$CuInSe_2$/POLYPYRROLE PHOTOVOLTAIC STRUCTURE PREPARED BY ELECTRODEPOSITION

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ABSTRACT: In this study, for the first time multilayer structures consisting of n-type $CuInSe_2$ (n-CIS) and p-type polypyrrole (PPy) thin films were prepared electrochemically using transparent glass/ITO substrates and investigated for photovoltaic applications. The phase composition and crystalline structure of the CIS films were characterized employing x-ray diffraction (XRD); the morphology of CIS and PPy films was studied using SEM and AFM microscopy methods. The chemical composition of the CIS films was determined by energy dispersive X-ray spectroscopy (EDS). The ionized carrier density, built-in potential, effective lifetime for photoinduced carriers and number of barriers in obtained structure were determined from impedance measurements. In order to study photovoltaic and C-V characteristics silver was vacuum-deposited onto doped PPy layers to obtain ITO/CIS/PPy/metal structures. The best structure showed V_{oc} = 92 mV and J_{sc} = 1.70 mA/cm^2 under white light illumination with 50 mW/cm^2. Our results show that the electrodeposition method gives the opportunity to prepare photovoltaic structures based on n-CIS and p-PPy thin films using relatively simple step-by-step technique.
Keywords: CIS – 1: Polypyrrole – 2: Photovoltaic structure – 3

1. INTRODUCTION

Thin film photosensitive junctions between conjugated polymers (polythiophene, PPy et) and various inorganic semiconductors (CdS, CdSe, CIS et) are currently investigated intensively with the aim to produce low-cost, large-area photodiodes and solar cells [1-5].

CIS is a ternary semiconductor compound, which offers several advantages for thin films applications [6]. In addition to its stability, CIS presents an optical absorption coefficient, which allows for optimum solar energy conversion efficiencies. The electrochemical techniques give several advantages for CIS thin film preparation such as the possibility of large-scale production, minimum waste of components and it does not require very pure starting materials [7-10]. One-step direct electrodeposition is one of the most promising electrochemical techniques to produce CIS films.

Although a lot of electrically conductive polymers were synthesized, the PPy film was one of the most intensively studied polymers during the last decade [11]. Beside its mechanical and chemical stability and high conductivity, its synthesis can be realized electrochemically in aqueous media with a wide range of doping anions. It was found that some sulfonic acids and salts (naphthalene sulfonates, toluene sulfonates et) used as dopants during electropolymerization lead to improved adhesion of PPy film with high conductivity [11-12]. As noted [12], the PPy films with good conductivity have also good mechanical properties.

Doped with sulfonic salts polypyrrole always has p-type of conductivity, but the type of conductivity of CIS strongly depends on the copper, indium or selenium content and may be n or p-type [6]. n-type of conductivity is more preferable for the formation of an hetero-junction between PPy and CIS layers. The main idea of our work was photovoltaic junction formation between n-CIS and p-PPy layers using step-by-step electrodeposition technique and investigation of obtained structures.

2. EXPERIMENTAL

The electrochemical synthesis of In-rich n-CIS films with a thickness of about 1 µm onto glass/ITO substrates was performed potentiostatically at a potential of -900 mV vs. SCE in a standard three-electrode cell using Wenking LT 87 potentiostat. The parameters for the electrochemical deposition were selected following literature data [13-14] to obtain adhesive n-CIS films. Aqueous solutions containing $CuSO_4/In_2(SO_4)_3/SeO_2$ in concentrations of 2/8/11, 3/7/11 and 4/6/11 mM respectively were used as a source for CIS(2-8-11), CIS(3-7-11) and CIS(4-6-11) films deposition. The solutions were prepared from Millipore water (18 Mohm·cm) and analytical grade reagents. Before the electrodeposition the glass/ITO substrates were cleaned and activated in saturated H_2SO_4 at 80 °C during 5 sec. Thermal annealing of as-deposited CIS films was performed at 400 °C for 20 min in vacuum. Such obtained CIS films were etched subsequently in 10% KCN aqueous solution during 5 min to remove possible secondary phases. The thickness of prepared CIS films was determined by electron microscopy to be about 1 µm. UV-VIS spectrophotometer Shimadzu UV-2401 PC was used for the light transmittance measuring. The films phase composition was characterized by X-ray diffraction (XRD) analysis using diffractometer of Bruker AXS D5005. Chemical composition of the CIS films was determined by energy dispersive X-ray spectroscopy (EDS).

The electrochemical syntheses of doped PPy films with the thickness of about 1 µm onto prepared glass/ITO/n-CIS substrates were performed galvanostatically between 0.55 V and 0.65 V vs. SCE in a current density range from 0.25 to 0.5 mA/cm^2 in standard three-electrode cell using VoltaLab™ 32 potentiostat/galvanostat. Pyrrole monomer (Aldrich) was distilled under vacuum prior to use. Polymerization was performed in the presence of _-naphthalene sodium sulfonate (Aldrich) as a dopant. Thin doped PPy films were synthesized in a 0.3 M pyrrole / 0.1 M _-naphthalene sodium sulfonate de-aerated aqueous solutions. All reagents were of analytical grade. The films

thickness was controlled by the charge transferred during electrodeposition using Faraday's law as demonstrated in [17]. Thermal annealing of PPy films at 100 °C for 6 hours in air markedly improved its adherence to the CIS. Finally, metal strips (Ag) were evaporated onto the polymer layer. Electrical contacts were made on the ITO and metal strip with silver epoxy. Photovoltaic structure ITO/CIS/PPy/Ag was fabricated in the sandwich configuration as shown in Figure 1.

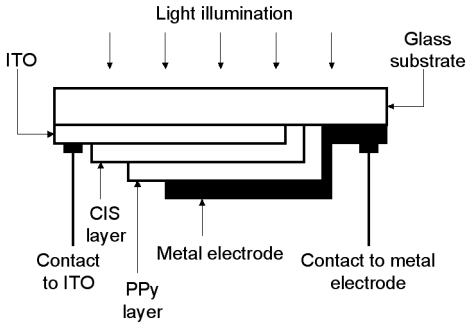

Figure 1: Schematic drawing of the ITO/CIS/PPy/Ag photovoltaic structure.

The impedance and frequency measurements were performed using an Autolab PGSTAT 30 potentiostat/galvanostat, the digital oscilloscope Tektronix TDS 220 and the low-frequency generator G3-112/1 (USSR) connected with an IR LED. The current-voltage characteristics were determined using VoltaLab™ 32 potentiostat/galvanostat. White light with an intensity of 50 mW/cm^2 from a tungsten-halogen lamp was used for irradiation.

3. RESULTS AND DISCUSSION

X-ray diffraction (XRD) was employed to characterize the structure of the electrochemically synthesized CIS films. Figure 2 shows the X-ray diffraction pattern for as-deposited, annealed and etched In-rich CIS(2-8-11) films. From the figure, it can be seen that the as-deposited film is polycrystalline in nature with weak and broad diffraction peaks. After annealing at 400 °C during 15 min the crystallinity is enhanced. The relative increasing of (220) peak compared to the others (112) and (116) indicates a preferential orientation in the (220) plane in annealed film. Comparing with Cu-rich films [15] the peak (112) is relatively wide and weak in diffractogramm on In-rich films even after annealing. The figure also indicates that etching in KCN had lead to a reduction of additional phases contained in the CIS film.

The photoelectrochemical characterizations for prepared CIS films were determined in 0.1 M sulfuric acid background solution under chopped white light. Figure 3 shows that obtained CIS films are photosensitive material and have the positive photocurrent in positive range of applied potential values. In the CIS electrode electron-hole pairs can be generated by light absorption. Therefore, photogenerated minority carriers are driven to the CIS surface by the electric field, at which they are consumed in photoelectrochemical processes. As it follows from the dependence, obtained CIS films had the n-type of conductivity and could be applied for n-p junction formation between n-CIS and p-PPy films.

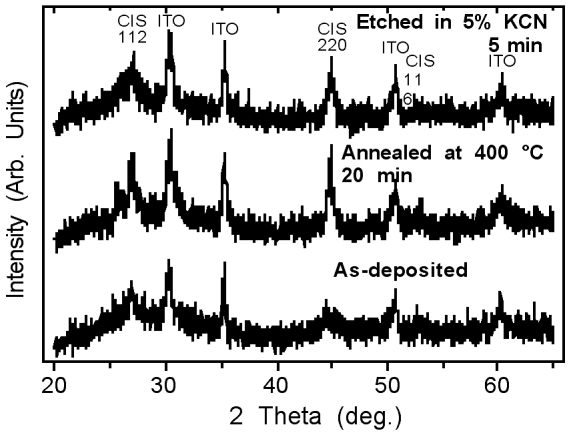

Figure 2: The XRD pictures for as-deposited, annealed in vacuum at 400 °C for 20 min and etched in 10% KCN for 5 min CIS(2-8-11) films.

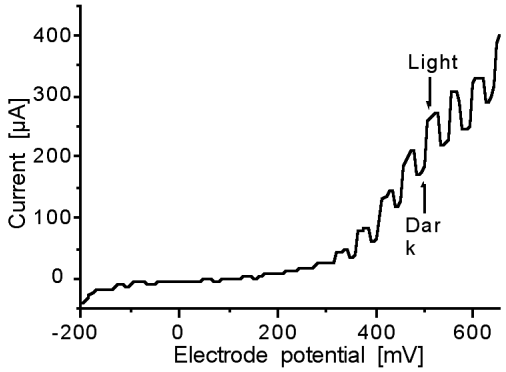

Figure 3: Typical dependence of photocurrent versus electrode potential for the CIS film under chopped light in three-electrode cell.

In order to guarantee high electroconductivity and good mechanical properties of PPy films, the polymerization of pyrrole was performed using a large organic dopant with a planar aromatic functional group - _-naphthalene sulfonate in situ. This counter anion induces structural regularity into the polymer chain. Also, it can more easily absorb at the electrode surface and thus enhance the first steps of the polymerization [12].

The morphology of obtained CIS and PPy films was studied using SEM and AFM technique. Figure 4 shows, that the CIS film has rather granular polycrystalline character with an average grain size of 200 nm. After PPy film deposition an essential smoothening of the granular surface by the amorphous polymer was observed.

The impedance measurements of such prepared ITO/CIS/PPy/Ag photovoltaic structures resulted in one symmetric semicircle for each structure attributable to a single barrier between n-CIS and p-PPy layers, Figure 5.

Figure 6 shows the results of C-V measurements (in the form of Mott-Schottky like plot) for representative ITO/CIS(2-8-11)/PPy/Ag structure. The value for the flat band potential or built-in potential, V_{bi} was determined by extrapolation to $C^{-2} = 0$. A more detailed analysis of the data is under way. The relatively high built-in potential at the CIS/PPy junction is noteworthy, because this potential determines the maximum photovoltage of a photovoltaic structure.

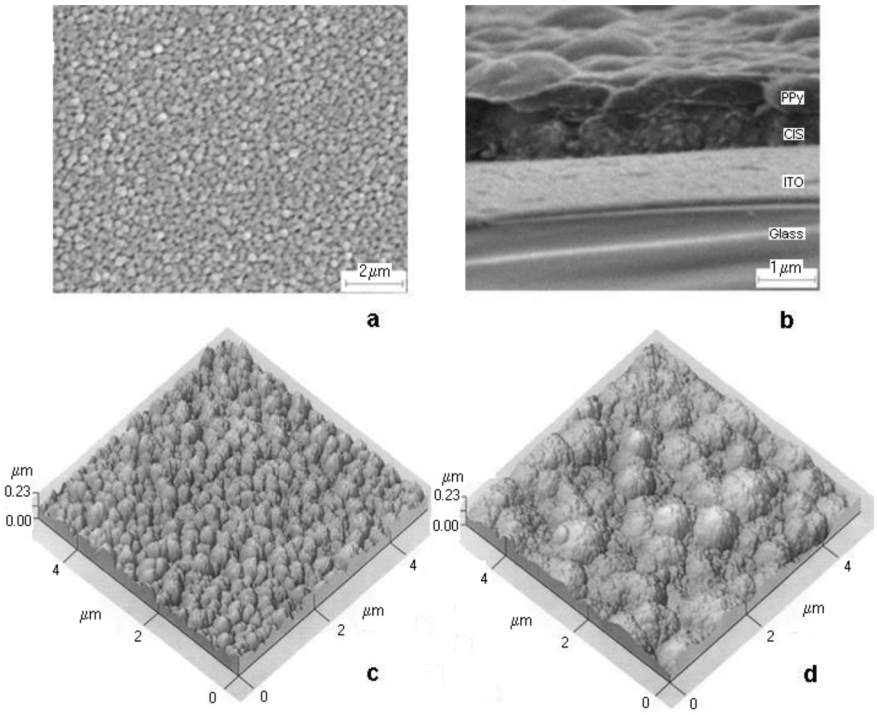

Figure 4: **a** – SEM photograph of a representative CIS film after annealing and etching. **b** – Cross-sectional SEM photograph for a representative glass/ITO/CIS/PPy structure. **c** – AFM image of a representative CIS film after annealing and etching. **d** - AFM image for PPy surface of a representative glass/ITO/CIS/PPy structure.

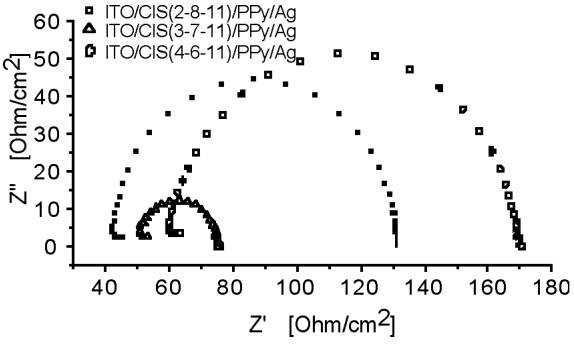

Figure 5: Complex impedance plot for ITO/CIS/PPy/Ag structures in the frequency range from 10 Hz to 1 MHz.

As noted [3], the positive slope for the Mott-Schottky plot corresponds to an n-type conductivity of the CIS films. Therefore, Figure 6 confirms the n-type of conductivity for the CIS films in a good agreement with photocurrent measurements in the electrochemical cell (See Figure 3).

The ionized carrier density N_D was calculated from the relation [18]:

$$1/C^2 = 2(V - V_{bi} - kT/q)/N_D q \_ _s S^2$$

where q is the electron charge, $\_ _s$ is the dielectric constant for CIS (13.6$_ _0$ [18]), S is the relevant interface area of the structure, C is the junction capacitance, V is the applied voltage and V_{bi} is determined built-in potential. Such determined N_D values are represented in Table 1 and provide only preliminaries values. A more careful analysis of the impedance data will follow in a later paper.

An example of the photovoltage changes induced by switching the IR "light on and off" on the prepared

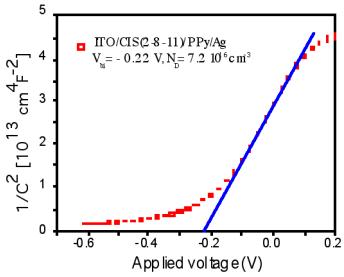

Figure 6: The Mott-Schottky plot for representative ITO/CIS/PPy/Ag structure.

ITO/CIS/PPy/Ag photovoltaic structures is shown in Figure 7. The photovoltage was induced reversibly and repeatedly by the on-off cycles of IR irradiation. The values of the effective lifetime of IR activated photogenerated charge carriers _ were determined from experimental curves represented in Figure 7 (See also Table 1).

Figure 8 shows the photovoltaic properties of obtained structures under white light illumination from tungsten-halogen lamp with intensity of 50 mW/cm^2. The incident light produced a short-circuit photocurrent density J_{sc} and an open-circuit photovoltage U_{oc} with the values represented in Table 1. It is evident that the behavior is fully controlled by the series resistance of the structure.

Table 1: The parameters of prepared ITO/CIS/PPy/Ag photovoltaic structures.

Structure	Cu/In/Se content in CIS (at. %)	N_D (cm^{-3})	τ (μs)	U_{oc}^* (mV)	J_{sc}^* (mA/cm^2)
ITO/CIS(2-8-11)/PPy/Ag	7.9/40.5/51.6	$7.2\ 10^{16}$	9	83	1.71
ITO/CIS(3-7-11)/PPy/Ag	10.9/37.3/51.8	$3.1\ 10^{17}$	4	92	1.70
ITO/CIS(4-6-11)/PPy/Ag	13.1/36.0/50.9	$1.6\ 10^{17}$	10	57	0.84

*Under white light irradiation 50 mW/cm^2.

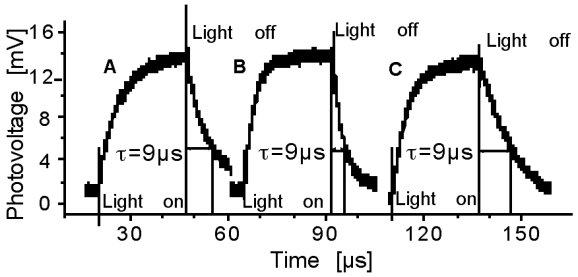

Figure 7: Photovoltage changes induced by switching the IR irradiation on and off (A – CIS(2-8-11); B – CIS(3-7-11); C – CIS(4-6-11)).

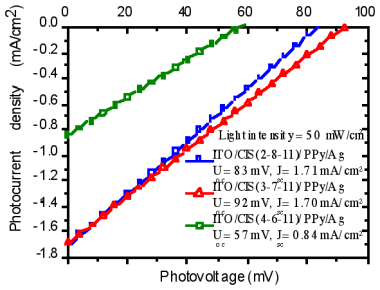

Figure 8: Photovoltaic characteristic of the ITO/CIS/PPy/Ag structures under tungsten-halogen irradiance of 50 mW/cm^2.

Also the voltage is a very small dues to the non-optimized band positions of the two contact behavior. As it follows from UV-VIS spectroscopy, the 1 μm CIS film absorbed about 95 % of the incident light, thus enabling only about 5 % of radiant power to reach the junction between the CIS and PPy layers. Nevertheless the short circuit current is remarkably high and proves the value of the chosen approach.

4. CONCLUSIONS

n-CIS/p-PPy hetero-junctions were prepared using electrochemical technique and characterized for photovoltaic application. The studies confirmed that a n-p barrier is formed between the n-CIS and p-PPy layers. A number of parameters, such as built-in potential V_{bi}, ionized carrier density N_D, effective lifetime of photogenerated charge carriers τ was determined. The best structure showed an open circuit voltage of V_{oc} = 92 mV and a short circuit current of J_{sc} = 1.70 mA/cm^2 under white light illumination of 50 mW/cm^2. The parameters of our structures are determined mainly by the CIS films and in further studies, thinner CIS films could be used to improve the parameters of this type of structures. One our further aim is to replace the as yet mainly flat interface by an interconnected network structure as used in polymer-C_{60} composites [19].

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