$CuInSe_2$/polypyrrole (polyaniline) photovoltaic structures

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Over the past few years, the structures based on inorganic-organic semiconductors are intensively studied due to their low-cost and simplicity of technology [1]. Although a lot of electrically conductive polymers were synthesized, the polypyrrole (PPy) or polyaniline (PANI) film was one of the most intensively studied polymers during the last decade [2]. Beside its mechanical and chemical stability and high conductivity, its synthesis can be realized in aqueous media with a wide range of doping anions. $CuInSe_2$ (CIS) is a ternary semiconductor compound, which offers several advantages for thin films applications [3]. In addition to its stability, CIS presents an optical absorption coefficient, which allows for optimum solar energy conversion efficiencies. In this study, for the first time multilayer structures consisting of n-CIS and p-type conductive polymers (PPy and PANI) thin films were prepared using transparent glass/ITO substrates and investigated for photovoltaic applications.

Photovoltaic structure ITO/CIS/Polymer/Ag was fabricated in the sandwich configuration as shown in Figure 1.

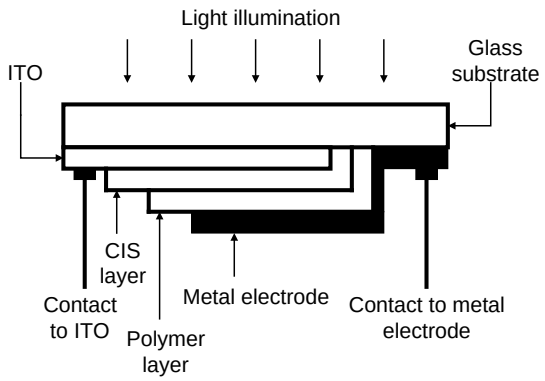

Fig. 1: Schematic drawing of the ITO/CIS/Polymer/Ag photovoltaic structure.

CIS thin films with a thickness of about 1 µm were directly electrodeposited onto transparent ITO/glass substrates using the potentiostatic mode at –900 mV vs. SCE. 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 the CIS (PPy) and 1/3.3/3.3 for CIS (PANI) films deposition. As-deposited polycrystalline CIS films were annealed in vacuum at 400 °C to improve the crystalline structure. After annealing films were etched subsequently in 10% KCN solution to remove secondary phases.

The high-quality adhesive PPy films with a thickness of about 1 µm were electrodeposited onto such prepared n-CIS films galvanostatically. Conductive soluble PANI was chemically

synthesized by the in situ doping oxidative polymerisation of aniline at the low temperature (0-2 °C). The p-PANI layer was cast onto the glass/ITO/n-CIS substrate from PANI solution in chloroform. Annealing of the doped PPy and PANI films was performed at 100 °C for 6 h in air and markedly improved its adherence to the CIS. The phase composition and crystalline structure of the CIS films were characterized employing x-ray diffraction (XRD); the morphology of CIS and conductive polymer 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 N_D, effective lifetime for photoinduced carriers τ and number of barriers in obtained structures were determined from impedance measurements (See Table 1). In order to study photovoltaic and C-V characteristics silver was vacuum-deposited onto doped PPy and PANI layers to obtain ITO/CIS/PPy(PANI)/metal structures.

Table 1: The parameters of prepared ITO/CIS/PPy (PANI)/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
ITO/CIS(1/3.3/3.3)/PANI/Ag	-	$3.7 \cdot 10^{17}$	14	31	0.56

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

The studies confirmed that a n-p barrier is formed between the n-CIS and p-PPy layers. The best ITO/CIS/PPy/metal structure showed V_{OC} = 92 mV and J_{SC} = 1.70 mA/cm^2 under white light illumination with 50 mW/cm^2. Mainly the quality of CIS films determines the parameters of structures and optimisation of CIS films and junction CIS/Polymer is planned in further studies to improve the parameters for 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 [4]. Our results show that the chemical and electrochemical methods give the opportunity to prepare photovoltaic structures based on n-CIS and p-PPy or p-PANI thin films using relatively simple step-by-step techniques.

References

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