Measurements of the Urbach tail for A2B6 mixed crystals by the photothermal method

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Abstract. This paper presents the influence of the composition of several mixed A2B6 crystals on the broadening of the optical absorption coefficient spectra. This broadening is observed as the change of the piezoelectric spectra associated with the change of the Urbach tail. This effect is interpreted as a result of the increase of the compositional disorder of the crystal lattice.

1. Introduction

Wide gap II-VI compounds are still the subject of the intense research, mainly because of their application in the band gap engineering, interband and intersubband transitions, dilute semiconductors, materials and devices [1–4]. For these materials it is possible to change electronic properties, lattice parameters and band gap energies by adjusting the composition of the mixed crystals. The change of the band gap energy gives the desired optical properties and emission in the entire visible and uv range of the spectrum.

The series of Zn\textsubscript{1-x}Mg\textsubscript{x}Se and Cd\textsubscript{1-x}Mn\textsubscript{x}Te mixed crystals of different composition were taken into consideration: all the investigated crystals were grown by the high pressure Bridgman method under argon overpressure. The change of their composition results in the change of energy gap values and also in the broadening of the absorption bands and formations of the band tails which can be associated with the worse quality of the crystal. The broadening is dissimilar for different materials. This paper deals with the investigations of Urbach tail of A2B6 bulk crystals by photothermal piezoelectric method (PP). The Urbach absorption edge is a nearly universal property of disordered solids, it arises from both static structural and dynamic phonon disorders [5].

The experimental amplitude PP spectra were the basis to calculate the theoretical PP spectra and then to estimate the optical absorption coefficient spectra. The PP amplitude and phase spectra exhibited not only Urbach tail which is a volume type absorption but also the absorption bands connected with the surface absorption on one or two surfaces of the samples connected with their mechanical and chemical treatment.
2. Theory

The simulation of the piezoelectric spectra in the rear configuration [6] for photon energies in the range of the main absorption band were performed for optical absorption coefficient spectra for the energies below and above the energy gap of the crystal with the equations 1 and 2 respectively.

\[ \beta(E) = \beta_0 \cdot \exp \left( \frac{E-E_g}{0.025} \gamma \right) \]  

(1)

\[ \beta(E) = A_0 \cdot \left( \frac{E-E_g}{0.025} \right)^{1/2} + \beta_0 \]  

(2)

![Graph on the left](image1)

![Graph on the right](image2)

**Fig.1.** Influence of the Urbach tail absorption band a) on the PP amplitude spectra b). \( \gamma = 1 \).

Equation 1 describes the Urbach tail optical absorption band, equation 2 - the band to band type transition absorption band associated with the direct electron type transitions. The quantitative analysis of the photothermal piezoelectric spectra was performed using the modified Jackson – Amer model [7]. Results of theoretical simulations of the influence of the Urbach edge on the piezoelectric
amplitude spectra are presented in Fig. 1 ($\beta_0=100 \text{ cm}^{-1}, \gamma=1, \alpha=0.05 \text{ cm}^2/\text{s}, f=100 \text{ Hz}, E_g=2.8 \text{ eV}$) and Fig. 2 ($\beta_0=100 \text{ cm}^{-1}, \gamma=0.3, \alpha=0.05 \text{ cm}^2/\text{s}, f=100 \text{ Hz}, E_g=2.8 \text{ eV}$). In the first case, $\beta_0$ is the Urbach absorption factor, $\gamma$ is the broadening parameter, $\alpha$ is the thermal diffusivity, $f$ is the frequency of modulation, $E_g$ is the energy gap value.

The simple dependence of optical coefficient (Fig 1a, 2a) is associated with quite complicated amplitude PP spectra (Fig 1b, 2b). As it is predicted by Jackson–Amer theory a maximum occurs in near energy gap region. It is associated with the change in phase spectra [7] and subtracting of the signal coming from piston and drum effects. Additionally, one can notice that the decreasing of $\gamma$ parameter causes the broadening of PP amplitude. That feature can be used to determine the crystal disorder directly from photoacoustic signal as the bigger value of $\gamma$ means the smaller broadening of the sub-band gap maximum and the better quality of the crystal. Small values of that parameter could be due to enhanced electronic distortion originating from the ordered defects and the structural disorder caused by compositional deviation from ideal stoichiometry. It was shown that the value of $\gamma$ increase with increasing structural ordering [5].

3. Experimental spectra

All experimental PP spectra were measured in the rear configuration [8] at room temperature. Experimental amplitude PP spectra of Zn$_{1-x}$Mg$_x$Se mixed crystals are shown in Fig. 3. The increase of energy gap values with increase of Mg content is clearly visible. The typical maximum in sub-band-gap region is observed for all the samples. The samples $x=0$ and $x=0.35$ are as grown ones, others are annealed in zinc vapor. For ZnSe, the broadening parameter $\gamma$ is estimated as $\gamma=0.3$, for the samples with magnesium content $0.12 \leq x \leq 0.28$ as $\gamma=0.5$ and for $x=0.35$ as $\gamma=0.3$. Annealing improves the quality of the samples, the increase of Mg contents is associated with the larger structural disorder of crystal.

![Fig.3. Amplitude of photoacoustic spectra of Zn$_{1-x}$Mg$_x$Se for different content of Mg](image)

The broadening of the Urbach tail, with an increase of $x$ parameter, is accompanied with the increase of the energy gap of the crystal from 2.7 eV to 3.2 eV. The quality dependence of the crystal on the manganese content is clearly visible for Cd$_{1-x}$Mn$_x$Te samples in fig 4. The broadening parameter $\gamma$ for CdTe systematically decreases with the increase of Mn content what means a broadening of the Urbach tail ($x=0, \gamma=1; x=0.27, \gamma=0.5; x=0.67, \gamma=0.3$ ). This effect is accompanied with the energy gap shift from 1.5 eV to 2.35 eV.
4. Conclusions
There are several effects associated with the change of the composition of mixed crystals. The first effect is the shift of the energy gap of crystals with the content $x$ of Mg and Mn in the alloys towards higher energies. It gives the possibility of tuning of the energy gap value. This effect is associated however with the other effect which is not desired. The quality of the mixed crystals gets worse with an increase of $x$ parameter. It is observed as the strong broadening of the Urbach tail described by a decrease of the $\gamma$ parameter. This effect was observed as the broadening of the respective piezoelectric photothermal amplitude bands for energies of photons below the energy gap of crystals.

References
[1] A. Mandelis, J. Batista and D. Shaughnessy, Phys. Rev. B 67, 205208-1-205208-18 (2003)
[2] A. Memon, A. Fukuyama, S. Sato and T. Ikari, Rev. Sci. Instrum. 74, 1, 592 (2003)
[3] D. Dietzel, S. Chotikaprapkhan, B. K. Bein and J. Pelzl, J. Phys. IV France 125, 87 (2005)
[4] D. M. Todorovic, Rev. Sci. Instrum. 74, 1, 582 (2003)
[5] Ken-ichi Noba and Yosuke Kayanuma, Phys. Rev B, 60 (7), 4418 (1999)
[6] M. Maliński Archives of Acoustics 27(3), 217(2002)
[7] W. Jackson, N. M. Amer, J.Appl.Phys. 51(6), 3343 (1980)
[8] M. Maliński, J. Zakrzewski, S. Łęgowski, H. Męczyńska Int. J.of Thermophysics 26, 1, 255 (2004)

Fig.4. Amplitude of photoacoustic spectra of Cd$_{1-x}$Mn$_x$Te for different content of Mn