TALLINN UNIVERSITY OF TECHNOLOGY
FACULTY OF CHEMISTRY AND MATERIALS TECHNOLOGY
DEPARTMENT OF MATERIALS SCIENCE

Electrodeposition of polypyrrole back contact to CdTe solar cell in acetonitrile.

Master Thesis

Andrei Ogloblin

Supervisor: Dr.Sergei Bereznev, Chair of Physical Chemistry,
Senior Researcher

Materials and Processes of Sustainable Energetics
2016

TALLINNA TEHNIKAÜLIKOOL

KEEMIA- JA MATERJALITEHNOLOOGIA TEADUSKOND

MATERJALITEADUSE INSTITUUT

Polüpürrooli tagakontakti elektrokeemiline sadestamine CdTe päikesepatareile atsetonitriili keskkonnas.

Magistritöö

Andrei Ogloblin

Juhendaja: Dr. Sergei Bereznev, Materjaliteaduse instituut,
vanemteadur

Materjalid ja protsessid jätkusuutlikus energeetikas

2016

Declaration

Hereby I declare that this master thesis, my original investigation and achievement, submitted for the master degree at Tallinn University of Technology has not been submitted for any degree or examination.

Andrei Ogloblin

Acknowledgments

I would like to thank my supervisor Dr. Sergei Bereznev for his help and guidance throughout this work. This research was carried out at the Department of Materials Science. Author is grateful to the financial support from the institutional research funding IUT19-28 of the Estonian Ministry of Education and Research. I have received assistance and help from many people and I would like to thank PhD Student Jelena Maricheva for support, assistance and advice, Prof. Andres Öpik and Dr. Marit Kauk-Kuusik for providing an excellent opportunity to carry out my studies and research at the Department of Materials Science, and Prof. Enn Mellikov for his support and encouragement during my Master’s course. I am thankful to Dr. Revathi Naidu, Dr. Olga Volobujeva and Dr. Taavi Raadik for regular helping during my study. I would like to express my gratitude to Dr. Natalia Maticiuc for valuable comments and corrections. Special thanks to Dr. Julia Kois for technical support and important recommendations. I would like to thank ANTEC Solar Company for providing CdTe samples.

Table of Contents

List of Abbreviations and Notations

ACN - Acetonitrile
CBD - Chemical bath deposition
CSS - Close space sublimation
CIGS - Copper Indium Gallium Selenide
CVD - Chemical vapor deposition
CZTS - Copper Zinc Tin Sulfide
ECP - Electrically conductive polymer
FTO - Fluorine-doped oxide
HVE- High vacuum evaporation
ITO - Indium Tin Oxide
LOF - Libbey Owens Ford
NP - Nitro phosphoric acid
PANI – Polyaniline
PCE - Photoconversion efficiency
PEDOT - Poly(3,4-ethylenedioxythiophene)
PLD - Pulsed laser deposition
PPy - Polypyrrole
PTSA - *para*-Toluenesulfonic acid
PV - Photovoltaic
PVD - Physical vapor deposition
SCE - Saturated calomel electrode
SLG - Soda-lime glass
TCO - Transparent conductive oxide
Χ - Electron affinity
ß-NSA- Naphthalene-1-sulfonic acid sodium salt

Introduction

Today the most common non-renewable energy sources are oil, coal and gas. World consumption and production of crude oil and gas are growing daily. According to the British Petroleum Statistical Review of World Energy in 2014 the worldwide consumption of crude oil and gas was about 92000 thousand barrels daily. In the comparison with the year 2004 this number is 10% higher. According to the CIA World Factbook the oil will be gone in the year 2052, while gas and coal will end in 2060 and 2088, respectively. Today scientists are trying to find other renewable sources, which could replace energy-rich nonrenewable sources such as oil. It is a problem to find such source that could cover all human needs. However scientists have found many renewable sources such as wind energy, water energy and one of them is the solare energy.

Solar energy is one of the most popular renewable energy sources, as it is wide spread and relatively simple to use. According to the World Meteorological Organisation, Earth receives 1.36 W/m^2 of Sun irradiation, which in its turn is transformed by photovoltaic (PV) devices from sun energy into electrical energy. This is an attractive technology for clean energy production. It is one of the most promising, cost-effective and thus fast-growing technologies in the renewable energy production. PVs could be used in different regions of the planet. Moreover, PVs can be used even in relatively cold regions as e.g. Estonia. In cold countries low temperature compensates the lack of the solar irradiation. In hot countries semiconductors are heated up and the resistivity of material is increasing, and thus decreases performance of the solar cell. However the ammount of the solar iradiation in northern countries is smaller. The highest average irradiation that could be transformed in Estonia, according to SolarGIS yearly data, can reach 1100 W/m^2. Unfortunately exist only few kinds of really powerful solar cells that could produce such amount of energy that could supply conventional houses. CIGS, CZTS, GaAs, Si and CdTe are the most effective and powerful PV in a market. CdTe is on of representative of thin film PV market. CdTe is covering 6% of a market. CdTe have band gap of 1.45 eV which perfectly covering AM 1.5 solar spectra. CdTe photovoltaic has a privilege in cold countries compared with other PV. CdTe is more sensitive in lower illumination, what make this technology preferable in Nordic countries.

It is hard to obtain CdTe PV with high performance. Scientists are trying to find most effective fabrication process. However, CdTe PV technology has some cons as toxic activation materials, imperfection in fabrication process and back contact problem.

Unfortunately, there is no existing material with work function higher than 5.5 eV. As a result, potential barrier for hole transport is formed, what in case decrease output power.

Present work is focused on fabrication of an organic back contact to industrial activated CdTe structure in order to replace conventional back contact and compare cell efficiency. Organic back contact of polypyrrole (PPy) doped with PTSA is formed onto glass/ITO/SnO_2/CdS/CdTe structure in non-aqueous media. Electrodeposition is an inexpensive method, which provide stable, smooth conductive polymer films with good electrical properties.

1. Literature review

1.1. Current status of photovoltaics

Solar cell technology has a growing importance and attracted many efforts during recent decades. Solar cells produce so called “green energy” directly from sunlight. The essential advantage of these cells is the reduction of CO_2 emission into the atmosphere. The renewable energy sources, however, produce insufficient energy amount to cover all human needs, and the cost of the green energy is presently too high. Major problem with the energy production from the renewable sources is a small part of total energy market compared to traditional energy production. Also, the energy production from traditional sources is more stable and reliable at the moment. Renewable sources unfortunately provide only cyclic energy production when the used for production renewable factor acts efficiently (e.g. solar light, wind or water stream). Nevertheless, due to expected shortage of oil and oil shale, people started to explore the renewable sources, such as wind energy, water and solar energy. Also, this kind of energy production minimizes the environmental pollutions. One of the commonly used renewable sources is solar energy according to solar energy stability and intensity [1,2,3].

Photovoltaic (PV) cell is a device for direct transformation of sunlight into electricity on the basis of internal photo-effect. PV module has usually a metal for substrate and glass for superstrate construction design. When substrate (or superstrate) is non-conductive, it is covered with transparent conductive oxide (TCO) in order to get low resistivity conductive front or back contact. Essential part of a PV cell is a layer of photoabsorber, which is responsible for the charge carrier’s generation. PV cells make use of semiconductor compounds that convert solar photon energy into electric current. The working mechanism could be described as follows: firstly, when the photons reach the p-type photoabsorber layer, they are absorbed and the energy is transferred to electrons, further electrons penetrate from p-type to n-type material, and the photocurrent is generated in a closed circuit [4].

In the decade since 2004 to2014 the energy generated by PV modules has increased to 177 GW from 2.6 GW. Top five countries in a 2014 with a highest PV electricity production were China, Japan, United States, United Kingdom and Germany, where China holds a leading position [2]. There are three main photovoltaic technologies known on market: crystalline silicon, thin film technology and multijunction photovoltaic technology.

1.1.1 Crystalline Silicon

Crystalline Silicon solar cells are made of silicon, which in turn is obtained from sand (mostly consisting of SiO_2). PV cells based on crystalline silicon are widespread in the world. Crystalline Silicon has highest single-junction efficiency according to NREL 2015 chart except GaAs shown in Figure 1[5].

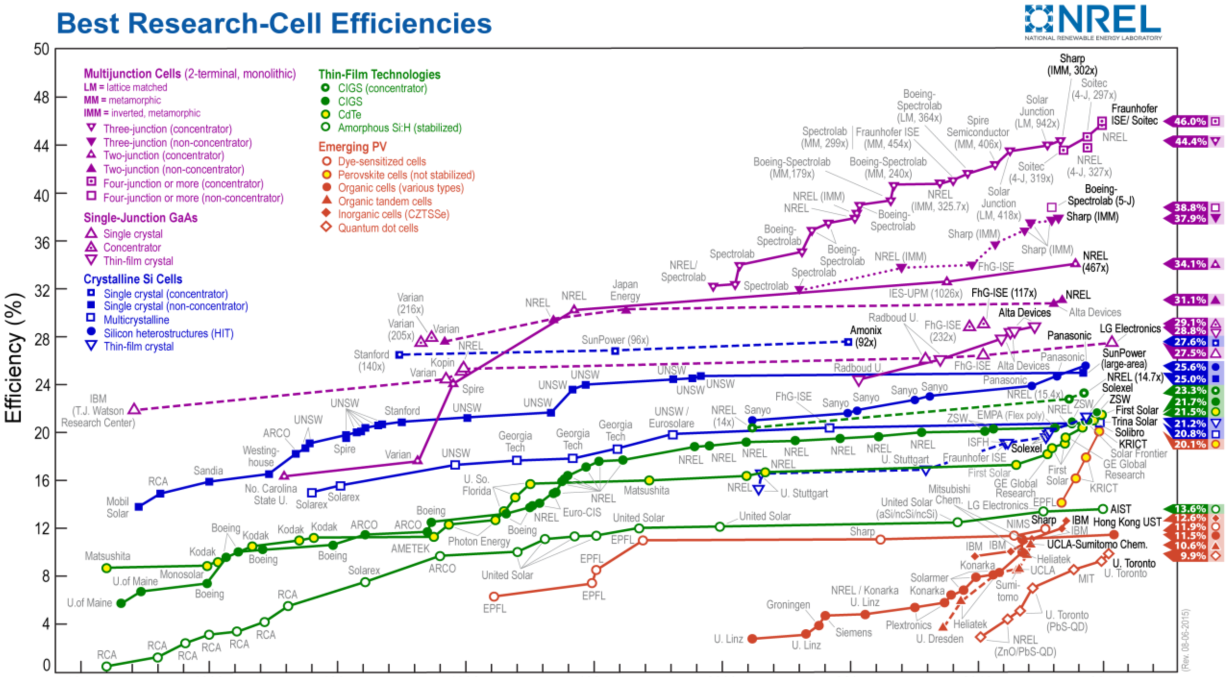


Figure 1. Best research-cell efficiencies published by U.S National Research Laboratory in 2015 [5].

However, the production technology of crystalline silicon is very expensive. Crystalline Silicon is used in the form of thin wafers (160-240 micrometers thick), sliced from single crystal ingot. Silicon single crystals have ordered structure and due to that some better parameters, and either more expensive production process compared to amorphous silicon. The highest research cell efficiency produced by Sun-Power Company has reached 25 %. Polycrystalline silicon plates for PV cells are made from a slab that is sliced into wafers. Polycrystalline silicon has grain boundaries in structure. They influence solar cell performance due to shunting paths for current. However, polycrystalline silicon has a lower price compared to silicon single crystals. Trina Solar company reached the best polycrystalline silicon efficiency, which is 20,8 %.

1.1.2 Thin film technology

Main idea of the thin film technology is to reduce the amount of expensive active materials in the solar cell (first of all - photoabsorber). Investigations of thin film materials have formed a new branch in solar cell development and design. The technology allowed producing flexible solar cells with high efficiency. The basic types of thin film solar cells are: amorphous silicon cells (a-Si), copper indium gallium selenide cells (CIGS) and cadmium telluride cells (CdTe).

The most developed thin film technology is based on amorphous silicon (a-Si). This technology is mostly used in pocket calculators, and as well as in supplying houses and building electrical systems. Amorphous silicon (a-Si: H) based solar cells are promising renewable energy sources due to their low cost, non-toxic raw material and lightweight. Amorphous silicon cells are prepared mainly by chemical vapor deposition technology. Amorphous silicon is deposited with thickness of about one micrometer. Si is commonly deposited onto substrate at the temperature of 140-200°C. The main advantage is the low manufacturing cost of amorphous silicon solar cells that makes these solar cells very popular in a market. Best a-Si laboratory cell efficiency has reached 13.6% [6,7].

Copper Indium Gallium Selenide (CIGS) based thin film technology is a less toxic than CdTe based solar cells. The World CIGS record, according to NREL efficiency chart, is 21.7% achieved by the ZSW Company. The efficiency of the CIGS solar cells remains high even being applied to the flexible substrate. The most efficient CIGS cells are generally deposited by HVE and sputtering method. However, indium is a rare element in the earth crust and thus expensive. Due to that research is concentrated on more cost-effective materials [8].

Cadmium telluride is one of the well-known and most promising thin film materials for relatively cheap photovoltaics production. CdTe is used in these thin film solar cells are based on CdTe as a photoabsorber material. Best reported efficiency according to NREL efficiency chart is 21.5% by First Solar Company. Production of the CdTe cell has small pollution footprint [9].

1.1.3 CdTe photovoltaics

Cadmium telluride (CdTe) is a stable semiconductor material with a band gap of about 1.5 eV. In 1981, Kodak built 10 % efficient solar cell by using close space sublimation (CSS) method [10]. Cadmium telluride photovoltaic cell is based on CdTe as absorber layer. Only few micrometers (μm) of CdTe is necessary to absorb sunlight due to its high optical absorption coefficient, which is greater than 10^3 cm^{-1} [11]. “First Solar” Company in 2015 achieved the best cell efficiency of 21.5 % [12]. CdTe photovoltaic is the mainly thin film technology with lower cost than usual crystalline silicon. Also CdTe production technology has the smallest carbon dioxide footprint, smallest energy payback time and minimal water consumption [13].

Advantages of CdTe over the other photovoltaics are easy and low cost technology (less than 1$ per watt), and capability to work in low-light conditions. CdTe PV cells are more powerful because CdTe matches well with sunlight, having absorption spectrum closer to sun spectrum than a number of other photoabsorber materials.

Unfortunately, CdTe PV has negative environmental and health impact, as Cd and its compounds are highly toxic. Cadmium oxide is most dangerous side-product. This side-product can be synthesized during PV manufacturing and damage breathing system or cause death.

Cd element is a long-term carcinogen and can cause detrimental effects on bones. However, CdTe is one of the most stable Cd compounds, insoluble in water and therefore less toxic than pure Cd. Pure Cd is a byproduct of zinc production. Zn is produced in a large scale and Cd without proper treatment as a byproduct can be harmful for environment. Cadmium consumption in production of photovoltaics prevents it from becoming dangerous pollution. Otherwise Cd will be buried in to the ground as a waste [14,15,16].

1.2 CdTe photovoltaic structure

1.2.1 Glass

There are two basic technologies of thin-film PV composing in industry: substrate and superstrate. For all types of thin film photovoltaics the main solid supporting frame is glass. Sometimes, polymer and metallic substrates are used as well. Substrate is the back-side of the PV module and superstrate is the cover layer. The layers are deposited in different order depending on whether it is a substrate or superstrate PV construction. The main requirements for glass properties are low absorption and reflection coefficient, environment resistivity, resistance to mechanical stresses and good temperature stability. There are many kind of glasses in a market providing these properties e.g. soda-lime glass (SLG), borosilicate glass (Corning 7059), etc. SLG or polymer should not be exposed to critical temperature to prevent the pollution of PV layers by diffusion of undesired components. Polymer substrate is a novel thin film technology, which allows forming flexible photovoltaic structures on top of the polymer surface [17].

1.2.2 TCO

Transparent conductive oxides (TCO) thin films are widely used in optoelectronic devices, photovoltaics and displays. Typically CdTe/CdS PV structures are fabricated in superstrate configuration. For high-efficiency, CdTe/CdS layers are basically grown onto TCO-coated borosilicate glass. CdTe solar cells consist of at least four layers.

Front contact is TCO, which is in contact with CdS and glass substrate. TCO can be deposited to the glass substrate by PLD, magnetron sputtering, and ultrasonic nozzle spraying or by chemical vapor deposition technique (CVD). Main goal of TCO is to reach high conductivity without losing transparency. TCO should have transparency over 90%. High conductivity is reached by doping of TCO. Most popular transparent conductive oxides are Indium doped tin oxide (ITO), Fluorine doped tin oxide (FTO), Aluminum doped ZnO (ZnO: Al) and Fluorine doped SnO_2 (SnO_2: F). Thickness of TCO can vary from 200 to 500 nm.

Ideally TCO should also have crystalline phase and lattice similar to that be grown up on it, in order to reduce strain and lattice defects [18,19].

1.2.3 CdS buffer layer

CdS is a yellow n-type semiconductor with band-gap around 2.4 eV. In case of build high efficiency PV, as much as possible radiation should reach CdTe layer. CdS is typically used as wide band gap n-type semiconductor. However, the blue portion of the spectrum is being absorbed. Due to this CdS layer is produced as thin as possible in order to reduce absorption. Basically in CdS/CdTe PV CdS layer thickness varies form 80 nm to 500 nm. However, the thickness should not be reduced below the limit 80 nm, otherwise cell will be shunted and voltage will be low. CdS is toxic especially in dust state. CdS is highly carcinogenic as Cd compound. CdS can be deposited by different techniques. Basically it is formed by high vacuum evaporation (HVE), but also can be deposited from chemical bath (CBD), by radio frequency sputtering and close space sublimation (CSS). In order to achieve high quality of films, CdS layers are exposed to the post-growth annealing treatment. Annealing treatment is required in case of recrystallization of CdS before CdTe deposition. Treatment is reducing the concentration of defects and improving CdS properties. To perform CdS annealing, deposited CdS is placed to pre-heated hot plate or furnace or heated in PVD system. Usually this process is performed in air or in the presence of N_2, at the temperature range of 300-600 ˚C for 5-30 min. Usually, $CdCl_2$ is deposited by PVD onto CdS prior annealing in order to increase cell efficiency [20].

D. Albin et al. [21] compared CSS and CBD of CdS films. Corning glass 7059 was used as substrate. SnO_2 was deposited to substrate as a TCO by a CVD. Also CdS films were prepared either by CBD or CSS method under pressure of 10 Torr. Layers were grown onto SnO_2 substrate with temperature of 475 ˚C. CBD film deposition lasted 35-40 min while CSS film preparation lasted only 4-15 min. To compare the resulting cells CdTe was deposited onto CdS at 300 ˚C in an atmosphere of O_2 (1 Torr) and helium (15 Torr). Thickness of CdTe was 10 µm. CdTe was deposited to substrate temperature of 525 and 600 °C and oxygen partial pressure of 0.1 and 2 Torr. Activation treatment was performed with $CdCl_2$. As a result CSS method yields to better quality of CdS films. The reason is higher crystallinity and grain size. Nevertheless, CBD films gave better final devices. CBD films have higher V_{oc} and higher FF, this is happen due to higher carrier life time around 500 ps while CSS 100-200 ps. Lower V_{oc} and FF can be described by different doping ratio of CdTe and CdS at interface.

CBD is based on a covering of a substrate with semiconductor material from a solution. This method is widely used due to low cost and performance simplicity.

1.2.4 CdTe

Thin-film CdTe is stable polycrystalline p-type semiconductor with band gap of 1.5 eV (at room temperature). This band-gap is very close to calculated theoretical optimum for a single junction absorber. CdTe is absorbing 99% of the incident solar radiation, that allows making relatively thin absorption layer with a minimal thickness of 1 μm. Basically the thickness of CdTe layer in solar cells is between 2 - 10 μm, because of the requirements needed for the proper electron hole depletion. It should be noted, that CdTe films are only about 8 μm thick while, crystalline silicon PV devices use 200 μm thicknesses. CdTe is more promising technology due to lower layer thickness and lower price, however CdTe is not the thinnest film absorber in the PV thin film technology. Typically CdTe can be deposited by HVE, CBD, sputtering, PLD, screen-printing, spray pyrolysis and CSS techniques. The most effective method is CSS [22]. Current highest CdTe photovoltaic record is 22.1% PCE according to NREL chart.

Ferekides et al. [23] described in detail conventional technology for a CdTe solar cell with an efficiency of 16% prepared by CSS method. They used typical superstrate configuration where borosilicate glass (Corning 7059) and soda lime-glass with SnO_2 coating were used as a substrate. Corning glass was shortly etched in dilute hydrofluoric acid before SnO_2 deposition. SnO_2 was deposited by metal organic chemical vapor deposition (MOCVD) to 7059 with a thickness 0.7-1.0 µm. SnO_2 bi-layer was deposited onto LOF in order to reduce sheet resistance R_{sh} from 20 Ω to less than 10 Ω. CBD and CSS techniques were used to deposit 60 – 100 nm of CdS. Then CdS was annealed after deposition process. CdTe was deposited onto CdS by CSS to a thickness of 4-8 µm. After deposition of CdTe structures were annealed in presence of $CdCl_2$. After CdTe treatment, etching was applied to back surface of CdTe in order to get good back contact. Etching was performed in (0.1 % by vol) bromine methanol solution. Back contact was formed by application of doped graphite paste or by deposition of Cu_xTe/Mo with following heat treatment. They found that CdS and CdTe could be deposited at high rates. Also they found that oxygen during CSS influence nucleation process by increasing the number of nucleation sites. They found that CdTe films are highly oriented when films are deposited at 600 ˚C and in presence of oxygen. At temperature below 550 ˚C films become porous and randomly oriented.

1.2.5 Activation of CdTe

Usually, as-deposited CdTe films do not provide high efficiency of PV cells without additional treatment. To get high efficiency solar cell, CdTe should be activated before application of a back contact and encapsulating. Different chlorides can be used to increase cell efficiency but only few of them are appropriate. $CdCl_2$ is the most commonly used compound that yields best efficiencies of manufactured CdTe solar cells. Activation process of CdTe is provided (i) by evaporation of about 100 nm $CdCl_2$ onto the surface of CdTe. The following stage (ii) is thermal annealing in presence of oxygen. Usually, annealing goes in temperature range between 400 °C and 500 °C for about 20 minutes. This procedure improves CdTe photoabsorbing properties [24].

Major et al. [25] investigated a low-cost non-toxic post growth activation step for CdTe solar cells. They deposited solar cell with CdTe/CdS/ZnO/FTO structure in substrate configuration. ZnO buffer layer 100-nm thick was deposited onto FTO by radio frequency sputtering. CdS window layer with a thickness of 120-nm thickness was deposited using radio-frequency sputtering technique at substrate temperature of 200 ˚C in Ar atmosphere. CSS technique was used to deposit 4 μm of CdTe with temperature of substrate and source 520 ˚C and 615 ˚C respectively under the pressure of 30 Torr. Then samples were immersed into nitric-phosphoric acid for 30 seconds. This was done to create Te-rich back surface. Few activation methods were compared. For basic activation with $CdCl_2$, 100 nm film was deposited by evaporation technique to CdTe layer. The optimum treatment temperature was 430 ˚C for 20 min. Also, activation method with non-toxic and low-cost chlorides was performed by applying drops of 10% $MgCl_2$ dissolved in 90% methanol to CdTe back contact. The results that are presented demonstrate that $CdCl_2$ can be potentially replaced with non-toxic $MgCl_2$, reducing the cost of solar cell and minimizing environmental risk. However, these results need to be confirmed by other studies.

1.2.6 Back contact to CdTe

Back contact is the final layer for superstrate CdTe/CdS solar cell. Back contact is very important part of PV devices. The critical issue in the CdTe/CdS cell production is to form low-resistive and stable ohmic contact with p-type CdTe. CdTe has a high electron affinity (x = 4.5 eV) with a work function higher than 5.7 eV. Due to this p-type CdTe and metallic back contact are forming Schottky barrier (a potential energy barrier that is formed by metal and semiconductor contact). This is the case when the work function for metal is smaller than for p-type material. Different treatments such as annealing, etching, doping are applied prior to back contact deposition. One of the most effective is etching with nitric-phosphoric acid NP. Also, to decrease diffusion and form better contact buffer layers are applied [26].

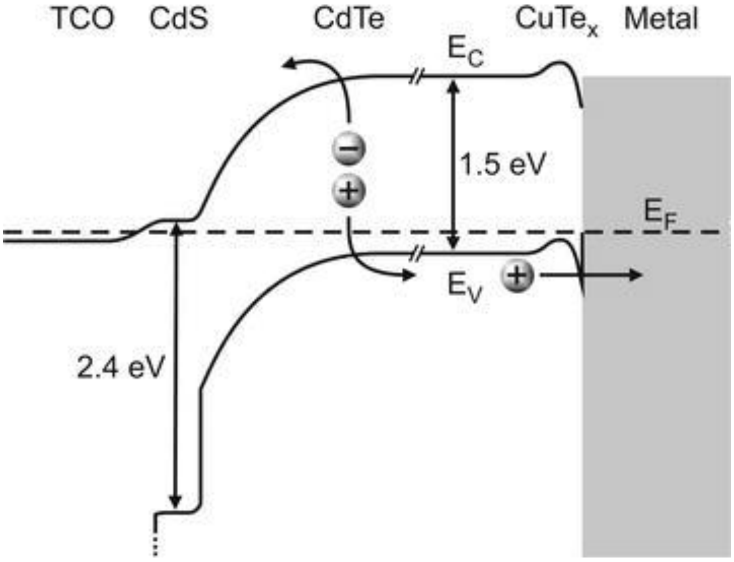


Figure 2. Energy band diagram of TCO/CdS/CdTe/CuTe$_x$/Metal solar cell [27].

Differently doped semiconductors show p- or n-type of conductivity. In p-type semiconductors Fermi level is shifted to valence band while in n-type Fermi level is shifted to conductive band. When two semiconductors n-type and p-type are connected, then Fermi level is equilibrated. Figure 2 shows a p-n junction (heterojunction) formed between CdS and CdTe layers. Heterojunction is a result of a connection of two or more p- and n-type semiconductors from different materials. As it can be seen from Figure 2 in the border between CdTe and metal is a highly p-doped region. This region was formed in order to reduce potential barrier and get low resistance ohmic back contact.

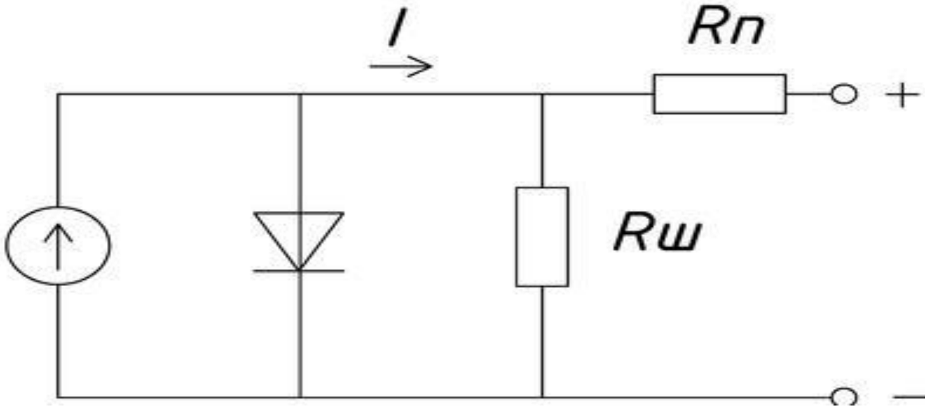


Figure 3.The equivalent circuit of the solar cell [28].

To illustrate the ideal solar cell model, the equivalent circuit was represented in Figure 3. This Figure is describing a ideal and simplest equivalent circuit of a photovoltaic cell.

In Figure 3 diode is in parallel connection with photo generated current source. Rn is the series resistance, which is caused by bulk resistance of materials in solar cell and Rw- is the shunt resistance of the solar cell, which is caused by cell defects. Series connection resistance Rn, for ideal cell should be zero and shunting resistance Rw should be as large as possible, ideally should be infinite. Series connection resistance is decreasing fill factor of the solar cell. As can be seen from Figure 4 increased series resistance can directly influence the slope and FF is decreased.

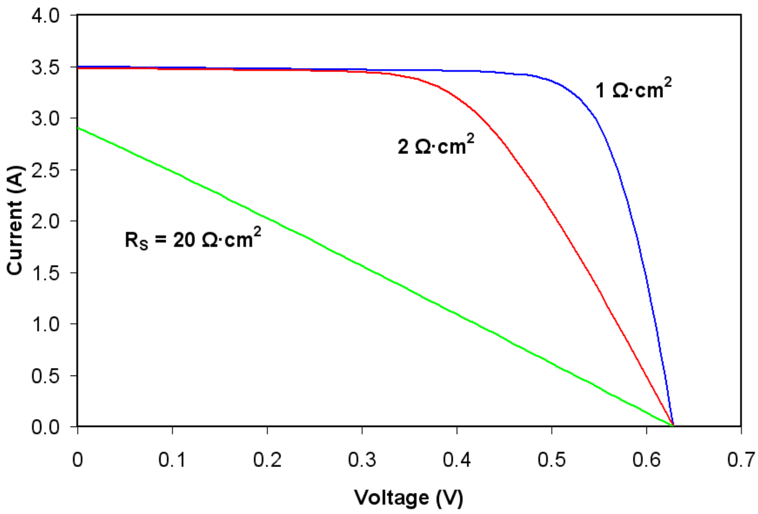


Figure 4. Series resistance influence to cell I-V curve [29].

Back contact with high resistivity can decrease PV efficiency. Interface of metal and n-type semiconductor create Schottky diode, which is in opposite direction from the main CdS/CdTe junction diode. It can decrease PV parameters by bending curve in other direction.

CdTe structures are typically exposed to etching after annealing. Etching is important step for formation of Te-rich (silver-gray) layer on top of the CdTe photoabsorber. Main idea and purpose of etching is to create quasi-ohmic p+ back contact to CdTe layer. It is difficult to form a highly doped p-type CdTe thin film with low-resistance contact. Etching process can be performed out in three typical solutions: NP, bromine-methanol and potassium dichromate sulfuric acids. NP provides better contact performance [30].

Fang et al. [31] claim that NP etching helps to form p+Cu_xTe alloy during Cu deposition. Also, they state that using ZnTe as a buffer layer between CdTe and Cu back contact can suppress the Schottky barrier and reduce the contact resistance. They noted that using Cu might reduce PV lifetime by diffusing through grain boundaries and cause shunt problem. Such metals as W, Al, Ni and Mo can be used as alternative to increase lifetime. Sb_2Te_3 is used as a low resistance high effective buffer layer material with Mo or W contact. High efficiency as high as 16% is provided by innovative As_2Te_3/Cu/Mo bilayer buffer structure. Furthermore, As_2Te_3 is deposited directly onto CdTe layer without etching process.

Bätzner et al. [32] studied influence of CdTe/CdS solar cell etching with different acids. They deposited CdTe and CdS with CSS method on TCO coated soda lime glass. After deposition structures were exposed to etching to produce Te-rich surface. Sb/Au back contact was deposited by evaporation. For a reference purpose Cu/Au back contact was prepared. Before depositing of a back contact onto CdTe layer-etching step was performed. They investigated three basic etching solutions: bromine-methanol, nitric-phosphoric acid and concentrated nitric-phosphoric acid. Etching with concentrated NP acid produce a low resistive Te-rich surface on top of the CdTe absorber layer. The efficiency of as deposited solar cell is up to 12.5% despite a strong rollover of JV-curve. They also found that Sb/Au is more stable and much better than Cu containing back contact.

1.3 Issues related to CdTe PV

CdTe is very prospective and fast developing object in PV thin film technology. As all real technologies, CdTe technology also has issues. Activation process using $CdCl_2$ in the presence of oxygen is not fully understood. One of the most important is back contact problem. Forming of a stable, low resistance back contact is hard and long procedure. To form a good contact, different techniques and different etching, annealing treatments must be applied. Sometimes interfacial layers are doped with additional impurities. Properties of a CdTe PV depend on deposition parameters. With changing of parameters, grain size, thickness the properties of PV can vary. Furthermore as mentioned above, back contact material play important role in diffusion, which can cause shunts or defects [33]. The alternative application of high work function electrically conductive polymers (ECPs) as effective and stable back contact functional layers for CdTe solar cells is the main idea of current work.

1.4 Electrically conductive polymers

A polymer is an organic chemical compound where molecules are bonded together in long repeating chains. Electrically conductive polymers (ECPs) have become very popular material and attracted attention of scientists and manufacturers in the last few decades. In the recent years, these materials have a wide range of applications in different fields of science and industry such as mechanical engineering, energy capacitors, electronics, PV, optics, and chemical manufacturing. The main reason why polymers have become popular is the variety of its properties: p- and n-type conductivity, variety of band gap, photoabsorbing and optical transmission properties, etc. ECPs are low cost organic materials with electrical properties of semiconductor. These properties are connected with the kind of polymer and its structure. High electrical conductivity can be reached by doping of backbone of ECPs. Such functional groups as halogens, nitrides, carboxydes that polymer contains, induce special properties as chemical resistivity, solubility etc. The first who discovered electroconductive properties of polymer was H. Shirakawa and Alan J. Heeger in the year 1977 [34].

Several most promising conductive polymers are attracting attention nowadays, are: PEDOT (poly (3,4 ethylenedioxythiophene)), PPy (polypyrrole), PANI (polyaniline), etc. represented in Figure 5. These polymers exhibit relatively high conductivity and demonstrate stability and a long lifespan. The conductivity of polymers is connected mainly with such factors as polymer structure, doping and deposition technique [35].

The mostly world-spread polymer is a polyethylene. This polymer chain consists of ethylene monomers that form sp^3-hybridized covalent bonds. These sigma bonding's have low mobility and do not promote electric current. ECPs have sp^2 hybridized carbon centers that form P_z orbitals and P_i bonds. After oxidation of sp^2-hybridized polymers, the mobility of electrons is increased which is due to removal of delocalized electrons. The band becomes conductive when electrons are partially displaced. The conductivity of normal polymers is around 10^{-10} S/m while some ECPs have conductivity close to10^5 S/m [36].

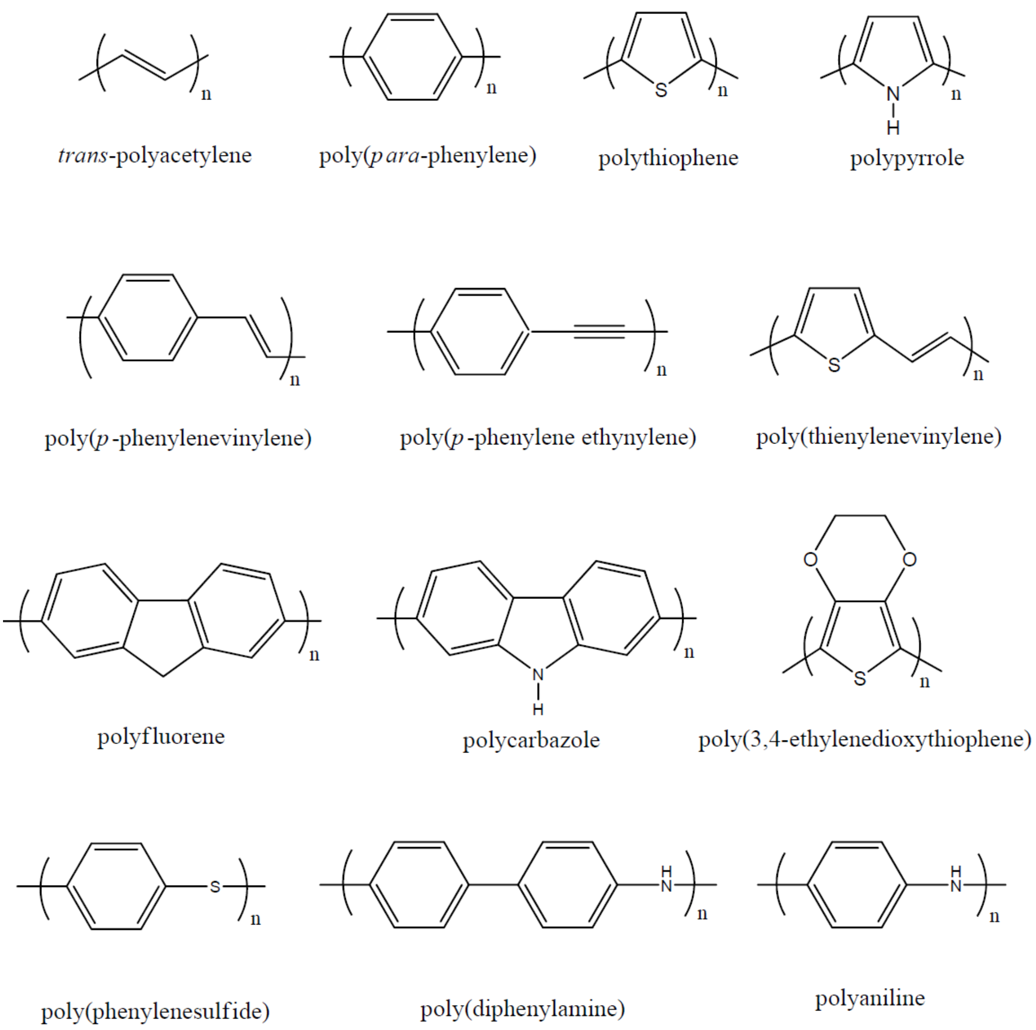


Figure 5. Main monomer structures of ECPs [37].

1.4.1 Polypyrrole

Polypyrrole (PPy) consists of four carbon atoms and one nitrogen atom that are connected to the ring and form a long chain of molecules (Fig. 5). PPy has been investigated over the last decades due to relatively high stability, low cost, low toxicity, and high electrical conductivity. The existence of nitrogen heteroatoms determines the resulting properties of PPy. PPy is a polymer that is produced from pyrrole by monomer oxidation process that forms a chain with the overlapping P_i-orbitals. PPy was chemically synthesized in 1916 by oxidation of pyrrole with hydrogen peroxide [38]. The first electrochemical synthesis of PPy was suggested in 1963 by B.A.Bolto et al [39].

1.4.2 Chemical synthesis of polypyrrole

PPy can be synthesized chemically and electrochemically. In chemical polymerization, dissolved pyrrole is treated by strong oxidizing agent. The first stage of polymerization is connected with forming of the radical-cations as the result of an initial oxidation of pyrrole molecule. These radical attacks another pyrrole monomer creating dimer radical cation, which becomes further, oxidized. The polymer chains are growing until the termination as shown in Figure 6 [40].

Typical chemical oxidants that are used for polymerization of pyrrole include iron(III) chloride, iron(III) perchlorate, ammonium peroxydisulphate and others. Certain organic oxidizing agents have been tested and films created by the use of these oxidants demonstrated low conductivity. The salts of transition metal are generally used [40].

PPy synthesis in vapor phase polymerization is rarely used. Coating of a surface by oxidant from the solution start this process. Then the surface is subjected to vapor of pyrrole monomer. In this case polymer is forming a film directly on the surface. This method employs such oxidants $FeCl_3$ or H_2O_2 [41].

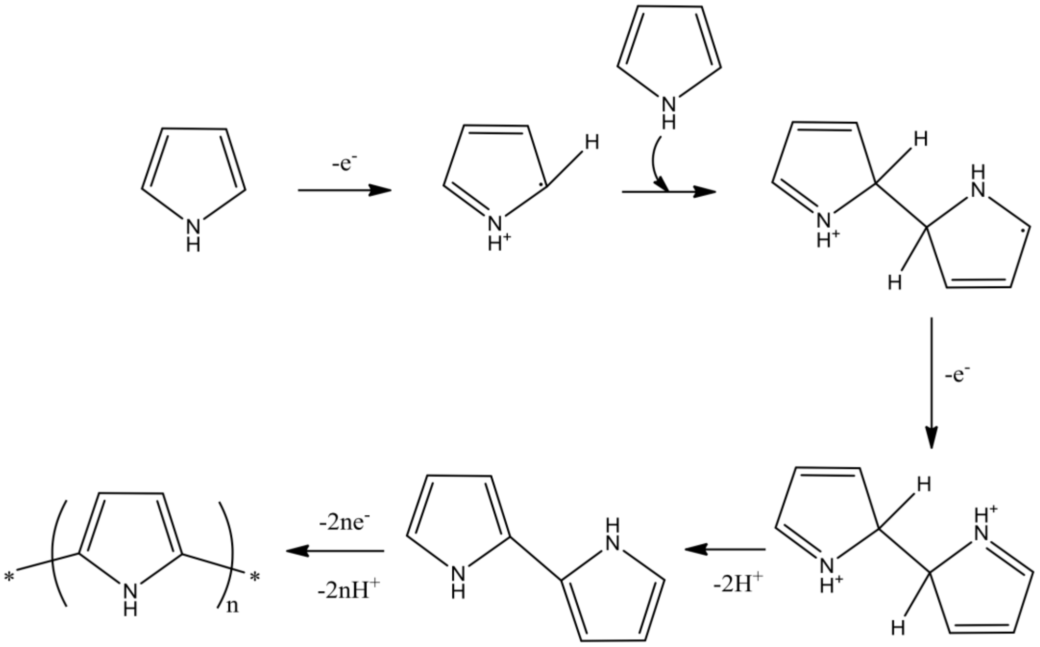


Figure 6. Mechanism of chemical synthesis of PPy [42].

Nakata et al [43] synthesized PPy by interphase oxidative polymerization. They cleaned pyrrole monomer in distillation column. Polymerization was performed in mixture of two solutions, which contained pyrrole solution in organic solvent, and the oxidants in aqueous media. The following oxidants were used: iron(III) chloride, iron(III) sulfate, iron(III) nitrate, and iron(III) perchlorate. Benzene, toluene, anisole, cyclohexane, n-pentane and n-hexane were taken as organic solvents for pyrrole. The two-phase solution was kept under constant reaction temperature. When polymerization process was finished, films were washed by water/methanol solution and dried under vacuum for 24 h under 45˚C. The diffusivity of pyrrole from organic to aqueous medium was found to be a primary factor of conductivity and film thickness.

1.4.3 Electrochemical synthesis of polypyrrole

In electrochemical synthesis of PPy, oxidative potential is applied to the working electrode in the electrolyte, which contains a pyrrole monomer dissolved in aqueous or non-aqueous media and doping salt or acid (sulfonates, etc.), which works as electrolyte and doping agent for synthesized PPy layer. Usually, three-electrode cell is used in order to control the polymerization process. Three-electrode cell includes working electrode (WE) for deposition of PPy layer, reference electrode (RE) e.g. saturated calomel electrode (SCE) and counter electrode (CE) e.g. Pt plate. WE is usually selected according to the work requirements, but basically there is used metal or transparent conductive oxide (TCO) electrodes. To initiate polymerization process, oxidative potential can be applied to the three-electrode electrochemical cell by potentiostat. The polymerization starts on the surface of the WE [44,45].

The mechanism of the electro polymerization of pyrrole consists of two main steps, initialization and propagation step [46].

The initialization step includes electron loss by pyrrole monomer due to applied potential, thus radical cation is produced Figure 7.

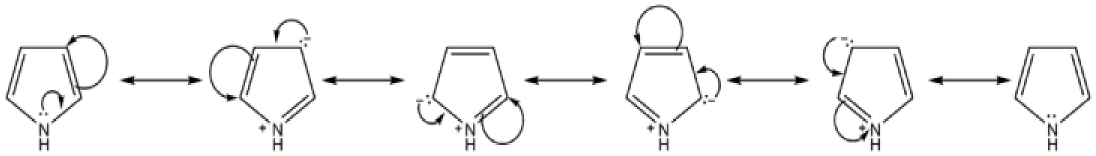


Figure 7. Radical cation formation scheme [47].

The propagation step is process of forming radical dimer with a second radical cation, Figure 8.

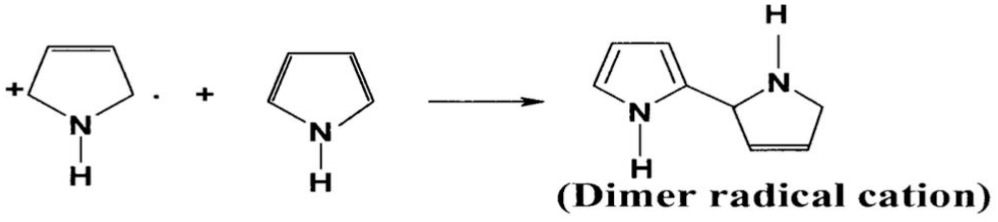


Figure 8. Radical cation dimer formation scheme [48].

The process of the radical linking can be continued until the brake of the chain. PPy chain is growing on the surface of the electrode and forms a thin polymer film. The form and length of the PPy chain depends on the applied current, density value, temperature, pH, electrode material, electrolyte, solvent and monomer concentration. The mass of the deposited polymer onto the electrode can be calculated by the Faradays law $m = \frac{Q}{F} * \frac{M}{Z}$ where m = mass (kg), Q = total charge (C), F = 96,500 (Faraday's Constant(C mol^{-1})), Z = valence, M = Molar Mass (kg/mol) [49, 50]

Different electrochemical deposition techniques are used to cover the different electrodes with thin PPy film: potentiostatic, galvanostatic, impulse and potentiodynamic method. The appropriate method can be selected according to the required final film structure and properties [51].

Also the result of PPy deposition depends on the solution temperature and concentration, applied potential, current density and nature of WE. The surface of the electrode, where the electro depositions take place, should not be oxidizable in the range of applied potentials, otherwise electrode surface oxidation process will compete with monomer oxidation process and thus reduce PPy deposition rate, adhesion and interface properties [52].

1.4.4 Photo-assisted electrodeposition technique

Conventional electrodeposition of PPy is commonly carried out in a solution of pyrrole and dopant (sulfonates, etc.). The required electro-deposition potential is around 700 mV vs. SCE in a water solution. This potential value provides covering of the surface of WE with highly conductive PPy layer. The amount of polymer that covers the surface is proportional to the applied current density [53].

In case of solar cell structures the conventional electrodeposition technique is not suitable sometimes. When the polymer is deposited onto photoabsorber layer as a functional layer, this polymer covers all surface, and penetrates into possible cracks and holes in photoabsorber layer. Therefore, this can cause the short circuits. These short circuits can reduce solar cell efficiency. Moreover, electrical resistance of the solar cells in the dark is relatively high and therefore current density and deposition rate of ECP can be reduced.

Photo-assisted electrodeposition technique uses light irradiation during electrodeposition process. The light beam is concentrated onto photoabsorber layer, which can absorb this light and produce extra charge carriers. In this case ECP is depositing only onto photoactive area, where the potential created by the photo absorber and potential created by the potentiostat in sum are equal or greater than minimal one required for monomer oxidative electro-polymerization. Photo-assisted method is providing active photo absorber covering. Damaged parts of a photoabsorber layer remain uncovered, due to lack of required potential in the cracks, holes, etc. [54].

Recently, our group [54] investigated photo-assisted electro polymerization of PPy in aqueous media. Polypyrrole was deposited potentiostatically onto CdTe layer in complete CdS/CdTe solar cell structure. Three-electrode cell was used. The concentration of 0.3 M pyrrole/0.1M Naphthalene-1-sulfonic acid sodium salt (ß-NSA) in solvent was used for deposition. Deposition potential was chosen in the range of 0.3-0.7 V vs. SCE. Xenon lamp was used to initiate polymerization process at lower applied potential. The PV structure with alternative PPy contact were shown to be comparable with conventional p+ CuTe back contacts. Also photo-assisted electrodeposition provides good uniformity and coverage of CdTe surface with PPy layer.

1.4.5 Electrodeposition in non-aqueous media

Electrodeposition processes are mainly carried out in aqueous solutions as appropriate media with predictable electrochemical properties.

On the other hand, different non-desirable processes for photoabsorber layer can take place during electrodeposition in water solution, such as hydrolysis and hydration. These two main processes can damage the photoabsorber interface, which in turn decreases cell efficiency. This could be caused by CdTe oxidation products such as salts, oxides and hydroxides, which can be formed during electro-polymerization of polymer on CdTe interface in aqueous solution.

Some semiconductors or metals are difficult to deposit from aqueous solution, they are deposited at higher potential than the reduction potential of water. Also some materials cannot be dissolved in water. Non-aqueous media are used for hydrophobic deposition. Non-aqueous solutions are based on organic solvents, ionic liquids and molten salts. These solvents have wide electrochemical window. Deposition in non-aqueous media can protect structure from degradation and provide better solubility for different compounds [55]. In this work acetonitrile (ACN) was used as a solvent to prepare electrolyte for PPy electrodeposition. ACN is stable, cheap and widely spread in organic synthesis as a solvent. ACN is a polar solvent, which is miscible with water and a number of organic solvents. ACN is a transparent liquid with molar mass of 41,05 g/mole and boiling temperature of 81.6 ˚C.

1.4.6 Doping of polypyrrole

Doping is a process of modification of chemical bonds in material, which leads to increase of electrical conductivity. The increase of conductivity in ECPs can be produced by partial chemical oxidation (p-doping) or reduction (n-doping). Almost all conjugated polymers can be partially oxidized or reduced by electron acceptors or donors. It was investigated that the n- and p-type dopants could compensate each other. The electron acceptors as I_2, AsF_5 can provide p-doping and electron donors (Na, K) provide n-doping.

The sulfonates are the salts or esters of the sulfonic acid. Sulfonates are well soluble in non-polar solvents such as organic solvents or oils. The sulfonates are mostly used in chemical synthesis as a doping material for conductive polymers. Sulfonates act as anionic dopants for the ECPs synthesis. During polymerization process, between sulfonate anions and polypyrrole cation electrostatic binding is being formed.

Bilal et al [56] studied chemical synthesis of PPy doped with dodecyl benzene sulfonic acid. They distilled pyrrole monomer prior to use. For experiment 0.29 mol of chloroform was added to flask and mixed with 0.00125 mol of benzoyl peroxide.

When mixture was stirred, 0.13 mol of 2-butanol, 0.00373 mol of DBSA and 0.00043mol of pyrrole was added into flask. Finally 0.28 mol of water was added to mixture.

Solution was filtered from organic precipitation (polypyrrole). They have obtained PPy-DBSA salt by dodecyl benzene sulfonic acid as a dopant and surfactant. Benzoyl peroxide was used as an oxidant and solution from chloroform and 2-butanol was used as a novel dispersion medium. They found that different concentration of oxidant and monomer can affect the yield of PPy-DBSA salt.

Moreover well-known and studied PEDOT: PSS polymer complex, where PSS (polystyrene sulfonate) is a doping agent. In case of PEDOT: PSS, sulfonate play doping role.

Also, PSS help to form stable aqueous suspension of the polymer, what could be further used for spin casting. This complex is often used to get uniform and highly conductive PEDOT:PSS coating.

The ECPs can be also doped using electrochemical potential. The doping can be obtained by application of a constant voltage to electrodes. Electrochemical doping is more precise than chemical and can be controlled by monitoring the current. Doping and undoing processes are highly reversible without chemical bi-products [57].

Alvaro et al [58] studied of kinetic formation and the electrochemical behavior of PPy films. PPy deposition was performed from three-electrode electrochemical cell, with ultrapure water solution as a solvent. Deposition was carried out at room temperature under constant potential of 0.8 mV vs. Ag/AgCl electrode in solution of 0.1 mol of H_2SO_4 and 0.2 mol of pyrrole (pH 6.5).

They reported that concentration of dopant in solution could directly affect the voltammetry response of PPy films and affect electrochemical formation. Also they noted that lower deposition potential is influencing the formation structure of PPy backbone. The films obtained at lower potential are more conjugated and therefore more electro-active than film obtained at higher potential. They noted that dopant is influencing to nucleation, growing and induction time.

1.5 Aim of the study

The aim of present investigation is connected with developing of highly conductive PPy back contact to a CdTe solar cell as alternative to conventional back contact in order to reduce production cost and increase cell efficiency. Work is focused on finding appropriate electrodeposition parameters of ECP back contact layer on CdTe layer in non-aqueous media of ACN. For this purpose, PPy has been selected as low-cost, relatively stable ECP with good electrical properties. In addition, the aim of study is focused on electrodeposition of PPy in non-aqueous media to avoid electrochemical degradation of CdTe interface.

2 Experimental Details

2.1 Materials and methods

Activated superstrate CdTe/CdS/SnO_2/ITO/glass cells without back contact have been received from Dr. Stefan Oelting and his group at ANTEC-Solar Company (Germany). According to ANTEC-Solar data, activated CdTe structures are based on low-iron float glass substrate of 4 mm thick that is coated with ITO/SnO_2 with thickness of 240/25 nm, respectively. CdS layer of 100 nm thick was deposited onto ITO/SnO_2, and finally CdTe with thickness of 4.5 µm was deposited on top of CdS by CSS technique.

Pyrrole monomer (reagent grade, 98%, Sigma Aldrich) was distilled under vacuum prior to use. *p*-Toluenesulfonic acid monohydrate (PTSA, SigmaAldrich) was used as a dopant for electrodeposition in ACN solutions. For aqueous media deposition Naphthalene-1-sulfonic acid sodium salt (ß-NSA) was used as a dopant. PTSA and pyrrole (anhydrous, 99.8%, Sigma Aldrich) and pyrrole with ß-NSA were dissolved in acetonitrile and water respectively. Electrochemical syntheses were performed by using Autolab PGSTAT30 potentiostat/galvanostat in a three-electrode electrochemical cell equipped with platinum counter electrode (CE), saturated calomel electrode (SCE) as a reference electrode (RE) and CdTe/CdS/SnO_2/ITO/glass structure as a working electrode (WE). Highly-conductive graphite suspension (Alfa Aesar) was used for the graphite dot-contacts preparation.

2.2 NP-etching

The CdTe/CdS/SnO_2/ITO/glass samples were etched in nitric-phosphoric (NP) acid. 1% of HNO_3, 70% of H_3PO_4 and 29% of H_2O were mixed according to NREL recipe to prepare NP acid solution. Samples were immersed into the acid solution for 30 sec to obtain Te-rich sub-layer on CdTe layer. After treatment samples were rinsed with Millipore water in case of the following PPy electrodeposition in aqueous media or rinsed in acetonitrile (ACN) in case of the following PPy electrodeposition in non-aqueous media (ACN). Finally, samples were dried under nitrogen flow.

2.3 Polypyrrole back-contact fabrication

A solution for PPy electrodeposition was prepared by dissolving of 0.1 mol/L PTSA and 0.1 mol/L pyrrole monomer in acetonitrile step-by step. First, PTSA was dissolved in acetonitrile using magnetic stirrer. Pyrrole was added dropwise in solution under continuous stirring in order to dissolve completely. The mixture was stirred for 15 min in order to get transparent homogeneous solution. Electropolymerization was carried out in a three-electrode cell potentiostatically by using potentiostat/galvanostat Autolab PGSTAT 30 at RT. To initiate a photo-assisted electrochemical polymerization process we used red semiconductor laser (670 nm, spot size 5 mm) with light intensity of 20 mW/cm^2 as illumination source. A laser was installed to illuminate the CdTe layer directly in an electrochemical cell. Figure 9 (a,b) shows setup for photo-assisted electrochemical polymerization.

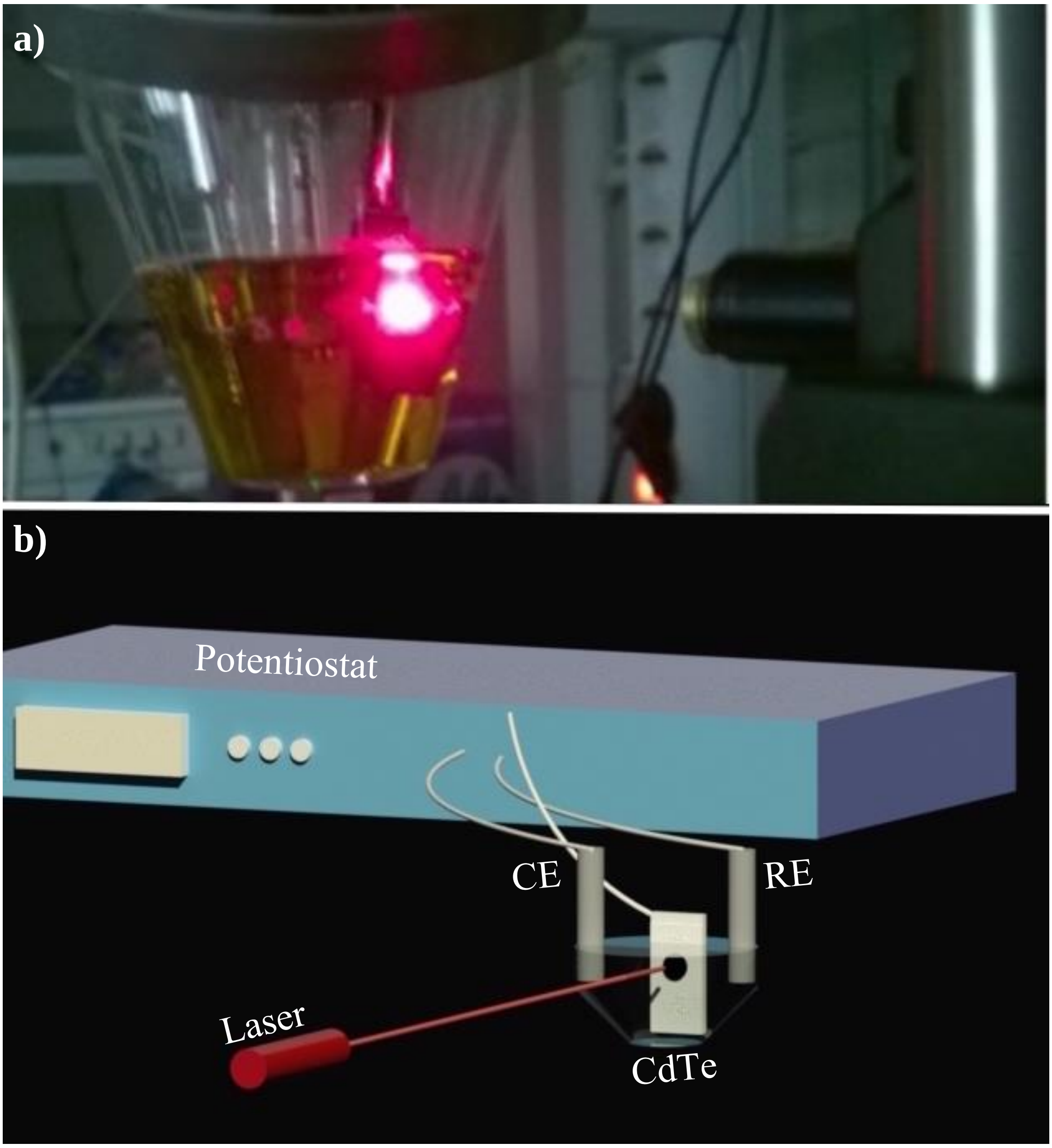


Figure 9 (a) – Photograph of electrochemical cell irradiated with laser and (b) – schematic drawing of setup for photoassisted electrodeposition.

The photo-assisted electrodeposition of PPy layers were performed potentiostatically in the range of applied potentials from 100 mV to 800 mV vs. SCE. Eight etched samples (d25-d32) were covered with PPy:PTSA films in acetonitrile media under laser-beam irradiation. Electrodeposition time was 20 min.

In order to compare the results of PPy back contact deposition in aqueous media and non-aqueous media, water based solution of 0.1 M of Naphthalene-1-sulfonic acid sodium salt (ß-NSA) and 0.3 M of pyrrole was also prepared. First, ß-NSA was dissolved using magnetic stirrer. Then, pyrrole was added dropwise under continuous stirring to dissolve completely. Photo-assisted electrodeposition in aqueous media was performed with the same conditions as for ACN solutions. After the polymerization, prepared glass/ITO/SnO_2/CdS/CdTe/PPy samples were rinsed with acetonitrile or Millipore water, depending on the media used for the electrodeposition, and finally dried under nitrogen flow. Graphite suspension dot-contacts were painted onto the prepared structures and dried at 60 ˚C for 10 min. Finally, CdS/CdTe/PPy layers were scribed around the graphite contact to limit the area for the I-V measurements.

2.4 Investigation of prepared hybrid structures

The morphology of prepared superstrate PPy/CdTe/CdS/SnO_2/ITO/glass structures was investigated by high-resolution scanning electron microscopy (HR-SEM, Zeiss Merlin). The compositional phase purity of the CdTe interfaces before and after NP-etching and electrochemical treatment was analysed by Raman Spectroscopy (Horiba LabRam HR spectrometer) using 532 nm green laser as an excitation source, which was focused to a 1 μm size spot and the spectral resolution of the system was around 0.5 cm^{-1}. All I-V measurements of prepared hybrid structures were performed by using potentiostat/galvanostat Autolab PGSTAT 30 equipped with laboratory-made spring contacts system.

3 Results and Discussion

3.1 Photo-assisted electrochemical synthesis

Prior to PPy deposition, the CdTe/CdS/SnO_2/ITO/glass structures were exposed to etching in NP solution for 30 seconds. Etching process is forming low resistant Te-rich interface on top of polycrystalline CdTe structure and clean the surface of CdTe from different impurities (organic and inorganic). PPy back contact was deposited potentiostatically onto glass/ITO/SnO_2/CdS/CdTe structures received from Antec SOLAR Company. According to Antec SOLAR data, these cells (10*10 cm) with conventional back contact (soft NP etched, sputtered Sb_2Te_3+sputtered Mo) have efficiency around 10%.

Photo-assisted electrodeposition technique uses light irradiation during electrodeposition process. The light beam is concentrated onto photoabsorber layer, which can absorb light and produce extra charge carriers. Therefore, overall resistivity of the PV structure can be decreased and additional oxidative potential can be induced on the CdTe interface in electrochemical cell.

Electrodeposited PPy thickness can be calculated by the Faradays law $= \frac{Q}{F} * \frac{M}{Z}$, where m = mass (kg), Q = total charge (C), F = 96,500 (Faraday's Constant (C mol^{-1})), Z = valence, M = Molar Mass (kg/mol).

All the electrodepositions were performed potentiostatically during 20 min. The dependence of current density vs. time at various applied potentials in electrochemical cell is represented in Figure 10. After the start of the electrodeposition process, decrease of current density is observed. This behavior can be attributed to the nucleation stage and growth of the polymer film that is accompanied with the increase of resistivity of the structure. When the polymer film has covered the CdTe surface the current density is slowly decreasing. It should be noted, that PPy films start to grow at minimal oxidative potential value of 100 mV vs. SCE under laser beam irradiation conditions. PPy films deposited without photo-assistance start to grow from the potential value around 600 mV vs. SCE.

Photographs of obtained structures with PPy back-contacts covered with graphite are represented in Figure 11 (left was deposited under 700 and right under 200mV vs. SCE). According to visual control, PPy polymerization process starts simultaneously in many places on the illuminated surface of CdTe. Polymerization process is divided to three steps: (i) CdTe interface layer starts to getting darker and then (ii) polymer nucleation centers became visible on surface of the CdTe, and finally (iii) growing step when PPy films keeps growing slowly.

As the result conductive PPy layer covers the whole illuminated area of CdTe. It should be noted, that samples illuminated with laser beam under applied electrodeposition potential of 800 mV vs. SCE, started to change their color after 100 sec of the deposition process, while under potential of 400 mV vs. SCE, CdTe structures started to change their color after 400 sec. The structures that were exposed at 100 mV vs. SCE changed color only after 10 minutes. The color of the CdTe layer has changed from silver-metal (Te-rich layer) to dark-green, that indicates the deposited PPy: PTSA layer. It should be noted, that the PPy films obtained in acetonitrile solution under applied potentials of 100-800 mV vs. SCE are smooth without any visible defects and holes, and with green color.

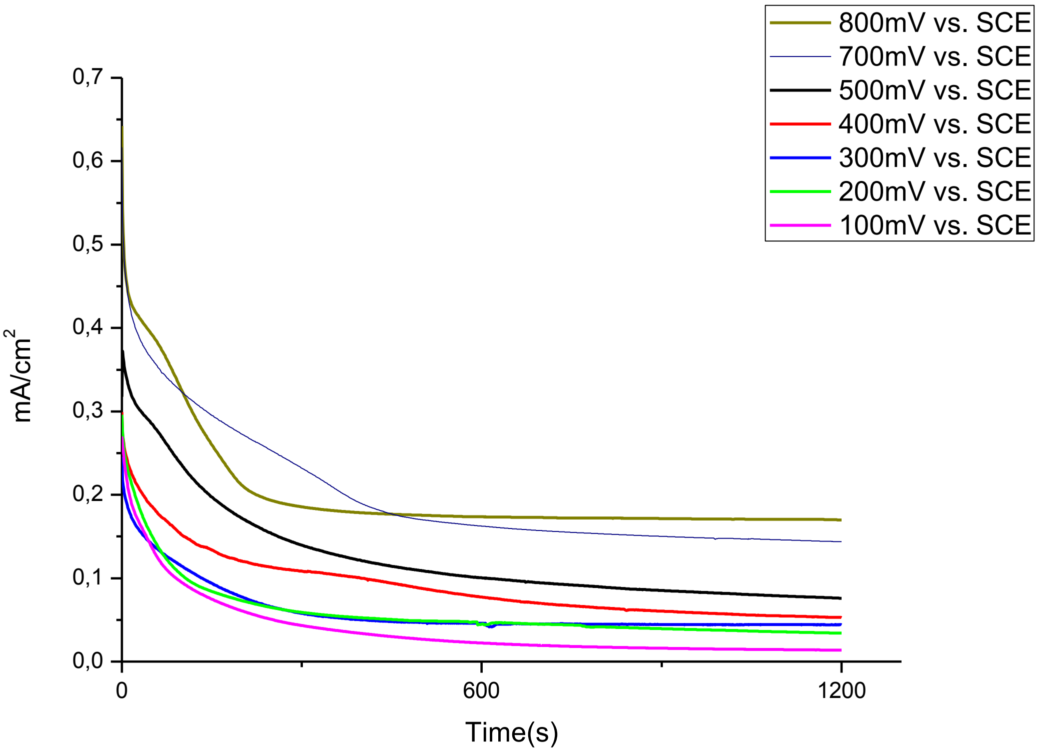


Figure 10. Electrodeposition curves of PPy: PTSA layers onto CdTe layer in ACN solution under laser beam illumination with an intensity of 20 mW/cm^2.

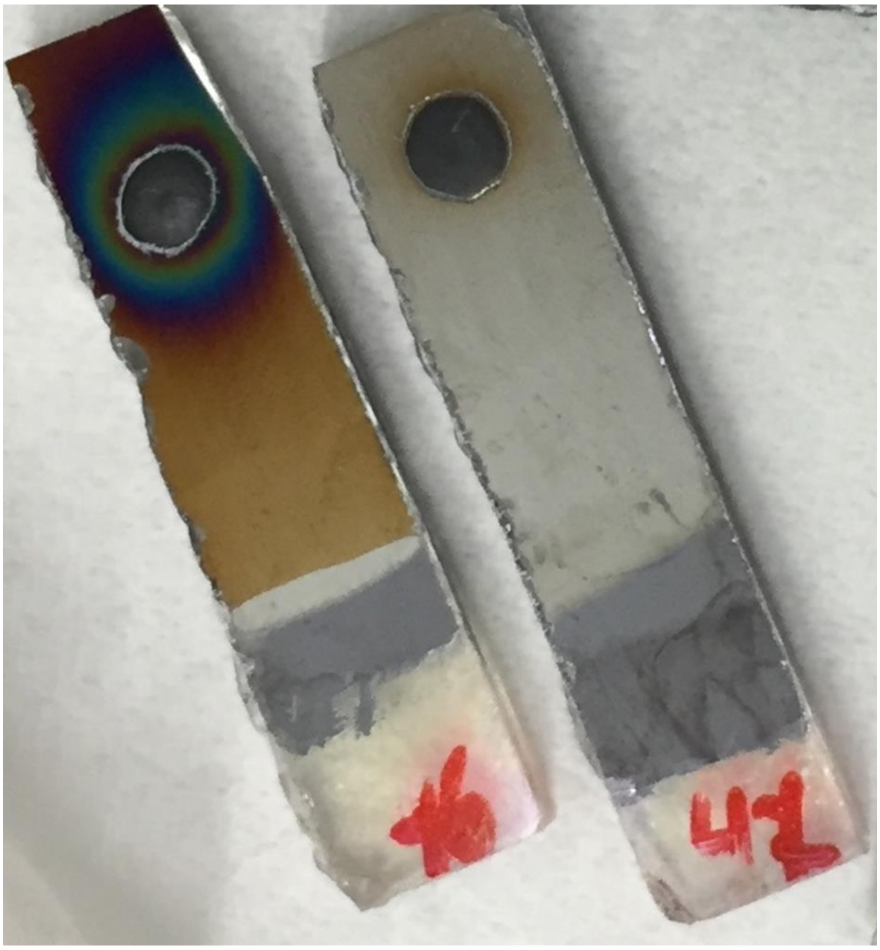


Figure 11. Photograph of scribed samples of graphite/PPy:PTSA/CdTe/CdS/SnO_2/ITO/glass structures (from left to right – PPy deposited at 700mV and 200 vs. SCE.

3.2 Study of morphology

The surface morphology of prepared PPy:PTSA/CdTe/CdS/SnO_2/ITO/glass structures were studied by high resolution scanning electron microscopy (HR-SEM) Figure 12 shows the micrographs of the surface of etched in NP-acid CdTe layer before PPy deposition. It can be seen, that CdTe layer is not smooth and includes non-deep holes and micro cracks.

Figure13 (a,b) show the morphology of PPy layer on CdTe surface at different magnifications. It can be seen, that PPy: PTSA film covers the CdTe surface continuously without cracks and holes in good agreement with the relief of the CdTe surface (Figure12 a, b).

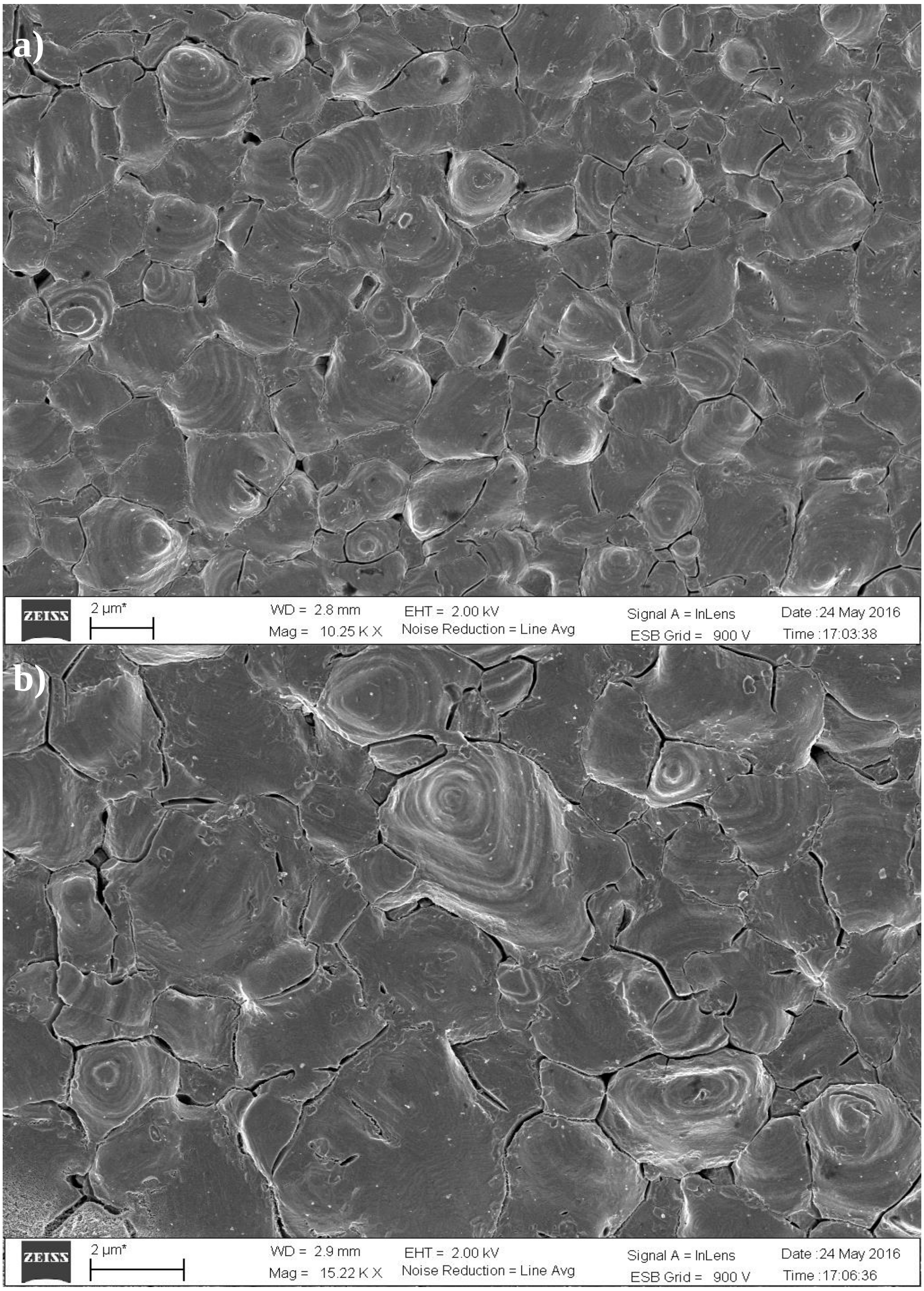


Figure 12 (a, b). HR-SEM image of CdTe surface of CdTe/CdS/SnO_2/ITO/glass structure etched in NP-acid during 30 sec.

It should be noted that PPy layer covers all holes and microcracks on CdTe surface that is appropriate for deposition of the final metallic contact without risk of possible short-cuts.

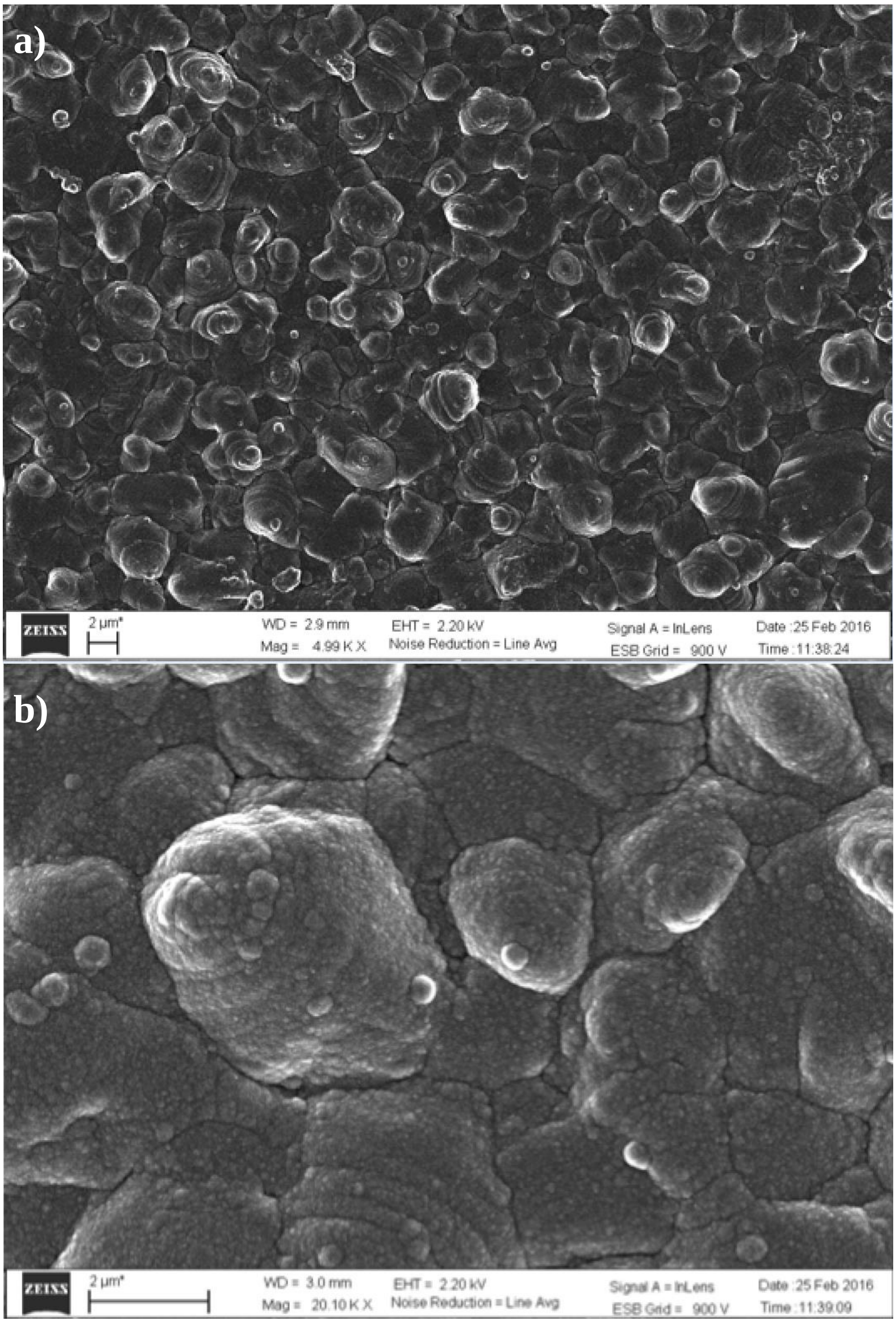
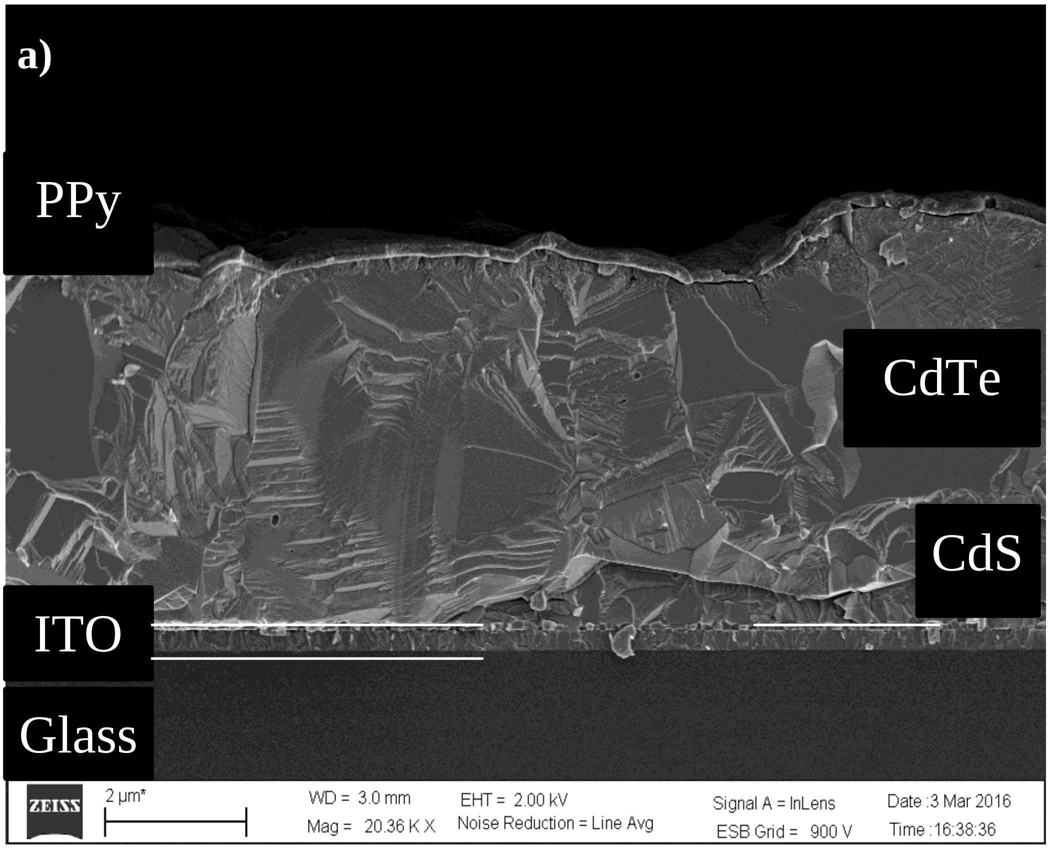


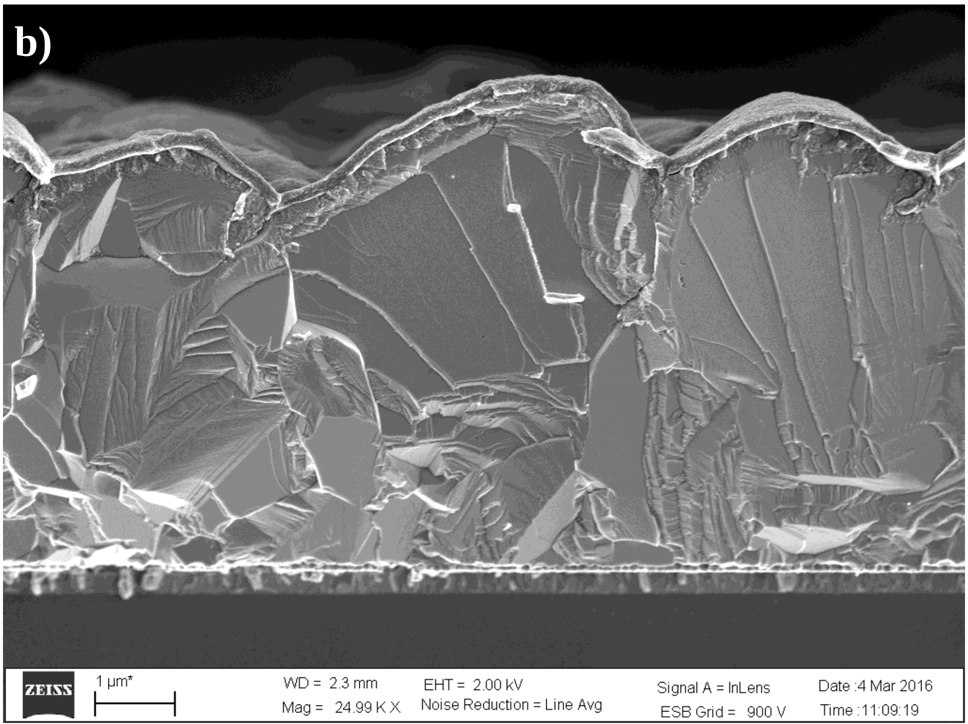
Figure 13 (a, b). HR-SEM surface image of PPy:PTSA layer in PPy: PTSA/ CdTe/CdS/SnO_2/ITO/glass structure (PPy film deposited at 200 mV vs. SCE for 20 min in ACN solution at room temperature under laser illumination).

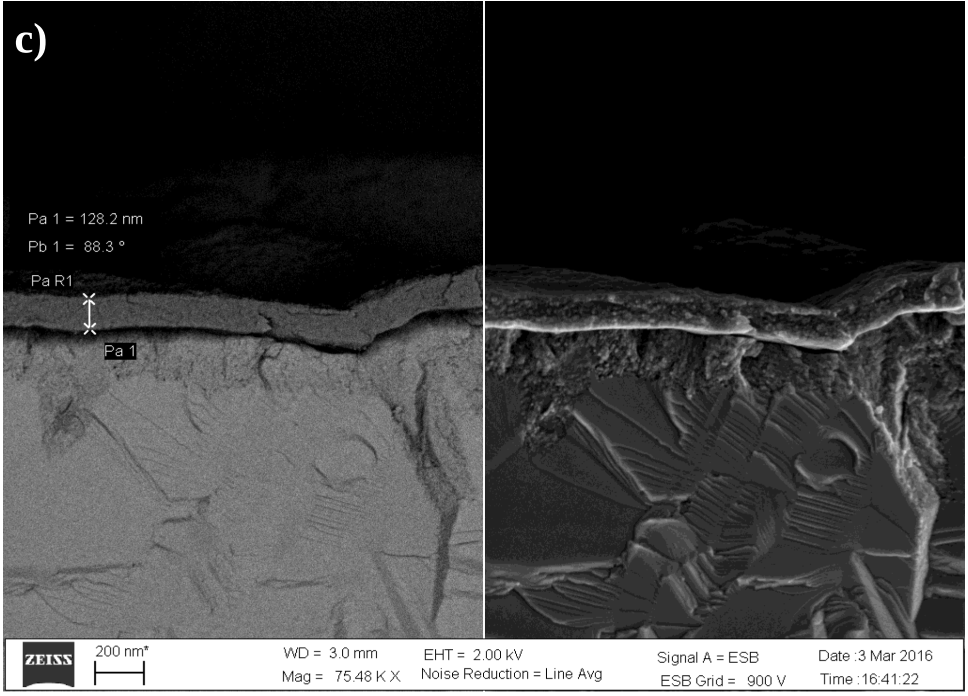
Figure 14 (a,b,c,d) shows HR-SEM cross-sectional images of complete PPy: PTSA/ CdTe/CdS/SnO_2/ITO/glass hybrid structure with PPy film prepared by electrochemical deposition at 400 mV vs. SCE for 20 min under laser illumination after NP-etching of the CdTe/CdS/SnO_2/ITO/glass structure.. According to ANTEC-Solar data the thickness of

ITO/SnO_2 is 240/25 nm, respectively, and CdS layer deposited onto SnO_2 is 100 nm thick. The thickness of the CdTe layer is about 4.5 µm (in good agreement with our micrographs). Figure 14a shows that the PPy film covers CdTe layer uniformly and continuously, that in a good agreement with the results obtained from the surface image (Figure 13a-b). The thickness of the PPy: PTSA layer is about 130 nm as shown in Figure 14c.

Figure 14d shows that on top of CdTe layer is a porous area with a thickness 200-250 nm. This area is formed after etching CdTe structure during 30 sec in NP-acid, and may be attributed to Te-rich part of the CdTe layer as shown in Raman spectrum (Figure 15). Etching creates Te-rich porous surface, which probably increase surface adhesion of PPy layer.




b)
ZEISS
1 µm*
WD = 2.3 mm
Mag = 24.99 K X
EHT = 2.00 kV
Noise Reduction = Line Avg
Signal A = InLens
ESB Grid = 900 V
Date :4 Mar 2016
Time :11:09:19


c)
Pa 1 = 128.2 nm
Pb 1 = 88.3 °
Pa R1
Pa 1
ZEISS
200 nm*
WD = 3.0 mm
Mag = 75.48 K X
EHT = 2.00 kV
Noise Reduction = Line Avg
Signal A = ESB
ESB Grid = 900 V
Date :3 Mar 2016
Time :16:41:22

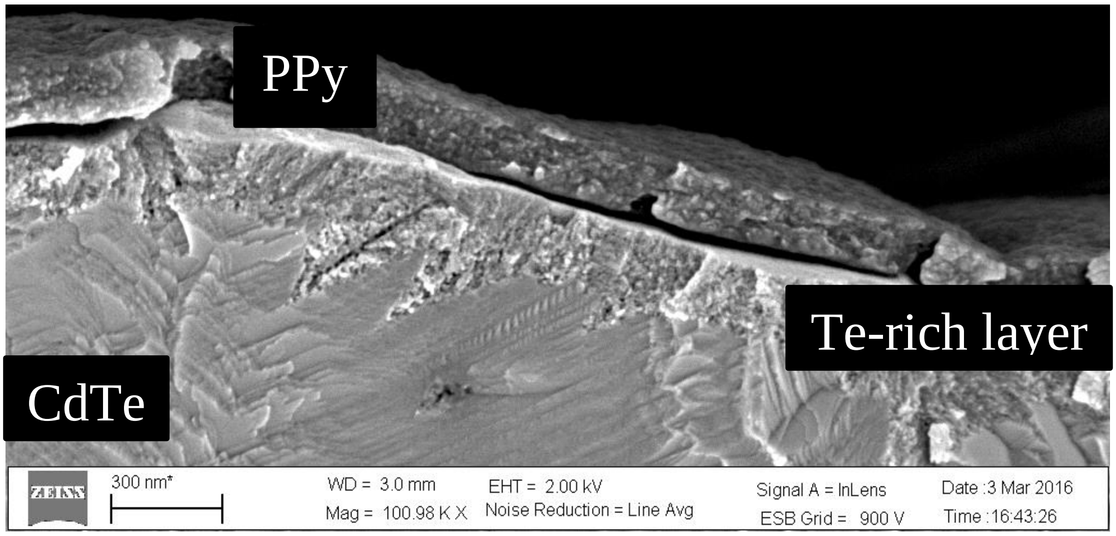


Figure 14 (a, b, c, d). Cross sectional HR-SEM micrograph at different magnifications of PPy:PTSA/CdTe/CdS/SnO_2/ITO/glass structure with PPy film deposited at 400 mV vs. SCE for 20 min at room temperature under laser illumination in ACN solution.

3.3 Raman spectra of CdTe layers

Figure 15 shows Raman spectra of the surface of CdTe deposited and activated by ANTEC Solar, etched and electrochemically treated in our Lab i.e. phase composition of the CdTe layers treated by different ways were investigated. In other words, we compare Raman spectra of activated CdTe; activated and etched CdTe; and activated, etched CdTe with following electrochemical treatment in ACN solution with PTSA during 20 min at applied potential of 200 mV vs. SCE.

Raman spectrum of the surface of activated CdTe shows peak at 165 cm^{-1} attributable to CdTe and peaks at 95 cm^{-1}, 122 cm^{-1} and 140 cm^{-1} attributable to Te. After the NP-etching, the CdTe surface color has changed from dark grey to metallic bright grey. According to the Raman spectroscopy, after etching CdTe peak at 165 cm^{-1} disappears. As expected, tellurium peaks height at 122 cm^{-1} and 140 cm^{-1} increase [59]. Raman spectra show that etching in NP-acid mixture According to our assumption, decrease of CdTe peaks height and increase of Te peaks height are connected directly with etching of CdTe layer in NP. Results observed can be connected with removing partial dissolving of Cd on the surface of CdTe. Peak at 331 cm^{-1} appears only for the CdTe layer electrochemically treated after NP-etching [60]. It should be noted, that Te-rich layer can be oxidized by applied anodic potential. As the result, decrease of the Te peaks height and appearance of CdTe peak at 331 cm^{-1} are observed.

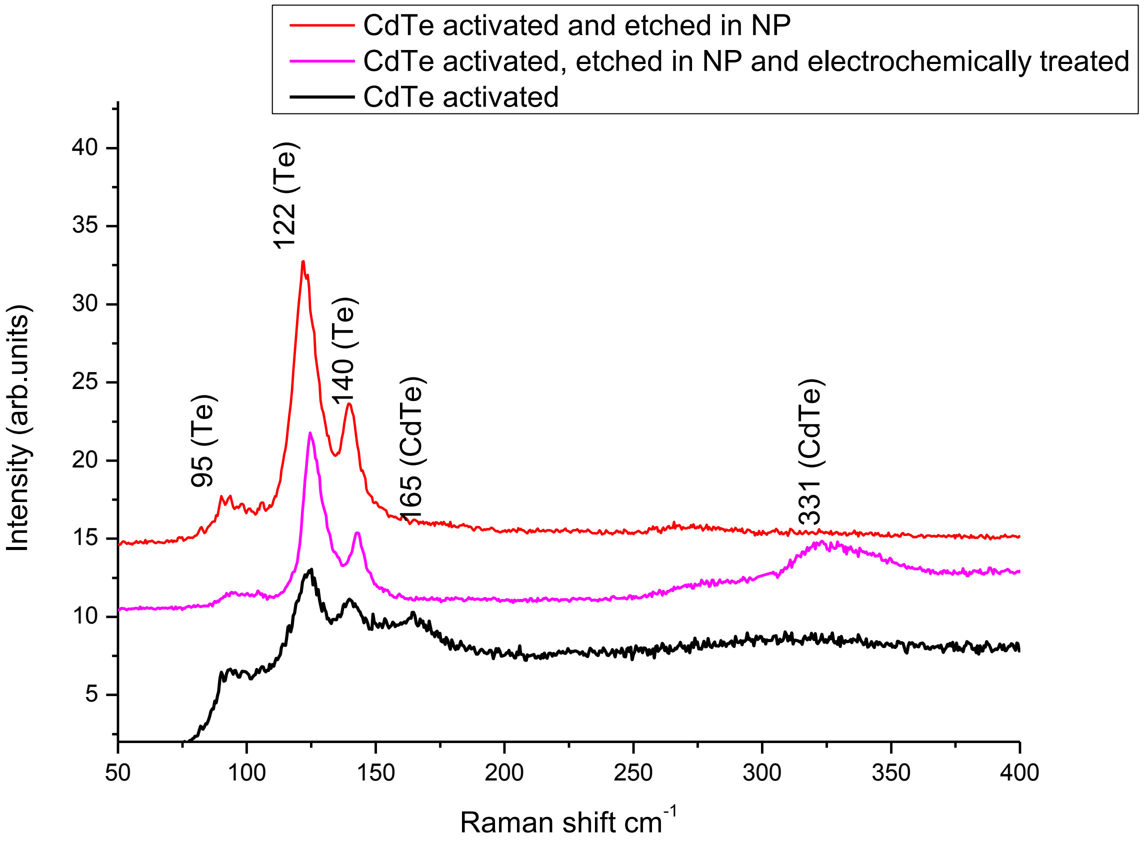


Figure 15. Raman spectra of activated CdTe surface; CdTe activated and etched in NP; CdTe activated, etched in NP and electrochemically treated in 0.1M PTSA solution in ACN during 20 min at applied potential of 200 mV vs. SCE.

3.4 I-V characteristics of prepared PPy: PTSA/CdTe/CdS/SnO$_2$/ITO/ glass hybrid structures

PPy back contact layers have been formed on the CdTe/CdS/SnO$_2$/ITO/glass structures in the applied potential range from 100 mV to 800 mV vs. SCE in ACN solution. Figure 16 show I-V curves for complete PPy:PTSA/CdTe/CdS/SnO$_2$/ITO/glass hybrid structures with PPy back contact electrodeposited under laser beam irradiation.

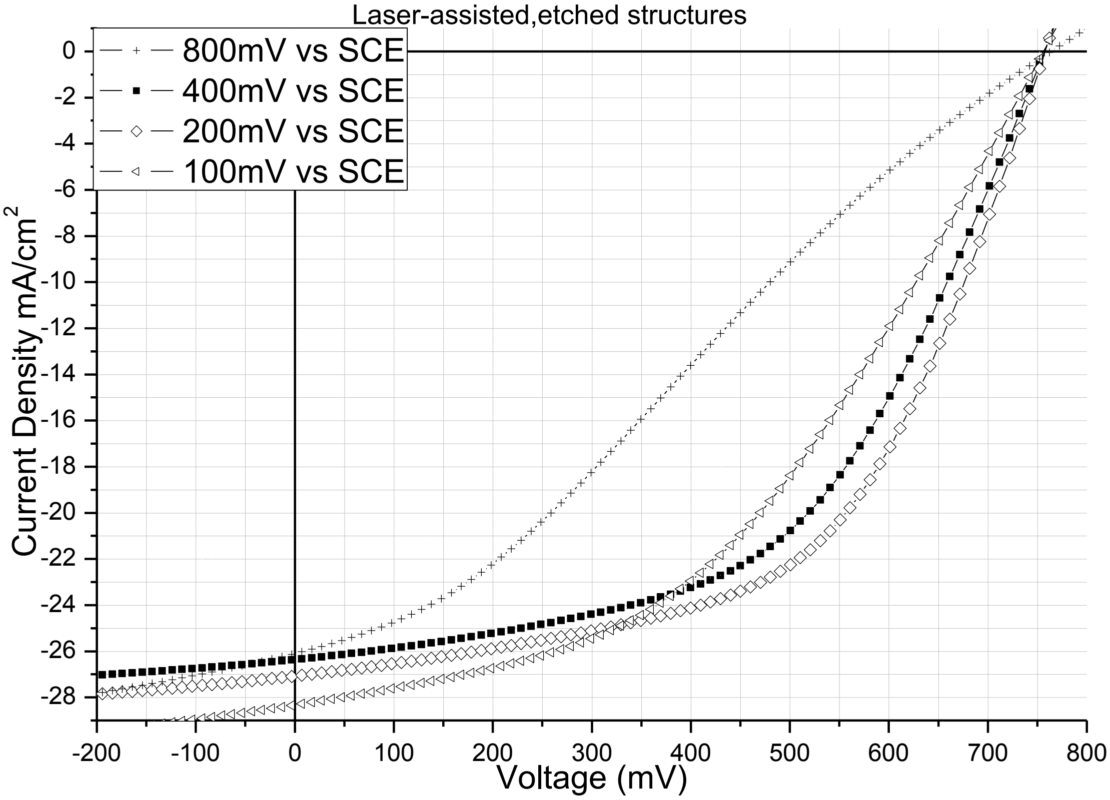


Figure 16. I-V curves of PPy:PTSA/CdTe/CdS/SnO$_2$/ITO/glass hybrid structures coated with electrodeposited PPy: PTSA layers under laser illumination at the applied potential range from 100 to 800 mV vs. SCE.

Table 1. PV parameters of PPy:PTSA/CdTe/CdS/SnO$_2$/ITO/glass hybrid structures coated

with electrodeposited PPy: PTSA layers under laser illumination at applied potential range from 100 to 800 mV vs. SCE..

Sample code	d26	d29	d31	d32
Potential vs. SCE	800 mV	400 mV	200 mV	100 mV
Area (cm^2)	0,13	0,10	0,10	0,10
I_{sc} (mA)	3,2	2,5	2,6	2,7
J_{sc} (mA/cm^2)	26,1	26,4	27,1	28,3
V_{oc} (mV)	763	757	757	756
FF (%)	27	52	54	44
Eff (%)	5,6	10,4	11,25	9,4
Deposition media	ACN	ACN	ACN	ACN

Table 1 shows PV parameters of obtained hybrid structures. According to Table 1, hybrid structure with PPy back contact electrodeposited at the potential of 200 mV vs. SCE demonstrates the highest photoconversion efficiency. On the other hand, the lowest efficiency was determined for hybrid structure where PPy layer was electrodeposited at the potential value 800 mV vs. SCE. It is not surprising due to possible electrochemical corrosion of CdTe interface under so high oxidative potential in presence of intensive light irradiation.

It should be noted, that photo-assisted electrodeposition in non-aqueous ACN media gives uniform and adhesive PPy layer to CdTe. All the PPy films were well reproducible. Photoconversion efficiency of obtained complete hybrid structures is comparable with ANTEC Solar CdTe structures with conventional inorganic back-contact. Therefore, photo-assisted deposition of PPy back contact in non-aqueous media has been found to be promising technique for CdTe solar cells technology.

3.5 Acetonitrile and aqueous media

In order to compare PPy back contacts deposited in aqueous and non-aqueous media, two electrolyte solutions were prepared. For electrochemical deposition in aqueous media, ß-NSA dopant was used. For electrochemical deposition in acetonitrile, PTSA dopant was used. Electrodeposition of PPy: PTSA and PPy: ß-NSA layers was performed in the potential range 200-400 mV vs. SCE under laser light illumination at room temperature.

According the obtained I-V characteristics for prepared PPy: PTSA/CdTe/CdS/SnO_2/ITO/glass structures from (Figure 16) the most appropriate potentials were chosen to be 200 and 400 mV vs. SCE. According I-V curves (Figure 18), complete hybrid structures with PPy back contact electrodeposited in ACN solution give higher efficiency in comparison with hybrid structures where PPy back contact was electrodeposited in aqueous electrolyte solution. In addition, PPy layers deposited in ACN solution had better adhesion to the CdTe surface in comparison with PPy layer deposited in aqueous media (small physical impact can remove PPy film deposited in aqueous solution from the CdTe surface, however films obtained from the ACN solution are strong enough to resist the impact). It was observed that the same exposure time into the ACN and aqueous solutions influences differently on quality of PPy films. CdTe structures had recognizable visual defects after 20 min deposition under 400 mV vs. SCE into aqueous solution that may correspond to the electrochemical corrosion of CdTe surface. According to the Pourbaix diagram (Figure 17), solid CdTe is very stable in wide range of pH at cathodic potentials. On Figure 17 shows, that line 5, 11 and 12 describe upper CdTe chemical equilibrium. In our study we used potentials from 200 up to 400 mV vs. SCE and aqueous solution pH was measured as 4. At potentials range from 100-500 mV vs. NHE, CdTe is dissolving by reaction (1). Potential that is higher than 500 mV vs. NHE bring corrosive reaction (2). Small increase of potential above to 200 mV leads to CdTe oxidation to TeO_2 (3). Aqueous solution is more aggressive than acetonitrile [61]. Potential in pourbaix diagram is given according to NHE, In order to calculate saturated calomel electrode potential, (E=+0.241 V) is summarized with NHE electrode potential.

$$CdTe \Leftrightarrow Cd^{2+} + Te + 2e^{-} \quad (1)$$

$$CdTe + 2H_2O \Leftrightarrow Cd^{2+} + TeO_2 + 4H^{+} + 6e^{-} \quad (2)$$

$$CdTe + 2H_2O \Leftrightarrow Cd^{2+} + TeO_2 + 4H^{+} + 6e^{-} \quad (3)$$

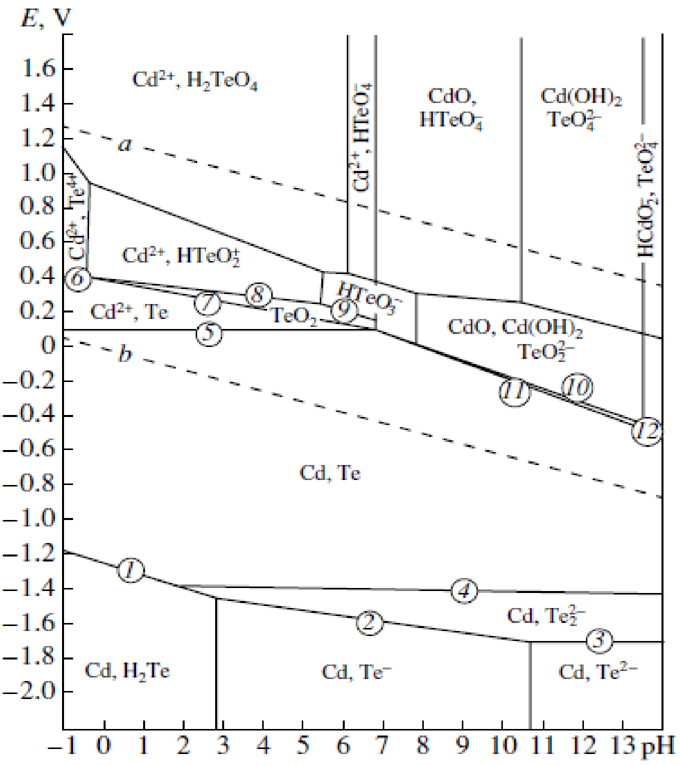


Figure 17. Pourbaix giagram of CdTe-H_2O system (potential is given vs. NHE).

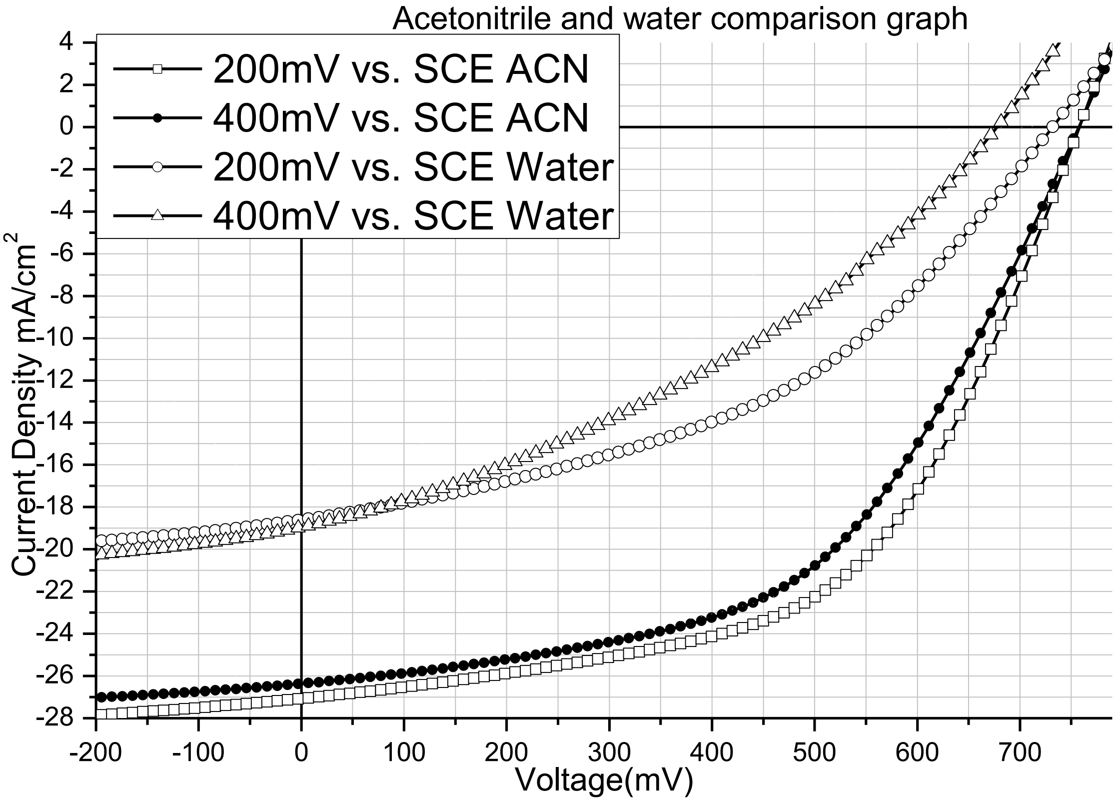


Figure 18. I-V curves for complete hybrid structures PPy/CdTe/CdS/SnO_2/ITO/glass with electrodeposited PPy: PTSA back contact layer in ACN media and PPy: ß-NSA back contact layer electrodeposited in aqueous media under laser illumination at the potentials 200 and 400 mV vs. SCE (all I-V curves were measured under white light irradiation of 100 mW/cm^2 intensity).

Table 2. PV parameters of the prepared hybrid structures (See also Figure 18).

Sample code	d46	d47	d29	d31
Potential vs. SCE	400 mV	200 mV	400 mV	200 mV
Area (cm^2)	0,0804	0,0962	0,0962	0,0962
I_{sc}(mA)	1,5	1,8	2,5	2,6
J_{sc}(mA/cm^2)	19	18,6	26,4	27,1
V_{oc}(mV)	677	731	757	757
FF%	35,5	43	52	54
eff%	4,5	5,8	10,4	11,25
Deposition media	Water	Water	ACN	ACN

Conclusions

The main purpose of this work was to prepare hybrid CdTe solar cell with electrically conductive polymer PPy back contact electrodeposited in non-aqueous medium.

1. A number of CdTe hybrid structures with PPy back contact was prepared by photo-assisted electrodeposition technique. Various oxidative potentials in non-aqueous solutions were used in this study.

2. It was found, that intensive light irradiation facilitates formation of the uniform and adhesive PPy layer onto CdTe at reduces deposition potential values and gives possibility to cover only photoactive area of CdTe layer. Also, preliminary etching of CdTe with NP improves quality of PPy back contact layer.

3. The glass/ITO/SnO_2/CdS/CdTe/PPy hybrid structures prepared in non-aqueous acetonitrile solution demonstrate higher photo conversion efficiency in comparison with similar hybrid structures with PPy back contact electrodeposited in aqueous medium. The adhesion of PPy layers deposited in acetonitrile solution is higher than PPy layers deposited in aqueous medium.

4. The best obtained CdTe solar cell with PPy back contact shows photoconversion efficiency around 11%. This result is comparable with efficiency of ANTEC solar cells with conventional Sb_2Te_3/Mo back contact (PCE around 10% for cells with active area of 10x10 cm). On the other hand, active area of prepared hybrid structures is less than 1 cm^2.

Résumé

Solar energy is available to everyone. On the other hand, main non-renewable sources such as coal, oil and gas are limited and using of these sources produces environmental pollutions. At the present time, a number of scientific groups are working in the research area of photovoltaics. In this field, thin film technology is one of the most promising and cost effective technologies today.

CdTe continues to be an important material in the photovoltaic research and a promising candidate for industrial-scale production of thin film based solar cells. However, some issues problems remain and require additional research. One of these problems is the fabrication of a stable ohmic or quasi-ohmic back contact to CdTe layer. In this work we investigated PPy organic back contact to CdTe solar cell as alternative to conventional inorganic back contacts. It should be noted, that PPy is cheap, non-toxic and, as covalent compound do not diffuse into CdTe photoabsorber layer as e.g. copper in widely distributed conventional copper-based back contact. PPy electrodeposition technique is relatively cheap and simple and do not pollute environment. Electrochemical synthesis has several advantages over other techniques e.g. film thickness can be controlled through the deposition current density and time, electrodeposited PPy layers demonstrate a highest conductivity etc. Electrodeposition can be performed in aqueous and non-aqueous solutions.

In our work PPy thin films were deposited onto CdTe/CdS/SnO_2/ITO/glass structure by using photo-assisted electrodeposition technique in non-aqueous media. Photo-assisted electrodeposition of PPy back contact in acetonitrile to CdTe is a novel approach and has not been studied yet. Different investigation techniques were used to characterize of obtained hybrid structures. It was found, that complete CdTe solar cell structures with PPy back contact electrodeposited in non-aqueous acetonitrile solution demonstrate PCE comparable with the same CdTe solar cell with conventional Sb_2Te_3/Mo back contact. The best-obtained hybrid solar cell PPy/CdTe/CdS/SnO_2/ITO/glass has PCE around 11%. These CdTe structures with organic back contact were deposited in acetonitrile media in presence of pyrrole monomer and PTSA dopant with concentration of 0.1 and 0.1 M respectively. Red light laser was used for photo-assisted electrodeposition. Deposition was carried out in three-electrode electrochemical cell at room temperature with applied potential of 200 mV vs. SCE.

Kokkuvõte

Põhilised mittetaastuvad energiaallikad on maagaas, nafta ja kivisüsi, nende varud maailmas on aga piiratud ja hakkavad ammenduma. Üks võimalikest taastuvenegia allikatest, mis neid asendada saaks on päikese energia. Päikeseenergia on kergesti kättesaadav ning selle muundamine elektriliseks energiaks on küllaltki odav. Viimastel aastatel teadustöö on suunatud suure efektiivsusega päikesepaneelide arendamisele. Teadustöö põhiprobleemiks on päikesepaneelide maksumus ja keskonnasõbralikkus. Antud valdkonnas õhukeste kilede tehnoloogia on kiirelt arenev suund, mis on hetkel kõige lootustandav tehnoloogia. Selle tehnoloogia põhimõtteks on materjali kokkuhoid ja suure efektiivsuse tagamine. CdTe baasil põhinevad päikeseelemendid on kõige efektiivsemad ja võimsamad ning seetõttu ka levinuimad õhukeste kilede tehnoloogial põhinevad paneelid. Antud tehnoloogia negatiivse poolena võib välja tuua materjalide, millest päikeseelemendid valmistatakse, kahjulikkus inimese tervisele ja väliskeskkonnale. Isegi omades kalleid materjale ja tootmistehnoloogiat, on küllaltki raske päikeseelemendi suurt efektiivsust tagada. Viimase aja teadustöö on suunatud efektiivsemate, odavamate ning samas ka keskkonnasõbralikke materjalide leidmisele. Selles töös me uurime polüpürrooli (PPy) orgaanilise taga kontakti CdTe päikeseelemendi jaoks. PPy on võetud levinud metallilise kontakti asenduseks. PPy on kovalentne ühend, mis on oma olemuselt odav, mittetoksiline ja ei levi valgust neelavasse kihti nagu levinud vase ühend. PPy elektrokeemiline sadestamine on lihtne ja ekoloogiliselt puhas meetod. Elektrokeemiline sadestamine omab mitmeid eeliseid võrreldes teiste meetoditega, näiteks, kile paksus on kontrollitatav läbitud voolu ning möödunud aja kaudu. Elektrokeemiliselt sadestatud kiled näitavad suurt elektrijuhtivust. Elektrokeemiline sadestamine võib olla tehtud nii vees kui ka orgaanilistes lahustes. Antud töös PPy õhukene kile on sadestatud fotoelektrokeemilise sadestamise meetodil laaseri valguse kasutamisel CdTe/CdS/SnO_2/ITO/klaas struktuuri peale orgaanilises lahuses. PPy fotoelektrokeemiline sadestamine on uudne lähenemine ning seda pole siiani uuritud. Erinevad meetodid olid kasutatud sadestatud polümeer kilede uurimiseks. Uuringu käigus leiti, et CdTe päikeseelement koos fotoelektrokeemiliselt sadestatud PPy-ga atsetonitriilis näitab sama suurt efektiivsust, mille saadi CdTe päikeseelemendi puhul tavalise kontaktiga Sb_2Te_3/Mo. Parima tulemuse saadi hübriidse PPy/CdTe/CdS/SnO_2/ITO/klaas päikeseelemendi puhul efektiivsusega 11% juures.

References

[1] Gail Tverberg Ten Reasons Intermittent Renewables (Wind and Solar PV) are a Problem published on January 21, (2014) accessed on November 9,2015 http://ourfiniteworld.com/2014/01/21/ten-reasons-intermittent-renewables-wind-and-solar-pv-are-a-problem/

[2] Renewables 2015 Global Status Report 58-66 ISBN 978-3-9815934-6-4 (2015).

[3] Dr. Simon P. Philipps, Dr. Andreas W. Bett Kelsey Horowitz, Dr. Sarah Kurtz, Current Status Of Concentrator Photovoltaic (CPV), Technology NREL (2016) TP-6A20-63916.

[4] Paul Hersch and Kenneth Zweibel Basic, Photovoltaic Principles and Methods, SERI (NREL) SERI/SP-290-1448 (1982).

[5] http://www.nrel.gov/ncpv/images/efficiency_chart.jpg

[6] Hitoshi Sai, Takuya Matsui, Takashi Koida, Koji Matsubara, Michio Kondo, Shuichiro Sugiyama, Hirotaka Katayama, Yoshiaki Takeuchi, and Isao Yoshida, Triple-junction thin-film silicon solar cell fabricated on periodically textured substrate with a stabilized efficiency of 13.6%, Applied Physics Letters 106, 213902 (2015).

[7] Jeehwan Kim, Ziruo Hong, Gang Li, Tze-bin Song, Jay Chey, Yun Seog Lee, Jingbi You, Chun-Chao Chen, Devendra K. Sadana1 & Yang Yang, 10.5% efficient polymer and amorphous silicon hybrid tandem photovoltaic cell, Nature Communications (2015).

[8] Solar Research: On the Hunt for the Super-cell Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg (ZSW) (2015).

[9] First Solar-Thin Film Module Technology Ideal for Converting Sunlight into Electricity, http://www.firstsolar.com/en/Technologies-and-Capabilities/PV-Modules/First-Solar-Series-3-Black-Module/CdTe-Technology accessed on November 15, (2015).

[10] Cadmium telluride photovoltaics, https://en.wikipedia.org/wiki/Cadmium_telluride_photovoltaics accessed on November 16, (2015).

[11] Kim Mitchell,Alan L. Fahrenbruh and Richard H. Bube, Photovoltaic determination of optical-absorption coefficient in CdTe, Journal of Applied Physics 48, 829 (1977).

[12] Mark Osborne, First Solar pushes verified CdTe cell efficiency to record 21.5%, published February 5,2015 accessed on November 9,2015 http://www.pv-tech.org/news/first_solar_pushes_verified_cdte_cell_efficiency_to_record_21.5 (2015).

[13] M.J. (Mariska) de Wild-Scholten, Energy payback time and carbon footprint of commercial photovoltaic systems Solar Energy Materials and Solar Cells 119:296-305, December (2013).

[14] Vasilis Fthenakis and Ken Zweibel CdTe PV: Real and Perceived EHS Risks National Renewable Energy Laboratory (2003).

[15] Sigel, Astrid, Sigel, Helmut, Sigel, Roland K. O. Cadmium: From Toxicity to Essentiality Metal Ions In Life Sciences (2013) 14-23.

[16] Vasilis M. Fthenakis National Photovoltaic Environmental Health and Safety Assistance Center Could CdTe PV Modules Pollute the Environment, November (2002).

[17] Adrian Chirilă, Stephan Buecheler, Fabian Pianezzi, Patrick Bloesch, Christina Gretener, Alexander R. Uhl, Carolin Fella, Lukas Kranz, Julian Perrenoud, Sieghard Seyrling, Rajneesh Verma, Shiro Nishiwaki, Yaroslav E. Romanyuk, Gerhard Bilger & Ayodhya N. Tiwari Highly efficient Cu(In,Ga)Se2 solar cells grown on flexible polymer films Nature Materials 10, 857–861 (2011).

[18] A. N. Tiwari, G. Khrypunov, F. Kurdzesau, D. L. Ba˙tzner, A. Romeo and H. Zogg, CdTe Solar Cell in a Novel Configuration Progress In Photovoltaics: Research And Applications, January (2004).

[19] X. Li, T. Gessert, C. DeHart, T. Barnes,H. Moutinho, Y. Yan, D. Young, M. Young, J. Perkins, and T. Coutts A Comparison of Composite Transparent Oxides Based on the Binary Compounds CdO and SnO2 National Renewable Energy Laboratory October (2001).

[20] Archbold, Martin David Polycrystalline CdS thin films and their role in CdS/CdTe photovoltaic devices, Durham theses, Durham University. accessed on November 20, 2015 http://etheses.dur.ac.uk/2138/ (2007).

[21] D. Albin, D. Rose, R. Dhere, D. Levi, L. Woods, A. Swartzlander and P. Sheldon Comparison of Close-Spaced Sublimated and Chemical Bath Deposited CdS Films: Effects on CdTe Solar Cells NREL CP-520-22949 (1997)

[22] M. A. Matin, Nowshad Amin, Azami Zaharim, And Kamaruzzaman Sopian Ultra Thin High Efficiency CdS/CdTe Thin Film Solar Cells from Numerical Analysis Department of Electrical, Electronics and System Engineering (2009).

[23] C.S. Ferekides, D. Marinskiy, V. Viswanathan, B. Tetali, V. Palekis, P. Selvaraj, D.L. Morel High efficiency CSS CdTe solar cells Thin Solid Films 361-362 (2000) 520-526

[24] B. Maniscalco , A. Abbas, J.W. Bowers, P.M. Kaminski, K. Bass, G. West, J.M. Walls The activation of thin film CdTe solar cells using alternative chlorine containing compounds Thin Solid Films 582 (2015) 115–119.

[25] J.D.Major, R.E.Treharne, L.J.Phillips and K.Durose A low-cost non-toxic post-growth activation step for CdTe solar cells Nature 511, 334–337, July (2014).

[26] S. Girish Kumar and K. S. R. Koteswara Rao Physics and chemistry of CdTe/CdS thin film heterojunction photovoltaic devices: fundamental and critical aspects The Royal Society of Chemistry July (2014), 45-102.

[27] Stephan Buecheler, Lukas Kranz, Julian Perrenoud, Ayodhya Nath Tiwari , CdTe Solar Cells, Encyclopedia of Sustainability Science and Technology, Springer , (2012), 10.1007/978-1-4419-0851-3_463

[28] Eduardo Lorenzo, Solar Electricity: Engineering of Photovoltaic Systems 8486505550, 9788486505554 316, 79-86, (1994)

[29] Chavali, R.V.K.; Wilcox, J.R.; Ray, B.; Gray, J.L.; Alam, M.A. "Correlated Nonideal Effects of Dark and Light I (2013);V Characteristics in a-Si/c-Si Heterojunction Solar Cells". *IEEE Journal of Photovoltaics* **4** (3): 763–771.

[30] Xiaonan Li, David W. Niles, Falah S. Hasoon, Richard J. Matson, and Peter Sheldon Effect of nitric-phosphoric acid etches on material properties and back-contact formation of CdTe-based solar cells Journal of Vacuum Science & Technology 17, 805 (1999).

[31] Zhou Fang, Xiao Chen Wang, Hong Cai Wu, and Ce Zhou Zhao Achievements and Challenges of CdS/CdTe Solar Cells International Journal of Photoenergy (2011).

[32] D. L. Bätzner, A. Romeo, H. Zogg, A. N. Tiwari,R. Wendt A Study Of The Back Contacts Of Cdte/Cds Solar Cells, Thin Film Physics Group, 361–362, February (2000) 463–467.

[33] Robert W. Birkmire and Peter E. Meyers Institute of Energy Conversion, University of Delaware, Processing Issues for Thin-Film CdTe Cells and Modules National Renewable Energy Laboratory (1994).

[34] Shirakawa, Hideki; Louis, Edwin J.; MacDiarmid, Alan G.; Chiang, Chwan K.; Heeger, Alan J. (1977). "Synthesis of electrically conducting organic polymers: Halogen derivatives of polyacetylene, (CH) x". Journal of the Chemical Society, Chemical Communications (16): 578. doi:10.1039/C39770000578

[35] Milica M. Gvozdenović, Branimir Z. Jugović, Jasmina S. Stevanović, Tomislav Lj.Trišović and Branimir N. Grgur Electrochemical Polymerization of Aniline, Electropolymerization by Ewa Schab-BalcerzakPublished by InTechJaneza Trdine 9, 51000 Rijeka, (2011)

[36] Himani Sharma, Conducting Polymers: Polyaniline, its state of the art and applications Thapar Institute Of Engineering And Technology, June (2006).

[37] Rajeswari Ravichandran, Subramanian Sundarrajan, Jayarama Reddy Venugopal, Shayanti Mukherjee, Seeram Ramakrishna, Applications of conducting polymers and their issues in biomedical engineering, J. R. Soc. Interface 2010 7 S559-S579; DOI: 10.1098/rsif.2010.0120.focus. Published 25 August 2010

[38] John Wiley & Sons, Flexible Flat Panel Displays (2005) 140-159.

[39] Bolto BA, McNeill R, Weiss DE. Electronic Conduction in Polymers III: Electronic Properties of Polypyrrole. Aust. J. Chem. 1963;16:1090–1103.

[40] S. A. Campbell, Y. Li, S. Breakspear, F. C. Walsh & J. R. Smithpages, Conducting polymer coatings in electrochemical technology Part 1 – Synthesis and fundamental aspects, Transactions of the IMF: The International Journal of Surface Engineering and CoatingsVolume 85, Issue 5, (2007), 237-244

[41] P. Subramanian, N. B. Clark, L. Spiccia, D. R. MacFarlane, B. Winther- Jensen and C. Forsyth, Vapour phase polymerisation of pyrrole induced by iron(III) alkylbenzenesulfonate salt oxidising agents, Synthetic Metals, 158, 704, (2008).

[42] S. M. Sayyah, S. S. Abd El-Rehim, M. M. El-Deeb Electropolymerization of Pyrrole and Characterization of the Obtained Polymer Films , Journal of Applied Polymer Science, Vol. 90, 1783–1792 (2003)

[43] Masakazu Nakata, Megumi Taga and Hideo Kise Synthesis of Electrical Conductive Polypyrrole Films by Interphase Oxidative Polymerization -Effects of Polymerization Temperature and Oxidizing Agents Nature Polymer Journal 24,No5, 437-441, (1992).

[44] M. Waleed Shinwari , David Zhitomirsky , Imran A. Deen , P. R. Selvaganapathy , M. Jamal Deen , and D. Landheer Microfabricated Reference Electrodes and their Biosensing Applications Sensors 1679-715, (2010).

[45] T.F.Otero,J.Rodriguez, Role of protons on the electrochemical polymerization of pyrrole from acetonitrile solutions, Journal of Electroanalytical Chemistry and Interfacial Electrochemistry;.379 (1994) 513–516.

[46] Seungjun Lee, Hyunkyung Sung, Sujung Han, Woonkie Paik, Polypyrrole film formation by solution-surface electropolymerization: influence of solvents and doped anions The Journal of Physical Chemistry 98, (1994) 1250.

[47] S. M. Sayyah, S. S. Abd El-Rehim, M. M. El-Deeb Electropolymerization of Pyrrole and Characterization of the Obtained Polymer Films, Journal of Applied Polymer Science, Vol. 90, 1783–1792 (2003)

[48] S. M. Sayyah, S. S. Abd El-Rehim, M. M. El-Deeb Electropolymerization of Pyrrole and Characterization of the Obtained Polymer Films, Journal of Applied Polymer Science, Vol. 90, 1783–1792 (2003)

[49] Stéphanie Carquigny, Olivier Segut, Boris Lakard, Effect of electrolyte solvent on the morphology of polypyrrole films: Application to the use of polypyrrole in pH sensors, Synthetic Metals 158,11, July (2008), 453–461.

[50] S. M. Sayyah, S. S. Abd El-Rehim, M. M. El-Deeb Electropolymerization of Pyrrole and Characterization of the Obtained Polymer Films Journal of Applied Polymer Science, Vol. 90, 7, 1783–1792 (2003).

[51] A.S. Liu and M. A. S. Oliveira, Characterization of polypyrrole films deposited on aluminum surfaces from oxalic acid aqueous solution Materials Science-Poland, 27, 1, (2009).

[52] Saïd Sadki,a Philippe Schottland,b Nancy Brodiec and Guillaume Sabouraud The mechanisms of pyrrole electropolymerization The Royal Society of Chemistry 29, (2000), 283-293.

[53] Gaber El-Enany, Matthew J. Lacey, Phil A. Johns, John R. Owen In situ growth of polymer electrolytes on lithium ion electrode surfaces Electrochemistry Communications 11(12), 2320-2323, (2009).

[54] Jarkov , S. Bereznev, O. Volobujeva, R. Traksmaa, A. Tverjanovich, A. Öpik, E. Mellikov Photo-assisted electrodeposition of polypyrrole back contact to CdS/CdTe solar cell structures Thin Solid Films, 535,15, (2013), 198–201.

[55] Y. Mido, S. Taguchi, M.S. Sethi S.A.Iqbal, Chemistry in aqueous and Non-Aqueous Solvents (1997).

[56] Salma Bilal, Fouzia Perveen, Anwar-ul-Haq Ali Shah Chemical synthesis of polypyrrole doped with dodecyl benzene sulfonic acid Journal of Scientific and Innovative Research (2015); 4 ,1: 33-42

[57] Liming Dai PhD, Intelligent Macromolecules for Smart Devices From Materials Synthesis to Device Applications, ISBN: 978-1-85233-510-6, 41-80, (2004).

[58] Arrieta, Almario, Alvaro A y Tarazona Caceres, Rosa l. Study of kinetic formation and the electrochemical behavior of polypyrrole films. *J. Chil. Chem. Soc.* [online]. 2009, vol.54, n.1, pp. 14-19. Issn 0717-9707.

[59] C. Frausto-Reyes, J.Rafael Molina-Contreras, C. Medina-Gutiérrez, Sergio Calixto CdTe surface roughness by Raman spectroscopy using the 830 nm wavelength Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy (2006).

[60] Magdalena Osial, Justyna Widera, Krystyna Jackowska Room temperature two-step synthesis of cadmium telluride films, American Journal of Chemistry and Materials Science (2014); 1-2: 11-17

[61] A. G. Voloshchuk and N. I. Tsipishchuk Equilibrium Potential–pH Diagram of the CdTe–H2O System Inorganic Materials, Vol. 38, No. 11, (2002), pp. 1114–1116