

LEC Growth of $\text{InAs}_x\text{P}_{1-x}$ Bulk Crystals

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Single crystal ingots of $\text{InAs}_x\text{P}_{1-x}$ alloy were successfully grown by the liquid encapsulated Czochralski (LEC) method. Seed melt-back, followed slow cooling for seeding and pulling rates less than 100 $\mu\text{m}/\text{min}$ were found necessary for suppression of polycrystallization. Lattice constant was relatively homogeneous, less than 0.1 % fluctuation along growth axis in the seed side half of an ingot. Growth striations existed outside of a round core. Striations changed in shape from round in the seed side region to hexagon in the tail side. Dislocation density in the core was 5×10^3 to 2×10^4 .

1. Introduction

Almost all the compound semiconductor devices have been fabricated on binary compound substrates such as GaAs or InP. However, if ternary or quaternary alloy substrates are available, the freedom in the design of device structures would be remarkably expanded. Especially, the relaxation from the lattice constant limit is of great importance. To date, several III-V ternary and quaternary single crystal ingots have been tried to be grown. Liquid encapsulated Czochralski (LEC) and gradient freeze methods have been used for growths of $\text{InGaAs}^{(1)}$, $\text{InAsP}^{(2)}$, $\text{InGaSb}^{(3)}$, $\text{GaAsP}^{(4)}$ and $\text{InGaAsP}^{(5)}$ with end-member-rich compositions.

Among them, InAsP is the one of the most attractive alloys because of its wide applicability to both microwave and optoelectronic devices. On InAsP alloy substrates, 1.7-3.0 μm InGaAsP lasers or InGaAs high speed transistors with higher performances than InP-lattice-matched InGaAs ones are expected.

A.G.Thompson and J.W.Wagner studied on the growth of InAsP bulk crystals with the Gremmelmaier method (magnet coupled sealed-tube Czochralski method) and the B_2O_3 LEC method.⁽²⁾ They tried to grow alloys covering the whole composition range and obtained a new pseudobinary phase diagram but no single crystal growth was succeeded.

2. Growth procedure

A 350 KHz RF-heated high pressure LEC puller was used. InAs and InP polycrystals with total weight of about 80 g was charged in a quartz crucible. The encapsulant was high purity dry (less than 150 ppm water) B_2O_3 with the thickness of 10 mm during growth. Counter pressure was applied by nitrogen gas with pressures adjusted to melt compositions. In the case of the growth from 80%-InP melt, 28 atms was needed to completely suppress the bubbling of the melt, while only 6.3 atms was sufficient in the growth from 10%-InP melt.

InP seed was used for InP-rich alloys, but for InAs-rich InAsP growth, previously grown InAsP

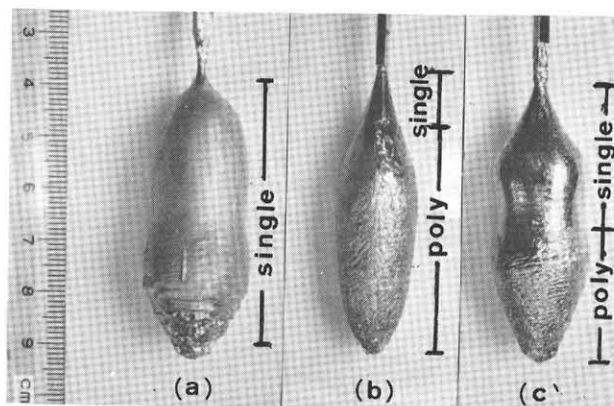


Fig.1 Photographs of LEC grown InAsP ingots grown (a) with pulling rate of 100 $\mu\text{m}/\text{min}$ from 80%-InP and 20%-InAs melt, (b) with 300 $\mu\text{m}/\text{min}$ from 80%-InP melt and (c) with 100 $\mu\text{m}/\text{min}$ from 70%-InP melt.

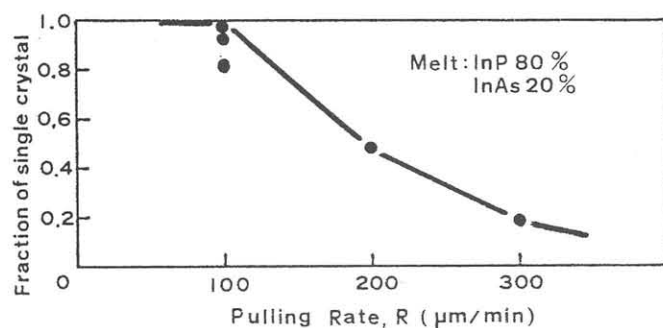


Fig.2 Fraction of single crystal as a function of pulling rate.

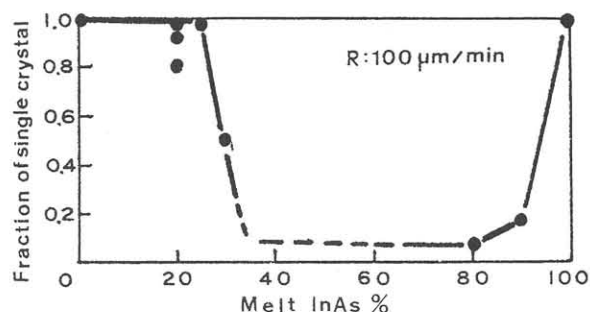


Fig.3 Fraction of single crystal as a function of melt InAs composition.

single crystal (arsenic mole fraction was about 0.15) was used as seed. The seed was rotated by 4 rpm with no crucible rotation. Seed orientation was $\langle 111 \rangle_B$. Several growths were tried using $\langle 100 \rangle$ InP seed but no single crystal ingot could be obtained. Slight melt-back of seed and very slow cooling rate were found absolutely necessary to suppress the growth of polycrystals just after seeding.

3. Single crystal growth

It has been well known in the growth of bulk alloys that the polycrystal growth is easily induced by a slight fluctuation of growth condition. One of the most important factors is the control of the degree of the constitutional supercooling just below the solid-melt interface. The constitutional supercooling is an essential problem for the alloy growth from its melt, arising from the non-unity distribution coefficient of an alloy component, i.e the spread of liquidus and solidus in the phase diagram. The degree of the constitutional supercooling is a function of pulling rate (growth rate), both temperature gradients along growth axis and radial direction, velocity of the melt convection (thermal and forced) flow and properties of the melt (viscosity and composition).

Figure 1 shows LEC grown InAsP alloy ingots obtained under different growth conditions. Usually, whole melt was converted to a pulled crystal even if polycrystallization occurred on the way.

Crystal diameter was manually controlled to be 15–20 mm. The ingot of Fig.1 (a) is the most successful case, where the more than 95 % charge could be converted to a single crystal. Faster pulling rates or higher InAs melt compositions resulted in polycrystallization in an earlier stage of growth as shown in Fig.1 (b) and (c).

Figure 2 shows the fraction of single crystal region (weight fraction) as a function of the pulling rate, where the melt composition was 80% InP and 20% InAs. Less than 100 $\mu\text{m/min}$ of pulling rate was needed to obtain an ingot without polycrystal grains. Fast pulling results in more accumulation of the alloy element having a distribution coefficient smaller than unity, arsenic in the present case. The large accumulation accelerates the constitutional supercooling, enhancing the interface breakdown or the initiation of dendritic growth.

Figure 3 shows the fraction of single crystal against the melt composition. More than 80 % conversion of the charged melt to a single crystal ingot was possible when the melt InAs composition was lower than 25%, where the solid composition was 12 % InAs at the seed end. The difficulty of InAs-rich alloy growth is arisen from the fact that the phosphorus distribution coefficient, which always exceeds unity, increases rapidly with decreasing the InP composition in the melt. The larger the distribution coefficient, the more the accumulation of arsenic occurs. The resultant heavy constitutional supercooling easily causes the breakdown of the solid-melt interface, the initiation of polycrystal growth, by a very small perturbation of growth conditions. This kind of the problem is always met when the melt composition of the higher-melting-point end member becomes low.

4. Uniformity of grown crystals

Alloy compositions were determined by the X-ray diffraction method with the Vegard's law. Figure 4 shows the variation of arsenic mole fraction of a single crystal ingot grown from the 20% InAs melt with 100 $\mu\text{m/min}$ pulling rate, shown in

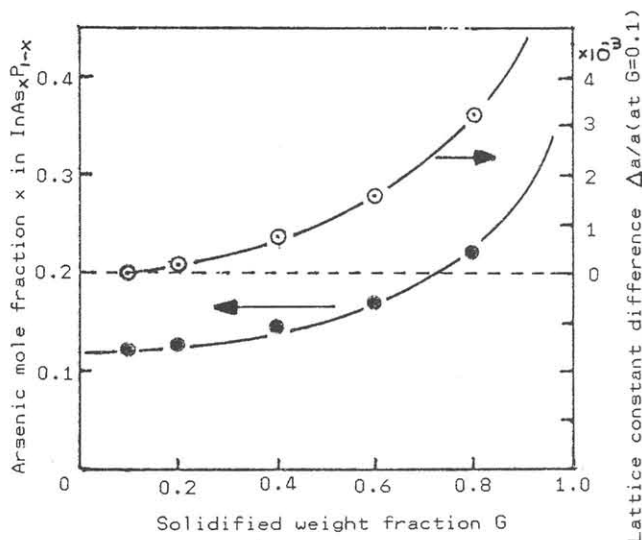


Fig.4 Arsenic mole fraction x as a function of solidified weight fraction G of the ingot shown in Fig.1 (a).

Fig.1 (a), as a function of the solidified weight fraction G . The distribution coefficient of arsenic was calculated to be 0.6 from the initial melt composition and the first-to-grow section alloy composition, which was well agreed with A.G.Thompson and J.W.Wagner's value. Arsenic mole fraction was changed from the 0.12 at the seed end to more than 0.25 at $G > 0.9$ in this sample. In the sample grown from the 25% InAs melt it varied from 0.15 to more than 0.3. The lattice constant normalized by that at $G=0.1$ was also plotted in the figure. In the seed-side half region, the lattice constant difference was within 1×10^{-3} , which was practically homogeneous. As expected from the phase diagram, homogeneous region becomes smaller with increasing arsenic composition.

5. Striation and dislocation

Striations and dislocations were revealed in (111) wafers by the boiling etchant of mixture of 4 cc HF, 6 cc HNO₃, 8 cc H₂O and 10 mg AgNO₃. The striation changed in shape from round in the seed side region to hexagon in the bottom region. Typical patterns of the two striation features are shown in Fig.5. A round core with a diameter of about half of the wafer size was always observed, within which no striation existed.

Although round striations are frequently observed in Czochralski crystals, no report was found concerning the hexagonal striation such as shown in Fig.5 (b). In the straight portion of the hexagon, which is aligned along $\langle 110 \rangle$ direction,

there is a lot of macrosteps. No striation exists between hexagonal striation bands.

Dislocations exist with a very high density in the interface region of the center core and peripheral striation region. Inside of the core, averaged dislocation densities ranged from less than

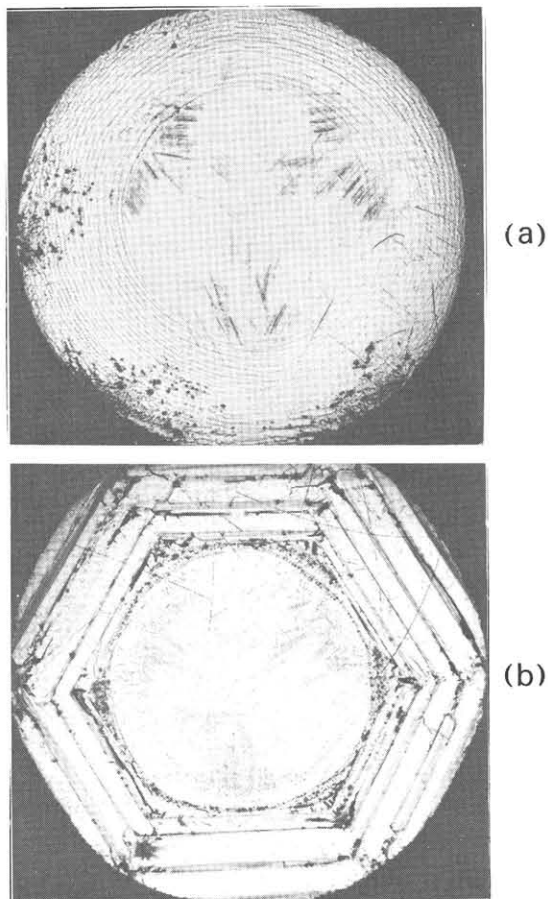


Fig.5 Striations and etch pit distributions of InAsP (111)A wafers cut from the ingot shown in Fig.1 (a); wafer position (a) at $G=0.4$ and (b) at $G=0.6$.

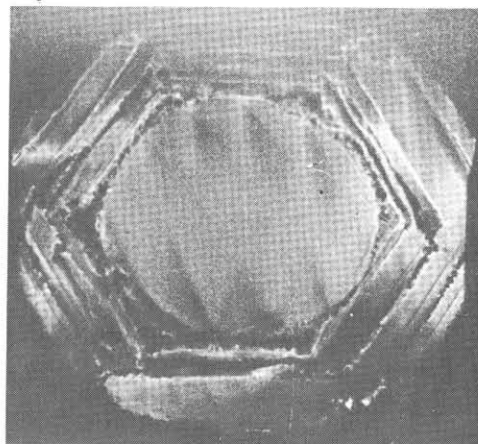


Fig.6 X-ray topograph of InAsP (111) wafer about 3 mm apart from the wafer shown in Fig.5 (b) (Cu K α /(511) reflection).

5000 cm^{-2} at $G < 0.5$ to $2 \times 10^4 \text{cm}^{-2}$ at tail end positions. Figure 6 shows an X-ray topograph of an InAsP (111) wafer about 3 mm apart from the wafer shown in Fig.5 (b). Since the reflected X-ray intensity was almost constant within the core, the lattice constant homogeneity was fairly good in the core. Also in the region between the hexagonal striation bands, the lattice constant was homogeneous, but changed abruptly at the hexagonal striation bands. A slight contrast observed in the core suggested the existence of internal strain or slightly wavy fluctuation of the alloy composition. Extremely high density dislocations are clearly observed as a strong contrast in the interface region between the round core and the adjacent striation band and on hexagonal striations.

6. Electrical properties

No intentional doping was made in the present study. Hall measurement of the crystal grown from 80 % InP melt showed electron concentration of 1.8 to $2.0 \times 10^{16} \text{cm}^{-3}$ and mobility of 2800 to 3000 $\text{cm}^2/\text{v}\cdot\text{sec}$ at room temperature and 1.6 to $1.8 \times 10^{16} \text{cm}^{-3}$ and 10100 to 10500 $\text{cm}^2/\text{v}\cdot\text{sec}$ at liquid nitrogen temperature. The difference along the growth direction was very small in spite of composition difference.

7. Discussions

The biggest problem in the growth of alloy bulk from its melt is how to eliminate the polycrystallization. The interface breakdown caused by the constitutional supercooling was extremely difficult to be suppressed. The constitutional supercooling is a result of the accumulation of a less-than-unity distribution coefficient element of the alloy. The accumulation will be reduced by three methods. One is to grow very slowly as compared with the diffusion velocity of the accumulated element. The second is to enhance the melt convection by increasing seed rotation rate or increasing temperature gradient. Thirdly, the growth from non-stoichiometric melt may be effective since the viscosity of the melt is decreased with being apart from the stoichiometric composition. Low viscosity results in strong thermal convection. From this point of view, magnetic field application should be said to be less effective.

K.J.Bachmann et al.³⁾ reported that high speed rotation rate and appropriate shaping of the cry-

stal ingot were essential for the suppression of the interface breakdown phenomena. However, as shown in Fig.1, tapering shape after seeding was not an important factor to suppress the polycrystallization. Although the lattice misfit was considerably large at the seeding point (4×10^{-3}), no problem was arisen if careful meltback of seed was carried out. This is contrary to K.J.Bachmann et al's result of LEC growth of InGaSb³⁾, where the angle of the taper must be smaller than some critical value. These differences from their results are probably due to the difference of the grown materials. As described below, InAsP was much easier to be grown because of the relatively narrow separation between liquidus and solidus curves as compared with InGaSb which includes two group-III elements.

Homogeneity in grown crystals is also an important parameter for the practical use. However, as far as the crystal growth is carried out under the equilibrium condition, it is impossible to grow a completely homogeneous ingot. The separation in the pseudobinary phase diagram of III-V alloys consisting of arsenic and phosphorus, such as InAsP or GaAsP, is smaller than those of alloys consisting of two group-III elements such as InGaSb, InGaAs or GaAlAs.⁶⁾ Consequently, InAsP is considered to be one of the highest homogeneity materials even the growth proceeds under equilibrium condition such as LEC or gradient freeze method.

Acknowledgements

The authors wish to express their thanks to Mr. A.Usui for his help to characterize the grown crystals. They are greatly indebted to Dr.T.Kawamura for his strong promotion of the present study.

REFERENCES

- 1) J.W.Wagner: J.Electrochem.Soc. 117(1970)1193
- 2) A.G.Thompson and J.W.Wagner: J.Phys.Chem.Solids 32(1971)2613.
- 3) K.J.Bachmann, F.A.Thiel, H.Shreiber, Jr. and J.J. Rubin: J.Electron.Mater. 9(1980)445.
- 4) F.Cerrina, D.Margadonna and P.Perfetti: J.Cryst. Growth 18(1973)202.
- 5) K.J.Bachmann, F.A.Thiel and S.Ferris: J.Cryst. Growth 43(1978)752.
- 6) G.B.Stringfellow: J.Phys.Chem.Solids 33(1972)665