Pulling large bismuth-silicon-oxide crystals

J. C. Brice, M. J. Hight, O. F. Hill and P. A. C. Whiffin

The use of acoustic waves on the surfaces of solids has made it possible to replace the present bulky intermediate-frequency filter of a colour-television set by a device of about the same size as a transistor. Such devices offer a considerable saving in space and materials and eliminate the need for i.f. alignment. They are also suitable for many other applications in which exactly tailored passbands and phase responses are required. However, the devices are only economically viable if suitable crystals can be produced. This article describes an investigation into the growth of crystals of a potentially suitable material and illustrates the difficulties experienced in bringing a new material from the initial research stage to a point at which industrial production can be contemplated.

Introduction

Crystals have always played a large part in science and technology. Most of the basic knowledge of solid materials is derived from investigations carried out on crystalline samples. Practical applications of the use of single crystals are gramophone styli, watch bearings and electronic devices, such as transistors, integrated circuits and quartz resonators.

Establishing the suitability of a crystal or class of crystals for application in a device is a long and complex process. It is necessary first to prove that useful devices can be made. Then it must be shown that likely variations in the growth process do not result in unacceptable changes in device properties. Thirdly, it has to be proved that the crystals can be grown in such quantities and sizes that economic device production is possible. All of the first stage and most of the second can be done with laboratory-scale crystals. However, the next stage and establishing the economic viability requires larger crystals to test both the device-production methods and the crystal-growth procedures.

In this article we shall touch upon a number of problems encountered in the growth of such large crystals. Examples include the problem of thermal strain — an analysis of this enables us to predict certain growth conditions that are independent of crystal size — and hydrodynamic effects in the melt which depend on the growth parameters. These effects are described on a semi-quantitative basis for bismuth-silicon-oxide crystals, but many of the results are found to be generally applicable to other crystals. Our examination of the economics of crystal growth show that, subject to some limits, growing bigger crystals does reduce costs in device production and that automation is very desirable. As we shall show, the economic and technological aspects are interlinked.

Bismuth-silicon-oxide crystals

The interaction between electrical and mechanical effects can be used to give components which transmit signals at some frequencies and reject all others. These components are usually based on a resonance effect; devices using effects in the bulk of quartz crystals have been known for many years (crystal oscillators). More recently, it has been shown that waves on the surface of crystals can be used in the same way with the advantage that by a simple fabrication it is possible to tailor the passband of frequencies to suit any application.[1]

The work to be described here was part of a project to make such devices suitable for use in television receivers, where one component about as large as a transistor can replace a large array of inductors and capacitors, giving a considerable saving of space, materials and time required for manufacture and alignment. It appeared likely that crystals of bismuth oxide would provide a material suitable for this purpose. A number of crystals of the $\gamma$-bismuth oxides were grown[2], and it seemed from the measured properties and the relative difficulty in growing the various crystals that $\mathrm{Bi}_2\mathrm{SiO}_5$ would be the best material. The correctness of this
The 'equilibrium' shape of Bi₁₂SiO₂₀ (BSO) is shown in fig. 1. Crystals like this could be produced from solutions or hydrothermally but growth by these methods is slow and the method adopted was the more rapid technique of pulling from the melt. However, in spite of the fact that this was a familiar technique, the investigation of the growth of BSO produced some unexpected results and required consideration of aspects which had previously been neglected. This was partly because the properties of BSO differ significantly from those of materials usually grown by this method and partly because of the need to grow large crystals to minimize device costs.

In the following sections of this paper we shall discuss the basic process, the composition of the crystals and its variation, the thermal strain and cracking, hydrodynamic effects during pulling and other technological aspects. The last section deals briefly with the economic aspects of crystal pulling. While the properties of BSO differ from those of other materials, as mentioned earlier, a great deal of knowledge which has been acquired during this study is generally applicable.

**Basic pulling technique**

In principle, the pulling method is simple. Fig. 2 shows the essential parts of the system. A melt made from weighed amounts of the component oxides (Bi₂O₃ and SiO₂) is contained in a platinum crucible heated by radio-frequency currents induced in it by the coil, which is connected to an r.f. generator. A seed crystal is brought into contact with the melt and the melt temperature is adjusted so that a small amount of the seed melts. Growth is started by slightly lowering the melt temperature and slowly raising the seed crystal. Material from the melt is pulled upwards and crystallizes. The seed crystal is rotated during growth to improve mixing in the melt and to increase the symmetry of the temperature distribution. The diameter of the crystal is controlled by changing the heat flow into the crystal. The most direct method for doing this is to change the melt temperature: lowering the temperature increases the crystal diameter and vice versa. Small crystals with diameters of about 10 mm could be grown at rates of about 6 mm per hour; the rotation rate was not critical. For larger crystals the conditions had to be adjusted with more care, as will be discussed later. Initially we used very pure starting materials contain-

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4. In the hydrothermal method, crystals are grown under very high pressure and at a high temperature, usually from a saturated aqueous solution. See for example A. Rabenau and H. Rau, Philips tech. Rev. 30, 89, 1969.
ing only one or two parts per million of impurities; the crystals were of a pale yellow colour.

When the curved growth face intersects the natural (100) and (110) faces of the crystal, flat regions are formed, the 'facets' (fig. 3). The material grown on these facets was slightly different in colour. There is, however, no measurable difference in composition inside and outside the facets. The lattice constant in the facets is at most 0.01 pm (i.e. 0.0001 Å) larger than elsewhere. We shall return to this later. Fig. 4 shows a BSO crystal obtained by pulling; its diameter is 42 mm.

Fig. 3. Diagram of the axial cross-section of a pulled BSO crystal, showing the facets (shaded).

Fig. 4. A pulled BSO crystal with a diameter of 42 mm; its weight is 1.4 kg.

Composition of the crystals

Since small variations in the growth process are inevitable, it is important to establish that these have no significant effect on the properties of the devices. Therefore it was necessary to grow crystals under slightly different conditions and with different compositions of the melt. As a starting point, changing the relative amounts of Bi₂O₃ and SiO₂ in the melt should change the relative amounts in the solid. Fortunately this proved to be only a weak effect. If we describe the material as Bi₂SiO₁₅+x², we found that the composition in the melt could be varied from Bi₁₀SiO₁₇ to Bi₁₂SiO₂₃ (x between 10 and 14) without affecting the composition of the crystals produced, provided the growth rate was low. At high growth rates, if x varied significantly from 12 in the melt, inclusions of the excess oxide were found in the crystals. It was found that x in the solid varied very little: the minimum and maximum values were 11.77 and 12.05. These values did not correspond to the minimum and maximum values in the melt. We can therefore conclude that the composition in the melt is not critical.

From the data it is possible to plot the relevant part of the phase diagram which is shown in fig. 5. On this diagram the melt composition is labelled Liq and the crystal composition is labelled Sol. Liquids and solids at the same temperature are in equilibrium, e.g. the melt m₁ is in equilibrium with the crystal having the composition c₁, and melt m₂ gives a crystal having the composition c₂. The compositions c₁ and c₂ are those with the minimum and maximum bismuth contents. If the composition of the melt differs from the composition of the crystal, the composition of the melt will change during the growth of the crystal, since the quantities of Bi and Si removed from the melt are different. However, crystals grown from a melt near the points m₁ and m₂ — the tangent to the curve is vertical there — have compositions which vary only very slightly down their lengths. For other melt compositions, x in the crystal can change by as much as 0.2 if half the melt is used up.

In surface-wave devices we could detect no change in properties when the composition was changed. A melt of composition m₁ or m₂ did however produce crystals which were less strained and therefore more robust.

Traces of impurities had no measurable effect on the surface-wave properties, but did affect the colour of the crystals, some of which were sensitive to light (photochromism): directly after growth the crystals were pale yellow, but some crystals became considerably darker on exposure to daylight.

Crystals were grown from many different batches of starting materials from different suppliers. The impurity contents ranged from less than 10 parts per million (ppm) to about 2000 ppm. Since most impurities fit
badly in the lattice, they are rejected by the growing crystal (see Table I) and the crystals typically contained from 2 to 10 ppm of impurities (measured relative to the silicon content). The results of the analyses did not enable the impurity causing the photochromism to be unambiguously identified, but crystals containing significantly less than 1 ppm of both iron and chromium always stayed yellow, while crystals containing more than 1 ppm of either iron or chromium always darkened.

As we mentioned earlier, the lattice constant on the facet is a little larger than in the crystal; see Fig. 6. This leads to mechanical strain around the facet. On the (100) facets this distortion amounts to about a third of the strain at which the crystal would break. Regions of high dislocation density can therefore be seen outside the facet.

The strain due to the facet is a function of the ratio of the facet area to the total cross-sectional area. Since in general the facet regions are relatively small,

The facets

The flat parts of the boundary surface where the crystal growth occurs arise because the growth mechanisms on the curved and natural faces are different. The growth on the curved face is due to a random deposition of molecules, while the growth on the natural faces requires the simultaneous deposition of a number of molecules.

The size of the facets increases as the growth face is made less curved. Increasing the rate of rotation of the seed crystal flattens the face and hence makes the facets larger; a similar effect can be produced by increasing the rate of pull. The faceted area in our crystals was typically 1 to 2% of the cross-section. At the greatest rates for stable growth facets were produced that occupied more than 20% of the cross-section.

The larger lattice constant cannot be explained by another composition for the facet material. Fig. 7

Table I. The ratio of the concentration in the crystal to the concentration in the melt of Bi₂SiO₅ for 24 impurities.

<table>
<thead>
<tr>
<th>Element</th>
<th>Crystal</th>
<th>Melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.2</td>
<td>Cu</td>
</tr>
<tr>
<td>Na</td>
<td>0.1</td>
<td>Zn</td>
</tr>
<tr>
<td>Al</td>
<td>0.7</td>
<td>Ga</td>
</tr>
<tr>
<td>S</td>
<td>0.07</td>
<td>Ge</td>
</tr>
<tr>
<td>K</td>
<td>0.3</td>
<td>Br</td>
</tr>
<tr>
<td>Ca</td>
<td>0.2</td>
<td>Ag</td>
</tr>
<tr>
<td>Ti</td>
<td>0.3</td>
<td>In</td>
</tr>
<tr>
<td>Cr</td>
<td>0.8</td>
<td>Sn</td>
</tr>
<tr>
<td>Mn</td>
<td>0.05</td>
<td>Te</td>
</tr>
<tr>
<td>Fe</td>
<td>0.2</td>
<td>Ba</td>
</tr>
<tr>
<td>Co</td>
<td>0.2</td>
<td>Pt</td>
</tr>
<tr>
<td>Ni</td>
<td>0.2</td>
<td>Pb</td>
</tr>
</tbody>
</table>

the total strain of the crystal is negligible, but crystals with large facets were usually more fragile.
shows the lattice constant of the crystal as a function of the ratio of bismuth to silicon $x$. To explain a difference in lattice constant of 0.01 pm, $x$ would have to be greater than 12 on the facet. However, chemical analysis of material grown on the facets and close to them showed no difference in the ratio of bismuth to silicon.

No significant difference in impurity content could be detected on and away from the facets, except that silver appeared to be preferentially absorbed on the facet. But even this impurity did not occur in the crystals in sufficient quantity to account for the observed lattice-constant variations; these would have required hundreds of ppm.

It has been suggested that the $\gamma$-bismuth-oxide structure can contain some Bi$^{5+}$ ions in addition to the Bi$^{3+}$ ions. If this is the case the lattice will contain some bismuth and oxygen vacancies. It can be postulated that if Bi$^{5+}$ is preferentially incorporated on the facets, its presence would increase the oxygen-ion content there and thus increase the lattice constant in the manner observed.

The growth rate

There are three effects that set a limit to the rate at which a crystal can be pulled. In the first place there is the latent heat, which must be removed; secondly, there is the formation of inclusions and the absorption of impurities from the melt, and finally the danger of cracking due to thermal stress. The first two set a limit to the rate at which thin crystals can be pulled; in thick crystals the chief danger is that the crystal may crack. We shall now examine these three limitations in order.

If the crystal grows at a rate of $f$ cm/s the quantity of latent heat evolved at the boundary surface between crystal and melt will be $\frac{L}{f}$ joules per cm$^2$, where $L$ is the latent heat per cm$^3$. This latent heat is conducted away via the crystal, since this is cooler than the boundary region, which is exactly at the melt temperature $T_m$, and the molten mass in the crucible is somewhat hotter. The heat flow in the crystal at the growth face is equal to $\lambda c (dT/dz)g$, where $\lambda c$ is the thermal conductivity of the crystal and $(dT/dz)g$ is the vertical temperature gradient at the boundary. This temperature gradient depends on the dimensions of the crystal and on the rate at which the crystal can give up its heat to the surroundings. This is proportional to the temperature difference $T_m - T_0$ between the hottest point of the crystal (the boundary) and the surroundings. As is shown in the Appendix, the temperature gradient at the boundary is given by:

$$(dT/dz)_g \approx c(T_m - T_0)/R^{1/2},$$

where $R$ is the radius of the crystal and $c$ is a constant of proportionality that depends on the thermal conductivity of the crystal and the heat-transfer coefficient of its surface.

It can be seen that the heat flow through the crystal does not depend on the pulling rate. This does however determine the contribution of the solidification process.
to the heat flow. Conversely, the given heat flow therefore determines the maximum permissible value \( f_{\text{max}} \) for the pulling rate. If this is exceeded, not all of the latent heat can be conducted away via the crystal and the temperature at the boundary rises; the contact between crystal and melt then fails.

At the rate \( f_{\text{max}} \) we have for the production and removal of heat

\[
 f_{\text{max}}L = \lambda_e (dT/dz)_g = c\lambda_e(T_m - T_0)/R^{1/2}.
\]

The maximum pulling rate is therefore given by

\[
 f_{\text{max}} = c(\lambda_e/L)(T_m - T_0)/R^{1/2}. \tag{1}
\]

This rate is clearly proportional to \( R^{-1/2} \).

From (1) it would appear that the maximum pulling rate could be increased by reducing the ambient temperature \( T_0 \). However, we then encounter some of the effects mentioned above that limit the pulling rate: the chance of formation of inclusions in the crystal and the absorption of impurities from the melt. We shall now examine this more closely.

The transport of material from the melt to the growth face is of course proportional to the growth rate of the crystal. The melt contains impurities, and, as mentioned previously, one of the main components can be present in excess. Since these are not absorbed by the crystal, a high concentration of these substances will be present in the melt near the growth face. These must mix with the melt again by diffusion.

The analyses were performed by J. B. Clegg, who used solid-source mass-spectroscopic methods with a detection limit of much less than 1 ppm. While the absolute accuracy of the method is uncertain without elaborate calibration, differences of a factor of 1.5 or more are obvious. See for example J. B. Clegg and E. J. Millett, Philips tech. Rev. 34, 344, 1974.

D. C. Craig and N. C. Stephenson, Structural studies of some body-centered cubic phases of mixed oxides involving Bi\(_2\)O\(_3\): the structures of Bi\(_2\)FeO\(_4\) and Bi\(_3\)ZnO\(_6\). J. Solid State Chem. 15, 1-8, 1975.
As we saw above, a reduction in $T_m - T_0$ requires a proportionate reduction in the growth rate $f$. If $e_b$ is the maximum permissible value of $e$, then by combining (1) and (2) we have an expression for the maximum permissible pulling rate $f_{\text{max}}$:

$$f_{\text{max}} \propto \frac{e_b}{\alpha} \cdot R^{-3/2}.$$

The maximum growth rate is thus no longer proportional to $R^{-1/2}$, as derived for smaller crystals, but to $R^{-3/2}$. This relation is shown as line $b$ in fig. 8. This line gives the relation between the radius of the crystal and the maximum growth rate at which the crystal will not crack. For BSO the lines $a$ and $b$ intersect at a crystal radius of about 1.5 cm.

**Cooling**

After the crystal has been grown, it has to be cooled to room temperature. If this is done too quickly, the temperature gradients will become too large, and the crystal may crack because of differences in expansion. It is clear that the heat loss through the crystal to its surroundings may be of about the same magnitude as the heat loss during the pulling process. We saw that the temperature difference between the hottest point of the crystal and the ambient temperature, $T_m - T_0$, must be approximately inversely proportional to the radius $R$. The heat loss $w$ per second and per cm of height is given approximately by

$$w \approx 2\pi R(T_m - T_0).$$

Since $T_m - T_0$ is proportional to $1/R$, the heat loss does not depend on the radius of the crystal.

The heat content of the crystal per cm of height is $\pi R^2 c T$, where $c$ is the specific heat per unit volume and $T$ is the mean temperature. Since the heat loss is constant, we should have:

$$\frac{dT}{dz} = \frac{1}{\gamma R^2}.$$

The proportionality constant $\gamma$ is determined by the specific heat, the thermal conductivity $\lambda$, the coefficient of linear expansion $\alpha$, and the maximum strain before cracking. It is given by:

$$\gamma = 8\frac{\lambda e_b}{\alpha c}.$$

Some of the properties of bismuth-silicon oxide are summarized in Table II and fig. 10. From these it can be shown that the greatest rate of cooling is equal to $74/R^2 \, ^\circ\text{C}/\text{hour}$ at the melting point and twice this value at room temperature. For crystals of radius 2 cm we find, in practice, a maximum rate of 20 °C per

<table>
<thead>
<tr>
<th>Table II. Some properties of bismuth-silicon oxide.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Quantity</strong></td>
</tr>
<tr>
<td>Density, solid</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Density, liquid</td>
</tr>
<tr>
<td>Linear expansion coefficient</td>
</tr>
<tr>
<td>Volume expansion coefficient</td>
</tr>
<tr>
<td>Specific heat/unit volume, solid [*]</td>
</tr>
<tr>
<td>Specific heat/unit volume, liquid [*]</td>
</tr>
<tr>
<td>Thermal diffusivity</td>
</tr>
<tr>
<td>Thermal conductivity</td>
</tr>
<tr>
<td>Viscosity</td>
</tr>
<tr>
<td>Young's modulus</td>
</tr>
<tr>
<td>Breaking strain</td>
</tr>
<tr>
<td>Latent heat [*]</td>
</tr>
<tr>
<td>Cooling constant ($\mu/\lambda$)</td>
</tr>
</tbody>
</table>

[*] The value shown relates to Bi₂O₃; value for BSO is not known.

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*Fig. 9. Diagram of a cracked crystal. Cracks are usually formed at 45° to the axis.*

*Fig. 10. The variation of thermal diffusivity $\alpha$ with temperature. (From data supplied by Dr T. M. Bruton, formerly with PRL.) The line $C$ applies to the crystal; line $M$ to the melt. The thermal conductivity can be found by multiplying $\alpha$ by the specific heat per unit volume (see Table II).*
hour — i.e. within 10% of the predicted value. Nearer to room temperature 35-40 °C per hour is satisfactory, as against a calculated value of about 50 °C per hour. For smaller crystals \( R = 1 \text{ cm} \) the rates are found to be about four times higher. These various values indicate that the treatment given above is satisfactory. We have also found these theoretical predictions to be valid for other crystals such as lithium niobate.

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The transition regime 12b is difficult to represent because the flow at any point varies with time. Temperature measurements in the transition conditions vary wildly. Fig. 13 shows the regions in which the various flow regimes exist. In region a an axially symmetrical flow occurs. Region b corresponds to an asymmetrical flow giving temperature variations with time at a fixed point and in region c the flow is again axially symmetrical. Detailed study was only made of the transition from a to b, so that only these measured

Hydrodynamic effects

In the investigation of the pulling of large BSO crystals it was found that the rate at which the crystal is rotated is also associated with an upper limit. This is related to the fact that the rotation of the crystal does not always bring about a rotation of the complete melt, which can therefore be inhomogeneous. We are not referring here to the well known growth striæ — the strains associated with these are small — but to effects that can have more serious consequences.

Our study of melt stirring started from the observation that in some instances dark swirl patterns were observed on the melt surface (fig. 11). If these patterns appeared, e.g. due to a change in the crystal rotation rate, the effect could be catastrophic: a large change in the interface shape occurred and the change in heat flow cracked the crystal. Similar effects had been seen in garnets and other investigators have reported the same effect in other materials. An experimental and theoretical investigation \(^{(7)}\) showed that the observed effect was the result of a change in the flow pattern from that shown in fig. 12a ultimately to that shown in 12c.

![Fig. 11. Swirl patterns observed on the surface of the melt. While these patterns are obvious to a human observer, they are difficult to photograph because they precess and the available viewing angles are not very suitable. (a) to (f) represent the views seen as the rotation rate increases.](image-url)
points are plotted. From the available data and the available theory it is likely that a maximum crystal-rotation rate is to be expected. This rotation rate is a function of the temperature gradient in the melt, the viscosity of the melt, the radius of crystal and crucible and the pulling rate \( f \). Table III summarizes the data for bismuth-silicon oxide. The same theory can be applied to gadolinium-gallium-garnet production and the predicted and observed crystal-rotation rates are in good agreement [8].

Table III. Temperature gradient, growth rate and critical rotation rate for five combinations of crystal and crucible diameter.

<table>
<thead>
<tr>
<th>Crystal diameter (cm)</th>
<th>Crucible diameter (cm)</th>
<th>Gradient ((^\circ\text{C/cm}))</th>
<th>Growth rate (mm/hr)</th>
<th>Critical rotation rate (rev/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>3.5</td>
<td>10</td>
<td>6</td>
<td>70</td>
</tr>
<tr>
<td>1.7</td>
<td>3.5</td>
<td>10</td>
<td>5</td>
<td>45</td>
</tr>
<tr>
<td>2.8</td>
<td>5.0</td>
<td>12</td>
<td>4</td>
<td>25</td>
</tr>
<tr>
<td>3.2</td>
<td>6.0</td>
<td>17</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td>3.7</td>
<td>8.6</td>
<td>20</td>
<td>2.5</td>
<td>15</td>
</tr>
</tbody>
</table>

**Automation**

The growth rate of large crystals is only a few millimetres per hour, as we saw in fig. 8. The complete process, including cooling down, takes five days for a large crystal like the one shown in fig. 4. This makes an automatic control not only economically desirable but a practical necessity. A number of experiments were carried out to detect the critical parameters to be measured and controlled to obtain a constant growth rate and a constant diameter. Attempts were made to control the process by regulation of the power in the r.f. coil and also by stabilization of the temperature of the melt. Our colleagues in Aachen also developed a laser-reflection system to measure the crystal diameter near the growth face. All systems failed on different points, however. They were not stable enough over long periods of time, not applicable to large crystals or the initial settings of the controls were not reproducible. The alternative approach of using a weighing system was therefore adopted [9].

**Fig. 12.** Elevation and plan views of flow in a crucible at three rates of crystal rotation. In (a) the central column under the crystal rotates almost as a solid body and there is little mixing of particles from this column with the outer annulus, but the column is itself well stirred. In (b) the flows in the column and annulus mix and in (c) the whole melt is stirred.

Fig. 14 is a block diagram of the system. With this system the melt weight is controlled so that it is always very near to a target value produced by a reference source. Since a constant crystal diameter gives a constant rate of reduction of weight, the programmer to produce the target can be a very simple electromechanical system. However, for greater flexibility a numerical technique has been adopted. In the initial phase of the growth, when the crystal is growing from seed to full diameter, the weight of the melt increases nonlinearly with time. The growth pattern is also nonlinear in the final phase, when the diameter of the crystal decreases. In between the weight of the melt increases linearly with time. The necessary digital data can easily be derived from a microprocessor.

This system has produced crystals with diameters within 5% of the target diameter and with variations in diameter of less than 2%. The discrepancy from the target diameter was caused by small variations in the pulling rate and in the crucible diameters; both affect the growth rate of the crystals.

**Other technological aspects**

The apparatus described at the beginning of this article needed little modification for pulling crystals of larger diameter. The only significant change was to mount the puller on anti-vibration mountings. This was done because our building vibrates at frequencies between 7.5 and 9.5 Hz, and the puller had a resonant frequency of 7.5 Hz. An antivibration mount with a resonant frequency of 4 Hz reduced the vibration on the puller by a factor of about 4. Seed crystals with square cross-sections were used; each side of the
caused by cutting damage. To reduce stresses on the seed crystal, it was wrapped in gold foil before being fastened in place and the holder for the crystal was attached to the pulling shaft by a series of ball-joints so that the system was self-aligning. These measures reduced seed-crystal failure from about 30% to 5%. The crucibles were made from platinum containing less than 200 ppm of rhodium. (A higher rhodium content gave rise to corrosion, which soon led to crucible failure.) The internal heights and diameters of each of the crucibles were the same within ±20% and we used successively diameters of about 35, 50, 60, 85 and 110 mm. The smaller crucibles had wall thicknesses of 1.5 mm and the bigger ones 2 mm. In use the crucibles distorted by about 5% before we discarded them; usually after about 20 runs. We looked for other materials but our tests showed that most metals, oxides and nitrides are rapidly corroded by the melt.

In order to obtain the temperature distributions necessary to prevent cracking heat shields were required.

Fig. 15 shows the assembly used for 40-mm diameter crystals. Table IV lists the sequence of operations, which can be fitted conveniently into a working week.

**Table IV. Operational sequence for pulling 40-mm diameter BSO crystals.**

<table>
<thead>
<tr>
<th>Time from start (hrs)</th>
<th>Phase of process</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>Start melt down</td>
</tr>
<tr>
<td>2</td>
<td>Put seed crystal into melt</td>
</tr>
<tr>
<td>2.5</td>
<td>Start pulling and cooling for expansion</td>
</tr>
<tr>
<td>10</td>
<td>Start parallel growth</td>
</tr>
<tr>
<td>60</td>
<td>Start tapering in</td>
</tr>
<tr>
<td>68</td>
<td>Growth complete</td>
</tr>
<tr>
<td>105</td>
<td>Crystal all inside heat shield. Start to cool melt</td>
</tr>
<tr>
<td>130</td>
<td>Power off</td>
</tr>
</tbody>
</table>

**Economic aspects**

Very little has been published on the economic aspects of crystal growing. Probably the reason is that the costs of the crystal production form only a small part of the production costs of a device. In this section we shall make a few comments on the costs of device production: it will appear that larger crystals are more economical than smaller ones, for both growth and processing.


[8] This attachment system was designed and made by V. E. Cox, of our Laboratories.
Fig. 15. The pulling apparatus used for growing crystals 40 mm in diameter. M melt in platinum crucible. C crystal. SH holder for seed crystal. FC flexible coupling. HS heat shield with viewing gaps. S. RFC r.f. heating coil with supply RFL. ST silica tube that insulates the water-cooled coil RFC from the hot crucible. Sup support for the crucible. W weighing cell.

Table V. The effect of crystal dimensions on the times necessary for various device-fabrication processes. The quantity $L$ can be identified with either the length or the diameter of the crystal, since these are in approximate proportion.

<table>
<thead>
<tr>
<th>Process</th>
<th>Time per device inversely proportional to</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal orientation</td>
<td>$L^3$</td>
</tr>
<tr>
<td>Crystal cutting</td>
<td>$L$</td>
</tr>
<tr>
<td>Slice processing</td>
<td>$L^2$</td>
</tr>
<tr>
<td>Device separation</td>
<td>$L$</td>
</tr>
</tbody>
</table>

After the BSO crystal has been grown there are six further stages necessary for the production of filters. The crystal directions are determined by X-ray methods and slices of known orientation are cut. These are polished, electrodes are evaporated on to them and patterns are etched in the electrodes. Finally, the filter elements are separated from the array on the processed slice. With large crystals the handling costs are lower. Table V shows how the time taken for various processes depends on a typical dimension $L$ of the crystal. (It is assumed that length and radius change in proportion, which is usually the case for pulled crystals.) The table suggests that the handling times decrease at least linearly with increasing size and that correspondingly large savings in man and machine time can be made. So even if the price per kilogram of the crystalline material is the same, there are good reasons for spending a great deal of effort to solve the problems of growing large crystals.

However, large crystals can be made more cheaply and more effectively than small ones. For a pulled bismuth-silicon-oxide crystal fig. 8 shows that $f R^{1/2}$ is a constant for smaller crystals and that for larger crystals $f R^{3/2}$ is a constant. The production per hour of single crystals can be calculated from this information. This is plotted in fig. 16, which shows the hourly production of a crystal as a function of crystal radius. It is clear that machines pulling larger crystals have a higher hourly output in spite of the lower pulling rate.

The automation, necessary for the long pulling times, gives an additional saving in money. The yield from automated production, in our experience, is 65-75% instead of 40-50% for the manual process. In addition, the predictability of the product from an automated system should not be overlooked.

Fig. 16. The volume $V$ of single-crystal bismuth-silicon oxide produced per hour, as a function of the radius $R$ of the pulled rod.
Device-production processes are most economic with a fixed size of crystal. Exceeding the target radius $R$ by an amount $\Delta R$ wastes a fraction $2\Delta R/R$. Hence if an error $\Delta R$ can arise, the target must be increased by this amount with the associated wastage. In our case automation at least halted this wastage at $R = 2$ cm. Further reduction in costs would be expected if resistance heating was used instead of radio-frequency heating. Finally, Table VI gives a few cost factors and shows how they contribute to the costs per unit volume of crystal pulled.

Table VI. The effect of the pulling rate $f$ and the radius $R$ of the crystal on the cost per cm$^2$ of the crystal produced, for the five most important factors.

<table>
<thead>
<tr>
<th>Factor</th>
<th>Cost inversely proportional to</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy</td>
<td>$fR/R$</td>
</tr>
<tr>
<td>Platinum crucible</td>
<td>$fR^2/R^2$</td>
</tr>
<tr>
<td>Manpower</td>
<td>$fR^2$</td>
</tr>
<tr>
<td>Material</td>
<td>$fR^2$</td>
</tr>
<tr>
<td>Machine time growth cooling</td>
<td>$fR^2$</td>
</tr>
</tbody>
</table>

[*] Decrease in the growth rate may allow less pure materials to be used.

Appendix: Calculation of the temperature distribution in a crystal

Let us assume (see Fig. 17) that a crystal C at the position $z = 0$ is in contact with a melt at the temperature $T_m$. The diameter of the crystal is $2R$, the thermal conductivity is $\lambda$ and the heat transferred from the surface of the cylinder to the surroundings (shown here as a heat shield $H$) is equal to $\mu(T - T_o)$, where $\mu$ is a constant determined by the method of cooling, the surface of the crystal, etc., and $T_o$ is the external temperature. If we also put $\mu R(1/\gamma)$, and if $J_0(x)$ is the zero-order Bessel function of argument $x$, then the temperature of the crystal at the position $r, z$ can be calculated [11]:

$$T(r, z) = T_o + 2(T_m - T_o) \sum_{n=0}^{\infty} \frac{\gamma}{\beta_n^2 + \beta_n \gamma} \times$$

$$\frac{J_0(\beta_n r/R)}{J_0(\beta_n)} \exp(-\beta_n z/R). \quad (A1)$$

The values of $\beta_n$ are calculated as solutions of the equation

$$\beta_n J_0'(\beta_n) - \gamma J_0(\beta_n) = 0,$$

where $J_0(\beta_n)$ is the first-order Bessel function of argument $\beta_n$.

For very small values of $\gamma$, i.e., for very thin crystals of high thermal conductivity, we only require the first term of this series. Since $\beta_0$ is small we can replace the Bessel functions by the first term of their power series. Equation (A2) then gives

$$\frac{1}{2} \beta_0^2 = \gamma,$$

so that

$$\beta_0 = (2\gamma)^{1/2},$$

and equation (A1) is reduced to:

$$T(r, z) \approx T_o + (T_m - T_o) \frac{1 - \gamma r^2/R^2}{1 - \gamma} \exp(-2\gamma r^2 z/R^2).$$

The gradient of the temperature at the growth face is therefore given by:

$$\frac{dT}{dz} \approx -(T_m - T_o) \frac{(2\gamma)^{1/2}}{R} \frac{1 - \gamma r^2/R^2}{1 - \gamma}.$$

Since $\gamma$ is small and equal to $\mu R(1/\lambda)$, a first approximation for the temperature gradient is

$$\frac{dT}{dz} \approx -(T_m - T_o) \frac{2\gamma}{R} \cdot \frac{1}{R^{1/2}}.$$

In the case of BSO $\gamma$ is approximately equal to 0.4$R$. A more accurate calculation [13], also valid for larger values of $\gamma$, gives:

$$\frac{dT}{dz} \approx -(T_m - T_o) \frac{(2\gamma)^{1/2}}{R^{1/2}}.$$

The difference between the accurate and the approximate values is therefore small.

If the temperature distribution is not uniform there will be strain, since the different parts of the crystal do not have the same expansion. The strain $\varepsilon_0$ of a ring of radius $r$ is given by [13]:

$$\varepsilon_0 = \frac{1}{R^2} \int_0^R \frac{r}{R} \frac{J_0(\beta_n r/R)}{J_0(\beta_n)} T_r dr.$$

If the strain is calculated from the approximate temperature distribution, it is found that the highest permissible temperature gradient at the boundary surface is given by:

$$\frac{dT}{dz} \max = \frac{4\varepsilon_0}{\pi R^{1/2}} \left(1 - \gamma^2\right) \left(1 - \gamma R^2 z/R^2\right)^{1/2}.$$

where $\varepsilon_0$ is the strain at which the crystal cracks. Since the strains

Fig. 17. Calculation of the temperature distribution in a crystal.

Table VI. Calculated and measured values of the maximum permissible temperature gradient $(dT/dz)\max$ in the crystal for four values of the crystal radius.

<table>
<thead>
<tr>
<th>$R$ (mm)</th>
<th>$(dT/dz)\max$ (°C/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>180</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
</tr>
<tr>
<td>19</td>
<td>20</td>
</tr>
</tbody>
</table>

in the axial and tangential directions are approximately equal (see fig. 7). $e_b$ is approximately equal to $2^{1/2}e_0$.

A more accurate calculation can also be made here; it gives:

$$\left(\frac{dT}{dz}\right)_{\text{max}} = 8 \frac{e_b}{\alpha} \left(\frac{\lambda}{\mu}\right)^{0.84} \frac{1}{R^{1.34}}.$$ 

The maximum permissible growth rate is found by substituting the expression just derived for $(dT/dz)_{\text{max}}$ in the relation

$$f_{\text{max}} = \frac{\lambda}{L} \left(\frac{dT}{dz}\right)_{\text{max}}.$$ 

Some calculated and measured values of the temperature gradient are summarized in Table AI.

**Summary.** Crystals with the cubic $\gamma$-bismuth-oxide structure, such as bismuth-silicon oxide, can be used to make surface-wave filters for TV and other applications. Large crystals of this material weighing several kilograms and with diameters up to 50 mm have been grown at PRL using a pulling technique. To avoid cracking due to thermal strain the maximum permissible axial thermal gradient has to be proportional to $R^{-3/2}$, where $R$ is the crystal radius, whereas for inclusion-free growth the axial thermal gradient has to be proportional to $R^{-1/2}$. The composition of the crystals is found to be highly independent of the composition of the melt. Effective control of the rotation rate is very important to avoid hydrodynamic instabilities. The long pulling times necessary for the growth of large crystals and the reproducibility required made an automated equipment desirable. This system keeps the diameter constant to within 2% and the maximum difference from the desired value is 5%. Devices are cheapest when made from large crystals.
Recent scientific publications

These publications are contributed by staff of laboratories and plants which form part of or cooperate with enterprises of the Philips group of companies, particularly by staff of the following research laboratories:

Philips Research Laboratories, Eindhoven, The Netherlands
Philips Research Laboratories, Redhill, Surrey, England
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Philips GmbH Forschungs laboratorium Aachen, Weißhausstraße, 51 Aachen, Germany
Philips GmbH Forschungs laboratorium Hamburg, Vogt-Kölln-Straße 30, 2000 Hamburg 54, Germany
MBLE Laboratoire de Recherches, 2 avenue Van Becelaere, 1170 Brussels (Boitsfort), Belgium
Philips Laboratories, 345 Scarborough Road, Briarcliff Manor, N.Y. 10510, U.S.A. (by contract with the North American Philips Corp.)

Reprints of most of these publications will be available in the near future. Requests for reprints should be addressed to the respective laboratories (see the code letter) or to Philips Research Laboratories, Eindhoven, The Netherlands.


V. Chalmeton: Chaîne de radioscopie 400 kV avec intensificateur à galette de microcaux. Acta Electronica 20, 53-64, 1977 (No. 1).


LSI

In about 1960 there was good reason to say that there had been a revolution in electronics, for in less than ten years the transistor had virtually replaced the thermionic valve in nearly all kinds of application. Today, however, we are in the midst of developments that are even more drastically changing the face of electronics — with no end in sight. When transistor manufacturers changed from the alloy to the planar technology — based on photolithographic processes — it only depended on the nature of the photomasks whether a small, simple circuit was produced or a large, complicated circuit consisting of hundreds of interconnected elements. Now it was possible in principle to make larger and larger integrated circuits. In 15 years integrated-circuit technology has advanced from SSI (small-scale integration; 10 gates per chip) via MSI (medium-scale integration; 100 gates per chip) to LSI (large-scale integration; 1000 gates per chip), and now we are on the threshold of the next great advance (VLSI, very-large-scale integration; $10^4$ gates per chip).

This evolution would not have been possible without detailed and extensive research in the large industrial research laboratories, including those of Philips. Readers will probably remember the contributions from Philips Research that have been described in earlier volumes of this journal: the issue on MOS technology, and many articles such as those on the LOCOS process, injection logic ($I^2L$), and the 'Optycograph'.

While the full impact of this later and greater revolution in electronics has only penetrated to the user in recent years, the research is by no means at an end. It therefore seemed appropriate to make LSI the subject of this special issue that completes our volume for the year. We start with an introductory article that gives a general picture of the evolution from the simple transistor to the LSI circuit and its repercussions on the designing of electronic circuits. Other articles include contributions on the subject of lithography — including the use of electron beams — and on the computer-aided design of large-scale integrated circuits. Three of the articles deal with specific LSI applications: an N-MOS circuit for telephony, an $I^2L$ circuit for data transmission, and an image sensor based on the charge-transfer principle.

An issue of this size cannot of course give anything like a full picture of Philips activities in the IC field — not even in research. The next volume will therefore contain a few other instances of advances in IC technology or applications. For the present, we will close by noting that developments in integrated circuits are now so rapid that those who are in the front line of the research may regard certain approaches as already out of date even before the work has left the IC development laboratory or has appeared in print.
Manufacturing ever-larger integrated circuits requires continuous improvement in the control of the processes and conditions of production. It is of the utmost importance, for example, that the least possible amount of dust should settle on the wafer during the different operations. At Philips Research Laboratories in Eindhoven all experimental integrated circuits are therefore made in a specially built department that has its own 'clean room'. The number of dust particles of half a micron and larger contained per unit volume of this room is about ten thousand times smaller than in an ordinary laboratory working-space. All the operations necessary for the fabrication of integrated circuits are performed in this room. The equipment is set up in 'lanes'. In the lane on the right of the photograph the silicon wafers are given a coating of photoresist and then illuminated through a mask. In the lane on the left the wafers undergo wet-chemical etching.