MATERIALS
SCIENCE

Effect of polymer layer deposition and annealing on photovoltaic properties of CuInS₂/polymer structures

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Abstract. The effect of deposition of various polymer layers and annealing in the air at different temperatures on the surface photovoltage of CuInS₂ photoabsorber films was studied. After polymer layer deposition onto the polycrystalline CuInS₂ surface, roughness and photovoltage somewhat decreased. The photovoltage decrease is greater for polymers with smaller flexibility of macromolecules and can be caused by the formation of micropores in polymer films. After thermal annealing close to the polymer glass transition temperature micropores disappeared and photovoltage increased. Photovoltage increase was higher in the structures with the functional layer of polymers having larger flexibility of macromolecules.

Key words: polymer materials, CuInS₂, photovoltaic properties, polymer, annealing.

INTRODUCTION

Polycrystalline thin film technology is one of the most promising technologies for the future. The chalcopyrite I-III-VI₂ semiconductors are now established as effective absorbers in thin film photovoltaic cells. The copper–indium chalcogenide materials, e.g. CuInSe₂ (CISe), CuInS₂ (CIS), Cu(InGa)Se₂ (CIGSe), and CuIn(SSe)₂ (CISSe), have been developed most extensively because they allow tailoring of the energy band gap and other material properties to enhance device performance [1–4].

Our previous studies [5,6] have shown that the polymer layer deposition onto the free surface of photo-absorber layers of CIS leads simultaneously to a small decrease in the surface photovoltage (V_s) and to a significant increase in the short-circuit photocurrent (I_{sc}). This can be explained by the decrease in the potential barrier height and increase in the efficiency of charge carriers transport through the CIS/polymer interface. The values of the V_s and I_{sc} change depend strongly on the molecular structure of the polymer [6]. Nevertheless, this does not lead to changes in spectral dependences of V_s and I_{sc}. Therefore a high concentration of the centres of charge carriers trapping and recombination remains on the CIS/polymer interface. These centres reduce the photosensitivity of CIS/polymer heterostructures in the energy (E) region of 2.0–2.5 eV [6].

According to our assumption, the main reasons for the high concentration of charge carriers trapping and recombination centres are the adsorption of oxygen molecules and solvent molecules in the process of polymer film formation. It is known [7] that both residual gases and solvent molecules are most effectively removed at the glass transition temperature of the polymer (T_g). Therefore, the annealing of structures at temperatures near or higher than T_g can result in a strong decrease in the concentration of the centres of charge carriers trapping and recombination on the CIS/polymer interface and a drastic rise in V_s.

Thus, the aim of this paper is to study how the annealing of CIS-based structures with deposited layers of different polymers affects photovoltaic properties of these structures.

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EXPERIMENTAL

CIS film preparation on a copper tape (CISCuT) by the method of indium electrodeposition, with following sulphurization is described in detail in [8].

To prepare CISCuT/polymer structures, we used the following polymers: polystyrene (PS), co-polymer of styrene with octylmetacrylate (TPN-10) containing 80% styrene, poly-N-epoxypropylcarbazole (PEPC), and poly(3-iodine-9-vinylcarbazole) octylmetacrylate (P-3I-9VC:OMA) (Fig. 1). PS, TPN-10, and PEPC polymers were produced by the 'Azot' plant (Severo-donetsk, Ukraine). The molecular weight of PEPC is 900–1000 g mol^{-1}, of PS – 2×10^5 g mol^{-1}. P-3I-9VC:OMA was synthesized in the Polymer Department of Kyiv National University, as reported in [6]. This polymer has a molecular weight of 5000–7000 g mol^{-1} and contains 70 mol% 3I-9VC monomer in the co-polymer structure [6].

The values of T_g for as-deposited polymers are as follows: PS – 100 °C, TPN – 75 °C, PEPC – 70 °C, and P-3I-9VC:OMA – 75 °C [9].

Polymer films were deposited by the method of spin casting from the solution of the respective polymer in 1,2-dichloroethane. Samples were annealed in the drying box in the temperature range of 50–130 °C during 12 h.

In the study of the surface morphology of CISCuT substrates and the polymer layer deposited onto CISCuT, a serial atomic force microscope (AFM) of NanoScope IIIa type was used in the periodical contact mode. The technique of V_s measurements and experimental setup for these measurements is described in [5,6].
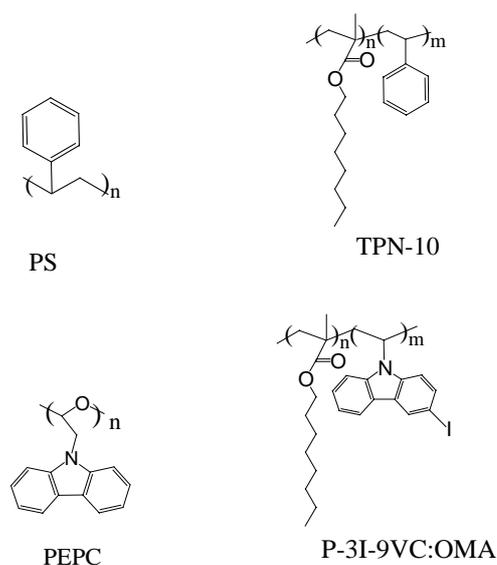
RESULTS AND DISCUSSION

Our studies show that the deposition of the polymer layer onto the free surface of CISCuT film in all cases leads to a small decrease in V_s (except for PEPC, where V_s is slightly higher, but in the range of the experiment accuracy of ±2.5%), while the annealing causes an increase in V_s for all studied structures. Figure 2 shows
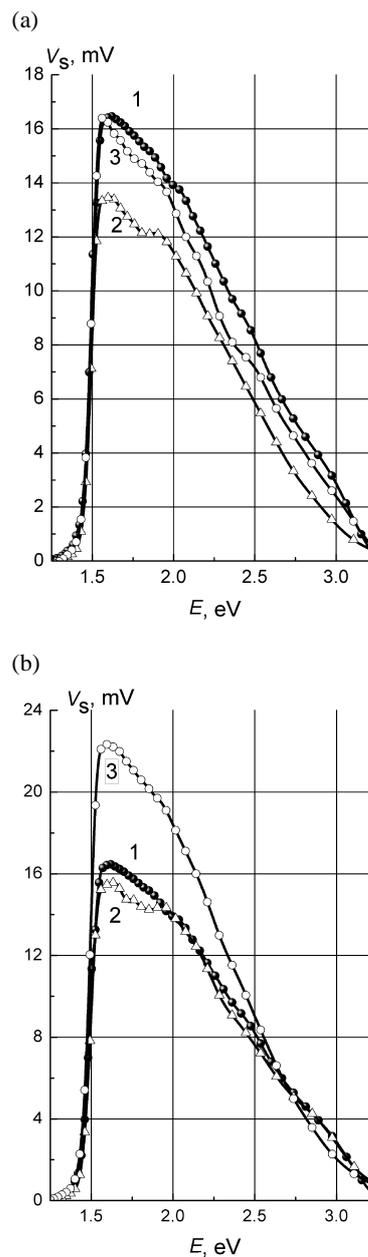

(a)

(b)

Fig. 2. (a) V_s spectra of the CIS film (curve 1) and CIS/TPN-10 structures before (curve 2) and after (curve 3) annealing. (b) V_s spectra of the CIS film (curve 1) and CIS/P-3I-9VC:OMA structures before (curve 2) and after (curve 3) annealing.

PS   TPN-10

PEPC   P-3I-9VC:OMA

Fig. 1. Molecular structure of deposited polymers.

V_s spectra for the CIS film (curves 1) and for the CIS/TPN-10 (Fig. 2a) and CIS/P-3I-9VC:OMA (Fig. 2b) structures before (curves 2) and after (curves 3) annealing at 130 °C.

It can be seen that the change in the V_s value after annealing significantly depends on the molecular structure of the polymer. The data in Fig. 2a and Fig. 2b show that V_s increase after annealing is a few times greater for CIS/P-3I-9VC:OMA structures (polymer with high flexibility of macromolecules) than for the structures with the PS layer, where the flexibility of macromolecules is lower. It should be noted that after annealing the V_s value for CIS/P-3I-9VC:OMA structures becomes even higher than V_s of the free surface of the CIS layer. The above results and comparison with analogous data for PEPC and TPN-10

polymers show that the change in V_s as a result of annealing can be associated with the elastic properties of the polymer layers. These properties are defined by the mobility of polymer macromolecules, which strongly increases at temperatures higher than T_g due to an increase in the flexibility of polymer macromolecules.

The increase in the mobility of polymer macromolecules (that can be the elasticity measure) of used polymers has the following trend: PS, PEPC, TPN-10, P-3I-9VC:OMA [7].

In order to clarify reasons for such correlation, we studied the surface morphology of the prepared structures. Figure 3 shows the AFM plots of CIS layers before (a) and after deposition of the P-3I-9VC:OMA layer (b), and the PS layer before (c) and after (d) annealing.
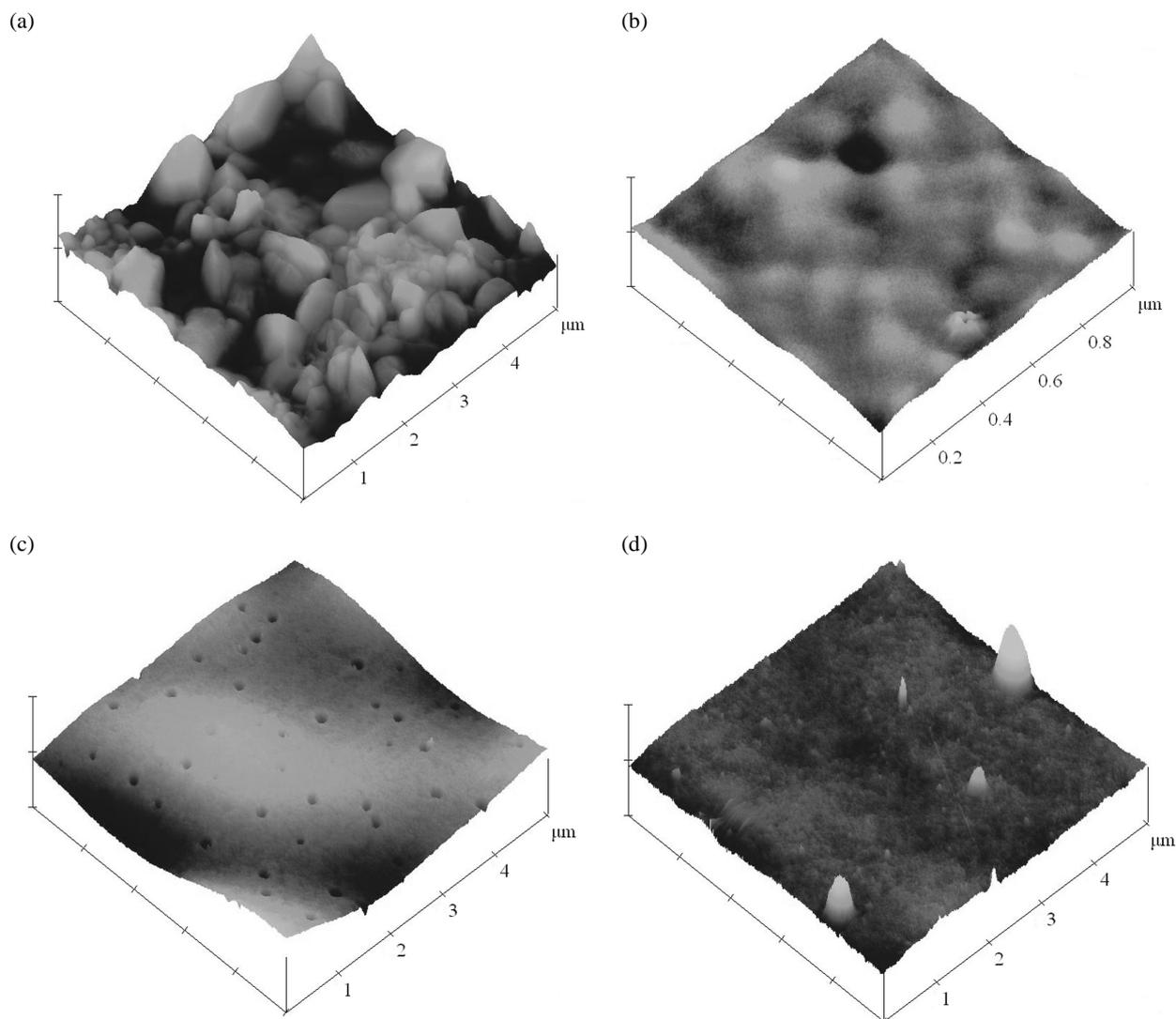

Fig. 3. AFM plots of CIS layers before (a) and after deposition of the P-3I-9VC:OMA layer (b); PS layer before (c) and after (d) annealing at temperature 130 °C. Z-scale values: (a) – 1 µm/div, (b) – 10 nm/div, (c) – 50 nm/div, and (d) – 20 nm/div.

Comparison of the images in Fig. 3 shows that the deposition of more elastic P-3I-9VC:OMA onto a polycrystalline CIS surface (Fig. 3a) leads to surface smoothing in the case of an amorphous polymer film (Fig. 3b). The picture was similar for the PEPC polymer layer. On the other hand, a significant amount of micropores was observed on a relatively smooth surface when we deposited the PS layer with a smaller flexibility of polymer macromolecules (Fig. 3c), which are filled during the process of annealing (Fig. 3d). Also, micropores disappeared after the annealing of the structures with the TPN-10 polymer layer. The changes in V_s and the surface roughness parameters are summarized in Table 1.

In Table 1 the value V_1 is the value of V_s at $E = 1.5$ eV (the region of weak absorption), V_{max} is the value of V_s at ca 1.65 eV, defined mainly by the rate of surface recombination of charge carriers on shallow surface centres. To characterize the efficiency of trapping onto deep surface centres, the value of the slope $\Delta V_s/V_s = (V_2 - V_3)/V_2$, where V_2 is the value of V_s at $E = 2.0$ eV (the beginning of a drastic decrease in $V_s(E)$ dependence), and V_3 is the value of V_s at $E = 2.5$ eV. Surface roughness parameters (Z_{range} – peak-to-valley difference in height values and RMS – root mean square average of height deviations) were analysed using fragments with 5×5 μm^2 dimensions by the help of routine AFM tools and software.

After the annealing of the structures, the change in V_s most probably occurs owing to the change in the barrier height on the CISCuT/polymer interface and to the change in the rate of the direct recombination of charge carriers on superficial centres. These centres are formed, for example, due to the adsorption of molecules of oxygen or solvent and effective trapping of non-equilibrium charge carriers on deep captures with their following recombination.

To estimate the contributions of these processes, we used the basic regularities of photovoltage spectrum

formation in the region of weak absorption, where V_s is defined mainly by the value of bands bending. On the other hand, the high rate of direct recombination of charge carriers on the surface centres should give $V_s(E)$ dependence on saturation in the region of strong absorption [10].

A drastic decrease in the short-wavelength region can only be caused by the trapping of non-equilibrium charge carriers onto deep surface centres, i.e. so-called trapping limited photovoltage rise [10].

Comparison of the obtained data (Table 1) shows that during annealing all structure bands bend and the decrease in the recombination rate is magnified at the CISCuT/polymer interface, due to the desorption of oxygen and solvent molecules during the annealing process. It should be noted that the concentration of deep trapping centres proportional to the parameter $\Delta V_s/V_s$ is practically not changed [5,6,10].

To determine the range of temperatures where the process of desorption is most effective, we studied the properties of structures with PEPC and P-3I-9VC:OMA polymer layers after annealing at different temperatures. We found that in the temperature range of 75–100 °C the influence of annealing is greater and magnification of V_{max} is higher than the values of V_s for a free CIS surface. The spectral dependences of V_s for structures with the layers of PEPC and P-3I-9VC:OMA after annealing at different temperatures are given in Figs 4 and 5.

Figures 4 and 5 show clearly that V_s changes essentially in the temperature range of 75–100 °C, i.e. the process begins at the point of T_g at which the effective desorption of oxygen and solvent molecules
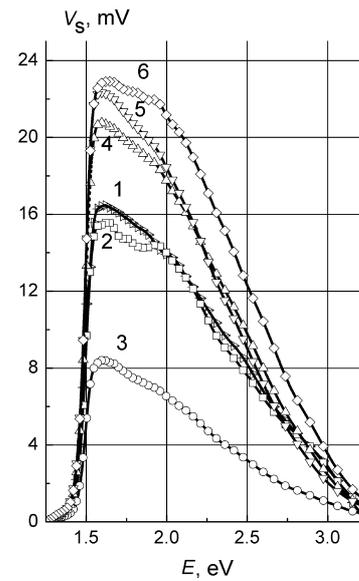
Table 1. The effect of annealing onto the surface and photovoltaic parameters of CISCuT/polymer structures

Structure	V_1, mV	V_{max}, mV	$\Delta V_s/V_s$	Z_{range}, nm	RMS, nm
CISCuT	10.62	16.47	0.409	872.14	128.21
PEPC/CISCuT	9.87	16.7	0.383	6.76	0.61
PEPC/CISCuT after annealing	11.93	20.11	0.396	5.29	0.64
P-3I-9VC:OMA/CISCuT	9.06	15.57	0.455	4.48	0.47
P-3I-9VC:OMA/CISCuT after annealing	13.84	22.33	0.417	2.02	0.25
PS/CISCuT	9.2	13.49	0.373	22.51	1.71
PS/CISCuT after annealing	9.62	16.03	0.485	9.62	0.68
TPN-10/CISCuT	8.3	13.48	0.487	24.07	2.68
TPN-10/CISCuT after annealing	10.14	16.46	0.453	11.39	1.12

Fig. 4. V_s spectra of CISCuT film (curve 1) and P-3I-9VC:OMA/CISCuT structures before (curve 2) and after annealing at temperatures 50 °C (curve 3), 75 °C (curve 4), 100 °C (curve 5), and 130 °C (curve 6).
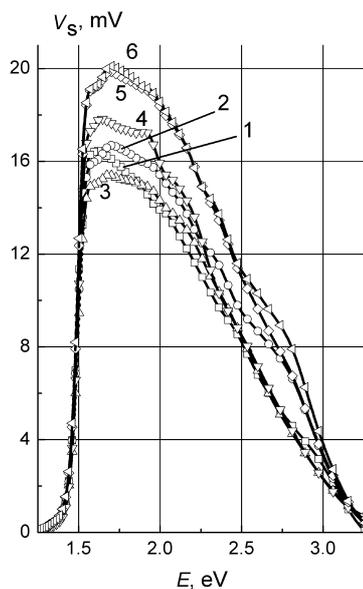
Fig. 5. V_s spectra of CISCuT film (curve 1) and PEPC/CISCuT structures before (curve 2) and after annealing at temperatures 50 °C (curve 3), 75 °C (curve 4), 100 °C (curve 5), and 130 °C (curve 6).

begins. When the annealing temperature is higher than 100 °C, the change in V_s is insignificant and frequently surface roughness is magnified and even defects on the polymer surface are observed (Fig. 3d). A characteristic feature of structures with a P-3I-9VC:OMA layer is an essential decrease in V_s after annealing at 50 °C. For the structures with other polymer layers the indicated changes are small and the process is ineffective in the applied temperature range. Measurements on AFM have shown that the surface of a film P-3I-9VC:OMA becomes rougher only after annealing at 50 °C. It becomes smoother before annealing and after annealing at temperatures higher than 75 °C. Probably, at this temperature the pores for the desorption of gases are already being formed, but the efficiency of desorption is still low. At higher temperatures not only desorption of gases is observed, but the mobility of molecules is already sufficient for filling pores.

CONCLUSIONS

The process of thermal annealing has significant influence on the morphology and photovoltaic parameters of hybrid CISCuT/polymer structures. Thus, active desorption of air (oxygen) and solvent from the polymer layer and subsequent filling of pores by molecules of a polymer take place during the annealing of the CISCuT/polymer structures at temperatures close to T_g (75–100 °C for different polymers). This leads to significant decrease in surface roughness, increase in the

height of a barrier, and reduction of the recombination rate at shallow surface levels, caused by the adsorption of molecules of oxygen and solvent.

However, annealing practically does not influence the concentration of deep surface trap centres of charge carriers, which define the decrease in photovoltage in the E region from 2 eV to 3 eV. The efficiency of the processes described above increases in the polymer range PS, PEPC, TPN-10, P-3I-9VC:OMA, i.e. it is connected with the flexibility of polymer macromolecules of a polymeric compound.

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Polümeerikihi ja termilise käsitluse mõju uurimine struktuuri CuInS$_2$/polümeer fotovoltomadustele

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On uuritud struktuuri CuInS$_2$/polümeer CuInS$_2$ absorberkihi fotovoltomadusi eri polümeere valides, sõltuvalt struktuuri kuumutamise temperatuurist õhukeskkonnas. On leitud, et pärast polümeerikihi sadestamist CuInS$_2$ pinnale struktuuri fotopinge mõnevõrra väheneb, samuti muutub pind siledamaks. Fotopinge väärtus sõltub valitud polümeeri plastilisusest ja on suurem plastilisemate polümeeride korral. Seda võib seletada väiksema arvu mikropooride tekkega. Järgnev termiline töötlus polümeeride klaasistumise temperatuuridel suurendab fotopinget ja vähendab pinna poorsust. Struktuuridel, mis sisaldavad suurema plastilisusega polümeeri, on fotopinge vastavalt suurem.