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Research in real time of some thermal and mass growth parameters of BGO and BSO crystals during the Czochralski process with weight diameter control

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The results obtained during the Czochralski (CZ) growth of $Bi_{12}SiO_{20}$ and Bi_{4-12} Ge_{1-3} O_{12-20}, BSO and BGO respectively, crystals in an apparatus with weight diameter control are analysed. Behaviour of some physical and technological parameters is investigated in real-time. The curves of temperature, conical angle, weight and first weight, and diameter derivative with respect to time, as functions of time or changing temperature, are presented. The best ratio between the crystal and crucible diameter related to radiative heat exchange is found. In the growth stages, both the cylindrical and conical crystal parts are analysed. The results are compared with well known numerical models of the CZ process.

1. Introduction

Czochralski (CZ) growth analysis dates from 35–40 years, when Billig [1] first derived an analytical relationship to describe the effect of pull rate on the radius of a germanium crystal. The advance of high speed digital computers was a possibility for extending one's understanding of the CZ process on the basis of numerical modelling. For example, thermal capillary models [2–4], or quasi steady state models [5, 6] and their extension for oxide systems [7], analysis of heat transfer after including thermal conductivity of the melt and the crystal, and fluid flow convection. Considering the CZ process as an inherent stable process, the idea was adopted that the main cause for destabilization of the process was decrease of the melt layer. Thus, the ability for assimilation of heat, and the axial temperature gradient, decrease too.

Most numerical simulations hint at the growing role of crucible wall radiation during the process (especially for oxide crystals, where the radiation number, $R_\alpha = 1$–10, [8]. But Derby [8] and coworkers [9] do not suppose that radiation exchange is able to provoke a process increase of the axial temperature gradient with time. Ramachandran and coworkers [10, 11] also model detailed radiation in the CZ process, but only in the case of a cylindrical crystal; their approximations are inapplicable of accounting for the moments of seeding and are poorly controlled batchwise. Dupret *et al.* [12] compute diffuse grey radiation in the CZ. When diameter fluctuations should considerably influence the realization of latent heat of crystallization; but they only consider cylindrical crystals and simplified interface surfaces, representative of the melt, crucible and ambient.

However, crucial questions concerning the inherent stability of the CZ process, suggested by Surek and coworkers [13, 14], can be answered only by discussion which allows the crystal radius to change in time and which results in a non-cylindrical crystal. Atherton *et al.* [9] present a similar discussion of the variation of crystal radius, provoked by radiation at ambient with regions of different temperature.

On the other hand, [15] proposes a mathematical model for the cooling crystal during Czochralski pulling, which accounts for radiative heat transfer between the crystal and an enclosure representing the crucible wall, heater and heat shields. The seed and the conical shoulder section are included, as well as a cylindrical crystal part.

The main purposes of the present paper are thus to

1. compare the results of the development of some thermal and mass growth parameters during experiments with predicted behaviour with well known models (especially in respect to radiation heat exchange and the relation between heater temperature and crystal weight), and
2. determine some useful technological parameters for automatic CZ growth of BSO and BGO crystals.

2. Experimental procedure

Crystal growth experiments have been carried out with crusilite resistive heater. The rotating speed was constant at about 15 r.p.m. During the different experiments the pull rate ranged from 0.8 to 1.2 mm h^{-1}, and was constant when the weight control was set into operation. The heater temperature was measured. The authors preferred to measure the weight of the melt remaining in the crucible [16, 17], which yielded a higher real signal-to-noise ratio as compared to the weight of the crystal itself [16, 18], and at the same

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time this procedure was simpler from the point of view of construction. The weight was measured by an electron digital balance, operating on the principle of electromagnetic compensation, with an accuracy of 0.01 g.

The signals for temperature and weight entered a computer device (based on a Z80 processor) communicating with the control computer, PC IBM.

The computer program was written in the high level language, C. A proportional-integral-differential (PID) regulating a temperature and weight closed loop was realized. The temperature regulator limited the temperature fluctuations in the melt. As Picone [19] mentions, the temperature fluctuations can worsen crystal quality and may cause, the appearance of a so-called "central core" in the crystal structure. In the weight closed loop, the difference between measured and calculated values of the weight loss rate during crucible weighing was a perturbation of the temperature and a basis for correction of the thyristors opening angle in the field thyristor block.

The special program arrangement allowed mathematical elimination of errors in the signals in a way in which n values (determined by the non-linear median method) went through a double average. Thus, the average value, dm_{av}, of the weight loss rate was determined by the formula

$$dm_{av} = \frac{\sum_{i=1}^{n} [(m_{i+1} - m_i)/i]}{n} \quad (1)$$

At every step of the cycle one of the measured values was assumed to be a basic one.

3. Results and discussion

$Bi_{12}SiO_{20}$, $Bi_{12}GeO_{20}$ and $Bi_4Ge_3O_{12}$ crystals with diameters, up to 50 mm, cylindrical parts length up to 100 mm and good optical characteristics were obtained (Fig. 1).

The interface shape was flat or slightly convex towards the melt for most of the crystal. Usually, a central core was absent from the structure.

Fig. 2 a–c shows the dependence of heater temperature, T_h, on time, t, during the whole process. The different temperatures of seeding (when $t = 0$) are due to different locations of the crucible. These values give information about the initial axial furnace temperature gradient. The curves show that to obtain large crystal diameters, larger temperature differences are not so necessary as longer cooling time. To maintain the desired diameter it was necessary to increase almost linearly the heater temperature to the end of these experiments (Fig. 2a). The duration of the temperature increase was longer for larger diameters.

When the ratio $d_{crystal}/D_{crucible}$ became more than 0.5, the program maintained the diameter by two temperature deviations displaced in 20 h, one behind another (Fig. 2a, b). The more the crystal diameter increased, the more deviations were increased and receded further and further (Fig. 2b). A tendency to decrease the heater temperature appeared. When this ratio became more than 0.67, the growth process represented a nearly linear decrease of the heater

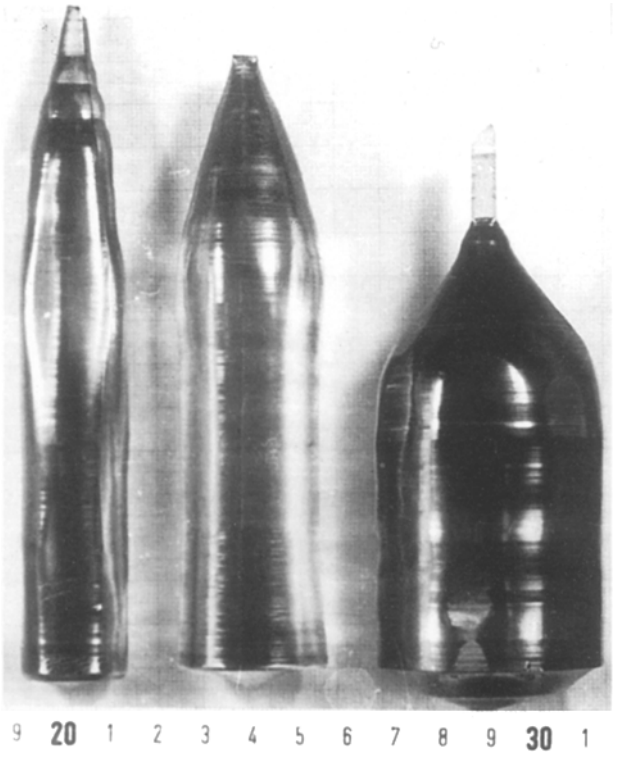

Figure 1 Some of the crystals obtained in the experiments with temperature–weight diameter control.

temperature, T_h, for the entire time after seeding. For example, cooling at a rate of 72 μV gave $dT_h/dt = 0.003\ \mu V\ min^{-1}$ (Fig. 2b). This software limitation of the heater temperature is evidence that the axial temperature gradient into the system increases with decreasing melt layer for large diameters of the investigated materials. Such a possibility is inadmissible in the field of well known numerical models of the CZ process.

Experiments showed (Fig. 2a, b) that systems with ratios $0.5 > d_{crystal}/D_{crucible} > 0.6$ are the most suitable for regulation. For example, the heater temperature was nearly constant during growth of a cylindrical body when the ratio $d_{crystal}/D_{crucible}$ was 0.62–0.63 (Table I). The result is in absolute accordance with numerical models which consider CZ growth as an inherent stable process. In the present case it was not process replenishment of the crucible, but radiation heat exchange between the crystal and the crucible wall, that played the role of a stabilizing factor.

For all that, Berkowski *et al.* [20] presented a well grounded investigation of the convectional fluid flows and the awaited change in the melt after $h_{melt} < d_{crystal}$(where h_{melt} is the melt layer thickness) and ratios $d_{crystal}/D_{crucible} > 0.5$. As far as [21] is categorical that the quality of crystals grown from the melt for use in microelectronic applications is strongly affected by the complex flow occurring in the fluid phase, adherence to these critical values is of great importance for semiconductor systems, especially in the absence of magnetic stabilization, suggested by [22]. Fortunately, for the investigated oxide crystal materials with optical applications, the connection between crystal quality and melt flow convection is not so drastic.

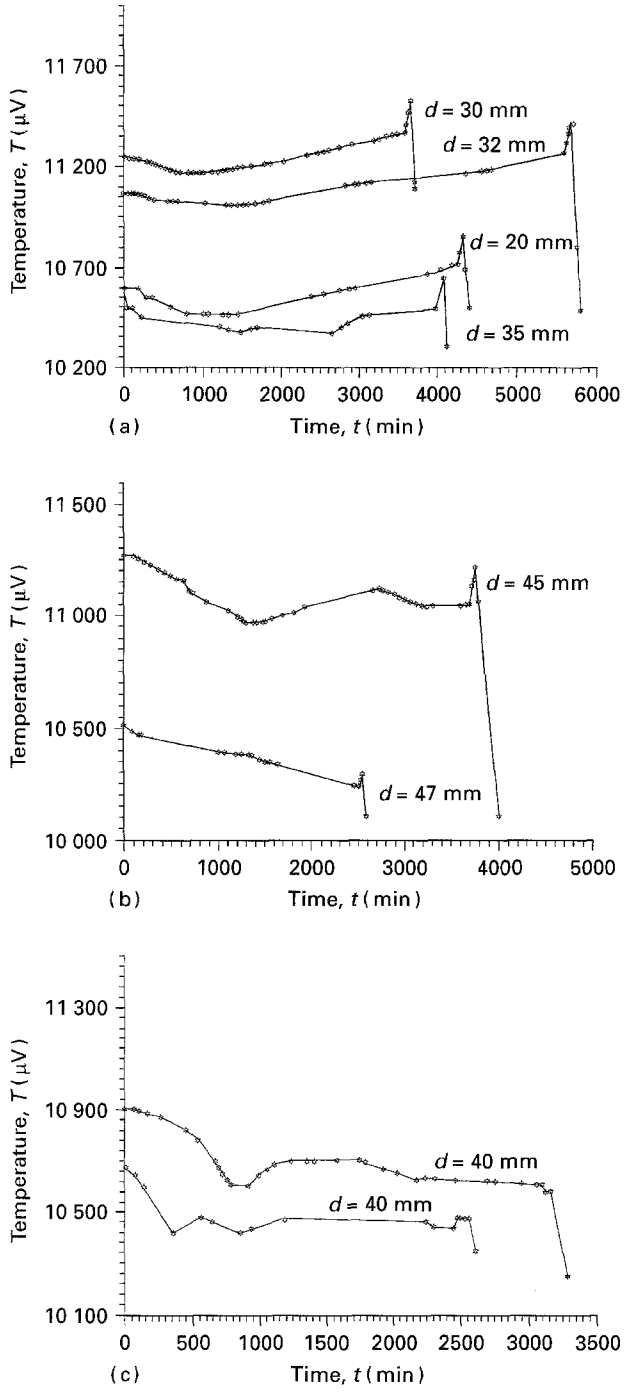

Figure 2(a–c) The dependence of $T = f(t)$ during the whole process.

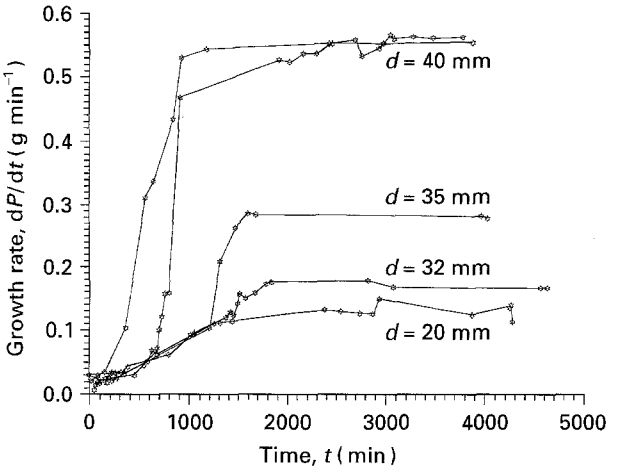

Figure 3 The dependence of $dP/dt = f(t)$ during the process.

In part of the present experiment, weight control was set into operation immediately after seeding. In these cases larger fluctuations of T_h were observed during growth of the crystal periphery (Fig. 2c). These fluctuations had an effect on the establishment of the weight growth rate, dP/dt, as a constant during the growth of the cylindrical part of the crystal (Fig. 3). The curves on Fig. 3 show the first weight derivatives with respect to time for the whole process. During cylindrical body growth, $dP/dt \approx$ constant for most of the curves.

Fig. 4 shows the relation between measured, P_m, and advisable P_c weight values for the crystal weight as a function of time. The curves show that P_m/P_c grew nearly equal to unity only during growth of the cylindrical part of the crystal. This is new evidence that conical and peripheral growth are a more complex test for the control system compared to the cylindrical growth.

Fig. 5 shows the first diameter derivatives with respect to time as functions of the temperature changes during conical growth. The average value of dD/dt is 23 μm-min^{-1} for BGO, and 35.5 μm-min^{-1} for BSO. The BSO-crystals show less dependence on the initial axial temperature gradient.

The dependence of the top conical angle on the first temperature derivative with respect to time is

TABLE 1 Some physical and technological parameters during the growth of crystals with different diameters

	Rotation rate (r.p.m)	Pull rate (mm h^{-1})	$d_{crystal}$ (mm)	$d_{crystal}/D_{crucible}$	Crystal weight (g)	Conical part ΔT (μV)	Conical part $(\Delta T/\Delta t)_{av}$ (μV min^{-1})	Conic angle (deg)	Cylindrical part ΔT (μV)	Cylindrical part $(\Delta T/\Delta t)_{av}$ (μV min^{-1})	Cylindrical part $(dP/dt)_{av}$ (g min^{-1})
$Bi_{12}GeO_{20}$	15	1.8	20	0.285	1382	− 145	− 0.156	24	261	0.088	0.14
$Bi_{12}GeO_{20}$	15	1.2	30	0.428	813	− 83	− 0.094	66	206	0.076	0.16
$Bi_{12}GeO_{20}$	15	1.2	33	0.457	728	− 60	− 0.042	45	258	0.062	0.17
$Bi_{12}GeO_{20}$	15	1.8	35	0.500	712	− 230	− 0.141	38	125	0.058	0.29
$Bi_{12}SiO_{20}$	15	1.7	40	0.571	1019	− 267	− 0.312	43	56	0.034	0.55
$Bi_{12}SiO_{20}$	15	1.7	40	0.571	907	− 253	− 0.252	55	47	0.030	0.55
$Bi_{12}SiO_{20}$	15	1.7	42	0.600	716	− 249	− 0.233	63	22	0.009	0.58
$Bi_{12}GeO_{20}$	15	1.8	43	0.614	734	− 247	− 0.123	67	13	0.005	0.64
$Bi_{12}GeO_{20}$	15	1.2	44	0.628	652	− 91	− 0.037	68	9	− 0.003	0.79
$Bi_4Ge_3O_{12}$	15	0.8	45	0.643	1405	− 125	− 0.122	81	− 158	− 0.069	0.65
$Bi_4Ge_3O_{12}$	15	1.2	47	0.671	896	− 102	− 0.029	62	− 172	− 0.031	0.92

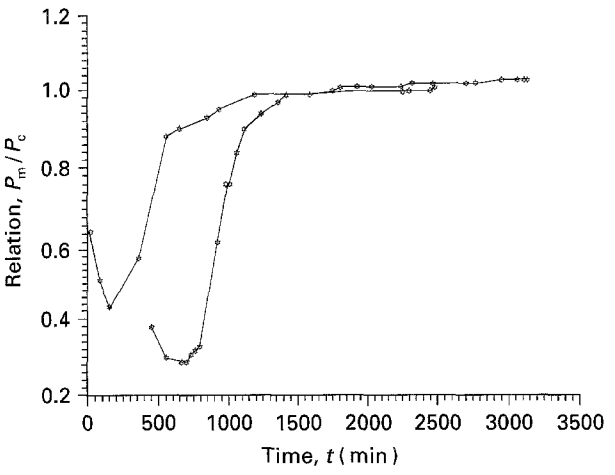

Figure 4 The relation $P_m/P_c = f(t)$ during the process.

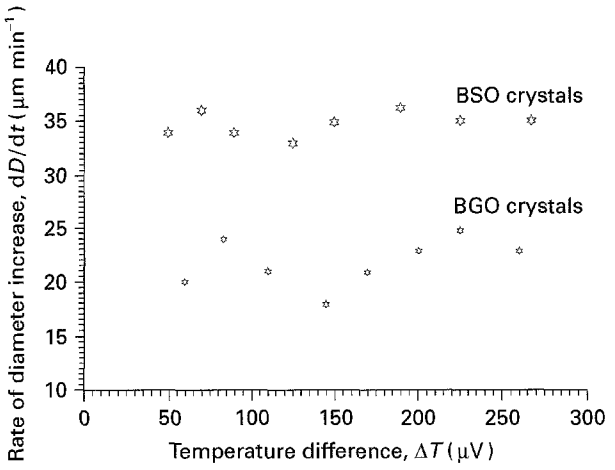

Figure 5 The dependence of $dD/dt = f(\Delta T)$ for BSO and BGO crystals during conical growth.

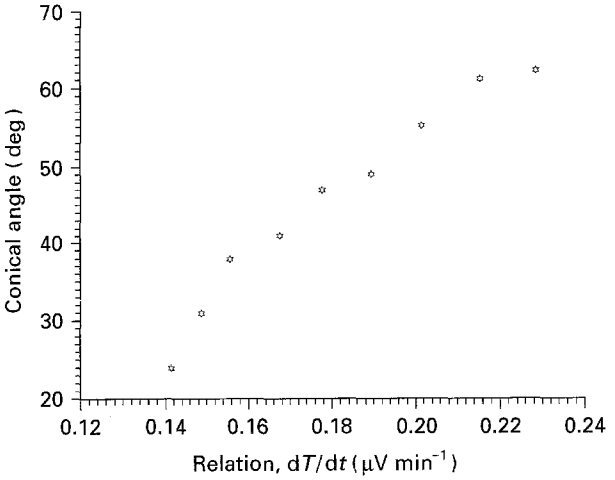

Figure 6 The dependence of conical angle $= f(dT/dt)$ during the growth of BGO crystals.

comparable for all investigated materials. Fig. 6 shows this dependence for $Bi_{12}GeO_{20}$ crystals.

Some numerical data of the process for different crystal diameters (see Table I) give further information. For example, the relation $\Delta T/\Delta t$ for the conical and cylindrical part of the crystal, respectively, decreases with increasing crystal diameter when the pull rate is constant.

4. Conclusions

About fifty crystal growth experiments have been carried out with the created control system and program. The dependence of heater temperature, conical angle, weight and first weight and diameter derivative with respect to time, on the time or temperature changes, has been established.

Experiments show that during conical growth not temperature, but time of cooling is essential to obtain the desired crystal diameter. The larger diameters needed small dT/dt rates.

Subsequent fluctuations of heater temperature and weight growth rate have been observed when weight control has been brought into operation immediately after seeding.

Systems with a $d_{crystal}/D_{crucible}$ ratio below 0.5 and above 0.6 are proved to be the most suitable to regulation during cylindrical growth. In the first case the heater temperature increased almost linearly after the beginning of cylindrical growth. However, in the case of $d_{crystal}/D_{crucible} > 0.67$, T_h decreased almost linearly during the whole process. When the $d_{crystal}/D_{crucible}$ ratio was ~ 0.62–0.63, the heater temperature was nearly constant for the entire time of cylindrical crystal growth.

The results confirmed the predictions of well known numerical models that the CZ growth is an inherent stable process. However, they established too that radiation heat exchange between the crystal and crucible wall can provoke an increase of the axial temperature gradient with melt layer decrease for oxide systems. The last fact contradicts them.

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