

Effect of Al-doping on the efficiency of chemically-deposited CdS/PbS thin film solar cells

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Using chemical bath deposition in an ammonia-free system, CdS/PbS solar cells have been synthesized with different Al content in their composition and varying its absorber layer thickness. Nanocrystalline CdS thin-films with an average thickness of 140 nm were prepared and, subsequently, PbS thin-films with two different thicknesses (330 and 790 nm) were grown on the CdS. X-ray diffraction studies shows that CdS and PbS thin films have a hexagonal and cubic structure, respectively. The illuminated current/voltage characteristic curves of these p-n junctions were measured using a 300 W solar simulator at air mass 1.5, and a frequency of 50-60 Hz. It was found that Al doping decreases the conversion efficiency of the solar cells with the thinnest absorber layer, from 0.19 % to 0.05 %, and for those with thicker layers, from 0.19 % to 0.03 %.

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1. Introduction

The use of solar radiation to generate electricity is a promising solution to the global energy crisis, due to its low carbon footprint and global availability. In this sense, thin film solar cells are an interesting alternative because of its good conversion efficiencies and the small amount of material needed for their manufacture [1]. On the other hand, nanostructured metal sulfides have been extensively studied due to their excellent properties and promising applications in electronic and optoelectronic devices, such as solar cells, light-emitting diodes, and non-volatile memories [2].

In this sense, CdS is a commonly used optical window material in thin film solar cells, due to its high optical transparency, wide bandgap energy (2.42 eV) and n-type conductivity. To use as an absorber layer, PbS has interesting features like direct bandgap energy (0.41 eV at 300 K) p-type conductivity, and large exciton radius (18 nm) which provides strong quantum confinement of electrons and holes, thus increasing the absorption for solar radiation in the near infrared region [3]. In this way, CdS/PbS thin film solar cells with layers deposited by means of chemical bath deposition have been investigated by several authors, where they have obtained good efficiencies between 0.44 % and 4.85 % [3-6]. Currently, chemical bath deposition (CBD) is a low-cost, scalable and easy technique to synthesize semiconductor thin-films [3-7].

Now, in both semiconductors it is possible to modify their properties by introducing metallic dopants into their structure, like its bandgap value and electrical conductivity. In this sense, doping with Al has been reported for chemically-deposited CdS and PbS films showing in both cases an improvement in their electrical conductivity and a modification of its bandgap

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energy and crystallite size [6-9]. Moreover, different optoelectronic devices have been reported recently using CBD Al-doped CdS thin films [10-13].

In this article, our aim is to study the joint effect that Al doping has in solar cells based on chemically-deposited CdS/PbS junction, for different thicknesses of the absorber layer, in order to evaluate its effect on the conversion efficiency and the modification of their photovoltaic parameters.

2. Experimental

Un-doped and Al-doped CdS thin films (CdS and CdS:Al) were synthesized by chemical bath deposition (CBD) on FTO/glass commercial substrates (Sigma-Aldrich, $7 \Omega/\text{square}$). The preparation steps and the synthesis process were described in our previous works [7,8]. Here, dopant concentration is measured by the molar ratio in solution $R_{Cd} = [\text{Al}]/[\text{Cd}]$, whose values are 0.00 (CdS) and 0.25 (CdS:Al). The deposition time of these films was 1 h., in order to obtain films with average thickness of 140 nm. The thicknesses of the films were determined by means of a fitting procedure of the transmittance spectra with a layer model, using the software *Filmeasure* [8].

To fabricate the solar cells, un-doped and Al-doped PbS layers of different thickness were deposited by CBD on CdS/FTO/glass. The aqueous solution was made up of 5 ml of lead (II) acetate 0.5 M, 5 ml of sodium hydroxide 2 M, 12 ml of thiourea 0.5 M, 2 ml of triethanolamine 1 M and 5 ml of pH 10 buffer. All reactants were provided by Sigma-Aldrich. *In situ* doping was performed by adding aluminum chloride to the mixture, with different molar ratios in the solution, $R_{Pb} = [\text{Al}]/[\text{Pb}]$, where the initial concentration of Pb remains constant. In this sense, the PbS films synthesized were labelled as $R_{Pb} = 0.00$ (PbS) and $R_{Pb} = 0.10$ (PbS:Al). The total volume of the deposition solution was equalled to 100 ml adding de-ionized water, and its pH value during the deposition was 12. These films were grown at a temperature of 70°C for 2 h. and 10 h., in order to obtain PbS absorber layers with an average thickness of 330 nm and 790 nm, respectively.

In order to determine the structural properties of the films, grazing incidence X-ray diffraction (GIXRD) measurements were carried out using a Bruker Endeavor D8 Advance unit (with 40 kV, 30 mA, Cu- $K\alpha_1$ radiation, $\lambda = 0.15406 \text{ nm}$) with grazing angle of 0.4° . Their surface morphologies were examined by Atomic force microscope (AFM) using a Nanosurf NaioAFM, in contact mode.

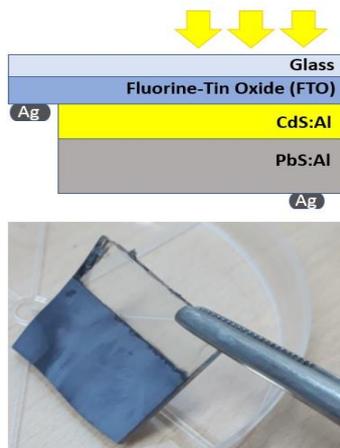


Fig. 1. Thin film solar cells CdS/PbS cross-sectional diagram and solar cell after the deposition of the PbS layer. The solar cell size is 5.0 x 3.0 cm.

Finally, Ag contacts were deposited on the surface of PbS films and the FTO by sputtering technique, to complete the solar cell structure (Fig. 1). To connect the solar cells devices, tab wires were pasted to the contacts with silver paste (EMS 12640). Their electrical parameters were

measured using an electrochemical cell, (model VersaStat 4 from Princeton Research Applied AMETEK) and a solar simulator from Photoemission (model SS50AAA, from Photoemission Tech.) with 300 W, air mass 1.5, and a frequency of 50-60 Hz. I-V curve was measured using this solar simulator for eight types of CdS/PbS solar cells, which have different concentrations of Al-doping in each layer, and different deposition times of PbS films.

3. Results and discussions

Fig. 2 shows the GIXRD patterns of the thin films that compose the solar cell. It is observed that CdS and CdS:Al films have the hexagonal wurtzite structure according to PDF No. 80-0006. The main peak position is located around $2\theta = 26.7^\circ$ and corresponds to the (0 0 2) planes. Also, a secondary peak is observed at about $2\theta = 48.2^\circ$ and is associated with the (1 0 3) crystalline planes. It is observed that Al doping does not modify the orientation of the lattice but their crystallite size. Using Scherrer equation, the average crystallite size for CdS and CdS:Al films were 38.5 and 19.4 nm, respectively.

In the case of PbS and PbS:Al films, their lattice has cubic galena structure according to PDF No. 05-0592. We observe that the most intense Bragg reflections are located at about $2\theta = 26.0^\circ$, $2\theta = 30.1^\circ$ and $2\theta = 43.1^\circ$, which correspond to the (1 1 1), (2 0 0) and (2 2 0) planes, respectively. The relative intensity of the peak (2 0 0) is enhanced with the inclusion of Al in the lattice. Their crystallite size estimated using this diffraction peak were 25.9 and 27.5 nm, for PbS and PbS:Al films, respectively.

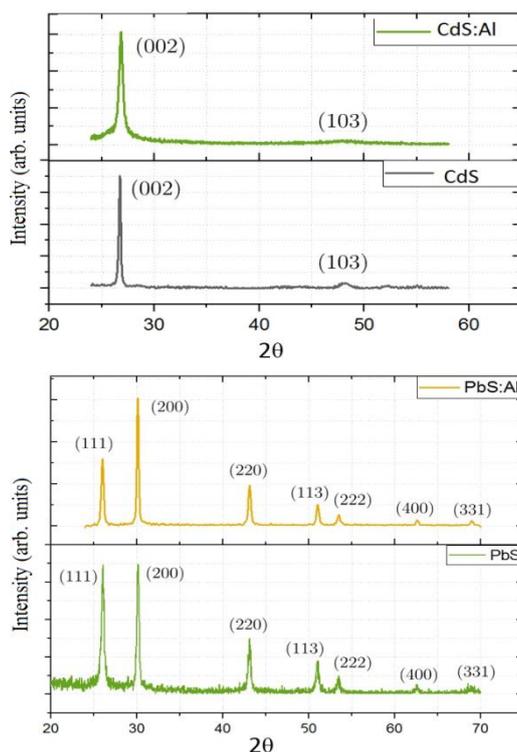


Fig. 2. GIXRD patterns of un-doped and Al-doped CdS and PbS thin films. In the case of CdS, an increase in the FWHM of the main peak is observed, which shows a decrease in its crystallite size with the inclusion of Al. On the other hand, in the case of PbS:Al, an increase in the relative intensity of the peak (200) is observed with respect to the other Bragg reflections, without modifying substantially its crystallite size.

AFM micrographs of the un-doped and Al-doped PbS and CdS films are shown in Fig. 3. From these images we calculate their RMS surface roughness, whose values were 73.7 nm (45.9 nm) and 85.7 nm (75.1 nm) for the PbS (PbS:Al) absorber layers deposited for 2 h. and 10 h., respectively. In the case of CdS and CdS:Al films, the values found were 7.5 nm and 8.4 nm, respectively. In the case of the PbS absorber layers, the surface roughness is much higher than CdS, which is in accordance with the diffuse reflectivity and high porosity of its surface.

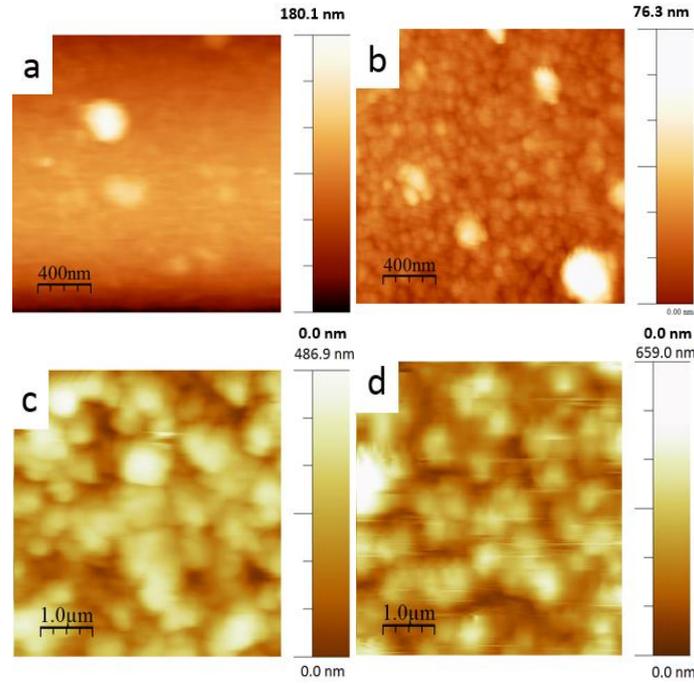


Fig. 3. Two dimensional AFM images of thin-films (a) CdS (b) CdS:Al (c) PbS (2 h.) (d) PbS:Al (2 h.). It is observed that the surface roughness of CdS films is much lower than PbS films.

The Figs. 4 and 5 shows the I-V characteristics curves of the eight different solar cells synthesized, with different combinations of un-doped and Al-doped CdS and PbS thin films, and for different thicknesses of the PbS absorber layers. Their solar cell parameters such as open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF), power conversion efficiency (η), and series resistance (R_s) are presented in Table 1. The equations to obtain these values are the same as the ones used in Refs. [3-6].

Table 1. Mean values and the confidence interval of photovoltaic parameters of solar cells CdS/PbS with and without Al-doping.

	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF	η (%)	R_s (Ω)
PbS deposited 2 h.					
CdS/PbS	85.0 \pm 8.0	8.26 \pm 0.74	26.5 \pm 0.7	0.186 \pm 0.009	66.8 \pm 5.8
CdS:Al/PbS	41.1 \pm 2.8	4.98 \pm 0.42	26.0 \pm 0.7	0.053 \pm 0.003	107.8 \pm 52.9
CdS/PbS:Al	63.9 \pm 5.9	5.11 \pm 0.23	26.4 \pm 0.5	0.086 \pm 0.007	13.1 \pm 5.7
CdS:Al/PbS:Al	58.0 \pm 2.8	8.60 \pm 0.31	25.8 \pm 0.5	0.130 \pm 0.009	39.8 \pm 12.8
PbS deposited 10 h.					
CdS/PbS	105.5 \pm 11.9	6.61 \pm 0.58	26.8 \pm 1.0	0.187 \pm 0.052	21.7 \pm 1.1
CdS:Al/PbS	88.2 \pm 10.4	5.58 \pm 0.51	26.4 \pm 0.6	0.130 \pm 0.005	66.7 \pm 8.3
CdS/PbS:Al	110.3 \pm 4.4	2.18 \pm 0.19	23.6 \pm 3.1	0.057 \pm 0.023	61.4 \pm 1.2
CdS:Al/PbS:Al	77.4 \pm 6.8	1.58 \pm 0.20	25.3 \pm 0.2	0.031 \pm 0.003	259.2 \pm 15.8

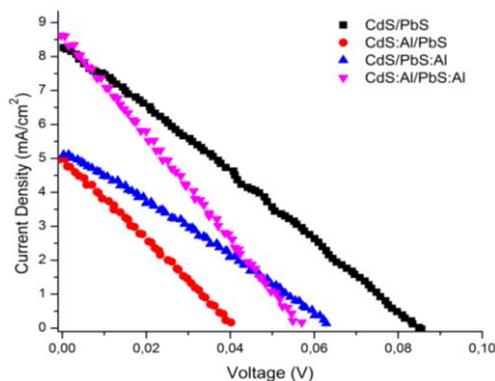


Fig. 4. Illuminated I-V characteristics curves for CdS/PbS solar cells, using the PbS layer deposited for 2 h.

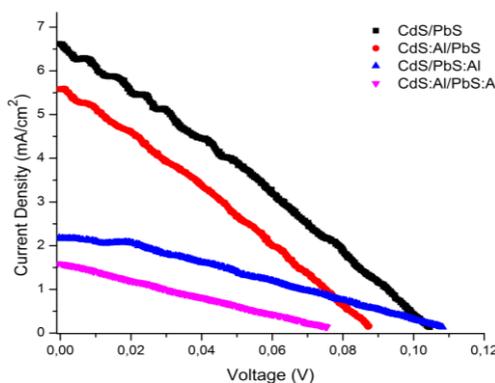


Fig. 5. Illuminated I-V characteristics curves for CdS/PbS solar cells, using the PbS layer deposited for 10 h.

In the case of cells fabricated with PbS films deposited for 2 h, when Al is introduced as a dopant in only one of the layers that compose the solar cell, there is a decrease in the conversion efficiency η . On the other hand, if both films of the cell are doped with Al, then the conversion efficiency decreases slightly compared to the solar cell made with un-doped films. In addition, it is observed that the series resistance R_s decreases when Al-doped PbS is used as an absorber layer. Having the electrical contact on it, it is possible to state that the electrical resistance of the solar cell drops, if a PbS:Al film deposited for 2 h. is used in its composition. It is important to note that similar values of R_s were reported for this type of cells in Ref. [4]. We note FF values remain slightly constant for all fabricated cells, but it is observed that V_{oc} values decreases when Al-doped films are used in the solar cells.

On the other hand, for the solar cells made with the PbS films deposited for 10 h, we observe solar cells composed of Al-doped layers have higher R_s than the solar cell made with un-doped films. Also, we note an increase in the average V_{oc} and a decrease in the average J_{sc} values, compared to those obtained for the cells made with PbS deposited for 2 h. The better adhesion of the thicker absorbent layers, due to their greater RMS surface roughness and porosity, allows for higher V_{oc} values for these types of cells.

It is observed that conversion efficiencies η are not improved using Al-doped films in our solar cells, even if the absorber layer increases its thickness. This leads us to think that Al has no effect on improving the performance of this photovoltaic device, and only modifies the other parameters of the solar cells shown in Table 1. Moreover, in the case of the cell made with two Al-doped layers, its R_s value is the highest of all the solar cells fabricated. In addition, the highest conversion efficiency of all fabricated cells is about $\eta = 0.19\%$ and corresponds to those composed of un-doped films, independent of the thickness of the PbS absorber layer.

Now, the low FF value for all fabricated cells is about 26%, which agrees with previously reported values for cells of this junction type [3,4,6,11]. This may be related to the porosity of the films synthesized by CBD allowing impurities to diffuse into the junction, in addition to the presence of voids in their structure, which affects their electrical properties.

The values obtained are comparable with the results of other authors using CdS or PbS in different types of solar cells. Among these, it is worth mentioning the article of Barote *et al.* who efficiently manufactured cells with $\eta = 0.041\%$ [14], and Moreno-García *et al.* who obtained efficiencies between 0.1 % and 0.4 % [15]. In our case, it is observed that the V_{oc} is higher in the case of cells with thicker absorbent layer, but the opposite happens with the I_{sc} , where the average value is higher in cells with thinner absorbent layer. This behavior causes that FF has similar values in all cases analyzed. In this sense, we can conclude that Al doping has no effect on improving the conversion efficiency of this kind of photovoltaic device.

4. Conclusions

Thin-film solar cells based on Al-doped CdS and PbS were synthesized using chemical bath deposition in an ammonia-free system. Mean thicknesses of CdS thin films was about 140 nm. A comparative analysis was made between CdS/PbS solar cells with different combinations between Al doped films, and for different thicknesses (330 nm and 790 nm) of the PbS absorber layer. It was found that Al doping does not modify the crystalline structure of the semiconductors but decreases the crystallite size of CdS films. It was found that the best efficiencies were achieved in solar cells made with un-doped thin films. In this sense, Al-doping causes the conversion efficiency η to decrease from 0.186 % to 0.053 % in cells with PbS deposited for 2 h., and from 0.187 % to 0.031 % for those with absorber layers deposited for 10 h. This results shows that *in situ* Al-doping in ammonia-free CBD-synthesized CdS/PbS solar cells, does not improve η but modifies the other photovoltaic parameters such as V_{oc} and J_{sc} , leaving FF values constant for all cases.

Acknowledgments

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References

- [1] N. Ali , A. Hussain , R. Ahmed , M. Wang , C. Zhao , B. Haq , Y. Fu, *Renew. Sust. Energ. Rev.* **59**, 726 (2016).
- [2] C. Lai, M. Lu, L. Chen, *J. Mater. Chem.* **22**, 19 (2012).
- [3] A. Obaid, Z. Hassan, M. Mahdi, M. Bououdina, *Int. J. Hydrog. Energy* **38**, 807 (2013)
- [4] J. Hernández-Borja, Y. Vorobiev, R. Ramírez-Bon, *Sol. Energy Mater. Sol. Cells* **95**(7), 1882 (2011).
- [5] F. Gode, S. Unlu, *Mater. Sci. Semicond. Process.* **90**, 92 (2019).
- [6] S. Rosario, I. Kulandaisamy, K. Kumar, A. Arulanantham, S. Valanarasu, M. Youssef, N. Awwad, *Physica B Condens. Matter* **575**, 411704 (2019).
- [7] A. Fernández-Perez, M. G. Sandoval-Paz, R. Saavedra, *Chalcogenide Lett.* **13**(11), 507 (2016).
- [8] A. Fernández-Perez, C. Navarrete, P. Valenzuela, W. Gacitúa, E. Mosquera, H. Fernández, *Thin Solid Films* **623**, 127 (2017).
- [9] K. Preetha, T. Remadevi, *Physica B* **407**, 4173 (2012).
- [10] I. Chávez, M. Pintor, F. Willars, Y. Vorobiev, R. Ramírez, M. Quevedo, *J. Appl. Phys.* **126**,

- 115702 (2019).
- [11] C. A. Rodríguez, A. C. Mera, L. Pizarro-Castillo, M. Ashfaq, M. G. Sandoval-Paz, M. J. Cortés-Burgos, P. Manidurai, S. Suárez, *Mater. Sci. Semicond. Process.* **131**, 105839 (2021).
- [12] F. Willars, I. Chávez, R. Ramírez, P. Vorobiev, Y. Vorobiev, *J. Alloy Compd.* **817**, 152740 (2020).
- [13] A. Fernández-Pérez, C. Navarrete, R. Muñoz, E. Baradit, M. Saavedra, G. Cabello-Guzmán, W. Gacitúa, *Mater. Res. Express* **8**, 016408 (2021).
- [14] M. Barote, A. Yadav, E. Masumdar, *Physica B Condens. Matter* **406**, 1865 (2011).
- [15] H. Moreno-García, M. Nair, P. Nair, *Thin Solid Films* **519**(21), 7364 (2011).