Effects of Cd compensation on the photoluminescence of Cd$_{1-x}$Zn$_x$Te single crystals grown by the modified Bridgman method

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ABSTRACT In order to deal with the phenomenon of Cd evaporation during the growth of Cd$_{1-x}$Zn$_x$Te ($x = 0.1$) crystals, Cd compensation was adopted during the growth by adding excess Cd into the raw materials. Photoluminescence (PL) spectra were used to investigate the effects of Cd compensation on the properties of Cd$_{1-x}$Zn$_x$Te. A free exciton (FE) peak appeared in the near band-edge region after Cd compensation, which indicated that the concentration of Cd vacancies ($V_{Cd}$) was reduced in Cd$_{1-x}$Zn$_x$Te crystals by Cd compensation. The donor–acceptor pair (DAP) peak became dominant in the PL spectrum and its first and second order phonon replica could also be easily identified after Cd compensation, which was only a weak hump in the case of Cd$_{1-x}$Zn$_x$Te crystals without Cd compensation. It possibly meant that impurities of Al and In were released from the $V_{Cd}$-related complexes. In addition, the deep energy level transition $D$ peak, decreased obviously after Cd compensation, which confirmed that Cd compensation could reduce the dislocation density effectively.

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1 Introduction

The development of room temperature nuclear radiation detectors eliminates complicated cooling systems, and therefore, enlarges the applications in medical imaging, industrial process monitoring, and environmental protection etc. [1–6]. The compound semiconductor Cd$_{1-x}$Zn$_x$Te is the most promising material for room temperature nuclear radiation detectors because of its unique physical properties, which include: (1) a high atomic number for efficient radiation–atomic interactions; (2) a large enough bandgap for high resistivity and a low leakage current; and (3) a high intrinsic $\mu$ $\tau$ product for effective charge carrier collection, where $\mu$ is the carrier mobility and $\tau$ is the carrier life [1]. These advantages allow Cd$_{1-x}$Zn$_x$Te nuclear radiation detectors to work at room temperature efficiently. The modified Bridgman (MB) method has been successfully employed in the production of spectrometer quality Cd$_{1-x}$Zn$_x$Te single crystals [1–3]. Compared with other growth techniques, Cd$_{1-x}$Zn$_x$Te grown by MB increases the processable area of usable wafers. In addition, MB equipment is relatively cheap, which reduces the production cost of Cd$_{1-x}$Zn$_x$Te single crystals to a large degree. However, due to the high Cd partial pressure, a lot of Cd evaporates from the raw material during the MB growth process and the as-grown Cd$_{1-x}$Zn$_x$Te crystals involve large numbers of Cd vacancies ($V_{Cd}$) and Te precipitates, which severely degrade the opto-electronic properties of Cd$_{1-x}$Zn$_x$Te crystals [4, 5]. Therefore, Cd compensation must be adopted to eliminate the influence of these defects. Generally speaking, there are two effective approaches to compensate for Cd levels in Cd$_{1-x}$Zn$_x$Te crystals. One is to anneal as-grown Cd$_{1-x}$Zn$_x$Te crystals in a Cd-rich atmosphere. The other is to add excess Cd into the stoichiometric raw materials. The latter method was applied in our research.

Photoluminescence (PL) measurement is a sensitive non-destructive technique for detecting intrinsic and extrinsic defects in semiconductors. It provides abundant information about energy states of impurities and defects, even at very low densities, which helps us to clarify different recombination processes in semiconductors. Hence, the analysis of PL spectra is very helpful for understanding the specific mechanism responsible for the variation of opto-electronic properties of Cd$_{1-x}$Zn$_x$Te caused by Cd compensation.

In this work, several Cd$_{1-x}$Zn$_x$Te ($x = 0.1$) single crystals were grown with the MB method, which were compensated by adding excess Cd into the raw materials. Their optical properties were analyzed in detail according to the results of the PL spectra. Some important features of the PL spectra were found.

2 Experimental procedures

Using the MB method, Cd$_{1-x}$Zn$_x$Te ($x = 0.1$) crystals were grown with Cd compensation in our laboratory. High purity raw materials of Cd (7N), Zn (7N) and Te (7N) were used to prevent the occurrence of unintended impurities. Excess Cd was added into stoichiometric raw materials to compensate for the evaporation. The following Clapeyron equation was used to calculate the mass of Cd evaporated from raw materials, $m_{Cd}$.

$$PV = nRT = (m_{Cd}/M_{Cd})RT$$  (1)
or,

$$m_{\text{Cd}} = \frac{(PV)}{RT} M_{\text{Cd}}$$  \hspace{1cm} (2)$$

where $P$ is the Cd equilibrium partial pressure at the growth temperature of 1423 K, which is approximately equal to $1.2 \times 10^5$ Pa [2], $V$ is the spare space above the Cd$_{1-x}$Zn$_x$Te crystal in an ampoule, $R$ is the gas constant, $T$ is the growth temperature of Cd$_{1-x}$Zn$_x$Te crystal, $n$ is the mole number and $M_{\text{Cd}}$ is the mole mass of Cd. In our experiment, excess Cd with the mass of $m_{\text{Cd}}$ was added into the raw materials to compensate for the evaporation. For comparison, a Cd$_{1-x}$Zn$_x$Te ingot without Cd compensation was also grown with the MB method.

The ingots produced in this way were cut along (111) faces with the dimensions of $5 \times 5 \times 2$ mm$^3$. The bulk resistivity of Cd$_{1-x}$Zn$_x$Te wafers are at the level of 10$^8$ $\Omega$ cm. Before PL measurements, all wafers were carefully mechanically polished with an MgO suspension and then etched with 5% bromine in methanol (Br-MeOH) for 4 min to reduce the mechanically-damaged surface layer.

In PL measurements, the samples were attached to a cold copper finger in a closed-cycle cryostat with thermal grease, and the sample temperature was varied from 10 K to 300 K. An argon ion laser with a wavelength of 458 nm was used to excite the PL spectra. A Triax 550 tri-grating monochrometer with a photo-multiplier tube (PMT), whose spectral resolution was better than 0.3 nm, was employed to collect and to analyze the emissions of the samples.

3 Results and discussions

3.1 Typical photoluminescence spectra

Figure 1 gives the typical low temperature PL spectrum of Cd$_{1-x}$Zn$_x$Te ($x = 0.1$) crystals with Cd compensation. For reference, the PL spectrum of a Cd$_{1-x}$Zn$_x$Te ($x = 0.1$) wafer without Cd compensation is also presented. Both of the spectra can be divided into three regions: region (I) the near band-edge region, from 1.68 eV to 1.64 eV, which consists of the free exciton (FE) peak, the neutral donor bound exciton (D$^0$, X) peak, the neutral acceptor bound exciton (A$^0$, X) peak and the LO phonon replica of the (A$^0$, X) transition ((A$^0$, X)–LO); region (II) from 1.64 eV to 1.55 eV, covering the donor–acceptor pair (DAP) recombination and its phonon replicas; region (III) from 1.55 eV to 1.38 eV, showing the deep energy level transition associated with some defects such as dislocations. Here, the band located in the defect-related Region is named as the D peak.

As shown in Fig. 1, when Cd$_{1-x}$Zn$_x$Te crystals were compensated with excess Cd, several interesting phenomena were found. First, a free exciton (FE) peak appeared, which was undistinguishable in the case of Cd$_{1-x}$Zn$_x$Te without Cd compensation. Secondly, in the case of no Cd compensation, there existed only a weak hump centered at 1.600 eV representing the donor–acceptor pair (DAP) recombination in the PL spectrum. However, when excess Cd was added into the raw materials, the DAP emission dominated in the whole PL spectrum. In addition, the first and second order phonon replica of DAP could also be easily identified. Thirdly, the intensity of the D peak was obviously reduced after Cd compensation was carried out.

3.2 Excitonic emission peaks

To show the near band-edge region in detail, the high-resolution PL spectra of Cd$_{1-x}$Zn$_x$Te crystals with and without Cd compensation are given in Fig. 2 respectively. The broad band might be caused by some overlapping emissions with different transition energies. Therefore, several Gaussian functions were used to fit the measurement results of PL spectra. In the case of Cd$_{1-x}$Zn$_x$Te without Cd compensation, three Gaussian curves could describe the experimental curve very well. The corresponding transitions were: (D$^0$, X) centered at 1.6540 eV, (A$^0$, X) centered at 1.6533 eV and ((A$^0$, X)–LO) centered at 1.6399 eV. However, in the case of Cd$_{1-x}$Zn$_x$Te with Cd compensation, four transitions were necessary to fit the curve perfectly, which separated the following transitions: (FE) centered at 1.6593 eV, (D$^0$, X) centered at 1.6540 eV, (A$^0$, X) centered at 1.6533 eV and ((A$^0$, X)–LO) centered at 1.6399 eV. However, in the case of Cd$_{1-x}$Zn$_x$Te with Cd compensation, four transitions were necessary to fit the curve perfectly, which separated the following transitions: (FE) centered at 1.6593 eV, (D$^0$, X) centered at 1.6540 eV, (A$^0$, X) centered at 1.6533 eV and ((A$^0$, X)–LO) centered at 1.6399 eV. However, in the case of Cd$_{1-x}$Zn$_x$Te with Cd compensation, four transitions were necessary to fit the curve perfectly, which separated the following transitions: (FE) centered at 1.6593 eV, (D$^0$, X) centered at 1.6540 eV, (A$^0$, X) centered at 1.6533 eV and ((A$^0$, X)–LO) centered at 1.6399 eV.