ppi 201502ZU4659

This scientific digital publication is continuance of the printed journal impresa p-ISSN 0254-0770/ e-ISSN 2477-9377 / Legal Deposit pp 197802ZU3



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REVISTA TÉCNICA

VOLUME 44

MAY - AUGUST 2021

NUMBER 2

Design, Manufacture and Characterization of Solar Cells p-CdTe / n-CdS with Thin Films

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 Received: 12 June 2020 | Accepted: 30 March 2021 | Available: 30 April 2021

Abstract

Venezuela, due to its geographical location, richness in sources and natural resources, has a valuable potential for the use of renewable energies, especially solar, a large part of its territory is characterized by an average insolation above 3 kWh/m², considered suitable for photovoltaic generation. CdTe is a well-known II-VI semiconductor, which has established itself as a leader in the photovoltaic industry, has optimal properties for solar cells. This research focused on design, manufacture and characterization of p-CdTe / n-CdS solar cells. The design was carried out looking for the simplest and lowest cost model. The manufacturing was carried out in an Ortus-700 equipment, using the thermal evaporation technique. For the characterization of the cells, the techniques of X-ray diffraction, optical absorption and current-voltage characteristic analysis were applied. Evidence of a typical preferential orientation of a cubic structure of Zinc Blenda, direct energy gap values between 2.15 to 2.85 eV and similar performance among prepared solar cells. The manufacture and characterization of nine p-CdTe / n-CdS cells was achieved through the formation of a p-n junction; with efficiencies of ~ 3%.

Keywords: Efficiency, optical absorption, p-CdTe/n-CdS solar cells, thin films, X-ray diffraction.

Diseño, Fabricación y Caracterización de Celdas Solares p-CdTe/n-CdS con Películas Delgadas

Resumen

Venezuela, debido a su ubicación geográfica, riqueza en fuentes y recursos naturales, tiene un valioso potencial para el uso de energías renovables, especialmente la solar, gran parte de su territorio, se caracteriza por una insolación media por encima de 3 kWh/m², considerada apta para la generación fotovoltaica. El CdTe es un conocido semiconductor II-VI, que se ha consolidado como líder en la industria fotovoltaica, posee propiedades óptimas para las celdas solares. Esta investigación se enfocó en diseñar, fabricar y caracterizar celdas solares p-CdTe/n-CdS. El diseño se realizó buscando el modelo más simple y de menor costo. La fabricación se llevó a cabo en un equipo Ortus-700, usando la técnica de evaporación térmica. Para la caracterización de las celdas, se aplicaron las técnicas de difracción de rayos-X, absorción óptica y análisis de característica corriente-voltaje. Evidenciándose una orientación preferencial típica de una estructura cúbica de la Zinc Blenda, valores de brecha de energía directa entre 2,15 a 2,85 eV y un rendimiento similar entre las celdas solares preparadas. Se logró la fabricación y caracterización de nueve celdas p-CdTe/n-CdS, mediante la formación de una unión p-n; con eficiencias de ~ 3 %.

Palabras clave: absorción óptica; celdas solares tipo p-CdTe/n-CdS; difracción de rayos X; eficiencia; películas delgadas.

Introduction

Venezuela, due to its geographical location and richness in sources and natural resources, has valuable potential for the use of renewable energy, especially solar. As can be seen in Figure 1, a large percentage of the national territory is characterized by an average insolation of the order of 4-5 kWh / m^2 per day (Solargis, 2017). Taking into account that values above 3 kWh / m^2 (Posso et al; 2013) are considered suitable for photovoltaic generation, it can be concluded that Venezuela is a country where the exploitation of solar energy is very convenient. In addition, it has been estimated that daily insolation in the territory is equivalent to 4.56 million barrels of oil, an amount that exceeds the daily oil production of Venezuela at any time in its history (Posso et al; 2013).



Figure 1. Map of solar resources of Venezuela (Solargis, 2017).

There are many types of solar cells (Bagher et al; 2019), however, from the point of view of their industrial production (Figure 2), they can be classified into three large groups: 1) polycrystalline silicon, 2) mono-crystalline silicon, and 3) thin films (Phillips and Warmuth, 2016). As can be seen in Figure 2, thin film technology has been growing in recent years, particularly CdTe-based cells (Figure 3).



Figure 2. World photovoltaic production by technology (in GWp) (Phillips and Warmuth, 2016).



Figure 3. Thin film technologies: global annual production of photovoltaic modules (Phillips and Warmuth, 2016).

CdTe (cadmium tellurium) is a well-known II-VI semiconductor (Strauss, 1977), which has optimal properties for solar cells. CdTe thin films have a high optical absorption coefficient that generally exceeds 104 cm⁻¹, absorbing approximately 92% of visible light in a thickness of only 1 μ m (Strauss, 1977; Rangel and Sobral, 2017); this efficiency is well above crystalline silicon, which needs around 200 μ m to reach the same absorption value (Burgelman, 2006). In addition, it has a direct optical energy gap of 1.606 eV at liquid helium temperature and 1.529 eV at room temperature, optimal for coupling with the solar radiation spectrum (Strauss, 1977; Rangel and Sobral, 2017). Also, its constituent elements, Cd and Te, are still relatively abundant in the earth's crust; this means that the commercial cost of CdTe powder in the international market is of the order of \$ 245 / kg (4 N purity) and \$ 280 / kg (5 N) (Alibaba, (2017). In fact, CdTe has been consolidated as a leader in the thin film photovoltaic industry, achieving efficiencies of up to 22% thanks to the optimization of the short-circuit current density (Jsc), which rose from 26.1 to 31.69 mA / cm² (Green, 2018).

CdS is also a well-known semiconductor of the II-VI family (Bube, 2001), naturally n-type, with an optical absorption coefficient, α of ~ 1.1x105 cm⁻¹, transparent, with a gap of direct optical energy of 2.41 eV (Oliva et al., 2001; Das and Pandey, 2011). Due to its optical characteristics and low cost (\$ 50-100 / kg) (Alibaba, 2016) it is the most used window material for solar cells with CdTe.

The objective of this research was to design, manufacture and characterize p-CdTe / n-CdS solar cells; using a design, versatile and simple, so that it can be easily replicated, and at the lowest possible cost, thus bridging the gap of the impossibility of easy access to most of the materials required for the manufacture of these photovoltaic devices.

Experimental

Solar Cell Design

The design of the experimental cell used for the manufacture of the solar cell, in the present work, is shown in Figure 4.



Figure 4. Details of the design of the p-CdTe / n-CdS cell. At the bottom, the experimental arrangement used in this work. In the upper part, photograph of the cell already made.

Solar Cell Manufacturing

The equipment used for the manufacture of the nine p-CdTe / n-CdS cells was an Ortus-700 (from the National Center for Optical Technologies adjunct to the Astronomy Research Center Mérida, Venezuela), which allows obtaining thin films using four different techniques: thermal evaporation, electron gun, ion gun and radio frequency. The substrate consisted of glass microscope slides, with dimensions of 25.4 x 76.2 x 1 mm. Before deposition, the chamber was subjected to vacuum levels on the order of ~ 10-4 Torr; once achieved, the substrates were subjected to an ABS (Assisting Beam Source) ion beam cleaning for 2 min, to remove impurities and achieve a rough nanometric surface that facilitates the adhesion of materials.

For the CdTe deposition process, polycrystalline powder with a nominal purity of 5 N (99.999%) was used, which was arranged in the form of granules with an approximate average value of 3 to 5 mm in diameter each piece, within a container made of molybdenum (Mo), which in turn was connected to the pair of electrodes of the thermal evaporation device inside the Ortus-700.

Films were made by gradually heating the CdTe inside the crucible until it evaporated. The vapor molecules, leaving the source, were deposited on the surface of the substrate. The equipment has a support for the substrates in the form of a spherical cap, which makes the distance between the heating source and the substrates vary between 45 and 53 cm, depending on their location on said support (Figure 5). To obtain homogeneous films, the mechanical rotation of said support was used, which was configured to rotate at 20 rpm, and the heating power was adjusted until reaching deposition rates of 2-6 Å / s.

The nomenclature l, m and c in Figure 5 is arbitrary, allowing the subsequent evaluation of the difference in thickness of the films as a function of position, since the concavity of the support makes the samples located in the most eccentric part closer to each other and to the heater fountain.



Figure 5. Side view of the support of the substrates in the Ortus-700. The nomenclature l, m and c is arbitrary and makes it possible to subsequently evaluate the difference in thickness of the films as a function of said position (Modified to Izovac, 2014).

For the CdS deposition process, polycrystalline powder with a nominal purity of 5 N (99.999%) was used, which was sintered into tablets with a diameter of 25 mm and a thickness of 0.5-0.8 mm. In a similar way to the CdTe compound, fragments of said tablets were placed inside a container of Mo, connected to the electrodes of the thermal evaporation device within the coating system. In this case, the substrate consisted of previously obtained CdTe thin film samples. Before deposition, the chamber was also subjected to a vacuum of the order of ~ 10-4 Torr, cleaning the CdTe samples by ABS ion beam for 2 min.

The thin films of CdS were also obtained by means of the resistive heating technique, where the substrate during the deposition reached temperatures similar to those of CdTe. Mechanical rotation was set at 20 rpm and the heating power was adjusted until reaching a deposition rate of 3 Å / s and a thickness of ~ 500 nm, measured in situ by optical transmission, which corresponds to T = 50% for incident radiation with λ = 550 nm. Once the CdTe and CdS layers were arranged on the glass substrate, the silver (Ag) finger-type contacts were fixed on them, which were obtained by the electron beam deposition technique, reaching a thickness of about 350 nm.

Characterization of Solar Cells

The first characterization carried out was the measurement of the films by X-ray diffraction (XRD), by means of the powder technique, using a SIEMENS Brukers-AXS D5005 equipment. The second characterization carried out was the measurement of the optical transmission, as a function of the incident wavelength for the films obtained, in Cary-UV-Vis-NIR-5000 equipment at normal incidence.

The third characterization that corresponded to the measurement of the efficiency of the cells, using their characteristic current-voltage density (J-V), is presented in Figure 6. The measurement circuit used is shown on the left side. Suitable RL values can be estimated by the following procedure. First, Voc and Jsc were measured, and the relationship of Voc, Jsc and RL was calculated. The value of RL is close to RL at the point of maximum power. Resistance values less than or greater than RL, by about an order of magnitude or more were chosen to score points in the JV characteristics towards Jsc or towards Voc, respectively, where more RL values should be chosen around the maximum power point to increase the accuracy of the fill factor (FF) measurement, defined below (Dittrich, 2018). On the right side of Figure 6, the home station that was used to manipulate the electrical contacts to the solar cell is also shown. Two bronze arms were used to hold the wire needed for each semiconductor material. Ohmic contacts were used for an adequate response. The CdTe contact consisted of 0.5 mm copper wire that was soldered to the surface of the thin film with silver paint, while a 0.2 mm diameter tungsten wire was used for the CdS. The ohmic behavior of the electrodes was verified by measuring the current density-voltage characteristic.



Figure 6. Arrangement of the electrical circuit used for the measurement of the current and voltage characteristics (J-V), using a potentiometer and two multimeters. R_{int}: internal resistance, RL: variable resistance, A: amperemeter, V: voltmeter.

Voltage and current readings were taken using two Keithley 2400 measuring instruments. J-V curves were obtained point-to-point under illumination. The incident light was provided by a tungsten incandescent light bulb (luminous efficacy 12.5-17.5 lumens / Watt), which was placed at a distance of about 1m above the solar cell sample to avoid undesirable heating of the device; luminosity was measured with a commercial PCL-VDL 16I lux meter.

The efficiency (η) of a solar cell is determined as the fraction of incident energy that is converted into electricity, and is defined as (Checa et al, 2015):

$$\gamma = \frac{P_{max}}{P_{in}} = \frac{V_{oc} J_{sc} FF}{P_{in}} \tag{1}$$

Where P_{in} is the incident power, V_{oc} is the open circuit voltage; J_{sc} is the short-circuit current density and FF is the fill factor, given by:

$$FF = \frac{V_{max} J_{max}}{V_{oc} J_{sc}}$$
(2)

Where V_{max} and J_{ax} are the coordinates of the point max.

The incident power P_{in} [W/cm²] is equal to the luminous flux Φ_V [lumens/cm²], divided by the luminous efficacy L_{ef} [lumens/W]:

$$P_{in} = \Phi_V / L_{ef} \tag{3}$$

In this case, the incident power measured on the solar cell $P_{in} = 0.1 \text{ W} / \text{cm}^2$.

Results and Discussion

Figure 7 shows the diffraction pattern obtained from the CdTe film. The diffraction pattern shows a preferential orientation of plane 111, typical of a cubic crystalline structure, similar to Zinc Blenda (Datta et al. 2011), crystalline structure of CdTe. The CdS diffraction pattern is shown in Figure 8. Comparison of the experimental pattern (red) with those calculated (blue and green,) unequivocally shows that the crystal structure corresponds to the known Wurtzite hexagonal phase of CdS. It should be noted that the patterns correspond to the films as they evaporated, without any subsequent heat treatment, due to the good crystallinity during their growth.



Figure 7. X-ray diffraction pattern of the CdTe thin film manufactured in this study. (°): degrees.



Figure 8. CdS thin film diffraction pattern (red line). For comparison, the calculated diffraction patterns of hexagonal CdS (blue line: ICDD 01-074-9663) and cubic CdS (green line: ICDD 04-006-3897) are also shown. (°): degrees.

Figure 9 shows the measurements of the nine CdTe films, each color groups three different measurements that practically overlap. The colors black, gray and blue, represent the positions l, m and c in Figure 6 and, therefore, three different thicknesses of the films: 355, 220 and 90 nm, for the curves of black, gray and blue, respectively.



Incident wavelength / λ [nm]

Figure 9. Optical transmission measurements as a function of the incident wavelength for the nine CdTe thin films. The three colors (black, gray, and blue) correspond to positions l, m, and c in Figure 5, respectively. Notice that there are three overlapping curves for each position. The numbers on the curve show the values of the two observed absorption bands.

It is known that the value of the energy gap (Eg) depends on the thickness of the film (Oliva et al., 2001; Goh et al., 2010; Khatri et al., 2010; Das and Pandey, 2011). In Figure 10 the values of Eg vs λ obtained from Figure 9 have been plotted with the values of the thicknesses of the CdTe films. An exponential type behavior is observed y = Ax^{-b}, with A = 5.68 eV and b = 0.195, which is coincident with that observed by other authors, for example for Ge (Goh et al., 2010), InSbBi (Khatri et al., 2010) and CdS (Oliva et al., 2001; Das and Pandey, 2011).



Figura 10. Values of Eg vs λ (nm) thicknesses of the CdTe films. Experimentals values, 1.000 nm thicknesses (Phixun et al; 2009).

The results of the nine CdS films are shown in Figure 11. In this case, all the curves overlap, so no change in the energy gap is observed. This result indicates that the thickness of the films is the same: 500 nm, measured in situ at the time of deposition. The value of Eg = 2.59 eV is within the range of the values obtained by other authors, also in thin films: 2.15-2.25 eV (Demir and Gode, 2015); 2.85 eV (Imran et al., 2018) and 2.42 eV (Oliva et al., 2001).



Incident wavelength / λ [nm]

Figure 11. Optical transmission measurements as a function of incident wavelength for the nine CdS thin films. The numbers on the curves are the values of the observed absorption bands. The value of the direct energy gap (Eg) is given.

The current-voltage (J-V) characterization for the nine cells is shown in Figure 12; the current density J [mA / cm^2] and the power output Pout [mW / cm^2] are represented as a function of the applied voltage V [mV] for a particular cell (cell number 1). In Table 1, the characteristic parameters of the nine cells are presented.





Figure 12. Current-voltage characteristic for the p-CdTe/n-CdS solar cell identified with number 1 in Table 1. The black points are the experimental values of J vs V. The red points are the output power. The yellow box represents the fill factor (FF).

| | | 1 | | | | |
|----------------------|--------------------------|---|-------------------------|--|-----------|----------|
| Solar cell number | V _{max} [mV] | J _{max} [mA/cm ²] | V _{oc} [mV] | J _{sc} [mA/cm ²] | FF [%] | η [%] |
| 1 | 88 | 3,6 | 160 | 6,2 | 32 | 3,2 |
| 2 | 95 | 3,5 | 191 | 5,0 | 35 | 3,3 |
| 3 | 92 | 3,5 | 178 | 5,8 | 31 | 3,2 |
| 4 | 93 | 3,4 | 175 | 5,9 | 36 | 3,2 |
| 5 | 101 | 3,1 | 181 | 5,4 | 32 | 3,1 |
| 6 | 99 | 3,1 | 178 | 5,6 | 31 | 3,1 |
| 7 | 99 | 3,5 | 169 | 5,9 | 35 | 3,5 |
| 8 | 97 | 3,6 | 165 | 6,1 | 35 | 3,5 |
| 9 | 91 | 3,4 | 163 | 6,2 | 31 | 3,1 |

Table 1. Photovoltaic behavior of the p-CdTe / n-CdS solar cells manufactured in the present study.

 V_{max} : maximum voltage; J_{max} : maximum current; V_{oc} : open circuit voltage; J_{sc} : closed circuit current corriente FF: fill factor; η : conversion efficiency.

As can be seen in Table 1, the performance of the solar cells prepared is very similar, this is because they were all prepared following the same methodology and under the same experimental conditions.

Conclusions

The manufacture and characterization of the nine p-CdTe / n-CdS cells, by forming a p-n junction capable of generating a potential difference when illuminated (photovoltaic effect). For this first prototype, a simple design was applied with the lowest possible cost; achieving efficiencies of ~ 3%. The short-circuit current was relatively low, probably due to a high value of the shunt resistance (Rs).

Acknowledgment

We thank the Crystallography Laboratory of the Universidad de Los Andes for the X-ray diffraction measurements; to Fonacit for the financing of the project "Measurement and optimization of the efficiency of photovoltaic solar cells manufactured in the National Center for Optical Technologies (CNTO)" (2018), and to the Ministry of Popular Power for Science and Technology, for the financing of the POA 2019 project "Manufacture and assembly of a photovoltaic module".

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REVISTA TECNICA

OF THE FACULTY OF ENGINEERING UNIVERSIDAD DEL ZULIA

Vol. 44. N°2, May - August, 2021____

This Journal was edited and published in digital format on April 2021 by Serbiluz Editorial Foundation

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