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Growth of GaAs Crystal by an Improved VGF Apparatus

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ABSTRACT

The construction details of VGF apparatus with a DM(direct monitoring) furnace for the growth of low defect crystal and characteristics of GaAs crystal grown by this apparatus are described. The average dislocation densities and EL2 concentration of as-grown undoped GaAs along the different solidified fractions exhibit $4\times10^{2}-7\times10^{3}cm^{-2}$ and $6\times10^{14}-4\times10^{15}cm^{-3}$, which are less than those observed for liquid encapsulated Czochralski(LEC) or high-pressure vertical gradient freeze(VGF) crystals. These remarkable reduction of the dislocation densities and EL2 concentrations were explained by the lower temperature gradient(dT/dx-10℃/cm) and slower rates of post-growth cooling (20℃/hr: 1240-1000℃, 30℃/hr: 1000-700℃). Also, The Hall mobilities, carrier concentrations show uniform distribution throughtout 80% of the ingot length.

1. INTRODUCTION

Low defect and large diameter GaAs substrates are increasingly required for electronic and opto-electronic devices. Various techniques have been employed to meet this demand. The most favorable growth techniques used in bulk growth are liquid encapsulated Czochralski(LEC) and horizontal Bridgman (HB) methods. While the LEC technique can produce a large diameter, undoped S.I. GaAs crystals, the dislocation density of the crystal is relatively high(typically $10^{4}-10^{5}cm^{-2}$) on account of excess thermal stress. On the other hand, the HB method is less favorable than the LEC method for the production of circular wafers and high purity GaAs crystals in spite of low dislocation density. In recent years, attentions have been paid to the vertical gradient freeze(VGF) method as one of the most promising techniques for the growth of low defect, large diameter GaAs since it has low temperature gradient(<20℃/cm) and no diameter control is needed and a good electrical uniformity across large of the wafer areas [1-3]. The details of this method was summarized by Woodbury [4].

In this point of view, we have constructed a vertical gradient freeze apparatus by using the direct monitoring(DM) furnace for the high temperature portion with a several design concepts which are an important aspects to the growth of Ⅲ-Ⅴ as follows: 1) the reduction of the temperature gradient which create high stress levels induced dislocation generation. 2) the control of the stoichiometry by maintaining a sufficient partial pressure of arsenic over the melt. 3) the maintaining of a flat or slightly

convex interface shape during the solidification. The major advantages involved in home-made VGF apparatus in our laboratory are the simplified hot-zone configuration and a fast response of the temperature profile with respect to the electrical power owing to the small heat capacity in compared with other conventional used furnaces and also having the advantages of cooling and the temperature control being easy.

The purpose of this paper is to report about the construction of the uniquely designed VGF apparatus using DM furnace for the crystal growth of low defect GaAs and to show the preliminary results for crystal qualities of VGF-grown undoped GaAs through the preferential etching, Hall effect and DLTS(deep level transient spectroscopy) PL(photoluminescence) measurements and the results for other gradient freeze and LEC are compared.

2. COSTRUCTION & EXPERIMENTAL PROCEDURE

Fig. 1 shows an overall view of our home-made VGF crystal apparatus. The VGF apparatus consists of a high temperature zone above

Fig. 1. Photograph of VGF apparatus used in the study with control units.

the GaAs melting point and a low temperature zone for arsenic overpressure control and mechanical parts for ampoule rotation. The main feature of this design is that a DM furnace with low thermal mass was used at the high temperature portion and a simple heater design compared to the more sophisticated furnaces which have several hot zones [2,3]. A more detailed drawing of the VGF apparatus arrangement is shown in Fig. 2. The DM furnace with a three zone heater assembly is used to melt the GaAs polycrystal and grow the crystal. The structure of DM furnace consists of heating elements, a quartz liner and a gold coated quartz water

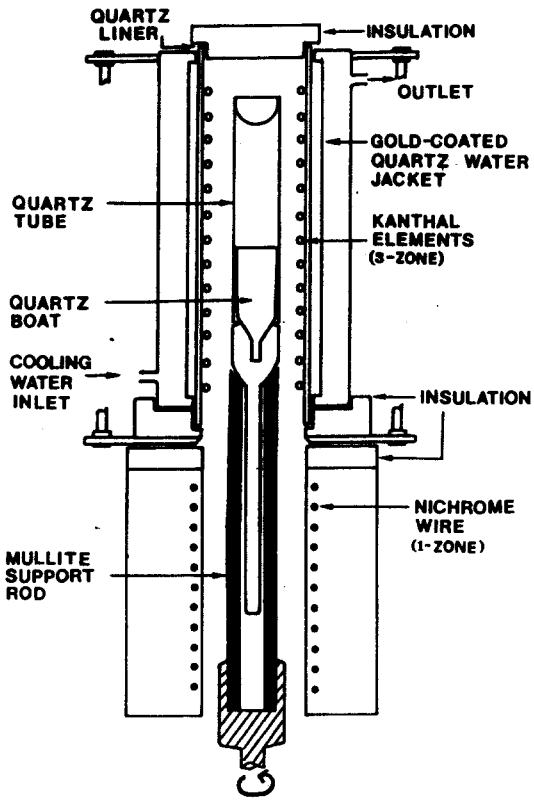


Fig. 2. Schematic drawing of the VGF apparatus with DM(direct monitoring) furnace in cross section.

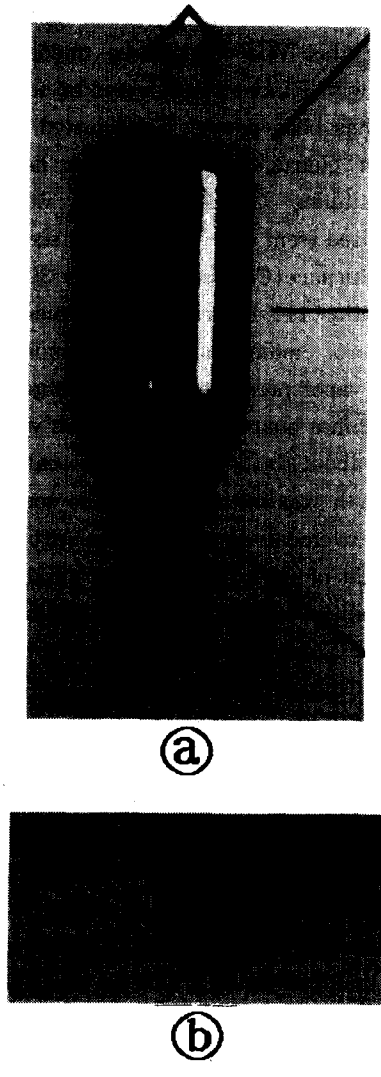
jacket. A three zone heater assembly disposed at the inside of the quartz liner tube for supporting, a cylindrical quartz water jacket arranged with cooling water inlet and outlet at the outer wall for circulation externally and coated with gold thin film on the internal wall surface of quartz water jacket. The heating zone was divided 3 sections which would be controlled separately by the each of the programmable temperature controllers and Kanthal heating elements was used as heating elements for all zones. Thereby whole process of the crystal growing can be observed by directly with naked eyes and a uniform distribution of temperature can be obtained at the temperature over than 1240℃. Other detail specifications of the DM furnace were illustrated in the proceeding paper [5]. The low temperature zone furnace is constructed of nichrome heating wire wound on a grooved mullite tube, embedded in alumina cement and surrounded by compacted layers of ceramic fiber blanket, the whole being enclosed in a stainless steel cannister. The both furnaces are mounted on sliding rod to readily allow relative movement so as to adjust the gap between zones, which can be used to control the temperature profile of the growth rigion.

Using this VGF apparatus, undoped GaAs crystal with 1 inch diameter and up to 10 cm in length has been grown. Sandblasted of 1 inch diameter quartz boat loaded with high purity polycrystalline GaAs of 150g which was synthesized from six−nine Ga and six−nine As in HB furnace(Crystal Specialties 301) and a seed with ⟨111⟩B orientation, excess arsenic amount of maintaining one atmosphere of arsenic vapor pressure inside the ampoule were enclosed in a quartz ampoule, which was evacuated to about 5×10^{-6} Torr before sealing. Crystal growth was initiated from the seed end by the m+ovement of temperature profile along the lenght of the melt. Then the axial temperature gradient at the seed−melt interface was about 10℃/cm, which is consistent with other low gradient growth techniques [6,7] and the crystal growth rate was about 2.5 mm/hr. During the growing crystal, temperature stability of the furnace in this apparatus has proved to be excellent with a deviation from set point seldom exceed ±0.1℃. The crucible is rotated at 2−3rpm during both growth & cooling processes to ensure thermal symmetry. Characterizations of the undoped GaAs grown by this VGF apparatus were determined by preferential etching, Hall effect measurements in the van der Pauw

configuration, schottky barrier deep level transient spectroscopy(DLTS) and low temperature photoluminescence(PL) measurement using He-Ne laser excitation at 20 K.

3. RESULTS AND DISCUSSION

Fig. 3 (a) shows a photograph of ⟨111⟩seeded, undoped GaAs crystal was grown by the VGF apparatus. The surface of grown crystal



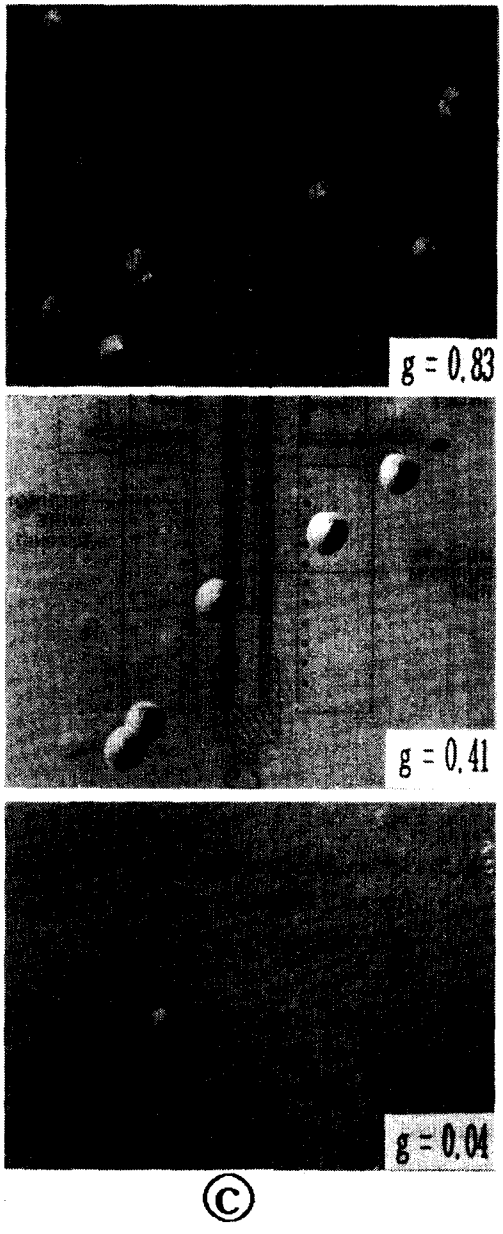


Fig. 3. (a) Undoped GaAs single crystal with 1 inch diameter and 10 cm length grown by VGF (b) Last-to-grown portion of VGF-grown GaAs. (c) Etch pits density (EPD) distribution across slices from the seed and tail ends of an undoped GaAs grown by VGF.

was observed very shiny without twinning and polycrystalline nucleation. It was good evidence of no sticking between quartz crucible and crystal during the growth proceeded. Also, Fig. 3(b) shows that the last-grown portion of crystal end has a slightly convex growth shape(center hotter than edge) and this convex interface eliminates the core facetting often seen in LEC material as well as markedly reducing twinning and spurious uncleation at the quartz crucible interface, it was found that the use of DM furnace can be produced the desired isotherms shape and decreased the interface curvature along the growing axis direction owing to a stong heat converging force and a convex crystal-melt interface was maintained during crystal growth. Photographs of $3H_2SO_4:1H_2O_2:1H_2O$ etched wafers from the seed, middle and tail part of an undoped GaAs grown by VGF are shown in Fig. 3(c). The dislocation density at the seed side is 450cm^{-2} and throughout 80% of the ingot length show low dislocation density less than 5000cm^{-2}, which is estimated the better than dislocation density of undoped GaAs crystals in recently published reports [1,2,8]. Several mechanisms for dislocation formation have been suggested in GaAs crystals grown from the melt by A.Grant Elliot et al [7]. Under the low thermal gradient environment, dislocations are predominantly created by the point-defect condensation and increase along the length of the crystal. Generally, the condensation of point-defect is a function of how rapidly the grown crystal is cooled from the melting point. In case of the slowness of the cooling process, excess vacancies will be annealed out and a condensation of vacancies which can be formed a dislocation loop will not occur. Therefore, this low dislocation densities in VGF-grown GaAs crystal was thought be as a results of the lower temperature gradient of-10℃/cm near the growth interface and slower rates of post-growth cooling through the step process to suppress defect interaction or dislocation generation during the cooling. Then, post-growth cooling rate was -20℃/hr for the first step(1240-1000℃) and -30℃/hr for the second(1000-700℃) respectively. By the reason above, this VGF apparatus is advantageous for the low defect crystal in comparison to conventionally used furnaces. The electrical properties for different solidified fraction measured at room temperature by van der Pauw method was represented in Fig. 4. As a results of, the

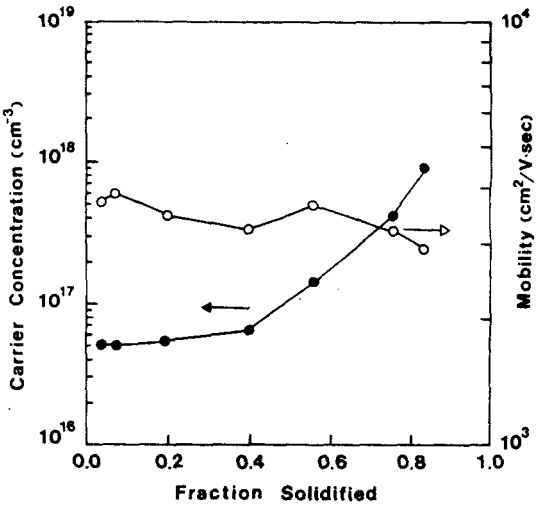


Fig. 4. Electrical properties of undoped VGF GaAs at room temperature along the different solidified fraction.

carrier concentrations exhibits about -5x10^{16} cm^{-3} about 50% of the melt solidified($g<0.5$) of VGF crystal and it increases about -9x10^{17} cm^{-3} near tail side. The Hall mobilities show fairly uniform distributions along the solidified fraction within the range of 3000-3900cm^2/V sec. The compensation ratio θ which is evaluat-

ed on the basis on Walukiewicz et al's predictions [9], varied from $\theta=0.5-0.7$ near the seed side to $\theta=0.2-0.4$ near the tail side. These variations of the compensation ratio θ arising from the self-compensation of amphoteric impurity(providing both shallow donors and shallow acceptors) which is introduced into the melt be decomposition of quartz crucible.

A DLTS spectra of VGF GaAs is shown in Fig. 5. It reveals the presence of three electron

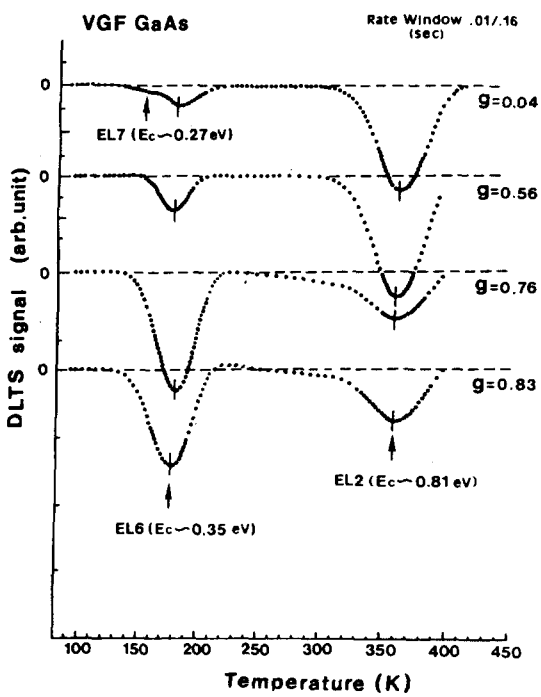


Fig. 5. DLTS spectra of electron traps in undoped. VGF GaAs.

traps EL7($E_C-0.27eV$), EL6($E_C-0.35eV$) and EL2($E_C-0.81eV$) which are typical for melt-grown GaAs [10]. EL2 and EL6 are clearly the dominant deep traps along the length of the crystal. As shown in Fig. 6, the absolute values of EL2 and EL6 concentration measured in VGF crystal were $6x10^{14}-4x10^{15}cm^{-3}$ and $4x10^{14}-1.5x10^{15}cm^{-3}$ along the different solidified fraction. The overall EL2 variation is much less than is typically found in "standard" LEC material($>1x10^{16}cm^{-3}$) and compares favorably with undoped HB material($>1x10^{15}cm^{-3}$). It has been shown that the EL2 concentration is directly related with a change in melt stoichiometry for undoped GaAs crystals as reported by others [11]. Fitting the concentration of EL2 obtained in the present crystal to data in Ref. 7 suggests that the melt stoichiometry should be near the arsenic fraction of 0.48. However, this is unlikely since we observe clear n-type from the Hall measurements and arsenic overpressure was maintained through the VGF growth process. Thus, the EL2 concentration in VGF GaAs crystal is expected to be depended upon the concentration of point defects induced during growth and post-growth cooling. Because, it has been proposed that EL2 originates in the migration of a gallium vacancy into a neighboring arsenic sites according to Lagowski et al [12]. As an example, in the case of In-doped ($-2\times10^{19}cm^{-3}$) HB GaAs with low dislocation density($<10^2cm^{-2}$) grown in our laboratory, the EL2 concentration is reduced to a concentration of approximately $<1\times10^{15}cm^{-3}$, it was explained by the reduction of V_{Ga}=concentration according to the incorporation of indium atom in Ga vacancy sites [13,14]. Therefore, the lower values of EL2 distribution and dislocation density in VGF crystal than LEC grown GaAs crystals lies in the low thermal stress during growth and cooing mode after growth. Since, the thermal stress enhances the formation of excess point defect (including V_{Ga}) which can be formed a dislocation loop and influences both the density of dislocation and EL2 distribution [12]. Meanwhile, the concentration of the EL2 trap was reduced to approximately $<7\times10^{14}cm^{-3}$, whereas that of the EL6

trap was found to be increased at the tail portion($g>0.7$) as shown Fig. 6. these phenomena

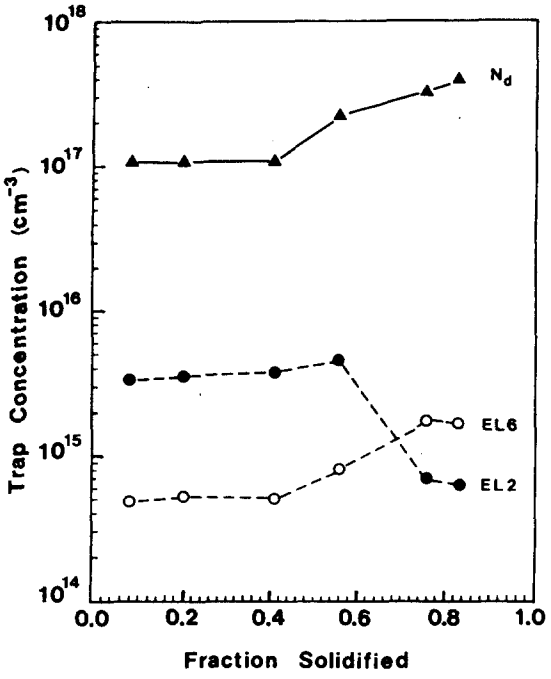


Fig. 6. Variations of deep level concentration (EL2, EL;6) along the different solidified fraction.

can be explained by defect reaction for the EL2 formation such as

$$V_{Ga}^{--} + As_{As} = As_{Ga} + V_{As}^{+} + 3e^{-}$$

According to the above reaction, the formation of As_{Ga} (EL2) has an n^{-3} dependence with higher electron concentration causing decrease in As concentration. Thus, it can be seen that the increase of donor concentration slightly above $10^{17}cm^{-3}$ in VGF GaAs suppresses the formation reaction of EL2 and that the EL6 trap has a possibility of a donor related defect [15,16].

We have examined the energy levels associated with impurities and how the VGF GaAs crystal was grown in certain circumstances by PL measurements at 20 K. Two emission bands are observed in the PL spectra at 1.512, 1.492 eV which are present along the different solidified fraction as shown in Fig. 7. The emissions

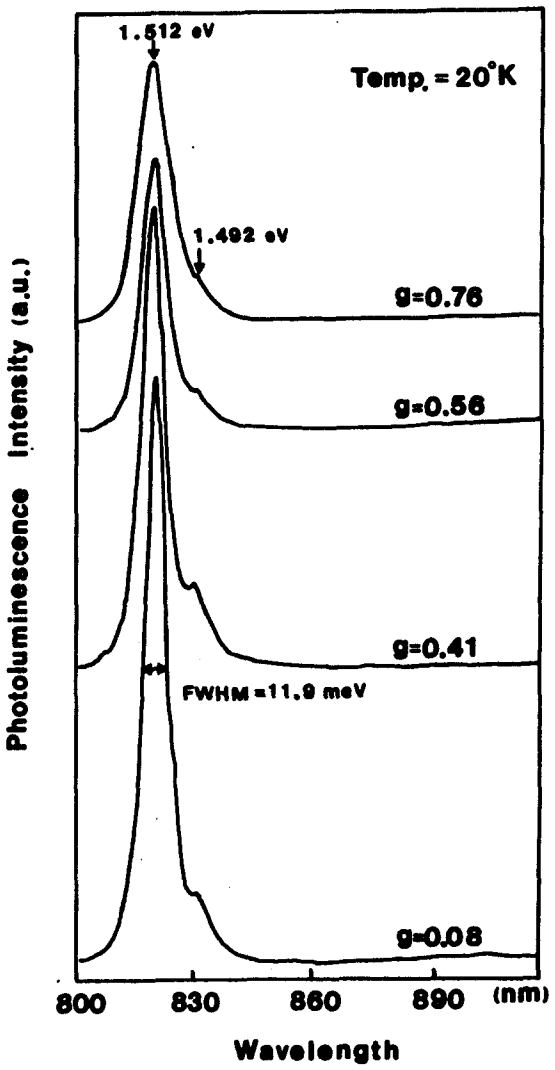


Fig. 7. PL spectra at 20K albng the different solidified fraction.

at 1.512 and 1.492 eV are attributed to the bound exciton or shallow donor to valence band

and conduction band to carbon(GaAs) transition, respectively [17]. Also, the full width at half maximum(FWHM) of the peaks at 1.512 eV were increased different solidified fraction were increased from 11.9 to 17 meV as the solidified fraction of melt increases from 0.08 to 0. 76 as shown in Fig. 8. When the above results

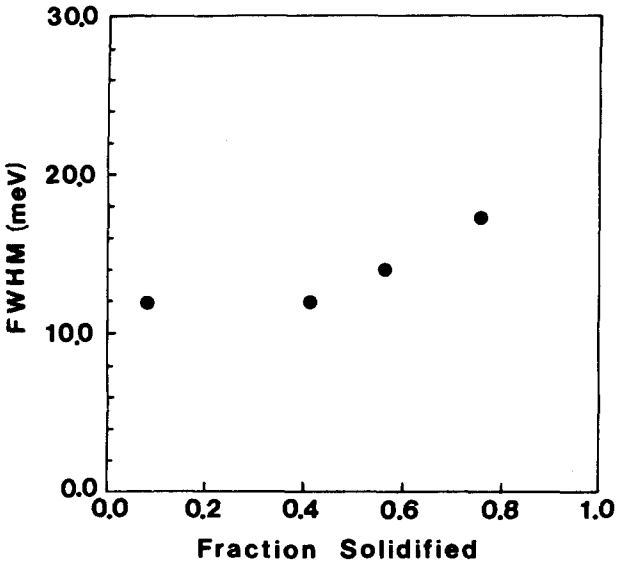


Fig. 8. Full width at half maximum(FWHM) of the peaks at 1.512 eV along the different solidified fraction.

compared with the half-width of the 1.512 eV luminescence peak as the arsenic concentration in the GaAs melt obtained by Driscoll et al's PL measurements at 20° K, it is found that the VGF grown GaAs has been grown on the slightly arsenic-rich condition [18].

In summary we have constructed an improved VGF apparatus which can be crystal growth in a low thermal stress environment by the use of DM furnace at the high temperature Zone. And, 1 inch diameter undoped GaAs was grown by this apparatus as a results of the low temperature gradients during growth and slower rates of post-growth cooling, the dislocation densities and deep traps, such as EL2 and EL6, along the length of a crystal are lower than crystals grown by the LEC or high pressure VGF techniques. Therefore we convinced that this apparatus will be applicable to grow high quality GaAs with low defect, large diameter.

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