration in the melt but only aimed at reducing concentration variations in the initial transient region of crystals which are grown in a diffusion limited regime. Our goal was to compensate both for solute concentration variations in the initial transient region and for the solute transport loss caused by residual acceleration at the growth interface throughout the crystal growth process.

With this method we need a well-balanced initial concentration profile, a suitable period of soaking before growth and an appropriate growth rate. If the soaking period is too long, the initial solute concentration profile will be averaged because any concentration difference in a melt causes mutual diffusion, and the preinstalled concentration profile then becomes meaningless. If the growth rate is inappropriate, the rate of accumulation of the solute will too great or too small, and no homogeneous crystals will be obtained. In this paper, we examine appropriate growth conditions experimentally and test the validity of the graded solute concentration method.

3. Experimental

Preparatory experiments of the graded solute concentration method have been done for $In_{0.5}Ga_{0.5}Sb$ on the ground. We simulated microgravity conditions and grew crystals using carbon capillary crucibles with a 1.5 mm bore. This bore diameter effectively gives the crystal growth the same Grashof number as obtained with 15 mm diameter bore at 10^{-3} G. First, we examined ways to avoid constitutional supercooling. Melts contained in carbon crucibles and sealed in quartz ampoules were directionally solidified at several solidification rates in a vertical Bridgman furnace. The temperature gradient measured in the furnace tube (outside the ampoule) at around the S/L interface temperature was about 25℃/cm.
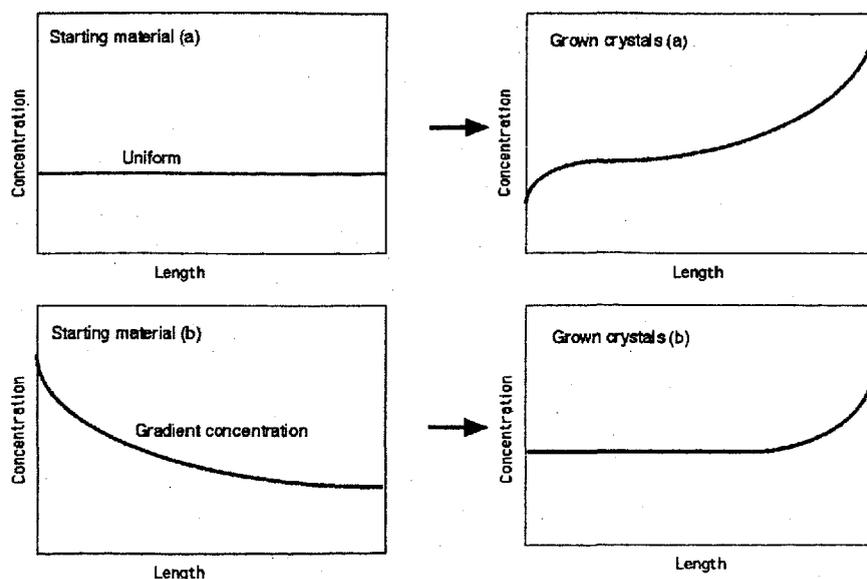
- 14 -

Fig. 1 Comparison of compositional profiles of feeds and grown crystals obtained with the Bridgman and graded solute concentration methods.
(a) Bridgman method, and (b) graded solute concentration method.

The resultant compositional profiles clearly revealed the constitutional supercooling boundary. A the temperature gradient of 25°C/cm requires a solidification rate of less than 1.7mm/h to suppress constitutional supercooling.

We carried out recrystallization using a solid ingot with a graded In concentration along its axis. We allowed the tail of the ingot with the higher In concentration to freeze first during the recrystallization in accordance with the principle of the graded solute concentration method shown in Fig. 1. In this case, the compositional profile in the original ingot compensates for the compositional variation due to partial mixing in the melt. A higher In concentration in the portion of the melt that is first to freeze results in a higher In concentration at the top of the crystal, and segregated In at the growth interface will be balanced more easily with the transport rate of In from the interface to ahead of the melt owing to the originally formed compositional profile in the melt. In our experiments, the bottom of the carbon crucible was set at the solidus temperature of $In_{0.5}Ga_{0.5}Sb$, and solidification was started. Sample translation rate was varied from 0.5 to 5 mm/h and the soaking time was chosen between 1 and 5 h.

4. Results and discussion

Figure 2 shows the In concentration profile along the growth axis for a sample solidified at a sample translation rate of 1 mm/h, and starting from a uniform $In_{0.5}Ga_{0.5}Sb$ melt composition. This compositional profile is similar to that for normal freezing of the melt. The dotted line shows the calculated profile based on the Scheil equation and the InSb-GaSb psuedobinary phase diagram. Note that the experimental data agree well with the normal freezing profile.
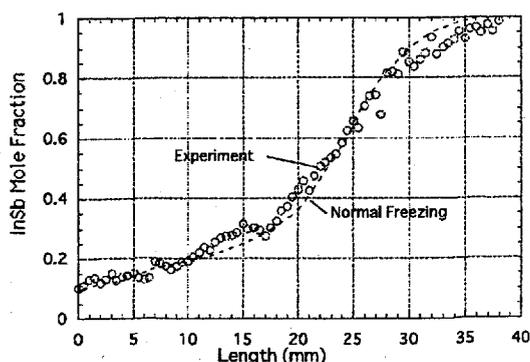

Fig. 2 In concentration profile along the growth axis for a sample solidified from a uniform melt composition and at a sample translation of 1 mm/h.

- 15 -

At higher solidification rates such as 3mm/h, the In/Ga ratios were scattered. Such scattering may be due to constitutional supercooling. Detailed experimental results on constitutional supercooling in the $In_{1-x}Ga_xAs$ system will be published elsewhere [15].

By using above prepared feeds, recrystallization of $In_{1-x}Ga_xSb$ by the graded solute concentration method was performed. As also described above, the sample translation rate and soaking period are two major factors which influence the concentration profile of recrystallized samples. Figure 3 compares the compositional profiles of recrystallized $In_{1-x}Ga_xSb$ at a sample translation rate of 1mm/h with soaking times of 1 and 5 h. For the sample with the 1 h soaking time, nearly homogeneous compositional profile is achieved from the beginning of recrystallization to a distance of about 15 mm. This shows the validity of the graded solute concentration method for obtaining homogeneous mixed crystals. The increase in the In concentration at a distance of 20 to 25 mm may originate from the diffusion boundary layer in the recrystallization process. Namely, the recrystallization rate may have been a little too fast and its rate has exceeded the InSb-GaSb interdiffusion rate, causing the solidification to move ahead of diffusion boundary layer. The high In concentration in the terminal region of the crystal growth is due to a shortening of the remaining melt length. If the recrystallization rate

and soaking time are adjusted more appropriately, we will obtain a longer homogeneous region. We beieve that a soaking time of 5 h is too long because high In concentration in the initial part of the feed is smeared out. The initial In concentration of the recrystallized sample is lower than that for a 1 h soaking time and a higher In concentration part is formed in the terminal region of the crystal growth. This is because In in the initial higher concentration part in the feed was transported toward the tail of the melt by diffusion during the soaking period.

Figure 4 shows the In concentration profile along the growth axis of a sample recrystallized at a sample translation rate of 0.5 mm/h after a soaking time of 1 h. Here, traces of the high In concentration region were only detected in the initial part of the crystal growth to a distance of 1.5 mm. With the exception of this initial part, the In concentration profile was very similar to that of normal freezing. The translation rate of 0.5 mm/h was too slow and In rejected at the growth interface as well as the initial In concentration difference in the feed was eliminated by diffusion.

Figure 5 shows the In concentration along the growth axis for a sample recrystallized at a furnace translation rate of 1.5 mm/h after a soaking time of 1 h. The initial In mole fraction was higher than 0.7 and the In concentration gradually decreased as solidification proceeded. Here, the sample translation rate was too fast and the solidification
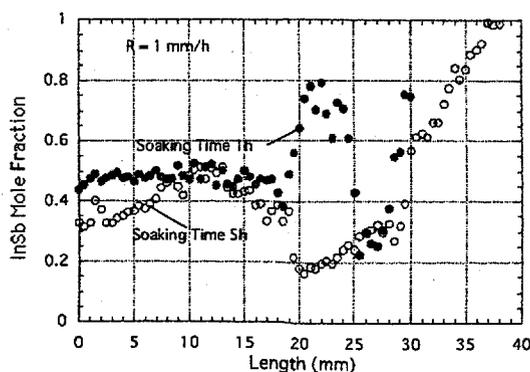
Fig.3 In concentration profiles along the growth axis for samples solidified by the graded solute concentration method at 1mm/h and different soaking times.
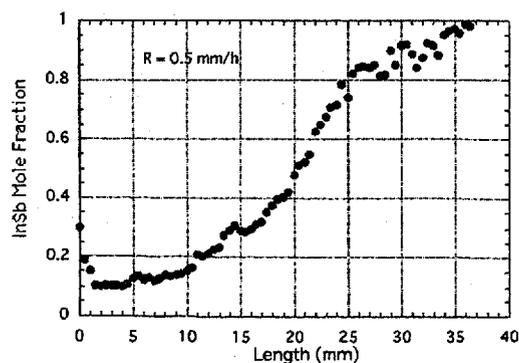
Fig.4 In concentration profiles along the growth axis for a sample solidified by the graded solute concentration method at 0.5 mm/h after a soaking time of 1 h.
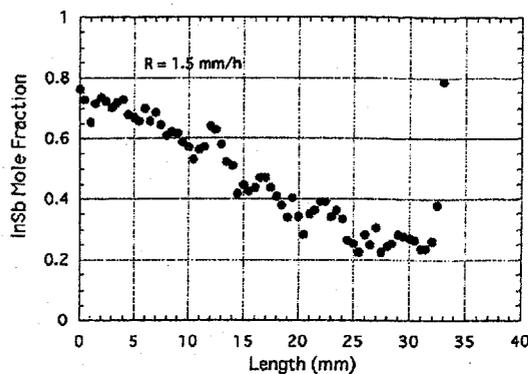
- 16 -

Fig.5 In concentration profiles along the growth axis for a sample solidified by the graded solute concentration method at 1.5 mm/h after a soaking time of 1 h.

proceeded before the In diffused into the remaining melt. Therefore, the initial In concentration profile in the feed was frozen in the regrown crystal almost unchanged.

We compared the concentration profiles for solidification at different sample translation rates, and found that 1 mm/h is the most appropriate rate among the tested rates for growing homogeneous $In_{1-x}Ga_xSb$ crystals, because the longest homogeneous region is formed at this rate with a 1 h soaking time. Based on these data, we analytically deduced the effective InSb-GaSb interdiffusion rate ahead of the S/L interface and found it to be about $2x10^9 m^2/s$. It should be noted that this value gives the interdiffusion rate at just above the solidus temperature and it is about 1/3 of that in the melt at temperatures higher than the liquidus line. At just above the solidus temperature, a mixed solid and liquid phase tends to form [16] and in such a mixed phase the interdiffusion rate should be lower than that in the melt. Therefore, we consider the obtained value to be reasonable. One dimensional numerical analysis showed that a solidification rate of about 3 mm/h is required for the growth of homogeneous mixed crystals of $In_{1-x}Ga_xAs$ [17] if the interdiffusion coefficient is assumed to be $1x10^8 m^2/s$. The effective interdiffusion coefficient just above the solidus temperature is smaller than that of the melt and this difference should be taken into consideration in the crystal growth.

5. Summary

We discuss the effects of residual acceleration on solute redistribution in space grown crystals and proposed a new growth method named the graded solute concentration method which is designed to provide more homogeneous crystals in the presence of residual acceleration. The results of preliminary experiments showed the validity of our new growth method because a 15 mm long homogeneous region was realized from the beginning of the crystal growth. At a temperature gradient of about 25°C/cm, a sample translation rate of about 1 mm/h provided the most homogeneous sample and we estimated the InSb-GaSb interdiffusion coefficient at just above the solidus temperature to be $2x10^9 m^2/s$.

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