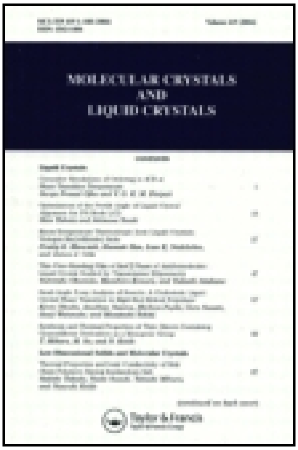

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Growing Condition of Anthracene Crystals

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Growing Condition of Anthracene Crystals

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Using the Bridgman method, anthracene single crystals were grown under several conditions. The parameters of the growth condition are both the lowering velocity of an ampoule and the temperature difference between the upper and lower furnaces. By measurement of the triplet lifetimes and observation of the etch pits of the non-basal dislocations, the quality of the crystals was estimated. The growth conditions under which the highest quality crystal (the triplet lifetime exceeds 25 ms) can be obtained, were found. These conditions are qualitatively established from a thermal equilibrium equation between the heat of solidification and the heat flow from liquid phase to solid phase.

Keywords: Bridgman method, triplet lifetime, anthracene single crystal

I. INTRODUCTION

The opto-electric properties of anthracene single crystals have been widely investigated and most studies are undertaken using crystals melt-grown by the Bridgman method. However, little attention has been paid to defining the optimum growth conditions on these crystals. For this reason, different experimental results have been obtained depending on the quality of the crystal. It has been found that the properties of anthracene single crystals are severely influenced by the impurities and lattice imperfections in the crystal.[1-3] Triplet lifetime is used as a probe for crystal quality estimation,[4,5] and it has been reported that crystals with a lifetime of 24–25 ms are the longest among the crystals available.[3]

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In this study, we report the triplet lifetime of anthracene single crystals which are influenced by the growth conditions. We take both the down velocity of an ampoule and the temperature difference between the upper and lower furnaces as parameters of the growth condition. Single crystals are melt-grown by the Bridgman method for several values of above parameters. The triplet lifetime of these crystals was measured and the number of etch pits was counted. Thus, the growth conditions for better quality can be determined. These conditions are qualitatively established from a thermal equilibrium equation between the heat of solidification and the heat flow from liquid phase to solid phase.

II. CRYSTAL GROWTH CONDITIONS

In the Bridgman method, the heat of solidification produced in the boundary layer between liquid and solid phases flows into the solid phase of the crystal and is dissipated through the ampoule wall. Therefore the heat of solidification produced per unit time is expressed as aRA, where A is the cross section of the inner diameter of an ampoule, R is the down velocity of the ampoule, and a is a proportionality factor. In Figure 1, the abscissa is the distance along the ampoule

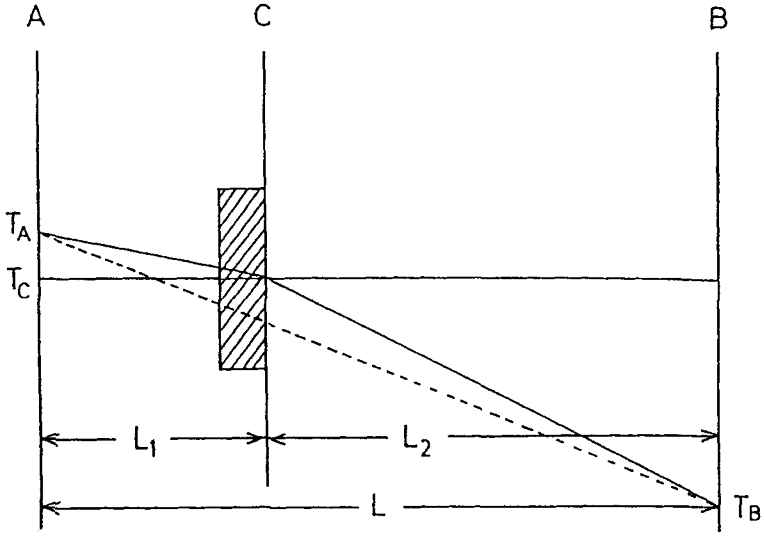

FIGURE 1 Schematic diagram at the solidification layer.

axis, the ordinate is the temperature, and the plane C is the boundary layer between liquid and solid phases. In this case, the liquid phase in the left portion of plane A is in thermal equilibrium with the upper furnace at temperature T_A, and the solid phase in the right portion of plane B is in equilibrium with the lower furnace at temperature T_B. Distance AB, AC, and CB are shown by L, L_1 and L_2 respectively. The shaded box to the left of plane C is R units thick, and expresses the portion of liquid which passes per unit time through the boundary layer and produces heat of solidification.

Considering thermal equilibrium in this box, with negligible heat flow in the radial direction, the following expression is obtained.

$$aAR + b(T_A - T_C)/L_1 = c(T_C - T_B)/L_2$$

where T_C is the temperature at plane C, b and c are proportionality coefficients for the thermal conductivity of the liquid and solid phases respectively. The second term on the left hand side expresses the heat flowing into the box, and the right hand side is the heat flowing out from the box.

For large values of R and constant $\Delta T = T_A - T_B$, a large amount of heat of solidification per unit time is produced, and thus the temperature gradient between C and B becomes large. As a result, the boundary layer moves toward the right and thermal equilibrium will be kept. On the other hand, for constant R and large ΔT, equilibrium is also kept with movement of the boundary layer toward the left. The boundary layer moves to the right when R is greater that the value of R corresponding to ΔT, and moves to the left when ΔT is greater than the value of ΔT corresponding to R.

The broken line in Figure 1 shows the temperature variation in the space outside the ampoule. If the boundary layer exists further to the right than shown in Figure 1, the heat flow in the outward and radial direction becomes large. As a result, disturbance occurs at the boundary layer during crystal growth. It is assumed that a small temperature difference between the ampoule and the outer space at the boundary layer produces a crystal of better quality. Thus there must exist a suitable value of $\Delta T/AR$ for crystal growth of better quality. Also, of course, thermal equilibrium can be more easily maintained for small values of $AR(\Delta T)$.

It should be noticed that temperature difference ΔT, rather than temperature gradient, should be used for the growth condition, because for large or small values of L with constant ΔT, that is, for large or small temperature gradients, the relative position of the C-plane with respect to the distance between the A- and B-planes changes little.

III. EXPERIMENTAL PROCEDURE

Sample powder (13076 Kodak scintillation grade) was purified by two azeotropic distillations, triple column chromatography and zone refining of 100 passes[6,7] under a pressure of 1/2 atmosphere of helium.[8] After zone-refining, the purified material was gently melted and transferred from the zone-refining tube to three ampoules without exposing by air, then the ampoules were sealed and separated from the tube. The schematic diagram of the crystal growth ampoule is shown in Figure 2. Crystallization starts in a tip of capillary. During the crystallization in a capillary, a crystallographic axis is fixed. The ab plane was perpendicular to the growing surface of the crystal for almost all cases.

In order to maintain the temperature inside each furnace constant, heat pipes (inner diameter 25mm, outer diameter 50mm) were used. The temperature of the upper furnace was kept at 230°C, and the

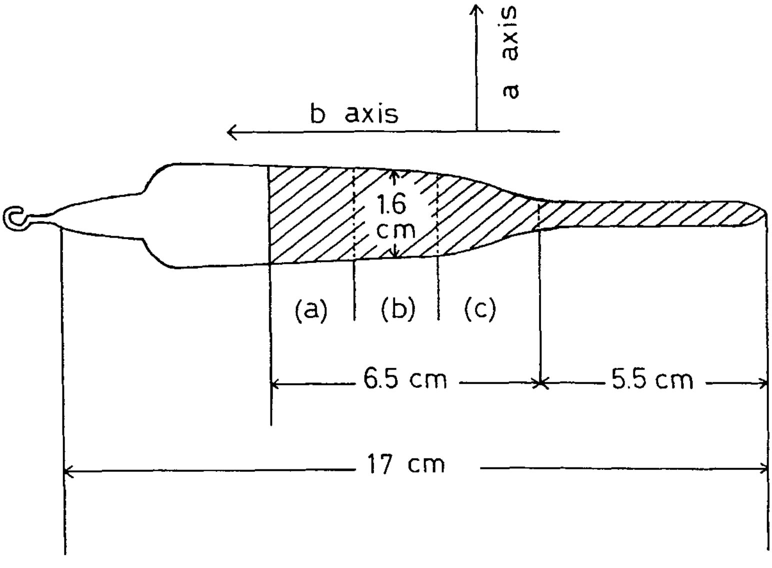

FIGURE 2 Schematic diagram of the crystal growth ampoule. (a), (b) and (c) are the upper, middle and bottom portion of the crystals in Table I and Table II, respectively.

lower furnace temperature was variable between 90°C and 200°C. The temperature fluctuation in the furnace was kept within ±0.1 °C by switching the heater power. The temperature variation along the axis is shown in Figure 3. The down velocity of the ampoule can be changed in six steps from 0.083 cm/h to 0.35 cm/h.

It should be noted that the annealing process, after the whole of the crystal has been transferred to the lower furnace, is very important. In this experiment, the temperature of the lower furnace was gradually lowered by switching the heater on and off to room temperature over a 24-hour period. Crystals were grown under several values of ΔT and R. The triplet lifetime was determined from analysis of the time decay of the delayed fluorescence caused by the mutual annihilation of triplet excitons.[9,10] Measurement was done on crystals which were not taken out of the ampoule.

The dislocation density on the cleavage surface of anthracene crystals was measured by counting the etch pits.[11-13]

IV. RESULTS AND DISCUSSION

Values for the triplet lifetime are shown in Figure 4. These values were measured along the axis of the ampoule for three crystals which had different lifetimes. In the middle portion of each crystal, lifetimes are long, and in the lower and upper portions lifetimes are short. These results may be attributed to the segregation of impurities in the lower and upper portions and/or to strain from the glass wall. It is found that the middle portion with the long lifetime expands for the crystal with a longer lifetime.

Values for triplet lifetime are shown in Table I for 12 crystals which were grown under different conditions. In the table, the values are classified for crystals with equal values of $C_{eq} = \Delta T/AR$. The values of the lifetime are mean values for respective portions. The longest triplet lifetime is obtained for $C_{eq} = 180$ °Ch/cm^3. For the same value of C_{eq}, the smaller $Q = AR(\Delta T)$ becomes, the longer triplet lifetime is obtained. Furthermore, a comparison is made of the etch pit concentration on the (001) surfaces of the crystals as a function of triplet lifetime. Bulk single crystals were carefully cleaved along the ab planes to make a specimen of approximately 2mm in thickness and cut to about 10×10 mm^2 in area. They were immersed in oleum for 30 seconds. The etched crystal faces are shown in Figure 5 (a) and (b). The triplet lifetimes are 23.9ms for (a) and 14.2ms for (b); the average non-basal dislocation density on the (001) plane is about 1×10^5 cm^{-2} and 2×10^6cm^{-2}, respectively. It is evident that the

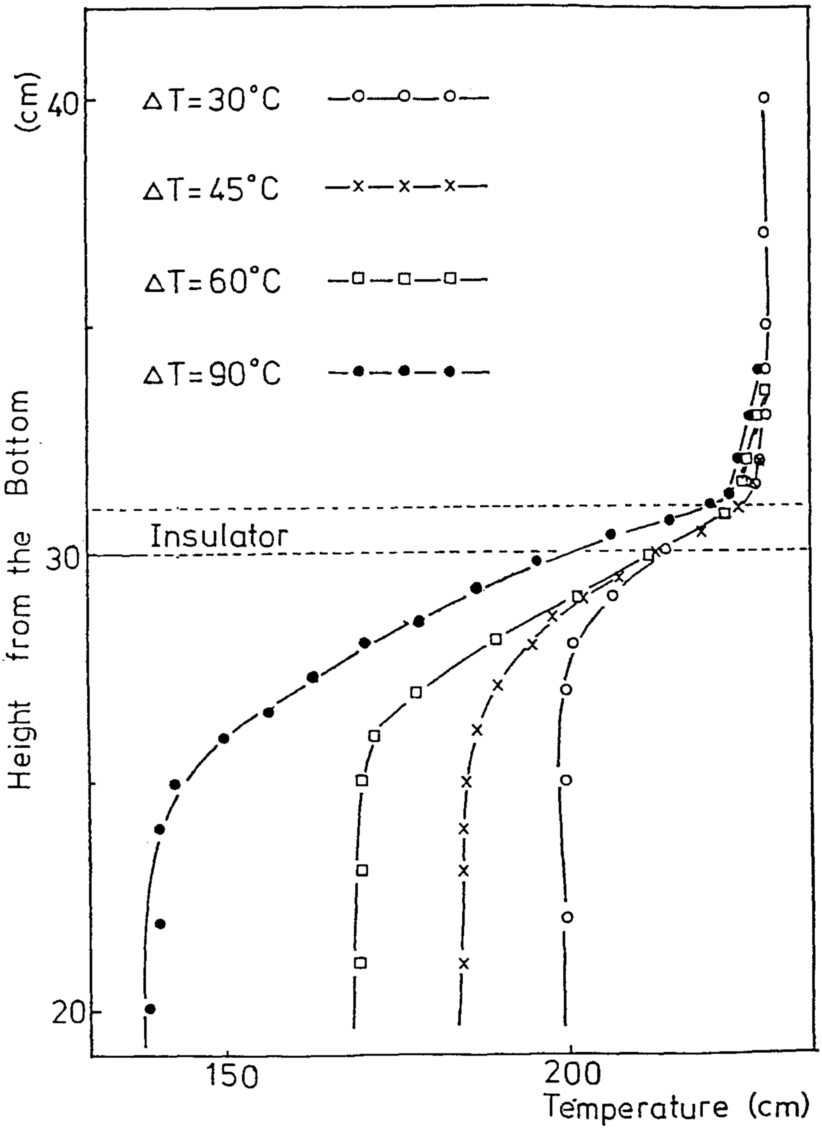

FIGURE 3 Temperature profiles in the space between furnaces.

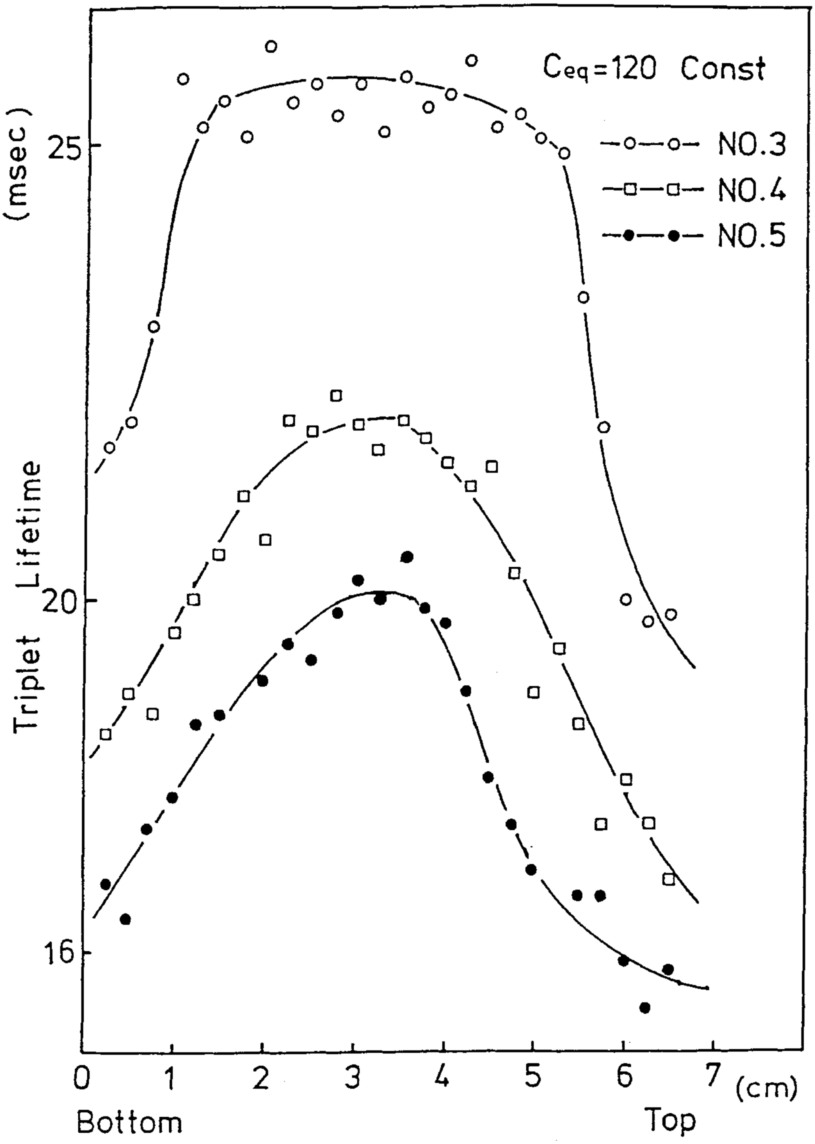

FIGURE 4 Triplet lifetimes for several portions of the crystal.

TABLE I

Growth condition and triplet lifetime. Cross section of ampoule is 2cm^2 for all cases. The value of the triplet lifetime is the mean value over the central axis of each crystal

	ΔT	R	$C_{eq} = \Delta T/AR$	$Q = AR(\Delta T)$	Triplet Lifetime (m sec)		
NO	(°C)	(cm/h)	(°Ch/cm^3)	(°Ccm^3/h)	Top	Middle	Bottom
1	30	0.25	60	15.0	20.3	21.9	20.2
2	45	0.38	60	34.2	17.1	19.5	17.6
3	30	0.13	120	7.8	22.9	25.5	23.5
4	60	0.25	120	30.0	18.4	21.7	19.8
5	90	0.38	120	68.4	16.5	19.6	17.7
6	30	0.083	180	4.98	23.7	26.2	24.4
7	45	0.13	180	11.7	23.4	26.3	24.8
8	60	0.17	180	20.4	23.5	25.8	23.6
9	90	0.25	180	45.0	20.2	23.0	21.2
10	60	0.083	360	9.96	24.0	24.9	21.2
11	140	0.18	389	50.4	19.8	21.6	22.7
12	140	0.083	840	23.2	21.8	20.4	21.3

number of non-basal dislocations decreases for the anthracene crystal with the longer triplet lifetime. Moreover, surface etching with oleum do not influence the triplet lifetime in the case of thick anthracene crystals, because the delayed fluorescence originates from the bulk of the crystals.

Taking AR as the abscissa and ΔT as the ordinate, crystals are classified in Figure 6 again. In the hatched area, the triplet lifetime is longer than 25ms, that is, if the crystal is grown under the conditions specified by AR and ΔT within this area, crystals of high quality could be obtained.

It is found that the temperature gradient G in the space between the upper and the lower furnaces is not important for obtaining crystals of high quality. Table II is another classification in which crystals are grouped for the same down velocity. Values of G and G/R are shown in the fourth and fifth columns of Table II respectively. It is difficult to find the relationship between these values and the values of the lifetime, that is, between the temperature gradient and the crystal quality.[14,15]

V. CONCLUSION

Using the Bridgman method, anthracene single crystals were grown under several conditions. By measurement of the triplet lifetimes and

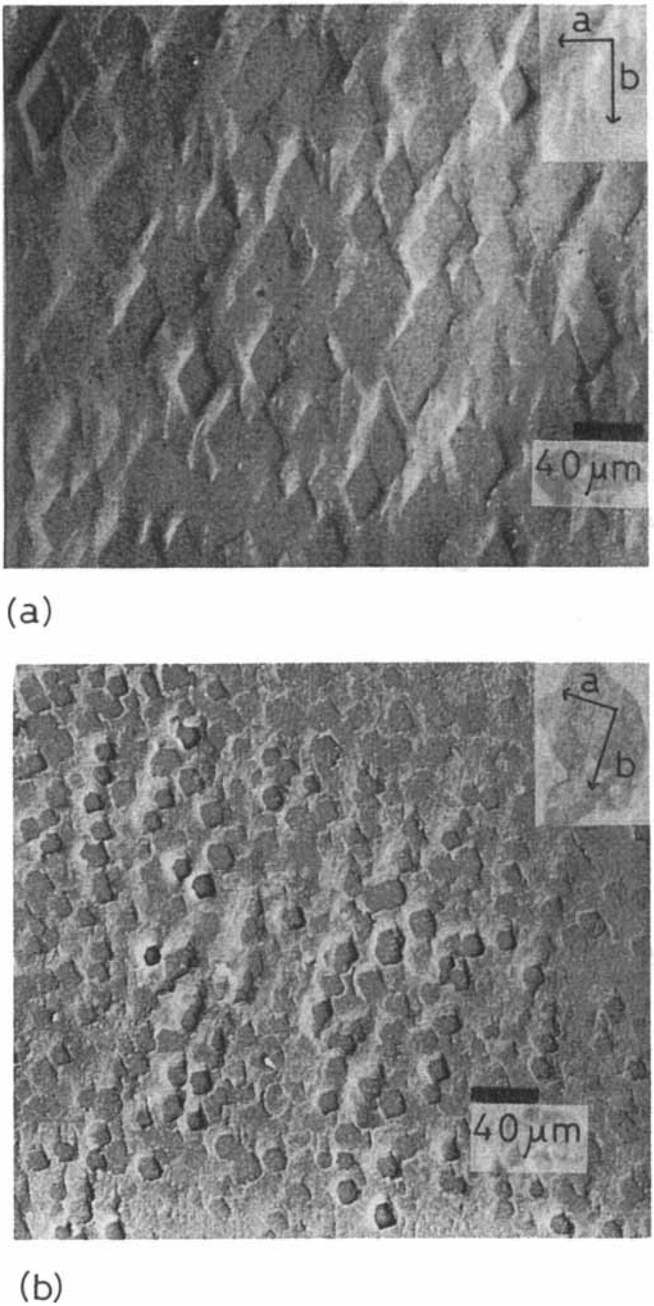

FIGURE 5 The etch pit distribution on the (001) face of anthracene single crystals. Triplet lifetimes are 23.9ms for (a) and 14.2ms for (b).

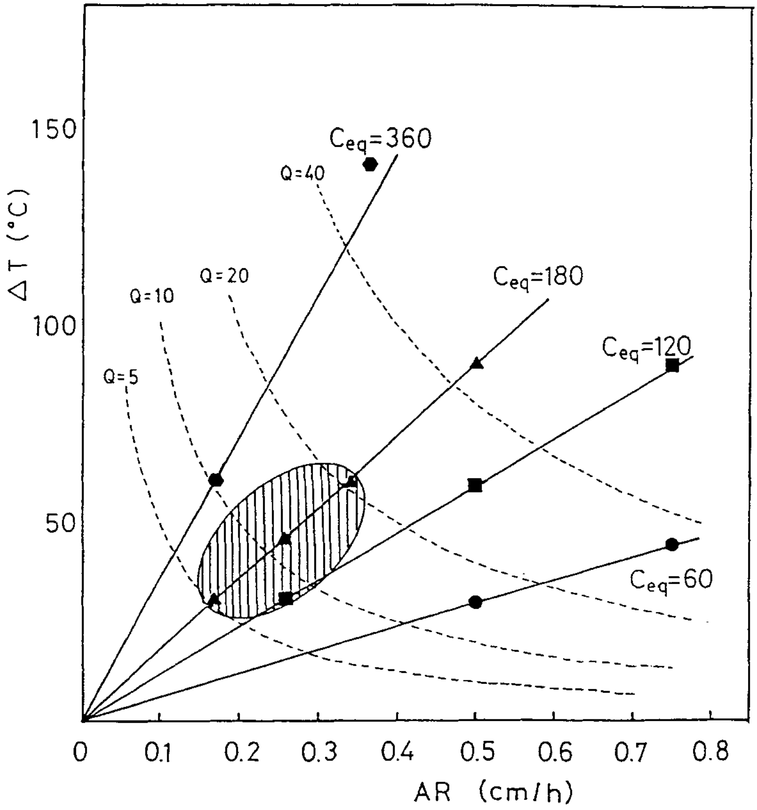

FIGURE 6 Dependence of crystal quality on C_{eq} and Q values.

TABLE II

Dependence of triplet lifetime on temperature gradient

	R	ΔT	G	G/R	Triplet lifetime (m sec)		
NO	(cm/h)	(°C)	(°C/cm)	(°Ch/cm^2)	Top	Middle	Bottom
2	0.38	45	11.9	31.3	17.1	19.5	17.6
5	0.38	90	18.1	47.6	16.5	19.6	17.7
1	0.25	30	8.7	34.8	20.3	21.9	20.2
4	0.25	60	12.5	50.0	18.4	21.7	19.8
9	0.25	90	18.1	72.4	20.2	23.0	21.2
8	0.17	60	12.5	73.5	23.5	25.8	23.6
11	0.18	140	20.3	113	19.8	21.6	22.7
3	0.13	30	8.7	67.0	22.9	25.5	23.5
7	0.13	45	11.9	91.5	23.4	26.3	24.8
6	0.083	30	8.7	105	23.7	26.2	24.4
10	0.083	60	12.5	151	24.0	24.9	21.2
12	0.083	140	20.3	245	21.8	20.4	21.3

observation of the etch pits of the non-basal dislocations, the quality of the crystals was estimated. The growth conditions under which the highest quality crystal can be obtained, were found. These were verified on the assumption that there exists no radial heat flow at the boundary layer. It was concluded that the temperature difference between upper and lower furnaces, rather than temperature gradient, is the important growth condition.

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