PVT-GROWN SINGLE CRYSTALS
OF $Cd_{1-x}Zn_xTe$ ($x \leq 0.25$) AND ZnTe
AS SUBSTRATES FOR EPITAXY

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The process of growth of single crystals of $Cd_{1-x}Zn_xTe$ ($x \leq 0.25$) and ZnTe by physical vapour transport has been optimized and the twin-free single crystals with a very good crystal structure and low density of dislocations are grown as substrates for MBE and other techniques of epitaxy. Characterization of the crystals is described.

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1. Introduction

The crystals of a very high quality are required as substrates for MBE and other techniques of epitaxy. In particular — the good real crystal structure is extremely important. We have optimized the process of growth of single crystals of $Cd_{1-x}Zn_xTe$ and ZnTe by a physical vapour transport (PVT) technique and we are growing large single crystals of those compounds.

Here we are going to show the results of characterization of the substrate crystals and of the source material used for the PVT process.

2. Growth of crystals

The characterized crystals are grown by the PVT technique, which was described for the first time by Piper and Polich [1]. The source material is placed in a closed horizontal quartz ampule with a conical tip at the colder end. The length of the ampule is about 12 cm and the internal diameter is 25 mm and the mass of the batch is 80–130 g. The temperature profile of the oven is the same as the profile described in the paper on CVT growth [2]. The ampule travels inside the oven 5–6 mm/day. The growth of the crystal takes 10–14 days.

3. Source material

We synthesize the compounds (ZnTe and $Cd_{1-x}Zn_xTe$) for the source material from the elements which are purified in our laboratory by the multiple vacuum (10^{-6} Tr) distillation. Purity of the elements is controlled by the Spark Source Mass Spectrometer. It is 6N for Te and 5N8 for Cd and Zn. Zinc and cadmium contain about 0.1–0.5 ppm of Na and K and less than 0.05 ppm of Li. The amount of Cu and the transition metals is also below 0.05 ppm in Zn and Cd. The synthesis of the compound is performed by a method similar to that described by Cantwell et al. [3]. The synthesized compound, in the form of a powder, is baked at a few consecutively increasing temperatures in the range 600–900°C. The resulting polycrystalline material of proper stoichiometry is used as the source material for the final crystal growth. The quality of this source material turned out to be one of the most important factors influencing the process of growth and the quality of the final crystals. This is why the source material was the object of characterization similar to that used for the final crystals. The composition was studied by the energy dispersive X-ray fluorescence (EDXRF) and reflectivity measurements in the region of free exciton. The photoluminescence excited by a He–Cd laser
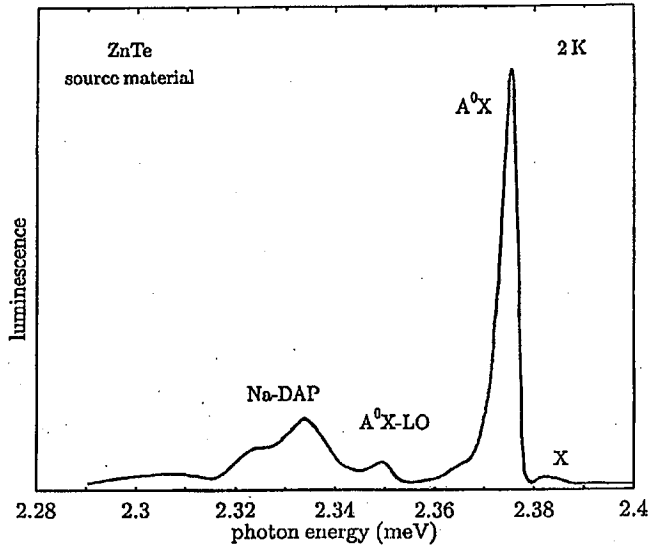

Fig. 1.   Luminescence spectrum at 2 K for ZnTe (polycrystalline) prepared as the source material for the PVT crystal growth.

was measured at 2 K. The photoluminescence spectrum typical of good source material for the growth of ZnTe crystals is presented in Fig. 1. The presence of the free exciton (X) line at 2381 meV testifies to the low concentration of impurities as the recombination of bound excitons competes with the recombination of free excitons. The dominating line belongs to the exciton bound to Na or Li acceptor. Na is more likely, because of the much higher Na content in the start-

ing elements (Cd and Zn). For both ZnTe and $Cd_{1-x}Zn_x$Te the source material, which gave good results of the PVT growth, was p-type and the resistivity at room temperature was 10^3-10^4 Ω cm.

4. Crystals

The twin-free monocrystalline blocks (cylinders) are usually 20–30 mm long and their diameter is 25 mm. The substrate plates (1–4 cm^2 in area) are cut from X-ray oriented single crystals with a multiwire saw. The various substrate surfaces (for example parallel to (100), (110), (111), (211), (311) crystal planes) were prepared. For the last three orientations — the tellurium side of the crystal was determined and prepared. The "epi-ready" surface of the substrate plates is finished by the etch attack polishing with the mixture of bromine, ethylene glycol, and methanol (4 ml : 75 ml : 125 ml).
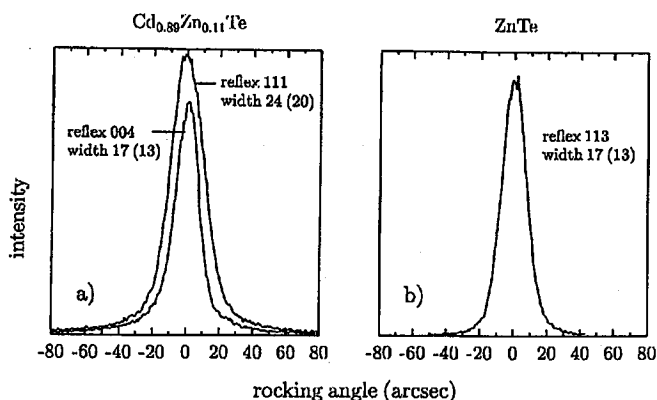

Fig. 2. X-ray rocking curves for a $Cd_{0.89}Zn_{0.11}$Te crystal (a) and a ZnTe crystal (b). The width (FWHM) in arcsec is given for each reflex. In paranthesis — the theoretical limit for the narrowness of the curve (for the diffractometer used).

The quality of the crystal structure of the substrate crystals was controlled by X-ray rocking curve measurements with a Philips High Resolution Diffractometer. The rocking curves for the ternary crystal $Cd_{1-x}Zn_x$Te and for ZnTe are presented in Fig. 2a and b, respectively. There are single narrow symmetric maxima. The theoretical lower limit for the width (full width at half maximum — FWHM) of the rocking curve, which is determined by both the physics of the X-ray diffraction and the parameters of the diffractometer, is written in each figure, to be compared with the actual result of measurement. One can see that the narrowness of the obtained curves is not far from this limit. The high quality of the crystal structure was confirmed also by the reciprocal space mapping of our crystals. This technique of measurement has shown that the stress, the presence of which was expected in ternary crystals (due to chemical disorder), is very small.

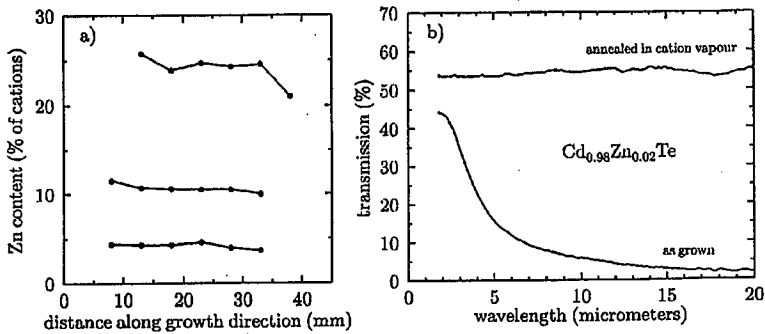The composition of the ternary $Cd_{1-x}Zn_x$Te crystals was studied by the EDXRF measurements. Figure 3a presents the composition distribution along the

Fig. 3. (a) Composition distribution along the crystal rod (in the growth direction) for the three $Cd_{1-x}Zn_xTe$ crystals. (b) Effect of annealing in cation vapour on the infrared transmission of a $Cd_{0.98}Zn_{0.02}Te$ crystal. The sample annealed in Cd vapours is compared with an as-grown sample. Annealing results in removal of the free carrier absorption.

growth direction for the three crystal rods with different compositions. Similar results were also obtained by measuring the position of the free exciton structure in the reflection spectrum and the position of the bound exciton line [4] in the luminescence spectrum. The small decrease in the Zn content can be seen in the growth direction, but there is usually a "plateau" in the middle of the rod. This region of the crystal is used to cut substrate plates.

To obtain information on the density of dislocations, the etch pit density (EPD) was measured for the "epi-ready" surfaces of the substrate plates. The EPD was in the range of $5 \times 10^3 - 10^4$ cm^{-2} for $Cd_{1-x}Zn_xTe$ crystals and about 10^4 cm^{-2} for ZnTe. After [5] NaOH was used to etch ZnTe, and after [6] — the EAg-1 etchant to $Cd_{1-x}Zn_xTe$. The shape of the etch pits [5] and the look of the surfaces [7] were used for ZnTe and $Cd_{1-x}Zn_xTe$, respectively, to distinguish between the two types of the surface: A (Zn or Cd) and B (Te).

To get information on the impurities — the luminescence, conductivity, Hall effect, and EPR measurements were carried out. The photoluminescence spectra of the as-grown crystals were measured at 2 K. The bound exciton line (A^0X) was usually weak and the spectra were dominated by the donor–acceptor pair (DAP) band corresponding to Na-acceptors but, opposite to our previous results [8], we were unable to detect DAP bands related to Cu-acceptors. We think that, due to the better purification of our materials, the concentration of Cu impurity is now well below 10^{15} cm^{-3}. At room temperature the crystals of both ZnTe and $Cd_{1-x}Zn_xTe$ are of p-type. For $Cd_{1-x}Zn_xTe$, for example, the concentration of holes is, according to Hall effect measurements, 10^{16} cm^{-3} (resistivity about 10 Ω cm) and the Fermi level lies about 190 meV above the top of the valence band. The acceptors are probably related to both native defects (cation vacancies) and impurities.

The EPR measurements did not reveal the microwave absorption due to paramagnetic impurities similar to Mn. This is very important if the magnetic properties of the structures deposited on the substrate crystals are to be studied.

The presence of free holes, mentioned above, is accompanied by the free carrier absorption (Fig. 3b). For some purposes (like the production of the infrared detectors), the substrate plates have to be transparent in the infrared part of the spectrum. It means that the free carrier absorption must be removed.

Such transparent, high resistivity substrate plates are prepared by annealing the crystals in the cation vapour. Figure 3b presents the effect of the annealing on the transmission up to the wavelength 20 micrometers.

The room temperature resistivity of the annealed crystals is about $10^6 - 10^7$ Ω cm. It means that, e.g., for $Cd_{1-x}Zn_xTe$ the Fermi level lies more than 500 meV above the valence band. In the luminescence spectrum of the annealed crystals the DAP bands are diminished and the bound exciton line begins to dominate the spectrum. We have not noticed the effect of annealing on the rocking curve and etch pit density.

Acknowledgments

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