Pinhole treatment of a CdTe photovoltaic device by electrochemical polymerization technique

Misle M. Tessema, Dean M. Giolando*

School of Green Chemistry and Engineering, Department of Chemistry, University of Toledo, 2801 W Bancroft S, Toledo, OH 43606, USA

ABSTRACT

An electrochemical treatment was developed to passivate pinhole defects in photovoltaic devices consisting of the device stack: glass substrate/SnO$_2$:F/CdS/CdTe/Cu/Au (metal/back contact). Samples were carefully examined and only those possessing a high density of pinholes through the CdS and CdTe layers were chosen for this study. The presence of a pinhole defect through these layers would lead to the formation of a wire-like connection through the photovoltaic device (shunt), which would seriously degrade the overall performance of the photovoltaic device, on deposition of the metal back contact. We report a solution to this problem wherein the pinhole defects are selectively filled with a resistive material such as polyaniline, using an electrochemical polymerization of the aniline monomer. After the polymer film deposition, this new layer acts as an insulator plug, and prevents the metallic back contact (Cu–Au) from making electrical contact with the transparent conductive oxide (SnO$_2$:F) layer, thus avoiding shunting of the photovoltaic device. Characterization techniques employed in this study are current–voltage measurements to measure the photovoltaic performance of treated and untreated devices and SEM–EDS microscopy and Grazing Angle X-ray diffraction to study the CdTe surface chemistry.

1. Introduction

During the fabrication process of CdTe photovoltaic devices material defects result in the formation of pinholes, which are small areas of missing portions of the semiconducting CdS/CdTe layers, and are areas of exposed transparent electrode. Pinholes can arise from random incomplete coalescence of the CdTe grains during deposition, or due to defects in the underlying surface [1]. Examination of the surface of a typical conductive oxide glass substrate using optical microscopy showed particulates consistent with surface contamination that can lead to pinholes during the growth of a thin film [1]. If these pinholes are left untreated, they lead to short-circuit or to shunting of the photovoltaic after deposition of the metal back contact. As early as 1982, a method was described wherein the pinhole defect was filled with a photochemically cured insulating polymer [2], but was not pursued further in the literature. Rather studies concentrated on destroying the shunt path or electrical short that resulted when the final electrode, which could be either the metal or transparent window electrode, was deposited. Usually, a current is passed though the short and the electrically conducting material of the shunt is converted to an insulator [3–7] and in one recent example the process is assisted by simultaneous photochemical activation [8]. Very recently it was suggested to locate the area of the shunt and to remove the electrode material or the current collecting grid connections and in so doing remove the defective portion of the photovoltaic device [9]. This current article presents an electrochemical treatment to passivate or seal the defect by selectively depositing insulating polyaniline onto the exposed portions of the transparent electrode into these pinholes; thus preventing shunting of the solar cells when the final electrode is deposited.

Polyaniline is known as a poorly conducting polymer, with high chemical stability [10,11]. Conducting polymers are of significant interest given their possible applications in numerous research areas including electronics, energy storage, and medicine [12–15]. Among such polymers, polyaniline has been studied extensively and has found increasing uses in various fields of technology such as in gas sensors [16], secondary cells [17], actuators [18], liquid crystal displays [19] and anticorrosion coatings [20,21]. This polymer is readily prepared electrochemically from aqueous solution (anodic polymerization onto the electrode surface), is insoluble in water, shows redox reversibility and is air stable [22]. Polyaniline comes in three oxidation states, known as leucoemeraldine base, emeraldine base and pernigraniline base. These oxidation states are shown in Fig. 1, where the value of Y varies: Y=1 to provide the fully reduced form (leucoemeraldine base); Y=0.5 for the form that is half oxidized

* Corresponding author. Tel.: +1 419 530 1511; fax: +1 419 530 4033.
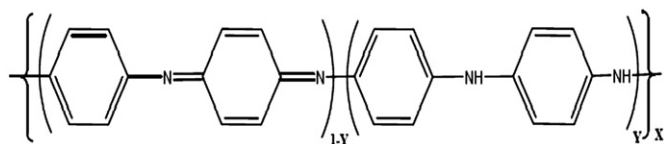 *E-mail address:* dean.giolando@utoledo.edu (D.M. Giolando).

Fig. 1. The base (i.e., neutral) polyaniline, which is half reduced/oxidized [14].

(emeraldine base, most stable form); and $Y=0$ giving the fully oxidized form (pernigraniline base) [11]. All three of these forms are electrically nonconducting. The fourth state of polyaniline is electrically conducting and is called emeraldine salt [23,24].

Electrochemical deposition is an interfacial reaction, performed by applying a voltage across a conductive substrate and an inert electrode while both electrodes immersed in an electrolyte rich solution containing aniline monomer, polyaniline grows on the conducting substrate. Usually, polyaniline is classified in the literature as a conducting polymer, however, as often prepared it has a high electrical resistivity of $\sim 10^6\ \Omega$, and as such acts as a poor conductor if not an insulator. The electrolytic cell setup, characterization and the growth rate of the polyaniline film are well studied. In our studies the transparent conducting oxide (TCO) is connected as the anode and a platinum mesh as the cathode of an electrolytic cell. Anode oxidation occurs at the surface of the TCO leading to polymerization of the aniline monomer to form polyaniline on the TCO surface [25]. Simultaneously, reduction of oxygen in the solution occurs at the cathode. The objective is to grow polyaniline by electrochemical polymerization in the pinhole areas of the CdS/CdTe photovoltaic device where the TCO layer is exposed. The high electrical resistivity ($\sim 10^6\ \Omega$) of the CdTe, and for the exposed CdS layer prevents polyaniline formation on its surface. In other words, our goal is to selectively coat only portions of the TCO layer that are exposed through the missing semiconductor layer. Thus, after the electrochemical polymerization treatment the polyaniline acts as an insulating material and provides a benefit by filling the pinhole defects, which prevents the formation of an electrical contact known as shunting between the TCO and Cu–Au back contact layers when completing the cell.

2. Experimental

The photovoltaic devices used in this study were donated by Calyxo USA, Perrysburg, Ohio. The samples on which the treatments were conducted, were cut from a 60 cm $\times$ 120 cm panel, and selected for having the presence of pinhole defects. Methanol (HPLC grade), $CdCl_2$ (Certificate A.C.S.), NaCl (Certificate A.C.S.), and HCl (Certificate A.C.S. Plus) were purchased from Fischer Scientific. Aniline (99.5%+A.C.S. reagent) and *p*-toluenesulfonic acid (*p*-TSA) (98.5%+A.C.S. reagent) were purchased from Sigma Aldrich. All chemicals were used as received, except for aniline, which was distilled prior to use. On exposure to air (oxygen) and light aniline changes color from colorless to dark brown. Impure and darkened aniline was purified by a simple distillation. All solutions were prepared with millipore water.

The $CdCl_2$-treatment was conducted as a "wet"-treatment, using 3 mL of a saturated $CdCl_2$ solution in methanol under standard conditions for each 7.62 cm $\times$ 7.62 cm sample. Therefore, approximately 50 μL of $CdCl_2$ solution is applied per centimeter square device area. After deposition of the $CdCl_2$ onto the CdTe surface the sample was placed in an oven at 390 °C where it remained for 30 min. The samples were rinsed with distilled water followed by methanol and then dried with a high pressure stream of nitrogen gas.

I–V-measurements were conducted on an Oriel 1000W Solar Simulator at 1.5AM, calibration of the current was done with a NIST certified crystalline photodiode – after the lamp was allowed to warm (circa 15 min) – and the intensity of the light is adjusted to provide a 24.9(1) mA current on the photodiode. The surface of the samples and the pinhole defects were examined using SEM, with a JEOL JSM-7500F scanning microscope. The changes in surface composition were analyzed by GIXRD on a PAN Analytical, X'PertPro PW3020Pro X-Ray diffractometer, at an incident beam angle of 1°.

2.1. Preparation of standard aniline solution

A freshly prepared solution containing 0.2 M aniline, 0.02 M *p*-toluenesulfonic acid monohydrate (*p*-TSA·H$_2$O), 1.0 M sodium chloride (NaCl) in de-ionized water was stirred for at least 0.5 h, resulting in a solution with pH 6.2–6.5 [26]. Since, aniline is toxic and light sensitive handling of all of the ingredients was done in a hood with the minimum light exposure and solutions were stored in an opaque container.

2.2. Electrochemical treatment

Samples of vapor transport deposited (VTD) CdS/CdTe photovoltaic devices were purposely prepared with widely distributed pinholes of various shapes and sizes that range from nanometer to micrometer in diameter across the whole device. Some of these pinholes can easily be seen with a naked eye using a bright light shining from one side through the typically opaque 4 μm of CdTe. The samples were cut into 2.5 cm $\times$ 5 cm dimensions suitable for our experimental setup [25]. A potentiostat (D.C. power supply), containing two wires terminating with alligator clips, was used to apply a potential to the TCO layer of a CdTe device and a platinum mesh electrode was used as an auxiliary electrode [25]. The TCO layer of the CdTe photovoltaic device acted as the anode/positive electrode and the platinum electrode as the cathode/negative. The electrodes were placed in a beaker filled to a height of 2.5 cm with the aniline solution. Half of the CdTe device is electrochemically treated by vertically immersing the sample half way into the aniline solution and applying an appropriate voltage of $\sim$2.0 V for 20 min, while the other half of the sample not immersed in the solution is left untreated and used as a control before placing the Cu–Au metal back contact metal, refer to Fig. 2. After the electrochemical treatment the device was rinsed with de-ionized water, dried with a stream of compressed air and then metallized using Cu ($\sim$35 Å) and Au ($\sim$200 Å) metals by thermal evaporation through a mask to provide a dot cell having an area of 0.031 cm^2. Finally, a copper diffusion heat treatment of 150 °C for 45 min was performed [27]. The completed CdTe photovoltaic device was characterized by measuring the current density versus voltage (*J–V*).

3. Results and discussion

After conducting the electrochemical treatment in the absence of light the color of the CdTe layer changed from dark to light gray indicating that the surface was lightly etched by the solution. Examination of the surfaces by SEM–EDS did not reveal notable differences in surface morphology; however, a significant difference in elemental composition was observed in the higher Te:Cd ratio, which was 58% Te to 42% Cd, for the treated surface of the sample while the ratio was close to stoichiometric for the untreated portions of the sample. A similar phenomenon was also observed at the CdTe surface during the *photochemical* non-uniformity treatment of CdTe photovoltaic device using the same
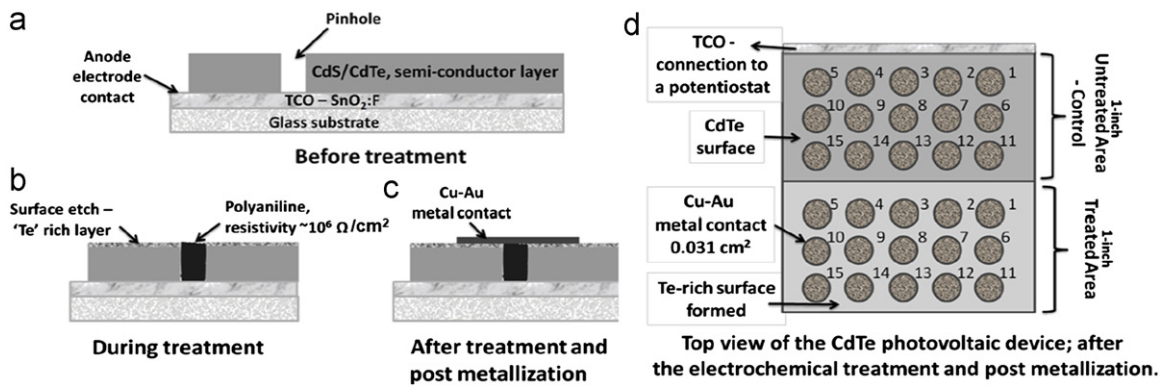
Fig. 2. (a) An illustration of a CdTe sample showing pinhole before the electrochemical treatment, (b) the polyanilne growth on the TCO sealing the pinhole and a formation of Te rich layer on the CdTe layer during the electrochemical treatment, (c) the metal back contact being placed on an area where the electrochemical treatments have been administered, and (d) top-view of a CdTe solar cell sample, which has been half treated using an electrochemical polymerization technique.

aniline monomer solution [26,28]. As indicated by Dobson et al. [28], the light gray coloration comes from the formation of a Te-rich surface on the CdTe layer during the photochemical treatment. Similar to Dobson et al. [28] we also used Grazing Incidence X-ray Diffraction-GIXRD with a PAN analytical, X'Pert-Pro X-Ray diffractometer, CuKα radiation at an incident angle of 1° to characterize the change in the surface of CdTe layer. A GIXRD pattern of the freshly electrochemically treated and untreated/ control regions showed clear differences, with "Te" phase peaks visible in the surface of treated region (Fig. 3). More experiments are needed to understand the reaction mechanism, the aniline effect on the CdTe surface and determining the thickness of the Te, which could not be done with SEM observations. The Te formed occurs only on the surface of the CdTe layer that is in direct contact with the aniline monomer solution and only when the electrical potential is applied. Similar to Dobson et al. [28] we have also noticed that as the CdTe surface becomes saturated with Te, then the reaction ceases. This phenomenon however works to our advantage because the Te rich material of the CdTe semiconductor layer increases p-type character of the surface, which is more suitable to forming a superior Ohmic-contact after the metallization process [29–31].

An additional benefit is filling of the pinholes of the treated portion of the sample with insulating material while pinholes in the untreated portion remained unaffected, which is readily demonstrated by holding a bright light behind the sample and observing light spots. The J–V measurement of the CdTe devices was measured for the control and electrochemically treated areas. For areas where a pinhole defect existed the completed cell will have shunted cells that provided a low open-circuit voltage (V_{OC}) and fill factor (FF), which in turn led to a loss in the overall cell efficiency of the cell. As shown in Fig. 4a–d, the electrochemical treatment improved the photovoltaic performance of the treated area cells. Cells from the treated portion measured a higher open-circuit voltage, fill-factor and efficiency. The short circuit current (J_{SC}) is not affected by the shunting of the solar cells (Fig. 4b). The 15 cells from the untreated portion gave a low average $V_{OC} \sim 0.3$ V and FF $\sim 31\%$, which is evidence for shunting or weak diode behavior. On the contrary, the 15 electrochemically treated cells gave a higher average of $V_{OC} \sim 0.7$ V and FF $\sim 62\%$. In Fig. 4a, the V_{OC} reading indicates strong evidence that the electrochemical treatment prevented shunting and gives a more uniform V_{OC} reading. The fill factor readings of the untreated area cells had lower than 45% as compared to the treated area sample cells that had FF of over 55% (Fig. 4c). These observations in turn reflected on the efficiency improvement in comparison to the control cells thus indicating the contact between the TCO layer and the metal back contact has been prevented. The average efficiency of the
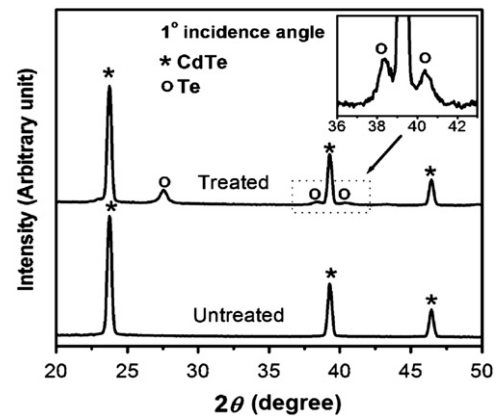

Fig. 3. GIXRD (1° incidence) of the untreated area and the electrochemically treated area of the CdTe device. The electrochemically treated area shows a formation of "Te" phase on the CdTe surface.

untreated area cell is ~1.6% while the electrochemical treated area had an average cell efficiency of 7.7% (Fig. 4d).

4. Conclusion

In conclusion, the electrochemical treatment consisting of the polymerization of aniline inside pinhole defects acts to prevent the shunting of the CdTe photovoltaic devices, as indicated by an improved average cell efficiency from 1.6% (untreated) to 7.7% (treated). The process is effective when the transparent electrode is exposed. In the event the pinhole defect results from the absence of only CdTe a thick layer of CdS may be resistive enough to provide an electrical barrier to the formation of a shunt. This treatment may provide a benefit for devices fabricated with a very thin layer of CdS, which might allow a short to form when contacted by the metal electrode. This electrochemical treatment can also be effectively used to seal an intentionally scribed sample, i.e. after laser scribing during the fabrication process used to separate a series of cell module. The Te formation on the CdTe surface should also be taken to our advantage as it can easily be used to substitute the much more vigorous acid or bromine etch of the CdTe surface for a better ohmic contact. Several compounds such as pyrrole [32], thiophene, 3,4-dihydroxy-3-cyclobutene-1,2-dione, adipic acid, stearic acid, pyrogallol, and oxalic acid have been tested show promising results that could be used as a substitute for aniline for the desired shunt passivation process.
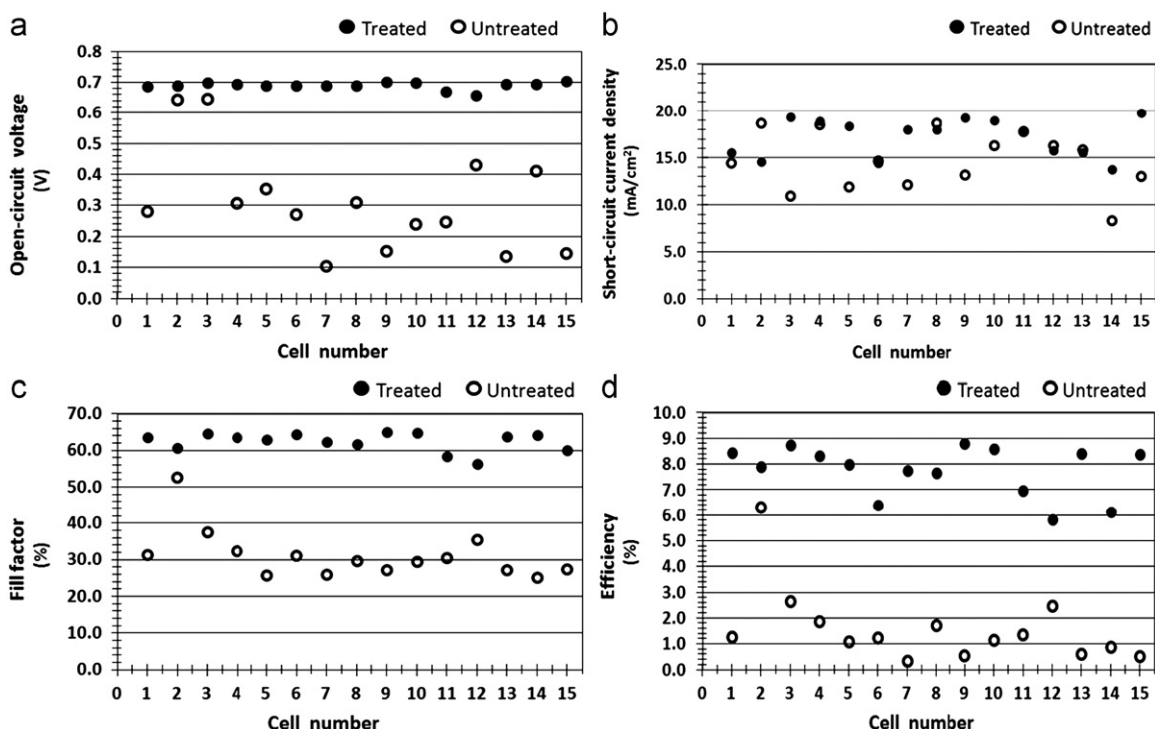
Fig. 4. (a) Open-circuit voltage—V_{OC} (V), (b) short-circuit current—J_{SC} (mA/cm^2), (c) fill factor—FF (%), and (d) efficiency—*Eff* (%) of the untreated/control (○) and electrochemically treated (●) CdS/CdTe photovoltaic cells.

References

[1] S.J.C. Irvine, V. Barrioz, A. Stafford, K. Durose, Materials issues in very thin film CdTe for photovoltaics, Thin Solid Films 480–481 (2005) 76–81.
[2] B. Basol, Plugged Pinhole Thin Film and Method of Making Same, European Patent, EP 0060487A1, Filing date 08.03.1982.
[3] G.E. Nostrand, J.J. Hanak, Method of Removing the Effects of Electrical Shorts and Shunts Created During the Fabrication Process of a Solar Cell, United States Patent, US 4,166,918, Patent date 04.09.1979.
[4] G.A. Swartz, Electrolytic Etch for Eliminating Shorts and Shunts in Large Area Amorphous Silicon Solar Cells, United States Patent, US 4,385,971, Patent date 31.05.1983.
[5] M. Izu, V. Cannella, System for Eliminating Short and Latent Short Circuit Current Paths in Photovoltaic Devices, United States Patent, US 4,510,675, Patent date 16.04.1985.
[6] J. Phillips, P. Lasswell, Method and Apparatus for Increasing the Durability and Yield of Thin Film Photovoltaic Devices, United States Patent, US 4,640,002, Patent date 03.02.1987.
[7] S. Kawakami, Method of Removing Short-Circuit Portion in Photoelectric Conversion Device, United States Patent, US 5,320,723, Patent date 14.06.1994.
[8] X. Deng, A. Vijh, Light-Assisted Electrochemical Shunt Passivation for Photovoltaic Devices, United States Patent, US 20070256729, Patent date 08.11.2007.
[9] B. Basol, Method of Detecting and Passivating a Defect in a Solar Cell, United States Patent, US 7,979,969, Patent date 19.07.2011.
[10] J.E. Albuquerque, L.H.C. Mattoso, D.T. Balogh, R.M. Faria, J.G. Masters, A.G. MacDiarmid, A simple method to estimate the oxidation state of polyanilines, Synthetic Metals 113 (2000) 19–22.
[11] E.T. Kang, K.G. Neoh, K.L. Tan, Polyaniline: a polymer with many interesting intrinsic redox states, Progress in Polymer Science 23 (1998) 277–324.
[12] T.A. Skotheim, J. Reynolds, Handbook of Conducting Polymers, 3rd ed., Marcel Dekker, New York, 2007, pp. 1–70.
[13] M.G. Kanatzidis, Polymeric electrical conductors, Chemical and Engineering News 68 (1990) 36–54.
[14] C.A. Mirkin, M.A. Ratner, Molecular electronics, Annual Review of Physical Chemistry 43 (1992) 719–754.
[15] J. Heinze, Electronically conducting polymers, Topics in Current Chemistry 152 (1990) 1–47.
[16] A.P. Monkman, M.C. Petty, N.E. Agbor, M.T. Scullys, Polyaniline Gas Sensors, United States Patent, US 5,536,473, Patent date 16.07.1996.
[17] T. Tsuji, K. Sakemura, T. Yamada, T. Miyake, S. Yanagisawa, Secondary Cell Comprising a Positive Electrode Containing Polyaniline and 4 Diazo Compounds, United States Patent, US 6,162,562, Patent date 19.12.2000.
[18] K. Kaneto, Y. Min, A.G. MacDiarmid, Conductive Polyaniline Laminates, United States Patent, US 5,556,700, 17.09.1997.
[19] S. Okada, S. Kaneko, Y. Inaba, K. Shinjo, H. Miyata, K. Katakura, Liquid Crystal Display Apparatus Having a Film Layer Including Polyaniline, United States Patent, US 5,689,320, Patent date 18.11.1997.
[20] P.J. Spellane, F.A. Via, Corrosion Resistant Non-ferrous Metal Article Coated With Emeraldine Base Polyaniline, United States Patent, US 6,117,558, Patent date 12.09.2000.
[21] A.J. Epstein, S.G. Jasty, Corrosion Protection of Iron/Steel by Emeraldine Base Polyaniline, United States Patent, US 5,972,518, Patent date 26.10.1999.
[22] C. Liao, M. Gu, Electroless deposition of polyaniline film via autocatalytic polymerization of aniline, Thin Solid Films 408 (2002) 37–42.
[23] A. Epstein, A. MacDiarmid, Polyaniline: an old polymer with new physics, Materials Research Society Symposium Proceedings 173 (1990) 293–303.
[24] S.C. Hobaica, Stability of polyaniline in air and acidic water, Journal of Polymer Science 41 (2003) 807–822.
[25] M.M. Tessema, Shunt Passivation Process for CdTe Solar Cell—New Post Deposition Technique, Master of Science Thesis, University of Toledo, 2009.
[26] Y. Roussillon, D.M. Giolando, D. Shvydka, A.D. Compaan, V.G. Karpov, Blocking thin-film nonuniformities: photovoltaic self-healing, Applied Physics Letters 84 (2004) 616–618.
[27] A.D. Compaan, A. Gupta, S. Lee, S. Wang, J. Drayton, High efficiency, magnetron sputtered CdS/CdTe solar cells, Solar Energy 77 (2004) 815–822.
[28] K.D. Dobson, S.A. Einstein, D.D. Sadowsky, B.E. McCandless, R.W. Birkmire, Understanding aniline surface treatment of CdTe, Materials Research Society Symposium Proceedings 865 (2005) 293–298.
[29] R.H. Bube, Photovoltaic Materials, Imperial College Press, London, 1998, pp. 1–281.
[30] R. Birkmire, Recent progress and critical issues in thin film polycrystalline solar cells and modules, in: Proceedings of the 26th IEEE PVSC, 1997, pp. 295–300.
[31] R. Ochoa-Landin, O. Vigil-Galan, Y.V. Vorobiev, R. Ramirez-Bon, Chemically-deposited Te layers improving the parameters of back contacts for CdTe solar cells, Solar Energy 83 (2009) 134–136.
[32] D. Giolando, D.K. Koll, A.H. Taha, Photochemical "Self-healing" pyrrole based treatment of CdS/CdTe photovoltaics, Solar Energy Materials and Solar Cells 95 (7) (2011) 1716–1719.