Growth of undoped and Te doped InSb crystals by vertical directional solidification technique

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Abstract. We have successfully grown high mobility undoped and Te doped InSb crystals of size 10–12 mm dia. and 60 mm length under inert argon atmosphere in closed quartz ampoules, by vertical directional solidification (VDS) technique. The crystals showed predominantly (220) orientation along the growth axis. The surface defects, such as voids were reduced drastically by selecting proper lowering rate, rotational speed and cone angle of the ampoule. The high mobility and quality crystals were obtained with the ampoule conical angle less than 20°, lowering rate 5 mm/h, and rotational speed 10 rpm.

Keywords. InSb crystals; directional solidification; quartz ampoule; cone angle; Hall measurement; inert atmosphere.

1. Introduction

InSb crystals are useful for infrared detectors in 3–5 μm wavelength range (Chen *et al* 1992). This material is also of increasing interest for large area detector arrays (Rayners *et al* 1993), high speed devices (Asauskas 1980) and optoelectronics devices (Baranski 1990). For epitaxial growth of InAsSb on InSb (Eagen *et al* 1994), substrates of high quality are required (Ohaski 1986; Lee *et al* 1993; Michel *et al* 1994). There have been reports of InSb bulk crystal growth using methods such as Czochralski (Witt *et al* 1968; Lin and Kou 1995), Bridgman (Kim 1978; Mulski and Neumann 1982), zone refining (Garanuet *et al* 1995), vertical gradient (Strauss 1959; Potard 1981; Jung *et al* 1991) and centrifuge (Weber *et al* 1990; Derabail and Wilcox 1992; Zhou *et al* 1993). We have undertaken the growth of undoped and doped bulk InSb crystals by vertical directional solidification (VDS) technique in conical quartz ampoule without using any seed. The VDS is a simple and suitable method for obtaining good quality InSb single crystals. To reduce the Sb loss related problem, the growth is done in closed ampoule and under optimization of inert atmosphere of argon. This paper reports the details of experiments carried out under various growth conditions such as cone angle of ampoule, lowering rate, rotation speed and inert gas for high quality single crystal growth without seed. As grown crystals are *p*-type while Te has been used for growing *n*-type doped crystals.

2. Experimental

2.1 Crystal growth

We performed the growth of InSb crystals in a vertical growth system by directional solidification (VDS) (Gadkari *et al* 1994). The system consists (see figure 1) of a vertical single zone resistance furnace. Quartz tube of 10 cm dia. and 100 cm length was used as the growth chamber. The tube was closed at both ends by end caps with Wilson seal arrangements for gas inlet and outlet. Water circulation was used for cooling the seals. Thermocouple (Cr–Al) was inserted from the bottom end of quartz tube for measurement of temperature inside the growth chamber. High purity In (6 N), Sb (6 N) and Te (6 N) were used as source materials. 9.7 g In and 10.3 g Sb in stoichiometric composition were filled in quartz ampoule of 10–12 mm in dia. and 100 mm in length with conical end on one side. Ampoules of various cone angles ranging from 15–70° were used in the growth experiments. Initially, growth was tried in open ampoule with flowing N_2 atmosphere. However, the resulting crystal was of poor quality. Subsequently growth was done in sealed ampoule and two variations of the procedure were used. In one case, the ampoule was sealed in vacuum and in the second case the ampoule was backfilled with argon before sealing. Growth of doped crystals was done by mixing Te dopant in the charge before sealing the ampoule for the directional solidification. Ampoule can be moved vertically as well as rotated in the growth chamber. The InSb charge was melted (see figure 2) by keeping the ampoule in the

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constant temperature of the furnace by raising the temperature to 800°C. This temperature was maintained for 10 h for synthesis and homogeneous mixing of the source materials. For the growth, the ampoule was lowered to the gradient zone of the furnace where the temperature was in the range 575–650°C and kept in this zone for 10 h for prolonged heating for thermal stabilization in the melt prior to starting the growth. The growth was done by further lowering the ampoule in the gradient zone. Different lowering rates in the range 5–10 mm/h were used. Further the rotation speed was varied in the range 10–30 rpm. After completion of the growth, the InSb ingot was annealed at a constant temperature of 200°C for about 18–24 h prior to its removal from the growth chamber. The typical growth profile is shown in figure 2. In good quality growth, the ingot can be removed from the quartz ampoule easily showing that the melt does not stick to the wall of the ampoule. As such the diameter of the grown ingot is slightly smaller than the internal diameter of the ampoule.

2.2 Sample characterization

Substrates of thickness about 500 µm were cut perpendicular to the growth axis. These wafers were cleaned and lapped by 5 µm carborundum powder. Further polishing of the wafers was done mechanically by using 0.3 and 0.05 µm alumina abrasive to mirror finish. We tried also chemi-mechanical polishing using 5% bromine-methanol solution and similar results were observed. Wafers were cleaned in warm TCE, acetone and methanol of electronic grade. These wafers were then used for various characterizations e.g. (i) the X-ray diffraction

for orientation determination and XRD patterns were recorded with step angle 0.02° and 0.5 s step time on JEOL JDX-8030 for 35 KV and 25 mA, (ii) growth morphology, and (iii) electrical transport properties by Hall measurements (Van der Pauw 1958; Look 1990). The EDAX measurements were used to identify the composition in the defect regions.

3. Results and discussion

3.1 Unsealed ampoule

Early growth experiments were performed in unsealed ampoules in flowing N₂. Ingots were grown by using ampoules with 4 different cone angles from 50°–70°. In all cases, growth showed severe distribution of voids on the surfaces. The XRD pattern of the InSb substrates cut from these ingots showed large FWHM for XRD peaks (see table I), indicating large heterogeneities and grain boundaries which may be due to polycrystalline growth.

3.2 Sealed ampoule

Since the open ampoule growth was of poor quality, the growths were carried out in ampoule with cone angle less than 30°. The source materials In and Sb inside ampoules were alternately evacuated and flushed with argon 10 times prior to vacuum sealing (10⁻⁵ torr), and growth was carried out at lowering rate 10 mm/h and rotation speed 30 rpm. Ingots were void free, 10 mm dia. and 60 mm length (figure 3). XRD measurements

Figure 1. A. Schematic diagram of the growth system and B. temperature profile of the furnace.

Figure 2. The crystal growth temperature versus time graph after optimizing growth conditions. The temperature is specified at the conical tip of the ampoule.

Table 1. Cone angles of ampoules and Hall measurements at 300 K.

Growth no.	Crystal	Ampoule ambient	Cone angle	Semicond. type	Mobility (cm ² /V.sec)	RH (cm ³ /coulomb)	FWHM (220) (arcsec)
3	InSb p3	A	64	p	—	—	1140
4	InSb p4	A	60	p	—	—	1290
5	InSb p5	A	50	p	—	—	1780
6	InSb p6	A	54	p	—	—	1740
7	InSb p7	B	30	p	—	—	1680
8	InSb p-1	C	25	p	3900	-39.6	580
9	InSb p-R	C	22	p	3500	-41.5	560
10	InSb n-1	C	25	n	3400	-0.35	482
11	InSb n-R	C	25	n	3145	-0.49	455
12	InSb p2-4	D	18	p	42000	-143.0	285
13	InSb n2-4	D	16	n	27000	-10.6	260
12	InSb p2-12	D	18	p	55000	-165	255
13	InSb n2-12	D	16	n	25600	-11.5	235

A, Open ampoule flowing N₂ ; B, ampoule closed in vacuum (10⁻⁵ torr) without argon flushing; C, ampoule prior to vacuum sealing (10⁻⁵ torr) was flushed by argon; D, ampoule closed under argon pressure (100 torr). Measurements were taken on two samples of growth nos 12 and 13 from different places.

Figure 3. The growth of undoped ingots performed by sealing the ampoules in vacuum (growth nos 8-9).

from powder of the as grown material showed agreement with ASTM data and JCPDS card no. 6-208 (Int. diff.

Figure 4. a. XRD pattern of the powder crushed from grown InSb ingots and b. XRD pattern of a substrate cut perpendicular to the growth axis.

(data 1994) (see figure 4a). Wafers prepared from the ingots showed prominent reflection for (220) orientation (see figure 4b). Sharp peaks of the XRD (table 1) showed improved crystallinity of the InSb ingots. Etching of polished wafers revealed regions rich in Sb as probed by EDAX. The etching of the undoped InSb substrate showed growth morphology such as conical etch pits, eutectic microstructures and ribs. While, heavily Te doped

Figure 5. Magnified photograph of Te-doped ingots with substrates (growth no. 13).

substrates (Gadkari *et al* 1995) showed absence of eutectic features but defects like striations, band formation, microcracks and precipitate were observed.

Hall–Van der Pauw measurements, the undoped and Te-doped samples at 300 K showed low mobility of $3900 \text{ cm}^2/\text{V}\cdot\text{sec}$ and $3400 \text{ cm}^2/\text{V}\cdot\text{sec}$ respectively. From these observations we concluded that the crystals contained excessive defects. In order to overcome this problem, we did next series of experiments in ampoules closed under Ar pressure.

3.3 Sealed ampoules with inert atmosphere

In this modified procedure, the source materials were at first evacuated and flushed with argon 10 times. Finally, the ampoule was backfilled with argon at 100 torr and sealed. All the ampoules used in the experiments had cone angle less than 20° , and growth was done at lowering rate of 5 mm/h and rotational speed 10 rpm . As grown ingots were free from voids (figure 5) with smooth surface. The ingots came out easily from the ampoules which showed that the melt did not stick to

the walls of the ampoules. Ingots surface were observed to be more shiny in conical region than the cylindrical regions as seen in figure 5.

X-ray diffraction measurements on the wafers cut from these ingots showed prominent (220) reflection and excellent agreement with the ASM data mentioned earlier. Further as seen from table 1, the FWHM had improved further as compared to the growth done in the evacuated ampoule. Improvement in the quality of the crystal grown under argon atmosphere was also seen from the Hall measurements. Undoped crystals were *p*-type with mobility reaching a value $55000 \text{ cm}^2/\text{V}\cdot\text{sec}$ at room temperature. The low (20 K) temperature Hall measurement on this sample showed doping concentration ($\sim 1 \times 10^{16} \text{ cm}^{-3}$) which shows reduction in the background defects by using this procedure. The Te-doped materials are also of better quality and show significant increase in mobility from $26000 \text{ cm}^2/\text{V}\cdot\text{sec}$ at room temperature to $29000 \text{ cm}^2/\text{V}\cdot\text{sec}$ at 40 K with the donor concentration of $6 \times 10^{17} \text{ cm}^{-3}$.

4. Conclusions

Nearly perfect single bulk crystal of InSb of high quality and degree of crystallinity have been grown from the melt by the VDS technique. Our experiments show the following.

(I) The wafers cut from the ingots show prominent (220) reflection indicating growth of nearly single crystal without seed.

(II) Maintaining inert argon atmosphere in the closed quartz ampoule is very crucial for growing high mobility InSb crystals. Other optimized growth parameters are (i) ampoule lowering rate 5 mm/h , (ii) rotation speed 10 rpm and (iii) conical angle less than 20° . Good quality ingots of 10–12 mm dia., 60 mm in length and 20 g weight have been grown by VDS technique in closed quartz ampoule.

(III) Undoped InSb is *p*-type. A very high Hall mobility $\sim 55000 \text{ cm}^2/\text{V}\cdot\text{sec}$ has been achieved in the optimized growth.

(IV) Te-doped *n*-type material with doping concentration $6 \times 10^{17} \text{ cm}^{-3}$ and Hall mobility $26000 \text{ cm}^2/\text{V}\cdot\text{sec}$ at 300 K have been grown.

These results indicate the effectiveness of vertical directional solidification method for the growth of high quality, uniform internal structure and high mobility InSb bulk crystals.

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References

- Asauskas R, Dobro Volskis and Krotkus A 1980 *Sov. Phys. Semicond.* **14** 1377
- Baranski P I, Gorodnichi O P and Shevchenko V V 1990 *Infrared Phys.* **30** 59
- Byueng-Su Yoo, Mark A McKee, Sang -Gi Kim and El-Hang Lee 1993 *Solid State Commun.* **88** 447
- Chen L P, Lou J J, Liu T H, Pang Y M and Yang S J 1992 *Solid State Electron.* **35** 1081
- Derabail R and Wilcox W R 1992 *J. Cryst. Growth* **119** 98
- Eagen R J *et al* 1994 *Semicond. Sci. Technol.* **9** 1591
- Gadkari D B, Lal K B and Arora B M 1994 *Solid State Phys. (India)* **C37** 198; *DAE Symp.* (Jaipur: Rajasthan Univ)
- Gadkari D B, Lal K B, Singh A J and Arora B M 1995 *Proc. VI national seminar on crystal growth* (Madras: Anna Univ.) p. 34
- Gadkari D B, Lal K B, Shah A P and Arora B M 1995 *Solid State Phys. (India)* **C38** 148; *DAE Symp.* (Calcutta: ACS)
- Garanuet J P, Differ T and Favier J J 1990 *J. Cryst. Growth* **106** 426
- International Centre for Diffraction Data 1994 Card No. 6-208, p. 327; NBS circular 539 (1955) p. 73
- Jung Y J, Park M K, Tae S I, Lee K H and Lee H J 1991 *J. Appl. Phys.* **69** 3109
- Kim K M 1978 *J. Cryst. Growth* **44** 413
- Lee G S, Thomson P E, Davis J L, Omaggio M K and Schidtt W A 1993 *Solid State Electron.* **36** 387
- Lin M H and Kou S 1995 *J. Cryst. Growth* **152** 256
- Look D C 1990 *J. Electrochem. Soc.* **137** 260
- Michel E, Singh G, Slivkeon S, Besikci C and Bove P 1994 *Appl. Phys. Lett.* **65** 3338
- Moorwood A F 1993 *SPIE Int. Soc. Opt. Eng.* **1946** 461
- Mulski G and Neumann G 1982 *J. Cryst. Growth* **59** 548
- Ohaski T 1986 *J. Vac. Sci. Technol.* **B4** 622
- Potard C 1981 *J. Cryst. Growth* **54** 558
- Rayners J *et al* 1993 *SPIE Int. Soc. Opt. Eng.* **1946** 490
- Straus A J 1959 *J. Appl. Phys.* **30** 559
- Van der Pauw L J 1958 Philips Res. Report 13, pp 1-9
- Witt A F and Gatos H C 1968 *J. Electrochem. Soc.* **115** 70
- Weber W, Neumann G and Muller G 1990 *J. Cryst. Growth* **100** 145
- Zhou J L, Wilcox W R and Regel L L 1993 *J. Cryst. Growth* **128** 173