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Growth and Characterization of Low Dislocation Large GaP Single Crystals

M. Watanabe, T. Fujii, J. Ushizawa and S. Washizuka

Toshiba Research and Development Center

Kawasaki 210, Japan

A new LEC technique has been developed for growing low dislocation large-diameter (2-inch) GaP single crystals. These crystals have dislocation-free areas in the interior region of the wafers. The new technique is featured by the modified temperature distributions in the B_2O_3 liquid encapsulant layer by optimizing the growth furnace configuration. GaP LEDs for green light emission using these crystals are almost twice as efficient as current LEDs.

§1. Introduction

Large diameter and high quality GaP single crystals are needed for the further LED development. Especially, crystals with low dislocation density are required to improve the emission efficiency of GaP green LEDs.

In the liquid encapsulated Czochralski (LEC) technique, the complicated chamber environment prevents the crystal growth with uniform diameter and low dislocation density. In the last few years, authors established the computer-controlled liquid encapsulated Czochralski (C-LEC) method.[1),2)]

The crystals with dislocation density as much as 5×10^4 cm^{-2} were successfully grown by this method.

This paper describes an advanced LEC technique which has been developed for growing large diameter GaP single crystals with extremely low dislocation density. Detailed characterization of the developed crystals is also presented.

§2. Experiment

In this experiment, <111> oriented crystals with 2-inch diameter were grown by the C-LEC method using resistance heating and a high pressure puller. The stoichiometric polycrystalline GaP was placed in a quartz crucible and was heated to the melting point (1467°C) by the furnace located in the side-wall and the bottom of the crucible. Molten GaP was covered with B_2O_3 liquid encapsulant to prevent phosphorous evaporation. 70 atmospheric nitrogen pressure was also required for this purpose. A crystal was pulled from this molten GaP. The crystals grown were sulphur doped n-type with carrier concentration of $1 \sim 5 \times 10^{17}$ cm^{-3}.

A novel base heater was developed for heating the crucible bottom in addition to heating the side-wall, as shown in Fig. 1. By using this heater, a uniform temperature distribution in the radial direction in the crucible was obtained as will be described later. Furthermore, to reduce the axial temperature gradient in the crucible, a graphite inner chamber was placed along with the high pressure chamber wall.

The temperature in the crucible was measured

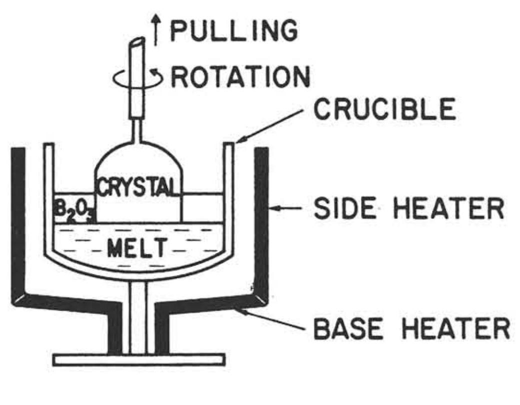


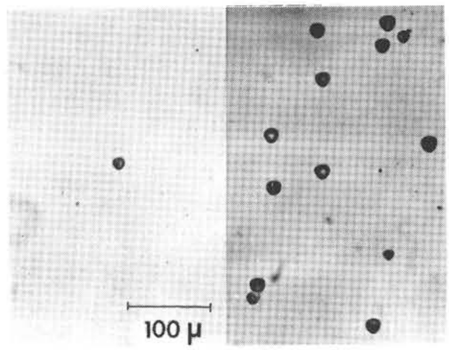
Fig.1 Schematic diagram of new heating method.

with two W/5%Re-W/26%Re thermocouples fixed to the pulling rod. One thermocouple was put in the core of the crucible and the other was mounted in the place 25 mm away from this inner thermocouple. These thermocouples were inserted into the molten GaP in the crucible with 96 mm inner diameter which contained 600 g GaP melt and 180 g B_2O_3 encapsulant melt.

Dislocation in the grown crystals were evaluated by preferential R-C etching on (111) phosphorous surfaces. Green LEDs were also fabricated by the LPE method on (111) phosphorous surfaces to characterize the quality of these substrates.

§3. Results and discussions

Figures 2 (a) and (b) show etching patterns observed on (111) surface at the position of 10 mm from the center of the crystal grown by using the present furnace. Both etching patterns are obtained in the middle of wafers. The dislocation densities are 10^3 cm^{-2} and 10^4 cm^{-2} for the (a) and (b), respectively. Figure 3 shows dislocation density distribution across the similar wafer to Figs. 2. The result for the reference crystal grown by using the conventional furnace is also shown for comparison. The present crystal has a dislocation-free core region. And, the dislocation density increases steeply from nearly zero in the core to $10^3 \sim 10^4$ cm^{-2} in the periphery region. On the contrary, the reference crystal has a dislocation density larger than 10^4 cm^{-2} in the core region. Both crystals have dislocation density of 10^5 cm^{-2} in the periphery. This characteristic of the dislocation density distribution in the present crystals were observed in more than 80 % portion of the grown ingot weighing 550 g. The tail portion of the pulled ingot had dislocation density of more than 10^5 cm^{-2} in the whole region. From these results, it is clear that the present furnace is effective to establish growth condition for suppressing dislocation generation in the interior region of the growing crystals.



(a) (b)

Fig. 2. Typical (111) surface etching pattern at the position of 10 mm from the center. Dislocation densities are 10^3cm^{-2} and 10^4 cm^{-2} for (a) and (b), respectively

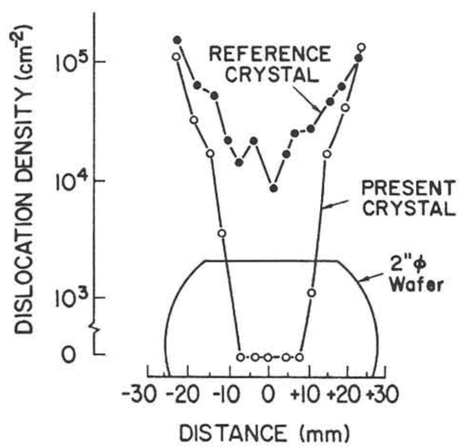


Fig. 3. Dislocation density distribution across 2 inch diameter wafers.

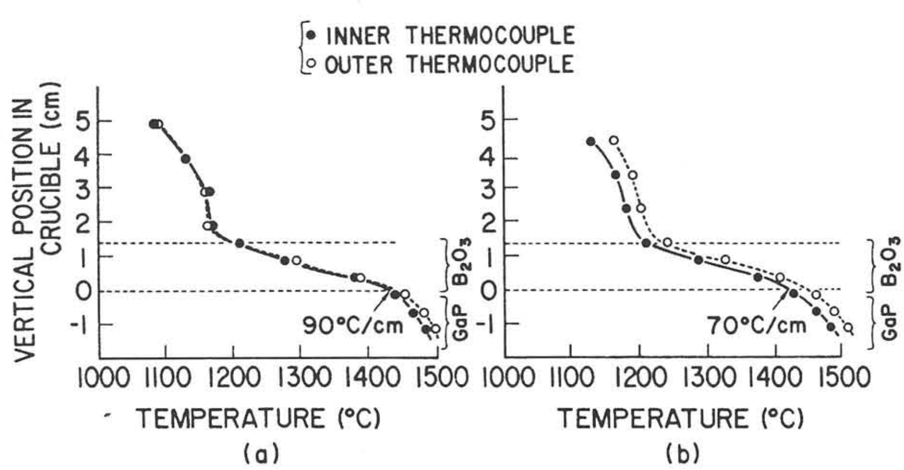


Fig. 4. Temperature distribution in crucible.
(a) Present furnace. (b) Conventional furnace.

Table. I Temperature measured in crucible

	ΔT_r (°C)	ΔT_a (°C)	dT/dZ (°C/cm)
Present furnace	10	210	90
Conventional furnace	40	210	70

ΔT_r : Temperature difference between the inner and outer portions in the radial direction. ΔT_a : Temperature difference between the upper and lower layers of the B_2O_3 melt. dT/dZ : Axial temperature gradient near the B_2O_3 /melt interface.

Figures 4 (a) and (b) show temperature distribution profiles in the crucible when using the present and the conventional furnaces, respectively. The essential results are summarized in Table 1. A more uniform radial temperature distribution can be obtained in the present furnace than in the conventional furnace. The temperature difference just above the melt, measured by a pair of thermocouples, was reduced to 10°C by using the present furnace as opposed to 40°C in the conventional furnace. On the contrary, the axial temperature gradient near the B_2O_3/melt interface was 90°C/cm which is larger than 70°C/cm obtained in the conventional furnace. The temperature difference between the upper and lower part of the B_2O_3 encapsulant for the present furnace was nearly the same as that for the conventional furnace. When taking off the graphite inner chamber from the present furnace, the axial temperature gradient near the B_2O_3/melt interface was increased sharply from 90°C/cm to about 110°C/cm, retaining the uniform radial temperature distribution. The temperature difference between the upper and lower layers of the B_2O_3 encapsulant was also increased to about 270°C. In accordance with this change of the temperature distribution in the crucible, the dislocation density in the periphery increased to more than 5×10^5 cm^{-2} and the dislocation density distribution became to be remarkably V-shaped across the diameter with dislocation-free core region. These results suggest that the radial temperature gradient distribution affects the dislocation density in the interior region of the grown crystal, while the vertical temperature gradient in the B_2O_3 encapsulant and/or near the B_2O_3/melt interface affects the dislocation density in the periphery.

Figure 5 shows the axial temperature gradient dependence of the average dislocation density for the conventional furnace.[2] The axial temperature gradient near the B_2O_3/melt interface was controlled by adjusting crucible position in the furnace. The average dislocation density was measured at 7 points with equal spatial interval. Growth under the low axial temperature gradient resulted in low dislocation density; a value less than 5×10^4 cm^{-2} was obtained in the crystal grown under the temperature gradient lower than 70°C/cm using the conventional furnace. On the other hand, the crystals grown with temperature gradient of 90°C/cm have average dislocation density of about 3.5×10^4 cm^{-2} when using the present furnace. In spite of the growth under the larger axial temperature gradient, lower average dislocation density can be obtained by using the present furnace than by the conventional furnace. The crystals grown with axial temperature gradient of 110°C/cm obtained by taking off the graphite inner chamber from the present furnace have the same average dislocation density of 1.5×10^5 cm^{-2}. The same value is obtained in the crystal grown with the same axial temperature gradient of 110°C/cm using the conventional furnace. These results suggest that under the lower axial temperature gradient condition, the more effective reduction of dislocation density will be achieved by flattening the radial temperature gradient in B_2O_3 encapsulant layer.

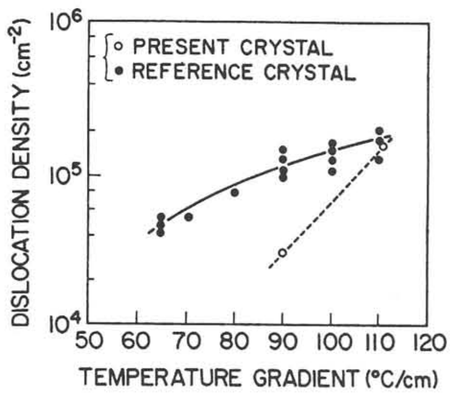


Fig. 5. Axial temperature gradient dependence of average dislocation density.

Billing suggested that dislocations are induced by the presence of axial and radial components of temperature gradient near the growth front.[3] A uniform radial temperature distribution, using the present furnace, is considered to make this radial

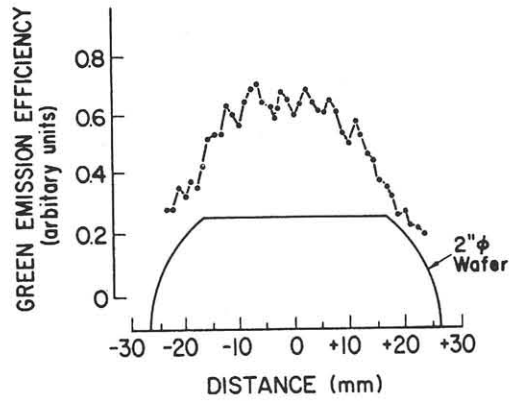


Fig. 6. Green emission efficiency distribution in GaP:N epitaxial layer using the present crystal as a substrate.

component less effective. For further improvement in dislocation density, it is necessary to realize a lower axial temperature gradient system with uniform radial temperature distribution and to develop stable growth technique even in lower temperature gradient environment.

Figure 6 shows the typical green emission efficiency distribution in GaP:N epitaxial layer using the present crystal as a substrate. By comparing Fig. 3 and 6, it is apparent that the green emission efficiency has strong relation with dislocation density, that is, green emission efficiency increases with decreasing dislocation density and the extremely high value of emission efficiency can be obtained in the interior of the wafer. This value is almost twice as high as current ones.

§4. Summary

A new LEC technique for growing large-diameter (2-inch) GaP single crystals with extremely low dislocation density has been developed. The crystals had $0\sim10^3$ cm^{-2} dislocation density.

The crystal quality effect on GaP green LED performance was investigated. The emission efficiency of GaP green LEDs, using the newly developed LEC-grown crystals, was almost twice as high as current values.

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