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Correlation between optical and thermal properties in ZnMgSe solid solutions

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HIGHLIGHTS

- Incorporation of Mg into ZnSe crystals plays a crucial role in properties.
- Refractive index decreases when Mg content introduced into $Zn_{1-x}Mg_xSe$ increases.
- Thermal properties decrease when the Mg content introduced into $Zn_{1-x}Mg_xSe$ increases.
- Energy band gap increases when Mg content introduced into $Zn_{1-x}Mg_xSe$ increases.

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ABSTRACT

The correlation between the optical (such as complex refractive index, energy band gap) and thermal (such as diffusivity, effusivity and conductivity) properties of $Zn_{1-x}Mg_xSe$ (with $0 \leq x \leq 0.50$) crystals are presented. The $Zn_{1-x}Mg_xSe$ mixed crystals were grown by the modified high-pressure Bridgman method and were studied using spectroscopic ellipsometry as well as photopyroelectric technique.

We found that when Mg content in $Zn_{1-x}Mg_xSe$ increases the value of E_g increases. Moreover, the values of thermal conductivity and refractive index of studied materials decrease with increasing Mg content in $Zn_{1-x}Mg_xSe$. Therefore, from the performed measurements, one can conclude that the incorporation of Mg as constituent into ZnSe crystals plays a crucial role in the observed optical and thermal response.

1. Introduction

Zinc selenide (ZnSe) is known as a material with high refractive index and a direct band gap of 2.7 eV at room temperature. In order to tune its optical and thermal properties over a wide range one should add different chemical elements (e.g. Mg, Be, Mn, S) into ZnSe lattice [1–8]. In this context, adding of Mg atoms make ZnSe crystals more interesting for potential optoelectronic applications and improved functional properties. Therefore, Mg-based II-VI compounds are interesting systems for the production of light emitting diodes operating in blue-green region of the visible spectrum.

For the design and construction of optoelectronic devices the knowledge of refractive index and absorption coefficient (determined from dielectric constants) as well as thermal diffusivity and thermal conductivity of these materials is important. Therefore, the goal of this work was study the correlation between optical and thermal properties of $Zn_{1-x}Mg_xSe$ (with $0 \leq x \leq 0.50$) crystals obtained by Bridgman method. This work is helpful in order to extend the knowledge of the optical and thermal properties of mixed ternary $Zn_{1-x}Mg_xSe$ semiconductor crystals depending on the Mg content introduced into ZnSe.

The systematic study of the optical and thermal properties of $Zn_{1-x}Mg_xSe$ mixed crystals can provide the information about the mechanisms responsible for them, which can enable a better understanding relation between optical and thermal processes

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occurring in the material and this is directly related to new practical applications. Therefore, the obtained results can be used for the possible design of other materials in this class with desired properties.

2. Experimental

2.1. Sample preparation

The mixed ternary crystals ($Zn_{1-x}Mg_xSe$ where $0 \leq x \leq 0.50$) were grown from a melt by the modified high-pressure Bridgman method under an argon overpressure of 11 MPa using ZnSe powder (6N Koch-Light) mixed with proper amount of metallic powdered Mg (purity of 99.8%) as a starting material. The prepared mixture was melted in the graphite crucible, kept at high (1850 K) temperature for several hours and then the crucible was moved-out of the heating zone with the speed 2.4 mm/h. The obtained crystals were cylindrical in shape with 10 mm in diameter and 5–7 cm in length. The crystals were cut into about 1.5 mm thick plates and mechanically polished. The final thickness of the investigated samples was about 1 mm [1–4,9–11].

The real contents of magnesium in this ternary alloys were determined with the standard SEM/EDS method, ICP chemical analysis, electron-probe analysis [12,13] and from lattice constant applying the Vegard's law. Energy-dispersive X-ray spectroscopy (EDS analysis) was performed with Quantax 200 X-ray spectrometer (Bruker-AXS Microanalysis GmbH, Berlin, Germany), equipped with EDX XFlash 4010 detector. For each sample the EDS analysis was performed in three different places of the crystal plate and the average values were calculated as the final results. Phase analysis was performed with the standard X-ray Brag-Brentano diffractometer and Ni-filtered Cu Kα radiation [12–17]. Philips high resolution transmission electron microscopy was used for investigation of crystal structure and lattice defects [15].

It has been established that $Zn_{1-x}Mg_xSe$ solid solution crystallize in sphalerite and wurtzite structure for low and high Mg content. The phase transition from sphalerite to wurtzite phase occurs at $x = 0.18$ [12–14,16,18]. At the transition region (x~0.18) the formation of 4H and 8H polytypes was observed [15,18–20]. In the samples with sphalerite structure formation of twins and edge dislocations has been found. The wurtzite phase exhibit better structural homogeneity. During the growth process with the method described above, some segregation of Mg along the crystal growth direction was observed. The concentration of magnesium was always larger at the end of the crystal boule. For $Zn_{1-x}Mg_xSe$ sample with Mg content about 50% ($x = 0.5$) and 10% ($x = 0.1$) the gradient of Mg content along the crystal axis was about 1.1%/cm and 0.04%/cm, respectively. For this reason the composition of each crystal plate investigated in this work was determined separately [15,21,22].

2.2. Methods

The real (n) and imaginary (κ) parts of the complex refractive index ($\tilde{n} = n + i\kappa$) of $Zn_{1-x}Mg_xSe$ crystals were determined from ellipsometric measurements in the spectral range from 0.6 eV to 6.5 eV using the V-VASE (J.A.Woollam Co., Inc.). The ellipsometric parameters, Ψ and Δ, were measured for three angles of incidence (65°, 70° and 75°). The three phase optical model (crystal/surface roughness/ambient) were used to determine the optical constants of the samples. A sum of Gaussian oscillators was used to parameterize the complex dielectric function of studied crystals [23,24]. Additionally, a band gap was determined using M0 critical point shape, and Sellmeier-type relation for real part of the complex dielectric function for energies lower than the absorption threshold [23,24]. The ellipsometry data analysis was performed using commercially available WVASE32 software [24].

The photopyroelectric technique (PPE) was used to measure the thermal properties of $Zn_{1-x}Mg_xSe$ crystals. This method is contact one compared to other photothermal methods such as IR thermography [11,25], photothermal radiometry [26–29], beam deflection spectroscopy [30–33]. The PPE directly measures heat oscillations. Analysis of measured heat oscillations gives the estimation of the thermal diffusivity and effusivity of studied samples using the thermal wave approach. Therefore, to estimate the thermal conductivity of investigated crystals one have to know the value of thermal parameters such as diffusivity and effusivity.

The experimental setup of standard PPE method for front and modified back measurements detection configuration was applied and is described elsewhere [9,10]. It consisted of a 300 mW power blue diode laser ($\lambda = 405$ nm), a 0.4 mm thick $LiTaO_3$ detector, provided with CrAu electrodes and a SR850 dual-phase lock-in amplifier. The excitation radiation was modulated electronically via lock-in TTL output.

3. Results and discussions

3.1. Optical properties

Spectroscopic ellipsometry (SE) is non-contact and non-destructive optical technique, which determines the optical constants of the material, which are represented by the complex dielectric function

$$\tilde{\varepsilon} = \varepsilon_1 + i\varepsilon_2 \quad (1)$$

or the complex refractive index

$$\tilde{n} = n + i\kappa = \sqrt{\tilde{\varepsilon}} \quad (2)$$

where ε_1 and ε_2 are the real and imaginary parts of the complex dielectric function, while n is the real part of the complex refractive index and κ is the extinction coefficient.

Spectral dependencies of the real part of the complex refractive index (n) and the extinction coefficient (κ) of mixed $Zn_{1-x}Mg_xSe$ crystals are shown in Fig. 1. In the non-absorbing spectral range (where $\kappa = 0$) the refractive index of studied crystals increase as the photon energy increases (Fig. 1a). We can also notice that for the selected wavelength the value of the refractive index decreases when the Mg content in $Zn_{1-x}Mg_xSe$ increases. For instance, for the ZnSe sample the n value at $\lambda = 532$ nm is 2.65 and decreases to 2.40 for the $Zn_{0.05}Mg_{0.50}Se$ crystal. From Fig. 1b we can see that all studied crystals are almost non-absorbing up to about 2.5 eV and exhibit noticeable absorption for photon energies above this value. We can also notice the shift of absorption spectrum in the direction of higher energy when the Mg content in $Zn_{1-x}Mg_xSe$ increases. For $x \geq 0.27$ we can see the differences in spectral dependencies of the real (n) and imaginary (κ) parts of the complex refractive index. This could be related to structural transformation of studied crystals at $x = 0.18$ [15,22].

The energy band-gap (E_0) for the ZnSe crystal is 2.65 eV and is in a good agreement with previous studies [34–37]. This critical point in the Brillouin zone corresponds to the direct transition from the highest valence band to the lowest conduction band at the Γ-point ($\Gamma_8 - \Gamma_6$) [27]. The spin-orbit splitting $E_0 + \Delta_0(\Gamma_7 - \Gamma_6)$ for the ZnSe sample is 3.56 eV. The critical point structures for higher energies, E_1 at 4.86 eV and $E_1 + \Delta_1$ at 5.14 eV can be attributed to ($L_{4,5} - L_6$) and ($L_6 - L_6$) transitions [37,38], respectively. The energy band-gap of MgSe is 3.6 eV at RT [35], thus the alloying of ZnSe and MgSe leads to the blue shift of the energy transitions; e.g. the