Optical Materials 79 (2018) 196–199

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Determination of the optical absorption spectra of thin layers from their photoacoustic spectra

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ARTICLE INFO

Keywords:
Photoacoustic spectroscopy
Optical absorption coefficient spectra
Thin semiconductor films

ABSTRACT

This paper presents a new method for computations of the optical absorption coefficient spectra from the normalized photoacoustic amplitude spectra of thin semiconductor samples deposited on the optically transparent and thermally thick substrates. This method was tested on $CuIn(Te_{0.7}Se_{0.3})_2$ thin films. From the normalized photoacoustic amplitude spectra, the optical absorption coefficient spectra were computed with the new formula as also with the numerical iterative method. From these spectra, the value of the energy gap of the thin film material and the type of the optical transitions were determined. From the experimental optical transmission spectra, the optical absorption coefficient spectra were computed too, and compared with the optical absorption coefficient spectra obtained from photoacoustic spectra.

1. Introduction

Thin semiconductor films deposited, on different substrates, have been investigated by the photoacoustic (PA) spectroscopy method for many years. Thin semiconductor layers such as $CuInSe_2$ or $Cu(In,Ga)Se_2$ have been studied because of their potential applications for use in photovoltaic devices as absorber layers to get the high efficiencies of the devices [1–3]. In order to improve the efficiency of solar cells, the band gap of the absorber should be adjusted to match it with the solar spectrum. Results of PA spectroscopic investigations of thin layers of several semiconductors deposited on the glass substrate are presented in papers: CdTe [4], CdS [5,6], SiC [7], $Cd_{1-x}Zn_xS$ [8], Cd_2SnO_4 [9]. The problem with thin layers is that for small values of the optical absorption coefficient the influence of multiple reflections of light on the photoacoustic signal should be taken into account. This problem was analyzed theoretically and experimentally in papers [10,11]. For thin samples, the problem of the interference of light can influence the photoacoustic signal too. The expression for the computation of the photoacoustic signal of the samples, in the presence of the interference of light, was presented in papers [1,12].

The main goal of photoacoustic investigations presented in the above papers was to determine the energy gap of thin semiconductor layers or their optical absorption coefficient spectrum and to find their optical parameters depending on the technological parameters of deposition of the layers. The goal of this paper is to present a method of computation of the optical absorption coefficient spectra of thin semiconductor layers deposited on the optically transparent substrates.

2. Theoretical model

The temperature of the front (illuminated) surface of the sample can be described by formula (1). It was derived in paper [13].

$$T = \frac{(1 - R_{opt})\beta}{\lambda\sigma(1 - R\cdot\exp(-2\sigma d))}\left(\frac{1 - \exp(-(\beta + \sigma)d)}{\beta + \sigma} + \frac{R\cdot\exp(-2\sigma d)\cdot(1 - \exp(-(\beta - \sigma)d))}{\beta - \sigma}\right) \quad (1)$$

The parameters of this formula are as follows. $\sigma = (1 + i)/\mu$, μ is the thermal diffusion length $\mu = (\alpha/\pi f)^{1/2}$, α is the thermal diffusivity, f is the frequency of modulation, β is the optical absorption coefficient, λ is the thermal conductivity, $R = (e_l - e_s)/(e_l + e_s)$ is the thermal reflection coefficient between the layer and the substrate e.g. air or glass, e_l and e_s are the thermal effusivities of the layer and the substrate respectively. R_{opt} is the optical reflection coefficient of the sample, d is the thickness of the sample.

For a big value of the optical absorption coefficient β when the sample is optically opaque i.e. $\beta \cdot d > 1$ formula (1) can be presented as:

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https://doi.org/10.1016/j.optmat.2018.03.043
Received 25 January 2018; Received in revised form 20 March 2018; Accepted 21 March 2018

$$T_{sat} = \frac{(1 - R_{opt})(1 + R\cdot\exp(-2\sigma d))}{\lambda\sigma(1 - R\cdot\exp(-2\sigma d))} \quad (2)$$

It is the case of the saturation of the temperature T_{sat}. The normalized PA amplitude is defined as:

$$q = \frac{P}{P_{sat}} = \frac{T}{T_{sat}} \quad (3)$$

where: P is the gas pressure in the PA chamber, P_{sat} is the gas pressure in the PA chamber for the big value of the optical absorption coefficient.

The normalized PA amplitude can be expressed by formula (4).

$$q = \frac{\beta}{(1 + R\cdot\exp(-2\sigma d))}\left(\frac{1 - \exp(-(\beta + \sigma)d)}{\beta + \sigma} + \frac{R\cdot\exp(-2\sigma d)\cdot(1 - \exp(-(\beta - \sigma)d))}{\beta - \sigma}\right) \quad (4)$$

The problem is that it is not possible to extract the value of the optical absorption coefficient β from the value of q, in the analytical form, from formula (4). It can be computed only with the iterative method.

For optically and thermally thick samples, the normalized PA amplitude can be expressed as:

$$q = \frac{\beta\mu}{\sqrt{(\beta\mu + 1)^2 + 1}} \quad (5)$$

From this formula, the optical absorption coefficient β can be determined with formula (6) [14–16].

$$\beta = \frac{1}{\mu}\frac{q^2 + q\sqrt{2 - q^2}}{1 - q^2} \quad (6)$$

This formula was also used for photoacoustic studies of $Zn_{1-x}Be_xSe$ mixed crystals [17].

For thin layers, however, formula (4) can be changed to much simple form if the following conditions are fulfilled: $1/\beta < \mu$ and $d/\mu \ll 1$ and the optically transparent substrate is thermally thick. Then, formulas (1), (2) and (4) can be presented as:

$$T = \frac{1 - \exp(-\beta d)}{\lambda\sigma(1 - R)}(1 + R) \quad (7)$$

$$T_{sat} = \frac{(1 - R_{opt})\cdot(1 + R)}{\lambda\sigma(1 - R)} \quad (8)$$

$$q = 1 - \exp(-\beta\cdot d) \quad (9)$$

The first condition means that the optical penetration depth $1/\beta$ is smaller than the thermal diffusion length μ. The second condition means that the sample is thermally thin.

In this simple model, the value of the optical absorption coefficient β can be determined from the value of the normalized PA amplitude q with formula (10).

$$\beta = -\frac{\ln(1 - q)}{d} \quad (10)$$

Let's consider an example thin semiconductor layer of the thickness $d = 0.5\,\mu m$, exhibiting the thermal diffusivity $\alpha = 0.01\ cm^2/s$, and the optical absorption coefficient spectrum given by formula (11), deposited on a thermally thick transparent substrate. Frequency of the modulation of the intensity of the illuminating light in the PA simulation, taken for computations, was $f = 36$ Hz. Thermal diffusion length equals to $\mu = 90\,\mu m$.

$$\beta(\lambda) = 3.33\cdot10^4\cdot\frac{\lambda}{1240}\cdot\left(\frac{1240}{\lambda} - 0.22\right)^3 \quad (11)$$

The results of computations of the absorption coefficient spectra, and normalized PA amplitude spectra are presented in Fig. 1a) and b) respectively.

The optical absorption coefficient spectrum, computed with formula (11), is presented as a solid line in Fig. 1a). The normalized PA amplitude spectrum, computed with formula (4), is presented as a solid line in Fig. 1b).

When we take the values of the q parameter from the spectrum of the normalized PA amplitude computed with formula (4) (solid line in Fig. 1b)), and compute the corresponding values of the optical absorption coefficient β, with formula (10), then we get values of β presented as a dashed line in Fig. 1a). One can see a perfect fit of the values of β computed with formulas (10) and (11).

The conditions of the correctness of this approach: $d/\mu \ll 1$ and $1/\beta < \mu$ are fulfilled in the whole optical range presented in Fig. 1.

One additional condition must be checked and fulfilled when the optical absorption coefficient spectrum of a thin layer is computed with formula (10) i.e. $\beta\cdot d < 8$. It is the result of the simplification of the formula for the normalized PA amplitude q, given by formula (4). For example, for the optical absorption coefficient spectrum presented in Fig. 1, for the biggest optical absorption coefficient value $\beta = 10^5\ cm^{-1}$ $\beta\cdot d = 5 < 8$ what means that this condition is fulfilled.

The dependence of the normalized photoacoustic amplitude q on the thermal reflection coefficient R, between the thin layer and a transparent substrate, is presented in Fig. 2. As one can see from this figure, the normalized PA amplitude q does not depend on the value of the parameter R. It means that the normalized PA amplitude spectrum is independent of the thermal parameters of the transparent backing and of the thin semiconductor layer.

3. Sample preparation

The photoacoustic method of determination of the optical absorption coefficient spectrum described above, was applied for investigations of $CuIn(Te_{0.7}Se_{0.3})_2$ thin films deposited on the glass substrates. The thickness of the layers was $d = 1\,\mu m$.

The $CuIn(Te_{0.7}Se_{0.3})_2$ thin films were deposited onto chemically cleaned Corning glass substrates by a pulsed laser ablation using Nd:YAG laser operating at a wavelength of 1.06 μm with a pulse duration of 10^{-3} s, and a repetition rate of $3\cdot10^{-2}$ Hz [18]. As a target material, Bridgman-grown, from high-purity elements, $CuIn(Te_{0.7}Se_{0.3})_2$ crystal was used [19,20]. Temperature of the glass substrate was maintained in the range 430–470 °C. The deposition process was carried out in a vacuum chamber at a pressure of $\sim10^{-5}$ Torr, the laser energy was in the range 150–200 J per pulse. A typical deposition rate was 10–12 nm per pulse.

The elemental composition of the deposited films was examined by the Energy-dispersive X-ray spectroscopy on the JEOL JSM-6400 scanning electron microscope. The analysis revealed that the overall films elemental composition corresponded to the formula of $CuIn(Te_{0.7}Se_{0.3})_2$ compound.

4. Results and discussion

The PA amplitude spectra of thin films were measured by using the experimental setup described in Refs. [21,22]. Self designed photoacoustic cell, with a G.R.A.S. microphone (type 26AK), has been used as a detector of the photoacoustic signal [23]. The experimental PA normalized amplitude spectrum of the $CuIn(Te_{0.7}Se_{0.3})_2$ samples is presented in Fig. 3a. The optical absorption coefficient spectra computed, from the normalized amplitude spectrum, with formulas (4) and (10) are presented in Fig. 3 b).

One can see that the spectra, presented in Fig. 3b, computed in the two models with formula (4) and formula (10), are almost identical. The advantage of the thin layer model is that it is very simple.

For the same thin films samples the optical transmission spectrum was also measured. The optical transmission spectra were measured by using Photon RT Spectrophotometer (Essent Optics) with a spectral