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Citation: Applied Physics Letters **50**, 86 (1987); doi: 10.1063/1.97827 View online: http://dx.doi.org/10.1063/1.97827 View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/50/2?ver=pdfcov Published by the AIP Publishing

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Technique for the direct synthesis and growth of indium phosphide by the liquid phosphorus encapsulated Czochralski method

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(Received 11 September 1986; accepted for publication 11 November 1986)

The direct synthesis and growth of InP have been successfully performed by the newly developed liquid P encapsulated Czochralski technique. We have developed a way to use liquid P both as a source element for the synthesis instead of P gas, and also as an "encapsulant" for the Czochralski growth instead of B_2O_3 . The existence of two distinct layers, liquid P and molten InP, has been discovered during the process. Grown single crystals showed a carrier concentration of as low as 5×10^{15} cm⁻³.

There is a strong need for cheap, high quality InP substrates for both optoelectronic and high-speed devices. However, it seems unlikely that commercially available substrates will be able to meet the demand, mainly because the crystals are grown by a "two-step" growth process. InP crystals are usually grown by the liquid encapsulated Czochralski (LEC) technique using polycrystalline InP presynthesized by the horizontal Bridgman (HB) technique. Another two-step growth technique is the vertical gradient freeze (VGF) method recently reported by Gault *et al.*¹ In any two-step operation, the cost performance is lower than in a one-step operation, and contamination by impurities is inevitable, although purification of source polycrystals has been reported in the HB method.^{2,3} So, the need for a onestep growth technique is strongly being felt.

Unlike GaAs, it is quite difficult to synthesize InP simply by heating a mixture of In and P. In the case of GaAs, Ga and As are covered with B₂O₃ during synthesis and the vapor pressure of As at the temperature of synthesis is a relatively low 30-40 atm. In contrast, in the case of InP, P cannot be covered with B₂O₃ because P sublimates at a lower temperature, about 100-200 °C, than the softening temperature of B_2O_3 , about 400-500 °C. Even if it were possible to cover P with an encapsulant with a lower softening temperature and prevent the sublimation of the P, the very high vapor pressure of P, as high as 200-300 atm⁴ during synthesis at about 1000-1100 °C, would preclude such a synthesis because it would be very difficult to obtain such a high temperature in an inert gas at high pressure. Another technique is the P injection technique.^{5,6} It is for pulling a single crystal from an in situ synthesized melt produced by injecting P gas into an In melt. It is presently being used commercially, though great care must be taken in regard to controlling the injection. All the above-mentioned methods commonly use P gas in the synthesis so as to compensate for the vapor pressure of P from the melt.

We have developed a new direct synthesis and growth technique for InP single crystals through the use of liquid P instead of P gas. This paper describes the growth process of our liquid P encapsulated Czochralski (LP CZ) technique and the characteristics of the grown crystals. Some mechanisms for the growth are also discussed.

Figure 1 shows a schematic diagram of the LP CZ system. A commercially available MSR-6RA puller (Cam-

bridge Instruments Ltd.) was modified and supplemented with an x-ray transmission image observation system. The whole direct synthesis and growth process were observed with this system as well as with a TV camera. Two zones, cooled and heated, were constructed in the chamber through the use of thermal baffles made of boron nitride (BN).

High-purity In and red P (both commercially available 6-9s grade) were charged in a 5-cm-diam container made of quartz. The charge weight of In was 100 g and that of P was 54 g. The 54 g of P included an amount 100% by weight in excess of that necessary for stoichiometric composition. Synthesis and growth were carried out under Ar gas at 60 atm.

Grown crystals were evaluated by Hall measurement at room temperature, by lattice parameter measurements with x-ray diffraction, and by measurement of the etch pit density. Etch pits were revealed with Huber etchant.

When the container was heated up to 200–300 °C, source solid red P sublimated to become a gas. The gas then cooled in the cooled part of the container and condensed on the inside wall. The gas became liquid white phosphorus and the liquid P flowed down onto the In melt and reacted with it at about 1000–1100 °C. As a result of the reaction, InP melt was produced.⁷ Most of the synthesis seemed to be completed within a couple of seconds, and after that, the melt was kept as it was for an hour so as to complete the synthesis. Then $\langle 111 \rangle$ single crystals were grown from the melt, using



FIG. 1. Schematic diagram of the LP CZ furnace.



FIG. 2. Temperature profile along the vertical axis. The temperature gradient near the surface of the melt was measured to be $27 \,^{\circ}$ C/cm.

the liquid P layer as an encapsulant. Cyclic phase transition of P, from gas to liquid and from liquid to gas, was observed during the whole synthesis and growth processes. We did not use an inert encapsulant, such as B_2O_3 , as is usually used in the LEC method. It is true that the major role of the liquid P layer as an encapsulant during growth is to prevent P evaporation from the melt, which is exactly the same as for B_2O_3 . But the greatest difference is that the encapsulant is one of the constituent elements of InP.

We measured the temperature profile in the container with a W-W.Re thermocouple. It is shown in Fig. 2. The profile showed a gradual change. The vertical temperature gradient near the surface of the melt was as low as 27 °C/cm. It was not only lower than the value for conventional processes, 100–150 °C/cm, but also lower than the value of 55 °C/cm reported⁸ as a condition for the growth of dislocation-free crystals. The neck portion of the container was cooled to less than 300 °C in order to produce liquid P.

Figure 3(a) shows an x-ray transmission image taken during growth at a cooling rate of 1.2 °C/h. While a $\langle 111 \rangle$ single crystal was growing, three-fold symmetry was confirmed in the image. However, when it became polycrystal, the image turned asymmetric.⁹ $\langle 111 \rangle$ single crystals were successfully grown at a cooling rate of 1.2 °C/h all during growth. Figure 3(b) is a photograph of a single crystal. The diameter was about 20 mm. The surface of the crystal was shiny and did not show any signs of either the dissolution or deposition of P.

Quite an interesting phenomenon was observed during the growth when the cooling rate was as high as 3 °C/h. Dendric crystals suddenly grew into the liquid P layer from both the surface of the crystal and the surface of the melt. This phenomenon is shown in the picture in Fig. 4(a) and in a schematic drawing in Fig. 4(b). This phenomenon implies that a certain amount of In is dissolved in the liquid P layer. A photograph of an actual dendric crystal is shown in Fig. 4(c). In this case, there was a single crystal inside the dendrites. The composition of the dendrites seems to be far from stoichiometry because they are more brittle than InP. The composition of the dendric crystals is now being analyzed.

The lattice parameter was measured to be 5.8683 Å, which is the same value as that for the commercially available LEC grown crystal. It is likely that the composition of the crystal is near stoichiometric, or almost the same as the LEC grown crystal. We observed neither In inclusions nor P inclusions in any crystals.

The carrier concentration was measured to be 5×10^{15} cm⁻³ and the mobility was $3500 \text{ cm}^2/\text{V}$ s. The etch pit density was on the order of $10^4 - 10^5 \text{ cm}^{-2}$, which is not very low in spite of the low-temperature gradient near the growth interface. This might be because of the high post-growth cooling rate, 20 °C/min, employed in these experiments. The reduction of dislocation is now under study.

The reason for the rather surprising phenomenon we discovered, namely, the separation of the liquid P and the molten InP, is very difficult to understand. In the x-ray transmission images, there was a dark region below the interface, meaning a very large x-ray absorption, and a clear region above, meaning a very low absorption. Also the interface between the two layers was very sharp. The details of the mechanism are not yet clear. However, the following is a possible explanation we can offer at present.

Considering the liquidus interaction parameter of InP near its melting point reported by Panish,¹⁰ In and P seem to react strongly with each other. So it seems that separation in the liquid phase is not likely to occur. One explanation for the phenomenon we observed is that it could be an intermediate phase before the reaction between In and P is completely finished. This speculation is supported by the fact that in some cases In inclusions were observed in the solidified residual melt. The In inclusions also support the possibility of gravity segregation. Although the phenomenon might be ex-



FIG. 3. (a) X-ray transmission image taken during growth of $\langle 111 \rangle$ single crystal and (b) a photograph of a grown single crystal with a diameter of around 20 mm.

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FIG. 4. (a) X-ray transmission image of dendrites, (b) a schematic drawing of (a), and (c) a photograph of grown dendrites.

plained using the phase diagram for InP, the one reported¹⁰ is not suitable for explaining the separation in the liquid phase, since our experiments were not performed under the equilibrium vapor pressure of P. So, another phase diagram is necessary, e.g., an asymmetric phase diagram which has some monotectic points on the P side of the diagram.

Further investigations of the compositions of the two layers are required in order to complete the phase diagram.

High-purity InP single crystals have been successfully grown by our newly developed LP CZ technique for the direct synthesis and growth of InP. In this technique liquid P, which is generated from solid red P, is used as one of the elements to produce InP, and it is also used as an "encapsulant" during growth as well as synthesis. Grown crystal showed a very low carrier concentration of 5×10^{15} cm⁻³. Two distinct layers, a liquid P layer above and a molten InP below, have been observed. Further investigation of the phase diagram for InP applicable to our experimental conditions is needed for a clear understanding of this phenomenon.

The authors are indebted to Dr. T. Iizuka, Dr. M. Hirano, and Dr. I. Hayashi for the fruitful and valuable discussion. They would like to express their thanks to Professor T. Nishinaga for the valuable discussion on the mechanism. They are also grateful to S. Ozawa for his advice and help in the experiments and to Dr. T. Obokata for his critical reading of this manuscript. The present research is supported by the Agency of Industrial Science and Technology, Ministry of International Trade and Industry.

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