Optical and Recombination Parameters of CdS$_{1-x}$Te$_x$ Thin Films Obtained by the CMBD Method

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Abstract: This paper presents the results of the photoacoustic, SEM, and surface photovoltage experiments performed on the series of CdS$_{1-x}$Te$_x$ thin films. These CdS$_{1-x}$Te$_x$ (0 ≤ x ≤ 1) thin films were obtained on the glass substrate by the chemical molecular beam deposition (CMBD) method. The polycrystalline character of these films was revealed by SEM pictures. From the experimental optical characteristics, the optical absorption coefficient spectra of the samples and values of their energy gaps vs. their composition were determined. From the surface photovoltage characteristics, the diffusion lengths of the carriers were also determined.

Keywords: CdS$_{1-x}$Te$_x$; thin films; chemical molecular-beam deposition (CMBD); surface photovoltage; photo acoustics

1. Introduction

During the last decade, the growing demand for thin-film solar cells and optoelectronic devices requires that they become cheaper, better quality, and more efficient [1–3]. This requires the use of simple and economical technologies for the production of photovoltaic and optoelectronic devices.

Various physical and chemical methods are used to obtain the main semiconductor polycrystalline layer in thin-film optoelectronic devices, such as photoresistors, photodiodes, transistors, etc. [4–11]. These methods use expensive vacuum devices and complex chemical processes to produce a semiconductor polycrystalline layer. Our chemical molecular beam deposition (CMBD) method avoids these processes and is simple [12]. In this method, the area of thin layers up to 50 cm$^2$ can be obtained at least for the investigated material. As a substrate, glass, ceramic, or Mo foil can be used. In the investigated samples, CdS and CdTe powders in stoichiometric ratios were used. The CMBD method has a number of advantages, such as

- The deposition process is carried out in a gas stream at atmospheric pressure, so an expensive vacuum and other equipment are not required. Therefore, this method is economical.
- The deposition process is controlled at the molecular level (10$^{10}$–10$^{14}$ cm$^{-2}$), which allows controlling the composition of the films accurately.
- The deposition rate varies in a wide range (10–10$^4$ Å/s).
- On the existing installation, the films are deposited over a large area (50 cm$^2$).
- Doping of the films is carried out during the growth process.
- No toxic gas is used.

By controlling the composition ratio in the vapor phase, it is possible to obtain films in the solid phase with different compositions from pure CdS to pure CdTe.
So far, the CMBD method has shown that ZnTe, CdS$_{1-x}$Te$_x$, CdTe, SnSe, SbSe, Zn$_x$Sn$_{1-x}$Se, and other thin-film polycrystalline layers can be obtained and used for efficient photovoltaic and optoelectronic devices [13–17].

Semiconductor films of ternary compounds based on solid solutions of CdS$_{1-x}$Te$_x$ have the advantage of being used in thin-film photoresistors. The band gap of the material can be adjusted in a wide range from 1.4 eV at $x = 1$ to 2.4 eV at $x = 0$. This means the material is sensitive to the UV to near-infrared spectral region, while the lattice parameters can also be adjusted in accordance with the absorber layer. In this work, we studied the optical properties of CdS$_{1-x}$Te$_x$ ($0 \leq x \leq 1$) thin films obtained by the CMBD method.

2. Materials and Methods

Glass substrates (dimension of 1.5 cm $\times$ 1.5 cm $\times$ 0.1 cm) were used for samples of CdS$_{1-x}$Te$_x$ thin films. The substrates were cleaned in an ultrasonic bath followed by acetone, methanol, rinsed in warmed deionized water for 7 min, and then dried in a stream of nitrogen. After that, the substrate was placed into a reactor chamber of CMBD. High purity 99.999% CdS and CdTe powders were used as the precursors. Before heating, the system was purged with hydrogen for 10 min to remove atmospheric pollutants from the reactor chamber. Then, the outer furnace of the reaction chamber was turned on. The heating level was determined by the specified deposition temperatures. Furnaces for the individual heating of the source were switched on to achieve the required heating of the precursors, and the temperature was adjusted to the required evaporation temperatures. The initial evaporation temperature of the sources for the obtained solid solutions was in the range from 400 $^\circ$C to 900 $^\circ$C, depending on the composition of the solid solution and the substrate temperature was 400 $^\circ$C. The flow of the hydrogen carrier gas was ~20 cm$^3$ min$^{-1}$. The duration of deposition depended on the required film thickness and was in the range from 30 to 90 min. The process of obtaining CdS$_{1-x}$Te$_x$ thin films by the CMBD method is described in detail in [18,19]. The thickness of the samples was measured by the micro interferometer (MII-4). In this article, the AFM data are not presented, but the roughness of the thin films ranged from 50 nm to 800 nm. The example SEM picture of such obtained samples is presented in Figure 1.

![Figure 1. The SEM picture of the CdS$_{0.95}$Te$_{0.05}$ layer.](image)

All samples were investigated with the photoacoustic (PA) and surface photovoltage (SPV) methods.

The PA method was used for the determination of the optical absorption coefficient spectra $\beta$(h$\nu$). The SPV method was used for the estimation of the diffusion length of carriers $L_d$. The experimental setup used for the PA spectral experiments was similar as in paper [20]. The sample, placed in the photoacoustic cell, was excited by the monochromatic light produced by the OMNI 300 monochromator, Zolix Ltd, China. The intensity of light was modulated with the frequency $f$ by the mechanical chopper SR540, Stanford Research Systems, USA. The monochromator was illuminated by the xenon or halogen
The xenon light was used for the ultraviolet and visible range of light (from 300 nm to 700 nm). The halogen lamp was used for the near-infrared range of light (from 700 nm to 1700 nm). The condenser microphone G.R.A.S. 40HL with a preamplifier was used for the detection of the photoacoustic signal. The two-channel lock-in amplifier SR830 measures both the amplitude and the phase of the photoacoustic signal. The setup was controlled by a computer.

Afterward, the optical transmittance spectra of the samples were measured. The transmittance spectra were measured by Jasco V-670 UV-VIS-NIR spectrophotometer JASCO Deutschland GmbH, Germany equipped with FLH-740 film holder.

The schematic diagram of the SPV measurement configuration was similar to what was previously described in the paper [21].

The excitation and measurement parts of the SPV setup were the same as in the photoacoustic setup. The monochromatic and chopped light went to the sample and the optical power meter (Thorlabs PM100) through the 2-fold optical fiber splitter. The sample was placed between two electrodes; the bottom electrode worked as a support and was electrically grounded, the top electrode was semitransparent. It was a metal grid of 250 \( \mu \)m mesh and the size of 8 mm \( \times \) 8 mm. The sample could be excited from both sides. The glass spacer, placed between the semiconductor top layer and the electrode, was used to provide equal conditions of excitation.

The different \( dV_s \) of electric potentials between the dark \( (V_s^*) \) and illuminated \( (V_s) \) surface of the sample was the source of the measured SPV signal [22]:

\[
dV_s = V_s - V_s^*
\]

Structural defects present on the surface (surface states) cause the density of free carriers to be different on the surface than in bulk. In effect, the electric potential profile \( V(x) \) changes. It is described in the literature as the energy band bending \( -qV(x) \). The generation and recombination processes that arise during the sample illumination change the electric potential profile and thus affect the SPV signal. In the adopted measurement method, the light intensity was periodically modulated. Therefore the amplitude of the SPV signal was proportional to the changes in the surface potential \( (dV_s) \) [23].

Both, the absorption light profile and the carrier diffusion length influence not only the electric potential of the illuminated surface \( V(0) \) but can also influence the electric potential of the opposite surface \( (V(d)) \). This can occur especially for thin layers, where the light penetration depth may be big enough to generate carriers near the back surface, and the carrier diffusion length can be enough to move carriers towards the back surface (Figure 2).

So, in the general case, the SPV signal is the difference between potentials prevailing on both surfaces—(Figure 3):

\[
U_{SPV} = dV(0) - dV(d)
\]
The electrical model of the SPV signal generation system in a situation where both surfaces are signal sources.

The electrical condensers $C_t$ and $C_b$ arose between the top, semitransparent electrode, and the top surface and between the bottom surface and the bottom electrode. The non-ohmic contact between the sample and the electrodes is the reason why the harmonic excitation was used. With a sufficiently high modulation frequency (several hundred Hz), the impedance of the $C_t$ and $C_b$ condensers is so small that it does not affect the decrease in the SPV signal.

When $dV_s < kT/q$ then changes of the surface potential are proportional to the excess carrier’s concentration $\delta n(0)$ [24], so SPV signal can be described as:

$$U_{SPV} \approx \delta n(0) - \delta n(d)$$ (3)

The equation for the excess carrier’s concentration can be found elsewhere, i.e., [24]. It is a function of several parameters: $\beta$ the optical absorption coefficient, $S_1$, $S_2$ surface recombination velocity coefficients, $L_d$ carriers’ diffusion length and $d$ thickness of the layer.

3. Results

The normalized experimental PA amplitude spectra—$q$ of the samples are presented in Figure 4. The frequency of the modulation of light $f = 128$ Hz.

Figure 3. The electrical model of the SPV signal generation system in a situation where both surfaces are signal sources.

Figure 4. Normalized, experimental PA amplitude spectra for CdS$_{1-x}$Te$_x$ samples. 1: $x = 0$; 2: $x = 0.016$; 3: $x = 0.05$; 4: $x = 0.07$; 5: $x = 0.1$; 6: $x = 1$. 
From the experimental amplitude PA spectral characteristics, the optical absorption coefficient spectra $\beta(h\nu)$ of the samples were computed. For this purpose, the following formulae were applied [25,26]:

$$\beta(h\nu) = -\ln\left(\frac{(1 - q)}{(1 - Rq)}\right)/d,$$  \hspace{2cm} (4)

where $d$ is the thickness of the sample, $R$ is the optical reflection coefficient.

The optical absorption coefficient spectra calculated this way for $R = 0.25$ and different composition $x$ of the layers are presented in Figure 5.

![Graph](image)

**Figure 5.** (a) Optical absorption coefficient spectra of CdS$_{1-x}$Te$_x$ samples computed with Equation (4), $R = 0.25$. (b) Tauc’s characteristics. 1: $x = 0$; 2: $x = 0.016$; 3: $x = 0.05$; 4: $x = 0.07$; 5: $x = 0.1$; 6: $x = 1$; 7: fitting.

The values of the energy gaps $E_g$ of the samples, determined by the Tauc method [27] from the optical absorption coefficient spectra presented in Figure 5, are collected in Table 1, column 4, and presented in Figure 6.
Table 1. Parameters of the investigated samples.

| No | x   | d   | $E_g$ |
|----|-----|-----|-------|
| 1  | 0   | 2.8 | 2.44  |
| 2  | 0.016 | 6.0 | 2.32  |
| 3  | 0.05 | 9.0 | 1.80  |
| 4  | 0.07 | 9.0 | 1.79  |
| 5  | 0.1  | 9.0 | 1.70  |
| 6  | 1    | 9.0 | 1.34  |

The relationship between the composition parameter $x$ and physical parameters and thickness of the layers was controlled by the ratio CdS/CdTe in the vapor phase. It is possible to obtain films in the solid phase with different compositions CdS$_{1-x}$Te$_x$ ($0 \leq x \leq 1$) from pure CdS to pure CdTe. Much evidence exists that a phase transformation from the cubic zinc-blend structure for CdTe to the hexagonal wurtzite structure for CdS occurs as the value of $x$ is varied. Increasing the $x$ parameters in CdS$_{1-x}$Te$_x$ ($0 \leq x \leq 1$) increased the thickness of the film.

The dependence of the energy gap value and the composition of the samples is presented in Figure 6.

![Figure 6](image_url)

**Figure 6.** Energy gap values $E_g$ vs. the composition $x$ of the CdS$_{1-x}$Te$_x$ samples. Full circles are experimental results. The solid line is the approximation curve.

The experimental and theoretical SPV spectra of the CdS$_{1-x}$Te$_x$ samples are presented in Figure 7.

From the fittings of theoretical curves to experimental characteristics, the diffusion lengths $L_d$ of carriers were determined. They are presented in Table 2.

Good results of theoretical fittings were obtained when $S_1$ (>50,000 cm/s) was much higher than $S_2$ (100 cm/s). The optical absorption coefficient spectra used for calculations were taken from PA measurements.
Figure 7. Experimental and theoretical SPV spectra of CdS$_{1-x}$Te$_x$ samples, excitation from the top side. Solid lines are theoretical fittings.

Table 2. Collected data of diffusion lengths of carriers for CdS$_{1-x}$Te$_x$ samples.

| $x$  | $L_d$ (SPV Spectra Fitting) |
|------|-----------------------------|
| 0    | 0.164 µm (from the literature) |
| 0.016| 5 µm                        |
| 0.05 | 17 µm                       |
| 0.07 | 7.7 µm                      |
| 0.1  | 15 µm                       |
| 0.1  | 5 µm                        |
| 1    | 0.1–3.3 µm (from the literature) |

4. Conclusions

The thin CdS$_{1-x}$Te$_x$ layers of the thickness from 3 µm to 9 µm, investigated in this paper, were obtained by the cheap and simple chemical molecular beam deposition (CMBD) method. By controlling the composition ratio in the vapor phase, it was possible to obtain good quality thin polycrystalline CdS$_{1-x}$Te$_x$ films. The quality of these films was proved by the SEM measurements. Results of the optical experiments presented in this paper showed the dependence of the optical absorption coefficient spectra and the energy gap values of the layers on their composition $x$. Depending on the value of the parameter $x$ the energy gap value changed from 2.44 eV (for $x = 0$) to 1.34 eV (for $x = 1$). What is important, it covers almost all the visible range of the optical spectrum from 509 nm to 927 nm, which can be important for the application of these thin layers. Results of the photovoltage experiments enabled the estimation of the diffusion length of carriers in the investigated samples. Mean values of the diffusion length of carriers changed from 5 µm to 17 µm depending on the composition of the samples. Taking into account the fact that the samples were direct energy gap semiconductors and were of the polycrystalline type, the diffusion lengths can be considered as big, which can be important from the application point of view in optoelectronic devices.

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