J Mater Sci (2007) 42:7176–7179
DOI 10.1007/s10853-006-1246-6

A study of the optical absorption in CdTe by photoacoustic spectroscopy

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Received: 19 April 2006 / Accepted: 10 November 2006 / Published online: 10 May 2007

Abstract We show that the Photo-Acoustic Spectroscopy (PAS) is an useful alternative method for the determination of the optical-absorption coefficient of CdTe thin films, in the spectral region near to the fundamental absorption edge, ranging from 1.0 eV to 2.4 eV, using an open cell in the transmission configuration. We applied this method to the optical characterization of CdTe layers for several values of their thickness. These CdTe samples were deposited by closed-space vapor transport (CSVT) technique under different growth conditions.

Introduction

CdTe thin films obtained by high-temperature processes such as closed-space vapor transport (CSVT) are typically fabricated with thicknesses ranging from 3 μm to 15 μm [1]. On the other hand, the absorption coefficient (α) is greater than 10^3 cm^{-1} and then is very difficult to determine optically because nearly full absorption of light should occur below 800 nm. The exact determination of the absorption coefficient in CdTe solar cells is very important, since the optimum layer thickness for high efficiency devices depends on this parameter. The highest efficiency CdS/CdTe polycrystalline thin-films solar cells reported up to now was made with a 10 μm thick CdTe layer [2]. For a layer with thickness higher than 4 μm it is necessary an alternative method to the traditional optical transmission ones. Spectral response of the solar cell was used by Michell et al. [3] for the determination of the optical absorption coefficient, but the method involves several approximations and the knowledge of some minority carrier related electronic parameters, reducing their application in general way.

Experimental procedure

CdTe thin films were deposited onto different substrates by the CSVT technique using CdTe powders (99.99% purity) and sintered CdTe:Bi crystals grown by Bridgman technique. The substrates used on these experiments were soda-lime glasses. Thermal gradients between source and substrate were 67 °C/mm and 100 °C/mm. The deposition time was varied for the different samples. Under these conditions, CdTe layers with thicknesses from 4 μm to 12 μm were obtained. For thermal annealing a 200 nm thick $CdCl_2$ layer was coated and then treated at 400 °C for 30 min in air.

Photoacoustic (PA) transmission spectra of the samples were obtained using an open cell configuration [4] in the region near the fundamental absorption edge. The PA cell is formed by a commercial electret microphone which uses

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its own chamber as the acoustic cell as reported elsewhere [4]. The sample, with the transparent glass-substrate facing the microphone, closes the (PA) chamber with the help of vacuum grease around the microphone hole to get it hermetically sealed. The microphone is composed on a metallized electret diaphragm and a metal plate separated by an air gap and connected through a resistor, *R*. The light provided by a Tungsten Lamp (Spectra Physics) operating at 700 W is intensity modulated at a fixed frequency of 17 Hz with a mechanical chopper (Oriel 75159) after it passes through a monochromatic (Spectra Physics 74000) with 1,200 lines/mm diffraction grating in order to obtain monochromatic light in the spectral range from 1.0 eV to 2.4 eV. The light was then focused, using an optical quartz fiber, onto the thin film side of the sample/glass system. A part of the incident light is absorbed by the film and become heat, which is transmitted toward the glass-substrate, but it is quickly attenuated by the low thermal diffusivity (and the great thickness too) of the glass-substrate. On the other hand, the other part of the light, pass through the film, and the glass-substrate too, and then it arrives to the membrane. Pressure oscillations in the air chamber deflect the membrane, generating a voltage across the resistor, which is supplied to a FET pre-amplifier already built in the microphone capsule. The signal is then sent to a Lock-In amplifier (SR-850) synchronized at the modulation frequency, where it is measured in amplitude and phase. More experimental details about this measurement configuration are given elsewhere [4].

In the spectral region near and bellow the energy band gap, where the film becomes transparent, the transmitted modulated light impinges directly on the metallized electret diaphragm, where it is absorbed generating a surface heat source causing pressure fluctuations in the PA chamber in a way similar to conventional Photo-Acoustic Spectroscopy (PAS) [5]. The signal is then proportional to the sample's transmittance. On the other hand, when the semiconductor absorbs photons with energies above its absorption edge minority free carriers are generated, whose thermalization and recombination give rise to plasma, acoustic and thermal waves [6], which can propagate through the film and the glass substrate to the PA air chamber, inducing also pressure oscillations there. Taking these mechanisms into account, and in order to eliminate the glass substrate and electret diaphragm contributions, the PA absorption spectrum was recorded by dividing the signal due to the sample/glass system, V_{sys}, by that due to the direct incidence of the modulated light on the diaphragm after passing through a glass substrate placing instead the sample/glass system, V_g. For thermally thick samples the absorption coefficient is then calculated as $\alpha = (1/l_{sys})\ln(V_g/V_{sys})$, where l_{sys} is the thickness of the sample/glass system, according to that reported elsewhere for a similar configuration using photopyroelectric detection [7].

Results and discussion

As a mean of calibration, in Fig. 1 we show a comparison between the transmission spectra taking by both, PAS and conventional optical transmission measurements for a CdS sample grown by CSVT on glass substrates, with 2 μm of thickness. The corresponding calculated optical absorption spectra are shown in the insert. As it can be seen the spectra are very similar, showing the potentiality of the above described PA method to perform the optical characterization of thin films deposited on glass substrate. In Fig. 2 we show the typical absorption spectra for undoped and Bi-doped CdTe thin films deposited on glass substrates with thicknesses of 12 μm. Changes in the band gap value and in the absorption tails can be observed. The exponential behavior of the absorption coefficient, near the fundamental absorption edge qualitatively agrees with the well-known Urbach rule: $\alpha = \alpha_0 \exp[(E - E_G)/S]$ [8], where α_0 and S are in general dependent on the doping level. *S* is a slope parameter, which can be calculated from the ln (α) vs. hν graph. Values of 250, 286, 155 and 201 meV were obtained for undoped, and Bi doped samples at 5, 40 and 520 ppm respectively as indication of variations in the tail states near to the band edge. The inset shows absorbance derivative versus photon energy plots of the undoped and doping films at 5, 40 and 520 ppm. The derivative spectra displays a well-resolved structure composed of one band,

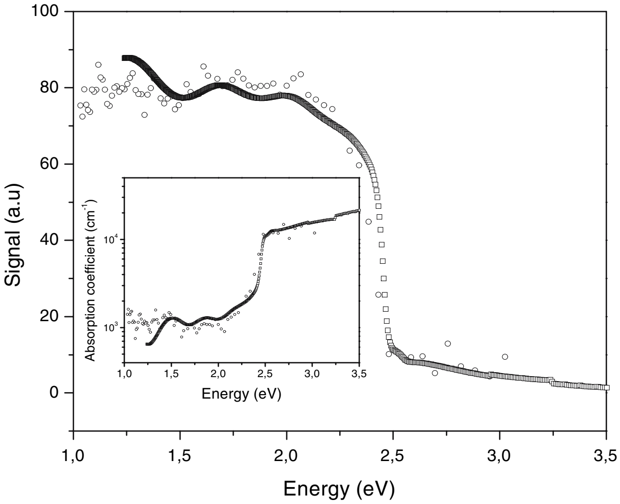

Fig. 1 A comparison between the optical properties obtained from PAS (circles) and conventional optical transmission (squares) measurements for a CdS sample (2 μm of thickness) grown by CSVT on glass substrates. The light modulation frequency used for PAS was 17 Hz

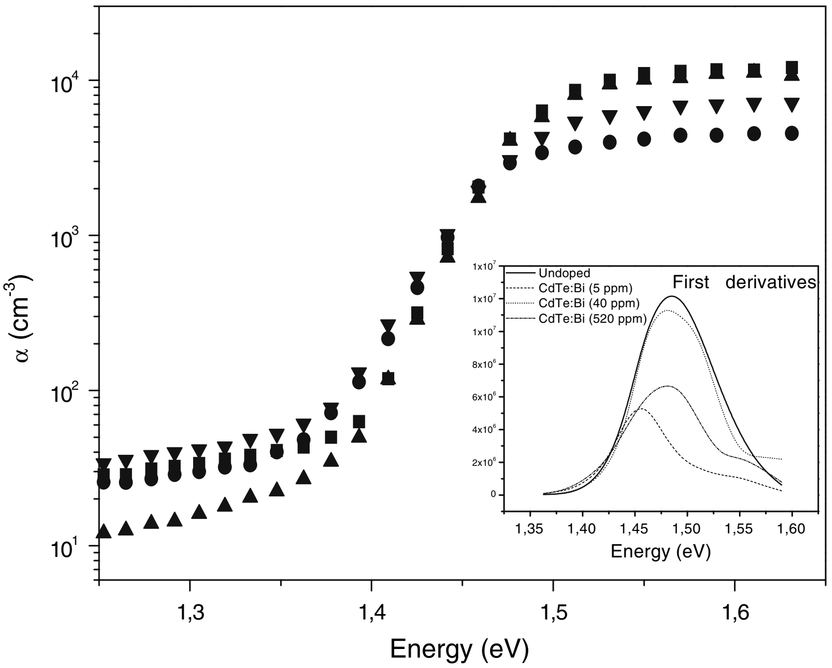

Fig. 2 Absorption spectra for undoped and Bi doped CdTe films deposited onto glass substrates: Undoped (square); CdTe:Bi (5 ppm) (circle); CdTe:Bi (40 ppm) (up triangle) and CdTe:Bi (520 ppm) (down triangle). In the inset the first derivates: Undoped (solid); CdTe:Bi (5 ppm) (dash); CdTe:Bi (40 ppm) (dot) and CdTe:Bi (520 ppm) (dash dot)

which permit us to calculated the exact value of the band-gap energy. This method was used in the calculation of the band-gap energy and the corresponding absorption length of the samples studied in this work.

Figure 3 shows the absorption coefficient as a function of the photons energy for two CdTe films deposited on glass substrates ($d = 4$ μm): as deposited and thermal annealed in $CdCl_2$ vapour atmosphere. Note that the absorption coefficient improves with $CdCl_2$ treatment, with slight shifts of the absorption edge to higher energies, as could be expected.

Finally in order to study the influence of the substrates in the absorption coefficient of CdTe thin films, layers of CdTe with thickness about 4 μm were deposited onto conducting glass/CdS substrates (where CdS films were grown by CSVT method). The absorption spectra are shown in Fig. 4. A better-defined absorption edge in the case of the CdS thin films with post thermal annealing in $CdCl_2$ atmosphere is observed.

Table 1 lists the band gap energy values and the corresponding optical absorption lengths (calculated at the band gap energy) for the CdTe thin films grown under different growth conditions.

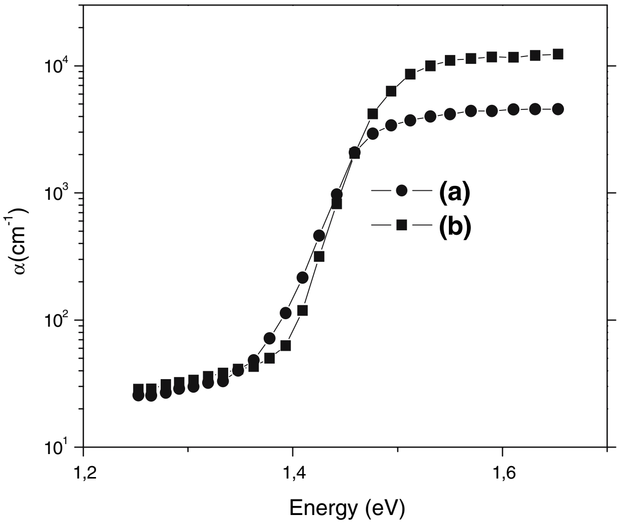

Fig. 3 Absorption coefficient spectra of CdTe thin films before (**a**) and after $CdCl_2$ thermal treatment (**b**)

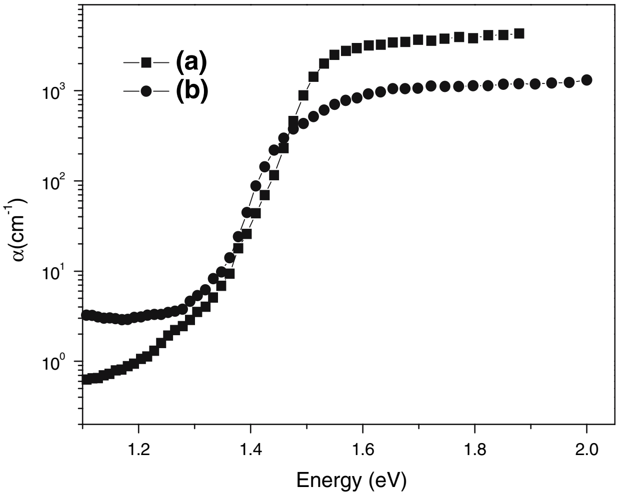

Fig. 4 Absorption coefficient spectra of CdTe thin films grown onto conducting glass/CdS substrates: (**a**): with post-thermal treatment of $CdCl_2$ of CdS layer; (**b**) without post-thermal treatment

Table 1 Values of the band-gap energy E_g and the absorption length for the CdTe thin films grown by CSVT under different conditions, with non thermal annealing (*) and thermal annealed in $CdCl_2$ atmosphere (**)

Growth conditions of CSVT-CdTe thin films	E_g(eV) (±0.05)	Absorption length (μm)
CdTe*/glass	1.46	2.50
CdTe**/glass	1.44	1.85
CdTe*:Bi (5 ppm)/glass	1.46	2.27
CdTe*:Bi (40 ppm)/glass	1.49	1.85
CdTe*:Bi (520 ppm)/glass	1.48	3.00
CdTe/CdS*/glass	1.46	2.87
CdTe/CdS**/glass	1.49	1.13

As it can be seen the absorption length value depends on the type of substrate, the post-thermal annealing and the doping level. Thermal annealing decreases the absorption length either in amorphous and polycrystalline substrates, but the type of substrates do not exhibit influence in this parameter. In the case of Bi doped CdTe samples, grown onto glass, the absorption length depends of the Bi concentration. The Bi has an amphoteric behavior, in dependence of its level doping in the CdTe crystals [9]. This fact must produce changes in the optical properties of the films.

Conclusions

We have demonstrated that PAS is a suitable method for the study of the spectral dependence of the optical absorption coefficient of CdTe thin films. The knowledge of this parameter is very important in polycrystalline thin films solar cells. For example, the knowledgement of α^{-1} allows the determination of the optimal CdTe thickness that improves a maximum short circuit current density and therefore the design of high conversion-efficiency CdS/CdTe solar cells. The values of α^{-1} depend on several aspects like, the growth method, type of substrate, post-thermal annealing and doping conditions. A full studied connecting the optical property of the CSVT-CdTe thin films and the CdS/CdTe solar cells fabricated with these layers is in progress.

Acknowledgements This work was partially supported by Consejo Nacional de Ciencias y Tecnología (CONACyT-México). ES also thanks to the MEK of Spain for the fellowship AP2003–1388.

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