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STRUCTURAL PROPERTIES OF CRYSTALS OF CdTe GROWN FROM THE VAPOUR PHASE

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The structural defects in large single crystals of CdTe grown from the vapour phase have been investigated using transmission electron microscopy and etching techniques. Twin bands, sub-grain boundaries and precipitates are the major features described.

1. Introduction

$Cd_xHg_{1-x}Te$ has a variable band gap in the infra-red region of the spectrum, and is therefore a strong candidate for the fabrication of photovoltaic thermal imaging devices. However, because of its poor mechanical properties and the difficulty of preparing it in bulk crystal form of suitable quality, considerable interest has evolved into techniques of growing epitaxial layers on foreign substrates [1,2]. The good lattice match between $Cd_xHg_{1-x}Te$ and CdTe for values of x in the vicinity of 0.2, makes CdTe a leading candidate for this application. Consequently, numerous attempts have been made to grow large single crystals of CdTe with minimal defect content. The techniques most frequently employed have been those concerned with growth from the liquid phase, i.e. from the melt using the Bridgman or allied techniques, or from solution as with solvent evaporation [3]. In contrast, work in our laboratory has been concentrated on growth from the vapour phase, since this offers the possibility of growth at a comparatively low temperature, together with some control over the stoichiometry.

The presence of defects in the substrate is particularly undesirable for epitaxy, since many of them can propagate into the growing layer, with deleterious effects on device properties. This paper is primarily concerned with a transmission electron microscope study of the defects in large crystals of CdTe grown from the vapour phase.

2. Experimental

The CdTe starting material for crystal growth was synthesised from the high purity elements (six 9s) supplied by MCP. Synthesis was carried out in a sealed evacuated silica tube at 900°C for a period of three days. The charge material produced in this way was loaded into silica growth capsules of the type described previously by Cutter and Woods [4]. The capsules, which ranged in diameter from 10 to 29 mm were evacuated and sealed, and then pulled through a vertical furnace so that nucleation occurred at the conical growth tip of the capsule, when an appropriate temperature gradient had been established. In some trials the inner walls of the capsule were first coated with carbon by the pyrolytic decomposition of high purity propane [5]. It was thought that this process would prevent the crystal boules from sticking to the silica tubes, thus eliminating one possible source of strain.

Thin sections of CdTe were prepared for examination in a JEM 120 transmission electron microscope (TEM) from 0.5 mm thick 3 mm diameter discs cut from the boules. Thinning was achieved by jet polishing using a solution of 2% bromine in methanol, and was terminated by immersion in clean methanol when a portion of the disc became sufficiently thin to transmit light.

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3. Results and discussion

Crystals of CdTe weighing up to 160 g with diameters up to 29 mm have been grown quite successfully. A photograph of the end face of a boule which was predominantly single grain is shown in fig. 1. Boules grown in the larger diameter capsules usually have larger grain sizes, although other factors are also known to be important. Twin bands such as those in fig. 1 were frequently present in the vapour grown boules. They could often be seen clearly with the naked eye, although their visibility could be enhanced by etching either with Inoue's EAg-1 reagent [6], which is acidified dichromate plus silver nitrate, or with the Nakagawa etch [7], which is $HF + H_2O_2 + H_2O$. The twin bands were up to several mm in breadth, and often extended across the width of single grains, see fig. 1.

Twins have also been observed in the transmission electron microscope. A micrograph of a narrow twin band some 3 μm wide is shown in fig. 2. The suggestion of some oscillatory contrast at A along the length of one of the twin boundaries may indicate that this boundary was only partially coherent. More detailed investigations of such twin boundaries will be reported elsewhere. The small features in the background of the micrograph should be ignored since they are artefacts introduced during sample preparation.

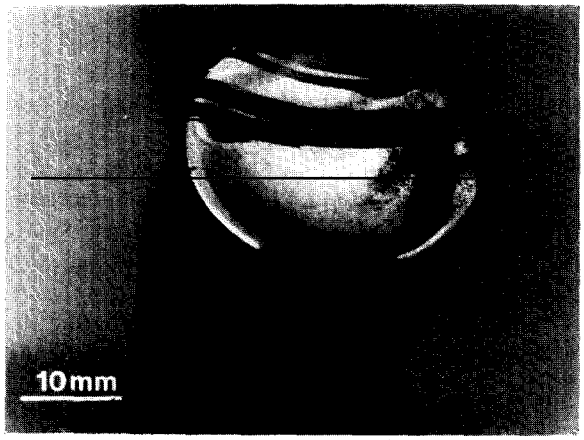

Fig. 1. Photograph of the end face of a boule showing twin bands.

Examination in the transmission electron microscope has revealed the presence of isolated dislocations which appear throughout the bulk material. One such dislocation is shown at A in fig. 3. However, the more prominent feature in that micrograph is the array of dislocations constituting a low angle grain boundary. The arrangement at this boundary is complex, with the inclinations of the dislocations to the surface of the foil, and their Burgers vectors varying along the length of the boundary. This is exemplified by the double image of the dislocation seen at B. Several similar low angle grain boundaries have been observed, and the density of dislocations along them was found to vary considerably. The densities of the dislocations and their Burgers vectors determine the orientational relationships between adjacent grains [8]. Measurements of the relative displacements of Kikuchi lines in electron diffraction patterns taken from either side of a number of sub-grain boundaries have shown that the misorientation of adjacent sub-grains was less than 0.3°. Sub-grains are known to form in material which has been stressed at high temperature [9]. Since the CdTe crystals were held at high temperatures for extended periods (~ several days) during growth, a similar process of dislocation polygonisation could be responsible for the formation of the sub-grain boundaries in this material. Preliminary etching studies have indicated that the sub-grains are of the order of 50 μm in width. This corresponds well with the sub-grain size of 100 μm reported by Chin [10] for CdTe supplied by the II–VI Corporation. However, Auleytner [11] observed a sub-grain size of several mm in Bridgman grown CdTe.

Small precipitates giving rise to strain contrast were also revealed during the TEM study. The only streaking observed in the diffraction patterns could be attributed to thermal diffuse scattering, rather than to precipitates [12]. When imaged in a two-beam condition, the strain fields about these precipitates appeared as a pair of light and dark lobes of contrast. A typical example is shown in fig. 4a. The "line of no contrast" separating the lobes was always perpendicular to the diffracting vector, regardless of its direction. Dark field imaging reversed the sense of the black–white lobe

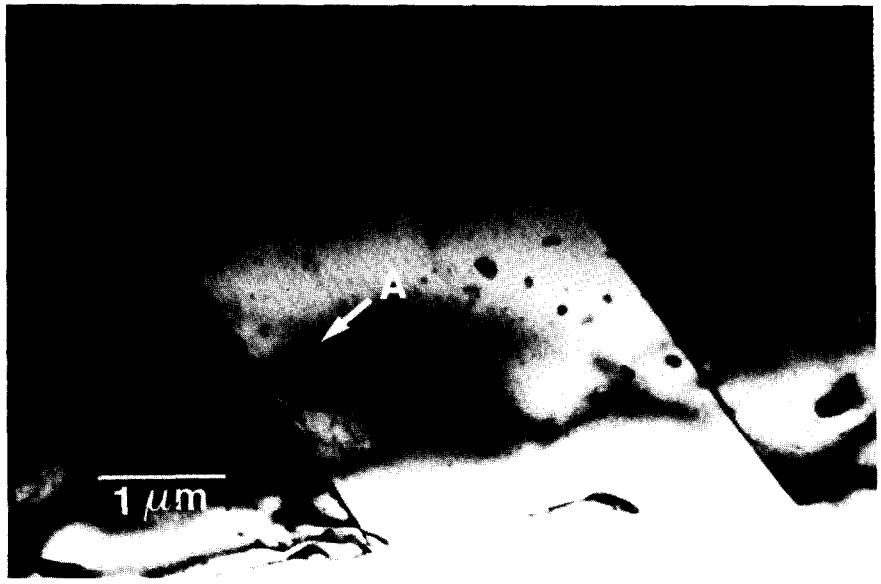

Fig. 2. Transmission electron micrograph of a twin band.

contrast, as shown in fig. 4b.

These contrast effects indicate that the strain field associated with the precipitates is radial [13]. it is well known that the retrograde solid solubility of tellurium in CdTe can lead to the precipitation of tellurium [14]. Indeed, tellurium precipitates have often been observed in CdTe, see for example Shin et al. [15]. It is quite likely therefore that precipitates such as that in fig. 4 are of tellurium. The stacking fault in the lower right-hand corner

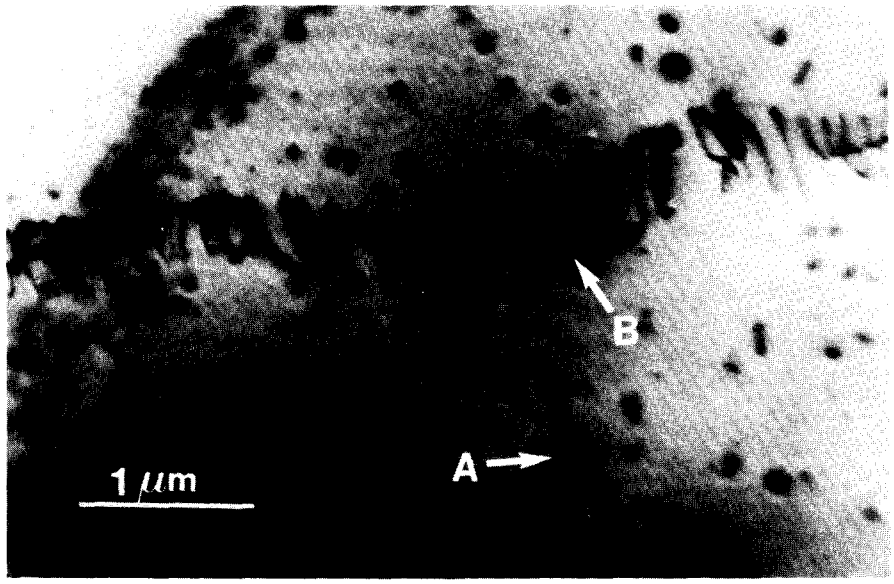

Fig. 3. Transmission electron micrograph of a sub-grain boundary.

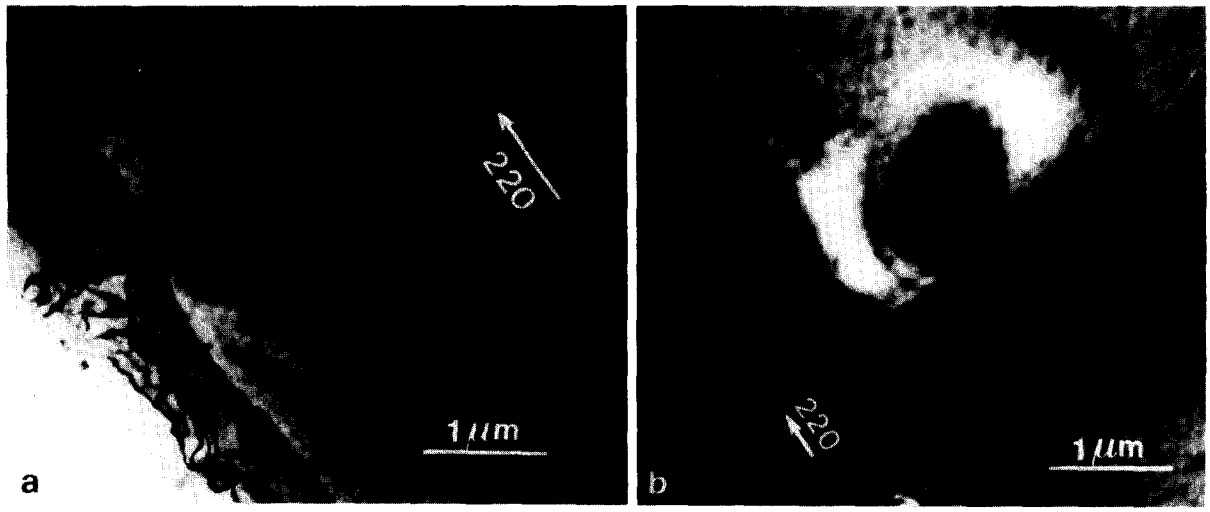

Fig. 4. Micrograph showing the strain field around a precipitate (a) bright field (b) dark field.

of the micrograph in fig. 4a was induced by the electron beam during the examination of the precipitate. This is confirmed by its absence from the dark field micrograph of the same area in fig. 4b which was recorded earlier.

Material grown in the carbon coated capsules was also examined in the TEM. Large irregularly shaped precipitates up to 2 μm wide were frequently observed. They were also accompanied by strain as demonstrated by the bright field micrograph in fig. 5. Vere [16] has suggested that carbon associates with tellurium to form precipitates in crystals grown in carbon coated capsules. In fact, the use of carbon coated growth tubes has been discontinued since sticking in uncoated tubes has not proved to be a particularly serious problem.

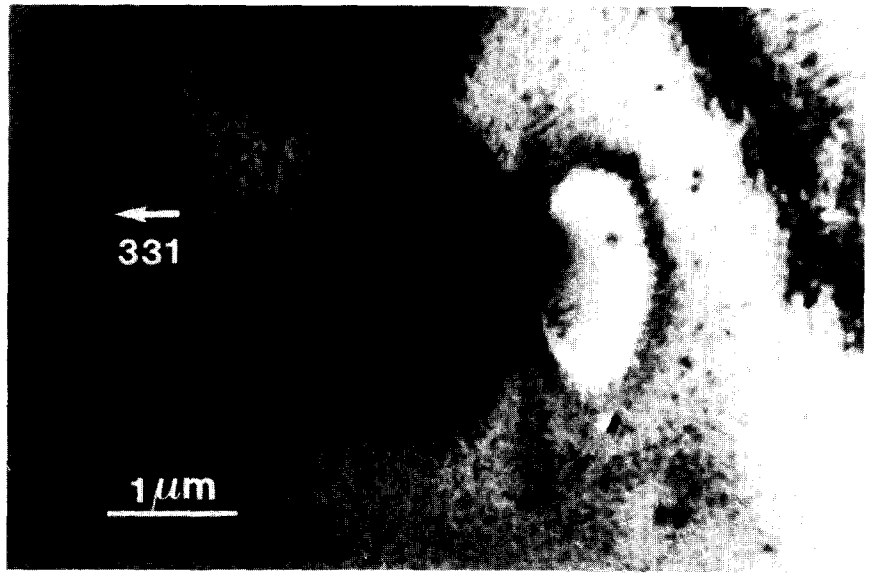

Fig. 5. Bright field micrograph of a precipitate in material grown in a carbon coated capsule.

In summary, the growth of large-grained boules of CdTe from the vapour phase has been successful. However, twins are frequently present and their examination in the TEM has shown that the twin boundaries may be only partially coherent. Isolated dislocations, and dislocations concentrated in low angle arrays generated by a polygonisation process have been observed in the TEM and by etching. The precipitates are associated with a radial strain field and are probably of elemental tellurium. Growth in carbon coated capsules resulted in the formation of larger precipitates which also gave rise to strain contrast, and are possibly related to those described by Vere [16].

Acknowledgements

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