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Photoluminescence of deep levels in (CdZn) Te-correlation with diffusion length measurement

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Abstract

Photoluminescence of deep levels near mid-gap in P-($Cd_{1-x}Zn_x$)Te ($x \approx 0.03$–0.05) grown by the vertical gradient freezing method was investigated. Correlation with recombination properties manifested by temperature dependence of diffusion length of minority electrons and the corresponding mobility-lifetime product was studied. Low-temperature photoluminescence (PL) in the spectral range 0.68–1.3 eV and a temperature dependence of diffusion length of minority electrons (DL) measured by EBIC in the temperature range 60–300 K on both as-grown and annealed samples (800°C and 900°C) were investigated. We observed, that while as-grown samples exhibited a steep increase in DL with decreasing temperature in the temperature range 60–140 K, annealing and subsequent quenching resulted in a significant decrease of DL at these temperatures. Photoluminescence band with a peak at approx. 0.84 eV in annealed samples with increased recombination and therefore low DL was observed, while no such peak was detected in the as-grown samples with high DL. Luminescence in the ≈ 0.8 eV band is usually attributed to a V_{Cd} related defect which is supposed to act as a recombination centre. It can be concluded, that a correlation between effects of increased recombination manifested by decreased values of DL at temperatures 60–140 K and detection of the ≈ 0.8 eV PL band was observed. Reduction of the mobility-lifetime product by increased recombination in (CdZn)Te single crystals is therefore probably connected with a presence of a V_{Cd}-related defect.

Keywords: (CdZn)Te; Photoluminescence; Diffusion length

1. Introduction

(CdZn)Te has been in the centre of interest due to its applications in detection of X- and gamma rays, in electro-optic devices and also as a substrate for epitaxial growth of mercury cadmium telluride. While crystallographic quality and good optical properties are crucial for (CdZn)Te substrates, electrical properties like a high mobility-lifetime product, high resistivity connected with a low leakage current are important for its use as a gamma and X-ray detector. For a production of (CdZn)Te with pre-defined optical and electrical properties and low concentrations of point defects and precipitates, identification of basic defects and their influence on material properties is necessary. One of the most commonly used experimental techniques for material characterization is the low-temperature photoluminescence (PL). In this paper we concentrate on PL results from spectral range 0.68–1.3 eV, that includes also signal from deep levels near the mid-gap. Properties of deep levels in CdTe and (CdZn)Te were investigated by several authors by PL, DLTS and PICTS methods. Generally, three groups of PL bands located at 0.5, 0.8 and 1.1 eV are observed in CdTe [1–3]. The 1.1 eV band is usually attributed to tellurium vacancy V_{Te}^{+} [4–6]. The 0.8 eV band was reported to consist of two subbands [2] at 0.72 and 0.81 eV. It has been attributed to an acceptor complex involving the native V_{Cd} defect and an impurity [7,8]. This level was also reported to be a good candidate

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to act as a recombination centre having comparable emission rates for electrons and holes [9].

The purpose of the present paper is to analyze deep PL bands in the spectral range (0.68–1.3 eV) in as-grown and annealed $Cd_{1-x}Zn_xTe$ ($x \approx 0.03$–0.05) and to investigate possible correlation with recombination effects in the samples analyzed from temperature dependence of diffusion length of minority carriers (DL) measured by electron beam-induced current (EBIC) method. This effect was already analyzed in Ref. [10], where correlation between DL and near band gap PL (≈ 1.5 eV) was looked for.

2. Experimental

(CdZn)Te samples used in this study were prepared in our laboratory by the Vertical gradient freezing method [11]. The as-grown samples were mostly P-type with a standard concentration of holes 10^{14}–10^{16} cm^{-3} and a mobility 30–70 cm^2/Vs at 300 K. Two sets of samples were fabricated. The first set was prepared from high-quality single crystalline (1 1 1) oriented P-(CdZn)Te slice (crystal A). Neighbor samples were annealed at 800°C and 900°C at different cadmium overpressures p_{Cd} (see Table 1) and after annealing quickly quenched to room temperature. The annealing procedure was performed in a one-zone furnace, when the p_{Cd} overpressure was created by additional Cd in the ampoule together with samples of (CdZn)Te powder being added in order to avoid surface damage during annealing. The annealing time was 10 days.

The second set of samples was prepared from the as-grown single crystal B by cutting samples along the [1 1 1] growth axis from the top to the bottom of the boule (height 2 cm) in order to characterize changing conditions during the growth (mainly due to changing p_{Cd} overpressure and Zn content) and their influence on basic electrical and PL properties.

PL measurements were performed in a FTIR spectrometer Bruker IFS66/S with a Ge and Si detectors in a spectral range (0.68–1.3 eV) at temperature 4.8 K in a continuous flow He cryostat. He–Ne laser with power ≈ 15 mW was used for excitation. Spectra were corrected with respect to sensitivity of the detectors. Diffusion length of minority carriers was measured by EBIC method in a JEOL-50 scanning electron microscope with a cooled holder for measurements in the temperature range 60–300 K [12]. Au-evaporated Schottky barrier was used for the separation of electron–hole pairs in the EBIC method.

3. Results and discussion

Results of measurements of DL of minority electrons on samples from the first set – annealed at 800°C and 900°C and different p_{Cd} overpressures together with an as-grown neighbor sample are presented in Fig. 1. Obviously, the as-grown sample shows a steep increase of DL and of the corresponding mobility-lifetime product (calculated from a standard relation $L^2 = (kT/e)\mu\tau$) at temperatures below 140 K. All three annealed neighbor samples show less steep increase of DL with decreasing temperature. The effect of increased recombination, which is manifested by shorter DL is stronger at higher annealing temperatures and lower p_{Cd} overpressure. These are experimental conditions that favor generation of cadmium vacancies V_{Cd} [13]. It is therefore a good reason to suppose, that the observed increased recombination is due to some V_{Cd} related defect or complex. Results of PL measurements are summarized in Table 1, where positions of the observed PL bands in the spectral range 0.68–1.3 eV are given for samples from both sets (the annealed set from single crystal A (samples No. 1–4), the as-grown set from single crystal B (samples No. 5–7). The PL band at 1.074–1.111 eV attributed to V_{Te} is present in all investigated samples and no correlation of its presence with recombination properties was found. The PL band at ≈ 1.23 eV is present only in one sample and also in this case we found no correlation with DL measurements. Other situation occurs in the case of the

Table 1

Crystal	Sample	T (anneal)	P_{Cd}	PL (eV) 1.2 eV band	PL (eV) 1.1 eV band	PL (eV) 0.8 eV band
A	1	as grown	×	×	1.08	×
A	2	800°C	8.7×10^{-4}	1.23	1.09	0.84
A	3	800°C	1.3×10^{-2}	×	1.07	0.75
A	4	900°C	0.3	×	1.07	0.85
B	5	as grown	×	×	1.08	×
B	6	as grown	×	×	1.09	0.84
B	7	as grown	×	×	1.11	0.84

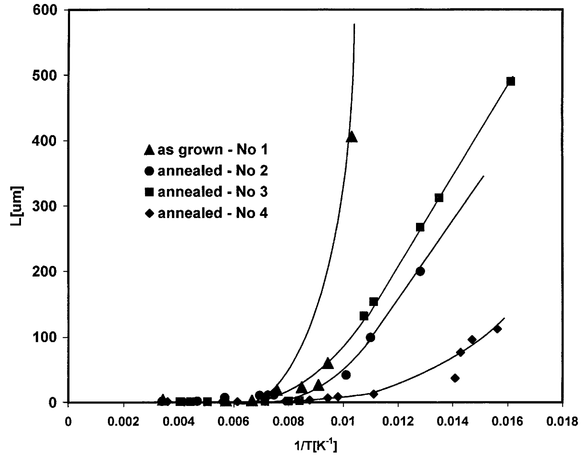

Fig. 1. Diffusion length of minority electrons in P-(CdZn)Te as-grown and annealed samples (crystal A).

PL band at ≈ 0.84 eV. All annealed samples have a significant PL signal in this spectral range. In the case of sample No. 3 the peak was slightly shifted towards lower energies. PL spectra of as grown sample No. 1 and the neighbor No. 4 annealed at 900°C, $p_{\mathrm{Cd}} \approx 0.3$ atm are given in Fig. 2. Dependence of the intensity of the ≈ 0.84 eV peak on DL of minority electrons at 100 K presented in Fig. 3 clearly shows the increase of PL intensity with decreasing DL.

Results of measurements of DL in samples from the second set (samples No. 5–7 cut along the growth axis of as-grown single crystal B) at room temperature and at 60 K are presented in Fig. 4. The top of the single crystal is N-type, the central part and the end are P-type. Diffusion length of both minority holes (N-type) and electrons (P-type) have a tendency to increase in the region, where P–N conversion occurs. Low-temperature (64 K) DL of minority electrons measured in the P-type part of the crystal are relatively long only in a very narrow region close to the P–N transition plain being very short in the rest part. PL analysis of these samples given in Table 1 shows, that the sample with relatively long DL at 64 K (No. 5) has only weak PL in the spectral range ≈ 0.84 eV, while the other two P-type samples representing the middle (No. 6) and the end of the single crystal (No. 7) have a clear PL band at ≈ 0.84 eV, whose intensity increases towards the crystal end.

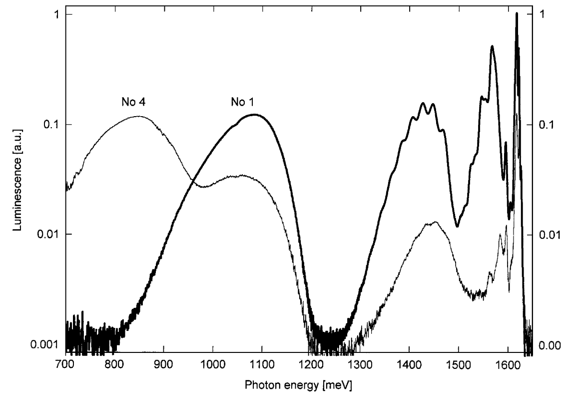

Fig. 2. Photoluminescence spectra of samples No. 1 and No. 4 (see Table 1).

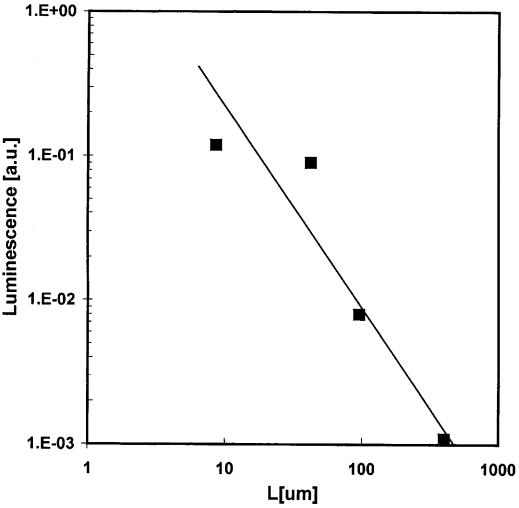

Fig. 3. Dependence of intensity of the ≈ 0.84 eV peak on diffusion length of minority electrons at 100 K (crystal A).

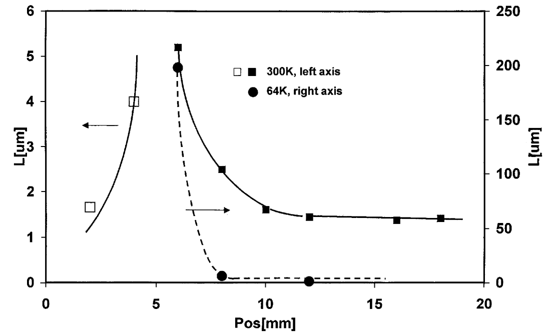

Fig. 4. Diffusion length of minority holes (open symbols) and electrons (full symbols) on a set of samples cut along the growth axis of crystal B at room temperature and at 64 K.

The results can be explained as follows. The growth of crystal B occurred in a p_{Cd} overpressure ≈ 1 atm. While the top of the crystal had direct contact with the surrounding Cd atmosphere, the central part and the end solidified under Te rich conditions, which resulted in a higher concentration of V_{Cd}. The same effect was reached by annealing and subsequent quenching of samples from the first set. The generated cadmium vacancies then could create complexes with some residual foreign impurities, which is manifested by increased PL at ≈ 0.84 eV. We conclude, that combined measurements of DL of minority electrons and PL in the spectral range (0.68–1.3 eV) indicate, that deep energy level ≈ 0.84 eV usually attributed to the V_{Cd} – foreign impurity complex, is responsible for increased recombination at temperatures below 140 K, which is manifested by shorter DL of minority electrons and of the corresponding mobility-lifetime product in P-(CdZn)Te samples.

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