Defense Technical Information Center Compilation Part Notice

ADP012637

TITLE: Effect of Marangoni Convection on InSb Single Crystal Growth by Horizontal Bridgman Method

DISTRIBUTION: Approved for public release, distribution unlimited

This paper is part of the following report:

TITLE: Progress in Semiconductor Materials for Optoelectronic Applications Symposium held in Boston, Massachusetts on November 26-29, 2001.

To order the complete compilation report, use: ADA405047

The component part is provided here to allow users access to individually authored sections of proceedings, annals, symposia, etc. However, the component should be considered within the context of the overall compilation report and not as a stand-alone technical report.

The following component part numbers comprise the compilation report:
ADP012585 thru ADP012685

Mat. Res. Soc. Symp. Proc. Vol. 692 © 2002 Materials Research Society H8.6

Effect of Marangoni Convection on InSb Single Crystal Growth by Horizontal Bridgman Method

K. Kodera[1], A. Kinoshita[1], K. Arafune[2], Y. Nakae[1], and A. Hirata[1]
[1] Department of Chemical Engineering, Waseda University,
Okubo 3-4-1, Shinjuku-ku, Tokyo, 169-8555, Japan
[2] Research Institute of Electronics, Shizuoka Univ., Hamamatsu, Shizuoka 432, JAPAN

ABSTRACT

It is necessary to clarify the effect of Marangoni convection on single crystal growth from a melt in order to improve the quality of the grown crystal. Particularly, the deviation of crystal-melt (C-M) interface from a planar shape is a major problem because it may deteriorate the quality of the grown crystal. In this paper, we investigated the effect of thermal and solutal Marangoni convection on C-M interface shape in an In-Sb binary system by the horizontal Bridgman (HB) method. The C-M interface concavity strongly depends on the cooling rate and the temperature gradient under uniform concentration distribution conditions in the melt. A large concavity was observed at low cooling rates and high temperature gradient conditions. The concavity was found to be caused by thermal Marangoni convection, by taking Péclet number into account. Then, we varied the composition of the In-Sb binary system to induce solutal Marangoni convection intentionally. The C-M interface was kept planar in case solutal Marangoni convection occurred in the direction opposite to the thermal one. Therefore, we believe that the utilization of solutal Marangoni convection will be a new control technique to make the C-M interface planar for the HB system. From these results, it was clarified that Marangoni convection plays a significant role in the HB crystal growth system.

INTRODUCTION

At present, most of the semiconductor bulk crystals are grown by melt growth methods such as the Czochralski (CZ) or the horizontal Bridgman (HB) method. During crystal growth by these methods, convection in melt affects the quality of the grown crystals. Therefore, it is necessary to clarify the mechanism of convection in melt and to control the convection to improve the quality of the crystal. The convection can be divided into buoyancy convection and Marangoni convection. The driving force of the former is the buoyancy difference in the melt, and that of the latter is the surface tension difference on the free surface. The convection can also be divided into thermal and solutal convection because those driving forces vary with temperature and concentration. Particularly, thermal buoyancy convection has been extensively investigated since as early as the beginning of the 20th century [1]. On the other hand, the importance of Marangoni convection, which has nothing to do with gravity, was recognized after semiconductor crystal growth experiments were conducted under microgravity conditions in the 1980s [2]. Since then, Marangoni convection has been investigated by many researchers [3,4].

Regarding solutal convection, although solutal buoyancy convection has been studied as a double diffusive problem, solutal Marangoni convection had not been studied so far. Therefore, we performed some experiments to measure surface velocities caused by buoyancy convection and Marangoni convection using a rectangular boat with a free surface. Consequently, we found that the surface velocities of solutal Marangoni convection are approximately 3-5 times higher than those of thermal Marangoni convection [5]. Moreover, in the case of coexistence of thermal and solutal Marangoni convection, solutal Marangoni convection was found to be dominant in the surface flow, and the flow direction could be opposite to that without solutal convection [6]. Also, we carried out parabolic flight experiments and found that Marangoni convection is dominant in the surface flow in case both buoyancy convection and Marangoni convection coexist [6]. From these results, we demonstrated that Marangoni convection, especially solutal Marangoni convection, is significant in a rectangular boat such as that used in the HB method. As one effect of Marangoni convection on the grown crystals, the change of C-M interface shape is often discussed. The deviation of the C-M interface shape from a planar one is a major problem because it is assumed to lower the quality of the grown crystals. Using the HB method, Lan et al. clarified numerically [7] and experimentally [8] that the effect of Marangoni convection on C-M interface shape is significant.

In this study, we performed InSb crystal growth experiments by the HB method to investigate the effects of thermal and solutal Marangoni convection on C-M interface shape. We varied the composition of the In-Sb binary system to induce solutal Marangoni convection intentionally in addition to thermal Marangoni convection. Based on the results, we suggested a simple way of controlling C-M interface shape.

EXPERIMENT

Concept of experiment

First, we discuss the interaction between thermal and solutal Marangoni convection. As described in the Introduction, Marangoni convection is induced by surface tension difference due to the difference of temperature or concentration on a free surface. In our previous study [6], it was clarified that the flow pattern of Marangoni convection could be divided into three cases as follows. Here, x denotes the composition of Sb in the In-Sb binary system ($In_{1-x}Sb_x$).

(a) Normal case (x=0.5)

In this case, there is no concentration difference in the melt. Flow of thermal Marangoni convection is induced in the direction shown in figure 1(a). This is because surface tension σ near the C-M interface is larger than that at the bulk of the melt.

(b) Acceleration case ($0<x<0.5$)

Thermal Marangoni convection is induced in the same direction as (a).When crystal growth proceeds, concentration of Indium C_{In} near the C-M interface becomes higher than that at the bulk of the melt. Because it is known that σ_{In} is larger than σ_{Sb}, surface tension near the C-M interface is larger than that at the bulk of the melt. This causes solutal Marangoni convection. Therefore, the flow direction of solutal convection is the same as that of thermal Marangoni convection.

(c) Deceleration case ($0.5<x<0.68$)

On the other hand, because C_{In} near the C-M interface becomes lower than that at the bulk of the melt, surface tension at the bulk of the melt becomes larger than that near the C-M interface. Therefore, the flow of solutal Marangoni convection is induced in the direction opposite to that of thermal Marangoni convection. Because it was clear that solutal Marangoni convection is stronger than thermal Marangoni convection [5], the flow direction becomes opposite to that without considering solutal Marangoni convection.

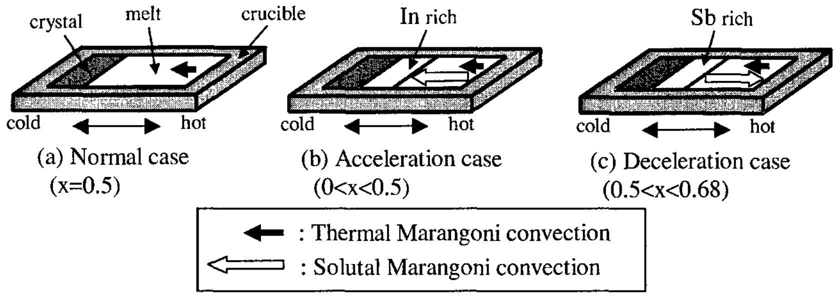

Figure 1. Flow pattern by interaction between thermal and solutal Marangoni convection

Experimental procedure

To avoid contamination and formation of metal oxide film on the free surface of the melt, special precautions were taken. In preparing the test sample, $In_{1-x}Sb_x$, In and Sb (5N, manufactured by Dowa Mining) were mixed at the desired ratio, and the mixture was dissolved and quenched in an oxygen reducing atmosphere (Ar97%+$H_2$3%). Then, chemical etching of the test sample was carried out. Moreover, a carbon crucible was baked for degassing. Figure 2 shows the cross section of the carbon crucible. The test sample was set in the reservoir tank, and InSb, which has a length of approximately 10mm, was also set at the cold side of the observation part as a seed crystal. After heating the crucible and the reservoir tank, the melted sample flowed into the observation part through a small hole and contacted with the seed crystal. The small hole prevents efflux of the remaining metal oxides in the sample. The experimental system is shown in figure 3. The temperatures of the hot side, T_H, the cold side, T_C, and the middle of the crucible, T_M were controlled by PID temperature controllers and power controllers. The temperature difference between T_H and T_C, and cooling rates of T_H, T_M, and T_C were kept constant as shown in table 1. To reduce buoyancy convection, we used a shallow crucible. The length, width and depth of the cavity of the crucible were 48, 10, and 5 mm, respectively. The test sample was solidified unidirectionally in the crucible. C-M interface shape was observed by means of a 3-CCD video camera. C-M interface shape was evaluated in terms of the degree of concavity (figure 4).

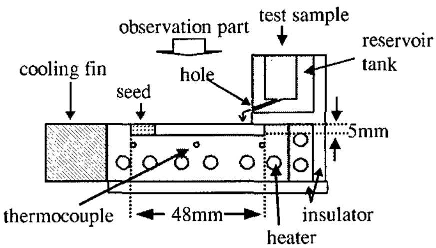

Figure 2. Cross section of the carbon crucible

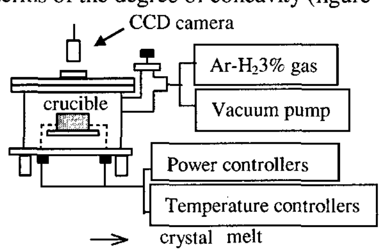

Figure 3. Experimental system

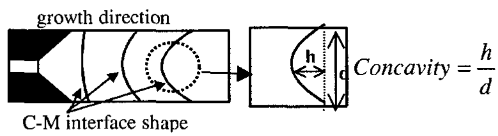

Figure 4. Top view of C-M interface shape

RESULTS AND DISCUSSION

We varied the control parameters such as cooling rate, temperature gradient, and composition of In-Sb in the experiments. The experimental conditions are shown in table 1. Figure 5 shows concavity as a function of L_C/L_0 at various cooling rates with the same temperature gradient of 14.1°C/cm. Here, L_C and L_0 denote the length of the crystal during growth, and the total crystal length after growth, respectively. Concavity increased as the growth proceeded, and then saturated at an L_C/L_0 of 0.5. Moreover, the C-M interface concavity obtained after the growth at low cooling rates was larger than that at high cooling rates. This is because long-term exposure to thermal Marangoni convection at low cooling rates resulted in the increase of the erosion of the C-M interface. Figure 6 shows concavity as a function of temperature gradient. The temperature gradient was varied from 8.4 to 14.1°C /cm at the same cooling rate of –5°C/h. The concavity was found to depend strongly on the temperature gradient. Although in figure 5, the concavity under the temperature gradient of –5°C/h was approximately 0.55, the concavity was kept 0 at 8.4°C/cm even if the cooling rate was –5°C/h in figure 6. The low temperature gradient indicates that thermal Marangoni convection is weak. From figures 5 and 6, there seems to be a strong correlation between driving force of Marangoni convection and C-M interface shape.

Table 1. Experimental conditions

Run No.	Cooling rate [°C/h]	Temperature gradient [°C/cm]	Composition x of In1-xSbx
1	-5	14.1	0.5
2	-11.7	14.1	0.5
3	-16.7	14.1	0.5
4	-19.7	14.1	0.5
5	-5	11.9	0.5
6	-5	8.4	0.5
7	-16.7	14.1	0.4
8	-16.7	14.1	0.6

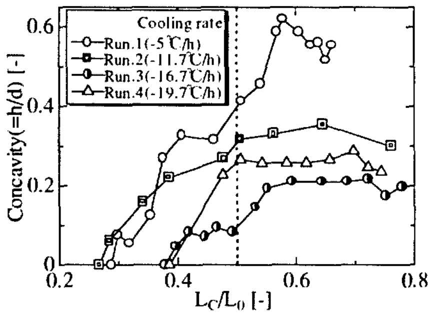

Figure 5. Concavity as a function of L_C/L_0. The dashed line indicates the saturation point of an increase of concavity.

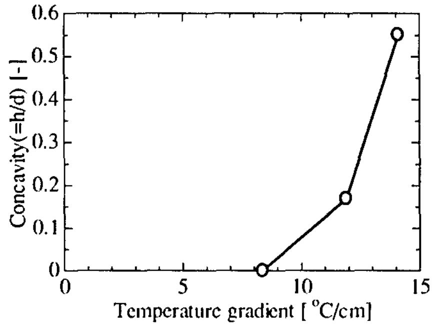

Figure 6. Concavity as a function of temperature gradient

In order to confirm this correlation, we determined Marangoni number (Ma) from temperature profiles and C-M interface position. Ma represents the driving force of Marangoni convection. Ma is defined by eq.(1).

$$Ma = \frac{\left|\partial\sigma/\partial T\right| \Delta T L_m}{\mu \nu} \qquad \text{eq.(1)}$$

In our previous study [9], we found a relationship between Ma, Pr, and Re, as shown in eq.(2).

$$\mathrm{Re} = 0.28 \cdot (Ma\,\mathrm{Pr}^{-1/2})^{2/3} \quad \text{eq.(2)}$$

Here, Re (Reynolds number) and Pr (Prandtl number) represent flow state of fluids and heat transport phenomena, respectively. Pr is defined by eq.(3).

$$\mathrm{Pr} = \frac{\nu}{\alpha} \quad \text{eq.(3)}$$

From eqs.(1), (2), and (3), we were able to estimate Re. After estimation of Re, we determined Péclet number (Pe) using eq.(4).

$$Pe = \mathrm{Pr} \cdot \mathrm{Re} \quad \text{eq.(4)}$$

Pe indicates whether convection or conduction dominates the heat transport phenomena. Therefore, Pe indicates the effect of Marangoni convection on the heat transfer through the C-M interface.

Figure 7 shows the calculated Pe as a function of L_C/L_0. Pe decreased gradually as growth proceeded up to an L_C/L_0 of 0.5, and then abruptly decreased thereafter. In other words, the effect of thermal Marangoni convection on the heat transfer decreased abruptly at L_C/L_0 =0.5. This value agrees with the saturation point of the increase of concavity shown in figure 5. From these results, it was clarified that concavity is mainly due to Marangoni convection.

As a simple way to keep C-M interface planar, we suggest that the Marangoni convection be restrained. The flow direction may be opposite to that of the normal case in the presence of solutal Marangoni convection, as reported in our previous study [6]. Therefore, we varied the composition of the In-Sb binary system to induce solutal Marangoni convection intentionally in addition to thermal Marangoni convection. Figure 8 shows the concavity as a function of L_C/L_0. Although the increase of concavity in the case of x=0.4 was larger than that in the case of x=0.5, increase in the case of x=0.6 was much smaller than that in the case of x=0.5. This is because flow velocity was accelerated in the case of x=0.4 and decelerated in the case of x=0.6. Moreover, we could keep the C-M interface planar in the case of x=0.6. From these results, we found that we can keep a planar interface by inducing solutal Marangoni convection intentionally in the direction opposite to that of thermal Marangoni convection.

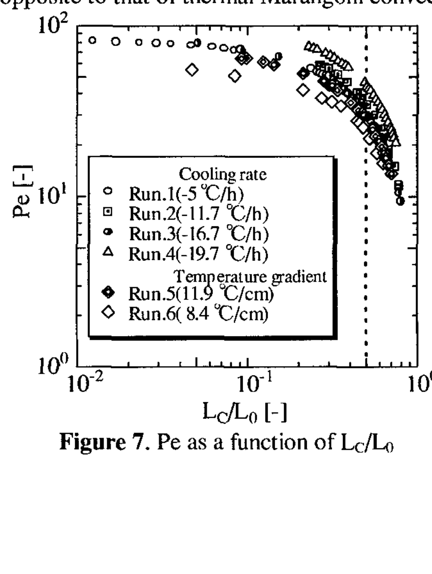

Figure 7. Pe as a function of L_C/L_0

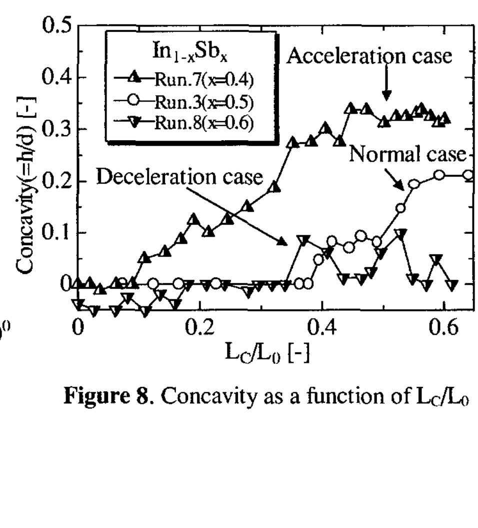

Figure 8. Concavity as a function of L_C/L_0

CONCLUSIONS

We investigated the effect of thermal and solutal Marangoni convection on crystal-melt (C-M) interface shape in the In-Sb binary system by the horizontal Bridgman (HB) method. The C-M interface concavity strongly depends on the cooling rate and the temperature gradient under uniform concentration distribution conditions in the melt. A large concavity was observed at low cooling rates and high temperature gradient conditions. The concavity was found to be due to thermal Marangoni convection, taking Péclet number into account. We varied the composition of the In-Sb binary system to induce solutal Marangoni convection intentionally. The C-M interface remained planar when solutal Marangoni convection occurred in the direction opposite to the thermal one. Therefore, we believe that the utilization of solutal Marangoni convection will be a new technique to control the planarity of the C-M interface in the HB system. From these results, it was clarified that Marangoni convection plays a significant role in the HB crystal growth system.

NOMENCLATURE

C_{In}	: concentration of Indium [at%]
L_0	: total length of crystal [m]
L_C	: length of crystal during growth [m]
L_m	: length of melt [m]
Ma	: Marangoni number [-]
Pe	: Péclet number [-]
Pr	: Prandtl number [-]
Re	: Reynolds number [-]
T	: temperature [°C]
T_C	: temperature at the cold side [°C]
T_H	: temperature at the hot side [°C]
T_M	: temperature at the middle of the crucible [°C]
h	: deviation of crystal-melt interface [m]
d	: width of melt [m]

Greek

ΔT	: temperature difference [K]
α	: heat diffusion coefficient [m^2s^{-1}]
ν	: kinematic viscosity [m^2s^{-1}]
μ	: viscosity [$kgm^{-1}s^{-1}$]
ρ	: density [kgm^{-3}]
σ	: surface tension [kgs^{-2}]
σ_{In}	: surface tension of Indium [kgs^{-2}]
σ_{Sb}	: surface tension of Antimony [kgs^{-2}]
$\partial\sigma/\partial T$	: temperature gradient of surface tension [$kgs^{-2}K^{-1}$]

REFERENCES

1. Rayleigh, Lord, *Phil. Mag.* **32**, 529-546 (1916)
2. A. Eyer, H. Leist, and R. Nitsche, *J. Crystal Growth*, **71**, 173-182 (1985)
3. D. Schwabe, and J. Metzger, *J. Crystal Growth*, **97**, 23-33 (1989)
4. Y. L. Yao, F. Liu, and W. R. Hu, *Int. J. Heat Mass Transfer*, **39**, 2539-2544 (1996)
5. K. Arafune, and A. Hirata, *J. Crystal Growth* ,**197**, 811-817 (1999)
6. K. Arafune, K. Yamamoto, and A. Hirata, *Int. J. Heat Mass Transfer*, **44**(13), 2405-2411 (2001)
7. M. C. Liang, C. W. Lan, *J. Crystal Growth*, **180**, 587-596 (1997)
8. C. W. Lan, M.C. Su, M.C. Liang, *J. Crystal Growth* **208**, 717-725 (2000)
9. K. Arafune, M. Sugiura, and A. Hirata, J. *Chem. Eng. Japan*, **32**, 104-109 (1999)