Journal of Crystal Growth 86 (1988) 471–476
North-Holland, Amsterdam

STRUCTURAL DEFECTS IN CdTe CRYSTALS GROWN BY TWO DIFFERENT VAPOUR PHASE TECHNIQUES

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The structural defects present in large single crystals of CdTe grown at the same temperature by two different vapour phase techniques have been investigaged using a range of techniques including TEM, SEM, EBIC, EDX and chemical etching. The contrasting defect content of the differently grown crystals can be explained by the considerable difference in the periods taken to grow the crystals by the separate techniques. In the crystals grown by the slower method, the development of both sub-grain boundaries and precipitates reaches a much more advanced stage than in those grown by the faster technique.

1. Introduction

The continuing demand for low defect content and lattice matched substrates for the deposition of $Cd_xHg_{1-x}Te$ has sustained a programme of vapour phase growth of bulk crystals of CdTe in these laboratories for a number of years. For epitaxial applications, the structural perfection of the substrates is of paramount importance, and consequently this has been monitored using a range of techniques including TEM, SEM/EBIC, EDX and chemical etching. Independent of the growth method used, our earlier work and that of others has demonstrated that the principal defects in single crystal CdTe are twins [1–4], sub-grain boundaries [5–9] and precipitates [7,10–13]. Only the latter two of these types of defect will be considered here as the important topic of twinning in these vapour phase grown CdTe crystals will form the subject of a separate publication. In particular, the present paper is concerned with a comparison of the sub-grain boundary structure and precipitate content of CdTe crystals grown from the vapour phase by two quite different techniques. These have been in regular use for the growth of a wide range of II–VI single crystals in these laboratories for many years. One of the methods has been pioneered at Durham [14] and employs an evacuated and sealed silica tube in which growth takes place in a period of 2–3 weeks. In contrast, the other technique, which is a modification of that due to Piper and Polich [15], uses an open ended silica tube in which growth takes place in an argon ambient at about atmospheric pressure, in a period not greater than ~ 3 days. The differences in the defect content of the crystals grown by the two techniques is attributed to the significantly different periods taken to grow the crystals.

2. Experimental

As the two separate methods of vapour phase growth used in this study have been described in detail previously [16], it will suffice to draw attention to the contrasting aspects of the two different techniques. Essentially the "Durham" method employs an evacuated and sealed silica capsule which is pulled through a temperature gradient at a rate of ~ 15 mm/day for 10–14 days, so that the charge material is transported in the vapour phase to the cooler end of the growth capsule. The grown crystal is subsequently cooled to room temperature over a further 3 day period. On the other hand, growth by the modified Piper–Polich technique takes place in an argon ambient at atmo-

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0022-0248/88/$03.50

spheric pressure in an open silica tube which is not pulled but is positioned in a steep part of the temperature profile of the furnace. With this method vapour phase transport is complete within 3 days whereupon the furnace is switched off and allowed to cool naturally. The same starting material was used for each technique and growth occurred at about 1000–1050 °C in each case.

For TEM studies, samples were prepared by chemical polishing using a solution of 2% bromine in methanol. Etching investigations were carried out using Inoue's E-Ag 1 etch [17], Nakagawa's etch [18] and a 0.5% solution of bromine in methanol with photostimulation [7,9]. To remove cutting damage all samples were prepared by mechanically polishing oriented slices with alumina down to a particle size of 1 μm. Prior to etching, these slices were chemically polished in a 2% bromine in methanol solution.

3. Results

3.1. Sub-grain boundaries

Fig. 1 shows a typical transmission electron micrograph of a sub-grain boundary in a sample of bulk CdTe grown using the "Durham" method. The dislocations which constitute the boundary are nearly all parallel and most have the same Burgers vector. There are, however, a few others lying in a direction different from the rest and it is likely that these have different Burgers vectors. By measuring the positions of Kikuchi lines relative to diffraction spots in selected area diffraction patterns recorded from either side of such boundaries, it was possible to make an accurate determination of the tilt angle between adjacent sub-grains. The tilt angle measured in this way for the boundary in fig. 1 was ~ 18′ and this was typical for the boundaries studied in this material. The parallel lines of contrast running down the left hand side of this micrograph were due to beam induced damage, while the dark speckled features are artefacts arising from chemical thinning.

In order to investigate the overall size and distribution of the sub-grains in the crystals grown by the "Durham" technique, chemically polished surfaces were etched in a 0.5% solution of bromine in methanol with photostimulation for 10 min. The special feature of this etch is that it reveals sub-grain boundaries on surfaces of all orientations. Its effect is illustrated in fig. 2 which is a low magnification optical micrograph showing an array of sub-grain boundaries with an average sub-grain size of about 150 μm. While fig. 2 is quite representative of the cellular sub-grain structure in CdTe grown from the vapour phase by the "Durham" method, elongated sub-grains such as those shown in fig. 3 were occasionally observed. A particularly interesting feature of sub-grain boundaries is the way in which they interact with twin boundaries. This is illustrated in the optical

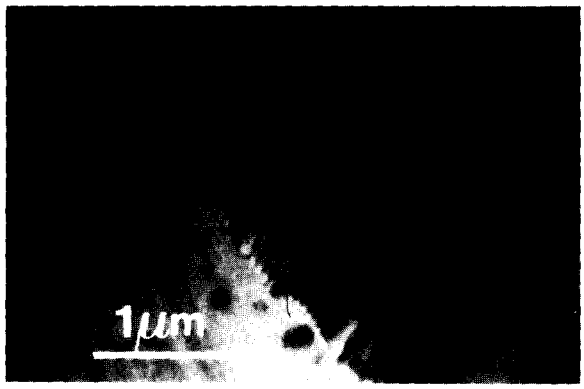

Fig. 1. Transmission electron micrograph of a sub-grain boundary in "Durham" grown CdTe.

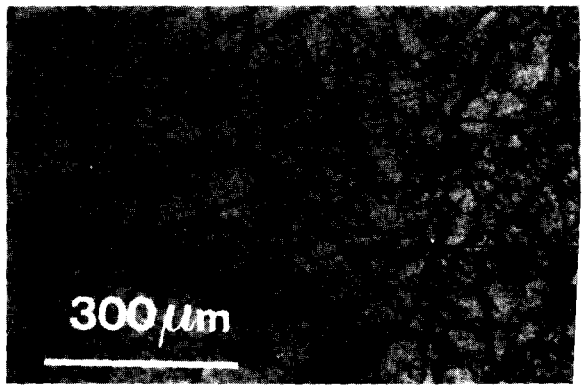

Fig. 2. Optical micrograph showing sub-grain boundary structure in "Durham" grown CdTe.

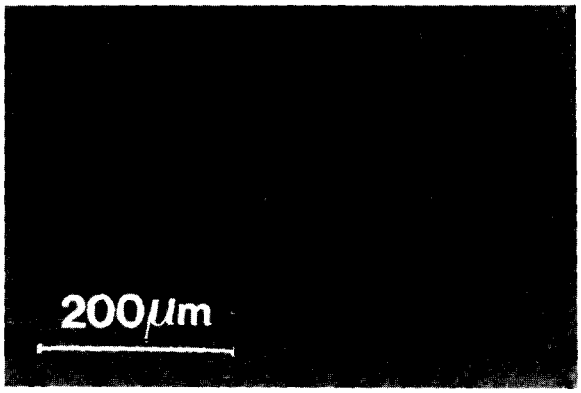

Fig. 3. Optical micrograph showing elongated sub-grain boundary structure in "Durham" grown CdTe.

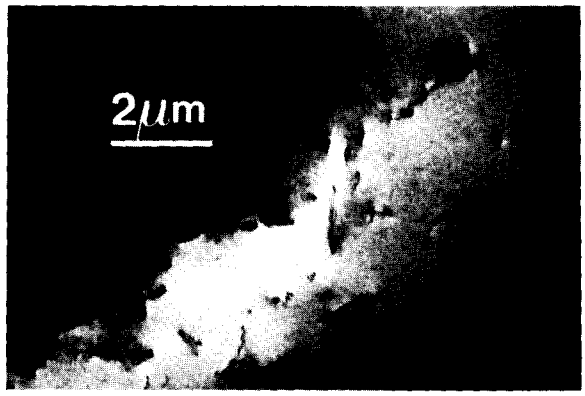

Fig. 5. Transmission electron micrograph of dislocations in Piper–Polich grown CdTe.

photomicrograph of fig. 4, in which the long straight and approximately parallel lines correspond to first order (i.e. $\Sigma = 3$) twin boundaries. Close inspection reveals that these are crossed by some sub-grain boundaries, as at A but they pin others, as at B. In addition, sub-grain boundaries are frequently associated with the points where these first order twin boundaries are terminated by lateral twin boundaries, as at C.

In contrast with material grown by the "Durham" method, that grown using the modified Piper–Polich technique exhibited an entirely different arrangement of dislocations in the sub-grain boundaries. This is demonstrated by fig. 5 which shows a transmission electron micrograph of what is considered to be the early stage in the formation of a sub-grain boundary in CdTe grown by this method. Not only are the dislocations present in a disordered fashion, but also there is no tendency for them to arrange themselves into any structures resembling the sub-grain boundaries in the CdTe grown by the "Durham" method (compare figs. 5 and 1). This point was further confirmed by etching studies which showed that the dislocations in Piper–Polich grown material were not concentrated into sub-grain boundaries but more of them were distributed throughout the sub-grains.

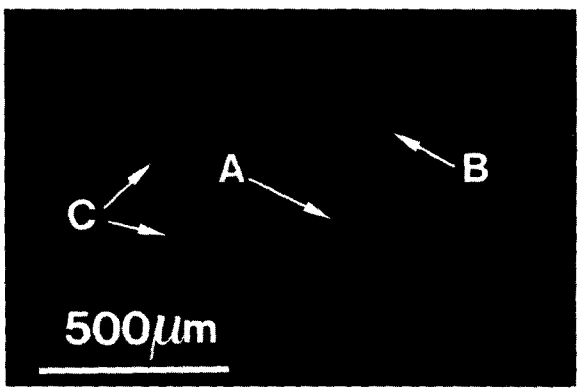

Fig. 4. Optical micrograph showing interactions of sub-grain boundaries with twin and lateral twin boundaries.

3.2. Precipitation

All three of the etchants employed in this study are capable of revealing precipitates in CdTe although they each have different effects on these defects. With material grown by the "Durham" method, while some precipitates were found within the bulk, many more were seen to be associated with the twin and grain boundaries. Fig. 6 is an optical photomicrograph which shows a precipitate situated on a first order twin boundary after etching with Inoue's E-Ag 1 reagent. The size of this precipitate ($\sim 10\ \mu$m) was typical for material grown by this technique. Analysis of such precipitates using EDX in the SEM indicated that they were comprised of Te. The optical micrograph in fig. 7 shows a twin band which is terminated by a lateral twin boundary lying on planes of the type

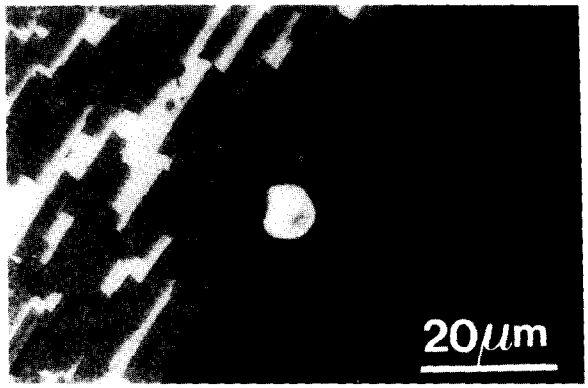

Fig. 6. Optical micrograph of a Te precipitate on a first order twin boundary.

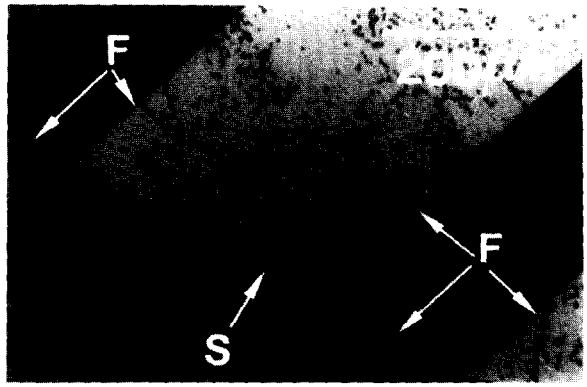

Fig. 8. Optical micrograph showing preferential decoration of a second order twin boundary by Te precipitates.

{115}–{111} when indexed with respect to both the twin and matrix orientations [19]. Close inspection of the lateral twin interface reveals that it is decorated by a number of precipitates along its length whereas none are visible on the first order twin boundaries. Similarly fig. 8 shows that there are more precipitates per unit length on second order twin boundaries (S) than there are on first order ones (F). An extensive study of precipitates in CdTe grown by the "Durham" method has shown that the concentration of precipitates generally decreases according to the sequence:

non-crystallographic random grain boundary
> second order twin boundary
> first order lateral twin boundary
> first order coherent twin boundary
> bulk CdTe.

As with sub-grain boundaries, the nature of the precipitation observed in material grown by the modified Piper–Polich technique similarly differed greatly from that for the CdTe grown by the "Durham" method. In particular, with the Piper–Polich grown material the precipitates were much smaller and were very much less likely to be associated with boundaries. A typical electron micrograph of them recorded under two beam conditions is shown in fig. 9. The distinctive black/white lobe-shaped contrast features associated with each precipitate is indicative of the presence of a radial strain field [20]. Even when these were observed in

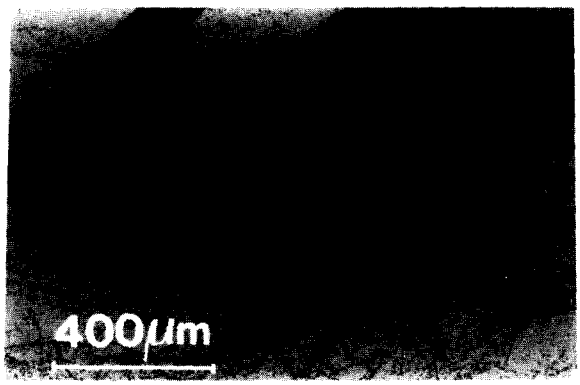

Fig. 7. Optical micrograph of a {115}–{111} first order lateral twin boundary decorated by precipitates.

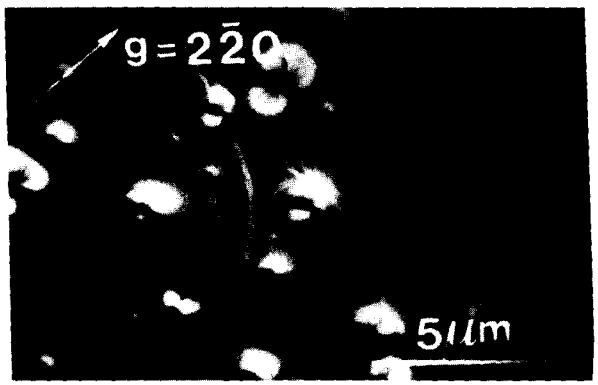

Fig. 9. Transmission electron micrograph of precipitates in Piper–Polich grown CdTe.

the vicinity of first order twin boundaries they showed no tendency to decorate such interfaces.

4. Discussion

Dislocation arrays are known to form in metal crystals which have been annealed following cold working. The formation of such arrays by a process of dislocation glide and climb (polygonisation) enables stress induced dislocations to achieve energetically stable configurations of the type described by Cottrell [21]. Stresses which are sufficiently large to introduce dislocations into CdTe crystals grown by either of the techniques used here could easily arise through the interaction of the silica capsules with the crystal boules since the coefficients of thermal expansion of the two materials differ by an order of magnitude [22]. Furthermore, it has been shown by Williams and Vere [9] that dislocation polygonisation occurs in CdTe at annealing temperatures as low as 440 °C. The long growth periods at relatively high temperatures associated with the "Durham" method are conducive to polygonisation and this process is able to explain the characteristics of the dislocation arrays which may be seen in the micrographs presented in this work. For example, if stress induced slip were to occur on only one set of close packed planes, then this would lead to a series of identical dislocations. During polygonisation these would assume a low energy configuration, that is, they would line up one above the other as in fig. 1. The resulting sub-grain boundaries would be long and straight like those in fig. 3. These boundaries resemble the polygonisation walls which are characteristic of metals which have been annealed following cold working. The polygonisation of stress induced dislocations having a range of Burgers vectors is expected to result in more complex sub-grain boundary configurations such as that illustrated in fig. 2. In this figure, the average sub-grain size of $\sim 150\ \mu m$ is comparable with that of some Bridgman grown crystals [5,6,9], although there have been reports of better quality Bridgman material with a sub-grain size of several hundred microns [6,8]. The association of sub-grain boundaries with other crystal defects such as lateral and coherent twin boundaries (fig. 4) may be taken as further evidence of the advanced stage in the development of polygonisation in these crystals.

In contrast to this, the comparatively short growth period employed in the modified Piper–Polich technique does not allow polygonisation to occur to anything like the same extent in crystals grown by this method. This is shown in fig. 5 which illustrates a sub-grain boundary consisting of dislocations which are present in a disordered arrangement. Not only do these sub-grain boundaries differ markedly in appearance from that shown in fig. 1, but they also do not separate the sub-grains with the comparatively large misorientations shown in fig. 1. Clearly the short time taken to grow CdTe by this technique results in a distribution of dislocations which deviates significantly from that which is expected at equilibrium.

As Te has a retrograde solid solubility in CdTe, any excess of this element which is present in the boules as a solid solution at the growth temperature will precipitate out on cooling to room temperature. Thermodynamically it is expected that, in the equilibrium state, precipitates of a second phase within a crystal will become associated with other defects such as dislocations, stacking faults and grain boundaries [23]. Furthermore, it has been shown by Gleiter [24] that, on energetic considerations, random grain boundaries become more heavily decorated than coincidence ones. The distribution of Te precipitates in the CdTe grown by the "Durham" method may be taken to be representative of the equilibrium situation. They decorate various types of crystal boundaries in numbers which reflect the relative interfacial energies of these boundaries, second order twin boundaries being more heavily decorated than first order ones for example. It may be concluded that this distribution of precipitates is a direct result of the long growth and cooling periods associated with the "Durham" method since these allow the precipitates to migrate to low energy sites. In contrast to this, the growth and cooling periods for the modified Piper–Polich technique are relatively short. While precipitation does occur, the precipitates are comparatively small presumably because this method of growth does not provide

the opportunity for them to coalesce. In addition, their distribution is random and there is no evidence that these precipitates are preferentially associated with twin boundaries.

5. Conclusions

The processes of dislocation polygonisation and Te precipitation in CdTe are significantly influenced by the crystal growth conditions employed. The long growth and cooling periods associated with the "Durham" method lead to more complete polygonisation and precipitation. The dislocations in this material are ordered into well formed arrays (sub-grain boundaries) while the Te precipitates preferentially decorate high energy crystal boundaries with a distribution corresponding to that expected for the equilibrium situation. In contrast to this, the shorter growth and cooling periods used for the modified Piper–Polich technique do not allow extensive polygonisation to occur and the precipitates tend to be comparatively small and they remain unassociated with crystal boundaries.

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