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Linear and nonlinear optical properties of $Zn_{1-x}Mg_xSe$ layers grown by MBE and PLD methods

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Ternary and quaternary $A^{II}B^{VI}$ mixing semiconductors are very attractive materials for various optical devices. Their optical properties such as the energy gap, linear refractive index, absorption coefficient and lattice constant can be changed with increasing component. For the practical application linear and nonlinear optical characterizations such as the two-photon absorption (TPA), linear and nonlinear refractive indexes are an important aspect. A practical motivation to measure the magnitude of TPA coefficient is that the performance of a device based on nonlinear refraction is strongly affected by the eventual nonlinear absorption.

The refractive index and TPA coefficient of $Zn_{1-x}Mg_xSe$ compounds grown on glass substrates by molecular beam epitaxy (MBE) and pulsed laser deposition (PLD) methods were systematically investigated as a function of Mg composition. The linear optical properties have been studied using transmission, reflection, and photoreflection spectroscopy. The nonlinear optical properties of these materials were investigated by the nonlinear transmission.

The energy gap and linear refractive index of these materials change with Mg content, hence the nonlinear optical processes such as TPA and nonlinear refraction index can be modified.

Keywords: $Zn_{1-x}Mg_xSe$ layers, reflection, transmission, refractive index, two-photon absorption, photoreflection.

1. Introduction

Wide-gap $A^{II}B^{VI}$ semiconductors have been subjected to extensive studies because these materials can be used to develop light-emitting diodes, lasers diodes and optoelectronic devices operating in the blue-green spectral region. We know that the compact coherent source with low cost and high efficiency operating in the blue and green regions of the visible spectrum are required for a broad range of applications, including compact displays, data storage and biomedical diagnostics.

In recent years, the promising candidates for optoelectronics devices in the blue-green spectral region are ZnSe-based materials. For these reasons, knowledge and control of linear and nonlinear optical properties such as energy bandgap, lattice constant, refractive index, absorption and two photon absorption coefficients of the studied materials are important in the design and analysis of laser structures and waveguiding devices [1].

Over the past few years, increasing attention has been denoted to the $Zn_{1-x}Mg_xSe$ ternary compounds because their optical properties can be changed with increase in Mg content [2]. So, the large bandgap of ZnSe semiconductors containing Mg makes these materials interesting for various optical devices in the whole visible and ultraviolet field.

Moreover, wide-gap $A^{II}B^{VI}$ semiconductors have been promising candidates for producing optical bistable switches, optical signal processing, optical computing and other nonlinear optical devices with low power, high speed and small size [3]. These semiconductors are also good candidates for many practical applications such as displays, high-density optical storage, modulators, etc.

Nonlinear materials with large optical nonlinearities and fast response speeds are fundamental requirements for future photonics devices. Also nonlinear absorption is important for sensor protection applications like multiphoton absorption induced optical power limiting. Thus, measurements of the magnitude and the transient response of optical nonlinearities, in particular the nonlinear refractive indices, of materials are becoming increasingly important.

In this paper, we report the experimental investigation of linear and nonlinear optical properties of $Zn_{1-x}Mg_xSe$ compounds grown on glass substrates by molecular beam epitaxy (MBE) and pulsed laser deposition (PLD) methods as a function of Mg content. The refractive indices with various Mg content were evaluated from the reflectance measurement. The two-photon absorption coefficient was calculated from nonlinear transmission measurements.

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2. Preparation of the samples

The $Zn_{1-x}Mg_xSe$ layers were grown on glass substrates by MBE and PLD methods. In MBE method, we used the elemental zinc, magnesium and selenium sources in independent carbon cells. The concentration of magnesium was controlled by Zn/Mg flux ratio changed. The temperature of substrate during the growth was kept in the range 560–575 K. All samples have zinc-blende structure with good structural quality, as monitored by *in situ* reflection high-energy electron diffraction (RHEED) and *ex situ* high-resolution x-ray diffraction. The value of the Mg content, x, was varied over a large range, but kept below 0.40 to avoid any structural phase change of the material. In PLD method, the vacuum chamber was evacuated down to 10^{-6} mbar pressure. The ultraviolet XeCl laser beam with 20 ns pulse duration, 10 Hz repetition rate, and 308 nm wavelength was focused at the target surface to induce material ablation. In order to achieve stationary ablation rate the target was rotated with angular speed about 18 rounds/min. A distance between the substrate and the target was about 4 cm. A thickness of the obtained layers was about 400–500 nm.

3. Experiment

The reflection and transmission spectra for the samples grown by MBE method were measured using a monochromator (SPM-2 Zeiss) with a photomultiplier (R-375 Hamamatsu). The reflectance measurements were performed using 100 W tungsten-halogen lamp as a light source. Optical spectra were measured for a series of $Zn_{1-x}Mg_xSe$ with different composition. The measurements were carried out at a room temperature.

The photoreflectance (PR) measurement for the samples grown by PLD method was performed using a monochromator (SPM-2 Zeiss) with 250-W halogen lamp as a probe source. Modulation of the sample surface electric field was produced by the photo-excitation of electron-hole pairs created by mechanically chopped 42 mW helium-cadmium laser (Omnichrome). The photon energy of the pump source was equal to 3.81 eV so, above the bandgap modulation conditions were satisfied. A chopper was tuned to the lock-in amplifier reference signal with frequency of 333 Hz. The change of reflectivity was measured by silicon photodiode using phase-sensitive techniques. To eliminate a parasitic signal, an appropriate long pass filter in front of a detector was used.

The TPA response of the samples grown by MBE method was measured using nonlinear transmission with a mode-locked Q-switched Nd:YAG laser with 30-ps pulse duration, 1-Hz repetition rate, and 532-nm wavelength. We assume that the intensity of the laser beam at the input face of the sample has a Gaussian distribution in space and time. The signal was detected by a photodiode Ph_1. A portion of the input beam was picked off and measured by a second photodiode Ph_2 to monitor the input energy. The photodiodes were averaged and displayed by a Tektronix TDS 3054 digital phosphor oscilloscope.

4. Results and discussion

In this work, we investigated $Zn_{1-x}Mg_xSe$ layers grown on glass substrates using MBE and PLD methods. Typical reflection and transmission spectra for the studied samples are shown in Figs. 1 and 2, respectively. As we can see, the reflection spectra indicate a periodic behaviour due to the interference effect between light reflected from the top and bottom interfaces of the $Zn_{1-x}Mg_xSe$ layer (Fig. 1). Periodical structures of fringes are observed in wavelength range of above 450 nm. The strong interference fringes can be seen in the reflection spectrum for $h\nu \leq E_g$ (in wavelength range longer than the band edge), where $Zn_{1-x}Mg_xSe$ layers are transparent. When the photon energy is larger than the bandgap energy $h\nu > E_g$ interference disappears. Oscillations rapidly decrease below 450 nm wavelength due to increasing light absorption in the $Zn_{1-x}Mg_xSe$ layers.

The oscillations, which we can see in Fig. 1, come from the interference due to reflection from the top surface of the film and the interface between the film and substrate. The period of the interference oscillations depends on the thickness and refractive index of the layer.

The measurement of the linear transmission of light through the $Zn_{1-x}Mg_xSe$ layers in the region of transparency is sufficient to determine the refractive index and the thickness (Fig. 2). We can see that transmission of the studied samples increases starting from about 400 nm and shows good transparency.

The refractive indices were calculated from oscillation in the reflection spectra using envelope method proposed

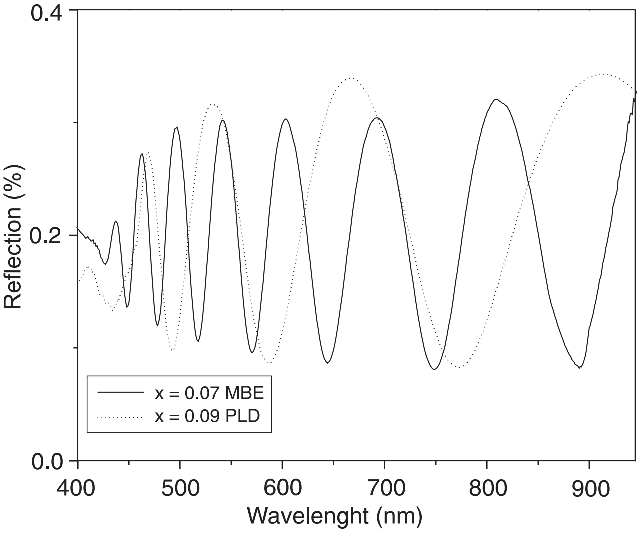

Fig. 1. Reflection spectra of $Zn_{1-x}Mg_xSe$ layers with different composition of Mg grown on glass substrates by MBE and PLD methods.

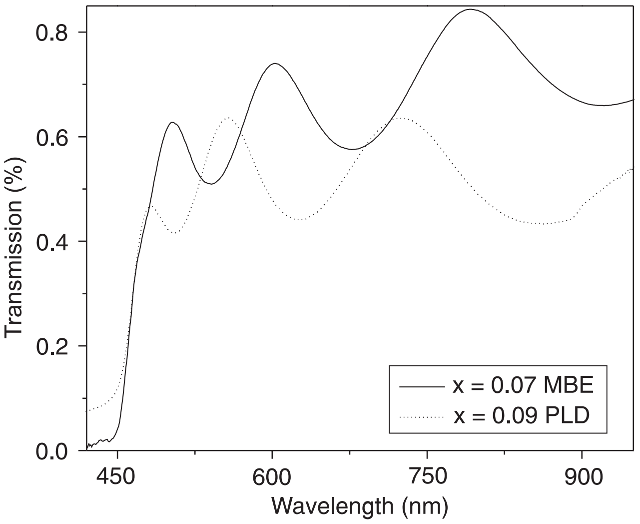

Fig. 2. Transmission spectra of $Zn_{1-x}Mg_xSe$ layers with different composition of Mg grown on glass substrates by MBE and PLD methods.

by Minkov [4]. The wavelength dependence of the estimated refractive indices for the $Zn_{1-x}Mg_xSe$ layers with different composition of Mg grown on glass substrates by MBE and PLD methods are shown in Fig. 3.

We can see that far from the absorption bands and beyond the gap wavelength, the refractive indices decrease continuously as the wavelength increases [5]. This behaviour can be described using a known first order Sellmeier relation [6]. Moreover, decrease in the refractive indices with increasing Mg content in $Zn_{1-x}Mg_xSe$ layers for the same wavelength range is observed. Also large refractive index differences were obtained for the $Zn_{1-x}Mg_xSe$ with different Mg content.

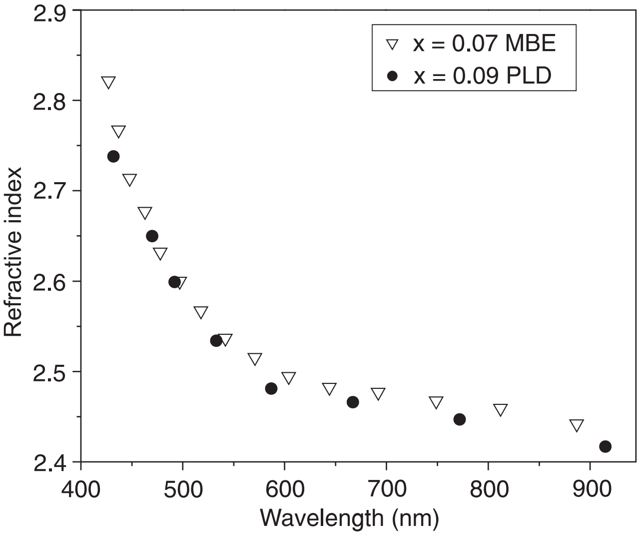

Fig. 3. Refractive index of $Zn_{1-x}Mg_xSe$ layers with different composition of Mg grown on glass substrates by MBE and PLD methods.

The knowledge of the TPA spectrum of semiconductors is important for development of all-optical switching elements, because TPA imposes a fundamental limitation on the performance of such devices. The TPA takes place when the laser photon energy $h\nu$ is larger than the half energy bandgap and lower than the energy bandgap of the sample ($E_g/2 < h\nu < E_g$). In our situation, we used Nd:YAG laser working at 532 nm, so the laser photon energy is 2.3 eV and energy bandgap of the investigated thin layer is about 2.7 eV, so the above dependence is satisfied [7].

We used the nonlinear transmission technique to obtain the TPA coefficient corresponding to the imaginary parts of $\chi^{<3>}\left[\beta = 24(\omega\pi^2/n^2c^2)\chi^{<3>''} \text{ in esu system}\right]$ [8]. This technique made possible to determine the TPA coefficient β by plotting the dependence of T on I_0 (Fig. 4), where I_0 is the intensity of the incident light. Taking into account the linear absorption coefficient α, the Fresnel reflection, and the scattered light, the nonlinear transmission formula becomes

$$T = (1-R)^2 \frac{\alpha \exp(-\alpha L)}{\alpha + \beta I_0[1-\exp(-\alpha L)]}, \tag{1}$$

where L is the thickness of the sample.

For the analysis described here beam propagation will be considered within the sample, so the irradiances are reduced from those measured experimentally by the factor $(1-R)^2$, where $R = (n_1^2 - n_2/n_1^2 - n_2)^2$ is reflectivity, n_1 and n_2 are the refractive indices of thin layer and substrate, respectively.

The linear absorption coefficient was determined from the linear transmission spectra (Fig. 2) for 532 nm. The obtained value equal to $(66 \pm 6.6)\times10^3$ 1/cm is in good agreement with the values determined from the interception of T with the ordinary axis at $\exp(-\alpha L)$ (Fig. 4). We can see that this value is different from unity. This says in a favour of one-photon contribution to the absorption. In our opinion the mechanism of absorption in the case $Zn_{1-x}Mg_xSe$ seems to be via uncontrolled impurity states localized in the forbidden gap with a one-photon contribution to the absorption. Also the main origins of the nonlinearities are known to be the two-photon transition, and the free charge carriers resulting from two-photon absorption.

The value of the TPA coefficient β extracted from the nonlinear transmission (Fig. 4) using the theoretical formula [Eq. (1)] is equal to 8.7 ± 0.8 cm/GW. The imaginary part of $\chi^{<3>}$ for $Zn_{0.93}Mg_{0.07}Se$ layer can be calculated by the formula $\beta = 24(\omega\pi^2/n^2c^2)\chi^{<3>''}$ and its value is equal to $(6.8 \pm 0.6)\times10^{-12}$ esu.

The photoreflectance (PR) spectroscopy is the sensitive, non-contacting and non–destructive technique for characterization of optical transition in semiconductors. Due to high sensitivity, the PR spectroscopy is a suitable method to determinate even poor energy bandgap shift caused by a

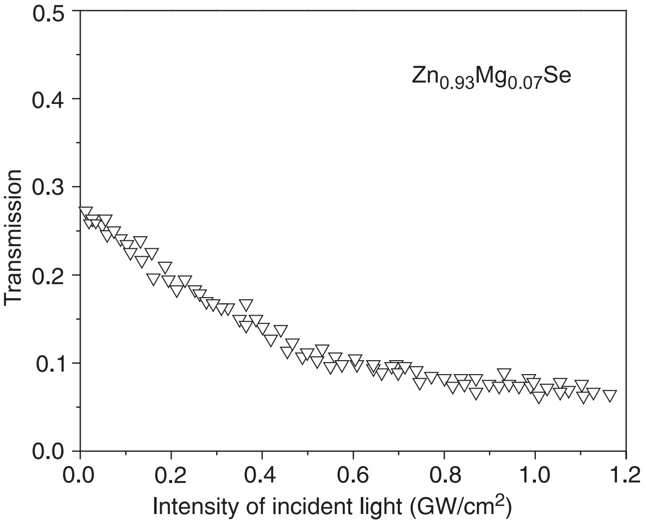

Fig. 4. Nonlinear transmission of $Zn_{0.93}Mg_{0.07}Se$ layer grown on glass substrate by MBE method.

change of alloy composition. Using an appropriate theoretical line shape it is possible to accurately determinate the amplitude, energy gap and broadening parameter of the given transition. In the case of a bulk material, where the low-field limit is performed, the line shapes of the modulated spectrum is directly related to the perturbed complex dielectric function and can be fitted using well known Aspnes formula [1,9,10]

$$\frac{\Delta R}{R} = \mathrm{Re}\left[Ae^{i\varphi}\left(E - E_g + i\Gamma\right)^{-m}\right], \qquad (2)$$

where E_g is the energy bandgap, Γ is the broadening parameter, A and φ are the amplitude and the phase factor, respectively. The parameter m depends on the type of the critical point and the order of the derivative. For a three-dimensional critical point, such as direct gap of $Zn_{1-x}Mg_xSe$, m is equal to 2.5.

In the case where the spectrum consists of n components, Eq. (2) which describes the shape of the spectrum becomes

$$\frac{\Delta R}{R} = \sum_j^n \mathrm{Re}\left[A_j e^{i\varphi_j}\left(E - E_{gj} + i\Gamma_j\right)^{-m_j}\right], \qquad (3)$$

where j denotes the number of spectral features.

Figure 5 shows typical PR spectrum obtained at a room temperature for sample with contamination of magnesium equal to 0.09 deposited by PLD method on a glass substrate. We can see that the PR spectra exhibit a double structure near the bandgap $Zn_{1-x}Mg_xSe$ alloys. The solid line shows a theoretical fit (Eq. 3) to the experimental data using a least-squares procedure and assuming two components spectrum. Obtained results from fitting procedure are shown in Table 1.

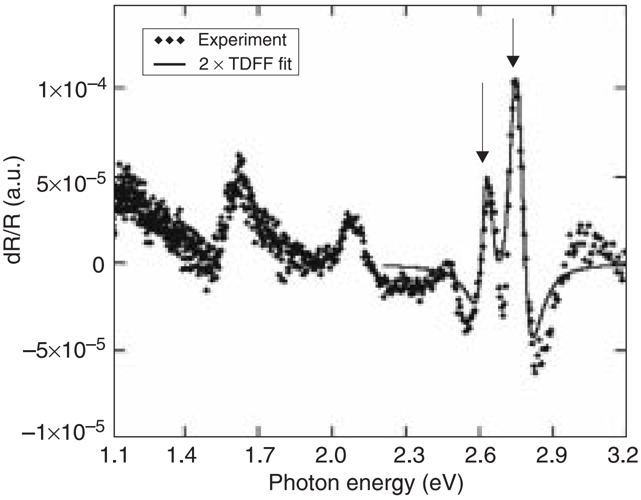

Fig. 5. Photoreflectance spectrum of $Zn_{0.91}Mg_{0.09}Se$ layer grown on glass substrate by PLD method.

Table 1. Results extracted from fitting procedure for two components spectrum (see Fig. 5).

Fitting parameters	1 component	2 component
A	1.005×10^{-7}	-1.199×10^{-7}
φ (rad)	2.601	1.365
E_g (eV)	2.62	2.75
Γ (eV)	0.04	0.064

Resonance about 2.75 eV corresponds to the direct band to band transition while energetically lower transitions (2.62 eV) may by attributed to unintentional impurity levels. The visible oscillations in infrared region were associated with so-called low energetical interference oscillation (LEIO). These oscillations were appeared because thin layers were investigated.

5. Conclusions

We calculated the refractive indices from reflection spectra using envelope method. We can see that far from the absorption bands and beyond the gap wavelength, the refractive indices decrease continuously as the wavelength increases. Also we can notice that the refractive indices decrease with increasing Mg content in $Zn_{1-x}Mg_xSe$ layers for the same wavelength range.

The photoreflectance spectroscopy (PR) was used for characterization of optical transition in semiconductors. We can see that the PR spectra exhibit a double structure near the bandgap $Zn_{1-x}Mg_xSe$ alloys. Resonance about 2.75 eV correspond to the direct band to band transition while lower energetically transitions 2.62 eV may by attributed to unintentional impurity levels. The visible oscillations in infrared region were associated with so-called low energetical interference oscillation (LEIO). These oscillations were appeared because thin layers were investigated.

The linear absorption coefficient was determined from the linear transmission spectra for 532 nm. The obtained value equal to (66 ± 6.6)×103 1/cm is in good agreement with the values determined from the nonlinear transmission. In our opinion, the mechanism of absorption in the case $Zn_{1-x}Mg_xSe$ seems to be via uncontrolled impurity states localized in the forbidden gap with a one-photon contribution to the absorption. Also the main origins of the nonlinearities are known to be the two-photon transition, and the free charge carriers resulting from two-photon absorption. The value of the TPA coefficient β extracted from the nonlinear transmission is equal to 8.7 ± 0.8 cm/GW. So, the imaginary part of $\chi^{<3>}$ for $Zn_{0.93}Mg_{0.07}Se$ layer is equal to $(6.8 \pm 0.6)\times10^{-12}$ esu.

We should notice that the TPA process occurs when the material has an electronic excited level at doubled the frequency ω of the input beam. We thus can conclude that these novel $Zn_{1-x}Mg_xSe$ thin layers show promising values of two-photon absorption for optical limiting applications. Two-photon absorption in semiconductors has been the subject of experimental and theoretical investigation. In the last decade, the employment of semiconductor components as nonlinear elements in optical communication and information processing system is demanding even more accurate and extended knowledge of their linear and nonlinear optical properties.

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