

Pulsed laser deposition and electrodeposition techniques in growing CdTe and Cd_xHg_{1-x}Te thin films

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Abstract

CdTe and Cd_xHg_{1-x}Te (CMT) thin films were grown by a cathodic electrodeposition technique. Also CdTe was deposited using a Pulsed Laser Deposition (PLD) technique. Optical and XPS analysis techniques have been used to characterise them. Important differences were found in adherence, composition, band gap, refractive index, absorption coefficient, really useful for these materials in solar cells. Variables like energy of the laser pulse and temperature of substrate are determinants to improve the structural and optical properties. The presence of Hg in CdTe films is able to control the bandgap although it carries some problems, like segregation and diffusion, found in XPS measurements, that have to be solved. PLD technique could be really of interest in order to avoid this kind of problems. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

CdTe is a very interesting semiconductor for the fabrication of polycrystalline thin films for making solar cells with a heterojunction of CdTe/CdS. (15.8% efficiency) [1]. Its direct energy band gap in the range of 1.4–1.5 eV and its high absorption coefficient $\sim 10^5 \text{ cm}^{-1}$ makes CdTe suitable for this purpose [2]. Small amounts of Hg in the CdTe lattice leads to Cd_xHg_{1-x}Te (CMT). The band gap of this semiconductor varies from negative values (semi-metal) to 1.5 eV (CdTe) when the Hg deposited in the Cd positions takes values in the range $0.2 < 1 - x < 1$. This band gap control for CMT makes it a very attractive material, not only for photovoltaic conversion, but also for infrared, X-ray and γ detectors and for electronic and opto-electronic devices [3,4]. Special attention should be paid to graded band gap structures with multilayers of this material, in order to get the maximum profit of the solar spectrum. These materials have been grown by different techniques: sputtering [5], electrodeposition [6], vacuum evaporation [7] and lately electrochemical atomic layer epitaxy (ECALE) and pulsed laser deposition (PLD) [8–10].

Electrodeposition is a very useful technique. It is a cheap method, easy to get in a large-scale production, and can

produce high purity material by purification of the plating solutions by pre-electrolysis.

Pulsed laser deposition (PLD) is a recent and successful technique for the growing of thin films of very different materials [11], and it has been shown to be specially suited for the development of films for optical applications [12]. It has also been applied to produce CdTe and related compounds [9,10]. The purpose of this work is to deposit CdTe by PLD technique and find, to a first order, its optical structural properties with composition. Characterisation of CdTe and CMT films grown by other techniques can be useful to compare with them.

2. Experimental

Electrodeposition of CdTe was carried out in an aqueous solution containing 1M CdSO₄; $3 \times 10^{-4} \text{ M HTeO}_2^+$ as TeO₂. Tin oxide glass was used as a substrate, Titanium plate as a counter electrode and saturated calomel electrode (SCE) as the reference electrode. For the deposition of the Cd_xHg_{1-x}Te samples, a solution $3 \times 10^{-5} \text{ M HgCl}_2$ was also introduced into the electrolyte. The temperature of the solution was maintained at 80°C and the pH was adjusted to 1.6 with H₂SO₄. The electrodeposition was favoured by stirring the solution. Nitrogen was bubbled before the deposition and passed over the electrolyte during the electrodeposition. In order to improve the adherence of the film to the tin oxide

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substrate, this was partially reduced before the deposition. Potentials applied were in the -600 to -650 mV SCE range. The influence of deposition potential on the properties of CdTe and CMT is demonstrated [13,14].

Sputtered samples were deposited in an Alcatel ASCM 451 deposition system equipped with a RF generator operating at 13.56 MHz. The deposition chamber was pumped down to 5×10^{-7} mbar prior to the introduction of the gas discharge (Ar) with pressure maintained at 10^{-2} mbar during deposition. The CdTe layers were deposited from a high purity (5N) polycrystalline CdTe target on Corning 7059 substrates placed at 6.5 cm in front of the target and which was grounded and water cooled. The power density on the target was kept at around 160 mW/cm^2 .

Ablation of a CdTe wafer was done in vacuum by 12 ns pulses of an ArF excimer laser ($\lambda = 193 \text{ nm}$). The focused beam deposits about 7 J/cm^2 in an area of 0.8 mm^2 , with an incidence angle of 45° . A glass substrate was positioned at 3 cm from the target (CdTe) surface and held either at room temperature or at 180°C . Continuous monitoring of the growing process was made by measuring the reflectivity change which allowed us to determinate the film thickness and the refractive index to a first approximation [15].

The PLD films have been optically characterised in the 1.5–4.5 eV range by spectral photomodulated ellipsometry using a SOPRA instrument. The calculation of n and k has been done using the matritial formalism Jones [16] and a Powell bidimensional minimisation method [17].

3. Results and discussion

3.1. Structural properties

X-ray diagrams of electrodeposited CdTe show the fcc structure with a (111) preferential orientation. More negative potentials lead to an increase of the crystallinity with peaks higher and narrower. At -650 mV Cd is observed as a single phase in the deposit, Similar effects were observed in the CMT samples [14].

The sputtered films exhibited also a polycrystalline structure with preferential orientation in the (111) direction when they are grown at RF power greater than 100 W. Samples grown using PLD show polycrystalline structure of CdTe, but it is only possible to sign two peaks corresponding to the values of the interplanar distance $d = 2.290$ and $d = 3.742$ of the (220) and (111) orientations, respectively. PLD samples grown using a low energy in the pulsed laser seems to be more crystalline and preferentially oriented (220). Structural properties are also sensitive to the substrate temperature previous to the deposition: the (111) orientation was clearly favoured in films whose substrates were at 180°C , as can be seen in Fig. 1. In conclusion, the energy of the laser pulse seems to be more determinant than the substrate temperature in order to get a better polycrystal. A right conjunction of both variables would improve structural properties.

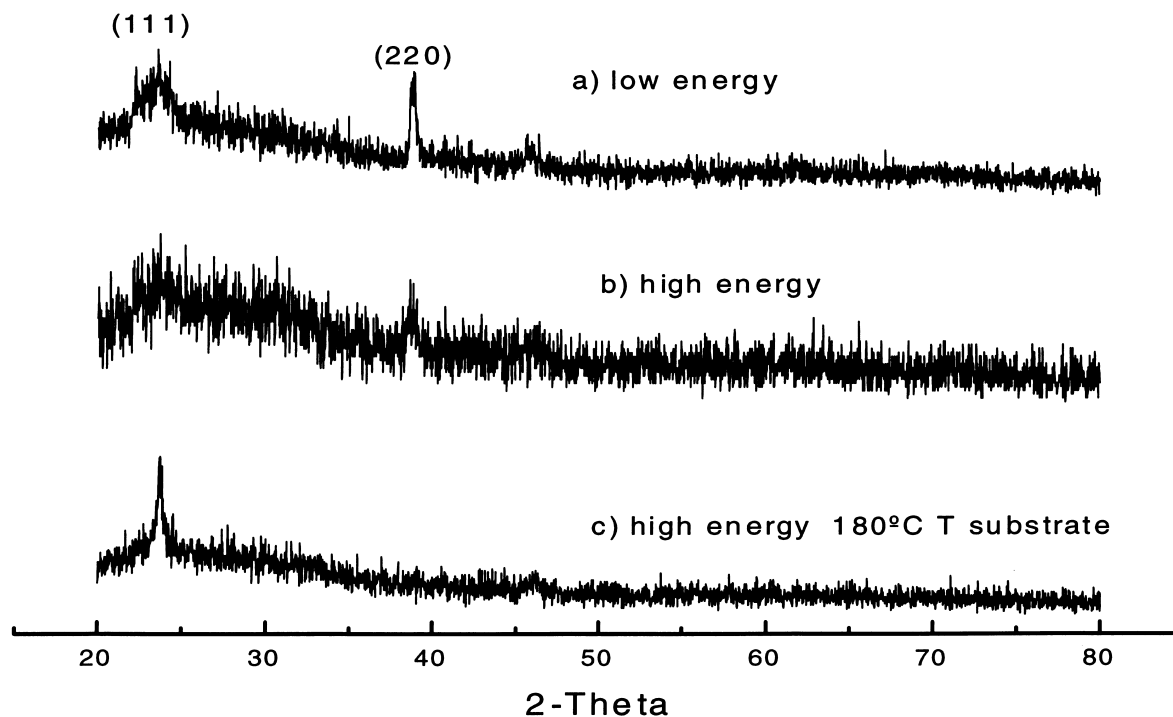


Fig. 1. Diffraction pattern of CdTe thin films deposited by PLD: (a) low energy laser pulse, substrate at room temperature, (b) high energy laser pulse, substrate at room temperature, (c) high energy and $T_{\text{substrate}} 180^\circ\text{C}$.

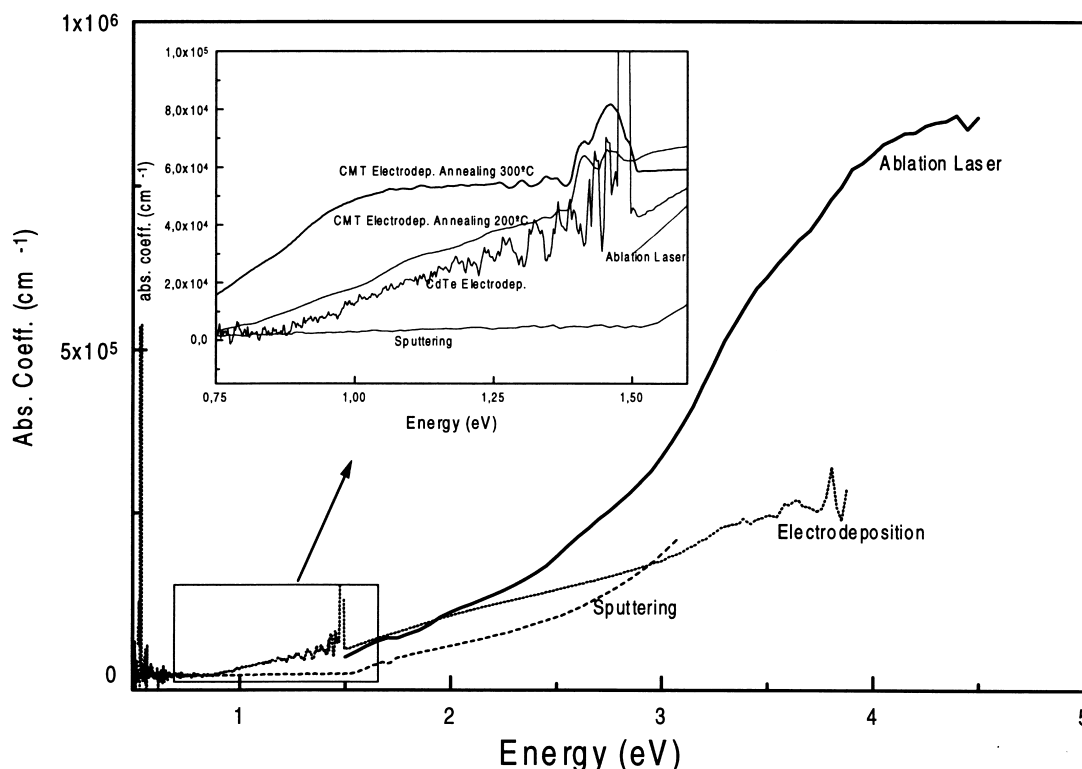


Fig. 2. Absorption coefficients for CdTe grown by different techniques.

3.2. Optical properties

Transmission and reflection spectra were obtained for electrodeposited and sputtered CdTe. Samples with interferences were analysed with a program developed at the Faculté des Sciences Semlalia, Dept. Physique, Marrakech [18]. For the PLD samples the method used was ellipsometry. Absorption coefficient (α) for these techniques is shown in Fig. 2. The PLD films were measured at different points with ellipsometry. The different points correspond to different thickness as can be seen in Fig. 3.

It can be observed that PLD samples have the best α in the visible range, giving values as high as $7 \times 10^5 \text{ cm}^{-1}$,

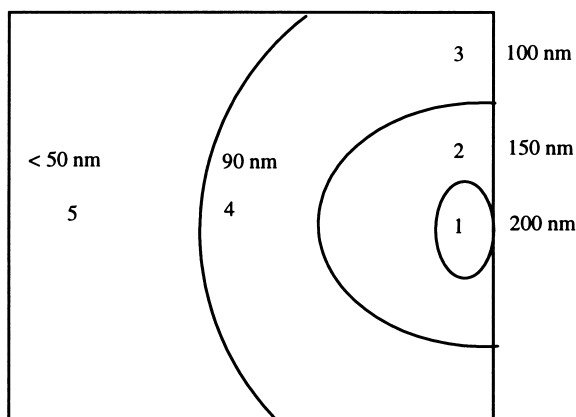


Fig. 3. Schematic diagram of a PLD sample and the different areas of measurement.

better than sputtered and electrodeposited samples. Electrodeposited films are as good as PLD ones until 2.0 eV and even better than sputtered until 3.0 eV. The noisy peaks at 1.5 eV (expected band gap energy) observed just in the cathodic deposition are probably due to different stoichiometries in the micro grains. This effect is partially solved annealing the film between 200 and 300°C in air [19]. For $\text{Cd}_x\text{Hg}_{1-x}\text{Te}$ films, where Hg content increases and the roughness grows up to 1000 Å, the absorption coefficient can present negative values. This is due to the impossibility of separating contribution from diffuse and specular reflectance. This effect is more important in samples with high Hg content ($1 - x > 0.2$) and deposited at relative more negative potentials $V_d = -650 \text{ mV (SCE)}$. Annealing of these samples improves the structural and optical properties, but must be controlled to temperatures below 400°C to avoid a massive evaporation of the film, or the creation of pin holes in the film that saturate transmittance. Annealing at 300°C in air for 20 min was studied and a notable improvement of the energy transitions between bands is clearly shown when the extinction coefficient is derivated respect to the energy.

The absorption coefficients for PLD films measured in different areas are very similar. The more absorbent, the thicker the film. This was also observed in the refraction index. The main differences are when the substrate is heated before deposition, this effect is clearly visible in Figs. 4 and 5, where the CdTe single crystal transition peaks at 3.3 and 3.9 eV are better defined in the heated sample and in Fig. 6, where the energy tail decreases not so slowly. Both effects

Table 1
Direct transitions in PLD (A1,A2,B1), sputtered (CdTe₁) and electrodeposited samples

Energy transitions					
Electrodeposition	Sputtering CdTe ₁	Ablation laser			Single crystal CdTe SC
		A1 high energy 25°C	B1 low energy 25°C	A2 high energy 180°C	
1.47 (d)	1.57 (d)	1.47 (d)	1.43 (d)	1.44 (d)	1.46 (d)

These results are better than those obtained for electrodeposited CdTe in which many kind of oxides and water were found in the film, and sometimes excess of Cd as a single phase. The effect of heating the substrate has clear advantages in order to improve the Cd/Te ratio.

Cd_xHg_{1-x}Te is more complicated to analyse because of the Hg. Hg tends to deposit on the surface or tries to migrate towards it from the bulk, so a good stoichiometry is not easy to obtain. Microareas with different (1 - x), Hg concentration, or formed by CdTe or even kinds of CdTe oxides are part of the multiple effects than can be get just changing the deposition potential. In this way PLD technique is a good alternative to deposit CdTe and surely Cd_xHg_{1-x}Te, stoichiometric thin films.

4. Conclusions

CdTe thin films have been deposited by pulsed laser deposition, and compared to sputtered and electrodeposited samples. PLD samples were polycrystalline showing fcc structure. PLD samples grown using a low energy in the pulsed laser seems to be more crystalline and preferentially oriented (220). Heating of the substrate leads to a diffraction pattern favoured to (111) direction with narrow peaks. A right conjunction of both variables would improve structural properties.

Optical properties of PLD samples are well fitted to the bulk material. These samples, compared to sputtered and electrodeposited present the highest absorption coefficient

maintained above the others from visible to UV range ($8 \times 10^5 \text{ cm}^{-1}$ at 4 eV). The energy band gap is slightly below 1.5 eV. Substrates heated to 180°C before deposition improve the energy transitions between bands and reduce the absorptions due to defects. Annealed electrodeposited films present the same effect. PLD variable thickness sample showed that the deposition rate has no meaningful influence on the optical constants, on the contrary, the substrate temperature produces notable effects on them. Electrodeposited CMT samples present changes in energy transitions depending on the Hg in the film, making it necessary to anneal them to improve the quality of the film.

Stoichiometry of PLD samples was achieved. Slight changes in Cd/Te ratio are observed on the same sample corresponding to different thicknesses.

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Table 2
XPS composition of PLD samples depending on substrate temperature and measurement location on the sample

$T_{\text{substrate}}$ (°C)		25			180
Position		1	2	3	1
Thickness (nm)		200	150	100	120
Cd (%)	CdTe	90	90	87	88
	CdO	10	10	13	12
Te	CdTe	85	91	87	83
	TeO ₂	15	9	13	17
O	H ₂ O	5	—	5	5
	OH ⁻	53	56	56	34
	O ²⁻	43	44	39	61
C	C=O	4	3	5	8
	C-C/C-H	96	97	95	87
Cd/Te		0.94	1.02	1.09	0.98