Photo-assisted electrodeposition of polypyrrole back contact to CdS/CdTe solar cell structures

A. Jarkov a,⁎, S. Bereznev a, O. Volobujeva a, R. Traksmaab, A. Tverjanovich c, A. Öpika, E. Mellikova a

a Tallinn University of Technology, Department of Materials Science, Ehitajate tee 5, 19086 Tallinn, Estonia
b Saint-Petersburg State University, 198503 Saint-Petersburg, Staryj Petergof, Ulyanovskaya 5, Russia
c Tallinn University of Technology, Materials Research Center, Ehitajate tee 5, 19086 Tallinn, Estonia

Available online 31 January 2013

Keywords:
CdTe
Back contact
Photo-assisted electrodeposition
Conductive polymer
Polypyrrole

Abstract
Glass/indium tin oxide/CdS/CdTe photovoltaic structures were prepared using the high vacuum evaporation method, followed by a typical activation procedure, which involves annealing of the structures at 415–430 °C in the presence of CdCl2, in air. The main purpose of this work was to prepare and evaluate the performance of complete CdS/CdTe solar cell structures with polypyrrole (PPy) back contact and compare it to the structures with standard, copper containing back contact. Back contact layers of PPy doped with 8-naphthalene sulfonate were deposited onto activated CdTe layers by photo-assisted electrodeposition technique in a three-electrode electrochemical cell. It was found that intensive white light illumination from a xenon lamp facilitates PPy deposition at a lower applied potential range as well as some Cu is diffused into the bulk of the CdTe layer to improve carrier density. As a result the height of back contact barrier decreases and tunneling of charge carriers through the junction is enabled. However, the diffusion of Cu+ ions from the back contact region towards the main junction may result in a Cu-depleted rectifying back contact and shunts through the structure.

The idea to use polypyrrole (PPy) for the back contact to CdTe is based on a high work function value (4.6–5.2 eV), high stability and relatively high conductivity of this conductive polymer (up to 100 S/cm) [8–10]. Furthermore, conductive polymers as covalent compounds are virtually free of broken chemical bonds and they should not provide any additional recombination and trapping centers at the interface with an inorganic photoabsorber. Meanwhile, large dimensions of organic molecules should limit the rate of their diffusion into a CdTe layer with the formation of new impurity centers and traps. Moreover, proposed photo-assisted electrodeposition
approach gives a possibility to deposit the polypyrrole doped with \(\beta\)-naphthalene sulfonate (PPy:\(\beta\)-NSA) conductive polymer strictly onto photo-excited CdTe surface, around pinholes, thus eliminating possible short-circuiting through defects in CdTe photoabsorber layer. Using relatively low deposition potential prevents electrochemical degradation of Cds/CdTe photovoltaic (PV) structure. During the synthesis \(\beta\)-NSA anions are incorporated into the polymer and are necessary to stabilize the delocalized positive charge on the polymer n-electron system (formed on the polymer back bone during simultaneous oxidation and polymerization of the pyrrole monomer) and achieve charge neutrality. The anion (counterion) used has a great influence on the general properties of the polymer and its thermal/environmental stability. In the present paper we have compared the performance of a Cds/CdTe structures with an electrodeposited PPy:\(\beta\)-NSA organic back contact and with a traditional inorganic p+CuxTe back contact. It should be noted that this approach is aimed to develop an alternative to the conventional copper/gold back contact fabrication technology and possibly to allow a reduction of the CdTe photoabsorber layer thickness due to inhibition of “parasitic” diffusion between front and back contacts in a complete CdTe solar cell structure.

2. Experimental details

Superstrate glass/indium tin oxide (ITO)/Cds/CdTe structures were fabricated by a typical high vacuum evaporation procedure [11]. Briefly, Cds (Aldrich, 99.995%) and CdTe (Testbourne, 99.9999%) layers with a thickness of around 300 nm and 4 \(\mu\)m respectively were sequentially deposited in a BOC-EDWARDS Auto500 high vacuum evaporation (HVE) system onto glass/ITO substrates ultrasonically cleaned in 2-propanol and de-ionized (DI) water consecutively. Before deposition of Cds, glass/ITO/CdTe substrates were annealed on a hot plate in Argon atmosphere at 450 °C for 45 min [12]. Substrate temperature of 200 °C was used during Cds deposition and 340 °C during deposition of CdTe layer. CdCl\(_2\) layers were deposited onto CdTe surface by soaking glass/ITO/Cds/CdTe substrates for 15 min in a 75%-saturated methanol CdCl\(_2\) solution. Next, the stacks were annealed on a hot plate at 415–430 °C for 25 min in air. After cooling, structures were thoroughly rinsed with DI water and blown dry with Ar.

Two types of back contacts to the p-CdTe layer have been fabricated for the structures prepared by HVE in our lab. Conventional Cu-containing back contacts were fabricated by HVE of ~6 nm of Cu and ~20–40 nm of Au onto CdTe layer, followed by heating in air to 200 °C for 30–40 min. Finally, highly conductive graphite suspension contacts (Alfa Aesar) were painted onto Cu,Te/Au layer and dried for 1 h in an oven at 60 °C. Alternatively, conductive polymer functional layers of PPy:\(\beta\)-NSA were deposited potentiostatically (Autolab PGSTAT-30 potentiostat–galvanostat) onto activated CdTe layer surface in a 0.3 M pyrrole/0.1 M \(\beta\)-NSA aqueous solution in a standard three-electrode electrochemical cell with platinum counter electrode and saturated calomel reference electrode (SCE). Prior to the deposition the pyrrole monomer (ALDRICH) was distilled under vacuum at around 35 °C. The deposition potentials were selected in the region from +0.3 to +0.7 V vs. SCE. Polymerization time (40–200 s depending on the applied potential) was calculated on the basis of Faraday’s law as described in [13] to deposit PPy films of 200–500 nm thickness. White light illumination of CdTe surface from a xenon lamp with an intensity around 100 mW/cm\(^2\) was used to facilitate PPy:\(\beta\)-NSA layer deposition at a lower applied potential range and to improve the quality of obtained polymer films. After polymerization, the PPy films were annealed on a hot plate in Argon atmosphere at 150 °C for 10 min in Omni Lab glove box. Finally, conductive graphite paste contacts (Alfa Aesar) were painted onto the PPy:\(\beta\)-NSA layer. PPy:\(\beta\)-NSA back contact has been also prepared for the structures received from the National Renewable Energy Laboratory (NREL) prepared by chemical bath deposition (CBD) and closed space sublimation (CSS) methods [14] and compared to standard NREL ZnTe:Cu back contact.

The morphology and crystal structure of the prepared glass/ITO/ Cds/CdTe samples were investigated by high-resolution scanning electron microscopy (HR-SEM) (Zeiss ULTRA 55, 2.65 kV SEM acceleration voltage) and X-ray diffraction (XRD) (Bruker AXS D5005 diffractometer equipped with Cu K\(_\alpha\) radiation source (\(\lambda = 0.154 \ nm\)), 40 kV/40 mA tube voltage/current, Bragg-Brentano configuration with graphite monochromator). Raman spectrometer with confocal microscope Senterra (Bruker) was used to study surface composition of CdTe layer before and after electrochemical treatment to determine the presence of possible additional sub layers. \(J–V\) characteristics were measured using the Autolab PGSTAT 30 potentiostat/galvanostat. A calibrated halogen lamp with an irradiation intensity of 100 mW/cm\(^2\) was used for measuring PV parameters of obtained cells. Agilent 4294A Precision Impedance Analyzer was used to measure the impedance spectroscopy of complete prepared Cds/CdTe solar cells.

3. Results and discussion

According to HR-SEM study the average grain size of the as-deposited CdTe layer is in the range of 0.7–0.9 \(\mu\)m, not exceeding 1 \(\mu\)m. The film is very compact, dense and free of visible defects. After recrystallization treatment with CdCl\(_2\) small CdTe grains are coalesced together under the influence of the relaxation of an internal lattice strain, CdCl\(_2\) sintering flux and a high temperature [4]. It’s reasonable to assume that the average grain size is increased, thus decreasing the total active grain boundary area, which is known to contain large number of recombination states.

The crystallographic orientation of as-deposited and annealed glass/ITO/Cds/CdTe structures was investigated using XRD and was found to be in agreement with literature data. The as-deposited structure exhibits a strong (111) preferred growth orientation belonging to cubic crystal structure of CdTe with additional small peaks at (311), (331), (322) and (511) reflectance planes (Fig. 1).

The (111) preferred orientation in the CdTe photoabsorber layer is completely lost after recrystallization. The intensity of (111) orientation is dramatically decreased; at the same time the intensity of (220) peak becomes similar to (111) peak, intensities of (400), (311), (422), (511) peaks increase and the (311) orientation becomes dominant. The peaks marked by asterisk (*) are signals attributed to the ITO substrate.

![Fig. 1. XRD diffraction patterns of as-deposited glass/ITO/Cds/CdTe structure and structures annealed in air with CdCl\(_2\) at different temperatures.](image-url)
PPy:β-NSA back contact layers have been electrochemically deposited onto the CdTe surface of activated glass/ITO/CdS/CdTe structures prepared in our Lab as well as onto glass/SnO2:F/SnO2:i/CdS(CBD)/CdTe(CSS) structures kindly provided by Dr. Joel N. Duenow from the National Centre for Photovoltaics, NREL. Fig. 2 shows cross-sectional micrographs of a PPy:β-NSA layer electrochemically deposited at 500 mV vs. SCE in complete glass/SnO2:F/SnO2:i/CdS(CBD)/CdTe(CSS)/PPy:β-NSA structure. It was found that PPy:β-NSA layers are readily deposited by the photo-assisted electrodeposition technique in the applied potential range from +300 mV to +700 mV vs. SCE. Resulting PPy back contact layers demonstrate excellent coverage of the CdTe surface, good uniformity and adhesion.

Results of J–V measurements for the glass/ITO/CdS/CdTe/Cu3Te and glass/ITO/Cds/CdTe/PPy:β-NSA structures are presented in Fig. 3.

According to J–V measurements, complete solar cell structures prepared by HVE with PPy:β-NSA back contact deposited at potential values of +400 mV and +500 mV vs. SCE demonstrate the best performance, comparable to structures with conventional back contact configuration. The conversion efficiency of a best device with PPy:β-NSA back contact of 8.0% is only slightly lower than that of a complete structure with conventional Cu3Te back contact (n = 9.2%).

J–V measurements of NREL structures demonstrate even more promising results. The structures with PPy:β-NSA back contact layer deposited at 500 mV vs. SCE are 10.4% efficient, which is very close to performance of the same structures with standard NREL back contact of 11.3%. It has to be noted that structures with PPy:β-NSA back contact deposited at potentials other than 500 mV demonstrate noticeably lower efficiencies (low FF and Jsc).

The reason of this phenomenon is not fully understood and needs to be additionally investigated. One of the possible reasons for such behavior is the formation of Te-rich sub layer on the surface of CdTe as a result of the electrochemical treatment during PPy deposition (according to the Pourbaix diagram of CdTe–H2O system Cd is more easily dissolved in an electrochemical cell than Te in positive region of potentials [15]). Properties of the synthesized PPy:β-NSA layer is another important factor. These properties depend on a number of parameters. The polymerization potential is affected by a Schottky-like potential barrier on the p-type semiconductor–electrolyte interface, causing a potential drop \[16\]. Next, an additional positive oxidative potential developed on the CdTe surface along with an excitation of the n–electron system of the organic molecules due to photo-excitation affects the deposition process. These factors could cause over oxidation of PPy layer at potential values over 600 mV vs. SCE and a reduction of its conductivity. It should be noted that mentioned factors are responsible for the fact that PPy films are synthesized on the surface of CdTe even when a potential of 0 V vs. SCE is applied during electrochemical deposition, when a potential of at least +0.7 V is applied for deposition of PPy onto metal electrodes. Finally, applying potential values higher than 600 mV vs. SCE together with additional developed potential might promote intensive electrochemical corrosion accompanied by hydrolysis of CdTe on the interface of CdTe/PPy with formation of a poorly conductive hydroxides and tellurium oxide sub layers between CdTe and PPy layers.

Raman spectra of all the structures show the presence of CdTe peak at 165 cm\(^{-1}\) and Te signal at 90 cm\(^{-1}\) (Fig. 4). CdTe films treated at the oxidative potential values of 400 and 500 mV vs. SCE in a background 0.1 M β-NSA aqueous solution demonstrate practically similar spectra with distinctive strong peaks at 125 and 141 cm\(^{-1}\) Raman shift value, corresponding to tellurium which are absent on the spectrum of the CdTe surface of a non-treated structure.

On the other hand the spectrum of the sample electrochemically treated at 600 mV vs. SCE has an additional peak around 470 cm\(^{-1}\), corresponding to TeO\(_4\)\(^{2-}\), evident of tellurium oxidation and hydrolysis at higher potentials, which can be responsible for the deterioration of the CdTe/PPy:β-NSA interface electrical properties in structures with PPy:β-NSA back contact electrodeposited at this potential.

The results of the impedance measurements using a two barrier model [7,17] of the best structures with PPy:β-NSA (back contact
deposited at 500 mV vs. SCE) and conventional CuTe back contact configurations, where one is the main diode barrier at the CdS/CdTe interface and the second is a back contact barrier, reveal that best structures with PPy:β-NSA back contact have about 3–4 times higher impedance value of the back contact barrier compared to structures with CuTe back contact (Fig. 5). It should be noted that comprehensive analysis of prepared back contact properties is out of scope of this current short paper and is the subject of further publications.

4. Conclusions

A number of glass/ITO/CdS/CdTe structures have been fabricated by HVE method and activated by annealing in air in the presence of CdCl₂. Photo-assisted electrodeposition of conductive polymer PPy:β-NSA back contact layers has been applied to prepare complete hybrid glass/TCO/CdS/CdTe/back contact solar cell structures. Resulting PPy back contact layers demonstrate excellent coverage of the CdTe surface and uniformity, and are able to form an electrical contact to CdTe layer without being too rectifying. It was found that PV performance of complete solar cell structures with the alternative configuration of back contact is comparable with performance of the same structures with conventional Cu containing back contact. Obtained CdS/CdTe structures demonstrate best PV performance when PPy:β-NSA layers are deposited in the potential range from 400 mV to 600 mV vs. SCE. Further study of PPy deposition procedure, e.g. in non-aqueous medias, applying of different dopants etc. is recommended to improve the PV performance of such CdS/CdTe hybrid solar cell structures with conductive polymer back contact.

Acknowledgments

Our group is grateful to the financial support from the Estonian Ministry of Education and Research under grant SF0140033s12, the Estonian Science Foundation (G8714) and the Archimedes Project “New materials for solar energetics” code 3.2.0501.10.0014. Also we would like to express our gratitude to Dr. Kristjan Laes for help with the impedance spectroscopy and to Dr. Joel Duenow from NREL for providing the structures prepared by NREL process for our experiments.

References