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The Capillary Seed Technique in Crystal Pulling

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The use and advantages of an inert capillary seed in crystal pulling are described. Examples are given of the use of the technique on various semiconductors and the effect on crystal purity is briefly discussed.

1. Introduction

On attempting to prepare single crystals of a new material by the Czochralski technique, or pulling, single crystal seeds of the material, on which to grow, are generally not available. In many cases it is possible to prepare suitable seeds by casting in a tubular mould or by the Stockbarger or Bridgeman techniques, but in some cases the production of seeds by these methods is inconvenient or impossible due to the reactivity, brittleness, vapour pressure, or melting point of the materials concerned. Another situation in which the preparation of seeds of the material to be pulled is sometimes to be avoided arises in the pulling of single crystal solid solutions such as $Pb_{1-x}Sn_xTe$. In such cases one is frequently concerned with pulling a range of crystals of different compositions and the preparation of a seed to match each starting melt is extremely laborious, even when the solidus—liquidus relationship in the phase diagram is sufficiently well known for this to be possible. Use of a seed of the wrong composition may lead to the melting off of the seed due to its having a lower melting point than the melt, and is bound to lead to the alteration of the initial melt composition in the inevitable first melting back of the seed.

2. The Capillary Seed

The problem outlined above has been solved for a number of semiconductors by the use of a capillary seed. Crystals of PbTe, SnTe, GeTe, GaSe [1], $PtSb_2$ [2], Cd_3As_2 [3], and $Pb_{1-x}Sn_xTe$ [4] of various compositions have been grown on tantalum capillary tubes and GaAs has been grown on a graphite capillary tube. In all of these cases it was also necessary to use the liquid encapsulation technique [5, 6] to prevent the vaporisation of the materials, and crystals were thus pulled through a layer of B_2O_3, or some other encapsulent, into a pressurised ambient of high purity nitrogen. The use of the liquid encapsulation technique was, however, incidental and was not a requirement of the capillary seed technique.

The capillary seed works by drawing up into its lower end a small amount of the melt. This solidifies and forms the effective seed on which the crystal is grown.

It is a prime requirement that the capillary material should not react with, or be soluble in, the melt, the ambient, or, where encapsulation is being used, the encapsulant. No evidence of reaction was observed between Ta and any of the semiconductor melts, although a vigorous reaction was observed when a Ta seed was dipped into a CdF_2 melt. As a check, samples of the starting materials PbTe and SnTe, and a $PtSb_2$ crystal grown on a conventional seed, together with Ta seed grown crystals of $Pb_{1-x}Sn_xTe$ and $PtSb_2$ were analysed spectroscopically. Increase in Ta content were of the order of 2 to 4 parts in 10^7 in Ta seed grown crystals (table I). A comparison of electrical properties between the two $PtSb_2$ crystals showed no significant difference in carrier concentrations. A thin brittle layer was formed on that part of the Ta which was immersed in the B_2O_3 for long periods at high temperatures. This appeared to act as a protective coating and did not pass into the B_2O_3 or affect the process in any way. At the highest temperatures used (~ 1200° C in the

TABLE I

Material	Ta (ppm atomic)
PbTe (starting material)	0.3
SnTe (starting material)	0.5
$Pb_{1-x}Sn_xTa$ (Ta seed pulled)	0.8
$PtSb_2$ ($PtSb_2$ seed pulled)	0.9
$PtSb_2$ (Ta seed pulled)	1.1

case of $PtSb_2$) that part of the tube exposed to the ambient became hard and brittle due, presumably, to nitride formation, although it retained adequate strength.

3. Experimental Arrangement

Capillary seeds, of 1.5 mm ID, 2.4 mm OD and 3 to 5 cm long, were prepared by inserting one end into a hole drilled into the head of a 2BA stainless steel bolt which screwed directly into the end of the pull rod of a standard RRE crystal puller. Capillaries were initially held in place with a grub screw but it was later found more simple, and equally satisfactory, to tap them gently into a slightly tapered hole. The seeds could be bent and thus easily centred. It was necessary to ensure that the top of the capillary was not sealed since this, especially where liquid encapsulation was being used, could prevent the entry of melt into the capillary.

Crystal pulling then proceeded in the usual way although the fact that the thin capillary has a rather lower thermal conductivity than most conventional seeds made temperature conditions more critical in seeding on. In most cases the first material grown was necked in to 1 to 2 mm for a short distance to ensure single crystallinity. Fig. 1 shows a crystal of SnTe which has been grown on a Ta capillary and then through a neck in this way, before removal of the encapsulant, B_2O_3, picked up in pulling. The junction between the Ta seed and the SnTe was extremely brittle and did not survive the removal of the B_2O_3 since seeding had only occurred within the capillary. In some cases, however, single crystals were obtained directly without further necking in.

4. The Ta Capillary

Fig. 2 shows a used Ta capillary seed before and after being sectioned. It may be seen that the melt has been drawn up about 1.6 mm into the tube while some 17 to 18 mm of the tube above the melt contains B_2O_3. The outside ridge at the base of the capillary is residual B_2O_3. The two "tide marks" on the outside of the capillary are of interest: the lower and less pronounced one indicates the level to which the seed was dipped in the B_2O_3 while the correct temperature was being sought. The part of the tube below this point is quite clean since it was never exposed to the ambient at high temperature. The higher, and main mark indicates the greatest level of dip during seeding on, and above this point the capillary is lighter in colour due to slight nitriding of the surface. It may also be seen that the internal level of the B_2O_3 is about 2 to 2.5 mm higher than the external B_2O_3 level, demonstrating the large capillary rise of B_2O_3 compared with that of the melt. The seed was originally simply touched onto the melt, so most, if not all, of the solidified melt in the bottom of the tube would have been introduced by capillary action. Finally it can be seen from fig. 2 that the inside burr formed in cutting the capillary has been left on. This was always done to provide a physical grip on the crystallite in the capillary should adhesion fail, perhaps through differential contraction.

5. Discussion

The capillary seed technique has now been used on a number of materials and on a large number of individual crystals with satisfactory results. The lower thermal conductivity of the capillary

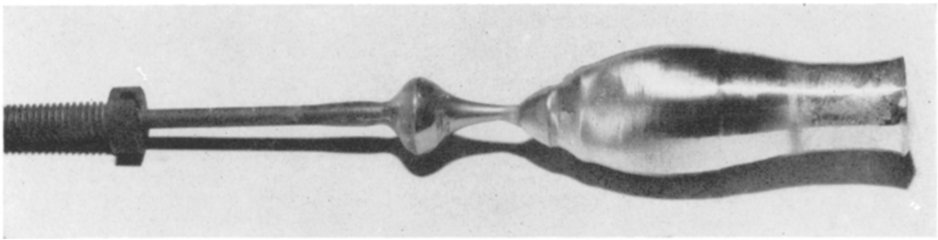

Figure 1 A crystal of SnTe pulled by the liquid encapsulation technique on a Ta capillary seed. The crystal is 45 mm from neck to base and the neck is 1.5 mm in diameter. The bottom of the neck and the lower part of the capillary seed still have a coating of B_2O_3.

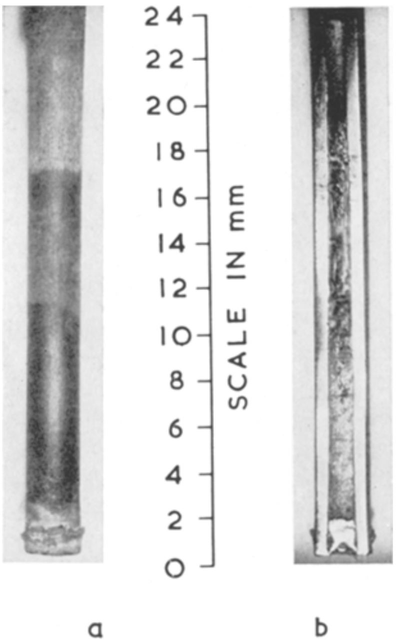

Figure 2 A Ta capillary seed (a) before and (b) after sectioning. The capillary has an ID of 1.5 mm, an OD of 2.4 mm, and has been sectioned to a length of 24 mm.

has not been found to be a serious drawback although its effects are noticeable. The use of a very short capillary, perhaps 5 mm, set in a thick walled tube of the same or a different material would provide a high thermal conductivity capillary seed should the problem ever be serious. It should also be pointed out that, while Ta and graphite capillaries have been satisfactory on all the materials mentioned above, many other metals and ceramics could be used should circumstances so demand.

Finally, the advantages of this technique should be reiterated. Firstly, capillary seed is effective where conventional seeds are difficult to prepare by techniques other than pulling and thus provides a means of preparing the first conventional seed of a new material. It has even been used where conventional, but polycrystalline, seeds were available simply because it has been more convenient. Secondly, when mixed crystals, e.g. $Pb_{1-x}Sn_xTe$, $Hg_{1-x}Cd_xTe$ etc, are being pulled, a capillary seed avoids the difficulties of matching the compositions of seed and melt and allows the first material to crystallise to be identified and analysed meaningfully to determine tie-lines.

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