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Growth of Large Diameter GaAs Single Crystals
in a Horizontal Configuration**

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EVALUATION OF THE MELLENN "EDG" FURNACE FOR GROWTH OF LARGE DIAMETER GaAs
SINGLE CRYSTALS IN A HORIZONTAL CONFIGURATION

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Abstract

An extensive evaluation of the Mellen "EDG" furnace has been conducted in order to assess its performance for growth of large diameter (2 and 3") GaAs crystals in the horizontal configuration. The axial and radial temperature gradients were found to influence strongly the crystal-melt interface shape and crystalline perfection of the crystals. When the axial thermal gradients are small relative to the radial thermal gradients, the shape of the crystal-melt interface fluctuates in time as growth proceeds, indicating the presence of oscillatory convective flows in the melt. The crystal-melt interface becomes stable as the axial component of the thermal gradient over the solid is increased. The crystals produced with optimized gradient conditions have a low and uniform dislocation density.

1. Introduction

It is remarkable that the simple design of the furnaces used by Bridgman [1] and Stockbarger [2] in 1925 and 1938, respectively, are still in use for many crystal growth applications. For the growth of GaAs crystals which exhibit a high dissociation vapor pressure, numerous modifications of the basic furnace design have been proposed and successfully implemented [i.e. 3,4]. A horizontal configuration, used to prevent excessive strain between the crucible and the crystal, represents one of these modifications. Most new designs make use of multi-zone furnaces, because a zone kept at a lower temperature than the melting point of GaAs is required to control independently the arsenic vapor pressure in the growth ampule which, in turn, affects the stoichiometries of melt and solid.

Commercially available since 1978, the Mellen "Electro-Dynamic Gradient (EDG) furnace, was designed with narrow heating zones which are used to shape the axial temperature gradient along the axis of the furnace. Each zone is independently microprocessor-controlled so that the axial temperature profile can be translated or modified in time as growth proceeds in a gradient freeze manner without motion of either the crucible or the furnace. The design of this furnace has been described in detail by Parsey and Thiel [5].

The purpose of this paper is to present the major results of an extensive study of the thermal environment provided by this furnace for growth of GaAs and to assess the furnace performance for growth of GaAs.

2. Experimental

Figure 1 is a schematic of the 5 1/8" I.D., "EDG" furnace used for

this study. It consists of the following parts:

- the low temperature zone: 15" long including four independently controlled zones of 6, 3, 3, and 3" lengths
- the radial loss section: 14" long without power input
- the EDG section: 18" long including ten 1" and four 2" independently controlled zones
- the high temperature zone: 8" long, including two independently controlled zones, 2 and 6" long.

Two sets of thermocouples were used. The first set is used for control and monitoring of each independent zone (No. 1 through 20 in figure 1). Their normal position is in contact with the growth ampoule. The second set (No. A through J) is used for temperature measurements along the radius (top) of the EDG section and their position can be varied from close to the heating elements down to the center of the growth chamber. The quartz ampoule shown in figure 1 (57 mm I.D.) has been specifically designed with small quartz tubes (1.5 mm I.D.), one inch apart, which extends to the center of the ampoule. Small measurement thermocouples can be inserted in these tubes in order to record the temperature just 2 mm above the melt.

We used sand-blasted quartz crucibles, 5 cm in diameter, for growth of <111> crystals about 25 cm long. The crucibles have a 5 cm long, 1 cm I.D. seed well and a cone angle of about 17°.

A typical thermal profile for growth of GaAs that makes use of the flexible control system of the EDG furnace is shown in figure 2. In all of the experiments presented here the low temperature zone that controlled the arsenic source temperature was kept at 617°C. Various "flat" temperatures were used for the profiles imposed in the EDG section. The

high temperature buffer zone was kept at 1245°C . The furnace was water cooled with a flow of about 1 liter/minute.

3. Results

3.1. Axial and radial thermal gradients

By simultaneously recording of the output of 30 thermocouples, positioned as shown in fig. 1, we were able to follow in time the motion of the temperature profiles during both simulated (no load) and real growth runs. The limited amount of space for this publication does not allow for a presentation of all the relevant data. We report only on a few profiles obtained during real growth runs that we believe are most representative of the overall furnace performance.

Figure 3 shows two temperature programs. The programs were written to translate temperature gradients of $10^{\circ}\text{C}/\text{cm}$ and $2.8^{\circ}\text{C}/\text{cm}$ over 2.5 cm on the crystal side and on the melt side, respectively, of the crystal-melt interface. The translation rate was 4 mm/hr. In the first program, the "flat" temperature was 1188°C . Curves a, b and c show that program at different times during the run. In the second program, shown at a later time during the run, the "flat" temperature was 1100°C . For each run, we monitored the actual temperature on the ampoule given by the control thermocouples and the temperature inside the ampoule, about 2 mm above the crystal and melt surfaces. The results (figure 4) show strong heat flow from the high temperature zones toward the radial loss section. Sharp angles in the temperature profiles are not maintained. The actual axial gradient, measured above the crystal-melt interface inside the ampoule, are shallower than those programmed. As growth proceeds, the axial

gradient decreases. Better tracking is obtained by lowering the "flat" temperature. Differences between the temperatures obtained from each set of thermocouples (5 to 14 and A to H) provides information on the magnitude of radial gradients along the furnace. The values of both axial and radial gradients, corresponding to figures 3 and 4, are summarized in Table I. When the axial gradient is about equal to the radial gradient above the melt, single crystal growth cannot be sustained. In this case, grains of random orientations nucleate on top of the melt and propagate toward the bottom of the crucible following the interface curvature.

3.2 Growth interface shape and convective flows.

Striations revealed by photoetching [6] have been used to investigate the growth interface morphology. In a horizontal growth configuration, the interface shape is mainly determined by the convective flows in the melt which, for high Rayleigh numbers ($Ra \geq 5 \times 10^3$), exhibit three-dimensional velocity components. Crochet et al. [7] have calculated such growth interface shapes by numerical simulation of horizontal Bridgman growth of GaAs. In order to adequately compare their theoretical results with experiments, a crucible without seed well and with a length-to-radius ratio of 6 was used. This design is a simplified growth geometry whose axial cross-section is equivalent to that used in Crochet's calculations. The crystal featured in figure 5(a) was grown with the "flat" temperature at 1188°C according to the program shown in figure 3, curves a, b, and c. The interface morphology is very similar to that calculated by Crochet et al. It shows that the shape of the crystal-melt interface fluctuates in time as growth proceeds, confirming the presence of oscillatory convective flows in the melt. It was also found that the

crystal-melt interface becomes stable as the axial component of the thermal gradient over the solid is increased and/or the radial component is decreased. An indirect way to reduce radial gradients is to position the melt centered with respect to the furnace axis. In a "normal" position, shown in figure 1, the top of the melt is at the level of the center axis of the furnace. Parsey et al. [5] found that lowering the flow of water used as coolant on the outside of the furnace, reduces the radial temperature gradients. Their findings have not been explored in the present study. It is important to note, as pointed out by Carruthers [8], that the flows and temperature distribution depend essentially upon the Grashof (Gr) number which indicates the relative importance of buoyancy driven forces with respect to viscous forces since the Prandtl (Pr) number is in fact an intrinsic property of the material and cannot be altered by changes in the growth parameters ($Pr = \nu / \kappa$, where ν is the kinematic viscosity and κ the thermal diffusivity). According to [7] the critical value of Rayleigh number above which instabilities occur is about 5×10^3 ($Ra = Gr \cdot Pr$) for a 4x1 horizontal geometry. Table II shows Grashof numbers calculated for various temperature gradients and melt height. These values were computed using the recent viscosity measurements by Kakimoto et al. [9] and the other parameters are from Jordan [10]. Table II, clearly indicates that unsteady periodic flows in deep melt can only be avoided if temperature gradients above the melt are as small as possible. The higher the Grashof number, the more stringent this requirement is. This was confirmed by our growth experiments since it was found that stable interfaces are obtained not only when radial gradients are reduced but also when the average temperature of the melt is decreased.

3.3. Arsenic source temperature and crystal perfection.

Due to end effects that influence the control of the first low temperature zone, the arsenic source temperature is best controlled with a thermocouple in contact with the end of the ampoule rather than in alignment with the other control thermocouples (see figure 1). The control parameters must then be adjusted to take into account the large distance that separates the thermocouple from the heating element. The arsenic source temperature (T_{As}) was found by Parsey et al. [11] to have a strong influence on the structural perfection of the crystals. A minimum in dislocation density was reached for $T_{As}=617^{\circ}\text{C}$. For our 5 and 7.5 cm diameter crystals, we observed the same phenomenon also for $T_{As}=617^{\circ}\text{C}$, however, the minimum is at about 2,000 to 5,000 dislocations cm^{-2} , (down from over 10,000 cm^{-2} at $T_{As}=620^{\circ}\text{C}$), while for small diameter crystals, Parsey et al. found that minimum at less than 500 dislocations cm^{-2} . A crystal representative of those grown during this study in the "EDG" furnace is shown in figure 6.

4. Conclusions

The "EDG" furnace operated in a horizontal configuration has been used successfully for growth of 2" GaAs single crystals. It provides reproducible growth conditions and allows the operator to shape the temperature profile to fit its specific needs. In the configuration that we used, axial temperature gradients are limited to less than $10^{\circ}\text{C}/\text{cm}$. For growth of GaAs, we operate at the upper limit of the heating element ratings. We found evidence of oscillatory flows and unstable growth interface for growth conditions yielding high Grashof number. Single

crystallinity cannot be sustained when the radial and axial components of the thermal gradients at the growth interface are about equivalent.

Crystalline perfection is improved by:

- increasing the axial temperature gradient over the solid
- decreasing the radial temperature gradient over the melt
- maintaining the arsenic source temperature to a constant value of 617°C.

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TABLE I. Axial temperature gradients on the solid side of the growth interface and maximum radial temperature gradients above the melt, corresponding to figures 3 and 4.

All values are given in $^{\circ}\text{C cm}^{-1}$.

Profile identification	Programmed values	Measured values on ampoule	Measured values inside ampoule	Maximum radial gradient
"flat" at 1188°C (a)	10	10	6	2.1
"flat" at 1188°C (b)	10	7	3	2.5
"flat" at 1188°C (c)	10	10	4	2.1
"flat" at 1100°C	10	10	7	1.1

TABLE II. Computation of Grashof numbers for various temperature differences across the melt and melt heights ($Gr = \beta g h^3 \Delta T \nu^{-2}$, where β is the coefficient of thermal expansion, g the acceleration of gravity, h the melt height, ΔT the difference in temperature between the cold and the hot end of the melt and ν the kinematic viscosity). The heavy line delineates the critical Grashof values for oscillatory flows. The bottom line indicates the corresponding maximum axial thermal gradients for stabilization of the convective flows in a 4x1 geometry.

Crystal diameter (cm)	2.5	5	7.5	10
h(cm) ΔT(°C)	1.25	2.5	3.75	5
1	3.1×10^2	2.5×10^3	8.3×10^3	2.0×10^4
3	9.3×10^2	7.4×10^3	2.5×10^4	5.9×10^4
5	1.5×10^3	1.2×10^4	4.2×10^4	9.9×10^4
10	3.1×10^3	2.5×10^4	8.3×10^4	2.0×10^5
15	4.6×10^3	3.7×10^4	1.2×10^5	3.0×10^5
20	6.2×10^3	4.9×10^4	1.7×10^5	4.0×10^5
25	7.7×10^3	6.2×10^4	2.1×10^5	4.9×10^5
30	9.3×10^3	7.4×10^4	2.5×10^5	5.9×10^5
Maximum axial temperature gradients (°C cm ⁻¹)	6.45	0.4	0.08	0.025

Figure captions

Fig. 1 Schematic of the "EDG" furnace used in this study.

Fig. 2 Typical temperature profile for growth of GaAs in the "EDG" furnace.

Fig. 3 Programmed temperature profiles for tests of the "EDG" furnace.

Fig. 4 Measured temperature profiles while using the programs shown in figure 3. The figure shows two sets of measurements for each profile: solid dots (●) are measurements on top of the ampoule, thermocouples 5 to 14, and open triangles (Δ) are measurements inside the ampoule during the growth run. Long dashes are profile (a), short dashes profile (b) and solid lines profile (c) and "flat" at 1100°C.

Fig. 5 (a) Growth interface shape of a crystal grown in a crucible without seed well and with a length-to-radius ratio of 6 (6x1 geometry);

(b) Interface shape calculated by Crochet et al [7] for a 6x1 geometry; $Gr = 2 \times 10^6$

(c) Isotherms calculated by Crochet et al. [7] for a 4x1 geometry; $Gr = 3 \times 10^5$.

Fig. 6 Example of 5 cm diameter crystal grown in the "EDG" furnace.

XBL 875-8896

Figure 1.

Figure 2.

XBL 875-10184

XBL 875-10186

Figure 3.

XBL 875-10183

Figure 4.

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