JOURNAL OF MATERIALS SCIENCE 2 (1967) 7–11

Single-Crystal Growth of Sapphire

B. COCKAYNE, M. CHESSWAS, D. B. GASSON
Royal Radar Establishment, Malvern, Worcs, UK

Received 17 August 1966

Two techniques are described by which single crystals of sapphire may be grown. One is a development of the vertical-pulling technique for the production of scatter-free, low-dislocation-density material, whilst the other is an extension of a floating-zone, recrystallisation technique previously used for calcium tungstate. The origin and control of defects in crystals grown by these techniques are discussed.

1. Introduction

Single-crystal sapphire (melting point 2050° C) is desirable as a substrate material for the epitaxial deposition of silicon [1]. It is mechanically hard and therefore capable of being polished to an accurately planar surface: this is an important, practical consideration in the manufacture of modern transistor devices based upon silicon layers. Additionally, sapphire is an insulating material, and a difficulty encountered in devices prepared by the conventional deposition of silicon upon silicon, namely the need to back-bias p-n junctions to achieve electrical isolation, is thus avoided. The use of sapphire therefore simplifies circuit design, and allows the preparation of devices which can operate at high frequencies.

Prior to this work, the sapphire used for substrates was grown primarily by a flame-fusion technique. Such material generally contains dislocation low-angle boundaries which propagate similar boundaries into the deposited silicon layer, and thus impair the electrical characteristics of the layer. Sapphire crystals can also be grown by flux techniques [2]. Flux-grown crystals often contain inclusions, but are free from low-angle boundaries; the crystals, however, generally form as thin plates, from which it is difficult to cut usable areas of crystal planes other than those of the type {0001}.

Earlier work in this laboratory has demonstrated that the vertical-pulling technique can be so controlled as to produce oxide crystals such as calcium tungstate (melting point 1600° C) [3] and yttrium aluminium garnet (melting point 1970° C) [4] with a high degree of crystalline perfection. The present paper describes the extension of this technique to the growth of sapphire single crystals (100 mm long × 15 mm in diameter) of similar perfection. The use of a modified, floating-zone, recrystallisation technique for the growth of sapphire crystals is also described. The only attempt to grow single-crystal sapphire yet reported in the literature [5] yielded small crystals and no evidence as to crystal perfection was presented.

2. Experimental Details

Three grades of aluminium oxide were used as starting material. In order of decreasing purity, these were crystalline boules grown by vapour-phase flame fusion, Johnson-Matthey high-purity grade available in powder form, and boules grown by powder flame fusion.

The general arrangement of the crystal-growing apparatus used in the vertical-pulling and floating-zone techniques has been described in previous papers [3, 6]. However, as it is the detailed changes made during the present work which permit the growth of sapphire by these techniques, the essential features of the apparatus are shown in figs. 1 and 2. The main change in the vertical-pulling apparatus is in the afterheater, which consists of an alumina jacket with an iridium liner. The afterheater totally encloses the volume into which the grown crystal is withdrawn, apart from a small hole to allow the seed crystal to be inserted and a viewing slot for the operator. If the afterheater is not used, the consequent steepening of the radial temperature gradients causes the iridium crucible to melt

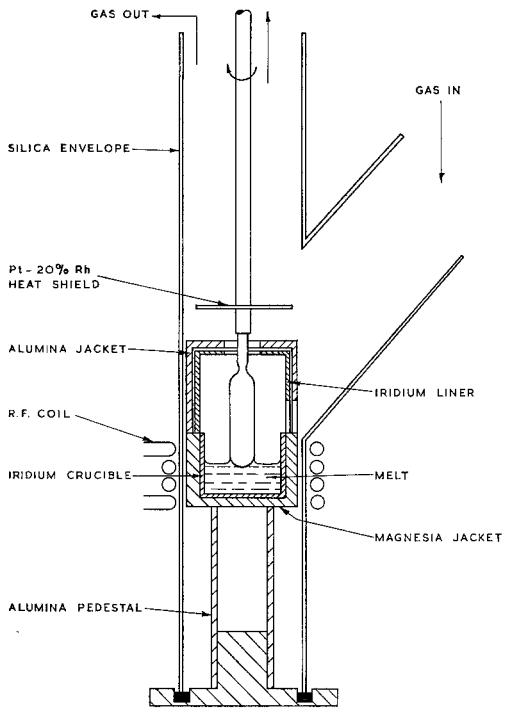

Figure 1 Vertical-pulling apparatus used for sapphire single-crystal growth.

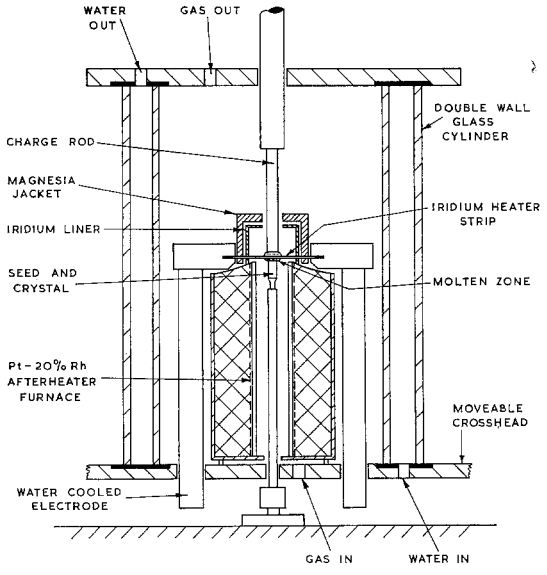

Figure 2 Floating-zone apparatus used for sapphire single-crystal growth.

before the charge is fully molten. The floating-zone apparatus is a modification of the version already described [3], to permit the use of a controlled atmosphere which prevents excessive oxidation of the heater strip. Additional heat-shielding around the strip and charge rod has also been provided in the form of a magnesia jacket containing an iridium liner. The after-heater furnace is wound with Pt-Pt/20% Rh, enabling working temperatures up to 1800° C to be achieved.

Pull rates of 6 to 50 mm/h and rotation rates 0 to 200 rev/min were used in the vertical-pulling experiments. The corresponding rates in the floating-zone experiments were respectively 6 to 12 mm/h and 10 to 20 rev/min. The atmospheres used were argon-oxygen or nitrogen-oxygen mixtures. For pulling, the latter mixtures were preferred, in order to prevent arcing between the crucible and seed holder. The crystal growth axes were $<0001>$, $<10\bar{1}0>$, or $<10\bar{1}1>$.

Sections of crystals required for optical examination were mechanically polished using successively finer grades of diamond paste. In order to reveal the dislocation distribution as etch pits, such sections were further polished chemically in either orthophosphoric acid at 350° C or molten lead fluoride at 800° C, and were etched in molten potassium persulphate at 650° C. This etchant is effective on $\{0001\}$ planes only.

3. Crystal Growth and Perfection

In sapphire single crystals grown by both the techniques described above, similar defects have been observed. These include particles causing Tyndall scattering, voids, iridium platelets, and dislocation low-angle boundaries. The formation of these defects has been studied as a function of growth conditions as described below.

3.1. Particle Scattering

Crystals grown in an inert atmosphere from the purest grade of material used, namely vapour-phase, flame-fusion boules, exhibit pronounced Tyndall scattering from particles 1 to 2 μm in diameter. As the original boules are free from such particles, and since their formation can be suppressed by the presence of oxygen in the gas ambient, it seems likely that the particles are formed by decomposition of the alumina into sub-oxides of aluminium, which are known to exist, and oxygen. Less than 0.5 vol % of oxygen prevents particle formation, and no further improvement is observed by raising the oxygen level above this limit. Crystals grown in an inert atmosphere from less pure grades of material

than described above show more intense Tyndall scattering. This is only partially removed by the presence of oxygen, which suggests that certain impurities in these grades of alumina are present in sufficient quantities to exceed the limit of solid solubility. No experiments have been undertaken to identify these impurities specifically.

It is desirable to keep the oxygen level in the gas ambient as low as possible, because high concentrations cause excessive oxidation of the iridium. This leads to entrapment within the crystal of triangular or hexagonal platelets which form by decomposition of the volatile oxide, IrO_2, at temperatures above 1020° C. In vertically pulled crystals, the platelets are 1 to 5 μm across and 1 μm thick. Their entrapment can be prevented, by directing the gas flow in such a manner that any IrO_2 formed is swept clear of the growing crystal and melt to deposit on cooler parts of the apparatus: in the pulling system described here, a gas flow of 300 cm^3/min is sufficient for this purpose. Iridium contamination is a greater problem in the floating-zone technique, where platelets up to 50 μm across and approximately 1 μm thick have been observed, as shown in fig. 3. In this technique, the ratio surface area of iridium/melt volume is greater

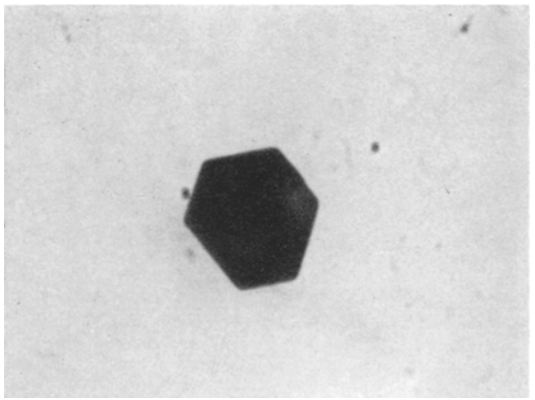

Figure 3 Iridium platelet in a sapphire single crystal grown by the floating-zone technique (×380).

than in the pulling technique, and more IrO_2 is formed for a given concentration of oxygen. Since the growing interface is very close to the iridium, entrapment of platelets is enhanced. Using the floating-zone technique, no sapphire crystals have yet been grown which are entirely free from iridium platelets, though their size and concentration have been reduced by directing the gas flow in such a way as to sweep IrO_2 away from portions of the heater strip not covered by the melt.

3.2. Voids

Voids of the form shown in fig. 4 have been observed in single crystals of sapphire grown by

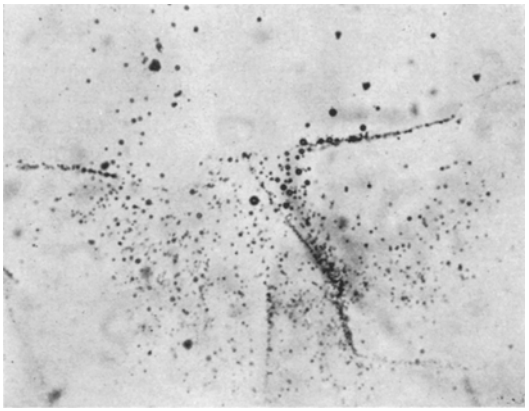

Figure 4 Voids in a sapphire crystal grown by the floating-zone technique viewed along the <0001> growth axis (×68).

both the above techniques. In the vertical-pulling system, void formation can be prevented by using pull rates of 12 mm/h or less for crystals of 8 to 10 mm diameter when these are grown from the purest starting material. At higher pull rates or larger crystal diameters, voids are readily formed. Crystal rotation rates up to 200 rev/min have no detectable effect upon void formation, and an arbitrary rate of 60 rev/min has been used in most cases. Crystals of 8 to 10 mm diameter which are grown from the more impure grades of starting material, or from melts doped with chromium to form ruby, exhibit void formation if the pull rate exceeds 6 mm/h. In the floating-zone system, crystals have been grown only from powdered alumina which is less pure than the crystalline boules. In this case, void formation occurs at growth rates greater than 6 mm/h for a crystal of 6 mm diameter, which is comparable with pulling from the same grade of material.

The voids are very similar in appearance to those previously reported in vertically pulled calcium tungstate ($CaO.WO_3$) [3] and yttrium aluminium garnet ($3Y_2O_3.5Al_2O_3$) [7] single crystals. These were shown to form by the solidification of trapped, impure melt, which contracts on freezing to create a cavity. The

impurities causing this effect can be those present in the starting material, those deliberately added as dopant, or gaseous matter derived from the gas ambient, provided that these have different solubilities in the liquid and solid (i.e. a segregation coeff $\neq 1$). In calcium tungstate, yttrium aluminium garnet, and in the present sapphire crystals, the voids first form in the central core of the crystal and subsequently extend in crystallographic directions which depict the symmetry of the growth orientation. The onset of void formation also depends markedly upon the growth rate and the purity of the melt in all three materials. The marked similarity in the appearance of the voids and in the factors controlling their formation in sapphire and the other two oxides suggests that voids also form in sapphire by the contraction of trapped, impure melt upon solidification.

3.3. Dislocations and Low-Angle Boundaries

Earlier work on oxide single crystals [3, 8] showed that thermal stresses imposed on the cooling crystal during growth can lead to the generation of dislocations which polygonise to form low-angle boundaries. Such boundaries impair the optical perfection of anisotropic materials, but their formation can be prevented by afterheaters which keep the thermal stresses below the yield stress of the crystal. The afterheater described in fig. 1 appears to satisfy this requirement for sapphire, since in general there is a complete absence of dislocation low-angle boundaries in the vertically pulled crystals, and the dislocation density is 10^2 to $10^3/cm^2$. The Twyman-Green interference pattern in fig. 5, taken through a 30 mm length of crystal, shows the high degree of optical perfection attained in such crystals. Occasionally, a single, low-angle boundary may be observed in a pulled crystal, and in such a case a few regions of higher dislocation density are found adjacent to the boundary.

The floating-zone apparatus uses only a small melt volume, and crystals grown by this technique are subjected to steeper thermal gradients than in vertical pulling. Consequently, greater thermal stresses are developed within the crystal, and, as yet, these have not been reduced sufficiently to prevent the formation of dislocation low-angle boundaries of the type and distribution shown in fig. 6.

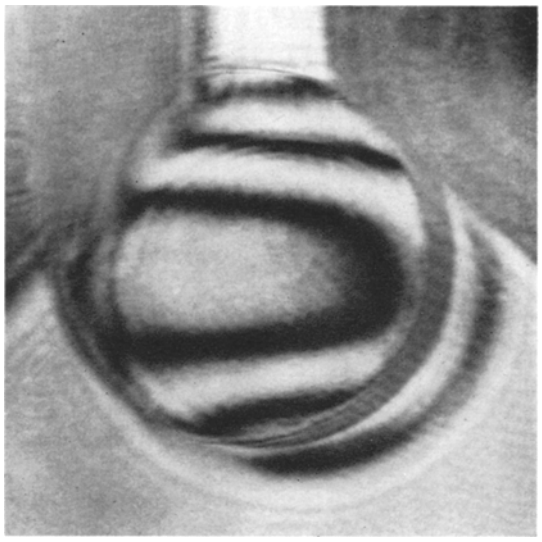

Figure 5 Twyman-Green interference pattern taken through a low-dislocation-density, sapphire single crystal (×4).

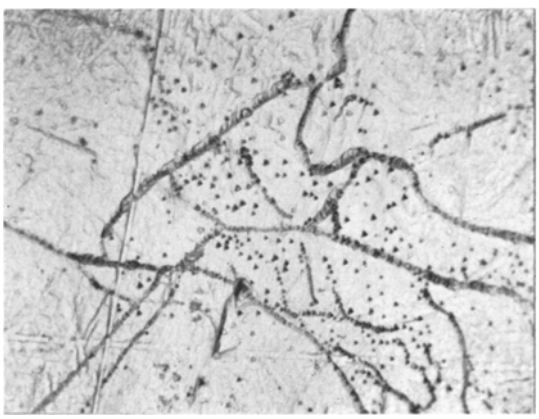

Figure 6 Low-angle boundaries in a sapphire single crystal grown by the floating-zone technique (×170).

4. Conclusions

Highly perfect, sapphire single crystals can be grown using the vertical-pulling technique. Single crystals can also be grown using a floating-zone, recrystallisation technique, but the higher thermal stresses associated with this method lead to the formation of dislocation low-angle boundaries and a lower degree of crystalline perfection.

Tyndall scattering can occur in these crystals

owing to impurities in the starting material, dissociation of the alumina in the absence of oxygen, and by entrapment of iridium. This latter effect can be avoided in pulled crystals and minimised in float-zone crystals by suitably directing the flow of the gas ambient. Voids can form in sapphire crystals by the contraction of trapped, impure melt on freezing, but their formation can be prevented by suitable control of growth rate, crystal diameter, and melt purity.

Acknowledgements

This paper is published by permission of The Controller, HM Stationery Office.

The authors wish to thank Dr D. A. Findlay and Mr G. W. Fynn for providing the interference pattern.

References

1. B. W. JOYCE, R. J. BENNETT, R. J. BICKNELL, and P. J. ETTER, *Trans. AIME* **233** (1965) 556.
2. K. NASSAU, *Lapidary J.* **18** (1964) 42.
3. B. COCKAYNE, D. S. ROBERTSON, and W. BARDSLEY, *Brit. J. Appl. Phys.* **15** (1964) 1165.
4. B. COCKAYNE, *J. Amer. Cer. Soc.* **49** (1966) 204.
5. A. E. PALADINO and B. D. ROITER, *ibid* **47** (1964) 465.
6. D. B. GASSON, *J. Sci. Instr.* **42** (1965) 114.
7. W. BARDSLEY and B. COCKAYNE, Conf. Proc. ICCG, Boston, *J. Phys. Chem. Solids* (1966), to be published.
8. B. COCKAYNE, D. S. ROBERTSON, and B. W. STRAUGHAN, *Nature* **203** (1964) 1376.