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Band gap energy determination by photoacoustic absorption and optical analysis of $Cd_{1-x}Zn_xTe$ for low zinc concentrations

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Abstract

In this paper we present a study of the optical properties of CdZnTe single crystal for low Zn concentrations at room temperature using photoacoustic spectroscopy and photoreflectance (PR) measurements. The photoreflectance measurements were carried out in order to determine the E_g value at room temperature of the CdTe sample to validate the criterion for the photoacoustic absorption measurements. The closed photoacoustic cell configuration (CPC) was used for the absorption measurements and, we use the knee method in the spectra for the energy band gap determination of CdZnTe as a function of the Zn concentration. The samples under study are commercial samples grown by the Bridgmann technique. X-ray diffraction was carried out in order to determine the Zn concentration of the samples and the FWHM of the diffraction peaks. The correlation between FWHM of the diffractograms and the photoacoustic absorption slopes shows that the absorption slopes could be associated with the crystalline quality of samples.

Keywords: A1. Crystal structure; A1. Optical properties; A1. X-ray diffraction; B2. Semiconducting II–VI materials

1. Introduction

$Cd_{1-x}Zn_xTe$ widely used as a material for X-ray detectors [1], other optoelectronic devices such as far infrared detectors [2], and as a substrate for lattice-matched growth of CdHgTe and ZnHgTe epitaxial films [3]. In the case of $Cd_{1-x}Zn_xTe$ crystals with Zn concentration near 4%, the material has been studied because its lattice parameter matches that of $Cd_{0.22}Hg_{0.78}Te$ for epitaxial growth [4]. Recent studies related to the crystalline quality for low Zn concentration (<0.08) have found that the thermal, structural and optical properties of these materials are strongly dependent on the zinc distribution in the sample [5].

Important issues in the study of semiconductor materials are the non-invasive, non-destructive and remote character of the techniques used to monitor their properties. Among the techniques, photoacoustic spectroscopy (PAS) has been used in the past few years to study the optical and thermal properties of semiconductors [6]. Using this technique Rodriguez et al. [7] studied the thermal diffusivity and electrical conductivity of $Cd_{1-x}Zn_xTe$ single crystals for low Zn concentration demonstrating that the crystalline quality affects the thermal properties of this semiconductor. With this technique, it is also possible to determine the band gap energy of different kinds of semiconductors, such as single crystals and polycrystalline materials, even if they are optically opaque at the energies near the band gap. The measurement of the absorption spectrum in semiconductors leads to the determination of the interband energy [8,9] involving non-radiative relaxation mechanisms.

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In the literature there exists a controversy about the criterion to determine the E_g value through absorption experiments. One of the most used criterion is based on the quantitative analysis of the whole absorption spectra using the Elliot–Toyozawa model [10,11]. Another model is based on the analysis of the first derivative of the PA signal as a function of the energy, but due to the non-symmetry of the derivative spectrum, it is necessary to include another criterion to determine the position of the peak. Finally, the model by A.K. Bhatnagar et al. [12], known as the knee method, uses the intersection between two tangents lines to determine E_g, located at the beginning of the absorption edge and the second one is tangent to the abrupt change of the slope in the absorption spectrum.

The three main processes involved in the photon interaction with a solid are absorption, spontaneous emission and stimulated emission. When the energy of the incident photon ($h\nu$) is equal to the band gap energy (E_g), it could be absorbed creating an electron–hole pair; this process corresponds to the so called intrinsic transition. On the other hand, when $h\nu$ is greater than E_g, the excess energy ($h\nu-E_g$) is dissipated as heat due to the interaction of electrons and holes with phonons. In the case that the incident photon energy is lower than E_g, it will be absorbed only if there are available energy states in the forbidden band gap due to the impurities and defects. These transitions are called extrinsic transitions.

The advantage of the PAS technique over photoluminescence (PL) is a clear absorption spectrum at room temperature, even for opaque samples. However, it is necessary to assure the same surface conditions for quantitative analysis of different samples.

Photoreflectance (PR) measurements were carried out to determine the E_g value at room temperature of the CdTe sample, in order to validate the criterion in the photoacoustic absorption measurements. PR is a modulation technique based on the reflectivity variation due to a periodic perturbation of the surface electric field. It is a powerful tool for the determination of optical properties of semiconductors, where the line shape could be described by the Aspnes theory [13]. It is possible to obtain the band gap energy value by fitting the experimental spectra to the theoretical expression, according to the order of the critical point. It is well known that the CdTe Van Hove singularity E_0 is a high symmetry critical point and its PR spectra is a third derivative Lorentzian line shape.

In this paper we present a study of the optical properties of CdZnTe single crystals at room temperature, for low Zn concentrations. We use photoacoustic spectroscopy and also include a PR measurement of a CdTe single crystal in order to chose a criterion for the CdZnTe band gap determination as a function of the Zn concentration, assuming the same surface condition for the samples.

2. Experimental procedure

Five samples were used in this study. One of them, a CdTe single crystal was purchased from II–VI Inc. USA, and the other four samples (see Table 1) are commercial samples from Cleveland Crystals USA. X-ray diffraction was carried out in order to determine the Zn concentration of each sample. It was determined using a Siemens D5000 diffractometer operating at 35 KV, 15 mA with CuK_α radiation. The concentration values and the crystalline quality of these samples were determined using a pure silicon $100\,\Omega\,cm^{-1}$ sample as internal standard to guarantee the alignment of the X-ray spectrometer and to avoid experimental mistakes [14]. For the photoacoustic measurements, the samples were mechanically polished on both surfaces with 0.3 μm alumina and washed in acetone for 3 min. The thickness were measured a Carl Zeiss Axiotech 100 optical microscope.

Fig. 1 shows the PAS experimental system used to study the E_g value as a function of the Zn concentration. In the photoacoustic technique, pressure waves created by a periodical-heated sample are detected by means of an electret microphone [15]. For the photoacoustic signal reading, we used a lock-in amplifier SR 830 DSP tuned with the chopper SR 540, which is used to periodically chop the light beam. In the CPC configuration [6,16], the cell is composed of an Al cylinder with a small channel at its periphery in which the microphone is inserted. The excitation source is monochromatic light, coming from a 1000 Watt QTH lamp and a monochromator SPEX 270 M. All the measurements were done at room temperature. In order to achieve the normalization process in which the microphone response function is included, it is necessary to read the spectrum of carbon black powder, which is almost a 100% absorber throughout the wavelength range used (720–1000 nm). The normalized amplitude signal, is taken as A_s/A_c, where A_s is the absorption spectrum of the sample, and A_c is the lamp spectrum.

Table 1
Band gap energy for $Cd_{1-x}Zn_xTe$ single crystal samples with different Zn concentrations, X-ray diffraction main peak at 2θ and its FWHM, and the slope of the PA absorption spectra

Sample	2θ [1 1 1]	Zn concentration (%)	E_g (eV) at RT ± 0.015	$FWHM^{-1}$	Slope
II–VI Inc.	23.746	0.00	1.505	7.37	5.753
2	23.793	2.34	1.515	9.85	5.739
D	23.802	2.84	1.530	10.46	8.503
W	23.833	5.18	1.540	10.06	6.921
B	23.837	5.68	1.547	8.40	5.480