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Characterization of thermal properties of $Cd_{1-x-y}Zn_xMg_ySe$ mixed crystals by means of photopyroelectric and infrared imaging techniques

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ABSTRACT

In this work a complete thermal characterization of $Cd_{1-x-y}Zn_xMg_ySe$ mixed crystals was carried out. Bulk $Cd_{1-x-y}Zn_xMg_ySe$ semiconductors with different x and y contents were grown from the melt by the modified high pressure Bridgman method. The photopyroelectric (PPE) method in the back configuration (BPPE) and the infrared (IR) lock-in thermography were applied to measure the thermal diffusivity. Values of thermal effusivity of the samples were obtained with the PPE technique in the front configuration (FPPE), coupled with a thickness thermal wave resonator cavity (TWRC) scanning procedure. Measured thermal effusivity together with the thermal diffusivity allowed calculating the thermal conductivity of the investigated materials. For the calculation of the specific heat, the densities of the samples were calculated from their weight and geometry. The effect of Mg/Zn molar ratio on thermal properties of these quaternary $Cd_{1-x-y}Zn_xMg_ySe$ compounds was analyzed and discussed.

1. Introduction

II–VI semiconductors are very promising materials from the point of view of their application in construction of visible radiation sources, green laser diodes, spintronics, photodetectors and many other applications in modern optoelectronics [1–3]. It is very important from the application point of view, that ternary and quaternary II–VI compounds allow almost smooth tuning of the band gap energy and lattice constant values by varying the composition [4]. $Cd_{1-x-y}Zn_xMg_ySe$ alloys are interesting materials for their potential applications in ultraviolet and visible light emitters [5,6], infrared IR photodetectors [7], distributed Bragg reflectors [8,9] and mid-IR quantum cascade lasers [10,11]. The knowledge of the basic thermal properties of these solid solutions is important for their applications in construction of optoelectronic devices. Thermal parameters are unique for each material, strongly dependent on the composition, structural characteristics of the sample and the preparation process. Quaternary $Cd_{1-x-y}Zn_xMg_ySe$ compound can be treated as the mixture of CdSe, ZnSe and MgSe binary semiconductors. Consequently, thermal properties of such an alloy exhibit a non-linear dependence on the content of individual components. The aim of this article is performing a complete thermal characterization (measurement of all static and dynamic thermal parameters) of the investigated materials and discusses the influence of the composition on their thermal properties.

Photopyroelectric methods have been extensively applied to study of thermal properties of condensed matter samples [12,13]. The major advantages of these techniques are their simplicity, high sensitivity, non-destructive character and adaptation on experimental restrictions for theoretical requirements. The thermal effusivity can be obtained in the front configuration (an incident radiation directly illuminates the sensor) coupled with TWRC method. On the other hand, the PPE method in the back configuration (the sample placed onto the sensor is excited by the incident radiation) requires a thin layer of the coupling fluid between the sample and the pyroelectric sensor. In this work the thermal diffusivities measured with PPE technique were underestimated (5% lower) compared to those obtained with lock-in infrared thermography. This fact is in agreement with results obtained by Salazar and Oleaga [14–16]. They have shown that the results obtained with BPPE technique are always underestimated due to the presence of the coupling fluid between the sample and the sensor. The influence of the coupling fluid in pyroelectric measurements of solids becomes significant especially for high conductive samples and at high modulation frequency of the incident radiation. One of the solutions to overcome this undesired effect could be a non-contact technique such as the infrared lock-in thermography.

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Table 1
The composition, geometry and mass of the investigated $Cd_{1-x-y}Zn_xMg_ySe$ crystals.

Starting composition		Results of analysis		Thickness [mm]	Diameter [mm]	Weight [mg]
x	*y*	*x*	*y*			
1	0	–	–	1.28	7.96	319.38
0.95	0.05	0.94	0.06	1	8.5	286.76
0.9	0.1	0.88	0.12	0.97	8.54	280.73
0.8	0.2	0.78	0.22	1.26	8.16	296.18
0.5	0.2	0.56	0.20	1.27	8.45	350.66
0.4	0.1	0.48	0.11	1.27	8.4	358.97
0.4	0.2	0.40	0.20	1.54	9.2	487.66
0.3	0.2	0.35	0.21	1.33	8.45	370.27
0.2	0.3	0.26	0.43	1.34	10.55	512.33
0.2	0.2	0.24	0.21	1.22	8.4	335.8
0.2	0.1	0.24	0.13	1.41	8.6	427.62
0.2	0.4	0.21	0.42	1.3	8.48	321.95
0.1	0.4	0.12	0.43	1.36	8.42	351.71
0.1	0.2	0.12	0.22	1.3	8.28	338.13
0	0	–	–	1.15	8.45	348.13

2. Materials and methods

2.1. Samples preparation

Quaternary $Cd_{1-x-y}Zn_xMg_ySe$ crystals were grown from the melt by the high-pressure, high-temperature modified Bridgman method using high purity powders of CdSe (99.995%), ZnSe (99.995%), metallic Mg (99,8%) and Se (99.9%) put in a graphite crucible in stoichiometric proportion. The crucible was then heated up to the temperature of 1850 K and kept at this temperature for 4–6 h. Then the crucible was moved out of the heating zone with the speed 2.4 mm/h. An argon pressure of 15 MPa was kept during the growth process. This method allows obtaining crystal rods of about 1 cm in diameter and up to few centimeters in length. Obtained crystal rods were cut perpendicular to the growth axis into about 1.4 mm thick samples. The plates were mechanically ground and then polished with diamond paste (1 μm). Their thickness and diameter were measured with a micrometer device (accuracy 10 μm). After such preparation samples were weighed with a Discovery OHAUS laboratory balance with the accuracy of 0.1 mg.

The real composition of investigated in this work crystal plates was measured. For determining Zn, Cd, and Mg contents in $Cd_{1-x-y}Zn_xMg_ySe$ solid solutions, the scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS) analysis was applied. Measurements were performed with scanning transmission microscope SEM-LEO 1430VP, made by LEO Electron Microscopy Ltd., Cambridge, England and X-ray spectrometer (energy-dispersive mode) Quantax 200, made by Bruker-AXS Microanalysis GmbH, Berlin, Germany, with EDX XFlash 4010 detector. The results showed that investigated samples were spatially uniform in composition. The EDS results as well as geometry and mass of the investigated $Cd_{1-x-y}Zn_xMg_ySe$ samples are listed in Table 1. The structure of the measured crystalline alloys was determined with X-ray diffraction method, which confirmed that the samples exhibited a wurtzite structure.

To check the change of the composition at both sides of the crystal plate, excitonic emission was recorded at the same temperature for two selected samples: $Zn_{0.78}Mg_{0.22}Se$ and $Cd_{0.45}Zn_{0.12}Mg_{0.43}Se$. The observed differences in position of the maximum of the emission are directly connected with the composition. Obtained values of the difference in Mg concentration between two sides of the crystal plate (1.4 mm) were about 0.00326 and 0.00644 for $Zn_{0.78}Mg_{0.22}Se$ and $Cd_{0.45}Zn_{0.12}Mg_{0.43}Se$ samples, respectively. These values are of the order of the accuracy of the method used for the composition analysis. To confirm results obtained from the luminescence measurements, additional elemental composition of three selected samples ($Cd_{0.45}Zn_{0.12}Mg_{0.43}Se$, $Cd_{0.63}Zn_{0.24}Mg_{0.13}Se$ and $Cd_{0.66}Zn_{0.12}Mg_{0.22}Se$) at both sides of the plates was carried out. The difference in the composition at both sides of the samples was not big and lied within the accuracy of the applied method. Obtained values of the concentration of each element were in good agreement with given in Table 1. However, the problem of the lengthwise gradient in the composition for ternary and quaternary compounds exist, therefore a more systematically research in this field would be undertaken in the future.

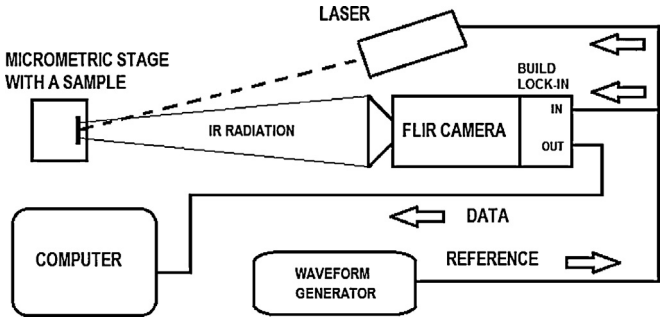

Fig. 1. Experimental setup for the lock-in thermography technique.

2.2. Experimental methods

An experimental setup for the BPPE measurement [17] consisted of a green, current-modulated DPSS (diode pumped solid state) laser (532 nm) with the output power of about 50 mW, a $LiTaO_3$ detector of the thickness 0.54 mm with Cr + Au electrodes and a SR830 lock-in processing of the measured signal. In this configuration the sample is placed onto the sensor and is directly exciting by the incident radiation. A thin layer of ethylene glycol served as a coupling fluid between the sample and the sensor. To protect the detector from the scattered light, a black diaphragm was used. Frequency scans were performed in the range from 0.3 Hz up to 15 Hz with 0.3 Hz single step. A blackening procedure with a thin carbon layer (<10 μm) was applied to the samples in order (i) to assure the optical opacity of the transparent samples and (ii) to avoid the influence of an optical exciting state of the semiconductor on its thermal properties (phonon scattering processes on free excited carriers).

The front configuration (FPPE) coupled with the thickness scanning procedure consisted of a red He–Ne laser (Melles Griot, 30 mW) modulated with an acousto-optical modulator, a 215 μm thick $LiTaO_3$ sensor coated with Cr + Au and a SR830 lock-in amplifier [18]. In this method the laser directly illuminates the sensor. The measured sample was put into the cell as a backing material. Between the sample and the sensor an ethylene glycol was inserted with the starting thickness of about 0.5 mm as coupling liquid with known thermal properties (effusivity: 890 $W\,s^{1/2}\,m^{-2}\,K^{-1}$, diffusivity: $9.36 \times 10^{-8}\,m^2\,s^{-1}$ [18]). The liquid was then compressed. Scanning procedure was performed by a 9062M-XYZ-PPP Gothic-Arch-Bearing Picomotor with a single step of 6 μm. The control of the parallelism between the backing and the sensor was assured by two 3 and 6-axis micrometric stages.

The experimental IR setup included a heat source, a waveform generator, an infrared camera and a computer for data acquisition (Fig. 1). The thermal images were collected from the blackened samples placed on a stage and excited with a green DPSS current-modulated laser (532 nm, 500 mW). The IR camera (FLIR 7200 Series) equipped with a 320×256 pixels array of InSb detectors with the spectral response in the range of wavelengths from 1.5 μm up to 5 μm recorded the changes in the surface temperature of the specimens. The noise equivalent temperature difference (NETD)