

MANUFACTURING PROCEDURES OF A CdS/CdTe THIN FILM SOLAR CELL

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ABSTRACT

This work reports the process used to manufacture CdS/CdTe thin film solar cells at the Instituto Militar de Engenharia (IME). The procedure consists of sequentially depositing several layers onto a glass substrate, configured as glass/TCO/CdS/CdTe/Au. Analysis of the individual layers showed that the films had the minimum requirements to yield efficient devices. The use of different TCOs did not improve the device efficiency, probably due to other more important loss mechanisms. The available system in the laboratory for the measurement of photovoltaic parameters yielded values near to the ones measured at NREL. The maximum efficiency of 4.4% is low compared with the worldwide record of 16.5%, but it can probably be improved by optimizing some steps of the manufacturing process such as the contact to CdTe and the thickness of the CdS layer.

1. INTRODUCTION

Thin film CdTe solar cells are one of the chief candidates for large scale photovoltaic applications. Conversion efficiencies of up to 16.5% have been recently reported at the National Renewable Energy Laboratory – NREL [1]. Modules with 60 Wp, 0.72 m² and 8% efficiency are currently commercialized, in modest scale, in Europe and in the USA. Recently, CdTe modules manufactured by First Solar, based in Ohio, were selected for a 1.3 MW German solar power plant, showing that these modules are beginning to be competitive in this market segment. This is due to a simple and fast deposition process, which permits that these 0.72 m² modules are manufactured at a rate of 1 module per minute, bringing about a huge reduction in the cost of PV modules.

Several groups have reported the manufacturing steps of this cell [2-5], but few of them have described the process in detail [5]. Manufacturing a CdS/CdTe thin film solar cell involves a set of physical and chemical procedures. Usually, the layers are sequentially deposited onto a substrate in a backwall configuration, which means that light is incident on the larger bandgap material. The commonest structure is glass/TCO/CdS/CdTe/BC, where TCO is the front contact, a transparent conducting oxide which is exposed to light, and the CdS film represents the n-

semiconductor, transmitting a large part of the sunlight into the absorber p-CdTe semiconductor. The sequence ends with a metallic back-contact (BC). Prior to BC deposition, the CdTe layer is submitted to a heat treatment in the presence of CdCl₂, which deeply affects the properties of the CdTe layer and is essential to achieve high efficiency [6].

The elemental layers of a CdS/CdTe solar cell have been the subject of several investigations at the Thin Film Laboratory of the Instituto Militar de Engenharia (LFF/IME) since 1996, with the purpose of optimizing the deposition processes [7-9]. These previous studies motivated the present work involving fabrication of the whole device [10]. To our knowledge, this is the first time this kind of device is manufactured in Brazil. This work details the whole process used to manufacture CdS/CdTe solar cells at the LFF/IME and also reports a 4.4% efficiency device as verified by NREL.

2. MANUFACTURING PROCEDURE

The fabrication procedure adopted at LFF-IME is analogous to the one carried out at NREL [5]. The difference lies on the deposition and heat treatment parameters of each layer, and on the materials selected as front/back contacts. Our procedure consists of sequentially depositing several layers onto a borosilicate glass substrate, configured as glass/TCO/CdS/CdTe/Au. Borosilicate glass was used due to the high temperatures involved in CdTe processing. By way of comparison, two TCOs were used as front contacts: a sputtered In₂O₃:Sn (ITO) film and a SnO₂:F/SnO₂ bilayer supplied by NREL. Gold was used as the back contact. Figure 1 shows the solar cell structure.

2.1 Front Contact (TCO)

The ITO layer was deposited onto a 9x14x1 mm borosilicate glass substrate in a RF magnetron sputtering system equipped with a 3 in magnetron gun from US'GUN. A ceramic In₂O₃:SnO₂ target (90:10 wt%, 99.99% purity) from Kurt J. Lesker was used. The 0.7 µm thick films were deposited in an argon atmosphere (3.0x10⁻³ Torr), at room temperature; the microwave power was 40 W. The deposition parameters were optimized in an earlier investigation [7]; they were chosen in order to achieve the best com-

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promise between high transmittance in the visible range and high electrical conductivity. The films had a sheet resistance of $60 \Omega/\square$ and a transmittance of 89%.

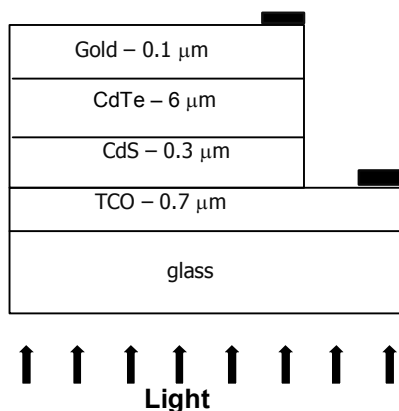


Figure 1 - Structure of the CdTe/CdS solar cell fabricated at LFF-IME.

The TCO supplied by NREL consisted of a tin oxide/fluorine-doped tin oxide bilayer deposited onto borosilicate glass by chemical vapor deposition [5]. The glass/SnO₂:F (0.45 μm)/SnO₂ (0.15 μm) structure has been used by that group as the front contact; the doped layer is the front contact itself and the undoped SnO₂ layer protects the device against short circuits, particularly when a very thin CdS is used. Also, this structure is chemically more stable than the ITO film [5]. The transmittance and resistance of the whole structure are 92% and $15 \Omega/\square$, respectively.

2.2 CdS Layer

The CdS film was deposited by chemical bath deposition (CBD) onto the TCO covered glass substrates. Prior to deposition, the TCO substrates were rinsed by sonication in hot DI water. The CBD technique is based on the decomposition of thiourea (the source of S) in an alkaline solution, in the presence of Cd²⁺ ions [5]. Our films were prepared by first immersing the substrates in a beaker containing 137.5 ml of DI water heated at 87 °C [10, 11]. Then, 2 ml of cadmium acetate (0.033 M) and 1.2 ml of ammonium acetate (1.0 M) were added. The cadmium acetate is the source of Cd and the ammonium acetate acts as a buffer solution, controlling the reaction rate. After 4 min, 3.7 ml of ammonia (3.7 M) were introduced very slowly in order to adjust the pH of the solution at 9.0. After that, 0.5 ml of thiourea (0.067 M) were introduced every 10 min up to a total of 2 ml. The total deposition time, after the addition of the first portion of thiourea, was 38 min. The substrates were then removed from the bath and rinsed in warm DI water. The films were 0.09-0.1 μm thick, which is the optimum thickness for the solar cell [12]. However, they were not uniform and this could lead to short circuits. Therefore, the CdS thickness was increased to 0.3 μm by repeating the above process three times. This procedure

ensured uniformity of the film but reduced its transmittance from 90% to 75-80% in the visible range of the spectrum.

2.3 CdTe Layer

The CdTe films were grown onto the glass/TCO/CdS stack by the close spaced sublimation (CSS) method. This technique has been pointed out as an attractive method for producing highly efficient CdTe/CdS solar cells [4]. Due to the high substrate temperatures used in this process, CdTe grain size is considerably larger than in CdTe films deposited by other methods. This is desirable, since grain boundaries are important recombination centers in polycrystalline films. The process consists of depositing CdTe using a source separated from the substrate by a very small distance, of the order of few millimeters. The reactor (a quartz tube) is evacuated by mechanical pumping and backfilled with inert gases and some oxygen or air up to a pressure of few Torr. The process allows film deposition at substrate temperatures close to the source temperatures while maintaining high deposition rates. The 6 μm thick films were deposited in a homemade CSS equipment. Details of our setup, deposition process, and film properties can be found elsewhere [13-15]. The CdTe source used in this work was a paste made of CdTe and propylene glycol [15], which was applied directly on a graphite block and dried at 120 °C for 1 h. The source and substrate temperatures were 750 °C and 560 °C, respectively. The source-substrate distance was 2.7 mm and the pressure of the system was kept at 1 Torr using pure argon. The properties of the films were extensively investigated [14]. The results showed that the films have the minimum requirements necessary to obtain efficient devices. They are slightly richer in Te and have a grain size in the range of 1 μm. In addition, the band gap of 1.46 eV and the absorption coefficient above 10^5 cm^{-1} ensure a significant absorption of the visible portion of the spectrum.

2.4 CdCl₂ Heat Treatment

The CdCl₂ heat treatment is a critical stage of the process. High efficiency solar cells are only obtained after this activation step, which consists of submitting the CdTe layer to a heat treatment in the presence of CdCl₂. Several authors have studied the influence of CdCl₂ treatment on the physical properties of CdTe films [2, 6]. Some of the reported effects are: grain growth, reduction in the density of defects and formation of an interfacial CdTe_{1-x}S_x layer, which is believed to reduce the interfacial stress caused by the lattice mismatch between CdS and CdTe. Our CdCl₂ heat treatment procedure and its effect on the properties of the CdTe layer have been described elsewhere [8-10]. Briefly, the glass/TCO/CdS/CdTe substrates were soaked for 15 min in a 75%-saturated CdCl₂/methanol solution that was previously heated at 55-60 °C in a hot plate. The substrates were taken out of the solution and submitted to an air annealing, inside the CSS reactor, at 420 °C for 40 min. After cooling, the substrates were rinsed in DI water

to remove the excess of CdCl_2 and blown with dry air.

2.5 Back-Contact

Obtaining low resistance ohmic contacts to p-CdTe is a difficult task because of the high work function of the compound, which leads to formation of a Schottky barrier. Several methods have been proposed in the literature [5, 16] to overcome this problem. The commonest (and the one that was used by our group) is to perform, prior to deposition of the contact, a p^+ doping at CdTe surface in order to reduce the barrier width. This doping can be achieved by preparing a Te-rich surface by means of a chemical etch. For this purpose, the surface of our CdCl_2 treated cells was etched in a 88:1:35 phosphoric acid: nitric acid: water solution (NP etch solution). Small droplets of NP solution were kept on the CdTe surface a few seconds past the point when the surface was completely covered with small bubbles. The total time for our samples was 50 s. Immediately after, the samples were rinsed in DI water and blown with dry air. The edges of the cell were then masked with Teflon tape in order to expose a known area to receive the contact and also to prevent shorting with the CdTe underlayers. The material used for the contact is an important factor in the process and needs optimization. Up to now, we have deposited 0.1 μm of gold onto the NP etched surface by e-beam evaporation; however, further studies are being carried out in order to find alternative contacts.

3. SOLAR CELL CHARACTERIZATION

Solar cell characterization was performed in a homemade system consisting of a 300 W halogen lamp, a silicon standard solar cell, a XY register, and the circuit shown in Figure 2. The standard solar radiation of 100 mW/cm^2 was simulated by illuminating the standard cell and adjusting the voltage applied to the lamp so that the open circuit voltage (V_{oc}) and the short circuit current (I_{sc}) were the same as those of standard cell. The current-voltage (I-V) diode characteristic curve under illumination was obtained by connecting the cell to the circuit of Figure 2 and varying the voltage supplied by a battery from -3.6 V to 3.6 V. The applied voltage was measured with a voltmeter and the current with another voltmeter connected to the ends of an $1\ \Omega$ standard resistor. The photovoltaic parameters were then extracted from the curve.

4. DEVICE RESULTS

Figure 3 and 4 show I-V curves for two illuminated CdS/CdTe solar cells. The cells are identical except for the transparent front contact: in Figure 3 the cell was fabricated on the ITO front contact deposited at LFF-IME whereas in Figure 4 the cell received the lower resistance $\text{SnO}_2\text{:F}/\text{SnO}_2$ bilayer supplied by NREL. The photovoltaic parameters extracted from the curves include the V_{oc} and

I_{sc} values, obtained respectively from the X and Y intercepts, the voltage for maximum power (V_{max}), and the current for maximum power (I_{max}), both obtained by visual inspection or, more accurately, by plotting the power output ($P=V.I$) versus the voltage and selecting the maximum power (P_{max}), as illustrated in Figure 5. One can also define J_{sc} , which is the ratio of I_{sc} to the area of the cell. The fill factor (FF) and the solar efficiency (η) are calculated using the following equations [17]:

$$FF = \frac{P_{max}}{V_{oc} \cdot I_{sc}} \quad (1)$$

$$\eta = \frac{P_{max} / A}{P_{inc}} \quad (2)$$

where A is the area of the cell exposed to light and P_{inc} is the incoming solar power of 100 mW/cm^2 . These values are summarized in Table A, which also shows the NREL standard I-V measurements for the cell characterized in Figure 3. R_s and R_{sh} are respectively the series and shunt resistances of the cells. It can be seen that the system used at LFF-IME for the measurement of photovoltaic parameters yielded values near to the ones measured at NREL. The highest values ever reported for a CdS/CdTe cell are [1]: $V_{oc} = 845$ mV; $J_{sc} = 25.88$ mA/cm^2 ; $FF = 75.5\%$; $\eta = 16.5\%$. The values listed in Table A are much smaller, but can probably be improved by optimizing some steps of the manufacturing process, such as the thickness of the CdS layer and the contact to CdTe. Losses by light absorption in the CdS layer should be avoided because they are detrimental to the quantum efficiency in the blue part of the spectrum; therefore, the CdS film should be made as thin as possible. As a matter of fact, the CdS films used in our devices are too thick for a window layer [12]. The 75-80% transmittance of this layer probably limited the photocurrent of the device.

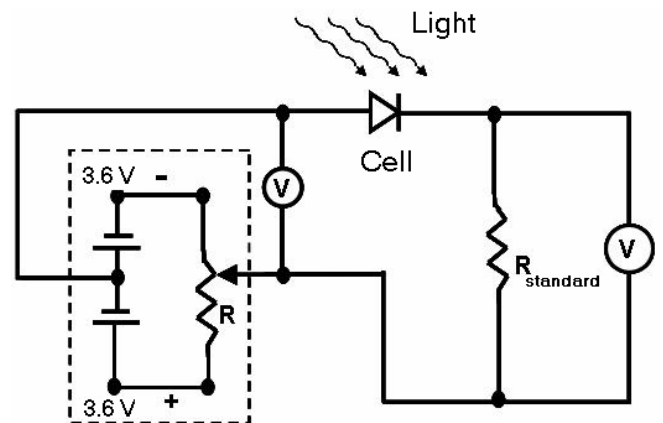


Figure 2 - Experimental setup for measuring the current-voltage characteristics of the device.

Table A also compares parameters of cells produced with different TCOs. It is well known that reducing TCO resistivity is essential for reducing R_s and improving the effi-

ciency of the cell [1]. However, Figure 3 shows that the use of the highly transparent and conductive TCO supplied by NREL did not improve the efficiency of our devices, probably due to other more important loss mechanisms, such as the existence of a barrier at the back contact. It is well established in the literature [17] that R_s is also affected by the back contact barrier, whose presence can be inferred in Figures 3 and 4 from the saturation signal known as *rollover* [18], an effect that limits the forward bias response of the device. This is probably the reason why our process did not benefit from the use of the lower resistance TCO.

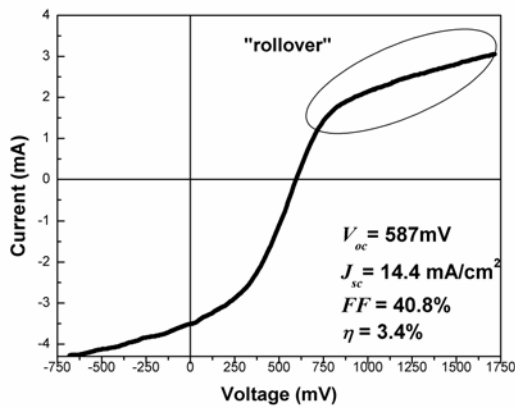


Figure 3 - Current-voltage curve for a 0.25 cm² illuminated CdS/CdTe solar cell fabricated with ITO front contact.

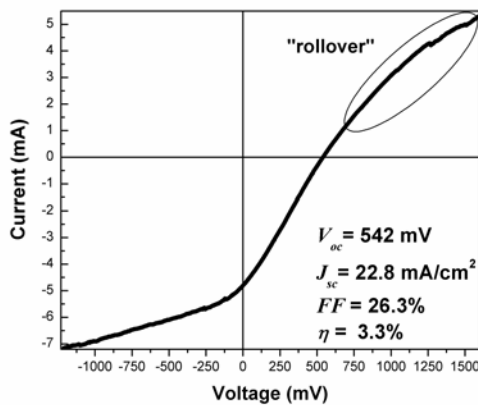


Figure 4 - Current-voltage curve for a 0.21 cm² illuminated CdS/CdTe solar cell fabricated with SnO₂:F/SnO₂ front contact.

It should finally be noted that the low R_{sh} value suggests the existence of shunting current paths which decrease the solar efficiency.

5. CONCLUSIONS

CdS/CdTe thin film solar cells were manufactured at LFF-IME and a 4.4% device is reported for the first time in Brazil. Except for the e-beam system used for gold deposition, the entire experimental setup used for deposition, chemical treatment, and characterization was built at LFF-

IME. Despite the simplicity of the process, which makes it attractive for cheap production, some technical difficulties have to be overcome. Many of the experimental steps are empirical and their influence on the cell parameters is still not well understood. The use of lower resistance TCO did not improve the efficiency of the devices, suggesting that other limiting mechanism may be present. Some possible mechanisms are: a) a high R_s resulting from the Au/CdTe barrier contact, since the I-V curves show the rollover signal; b) the excessive thickness of the CdS layer, which probably absorbed a significant part of the incident light, decreasing the photocurrent; c) a low R_{sh} , probably caused by shunts between the layers. Our group is presently trying to correct these defects.

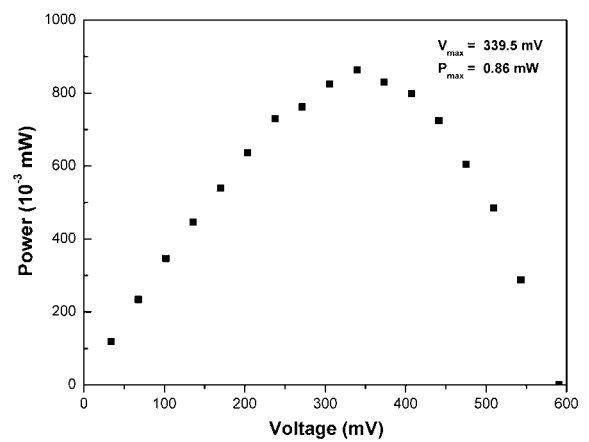


Figure 5 - Power-voltage curve for the illuminated CdS/CdTe solar cell fabricated with ITO front contact; V_{max} is the voltage at maximum power.

Table A – Photovoltaic parameters of the CdS/CdTe solar cells characterized in Figures 3 and 4 as measured at IME and NREL.

	ITO contact IME data	ITO contact NREL data	SnO ₂ :F/SnO ₂ contact IME data
V_{oc} (mV)	587	605	542
I_{sc} (mA)	3.6	5.1	4.8
V_{max} (mV)	340	340	292.6
I_{max} (mA)	2.54	3.66	2.34
J_{sc} (mA/cm ²)	14.4	18.0	22.8
P_{max} (mW)	0.86	1.24	0.68
FF (%)	40.8	39.9	26.3
η (%)	3.4	4.35	3.3
Area (cm ²)	0.25	0.29	0.21
R_s (Ω)	-	67.32	-
R_{sh} (Ω /cm ²)	-	665.91	-

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