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Relationship between the cathodoluminescence emission and resistivity in In doped CdZnTe crystals

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Cadmium zinc telluride, CdZnTe, bulk single crystals doped with 10^{19} at./cm^3 of indium in the initial melt were grown by vertical Bridgman technique. The samples were investigated by energy dispersive spectroscopy, cathodoluminiscence (CL), and current-voltage behavior at room temperature. The results shows that Cd and Te vacancy concentration depend on the indium and zinc concentrations. CL measurements indicate a relationship between radiative centers associated to Cd and Te vacancies and resistivity values. © *2009 American Institute of Physics*.
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I. INTRODUCTION

Cadmium zinc telluride (CZT) is a promising semiconductor material for application such as room-temperature radiation detector, photonics, and infrared imaging.[1–4] In the last decades, CZT in bulk and epitaxial form has been growth by different techniques, but its commercial use is still limited due to different problems, principally related to the growth process.

In particular, CZT presents very interesting features required for x-ray and γ-ray detector and numerous works have been carried out to improve the properties of this material. One important property is the resistivity of the sample for its use as detector that has to reach values higher than 10^{10} Ω cm. In fact, it is well recognized that zinc concentration is a determining factor to obtain such high resistivity because the incorporation of Zn induces and increases in the band gap, which allows for a high electrical resistivity with low leakage current.[5,6] According to these previous works, in the case of $Cd_{1-x}Zn_xTe$ crystals, Zn concentration should not overcome the value of 20 at. % and the optimum value is around 10 at. %. However, in the crystal growth process, there is Cd and Te losses causing generation of native Cd and Te vacancies. These vacancies can reduce the resistivity and change the conductivity type of the CZT crystals. Different studies show that by addition of certain concentrations of dopants, the resistivity of the material increases up to four orders of magnitude, by constant Zn concentration. In this way, an appropriate doping element is necessary for compensation. Indium (In) has been selected as the most adequate dopant in a concentration range of 1×10^{19} at./cm^3 to 8×10^{19} at./cm^3. In this work, the relation between the In induced variations of native vacancies, detected by cathodoluminescence (CL) and the resistivity of CZT single crystals has been investigated.

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II. EXPERIMENTAL DETAILS

High-purity 99.9999% Cd, Zn, and Te (initial stoichiometry 85% Cd, 15% Zn, and 100% Te, and 61.6880, 6.3138 and 82.4482 gr., respectively) elements were used as starting material to grow two In-doped CdZnTe crystals with a doping level of 1×10^{19} at./cm^3, in high-quality quartz ampoules by vertical Bridgman method. Details on this technique can be found elsewhere.[7,8] The samples were mechanically polished with alumina powder and chemically etched with 2% bromine-methanol solution to remove any mechanical surface damage; afterwards the samples were washed with methanol to remove any rest of the chemical solution.

CL measurements, spectra, and images were carried out in a Leica 440 scanning tunneling microscopy (SEM) and in a Hitachi 2500 SEM at liquid nitrogen temperature in both cases. The electron beam energy used during the measurements was of 20 keV and a R5509 Hamamatsu photomultiplier tube was used for the CL signal detection. Energy dispersive x-ray spectroscopy (EDX) measurements were carried out in a Leica 440 SEM electron microscope equipped with a BRUKER AXS QUANTAX system. In order to investigate the resistivity of the samples, current-voltage (I-V) characterization was carried out at room temperature, using a Keithley system Electrometer (6514 model) and ET NHQ 105L dc high voltage power supply.

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TABLE I. EDX measurements of sample 1 and sample 2.

CdZnTe:In	Te (at. %)	Cd (at. %)	Zn (at. %)	In (at. %)
Sample 1	47.95	40.58	10.18	1.24
Sample 2	47.48	39.39	11.78	1.3

III. RESULTS AND DISCUSSION

In order to obtain the concentration of elements in the samples, energy dispersive spectroscopy (EDS) measurements were carried out. Both samples (sample 1 and sample 2) present similar Te concentration as Table I shows. Similar In concentration values of 1.24% and 1.3% were measured in samples 1 and 2, respectively. On the contrary, Cd and Zn concentrations change from one sample to another, and a higher value of Zn concentration corresponds with a lower concentration of Cd, which indicates that Zn atoms are incorporated into the Cd sublattice.

After gold contacts deposition on the surface of both samples, current-voltage measurements were carried out. *I-V* curves were recorded at room temperature and a typical curve, recorded on sample 1, is shown in Fig. 1. The resistivity values measured on sample 1 are in the range of $(2.87-7.85)\times 10^7\ \Omega$ cm, whereas the resistivity values measured on sample 2 are in the range of $(3.1-4.8)\times 10^3\ \Omega$ cm. In fact, the Ohmic behavior of sample 1 is clearly noticeable; while a rectifier behavior is observed in sample 2.

In order to investigate the origin of this high difference in resistivity values, which in principle could be attributed to the difference in Cd and Zn compositions and to native defects in the material, such as Cd and Te vacancies, CL measurements have been carried out. CL enables to investigate the change in the Zn concentration through the bandgap emission and the presence of Cd and Te vacancies through radiative transitions.[9–11] It is established that for example, Cd vacancies introduce a radiative center labeled A-band, which is related to a luminescence band centered around to 1.4 eV. Figure 2 shows typical CL spectra of the two samples. In both cases, three emission bands are observed, but no bands related to band-to-band transitions appear in the spectra. Both samples present a very high CL signal with the main emission bands centered at 1.4 and 0.75 eV. The band at 1.4

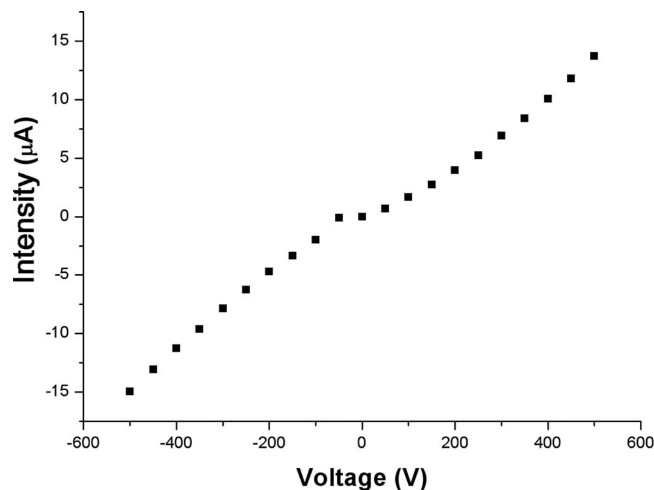

FIG. 1. *I-V* curve of CdZnTe (set 1) at room temperature.

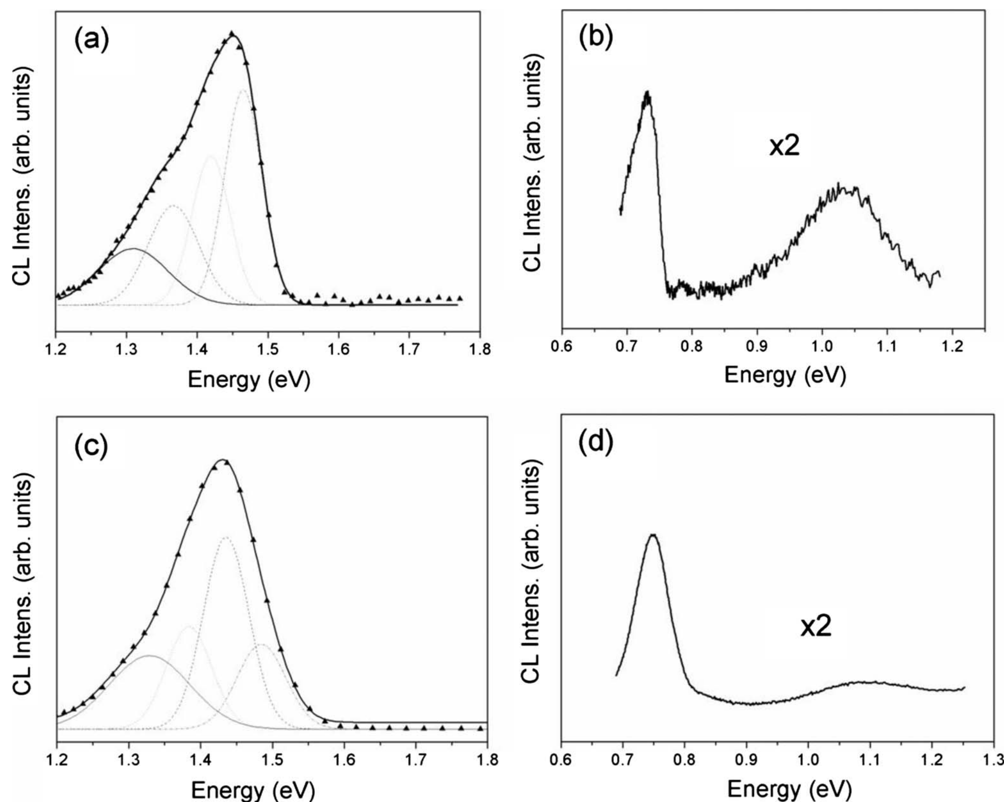

FIG. 2. CL spectra of set 1 [(a) and (b)] and set 2 [(c) and (d)] at 78 k.

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eV, often referred as band A, is related to complex defects involving Cd vacancies and impurities.[12] Gaussian deconvolution of this band shows that at least, four emissions are involved with some differences between sample 2 and sample 1. In sample 1, a broader band is observed. Deconvolution shows that another emission, centered at 1.32 eV, contributes to the broadening. This additional emission, only observable in samples of CZT doped with In, could be associated to the presence of this dopant. The intensity of this band is similar in both samples and it is in agreement with the fact that In concentration is similar in both samples. The 0.75 eV band is a complex band too. Gaussian deconvolution of this emission shows that it is composed of at least two emissions. Its intensity is very similar to that of A-band and its origin is related to double ionized Cd vacancies.

Another emission band, centered at about 1.1 eV, is present in both samples. This band, which has a lower intensity than the 1.4 and 0.75 eV, is related to Te vacancies and it has been previously reported in CdTe and CdZnTe.[13] The different intensities of the 1.1 eV in both samples shows that concentration of the defects responsible of this emission is lower in the sample 2 that in sample 1. We suggest that the different resistivities from sample 1 and sample 2 could be related to the concentration of electrically active defects. In particular, the 1.1 eV band has a higher relative intensity in sample 1, which shows higher resistivity. The Te vacancies related to this emission could partially compensate the effect of Cd vacancies, which act as donors, and contribute to an increase in resistivity.

IV. CONCLUSIONS

The relationship between the resistivity and the native vacancies present in In-doped CdZnTe crystals has been investigated. A relationship between the values of the resistivity and the presence of luminescence band related to vacancies has been found. Normally, a high concentration of Cd vacancies induces a drastic decrease in resistivity. However, the presence of Te vacancies, detected by a luminescence band centered at 1.1 eV, appears to compensate the effect of the Cd vacancies and to contribute to an increase in resistivity. CL measurements reveal an emission band related to In as a dopant in CZT and centered at 1.32 eV. This additional band is present in both samples with the same intensity and consequently is not related to the different resistivities of samples 1 and 2.

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