Determination of the Optical Absorption Coefficient of Zn$_{1-x-y}$Be$_x$Mg$_y$Se Mixed Crystals from the PAS Experiments - Improved Approach

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In this paper the results of the photoacoustic spectroscopic experiments performed on Zn$_{1-x-y}$Be$_x$Mg$_y$Se mixed crystals are presented. In the course of the study the PA spectra of the amplitude and phase of the PA signals were measured at different frequencies of modulation. The measurements were performed for the series of samples at $x=0.14$ $y=0.06$ after different technological treatment e.g. as grown, annealed, polished and unpolished samples. From the measurements were determined: energy gap value, optical absorption coefficient, Urbach edge contribution, contribution of the surface signal to the total PA signal. The influence of the technological treatment of the samples on the above parameters was determined and the results were discussed in one layer and two layers models.

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Photoacoustic spectroscopy PAS has been an important measuring technique for several years for the nondestructive characterization of semiconductor materials. Analysis of the PA amplitude and phase spectra can give information about the values of energy band gap, the optical absorption coefficient, thermal and chemical disorder broadening of the absorption band and the state of the surface of the samples. In general the theory applied for the data processing is based on the theory of the photoacoustic effect developed by Rosencwaig and Gersho [1], Bennett and Patty [2], Ouzafe [3], Charpentier [4], Lachaine [5] and others.

The II-VI mixed compounds are very promising from the point of view of visible radiation sources in laser diodes and a lot of work has already been done [6-11]. There are however areas of interest that are still interesting as: the influence of the state of the surface on the PA signal, different approaches to the problem of determination of optical parameters [12,13] and the influence of the after growth treatment of the samples on the PAS signal and material parameters of samples. The results for Zn$_{1-x-y}$Be$_x$Mg$_y$Se are compared with the results obtained for the mixed crystals Zn$_{1-x}$Be$_x$Se.

Experiment

Experiments presented in this paper were performed on the computer controlled photoacoustic spectrometer with the microphone phase sensitive detection. The main idea of the construction of this apparatus is similar to that described in ref.[7,14]. The samples of Zn$_{1-x-y}$Be$_x$Mg$_y$Se mixed crystals were cut from the bulk crystal grown by the high pressure Bridgman method [8]. The samples were in the form of parallel plates of the thickness 0.1cm. Three groups of samples were measured: as-grown samples, after growth samples annealed in the zinc vapor for 24 hours at 1230 K and samples mechanically polished after annealing. The influence of this treatment on PAS results was next investigated.

Experimental procedures

The value of the thermal diffusivity was determined from the frequency domain phase-lag method as $0.1 \text{ cm}^2 \text{s}^{-1}$. In the first stage of experiments the amplitude spectra of the samples were measured at 21 Hz and 42 Hz. From the relative change of the amplitude of PA signals versus the photon energy of the exciting light and after the normalization of the amplitude spectra to unity in the saturation region i.e. for energies above $3.0 \text{ eV}$ the optical absorption coefficient was determined according to the expression:

$$\beta = \frac{1}{\mu} \cdot \frac{q^2 + q - \sqrt{2 - q^2}}{(1 - q^2)}$$

where $q = \frac{A_m(h\nu)}{A_m(h\nu_{sat})}$; $\mu = \sqrt{\alpha/\pi f}$ - thermal diffusion length; $\alpha$ - thermal diffusivity of the sample; $f$ -
frequency of light modulation, \( A_m \) is experimental value of the amplitude of PA signal. 

The values of the energy gap were determined from the fitting of the theoretical expression \( \beta \cdot h \nu = A_0 (h \nu - E_g) \) to experimental results. This formula describes the character of the optical absorption coefficient for direct allowed transitions in the quantum mechanical sense.

In the second stage of investigations the phase spectra of the PA signals were investigated. The spectra were analyzed in the frame of the model of Ouzafe [3]. In this model the phase spectra can be calculated as:

\[
P(\beta, \alpha, f) = -\pi + \tan^{-1}(\beta \cdot \mu + 1),
\]

where the \( \beta(h\nu) \) spectra were taken from the computations according to formula (1) valid for a model of one layer thermally thick samples.

The comparison of the phase spectra and experimental results shows that the predictions of one layer model don’t correlate with experimentally obtained spectra. They can be explained however in the frame of two layer model. In such a model the complex signal can be described as:

\[
\text{Pas}(f, \beta, K) = A_m \cdot e^{i \cdot P_{\text{h}}} - \frac{1}{K} e^{-i(\pi / 4)}.
\]

\( \beta = \beta_0 \cdot \exp(\nu / (h \nu - E_g / k_B \cdot T)) \) for \( h \nu < E_g / T \).

Experimental results.
The photoacoustic results of the measurements of as-grown \( Zn_{1-x-y}Be_xMg_ySe \) samples.

The spectrum of the optical absorption coefficient determined from the amplitude PA spectrum is shown in Fig.2.

![Fig.1. Schematic diagram of the sample (B) with the semitransparent thin insulating surface oxide layer (A).](image1)

Fig.2. The spectrum of the optical absorption coefficient experimental results and fitting to the theory in the region of band to band absorption and in the Urbach’s edge region for as grown \( Zn_{1-x-y}Be_xMg_ySe \) sample.

![Fig.3. The phase spectra of the PA signals measured at 21Hz (upper figure) and 42 Hz (bottom figure). ‘Ideal’ means the prediction of Uzafe’s model, ‘corrected’ means predictions of two layer model for \( K=35 \) where \( K \) is the fitting parameter see expression (4).](image2)
From the fitting of the theoretical expressions to experimental results the following parameters were determined:

\[ A = 2400 \text{ cm}^{-1} \text{ eV}^{-1/2}; \quad \beta_0 = 150 \text{ cm}^{-1}; \quad E_g = 2.89 \text{ eV}; \quad K = 35; \quad \gamma = 1 \]

The phase spectra of the samples are shown in Fig.3.

The spectrum of the optical absorption coefficient in the region of the Urbach’s edge is shown in Fig.4.

The photoacoustic results of the measurements of Zn\(_{1-x-y}\)Be\(_x\)Mg\(_y\)Se samples after annealed in Zn vapour.

The spectrum of the optical absorption coefficient determined from the amplitude PA spectrum is shown in Fig.5.

From the fitting of the theoretical expressions to experimental results the following parameters were determined:

\[ A = 1000 \text{ cm}^{-1} \text{ eV}^{-1/2}; \quad \beta_0 = 90 \text{ cm}^{-1}; \quad E_g = 2.74 \text{ eV}; \quad K = 10; \quad \gamma = 1 \]

The phase spectra of the samples are shown in Fig.6.

The photoacoustic results of the measurements of Zn\(_{1-x-y}\)Be\(_x\)Mg\(_y\)Se samples annealed in Zn vapor and next mechanically and chemically polished.

The spectrum of the optical absorption coefficient determined from the amplitude PA spectrum is shown in Fig.8.

From the fitting of the theoretical expressions to experimental results the following parameters were determined:

\[ A = 1700 \text{ cm}^{-1} \text{ eV}^{-1/2}; \quad \beta_0 = 160 \text{ cm}^{-1}; \quad E_g = 2.90 \text{ eV}; \quad K = 25; \quad \gamma = 0.6 \]
The phase spectra of the samples are shown in Fig.9.

![Phase spectra of the PA signals measured at 21Hz (upper figure) and 42Hz (bottom figure).]

Fig.9. The phase spectra of the PA signals measured at 21Hz (upper figure) and 42Hz (bottom figure).

The spectrum of the optical absorption coefficient in the region of the Urbach’s edge is shown in Fig.10.

![Spectrum of the optical absorption coefficient in the region of the Urbach’s edge.]

Fig.10. The spectrum of the optical absorption coefficient in the Urbach’s edge region. The experimental results (circles) and theoretical curves for the fitting parameter γ=1 and γ=0.6.

Summary

When the results of the above photoacoustic experiments are collected together, the influence of the after growth treatment is clearly visible. This influence on the values of following parameters: energy gap $E_g$, the value of the optical absorption factor $A$, quality of the crystal $\gamma$ and the state of the surface of the sample $K$ was observed.

The values of physical parameters for as-grown crystals $E_g=2.74$eV and $A=2400$cm$^{-1}$eV$^{-1/2}$ agree with the results obtained for similar mixed crystals $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ for the similar beryllium concentration ($x=0.20$) when $E_g=2.9$eV and $A=1700$cm$^{-1}$eV$^{-1/2}$. The parameters of $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ mixed crystals used for comparison were obtained for similar mixed crystals $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ for the similar $E_g=2.9$eV and $A=1700$cm$^{-1}$eV$^{-1/2}$ similar to the ones of as-grown crystals. The three groups of samples exhibited most often $\gamma$ parameter equal to unity what indicates that the quality of the crystals was high and the broadening had mainly the thermal character. The results obtained for $\text{Zn}_{1-x}\text{Be}_x\text{Se}$ crystals grown with higher concentration of beryllium exhibited the considerable increase of the broadening of the Urbach’s edge and $\gamma=0.45$. The value of the $K$ parameter was different $K=10$-35 for different samples depending on the conditions of surface preparation and was taken into account in the process of computations.

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References