

Improvement of Electrical Properties of Grätzel Cells by Tuning the Dye Layer with CdS/ZnO Junction

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(Received 21 March 2021; revised manuscript received 02 August 2021; published online 20 August 2021)

Solar cells based on organic dye have been widely used for the reason of their simplicity of manufacture. A simple structure is composed of a colored layer of TiO₂, an electrolyte and a counter electrode. In this study, the layers of TiO₂, CdS and ZnO were deposited on conductive glass by different methods to replace organic dye. Metal organic chemical vapor deposition (MOCVD) method was used to prepare the TiO₂ layer, chemical bath deposition (CBD) to prepare the CdS layer, and spray pyrolysis (SP) for the preparation of the ZnO layer. Morphological and structural studies have shown a homogeneous morphology of the superposition of TiO₂/CdS/ZnO layers. XRD and SEM characterizations have shown that annealing of the CdS layer must be done under a controlled atmosphere in order to avoid the formation of cadmium oxide and to control the particle size. The aim of this work is the substitution of organic dye in the Grätzel cell by CdS(*n*)/ZnO(*n*⁺) junction. Morphological and optical properties of TiO₂/CdS/ZnO in addition to photovoltaic performance of this structure junction were investigated with different deposition times of the CdS layer. It is found that the nature of the substrate has no influence on the realization of the junction. It is noticed that each layer added leads to a decrease in the transmittance of the substrate. Characterization of the photovoltaic properties of cells based on the CdS/ZnO junction shows a higher yield compared to conventional cells based on organic dye. It is also recommended to undertake annealing under a controlled atmosphere such as nitrogen in order to eliminate the CdO secondary phase and decrease the size of the grains which may enhance the efficiency of the solar cells.

Keywords: TiO₂, MOCVD, CBD, Spray pyrolysis, CdS/ZnO junction.

DOI: [10.21272/jnep.13\(4\).04004](https://doi.org/10.21272/jnep.13(4).04004)

PACS numbers: 68.55. – a, 82.33.Ya –, 81.10.Dn, 81.15.Rs, 81.05.Hd

1. INTRODUCTION

Renewable energies are a solution to reduce side effect of other energies. Solar energy is one of the alternatives that can preserve the environment. Solar cell technology is in continuous progress since the appearance of its first generation. The material used is a different form of silicon. Solar cells based on thin films or second-generation solar cells are a choice to replace conventional cells based on silicon [1].

Due to their features, the third-generation solar cells or so-called Grätzel cells represent one of the solutions to promote the solar cell performance. Its structure is based on a colored photo-anode, a counter electrode and an electrolyte [2]. Several materials are used to prepare an active layer; among them titanium dioxide TiO₂ [3], cadmium sulphide CdS [4] and zinc oxide ZnO [5].

The ruthenium-based dye is frequently used to assemble cells [6]. It will be interesting to replace its lifetime and high cost. Using a junction is one way to reduce cells cost and improve performance.

Previous studies on TiO₂ have shown that it is a 3.2 eV wide band gap semiconductor [3], it exists in three crystalline forms: anatase, rutile and brookite [2]. To increase the efficiency of Dye Sensitized Solar Cells (DSSCs), the optical, structural and crystalline studies have been favored [7]. Solar cells structures containing

CdS show better optical captivity and high current outputs [4, 8]. CdS films deserve our attention because of their ease of manufacture and their gap, it varies between 2 and 2.8 eV depending on the deposition methods [9]. ZnO thin films are transparent in the visible and infrared range [10]. Their energy gap at room temperature is 3.3 eV [11].

The present work studies the properties of solar cells based on thin films of TiO₂, CdS and ZnO. The choice of a solar cell based on thin films is to find a solution for the dryness of the organic dye, and the deposition processes are extremely fast (from a few seconds to a few minutes), which makes it possible to achieve high production rates and therefore reduce production costs. Also for their efficiency, which has already reached 11 % in industrial production and 20.3 % under operating conditions [12].

These thin film layers have been produced by chemical methods such as Metal Organic Chemical Vapor Deposition (MOCVD), Spray Pyrolysis (SP) [5] and Chemical Bath Deposition (CBD) [13]. MOCVD is a very simple method which is done in a controlled atmosphere, and the choice of it is due to mastery of the method and because there are studies carried out on TiO₂ developed by MOCVD. We opted for the SP and CBD methods for their ease of manufacture and their

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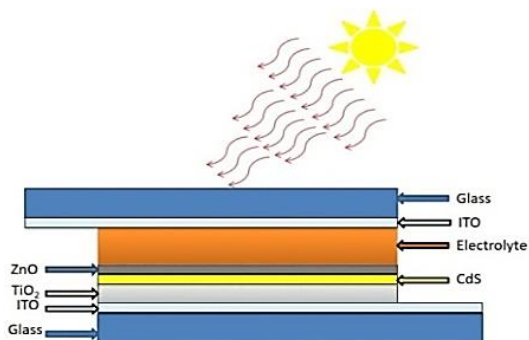


Fig. 1 – Diagram of the elaborated cell

homogeneous thin films. The cells have the following configuration: glass/ITO/TiO₂/CdS/ZnO/electrolyte/ITO/glass. Fig. 1 shows the diagram of the performed cell.

2. EXPERIMENTAL DETAILS

2.1 Preparation of Thin Films

The substrates used are glass/ITO, glass slides covered with a layer of Indium Tin Oxide (ITO). ITO was deposited by magnetron cathode sputtering on glass of 1.1 mm thick, resistance 30-50 Ohms, layer thickness ~ 1000 Å, manufacturer Solems. Retrogradation of the substrates for solar cell assembly and heat treatment in a 3 cm × 2 cm oven under nitrogen resulted in a small width. TiO₂ layers were prepared by MOCVD. Titanium isopropoxide (TIP) was used as a precursor of TiO₂ concentrated to 99.999 %. The growth was carried out under nitrogen at a temperature of 550 °C and deposition time of 30 min [14]. In the second step, the optimization of CdS layers was done by CBD under several temperatures (30, 50, 80 °C). The product used as a source of cadmium was CdCl₂. The composition of the bath was CdCl₂, thiourea CH₄N₂S and ammonia NH₄OH, with stirring. The deposition temperature was chosen to be 50 °C according to the optical and morphological characterization of the layers carried out at 30, 50 and 80 °C for 60 min. Once deposited, CdS layers were annealed under purge of air and nitrogen at a temperature of 500 °C for 30 min. We have chosen the annealing time of 30 min because with less time CdO particles still remain. Zinc acetate was the precursor used in the SP, the preparation protocol was the same as the reference, the temperature of the hot plate was 220 °C and the deposition time was 15 min with 30 s spray jets after 1 min of drying [15]. Then, the electrolyte layer made of potassium iodide KI and iodine I was prepared. Finally, the cells were assembled according to the configuration mentioned above.

The layers produced were characterized using a thermo brand Spectorphotometer, SEM scanning electron microscopy, JEOL JSM 7600F, a HITACHI SUI510 X-ray microprobe, a D5000X-Ray type diffractometer and UV-VIS-IFR transmittance spectroscopy. The solar simulator (Riels Instruments) was used to get the photovoltaic performance as prepared cells.

3. RESULTS AND DISCUSSION

Fig. 2a shows a homogeneous TiO₂ layer with nanometer grains (50 nm) and a thickness of 150 nm;

these results are consistent with Siddhartha K. [16]. Fig. 2b shows a CdS layer deposited on glass, the thickness of the CdS layer is 80 nm. It is composed of regularly connected islets completely covering the surface depending on the film deposition time. It can be seen that the CdS layers have a sheet-like shape on the TiO₂ mat, the height of the sheets is of the order of a few hundred nanometers, and the thickness is a few tens of nanometers, which seems to completely cover the surface of TiO₂. Fig. 2c clearly shows that the CdS layer after annealing at 500 °C for 60 min under nitrogen conditions does not have a constant thickness, but it seems that the entire TiO₂ layer is well covered with CdS [8]. EDX analysis confirms this point. Fig. 2d shows the deposition of ZnO by sputtering on a glass substrate. We notice a hexagonal shape of the crystal, and its crystallites rest on less structured agglomerations. Despite the homogeneous distribution, the layer does not appear to be perfectly continuous.

Fig. 3a shows the overall structure of the junction (Si/TiO₂/CdS/ZnO). The thickness of each layer can be extracted. The thickness of the TiO₂ layer is 150 nm, the CdS layer is 80 nm and the ZnO layer is 150 nm; the thicknesses are measured in situ using the scanning electron microscopy. Fig. 3b shows the following configuration: glass/ITO/TiO₂/CdS/ZnO. The thicknesses of TiO₂ and CdS layers are identical to the previous configuration, while the thickness of ZnO increases slightly keeping the same deposition conditions. It can be noted that the nature of the substrate has no influence on the realization of our junction.

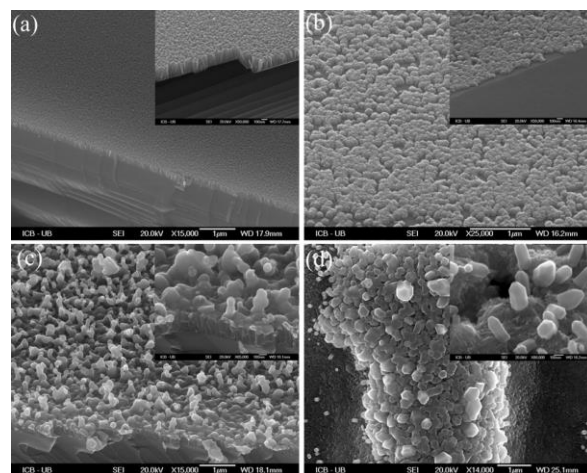


Fig. 2 – SEM images of (a) TiO₂ layers on silicon, (b) CdS layers deposited on glass, (c) a layer of CdS deposited on the Si/TiO₂ substrate after annealing, and (d) ZnO deposits on the glass substrate

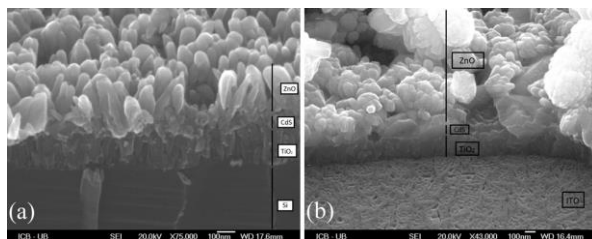


Fig. 3 – Junction of the annealed deposited layers: (a) silicon substrates, (b) glass substrates

Table 1 shows the chemical composition of the Si/TiO₂/CdS/ZnO junction determined by EDX elements detected before and after heat treatment and before annealing. The EDX elemental analysis reveals the presence of Cd probably in the form of CdS as well as N, O, Cl, C residues of the products of synthesis (thiourea, ammonium chloride, ammonia and cadmium chloride). After annealing, the surface contains 8 at. % of titanium. The presence of Ti and an increase in oxygen identify the perfect formation of CdS layers. Note the ratio Cd/S = 1 indicating the presence of the only compound containing cadmium, CdS.

Table 1 – EDX evolution of the Si/TiO₂/CdS/ZnO junction: (a) as deposited, (b) after annealing

Elements	As deposited		After annealing	
	Norm wt%	Norm at%	Norm wt%	Norm at%
Carbon	2.52	8.46	-	-
Oxygen	17.14	43.27	15.59	33.27
Silicon	2.26	3.26	32.62	39.67
Sulfur	4.58	5.77	4.76	5.07
Chlorine	0.95	1.08	-	-
Titanium	1.56	1.31	11.96	8.52
Zinc	43.94	27.13	12.86	6.72
Cadmium	27.05	9.72	22.22	5.07

Most of the synthetic residues decomposed and precipitated. Residual carbon can come from pollution and carbon formed during the breakdown of carbon chains in a non-oxidizing atmosphere.

At this stage of our study, we can conclude that after thermal treatment at 500 °C, 60 min under nitrogen scavenging, a CdS layer is formed by CBD, without the presence of CdO and contains some carbon impurities. The thickness of this layer is fine as allowed by the SEM image and the observation of titanium by EDX through the layer. It is reasonable to exclude the presence of holes in the CdS layer because before heat treatment titanium is not visible.

The results of the EDX analysis for the Si/TiO₂/CdS/ZnO junction before annealing in Table 1 represent the EDX results of the same structure after annealing. This analysis allowed us to affirm that the densification heat treatment of the ZnO layer does not modify the composition or the texture of this layer.

The XRD measurement is performed to determine the crystalline structure of the samples. Fig. 4 shows the crystalline structure of anatase TiO₂; the peaks positions of 2θ angles 25.28°, 38.56°, 48.06°, 54.58°, 55.12°, 62.77°, 68.81°, 70.42°, 75.15° and 76.18° are respectively equivalent to the crystallographic planes (101), (112), (200), (105), (211), (220), (116), (220), (215) and (301). Rodrigo T. et al. [17] have already proven these results. The studies carried out by A. Crisbasan have shown that the TiO₂ layer obtained by MOCVD consists of monocrystalline columns perpendicular to the substrate [14]. Before doing our grain size calculations, we will correct the FWHM measurements by instrumental enlargement before applying the formula. Using the Scherrer's formula [5, 13], the grain size *t* was calculated and is shown in Table 2; its range from 30 to 60 nm is similar to Kibasomba study [18].

Fig. 5 shows the XRD peaks of CdS layers: as-deposited (a), after annealing under nitrogen (b), and after annealing under air (c). The diffractogram indicates the presence of CdS peaks only after heat treat-

ment, which is visible by comparing (a) before annealing with (b) after annealing under nitrogen and (c) after annealing under air. The presence of peaks characteristic of the majority CdS phase is noted as well as the presence of peaks characteristic of the CdO phase after heat treatment in air. The size of CdS crystals is smaller after treatment under nitrogen compared to treatment in air. This is due to the presence of CdO particles [19]. The type of annealing affects the size of crystallites. Table 3 shows the size of the crystals annealed under nitrogen and annealed under air. The grain size of CdS upon annealing in nitrogen is from 18 to 31 nm, and upon annealing in air from 38 to 82 nm. Nonmetric dimensions of the films are very important in the results in order to improve proprieties and operating materials.

XRD analysis confirms the formation of pure CdS compound for samples treated in nitrogen. Consequently, densification of the ZnO layer must be done in a non-oxidizing atmosphere to avoid the appearance of CdO particles.

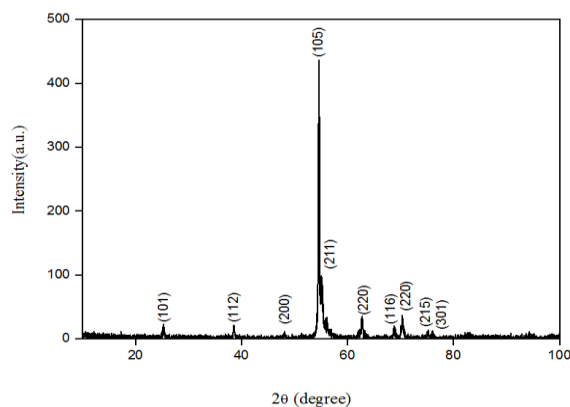


Fig. 4 – X-ray diffraction pattern of TiO₂ samples deposited on silicon

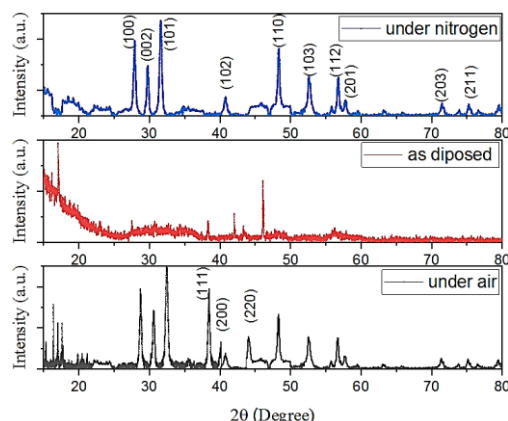


Fig. 5 – X-ray diffraction spectra of the CdS layer deposited on glass substrate: (a) deposited just before annealing, (b) after annealing in nitrogen, (c) after annealing in air

Table 2 – TiO₂ crystallite size of the sample

hkl	101	112	200	105	211	220	116	220	215	301
t (nm)	32	36	40	58	58	46	50	64	64	62

The transmittance of our studied glass/ITO/TiO₂/CdS/ZnO junction is shown in Fig. 6. From the spec-

trum, we notice that each time we add a layer the transmittance of the substrate decreases, and this is logical due to the thickness of the layers.

Table 3 – Sizes of crystals annealed under nitrogen and air

hkl	100	002	101	111	200	102	220	110	103	200	112	104	203	211
t(a) (nm)	31	23	26	-	-	25	-	25	21	18	24	29	22	24
t(b) (nm)	74	67	53	82	69	60	64	78	46	47	38	46	89	84

Table 4 – Photovoltaic performance of the TiO₂/CdS/ZnO junction for different deposition times of the CdS layer

Cells	J _{sc} (mA/cm ²)	V _{oc} (V)	η (%)	FF (%)
TiO ₂ /CdS(20')/ZnO	3.78	0.18	0.32	0.47
TiO ₂ /CdS(30')/ZnO	3.76	0.22	0.37	0.68
TiO ₂ /CdS(50')/ZnO	3.18	0.17	0.22	0.41

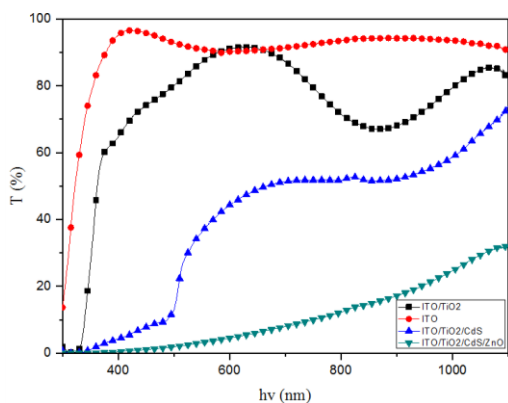


Fig. 6 – Transmittance spectra of the glass/ITO/TiO₂/CdS/ZnO junction in the UV-Vis-IR spectrum

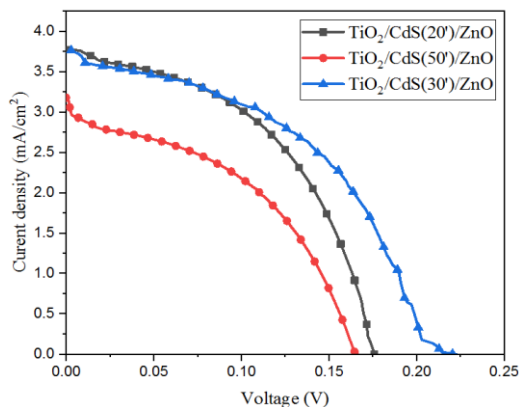


Fig. 7 – J - V curves of the fabricated TiO₂/CdS/ZnO junction with different deposition times of the CdS layer

After the completion of our junction, we prepare the electrolyte based on polyethylene glycol C_{2n}H_{4n+2}O_{n+1}, potassium iodide KI, iodine I and ethanol. In the end, the assembly of solar cells is done by depositing the

electrolyte on the sandwich prepared beforehand of ITO/TiO₂/CdS/ZnO thin films. Then we deposit an ITO-conducting substrate and make our contact with silver lacquer as shown in diagram of the cells in Fig. 1.

The electrical measurements were carried out using a solar simulator (Riels Instruments) at the CRTSE research center. Fig. 7 represents the current density-voltage $J(V)$ characteristics of solar cells produced under lighting. The cells were selected based on the window layer deposition time (CdS). The deposition time for cells of group (1) (TiO₂/CdS(20')/ZnO) was 20 min, cells of group (2) (TiO₂/CdS(30')/ZnO) was 30 min and cells of group (3) (TiO₂/CdS(50')/ZnO) was 50 min.

Table 4 shows the photovoltaic performance of the TiO₂/CdS/ZnO junction for different deposition times of the CdS layer. It is noted that the performances of group (2) have the best efficiency in comparison with other cells of group (1) and group (3). Cells of group (3) have lower efficiency (1.76 % less than cells of group (2)); this is due to the low current intensity and voltage generated by cells of group (3). In the work of Guang Zhu et al. [20], they developed cells of TiO₂/CdS and TiO₂/ZnO/CdS types. The results found are TiO₂ with the efficiency $\eta = 0.99$ %, fill factor FF = 0.36 %, open-circuit voltage V_{oc} = 0.49 V and short-circuit current density J_{sc} = 5.52 mA/cm², and in the cell with the TiO₂/CdS/ZnO junction the efficiency $\eta = 1.56$ %, FF = 0.35 %, V_{oc} = 0.58 V and J_{sc} = 7.66 mA/cm².

4. CONCLUSIONS

The substitution of organic dye by the CdS/ZnO junction was carried out in this work. CBD and SP techniques were used to prepare these layers. Then, each thin layer was characterized morphologically, structurally, and optically.

Through these characterizations, we have shown that annealing of the CdS layer must be done under a controlled atmosphere in order to avoid the formation of cadmium oxide and to control the particle size.

Following the characterization of the photovoltaic properties of cells based on the CdS/ZnO junction, a higher yield is shown compared to conventional cells based on organic dye. It is also noted that annealing under a controlled atmosphere such as nitrogen will eliminate CdO particles and also decrease the grain size. The efficiencies of our solar cells are $\eta_1 = 0.37$ %, $\eta_2 = 0.22$ %, and $\eta_3 = 0.32$ %.

ACKNOWLEDGEMENTS

The authors wish to thank the General Directorate for Scientific Research and Technological Development (DGRSDT) and the Research Center on Semiconductor Technology for Energy (CRTSE).

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Покращення електричних властивостей елементів Гретцеля шляхом заміщення шару барвника переходом CdS/ZnO

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Сонячні елементи на основі органічного барвника широко використовуються через простоту їх виготовлення. Проста структура складається з кольорового шару TiO₂, електроліту та антиелектроду. У дослідженні шари TiO₂, CdS та ZnO наносились на електропровідне скло різними методами для заміни органічного барвника. Для підготовки шару TiO₂ використовували метод метал-органічного хімічного осадження з газової фази (MOCVD), хімічне осадження у ванні (CBD) для підготовки шару CdS та спреї-піроліз (SP) для приготування шару ZnO. Морфологічні та структурні дослідження показали однорідну морфологію суперпозиції шарів TiO₂/CdS/ZnO. XRD та SEM аналіз показав, що відшару CdS повинен проводитися в контрольованій атмосфері, щоб уникнути утворення оксиду кадмію та регулювати розмір частинок. Метою роботи є заміщення органічного барвника в елементі Гретцеля переходом CdS(n)/ZnO(n⁺). Морфологічні та оптичні властивості TiO₂/CdS/ZnO на додаток до фотоелектричних характеристик цього структурного переходу були досліджені з різним часом осадження шару CdS. Встановлено, що природа підкладки не впливає на реалізацію переходу. Помічено, що кожен доданий шар призводить до зменшення коефіцієнту пропускання підкладки. Характеристика фотоелектричних властивостей елементів на основі переходу CdS/ZnO показує більш високий вихід в порівнянні зі звичайними елементами на основі органічного барвника. Також рекомендовано проводити відшару в контрольованій атмосфері, такий як азот, щоб усунути вторинну фазу CdO і зменшити розмір зерен, що може підвищити ефективність сонячних елементів.

Ключові слова: TiO₂, MOCVD, CBD, Спреї-піроліз, Перехід CdS/ZnO.