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MORPHOLOGICAL AND STRUCTURAL STUDY OF THE GROWTH OF SOME CDTE THIN FILMS ON AL_2O_3/HD-SI, HFO_2/HD-SI AND SIO_2/HD-SI SUBSTRATES, BY PULSED LASER DEPOSITION

L. I. LOMELI-GALAZ[a], M. A. QUEVEDO-LOPEZ[b,c], A. G. ROJAS-HERNANDEZ[a], A. DE LEON[e,*], A. APOLINAR-IRIBE[d], R. OCHOA-LANDIN[d], G. VALENCIA-PALOMO[f], S. J. CASTILLO[a]

[a]*Departament of Physics Research, University of Sonora, P.O. Box 5-088, ZIP code 83000, Hermosillo, Sonora, México*

[b]*Department of Materials Science, University of North Texas, Denton, Texas 76203*

[c]*Departament of Polymers and Materials Research, University of Sonora, P.O. Box 130, ZIP code 83000, Hermosillo, Sonora, México.*

[d] *Departament of Physics, University of Sonora, P.O. Box 1626, ZIP code 83000 Hermosillo, Sonora, México.*

[e]*Departament of Biological and chemical science, University of Sonora, ZIP code 83000, Hermosillo, Sonora, México.*

[f] *Technological Institute of Hermosillo, Tecnológico y Periférico Poniente S/n Ave, C.P. 83170, Hermosillo, Sonora, México*

In this research we utilized pulsed laser deposition (PLD) to deposit layers of the material Cadmium telluride, which is grown on 3 different substrates: Al_2O_3/HD-Si, HfO_2/HD-Si y SiO_2/HD-Si. Afterwards, the material was characterized to observe its morphological and structural properties. The first results show us the compactness and the transversal to the substrate surface CdTe growth. It portrayed a fluctuating kinetics in its thickness of 446, 892, 814 and 742 nm at substrate temperatures of 100, 200 and 400ºC, respectively. When the substrate is treated previously at 1000ºC and the substrates are maintained at the same temperatures during growth, thickness variation decreased, with values of 999, 964, 818 and 591 nm, respectively. A condition where the CdTe films only show a cubic phase and another one with a mixture of hexagonal and cubical phases (PDF#65-1085, PDF# 19-0193). Crystallite size calculations were performed using X-ray patterns, which range from 8.74 to 26.09 nm. SEM micrographies were obtained where diverse morphologies are observed. These can be useful on photovoltaic devices, sensors or optoelectronics in general.

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Keywords: Cadmium telluride, Pulsed laser deposition, Semiconductors, Electronic devices

1. Introduction

CdTe has a forbidden band width between 1.4 and 1.6 eV [1-4] which is the fundamental one of the main candidates in the field of photovoltaic energies [3] among other things, due to an absorption coefficient close to $5x10^5$ cm^{-1}, an absorption near 99% with a width of 2 μm of the incident solar light [3, 5, 6, 10]. CdTe films can be obtained through different methods, such as chemical bath deposition (CBD), closed-spaced deposition (CCS), metallo-organic chemical vapor deposition (MOCVD), vacuum evaporation deposition, advanced pulsed laser (APL), electron beam physical vapor deposition (EBPVD), sputtering, electrodeposition, electrochemical atomic layer epitaxy (ECALE) and pulsed laser deposit (PLD) [5, 10, 11, 12, 13, 14].

* Corresponding author: d_aned@hotmail.com

In the past few years, the PLD technique has shown a strong development. The interest on this technique is due to the possibility of elaborating thin films in a wide range of substrate temperatures, vacuum chamber pressure, simultaneous codeposits or multilayers, with which several compositions are obtained [4, 5]. For the films's growth, the goal is to achieve the greatest uniformity on the deposited material. If the layer has a great amount of defects, these imply a smaller distance between collsions, affecting the mobility and as a consequence a low electric conductivity [3,15].

The pulsed laser deposit is preferred in compound thin films since the stoichiometry can be replicated since the incident beam on the substrate produces a quick rise in temperature on the target ($>10^{11}$ Ks^{-1}). Multilayers including metals, semiconductors and dielectrics [5,16] can be deposited and it is an appropriate method for the in situ fabrication. Through this method, there is a controlled deposit rate for our case of 0.07 nm/s.

The high kinetic energy (1-100 eV) allows for the preparation of the thin films at low substrate temperatures due to the high superficial mobility [4, 17, 18].

The CdTe films have applications in semiconductor junctions with CdS as solar cells. Small quantities of Hg on the Cd positions of the CdTe lattice control the bandgap to become an attractive material not only for photovoltaic applications, but also as X- and γ-rays and in general in optoelectronic devices [1, 3, 18, 20]. The structural and electrophysical properties of the films obtained through PLD depend strongly on several parameters, such as substrate temperature, the distance substrate target, the pulse repetition rate, the laser energy and the deposit pressure, among others, [1, 21].

2. Experimental

This work consits on depositing material layers of CdTe by the means of PLD on three different substrates with the goal of understanding and correlating deposit conditions; morphological, structural and electrical properties to establish the possible applications of the material layers on electronic devices. The three different substrates deposited on the CdTe layers were: Al_2O_3/HD-Si, HfO_2/HD-Si y SiO_2/HD-Si.

12 layers of CdTe were grown with the fixed conditions of 100 mT of pressure, a frequency of 10 Hz and 75,000 shots. Of these 12 samples, 2 were grown on substrates of Al_2O_3/HD-Si, 8 were grown on substrates of HfO_2/HD-Si and 2 on substrates of SiO_2/HD-Si for certain substrate temperatures. The list of samples is shown on Table 1, which relates their names to the conditions on which they were created. A pre-deposit thermal annealing treatment on the substrate took place for 30 min at a temperature of 1000ºC on an O_2 atmosphere

Chemical-thermal annealing treatments on samples S2-2 and S2-4 were also performed in which the samples were covered by adhesion by a saturated solution of $CdCl_2$ and afterwards heating on a nitrogen atmosphere up to 415ºC during 15 minutes.

Table 1. General scheme of the design of the deposited samples with the PLD technique.

Sample LABELS	Material	Substrate	Substrate Temperature	Pressure (mTorr)	Frequency (Herz)	Shots
S1-1	CdTe	Al_2O_3	RT	100	10	75000
S1-2	CdTe	Al_2O_3	400°C	100	10	75000
S2-1	CdTe	HfO_2	RT	100	10	75000
S2-2	CdTe	HfO_2	100°C	100	10	75000
S2-3	CdTe	HfO_2	200°C	100	10	75000
S2-4	CdTe	HfO_2	400 °C	100	10	75000
S2-5	CdTe	HfO_2 (AN)	RT	100	10	75000
S2-6	CdTe	HfO_2 (AN)	100°C	100	10	75000
S2-7	CdTe	HfO_2 (AN)	200°C	100	10	75000
S2-8	CdTe	HfO_2 (AN)	400°C	100	10	75000
S3-1	CdTe	SiO_2	RT	100	10	75000
S3-2	CdTe	SiO_2	400°C	100	10	75000

List of the equipment used for the manufacture of the samples and their characterizations:

To grow HfO_2 and Al_2O_3 layers, an ALD Cambridge Nanotech Savannah model was used. The thickness measurements were performed by a Sentech SE800 Ellipsometer. For the CdTe doposit layers, a PLD Neocera brand, was used, coupled with a GAM LASER, INC EX200 Model. A Temescal BJD-1800 Model, a Spin coating Cee LS02 model and a Mask aligner Karl Suss MA 6/BA 6 were used for metal contact evaporations and Lift-Off processes, the characterizations were carried out with Rigaku Ultima III-XRD, SEM ZEISS Supra 40 model, Alessi Four-Point Probe and CASCADE Summit AP model proof station (Measurements I-V)

3. Results

Fig. 1 shows the comparison made by the SEM cross section between theCdTe layers. The temperature of the three substrates was room temperatures. The labels of these samples are S1-1, S2-1 and S3-1. Their respective thicknesses were of 438, 446 and 556 nm, measured also through ellipsometry. The S2-1 sample grown over HfO_2, looks isotropically more compact than S1-1 and S3-1 samples, however, the CdTe grows with a greater ratio on the substrate of SiO_2.

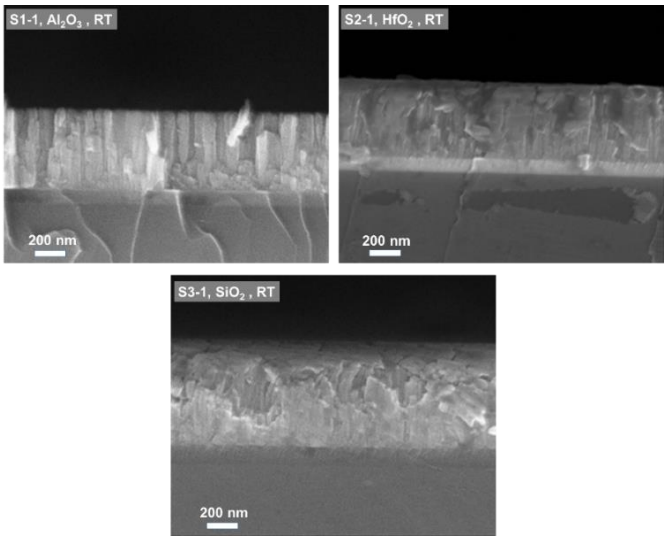

Fig. 1. SEM images of the transversal sections of the layers of CdTe, S1-1, S2-1 y S3-1. The substrate is at room temperature.

For the same group of samples of the layers of CdTe, S1-1, S2-1 y S3-1, X-ray diffractograms were performed, where it can be observed that at 75,000 shots with the substrate at room temperature, the CdTe layers are policrystalline with a mixture of cubical and hexagonal phases. Fig. 2 shows these diffractograms where the grain sizes calculated were of 8.74 (on Al_2O_3), 19.46 (on HfO_2) and 19.55 nm (on SiO_2).

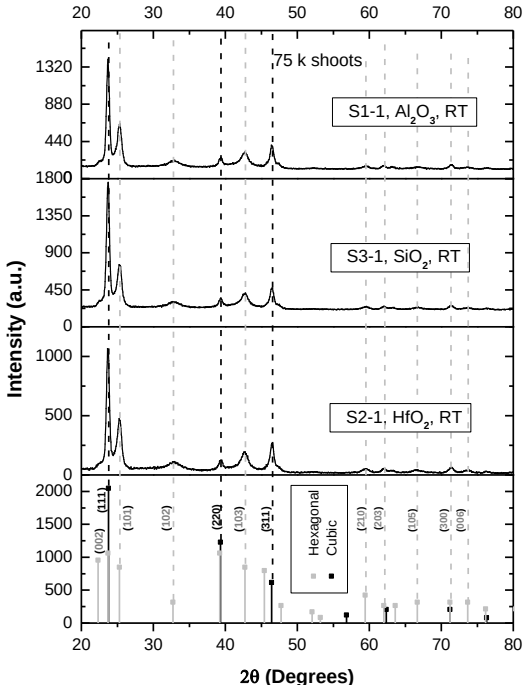

Fig. 2. X-ray diffractograms of CdTe layers, S1-1, S3-1 and S2-1, showing a mixture of cubical and hexagonal phases and its substrate at room temperature.

Similarly, Fig. 3 shows comparison of the SEM cross sections between CdTe layers at a substrate temperature of 400ºC. The labels of these samples are S1-2, S2-4 and S3-2, with their respective thicknesses of 597, 742 and 662 nm, also were measured by the ellipsometer. The S2-4 sample, grown over HfO_2, looks isotropically more compact than S1-2 and S3-2 samples, however, CdTe grows at a greater ration over the HfO_2 substrate.

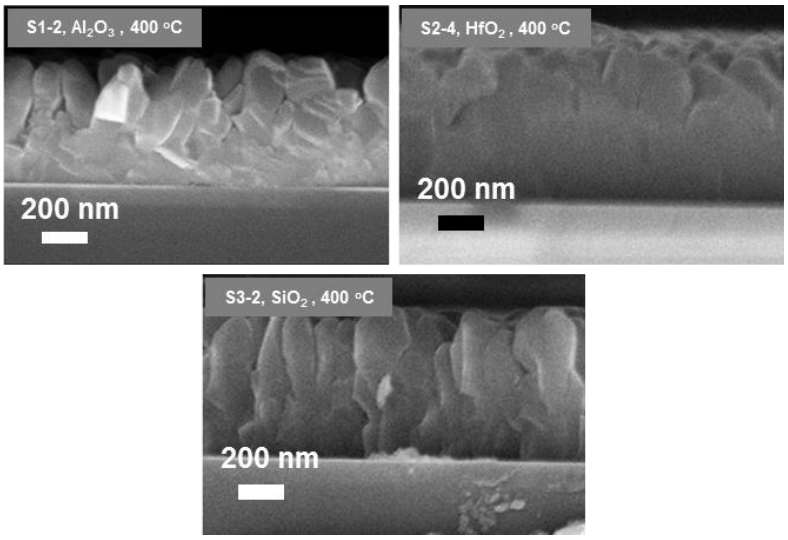

Fig. 3. SEM images of the transversal sections of the CdTe layers S1-2, S2-4 y S3-2 at a substrate temperature of 400 ^oC.

This second group of samples compares the layers of CdTe S1-2, S2-4 y S3-2, where the substrate was maintained at a temperature of 400ºC. The X-ray diffractograms performed show evidence of a phase depuration, leaving essentially the CdTe cubical crystallographic structure.

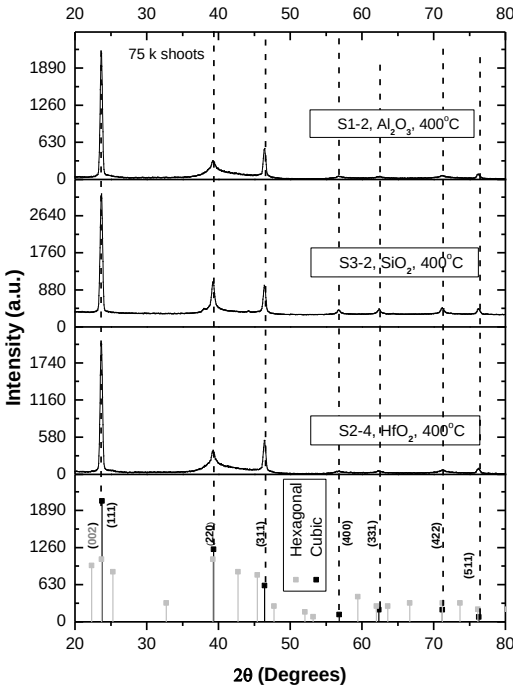

Fig. 4. X-ray diffractograms of CdTe layers, S1-2, S2-4 and S3-2, showing only the cubical crystallographic phase.

In the following paragraphs we analyze the intermediate growth of CdTe over HfO_2, at intermediate substrate temperatures between room temperature (RT) and 400ºC (samples S2-1 and S2-4). Fig. 5 depicts a fibrillary growth for the intermediate temperatures of 100 and 200 ºC (samples S2-2 and S2-3), of 892 y 814 nm, respectively.

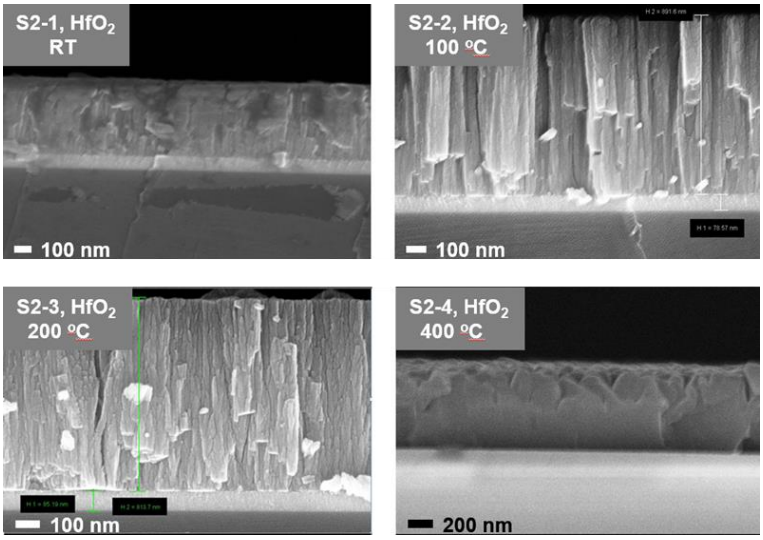

Fig. 5. Transversal sections of the CdTe films S2-1, S2-2, S2-3 y S2-4. S2-2 and S2-3 show an axial growth, while S2-1 and S2-4 show a compact growth.

Next, we performed a thermal annealing treatment previous to the CdTe deposit on the silicon substrates with the aluminum oxides of hafnium and silicon. This consisted on heating for 30 min at 1000ºC on an O_2 atmosphere. This effect can be observed on Fig. 6, where the

thicknesses of the samples S2-5, S2-6, S2-7 and S2-8 can be observed to be decreasing with the substrate temperature, see Table 2.

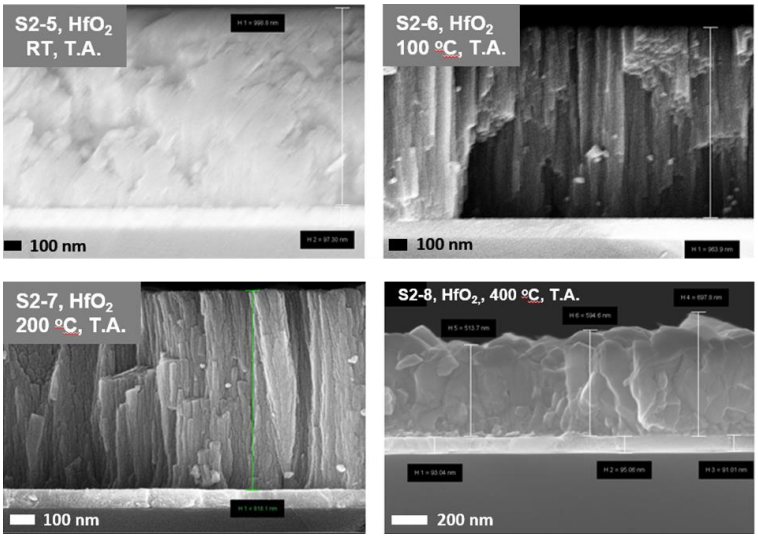

Fig. 6. Transversal sections of the CdTe films S2-5, S2-6, S2-7 and S2-8. S2-6 and S2-7 show an axial growth, while S2-5 and S2-8 show a compact growth. IN these CdTe samples HfO_2/Si underwent a thermal annealing treatment of 1000^{o}C during 30 min before the growth process.

Table 2 shows a summary of the thicknesses obtained of all the samples obtained in this work, grown with 75,000 shots.

Table 2. Thicknesses for samples with 75000 shots.

Sample	Tickness (nm)	Figure
S1-1	438	1
S1-2	597	3
S2-1	446	1
S2-2	892	5
S2-3	814	5
S2-4	742	3
S2-5	999	6
S2-6	964	6
S2-7	818	6
S2-8	591	6
S3-1	556	1
S3-2	662	3

Fig. 7 displays a strong effect of the growth of CdTe when the substrate undergoes a thermal annealing treatment with the oxide, HfO_2/Si, of 1000^{o}C during 30 min previous to its deposition on a RT substrate during growth going from 446 nm up to 999 nm. A difference of 72 nm is obtained when the substrate is maintained at 100ºC; almost the same thickness if the substrate is maintained at 200ºC and inverting the growth kinetics for the substrates maintained at 400ºC.

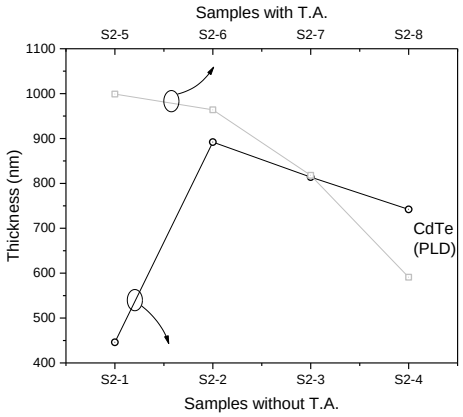

Fig. 7. Two growth processes are shown (black and gray lines) varying the temperatures of the growth surface, HfO_2/Si, with and without thermal annealing of 1000^{o}C during 30 minutes, before the conditions of the PLD.

Table 3. Estimated cristallite size of the denoted samples obtained from the X-ray diffractograms that were included as Figs. 2 and 4. The Debye-Sherrer [22] procedure was used to calculate these results.

Sample	Cristallite Size (nm) 75000 shoots	Figure
S1-1	8.74	2
S1-2	23.8	4
S2-1	19.46	2
S2-4	24.74	4
S3-1	19.55	2
S3-2	26.09	4

The following characterization performed on the films obtained as a comparison between the substrate's deposit temperature of RT vs 400ºC is shown on Fig. 8. This characterization corresponds to the SEM top view micrographies. In here, the formation of fibrilar clusters can be appreciated for the three different oxides where CdTe was grown when this oxide was maintained at room temperature. Anyhow, the morphology of the clusters when the oxides were maintained at 400ºC was displayed as angled geometric shapes of flat faces. The labels in the samples are as reported in Table 1. At this stage, the used celeration voltage in SEM was of 15 kV with a magnification of 250 kX.

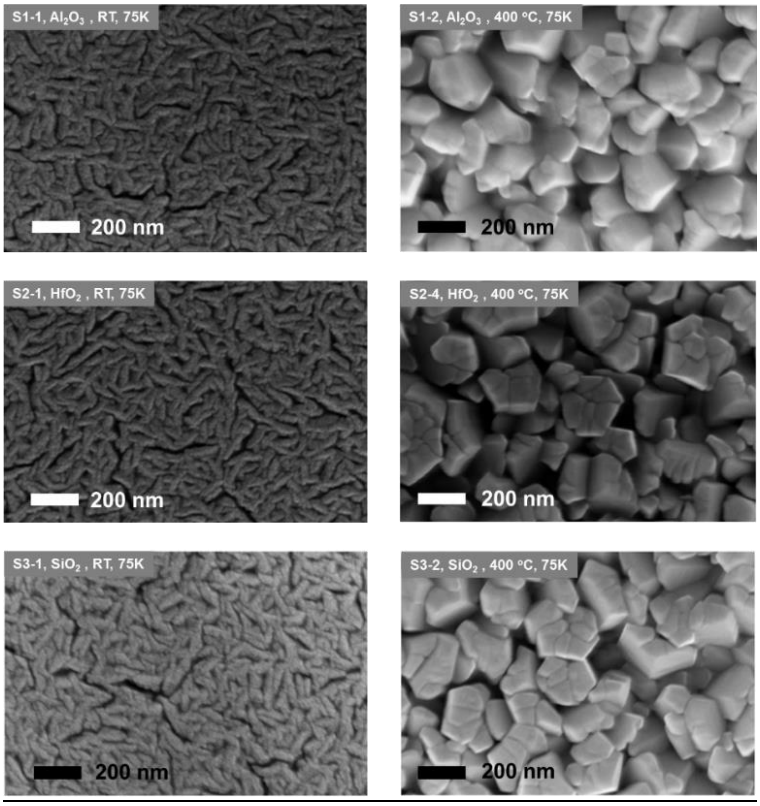

Fig. 8. Morphology for 2 substrate tempertures, RT and 400ºC of CdTe depending on the conditions indicated for the three oxides used.

On Fig. 9, we establish a morphological comparison also through SEM of the set of CdTe films grown over Hafnium oxide, where a group of four samples underwent a thermal annealing previous to the deposit process through PLD, indicated on the TA images. As it is shown on Table 2, complemented by Table 3, the higher and lower thicknesses are from samples S2-1 and S2-5 of 446 and 999 nm, respectively. Sample S2-6 has a thickness of 964 nm, 72 nm more than that of S2-2 (892 nm). Samples S2-3 and S2-7 show thicknesses almost the same size. At this stage, the celeration voltage used in SEM was of 10 kV and the magnification was of 250 kX.

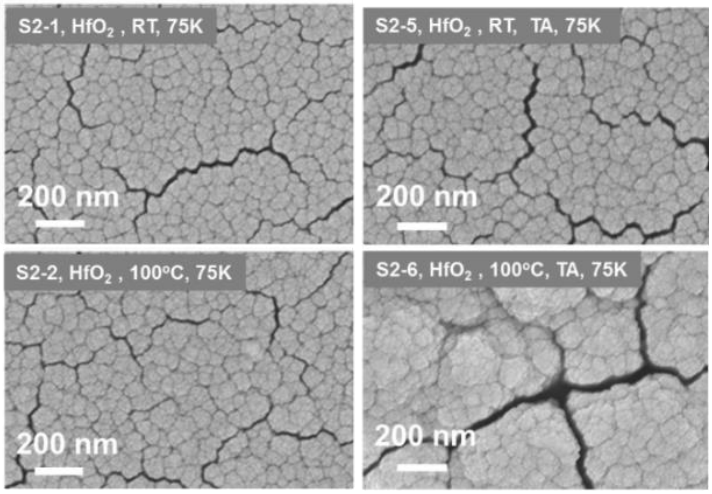

Fig. 9.1 The columns of this image show both growths at their different growth conditions, together with the morphological similarities. However, there is a marked difference on the cracking of sample S2-6.

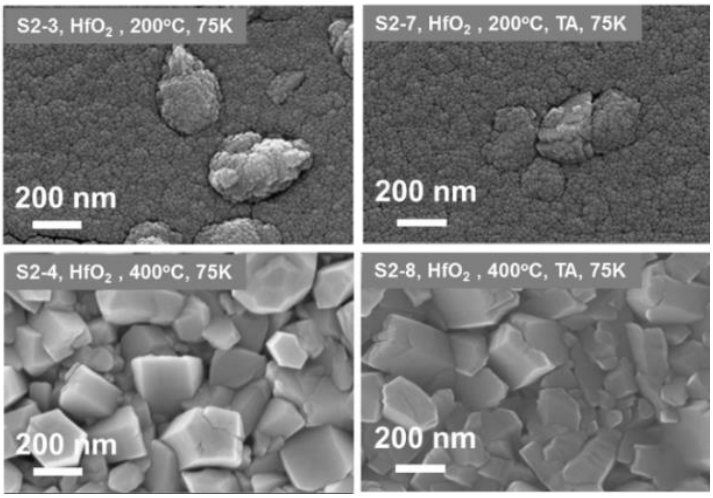

Fig. 9.2 The columns of this image show both growths at their different growth conditions, together with the morphological similarities. However, there is a marked difference on the cracking of sample S2-6.

On Fig. 10 the morphological changes are presented when the samples S2-2 and S2-4 were covered by adhesion by an $CdCl_2$ saturated aqueous solution which later underwent a thermal annealing at 415ºC during 15 minutes on a nitrogen atmosphere. The top pictures correspond to the morphological changes from a top view of CdTe sample S2-2. A coalescence and growth of the aggregates is promoted, leaving certain profiles of rugosity. The corresponding evolution of S2-4 shown on the inferior images portrays an even greater coalescence, yet formations of isolated pin holes are left.

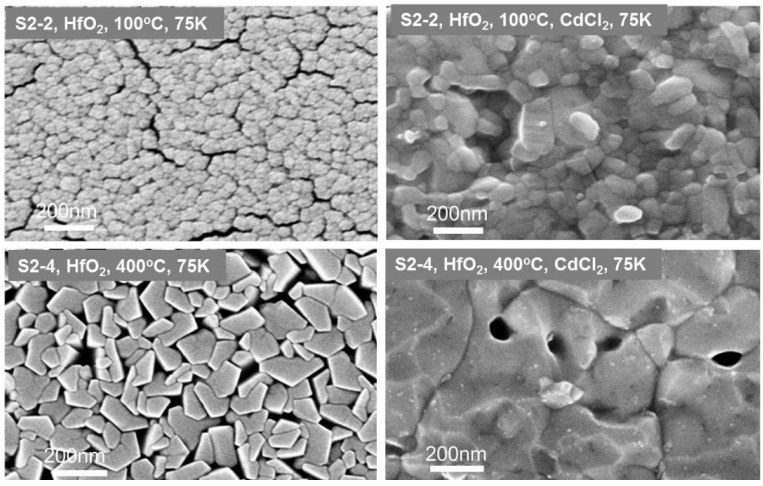

Fig. 10. Top images: morphology changes of samples S2-2 by being submitted to a thermal annealing. Bottom images: changes on the morphology of the samples S2-4 by being submitted to a thermal annealing.

The following characterization corresponds to the X-ray diffraction patterns. Figure 11 corresponds to sample S2-2 of CdTe. The changes obtained in the CdTe S2-2 demonstrate that the film has a mixture of cubical and hexagonal phases, with an orientation on the cubical direction (111) which coincides with the hexagonal direction (002) and as a result of the thermal chemical annealing explained, the crystallite growth is promoted with other orientations (220) and (311), this last orientation pertains only to the cubic structure.

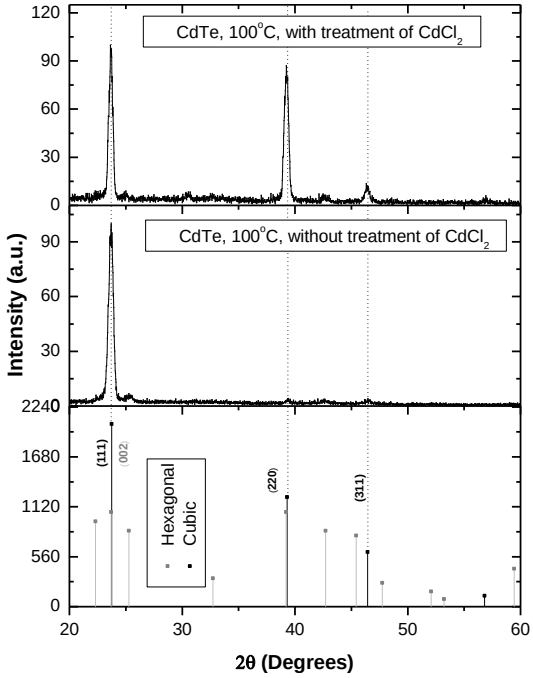

Fig. 11. X-ray pattern comparison with and without $CdCl_2$ treatment. The treatment promoted significantly two crystallographic orientations (220) and (311) simple cubic phase S2-2.

Fig. 12 shows the X-ray diffraction patterns for the CdTe sample S2-4 before and after the chemical-thermal annealing designed. The obtained changes on CdTe S2-4 show that from a film with an essentially cubic structure with an orientation on the direction (111), through this combined treatment, growth of crystallites with other orientations (220), (311) and (400) is promoted. We assume that also of a cubic structure since the las two directions are only characteristic of the cubic phase of CdTe.

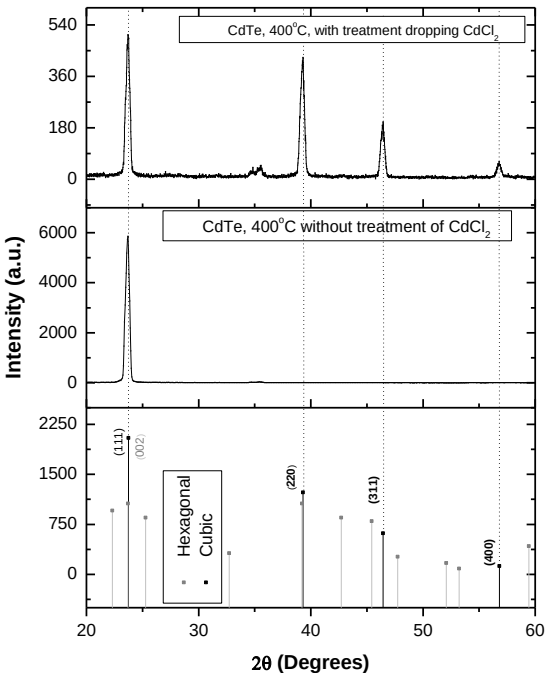

Fig. 12. Comparison of X-ray diffraction patterns with and without $CdCl_2$ treatment. In this case the treatment promoted significantly three crystallographic orientations (220), (311) and (400) simple cubic phase S2-4.

Fig. 13 shows the electrical responses I-V, also for sample S2-4, but with two different ways to deposit the electrical contacts. Graphs a) and b) were obtained when the film S2-4 was not treated with $CdCl_2$ and it an ohmic behavior of lower ressistance can be noted when the gold contacts are deposited by lift-off. The application of the chemical thermal annealing with $CdCl_2$ produced a drastic change on the behavior of the curves (see graphs c) and d) I-V) on both deposit processes of Au contacts. This was shown with a rectifying-type growth which could be due to a combination of junctions between the base semiconductor and the enriched semiconductor base with Cd atoms from the treatment with $CdCl_2$ and Au, the metal contact. For lift-off deposited contacts, better ohmic response and rectifying curves were obtained (Von=1.15 V).

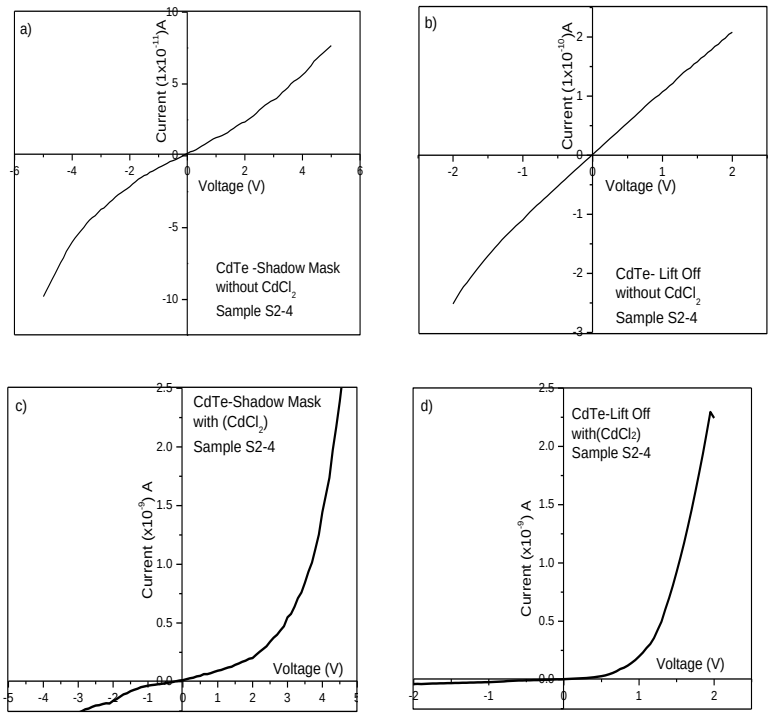

Fig. 13. Responses I-V of CdTe sample S2-4 a) without $CdCl_2$ treatment and shadow mask contact, b) without $CdCl_2$ treatment and lift-off contact, c) with $CdCl_2$ treatment and shadow mask contact, d) with $CdCl_2$ treatment and lift-off contact.

Finally the CdTe sample S2-4, also was selected to calculate the sheet resistance and resistivity, by the Transmission Line Method [23], getting the following values: Rsh=3.64 x 1011 Ω/sq and ρ= 27.3 MΩ-cm, the considerate thickness was of the order of 750 nm.

4. Conclusions

A growth kinetics was elaborated for CdTe thin films deposited on three different oxide layers using the PLD method.

It was demonstrated that a previous thermal annealing before a typical growth process increases the thickness of sample S2-5 compared with sample S2-1, which carries on to an anomalous kinetic behavior, strictly decreasing when this previous annealing treatment is applied; and fluctuating when the treatment is not applied.

On CdTe grown over HfO_2 the effect of the substrate temperature remaining constant during the deposit process produces a compact material for RT and 400ºC and a column-axial material for deposit temperatures of 100 and 200ºC.

The chemical thermal annealing with $CdCl_2$ to CdTe/HfO_2/Si, in general rises the size of the aggregates formed by coalescing CdTe and the Cd atoms. The tests were performed for

substrate temperatures of 100 and 400ºC. On the X-ray patterns this shows different crystallographic orientation numbers. On the other hand, this is displayed on the curves I-V through a smaller ressistivity.

Acknowledgements

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