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Identification of the Volume and Surface Type Absorption by the Nondestructive Photoacoustic Method

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Introduction

The technology of production of semiconductor samples requires a series of surface processes. Surface of the samples is modified by several processes such as: cutting, grinding, polishing, etching, implantation, annealing, RF sputtering cleaning and others. After each of these processes the surface of the sample is strongly modified. For the analysis of the influence of these processes on the quality of the surface of the samples different measuring methods can be applied. One of them is the photoacoustic method. The photoacoustic method can be applied with the piezoelectric or the microphone method of detection. These methods have a strong advantage as the phase of the photoacoustic signal depends on the location of the absorbing region in the sample. The effect of surface states on the experimental piezoelectric photothermal spectra of silicon single crystals was presented in paper [1]. The influence of the surface preparation on the piezoelectric spectra of $Zn_{1-x-y}Be_xMn_ySe$ mixed crystals was presented in paper [2]. The piezoelectric theory of detection of surface states enabling computations of the piezoelectric amplitude and phase spectra in the presence of the surface absorption was presented in paper [3]. The photoacoustic spectra of ZnBeMgSe mixed crystals in the piezoelectric method of detection, exhibiting surface states, were presented in papers [4,5]. The photoacoustic spectra of surface defects states of semiconductor ZnBeSe mixed crystal samples, in a microphone detection, were presented in paper [6].

Theoretical Model

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: A. Mandelis et al. [7], N. C. Fernelius [8] or N. Takabatake et al. [9]. The model of a photoacoustic signal of a thin semiconductor layer on a thermally thick semiconductor backing was presented in paper [10].

For the case of the surface absorption when the thickness of the surface layer is much smaller than the thickness of the sample and thermal parameters of both layers are similar the mathematical model describing the structure 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 the computations of the theoretical spectra and performing the fitting of the spectra to the experimental characteristics is presented below.

$$PA(f,l,\alpha_1,\alpha_2,d,\beta_v(\lambda),\beta_s(\lambda),\lambda_1,\lambda_2) = \frac{D(f,l,\alpha_1,d,\beta_s(\lambda),\lambda_1)+C(f,l,\alpha_2,\beta_v(\lambda),\lambda_2)\cdot\exp(-\beta_s(\lambda)\cdot d)}{\sigma_1(f)} \tag{1}$$

$$\sigma_i=(1+i)\cdot\sqrt{\frac{\pi\cdot f}{\alpha_i}} \tag{2}$$

$$D(f,l,\alpha_1,d,\beta_S(\lambda)) = \frac{[1-\exp[-\beta_S(\lambda)\cdot d]\cdot[1+\exp[-2\cdot\sigma_1(f)\cdot l]]}{\lambda_1\cdot\sigma_1(f)\cdot[1-\exp[-2\cdot\sigma_1(f)\cdot l]]} \tag{3}$$

$$C(f,l,\alpha_2,\beta_v(\lambda)) = \frac{\beta_v(\lambda)\cdot[A(f,l,\alpha_2,\beta_v(\lambda))+B(f,l,\alpha_2,\beta_v(\lambda))]}{\lambda_2\cdot 2\cdot\sigma_2(f)\cdot[1-\exp[-2\cdot\sigma_2(f)\cdot l]]} \tag{4}$$

$$A(f,l,\alpha_2,\beta_v(\lambda)) = \frac{[1-\exp[(-\sigma_2(f)-\beta_v(\lambda))\cdot l]]}{\beta_v(\lambda)+\sigma_2(f)} \tag{5}$$

$$B(f,l,\alpha_2,\beta_v(\lambda)) = \frac{\exp(-2\cdot\sigma_2(f)\cdot l)\cdot[1-\exp[(\sigma_2(f)-\beta_v(\lambda))\cdot l]]}{\beta_v(\lambda)-\sigma_2(f)} \tag{6}$$

$$Am(\lambda) = |\, PA(f,l,\alpha,d,\beta_S(\lambda),\beta_v(\lambda))\,| \tag{7}$$

$$Phase(\lambda) = \frac{180}{\pi}\cdot\arg\left[PA(f,l,\alpha,d,\beta_S(E),\beta_V(E))\right] \tag{8}$$

Where: f – is the frequency of modulation, λ is the wavelength of light, l is the thickness of the sample, α_1 is the thermal diffusivity of the surface layer, α_2 is the thermal diffusivity of the sample, λ_1 is the thermal conductivity of the surface layer, λ_2 is the thermal conductivity of the sample, d is the effective thickness of the surface 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.
$exp(-\beta_s\cdot d)$ represents that part of the intensity of light transmitted past the surface layer and is absorbed in the volume of the sample. In the fittings it was assumed that: $\alpha_1=\alpha_2$, $\lambda_1=\lambda_2$ i.e. the thermal parameters of the surface layer and volume of the sample are the same.

Experimental Set Up

The experimental setup for spectral measurements consisted of 300 [W] xenon lamp, as a source of light, grating monochromator, mechanical modulator, PA chamber with the electret microphone, low-noise preamplifier, lock-in type amplifier and the computer which controlled the measuring process. The schematic diagram of experimental set up is shown in Fig.1. The PA spectra were measured at room temperature at the frequency of modulation f=30 [Hz] in the front experimental configuration with the conventional photoacoustic spectrometer described in papers [11-12].

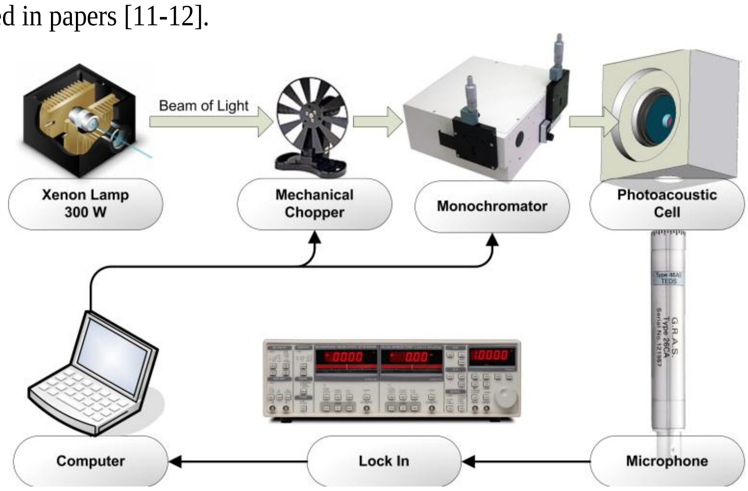

Fig. 1. The experimental photoacoustic set up used for the spectral experiments.

Sample Preparation

ZnBeMgSe crystals used for experiments were grown from the high purity powder using the high-pressure Bridgman method. The crystal rod was cut into 1mm thick samples which were first ground using the grinding powder (10 μm diameter), then polished with diamond paste (1 μm diameter) and finally chemically etched. A solution of H_2SO_4 (96 %), $K_2Cr_2O_7$ and water was used for etching the samples. After etching, the samples were rinsed in distilled water and then immersed for a few seconds in boiling NaOH. Then the samples were rinsed again in cold water, next in boiling distilled water, and finally in ethyl alcohol. The value of the thermal diffusivity of the samples, necessary for computations of the optical absorption spectra, was determined from the independent frequency PA measurements as α=0.1 cm^2/s.

Experimental Results

The photoacoustic experimental and theoretical amplitude spectra of ZnBeMgSe sample are presented in Fig.2.

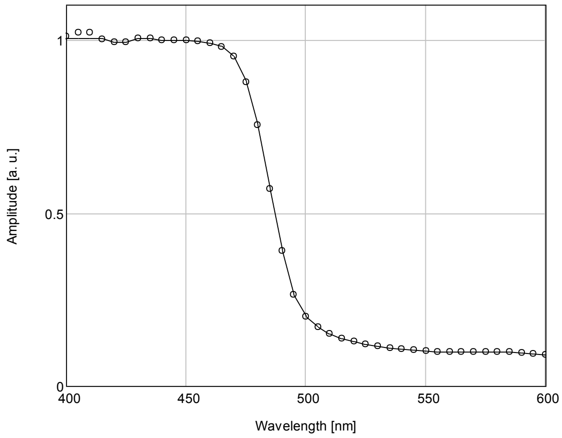

Fig. 2. Photoacoustic amplitude spectra of ZnBeMgSe sample. Circles – experimental data, solid line – a theoretical curve computed in a volume absorption model.

The fitting of the theoretical curve to the experimental amplitude spectrum was performed in a volume absorption model. From the amplitude PA spectrum the volume optical absorption coefficient spectrum was extracted $\beta_V(\lambda)$.

The corresponding photoacoustic phase spectra of the same sample measured and computed in a volume absorption model for the optical absorption coefficient spectrum $\beta_V(\lambda)$ are shown in Fig.3.

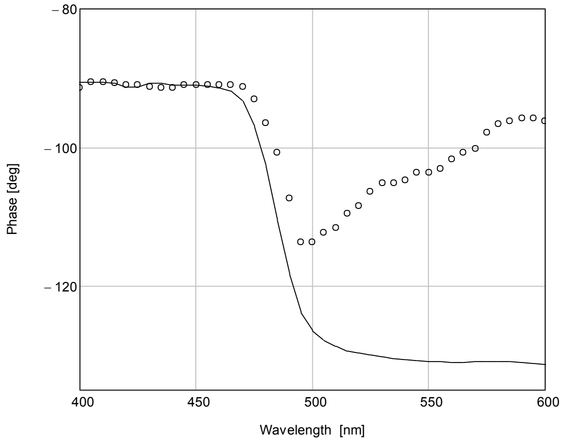

Fig.3. Photoacoustic phase spectra of ZnBeMgSe sample. Circles – experimental data, solid line – a theoretical curve computed in a volume absorption model.

The comparison of the experimental and theoretical phase spectra computed for the optical absorption spectrum $\beta_V(\lambda)$ presented in Fig.3 show that the volume absorption model is not appropriate for interpretation of the photoacoustic experimental spectra of the analyzed sample. In the other approach in the first step the fitting was performed for the phase spectrum. It is presented in Fig.4. From the fitting of the theoretical curve, computed in the volume absorption model, to the experimental phase spectrum the optical absorption spectrum $\beta_V(\lambda)$ was extracted. It is also possible to get the perfect fitting of theoretical and experimental phase spectra. Then the optical absorption spectrum $\beta_V(\lambda)$ was applied for the computations of the amplitude PA spectrum of the same sample. It is presented in Fig.5. It turned out that the model again is inappropriate for the interpretation of the experimental spectra.

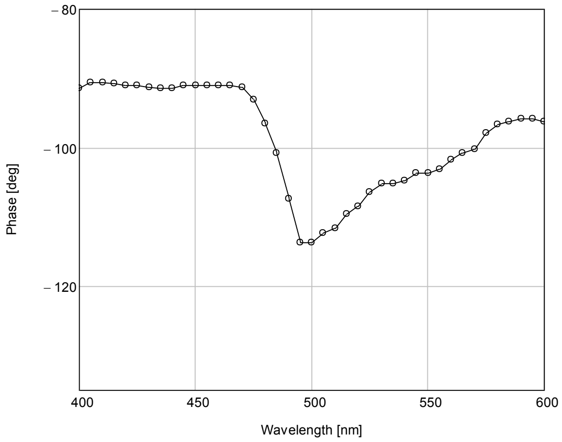

Fig. 4. Photoacoustic phase spectra of ZnBeMgSe sample. Circles – experimental data, solid line – a theoretical curve computed in a volume absorption model.

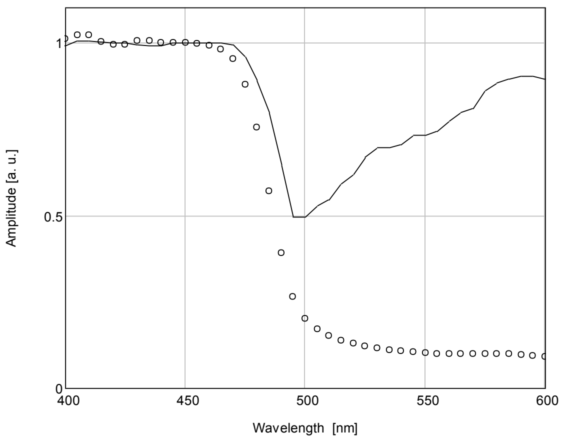

Fig. 5. Photoacoustic amplitude spectra of ZnBeMgSe sample. Circles – experimental data, solid line – a theoretical curve computed in a volume absorption model.

To explain the amplitude and phase PA spectra of the sample the volume and surface absorption model had to been applied. The results of the fittings performed in this model are shown in Figs.6 and 7.

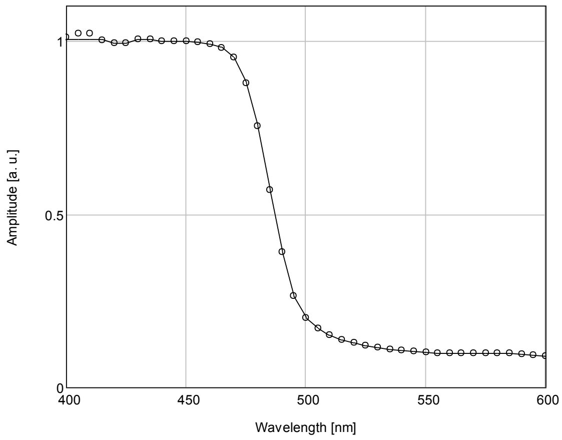

Fig. 6. Photoacoustic amplitude spectra of ZnBeMgSe sample. Circles – experimental data, solid line – a theoretical curve computed in a volume and surface absorption model.

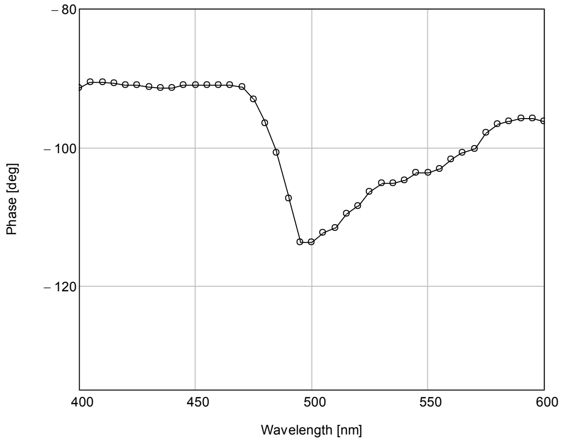

Fig. 7. Photoacoustic phase spectra of ZnBeMgSe sample. Circles – experimental data, solid line – a theoretical curve computed in a volume and surface absorption model.

The resulting volume and surface absorption spectra of the sample are shown in Figs.8 and 9. The volume and surface absorption coefficient spectra $\beta_v(\lambda)$ and $\beta_s(\lambda)$ were computed as the solution of the set of equations for each wavelength of the absorbed light. For computations the thickness of the damaged surface layer d=10 μm was assumed.

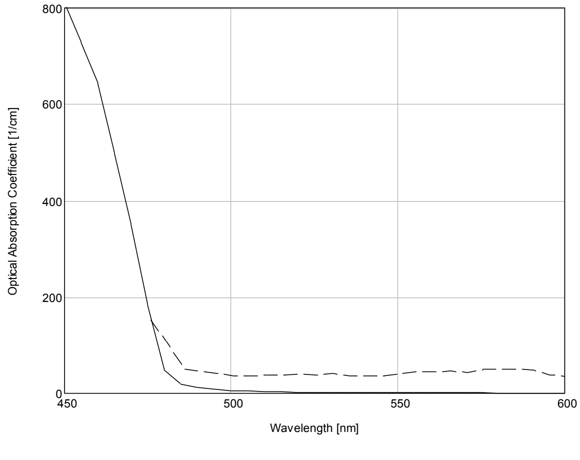

Fig. 8. Volume (solid line) and surface (dashed line) optical absorption spectra computed from the PA spectra in a volume and surface absorption model.

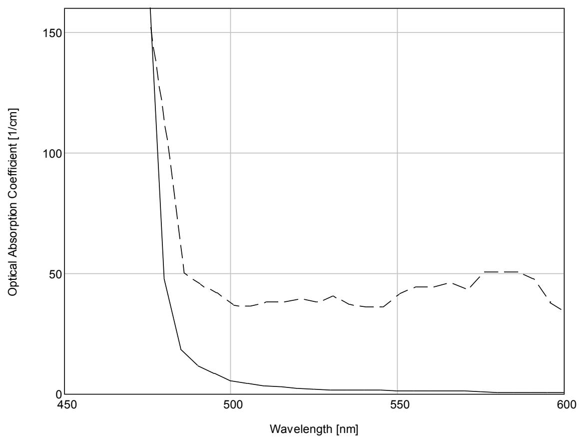

Fig. 9. Volume (solid line) and surface (dashed line) optical absorption spectra computed from the PA spectra in a volume and surface absorption model.

Conclusions

This paper shows that the character of the optical absorption i.e. a volume or a surface one can be identified only by the simultaneous fitting of the theoretical PA amplitude and phase spectra to the experimental ones. From the solution of the appropriate set of equations it is possible to determine the values of $\beta_S(\lambda)\cdot d$ as also $\beta_V(\lambda)$. The parameter $\beta_S(\lambda)\cdot d$ is suggested to be applied as describing the quality of the surface of semiconductor samples. Its value enables comparison of the quality of the surface of semiconductor samples after different surface treatments.

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Abstract

This paper presents experimental and theoretical amplitude and phase photoacoustic spectra of the mixed crystal ZnBeMgSe. The experimental photoacoustic spectra with the microphone detection were analyzed in a surface and volume absorption model. This paper proves that it is not possible to draw conclusions about the character of the absorption i.e. volume or surface only from the amplitude or phase photoacoustic spectra. It is possible to identify the character of the absorption only from the amplitude and phase photoacoustic spectra together.

Streszczenie

W artykule przedstawiono eksperymentalne i teoretyczne fotoakustyczne widma amplitudowe i fazowe kryształu ZnBeMgSe. Eksperymentalne widma fotoakustyczne uzyskane przy zastosowaniu detekcji mikrofonowej zostały zinterpretowane w modelu absorpcji objętościowej i powierzchniowej. Artykuł dowodzi, że nie jest możliwe wyciągnięcie wniosków odnośnie optycznej absorpcji objętościowej i powierzchniowej tylko z charakteru fotoakustycznego widma amplitudowego lub fazowego. Możliwe jest to przy jednoczesnej interpretacji zarówno fotoakustycznego widma amplitudowego jak i fazowego.