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The photoacoustic spectroscopic investigations of the surface preparation of ZnSe crystals with the use of the optimization methods

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ABSTRACT

This paper shows results of the photoacoustic (PA) spectral studies, with the microphone detection, of a series of ZnSe crystals with differently prepared surfaces. All samples exhibited the surface absorption connected with defects states located on their surfaces. The quality of the surface preparation is expressed by the surface absorption coefficient spectra of the samples times the thickness of a damaged layer. In this paper both theoretical and experimental photoacoustic amplitude and phase spectra as also the corresponding computed surface and volume optical absorption coefficient spectra of the samples with differently prepared surfaces are presented and discussed. The procedure of computations of the volume and surface absorption spectra with the use of the optimization method is presented in the paper too.

1. Introduction

Wide gap AII–BVI mixed crystals have potential applications in optoelectronics, such as short wavelength emitters and photo detectors [1,2]. ZnSe has been of great interest for fabricating light emitting devices in the blue-green-yellow spectral regions. These are of interest for many devices for example green solid-state lasers. AII–BVI type semiconductors are also interesting materials for spintronics and other applications in modern electronics [3].

The photoacoustic spectroscopy is an important method for nondestructive characterization of semiconductors materials. The PA effect is based on the generation of the thermal waves in the sample as a result of its periodical illumination and next heating of the gas in the PA cell. The PA signal is detected as periodical changes of the air pressure in the PA chamber. The thermo diffusion mechanism of the PA effect was described by Rosencwaig and Gersho [4]. For the first time this method was applied by Gosh for investigations of ZnSeTe mixed crystals [5]. The application of the PA method, with the microphone detection, for measurements of ZnBeSe crystals was described in papers [6,7].

Investigated samples exhibited a two-layer character as a result of their different surface preparation, which changed the optical parameters of the surface layer of the ZnSe samples. The experimental literature PA results indicate a strong dependence especially of the PA amplitude spectrum on the surface quality of different semiconductor samples [8–12]. Obtained, and presented in this paper, experimental results have been interpreted theoretically in a two-layer model [13,14] with the optimization method of computations.

2. Sample preparation and the theory

ZnSe crystals grown from the melt by the high-pressure high temperature Bridgman method [15] were cut into the plates of the thickness $l = 0.13$ cm. Two groups of samples were investigated. The first ZnSe sample was [1,1,1] oriented, grinded, polished and chemically etched in NaOH. The second ZnSe sample was [1,1,1] oriented, grinded and polished only.

The photoacoustic (PA) spectra of the samples were measured at the frequency of modulation $f = 20$ Hz in the front experimental

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configuration with the conventional photoacoustic spectrometer described in paper [16]. General requirements concerning the apparatus for measurements of the photoacoustic effect were described by Rosencwaig in paper [17]. The experimental setup consisted of: a 300 W Cermax xenon short arc lamp as a source of light, a grating monochromator, a mechanical chopper, a set of lenses, a PA chamber with an electret microphone, a low noise preamplifier, a lock in phase selective amplifier and a computer. All measurements were performed at room temperature and were computer controlled. A carbon black sample was used as a reference sample for calibration of the PA spectra. The thermal diffusivities of the ZnSe samples, necessary for computations, were known from the independent frequency PA measurements and their values determined as about $\alpha = 0.1\ cm^2/s$.

From the theoretical point of view the mathematical model of the photoacoustic signal of the sample with the surface states is a two-layer model. In a general case, when both layers have different thickness and different thermal parameters, one of the existing models can be applied: Mandelis et al. [18], Fernelius [19] or Takabatake et al. [20]. The model of a photoacoustic signal of a thin semiconductor layer on a thermally thick semiconductor backing was presented in paper [21].

When the thickness of the surface layer is much smaller than the thickness of the sample and thermal parameters of both layers similar then the mathematical model can be simplified.

The model of the photoacoustic signal, in the microphone detection, of the sample exhibiting both the surface and volume absorption applied for computations of the theoretical spectra and the fitting of the spectra to these experimental characteristics is presented below:

$$Am(PA) = |PA[f, l, \alpha, d, \beta_S(\lambda), \beta_v(\lambda)]| \quad (1)$$

$$Phase(PA) = \frac{180}{\pi} \cdot \arg[PA[f, l, \alpha, d, \beta_S(\lambda), \beta_v(\lambda)]] \quad (2)$$

$$PA[f, l, \alpha, d, \beta_S(\lambda), \beta_v(\lambda)] = I_0 \cdot \left[\frac{D(f, l, \alpha, d, \beta_S(\lambda))}{\sigma(f, \alpha)} + \frac{C(f, l, \alpha, \beta_v(\lambda)) \cdot \exp(-\beta_S(\lambda) \cdot d)}{\sigma(f, \alpha)}\right] \quad (3)$$

$$\sigma(f, \alpha) = (1 + i) \cdot \sqrt{\frac{\pi \cdot f}{\alpha}} \quad (4)$$

$$D(f, l, \alpha, d, \beta_S(\lambda)) = \frac{1 - \exp[-\beta_S(\lambda) \cdot d] \cdot [1 + \exp[-2 \cdot \sigma(f) \cdot l]]}{\sigma(f) \cdot [1 - \exp[-2 \cdot \sigma(f) \cdot l]]} \quad (5)$$

$$C(f, l, \alpha, \beta_v(\lambda)) = \frac{\beta_v(E) \cdot [A(f, l, \alpha, \beta_v(\lambda)) + B(f, l, \alpha, \beta_v(\lambda))]}{2 \cdot \sigma(f) \cdot [1 - \exp[-2 \cdot \sigma(f) \cdot l]]} \quad (6)$$

$$A(f, l, \alpha, \beta_v(\lambda)) = \frac{2 \cdot [1 - \exp[(-\sigma(f) - \beta_v(\lambda)) \cdot l]]}{\beta_v(\lambda) + \sigma(f)} \quad (7)$$

$$B(f, l, \alpha, \beta_v(\lambda)) = \frac{2 \cdot \exp(-2 \cdot \sigma(f) \cdot l) \cdot [1 - \exp[(\sigma(f) - \beta_v(\lambda)) \cdot l]]}{\beta_v(\lambda) - \sigma(f)} \quad (8)$$

where f is the frequency of modulation, λ is the wavelength of light, l is the thickness of the sample, d is the effective thickness of the damaged layer, D denotes the temperature contribution to the total temperature of the illuminated side of the sample associated with the surface absorption in a damaged layer, while C denotes the temperature contribution associated with the volume absorption in the sample. $\text{Exp}(-\beta_s \cdot d)$ represents that part of the intensity of light that is transmitted past the surface and is absorbed in the volume of the sample.

Extraction of volume and surface absorption coefficients by the fitting of photoacoustic theoretical amplitude and phase spectra to experimental spectra was performed by the application of polioptimization algorithms implemented in Matlab® environment. The polioptimization is the optimization with the vector goal function, whose goal is to find the best solution for several criterions simultaneously. In this case the criterions are the best fittings of amplitude and phase theoretical to experimental photoacoustic spectra. For the solution of that problem a procedure was applied, which minimalizes a vector of distance values of given criterial functions F_i to goal functions vector keeping importance of their weights. This problem can be written as Eq. (9):

$$\min_{x,\lambda}\{F_i(x) - weight \cdot \lambda \le goal\} \quad (9)$$

Minimalization is usually performed in the presence of linear and nonlinear constraint functions and boundaries given as follows: $c(x) \le 0,\ c(x) = 0,\ A \cdot x \le b,\ Aeq \cdot x = beq,\ lb \le x \le ub$. The procedure finds the best solution, in the form of the vector of optimal values of decision variables, which fulfil all linear and nonlinear constraints and boundaries. Criterion functions reach their desired values with their own weights.

For each of experimental points, a solution of the equations system (10) is searched:

$$\begin{cases} Am_{\exp}(\lambda_j) = |PA[f, l, \alpha, d, \beta_S(\lambda_j), \beta_v(\lambda_j)]| \\ Phase_{\exp}(\lambda_j) = \frac{180}{\pi} \cdot \arg[PA[f, l, \alpha, d, \beta_S(\lambda_j), \beta_v(\lambda_j)]] \end{cases} \quad (10)$$

So the goal function describing particle criteria for each of the measured points can be presented as

$$F_i(x_j) = [Am_1(\lambda_j)\ \ Ph_2(\lambda_j)] \quad (11)$$

where

$$x_j = [BetaV(\lambda_j)\ \ BetaS(\lambda_j)] \quad (12)$$

is a decision variable vector that is searched. Volume and surface absorption coefficients, in each measured point, are the values of this vector.

For each of the criteria the most desired values have been defined as the values of the experimental amplitude and phase for each point in the form of Eq. (13):

$$goal_j = [AmExp(\lambda_j)\ \ PhExp(\lambda_j)] \quad (13)$$

For each of the criterion the same weight values have been assumed what means that the amplitude fitting criterion is as important as the phase fitting criterion and they must be fulfilled at the same time:

$$weight_j = [1\ \ 1] \quad (14)$$

In this case linear and nonlinear constraints functions are not necessary. Only lower and upper boundaries are superimposed on the values of volume and surface absorption assumed according to the literature values.

The solution for each measured point are the two optimal values of volume and surface absorption for which the amplitude and phase fitting is obtained. This procedure is performed for each value of the wavelength. The results are searched volume and surface absorption spectra.

The alternative manual solution method can be applied, however this approach is time consuming and requires more work than an application of the polioptimization technique.

The application has been written in Matlab® environment where optimization algorithms are implemented already. Using the computer with the quad core processor calculations of that problem take about 3 s. Instead manual calculations need about 2 h of work.