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Improving the optical and crystalline properties on CdS thin films growth on small and large area by using CBD technique

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CdS polycrystalline thin films have been used as window layer in solar cells; the optical and crystalline quality of the CdS-partner plays an important role in the photovoltaic device performance. CdS thin films were deposited by using Chemical Bath Deposition (CBD). The SnO_2:F substrates used were chemically treated with HCl (0.1M) and others were thermally annealed in different atmospheres (Ar y O_2). The physical properties of CdS thin films were influenced by the HCl treatment, position, size and the substrates movement inside the reaction beaker. The CdS samples were deposited in areas of 4 cm^2, 50 cm^2 and 100 cm^2. Finaly CdS thin films with thickness of 35-300 nm with good optical and crystalline quality on a uniform morphology were obtained. Transmittance values were obtained for all samples about 85-90% with an average of gap energy of 2.5 eV.

Keywords: CdS; CBD; solar cells.

Las películas delgadas policristalinas de CdS han sido usadas como el material ventana en celdas solares; la calidad óptica y cristalina de la película delgada de CdS juega un papel muy importante en el desempeño del dispositivo fotovoltaíco. Películas delgadas de CdS fueron depositadas utilizando la técnica de baño químico (DBQ). Los substratos de SnO_2:F utilizados fueron tratados químicamente con HCl (0.1M) y algunos otros fueron térmicamente recocidos en diferentes atmósferas (Ar and O_2). Observamos que las propiedades físicas de las películas delgadas de CdS se ven influenciadas por el tratamiento con HCl, la posición, el tamaño y el movimiento del substrato dentro del vaso reactor. Las muestras de CdS se depositaron en areas de 4 cm^2, 50 cm^2 and 100 cm^2. Finalmente se obtivieron películas delgadas con espesores de 35 - 300 nm con buena calidad óptica y cristalina en una morfología uniforme. Los Los valores de transmitancia en las muestras obtenidas se encuentran entre un 85 y 90% con una brecha prohibida de energía promedio de 2.5 eV.

Descriptores: CdS; CBD; celdas solares.

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1. Introduction

The CdS thin films as window material is the most used in the technology of thin film photovoltaic solar cells (CdTe, Cu(In,Ga)Se_2, Cu_2ZnSnS_4). The technology of thin films solar cells requires deposit methods to ensure simplicity, low production cost and high efficiencies. Chemical bath deposition has proven to be one of these methods.

The efficiency is influenced by the transport of charge in the hetero-junction between both, the window and absorbent materials when solar cells are fabricated. CdS as window material must be free of defects such as intergranular caves and pin-holes [1]. The record efficiency into CdS/CdTe Solar cells are 21% ± 0.4% laboratory level [2] and 10% in solar panels [3]. These efficiencies, however, are well below the theoretical limit of about 30% calculated [4]. ZnO/CdS/CIGS thin-film solar cells have a new record efficiency of 20.5% ± 0.6% and the record efficiency based on CZTSSe solar cells close to 12.6% ± 0.3% value [2]. Larger improvements in current collection can be achieved by using window layers of thinner CdS. Chemical bath deposition (CBD) technique is well suited for producing thin films of large area and can be applied in solar cells. Furthermore, exist a variety of materials that can be produced by this technique in later years; this is because of the viability to produce multilayer films. CBD has proven to be a simple and low cost technique to prepare CdS films as optical window material for solar cells. Many options are required to improve CBD for technological applications. The aim of this work is to study the impact on the main physical properties of the CdS thin films deposited by chemical bath deposition technique (CBD) by using substrates with different thermal and chemical treatment and considering different growth conditions in order to obtain CdS thin films with suitable properties for use them in solar cells technology of large area.

2. Experimental

The CdS semiconductor thin films were deposited on SnO_2: F substrates (FTO) by using CBD technique. As precursor solution was used $CdCl_2$ (0.1M), NH_4Cl (0.2 M), NH_3 (2 M) and $(NH_2)_2CS$ (0.3 M). Some substrates were treated with HCl (0.1M) during 30 min, and others were thermally annealed at 500°C in different atmospheres (Ar and O_2). Bilayers of CdS with deposition time of 10 min. at 75 ± 2°C were obtained. Figure 1a shows the reaction beaker with the

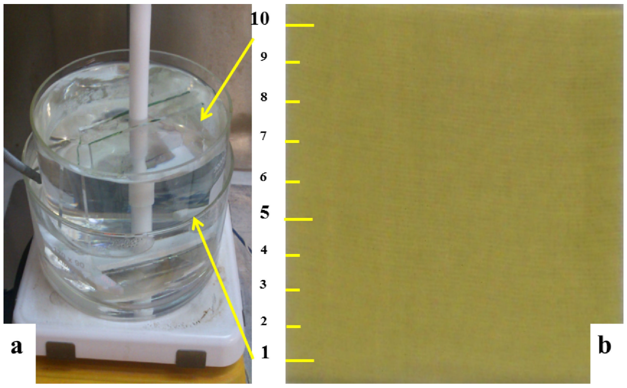

FIGURE 1. CBD arrangement, (a) Reaction beaker with the FTO substrates inside of this before de chemical reaction, (b) Specific points (1, 5 and 10) along the CdS thin films are shown; these points were considered for a subsecuent characterization and analysis.

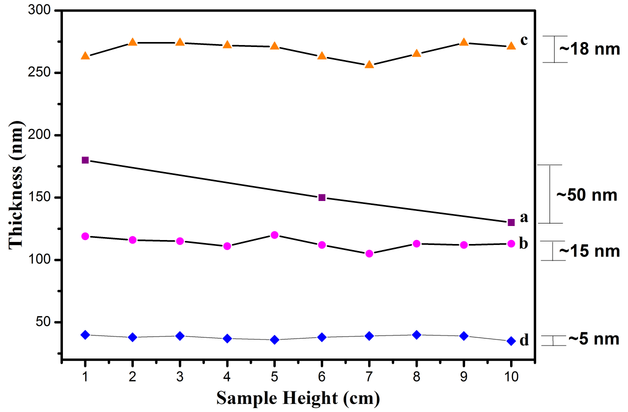

FIGURE 2. (a) ^{1}CdS$_{50}$ (15 min.), (b) ^{2}CdS$_{50}$ (10 min.), (c) ^{2}CdS$_{50}$ (20 min.), (d) ^{2}CdS$_{100}$ (14 min.). Consider: 1 magnetic stirrer of 0.8 cm; 2 magnetic stirrer of 2 cm.

substrates inside it and Fig. 1b shows the CdS thin film deposited on areas of 100 cm^2. These samples were labelled considering specific points (1 to 10) respect the bottom to top inside the reaction beaker respectively. CdS thin films were obtained in areas of 4 cm^2, 50 cm^2 and 100 cm^2. Some CdS thin films were deposited on areas of 4 cm^2 (bi-layers), but nevertheless, mono-layers of CdS thin films were deposited on areas of 50 and 100 cm^2 (CdS$_{50}$ and CdS$_{100}$) respectively. The structural characteristics of the samples were determined by the X-ray diffraction patterns (XRD), by means of a D-500 Siemens X-ray system using the CuK$_\alpha$ line. The layer thicknesses were measured with a step profiler (Sloan Dektak II). Morphological analysis was made using a scanning electron microscope (SEM) JEOL JSM-6300 model with an acceleration voltage of 5 kV, allowing a resolution of 2 nm, and an Innova Veeco AFM by using contact mode with phosphorus tipped (n) doped with Si was used for this purpose. Optical properties were obtained using a Shimadzu UV 2401-PC spectrometer. Photoluminescence (PL) spectra were measured by using a conventional phase-sensitive technique and a laser to 514.5 nm at 10 K. The CdS/CdTe solar cell were completed using CdTe thin films (thickness of 4 μm) deposited by

TABLE I. Variation of the thickness of CdS thin films considering the growth on different substrates.

Sample	Area (cm^2)	Deposited Time (min)	Thickness (nm)
CdS	4	10	125
CdS-HCl	4	10	120
CdS-M$_{35}$	4	10	120
CdS-M$_{52}$	4	10	140
^{1}CdS$_{50}$	50	15	153*
^{2}CdS$_{50}$	50	10	113*
^{2}CdS$_{50}$	50	20	268*
^{2}CdS$_{100}$	100	14	38*
CdS-Ar	4	5	50
CdS-O$_2$	4	5	62

^{1}Magnetic stirrer of 0.8 cm^2; ^{2}Magnetic stirrer of 2 cm^2; *Average (see Fig. 2).

TABLE II. Grain size averages of different FTO substrates and CdS thin films.

Sample	Grain Size average (nm)
TCO	35
TCO-HCl	18
TCO-Ar	29
TCO-O$_2$	35
CdS	25
CdS-HCl	36
CdS-M$_{35}$	24
CdS-Ar	27
CdS-O$_2$	24

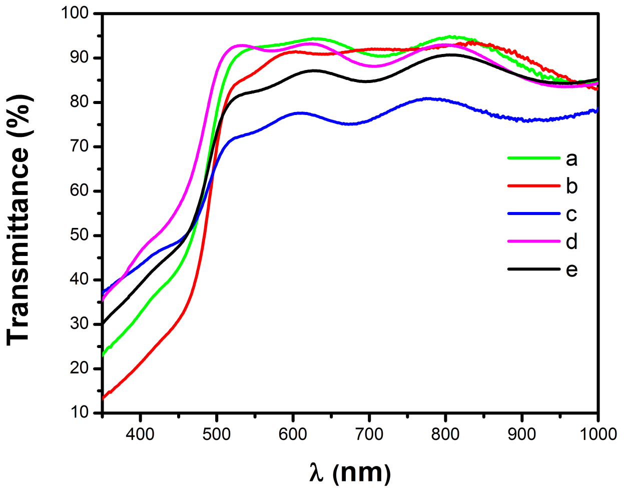

FIGURE 3. Transmittance spectra of (a) CdS, (b) CdS-M$_{35}$, (c) CdS-M$_{52}$, (d) CdS-HCl, (e) ^{2}CdS$_{50}$ (15 min).

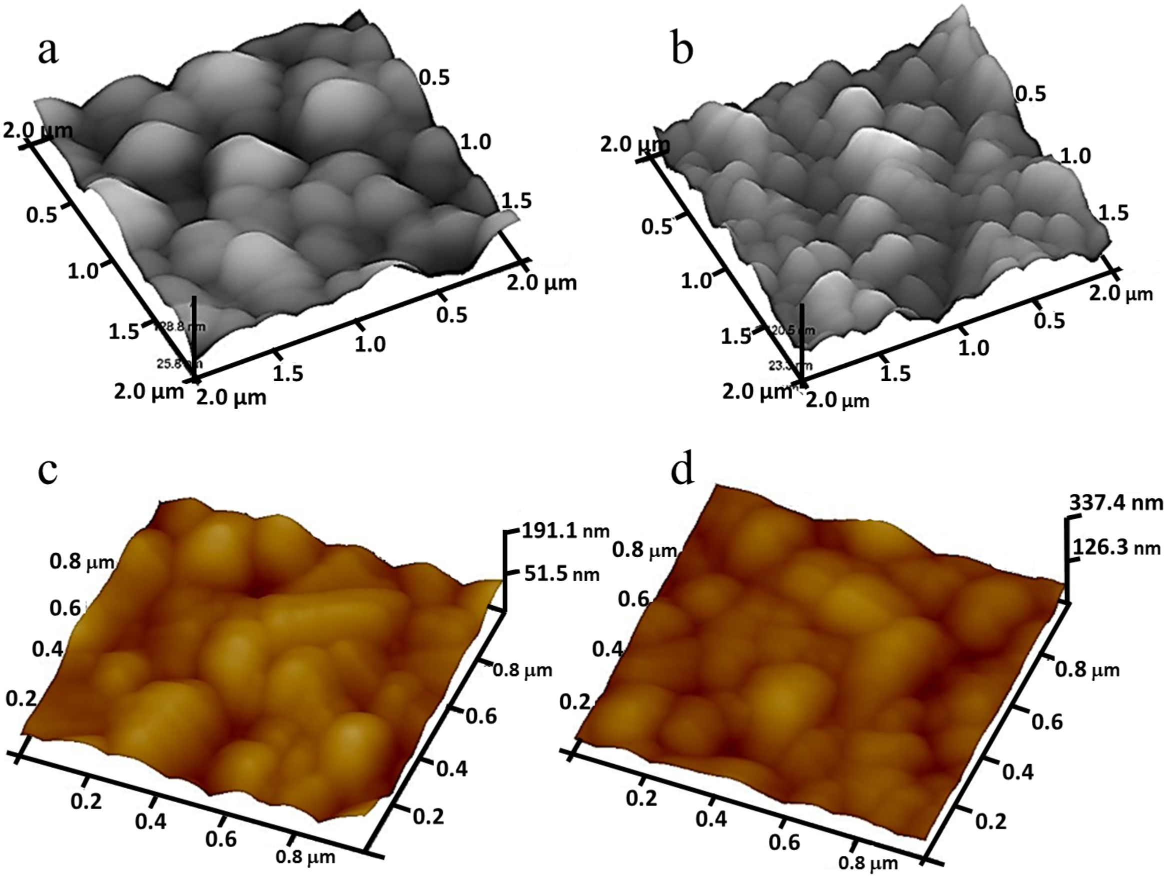

FIGURE 4. AFM images of different FTO substrates (a) FTO without treatment, (b) FTO treated with HCl, (c) FTO with Ar treatment and (d) FTO with O_2 treatment.

Close Space Vapor Transport (CSVT). The CdTe thin films were also thermally treated with $CdCl_2$; as back contact were used two evaporated layers of Cu and Au (20 Å and 350 nm respectively) with an area of 0.08 cm^2 onto the CdTe, and finally the films were annealed at 180°C in Ar.

3. Results

Table I shows the influence of different growth conditions and substrate treatments on the layers thickness. The samples named as CdS-M_{35} and CdS-M_{52} were deposited by rotating the substrate holder at 35 and 52 rpm, respectively, while the samples named as CdS-HCl, CdS-Ar and CdS-O_2 were deposited on FTO substrates previously etching in HCl or treated on Ar or O_2 atmospheres respectively. The movement of the substrate holder produces an increase on the CdS thickness (CdS-M_{35} and CdS-M_{52}); the CdS thickness increases as deposit time increases too. Comparing the CdS-Ar and CdS-O_2 samples, it is noted that the thermal annealing in oxygen promotes the CdS growth.

Figure 2 shows the variations of the CdS thickness considering the influence of the specific FTO substrate used; for this characterization, we considered 10 points along the CdS sample, and these points were labelled as indicated Fig. 1. Analysing Figs. 2(a-c); CdS growth is influenced by magnetic stirrer used inside the reaction beaker; in this case two different magnetic stirrer were used (^{1}magnetic stirrer of 0.8 cm and ^{2}magnetic stirrer of 2 cm of length: ^{1}CdS and ^{2}CdS respectively). When a small magnetic stirrer (0.8 cm) is used, this causes insufficient agitation to allow the CdS solution inside the reaction beaker and then, there is a greater movement of fluid at the bottom compared with at the top reaction beaker; previous results (see Table II), show that further movement creates a thicker film. On the other hand, the pressure inside the reaction beaker decrese as a function of the height due to the fluid column. Figures 2(b, c, d) show a more uniform thickness along the film; in this case a magnetic stirrer of 2 cm was used. the results of Fig. 2 are very important because we can determinate the appropriated growth parameters to obtain homogeneous CdS thin films in areas of 50 cm^2 and 100 cm^2 (see Fig. 2d), these films should be used in the solar cells development.

The Fig. 3 shows the transmission spectra of some different CdS samples grown under different conditions. All samples have an optical transmittance average about 85-91 % and present multiple reflections; that suggest a good crystalline quality. The average energy gap of 2.5 eV. was calculated. The Fig. 3c shows a tail defect greater than others, this cor-

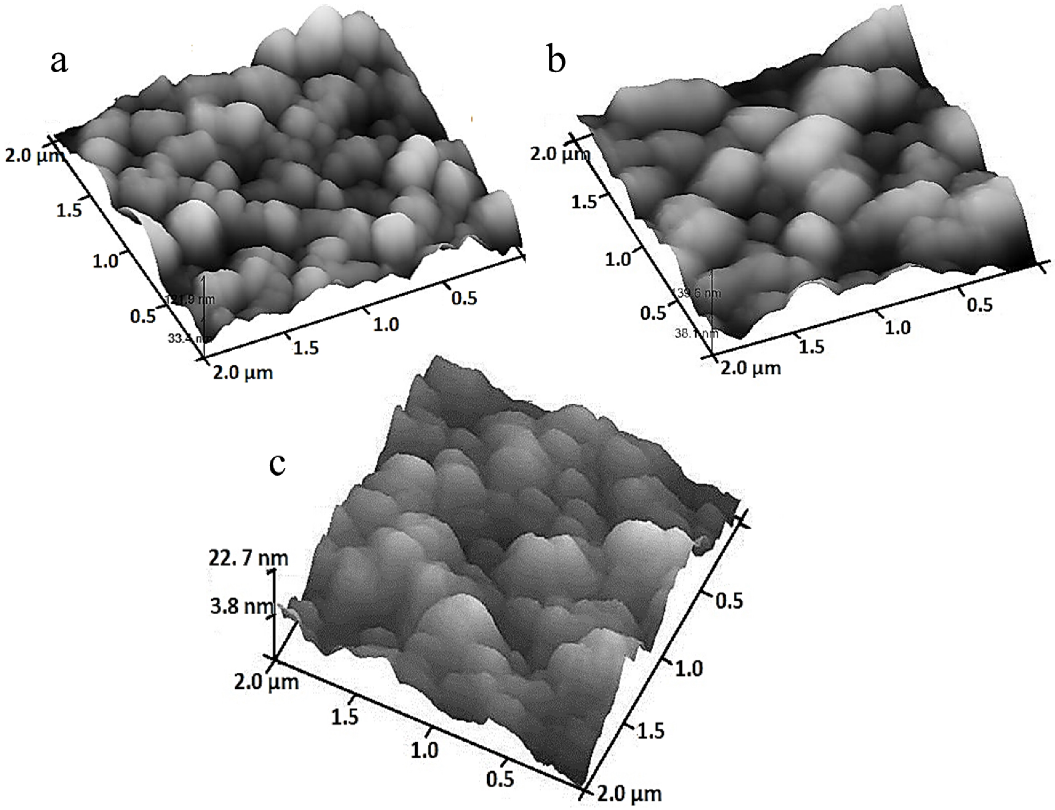

FIGURE 5. AFM images of CdS growth by using different FTO substrates (a) CdS, (b) CdS-HCl and c) CdS-$M_3$5.

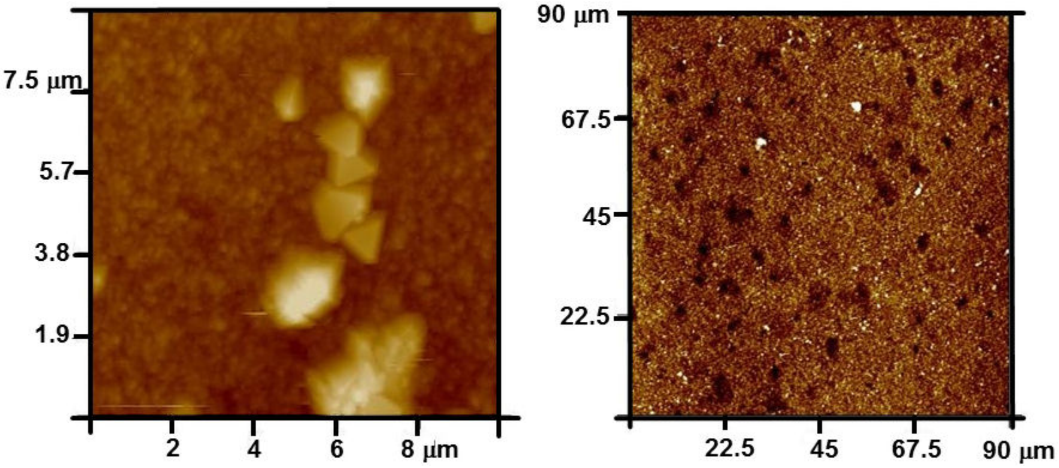

FIGURE 6. AFM images of CdS thin film thermally treated with $CdCl_2$ (a) $CdCl_2$ crystals onto CdS surface, (b) Deep caverns onto CdS surface due to $CdCl_2$ crystals were removed.

respond with the sample CdS-M_{35}; therefore it is concluded than to an excessive agitation causes an increased amount of defects on CdS thin films.

The Fig. 4 shows AFM images of FTO substrates with different treatments previous the CdS growth. Figure 4a shows a FTO without treatment with average grain size about 35 nm; after treating the FTO substrates with HCl the grain size changed from 35 nm to 18 nm, in last case we obtained more capture centres (see Fig. 4b). Ar treatment changed the size grain in FTO substrate to 29 nm and finally, treatment under O_2 atmosphere does not produce any appreciable change compared with the substrate without treatment (see Figs. 4c, d).

Figures 5(a, b, c) show AFM images of CdS thin films deposited on different FTO substrates by using CBD technique; in these images we can appreciate the morphology properties of the samples. The CdS morphology is influenced by the substrate used during the growth. Comparing these images

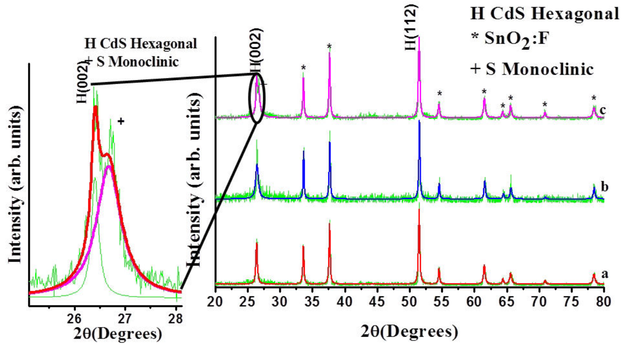

FIGURE 7. XRD patterns of (a) CdS, (b) CdS-HCl and (c) CdS-M_{35}.

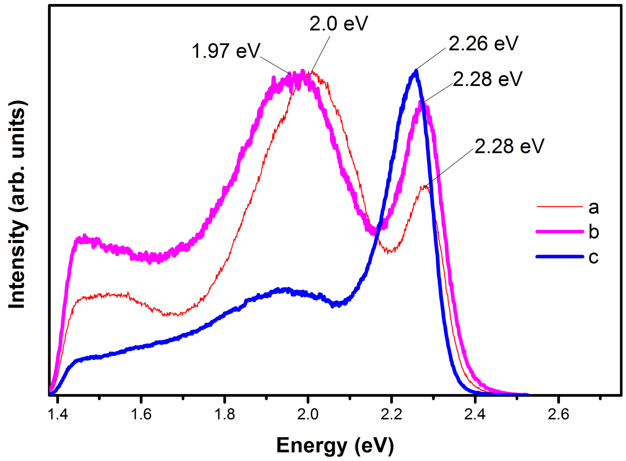

FIGURE 8. Photoluminescence spectra of CdS thin films in large area measured in three different sections corresponding with the sample (a) 1 - lower section, (b) 5 - midsection and (c) 10 - top section.

we obtained the grain size changed; Fig. 5a shows a CdS sample deposited onto FTO substrate without treatment, this sample presents a grain size about 25 nm. On the other hand the CdS films deposited on FTO treated with HCl and CdS-M_{35} samples showed a grain size about 36 nm and 24 nm respectively (see Figs. 5b, c); for CdS-HCl the grain size increases and then we have a better morphology in the sample. Analysing the morphological properties, CdS-HCl is the best sample from morphology and cheaper process point of view.

After depositing the CdS films, it is required a thermal treatment on the samples in order to recrystallize them. An important result was obtained when the CdS thin films were thermally treated with $CdCl_2$ at 350°C for 3.5 min by using CSVT (close space vapour transport) technique, in this case, crystals of $CdCl_2$ formed onto CdS surface. Figure 6a shows an AFM image of this; some of these $CdCl_2$ crystals onto CdS surface are seen. Later these films were washed with hot deionized water in order to remove the cadmium salt and then carry out the deposit of CdTe thin film. Figure 6b shows the morphological defects caused when $CdCl_2$ salt is removed and finally deep caverns are seen. This damage on the CdS sample surface can cause the CdTe deposition reaches until

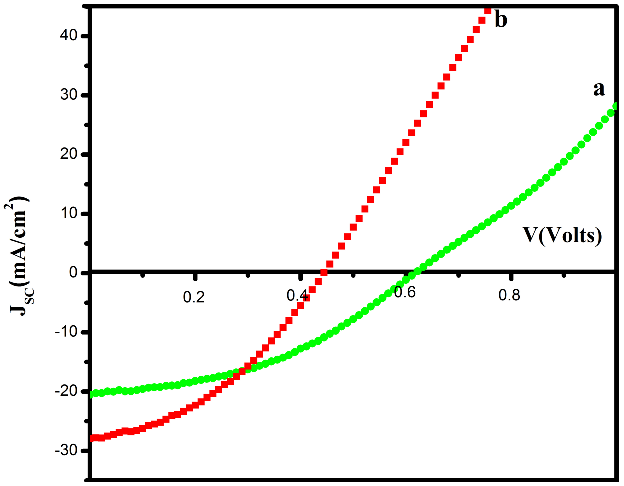

FIGURE 9. IV characteristics of CdTe solar cells using as window material CdS and CdS-HCl respectively (a) CdS/CdTe and (b) CdS-HCl/CdTe.

the FTO substrate; this will cause a short circuit in the photovoltaic device.

Table II shows the grain size average of CdS thin films deposited by using CBD technique considering different FTO substrates.

Figure 7(a) shows a typical XRD pattern of CdS thin film with (002), (112) and (004) phases, identified with JCPDS 41-049 star quality. In general all samples show the same diffraction pattern except CdS-M_{35} sample. Figures 7(a, b) show that there is not change in CdS phase regardless if HCl is used or not; Fig. 7(c) shows an additional peak related with monoclinic sulphur, these results are consistent with data obtained from chemical composition of elements. From this, it can be conclude that excessive agitation inside the reaction beaker may cause additional phases of sulfur.

CdS thin films on large area with suitable properties for application in photovoltaic devices plays an important roll. In this way, the photoluminescence (PL) measurements were used to study the optical and polycrystalline properties of CdS films in large area (100 cm^2); for this purpose we selected three sections in CdS films labelled as 1, 5 and 10 (see Fig. 1b). Figure 8, shows the photoluminescence spectra of the three sections mentioned above. The PL spectra are different in all cases; the peaks located at 2.25 eV and 2.28 eV are related with the green band (2.18 eV - 2.54 eV); 2.2 eV is a donor (Cd_S) to VB transition. The peak located at 2.0 eV corresponds to Orange band (2.00 eV - 2.07 eV) [5,6]. The peaks related with CdS defects (1.96 eV and 2.0 eV) are present with major intensity in section labelled with the number 1; this part of the sample is at the bottom of the reaction beaker and near the magnetic stirrer; so this part of the sample is where the fluid moves faster. Comparing these results with the properties of CdS-M_{52} the rapid movement of fluid causes the film to be deposited faster but with more defects. On the other hand, the PL spectrum of section labelled as 10 in CdS film presents major crystalline quality compared with the Sec. 1 and 5 (see Figs. 8a,b) due to the peak located at 2.26 eV is larger than the others; in this section; corresponding to the top of the reaction beaker we have a slower movement of the fluid. Therefore, the magnetic stirrer located at the bottom of the reactor produces a major quantity of defects due to the movement of atom collisions producing an increase of disorder inside the lattice and secondary faces appear (see amplification of Fig. 7c).

On the other hand, CdS-HCl thin films presented the best physical properties making them candidates for use them in solar cell technology. We have processed a CdS/CdTe solar cell in order to evaluate the photovoltaic efficiency. Figures 9(a, b) shows the IV curves of the CdS/CdTe cell; we use as window material CdS and CdS-HCl thin films respectively; the photovoltaic efficiency increase from 5.2% to 7.7%.

4. Conclusions

CdS thin films were deposited by CBD technique considering different areas (4 cm^2, 50 cm^2 and 100 cm^2), we used FTO substrates treated with HCl, Ar and O_2. In general, the rotation of the substrates inside the reaction beaker was not favourable because the optical transmittance decreases up to 75 - 80 %, the rest of CdS samples showed transmittance values around to 85 - 91 % with multiple reflections that suggest good crystalline quality. The CdS grain size is increased when FTO substrates previously treated with HCl are used. Probably, this treatment can reduce the stress on the lattice generated between the CdTe and CdS coupling. We obtained CdS thin films with good physical properties and for films of large area is better not to rotate the substrate or fluid. The CdS-HCl samples can be use as window material in CdTe, CIGS and CZTS solar cells to improve the photovoltaic efficiency.

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