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OPTICAL AND MORPHOLOGICAL PROPERTIES OF CdS NANOPARTICLES THIN FILMS DEPOSITED BY CBD PROCESS

MIGUEL ÁNGEL GRACIA-PINILLA[a,b*], LUIS CARLOS MORENO[b], GERARDO GORDILLO GUZMÁN[c]

[a]*Actually adress: Laboratorio de Nanociencias y Nanotecnología –Centro de Investigación en Ciencias Físico Matemáticas- Facultad de Ciencias Físico Matemáticas, Universidad Autónoma de Nuevo León, Monterrey, Nuevo León, 66450, México.*

[b]*Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Sede Bogotá, Bogotá. D.C. Colombia*

[c]*Departamento de Física, Facultad de Ciencias, Universidad Nacional de Colombia, Sede Bogotá, Bogotá. D.C. Colombia*

CdS nanoparticles thin films have been fabricated using the chemical bath deposition (CBD) process; $CdCl_2.2,5H_2O$, thiourea [$SC(NH_2)_2$] and ammonium chloride [NH_4Cl] were used as reagents. Special emphasis was placed on the study of the influence of the substrate and thiourea/$CdCl_2$ ratio on the optical and morphological properties of the films; for that, samples deposited on glass, $CuInSe_2$(CIS) and SnO_2 substrates were characterized through Visible spectroscopy and AFM (atomic force microscopy) measurements. Through a parameter study it was found that CdS nanoparticles thin films with good substrate coverage and high transmittances (≈80 %) can be achieved by varying the molar concentration of thiourea between 0.5 and 1M and keeping the $CdCl_2$ concentration in 0.1M. nanoparticles CdS thin films with these characteristics are desirable for using them as buffer layers in solar cells. The best parameter set found for the preparation of CdS nanoparticles thin films by the CBD method is the following: [$CdCl_2$]= 0.1M, [thiourea]= 0.75 M, [NH_4Cl_2]= 0.2M, pH=10.2, Tsol=80°C.

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1. Introduction

Cadmiun Sulfide (CdS) is one of the best buffer materials for the fabrication of high efficiency polycrystalline thin film solar cells, either based on Cadmium Telluride [1,2], Copper Indium Diselenide (CIS) [3,4,5], Copper Indium Gallium Diselenide (CIGSe) [6.7] and Copper-Indium-Gallium-Disulfide (CIGS) [8,9]. In all cases are used CdS with buffer layer between transparent conductive Oxide and light absorbing materials, the actually use of CdS are discussed for toxicity but the optimal optical, electrical, morphological and structural properties are reflected in the record efficiency showed the excellent performance in this devices, so then, for polycrystalline CdS/CdTe solar cells with a record efficiency of 16.5%[10], for CdS/CIS with a record efficiency of 15.3% [11], for CdS/CIGSe with a 19.9% [12], and finally for CdS/$CIGS_2$ solar cells with a record efficiency of 11.9%[8], in general theses results showed the high relevance of optimal control of the thickness in the buffer layer in the efficiency of the solar cell.

Nanoparticles CdS thin film have been prepared by several methods such as close spaced sublimation (CSS) [13], electrochemical deposition [14] and Chemical Bath Deposition (CBD) [15-16]. However, the CBD process appears to be the best technique for depositing CdS with

*Corresponding author: miguel.graciapl@uanl.edu.mx

suitable properties for the fabrication of solar cells. This method allows the preparation of CdS thin films with the thickness at nanometric scale and good substrate coverage leads to a diminish in the charger carrier trapping effects in grain boundaries; these characteristics must be true for buffer materials in order to achieve high conversion efficiencies [1].

In this work, we focus the attention to study the influence of the thiourea-concentration and substrate type on the growth rate and in the optical and morphology properties of CdS nanoparticles thin films; the CdS nanoparticles thin films will be used later as buffer layer either in CdTe or CIS based solar cells. For that, the CdS nanoparticles films were deposited on soda lime glass substrates and on a glass substrate covered with a CIS or SnO_2:F thin layer substrates In the next section we make a detailed description of the experimental conditions for the growth of CdS nanoparticles films, followed by a section that presents and discusses our results. Finally, in the preceding section we remark the most relevant conclusions of this work.

2. Experimental Setup

CdS nanoparticles thin films were deposited on soda lime glass, glass/SnO_2:F and glass/CIS substrates from an aqueous solution containing Cadmium Chloride ($CdCl_2$), Thiourea (Tu)($CS(NH_2)_2$), Ammonium Chloride (NH_4Cl) and Ammonium Hydroxide (NH_4OH). The CdS nanoparticles thin films samples were deposited using a reactor similar to the one reported in Ref. [17]. The nanoparticles thin films preparation parameters and their variation ranges are listed to continued:

- The solution temperature between 70 and 85°C.
- [Tu]/[$CdCl_2$] ratio between 1:1; 2.5:1; 5:1; 7.5:1; 10:1
- pH between 10.2 and 12.
- The deposition time was varied between 5 and 20 minutes.
- Substrate type used : Glass ; Glass/SnO_2 ans Glass/CIS.

During the deposition process the concentrations of $CdCl_2$ and NH_4Cl were kept in 0.1 M and 0.2 M respectively.

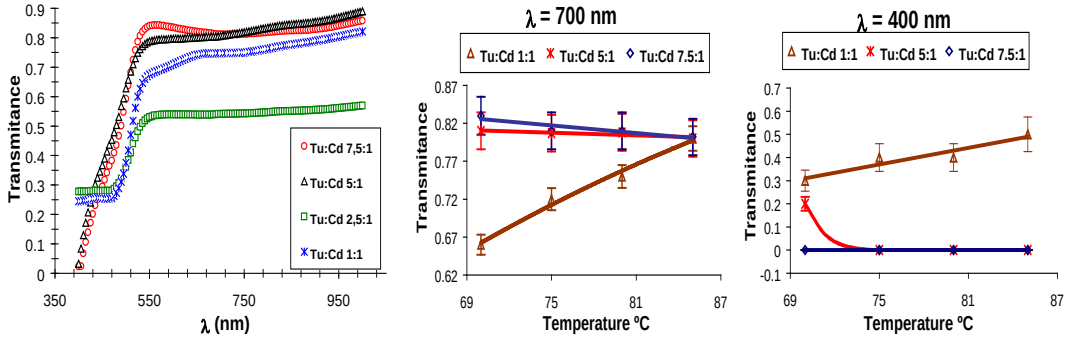
The SnO_2:F films were deposited by the technique of Spray Pyrolysis (reactor home made), using Tin Chloride ($SnCl_4$) 0.1M in Ethanol as precursor solution and HF (0,08M) as doping solution, more details are shown on reference [18-19]. The deposition of the CIS layers was accomplished in a two stage process, where the metallic precursor is sequentially evaporated from a tantalum effusion cell. For more detailed of this process are shown on reference [4].

The optical (transmittance) properties were carried out with a spectrophotometer Oriel between 300 and 1000 nanometers, and the surface morphology of the films is investigated by Atomic Force Microscopy (AFM), using the AFM CP from Park Scientific Instruments (all measurements were made in contact mode).

3. Results and discussions

3.1 Influence of the solution temperature and the [TU]/[$CdCl_2$] ratio on the transmittance and morphology of CdS nanoparticles thin films deposited on glass substrates

In Fig. 1a are depicted typical spectral transmittance curves corresponding to CdS nanoparticles thin films samples deposited using solutions at 80 °C, pH=10.2 and TU-concentrations varying between 1 and 10 with respect to the $CdCl_2$-concentration. Fig. 1b and 1c, show the effect of the solution temperature on the transmittance of the CdS nanoparticles thin films measured at wavelengths λ of 700nm and 400 nm respectively.



a) b) c)

Fig. 1. a) Influence of the TU-concentration on the spectral transmitance and b) and c) of the solution temperature on the transmittance measured at wavelengths of 700nm and 450 nm respectively.

The results of Fig. 1 show that at λ values greater than the cut off λ_c, the transmittance is significantly reduced by decreasing the TU-concentration. In samples prepared at TU-concentrations smaller than 5 (respect to the $CdCl_2$-concentration), the transmittance is also reduced by decreasing the solution temperature. The reduction of the transmittance seems to be related with an increase of the nanoparticles thin film roughness and/or the reflectance, caused by decreasing the TU-concentration and the solution temperature. On the other hand, a strong decrease of the transmittance is in general observed in samples prepared at 80 °C, pH=10.2 and TU-concentrations around 2.5. Since this unexpected behavior can not be explained by roughness and reflectance effects, absorption via states within the gap could be pointed out as responsible for the strong absorption at λ values greater than λ_c.

The high values of transmittance at $\lambda < \lambda_c$, which are typically observed in samples prepared at low TU-concentrations (less than 5, respect to the $CdCl_2$-concentration), seem to be caused by the presence of substrate areas not covered by the CdS nanoparticles thin films. In this case, high transmittance of light through areas not covered by CdS, is added to the low portion of light transmitted through the areas covered by the CdS nanoparticles thin film. Therefore, the transmittance at $\lambda < \lambda_c$ could be used as a qualitative measure of the porosity degree of very thin films. AFM measurements confirmed some of the explanation given above for the results of Fig.1 (see fig.2 and table 1).

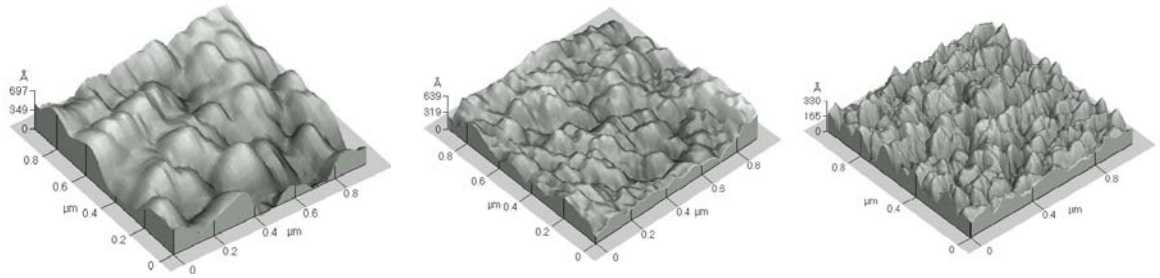
Table 1. Values of Rp-v, roughness, grain size and porosity of CdS nanoparticles thin films as functions of the TU-concentration and deposition time.

	[Tu]:[$CdCl_2$] (1:1)			**[Tu]:[$CdCl_2$] (5:1)**			**[Tu]:[$CdCl_2$] (7,5:1)**		
Deposition time (min.)	5	10	15	5	10	15	5	10	15
Rp-v (nm)	74.9	102	81.4	16.4	39.3	38.1	21.4	23.6	42.8
Roughness (nm)	16.9	27.2	81.4	3.5	9.6	8.8	4.6	5.2	9.05
Grain size (nm)	251	275	309	101	102	80.2	72.8	84.6	97.9
% Porosity	50.1	49.48	49.24	48.85	48.5	46.78	42.36	34.75	34.9

Table 2. Comparison of the growth rate of CdS nanoparticles thin films deposited on CIS thin films with the one deposited on SnO_2:F. pH as parameter.

pH	Growth Rate of CdS on SnO_2:F (nm/min)		Growth Rate of CdS on CIS (nm/min)	
	Growth Phase	**Terminal Phase**	**Growth Phase**	**Terminal Phase**
10.2	11.3	1.4	30.2	4.1
11.2	13.6	6.6	44.9	3.6
12	24.3	7.5	44.1	6.7

Fig. 2 shows typical AFM images of CdS nanoparticles thin films prepared at 80 °C, pH=10.2 and TU-concentrations varying between 1 and 7.5 respect to the $CdCl_2$-concentration. In table 1 are listed data of roughness (Rms value), Rp-v (distance between the highest peak and the deepest valley), grain size (average values) and porosity (given by the relation between the surface of the grains projected on the substrate plane and the substrate area) as a function of the TU-concentration and thickness (given by the deposition time). These data were obtained analysing statistically the AFM images using the Program "Proscan Data Acquisition".



a) b) c)

Fig. 2. AFM images of CdS nanoparticles thin films indicating the effect of the TU-concentration on the morphology a) [TU]/[$CdCl_2$]=1:1, b) [TU]/[$CdCl_2$]=5:1, and c) [TU]/[$CdCl_2$]=7,5:1. In all case the area of scan is 1x1μm.

It is observed that the roughness and grain size increase by decreasing the TU-concentration, indicating that the TU-concentration significantly affects the growth mechanisms of the CdS nanoparticles thin films. On the other way, it was found that samples deposited at low TU-concentrations and low temperature present Rp-v values much greater than the film thickness; this result seems to be associated to an incipient formation of aggregates or clusters an the surface . The results also reveal that the porosity increases when the TU-concentration decreases indicating that the substrate coverage with a continuous CdS nanoparticles thin film decreases by decreasing the TU-concentration.

3.2 Influence of the pH and the substrate type on the growth rate and morphology.

From the studies carried out in the previous section with CdS nanoparticles thin films deposited on glass substrates, a solution temperature of 80°C, and a [TU] to [$CdCl_2$] ratio of 7.5:1 were selected as optimum deposition parameters and afterwards used to deposit CdS nanoparticles thin films on glass/SnO_2:F and glass/CIS substrates. Initially the growth rate of the CdS nanoparticles films was determined by dividing the film thickness by the deposition time. The

thickness of the CdS nanoparticles films was determined subtracting the thickness of the CIS (or SnO_2:F) film from the CIS/CdS (or SnO_2:F/CdS) bilayer. The thickness of both, the single CIS (or SnO_2:F) and CIS/CdS (or SnO_2:F/CdS) bilayers were determined using the interference fringes observed in the transmittance spectra and the relation: $\delta=\lambda_1\lambda_2/[2(n_1\lambda_1- n_2\lambda_2)]$ were λ_1, λ_2 are the wavelengths of two consecutive maxima or minima and n the corresponding refractive index determined using the procedure described in ref. [19-20].

Fig.3 shows the behavior of thickness versus the deposition time of CdS nanoparticles thin films grown on CIS and SnO_2:F substrates. In this case the CdS nanoparticles thin films samples were deposited using a solution with a [TU] to [$CdCl_2$] ratio of 7.5:1, a pH of 10.2 and a solution temperature of 80°C.

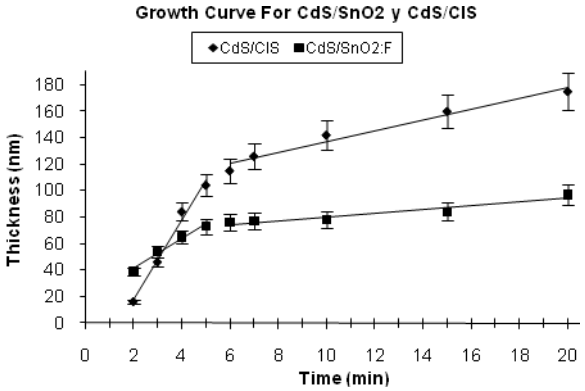


Fig. 3. Variation of the thickness of CdS nanoparticles thin films grown on CIS and SnO_2:F substrates as a function of the deposition time.

The results of Fig.3 show that the substrate type affects de growth rate of the CdS nanoparticles thin films, being the growth rate on CIS substrates significantly greater than the growth rate on SnO_2:F. It is also observed that during the first 5 minutes the CdS nanoparticles thin films growths at a constant rate or quickly rate growth, defining the so called growth phase [16]; afterwards, during about 1 minute a transition occur from the growth phase to a new growth regime called terminal phase, were the CdS nanoparticles thin films grows at a much smaller rate.

In table 2 are listed values of the growth rate of CdS nanoparticles thin films on SnO_2:F and on CIS substrates (during the growth and terminal phases) as a function of the pH. These results show that the increase of the solution pH leads to a strong increase of the growth rate of CdS nanoparticles thin films on both, CIS and SnO_2:F substrates, as a consequence of the solubility improvement.

In the future, the growth curves of CdS obtained in this work will be used as reference curves for the determination of the thickness of CdS nanoparticles thin films deposited by CBD method. This is an important result for us, because from now on it will be possible to know the thickness of the nanoparticles CdS thin film only by controlling the deposition time; the nanometric thickness of the CdS buffer layer is one of the parameters most critically affecting the current generated by the solar cell.

Fig. 4 compares AFM images of nanoparticles CdS thin films deposited in the same run on glass, on Glass/CIS and on Glass/SnO_2:F substrates and in table 3 are listed the corresponding data of roughness, Rp-v, average values of grain size and porosity.

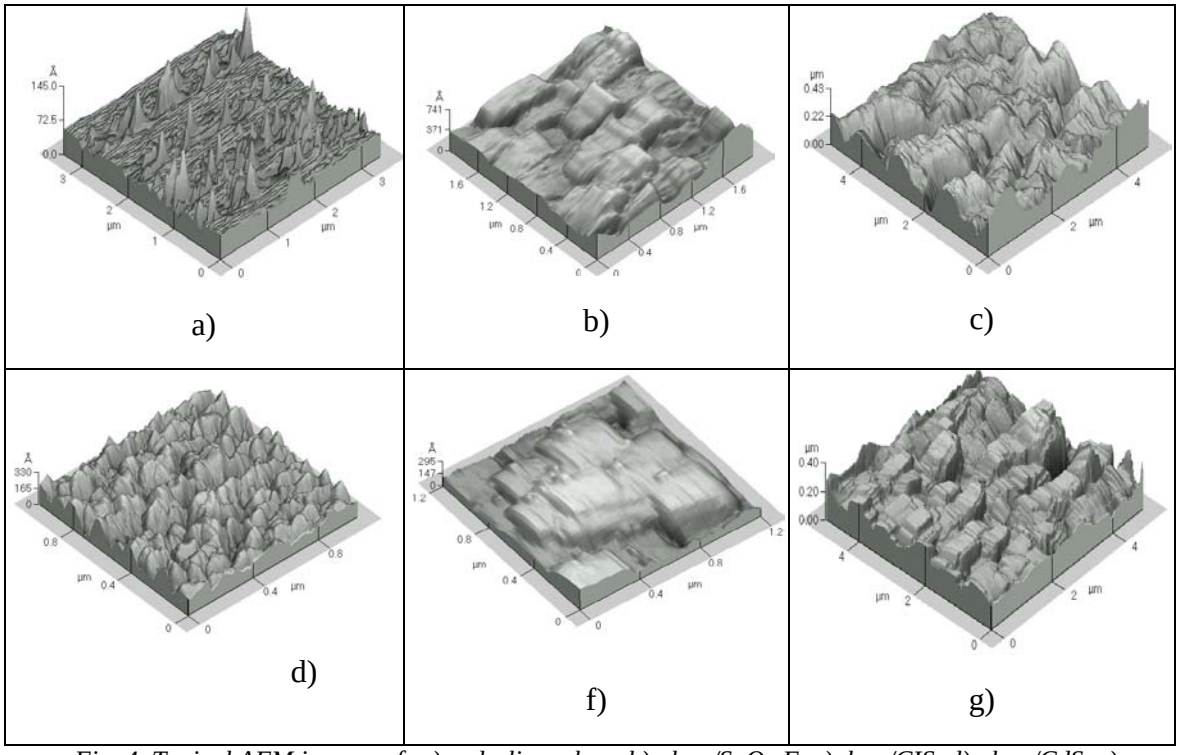


Fig. 4. Typical AFM images of: a) soda-lime glass, b) glass/SnO_2:F, c)glass/CIS, d) glass/CdS, e) SnO_2:F/CdS and f) CIS/CdS. Deposition time of 5 min.

The images of Fig.4 and the dates of the table 4 indicate that, with the exception of the porosity, the morphological properties of the CdS nanoparticles thin films are significantly affected by the type of substrate on which the CdS nanoparticles thin films grows. In particular the grain size of the CdS nanoparticles thin films deposited on CIS or on SnO_2 substrates is greater than that SnO_2:F and lower for CIS substrates films.

Table 3. Comparison of the values of: Rp-v, roughness, grain size and porosity of CdS nanoparticles thin films deposited on different types of substrates (glass, SnO_2:F and CIS), deposition time of 5 minutes.

Parameters	**Substrates**			**Nanoparticles CdS thin film /substrates**		
	SnO_2:F	**CIS**	**Glass**	**CdS/SnO_2:F**	**CdS/CIS**	**CdS/Glass**
Rp-v (nm)	72	227	11	17.5	88	21.4
Rms (nm)	14.5	63.8	2.1	3.8	19	4.6
Grain Size (nm)	362	741		419	377	72.8
% Porosity	51.3	48.2		44.3	42.8	42.3

Table 4. Comparison of the electrical output parameters of CIS solar cells using CdS and inxSey those buffer materials. Ilumination of 100mW/cm^2. [Taken from ref 21, Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission]

Cell structure	Voc (V)	Jsc (mA/cm2)	FF	η (%)
Mo/CIS/IS/n-ZnO	0.445	30.8	0.6	8.3
Mo/CIS/CdS/n--ZnO	0.43	34	0.63	9.2

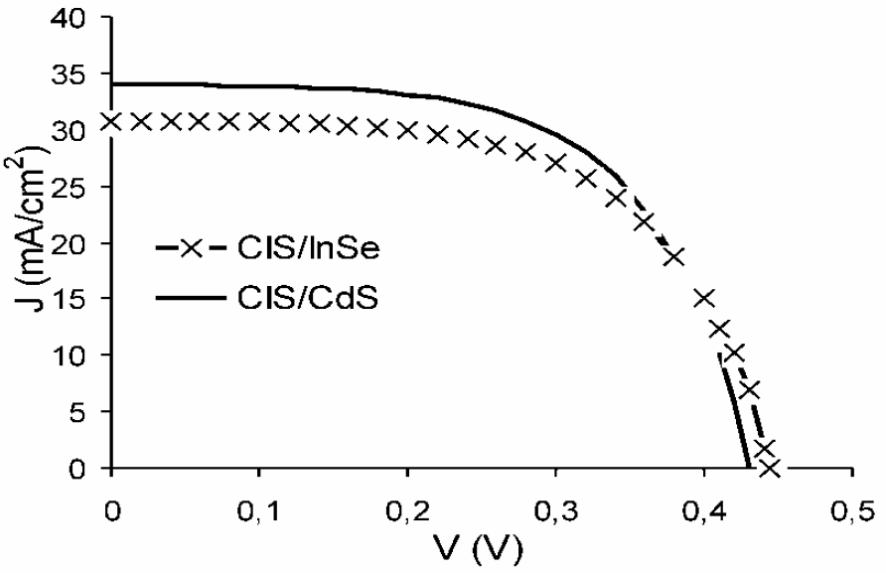


Fig. 5. Comparison of the I-V curve of a CIS solar cell fabricated using CdS and In_xSe_y as buffer layers . Irradiance of 100mw/cm^2. [Taken from ref 21, Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission]

For the evaluate the high efficiency of Nano CdS thin films , this has compared with InxSey buffer materials, in both case used with buffer layers over CuInSe, in the Fig 5 compares the I-V characteristic of the CIS solar cells. Other parameters to evaluate are the electrical output parameters. In the table 5 are enumerated the resultant electrical output parameters of both solar cells.

4. Conclusions

In this work, the conditions were found to deposit CdS nanoparticles thin films by the CBD method with adequate properties to be used as buffer layer in solar cells ¨most favorable optical and morphological properties, also, with thickness between 20 and 120 nanometeres¨. CdS nanoparticles thin films with high transmittance and high substrate coverage can be deposited using the following parameter set: pH=10.2, [TU]/[$CdCl_2$]=7.5:1, solution temperature 80°C, $CdCl_2$-concentration=0.1M and NH_4Cl-concentration=0.2 M.

The studies showed that the TU-concentration and the solution temperature affect significantly the transmittance, substrate coverage and the morphological properties of CdS nanoparticles thin films. In general the CdS nanoparticles thin films prepared at low values of TU-concentrations (<5 respect to the $CdCl_2$-concentration) and of solution temperature (<75 °C) present low transmittance and low substrate coverage. Correlating transmittance and AFM measurements, it was found that the decreasing of the transmittance of the CdS nanoparticles thin films is related with increasing of roughness and aggregates formation as well as with increasing of the reflectance.

It was found that the pH and substrate type strongly affect the growth rate of the CdS nanoparticles thin films. The CdS grows faster on CIS substrates than on SnO_2:F substrates and the increase of pH leads to an increase in the growth rate. Typically, the CdS nanoparticles thin films prepared under the parameter set given previously in this section, growth on CIS at a rate of 30.2 nm/min. during the growth phase and 4.1 nm/min. during the terminal phase, whereas the growth on SnO_2:F occurs at a rate of 11.3 nm/min. during the growth phase and 1.4 nm/min during the terminal phase. This is a very important result for us, because from now on it will be possible to know the thickness of the CdS nanoparticles thin film only by controlling the deposition time; remember that the nanometric thickness of the CdS buffer layer is one of the parameters most critically affecting the current generated by the solar cell. Finally we show evidence of the high quality of the Nano CdS thin films by the measurement of the I-V curves of the CIS solar cells where the efficiency was η=9.2%.

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