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IMPACT OF THE ANNEALING TEMPERATURE OF In_2O_3 FILMS ON THE PHOTOVOLTAIC CHARACTERISTICS OF A POLYMER SOLAR CELLS

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It is necessary to determine the effect of thermal annealing on morphology, absorption, and photoelectric properties for increase the efficiency of electronic transport of In_2O_3 films. The paper presents the results of a study the effect of the annealing temperature of In_2O_3 films obtained by spin-coating on the optical and photoelectrophysical characteristics of a polymer solar cell. It is established that an increase in the annealing temperature of films leads to an increase in the absorption and optical width of the band gap of the film. Has been determined the optimal annealing temperature of the films $T = 300^\circ\text{C}$, at which the electrons in the photoactive layer has the maximum lifetime of charge carriers and a low probability of recombination. At this temperature is observed, the maximum value of the efficiency of polymer solar cell.

Keywords: In_2O_3 , polymer solar cell, voltage characteristics, impedance spectra.

Introduction

Currently, semiconductor complex double and triple oxides, such as In_2O_3 , ZnO , SnO_2 , CdO , Ga_2O_3 , TiO_2 , are intensively studied. This is due to the fact that such materials have a fairly high transparency ($\sim 90\%$) in the visible range and the ability to conduct electric current. Therefore, they are used in the manufacture of thin displays, organic light-emitting diodes, solar panels, thin-film transistors, gas sensors, spacecraft, etc.

Relatively have a low mobility of charge carriers films based on ZnO and TiO_2 . Indium oxide (In_2O_3) having a band gap width (3.7-3.85 eV), optical transparency and relatively high electron mobility ($14 - 226 \text{ cm}^2 * \text{V}^{-1} * \text{s}^{-1}$) is an alternative [1].

There are many known methods for producing transparent conductive films based on indium oxide. In_2O_3 thin films can be obtained by pulsed laser deposition (PLD) [2], magnetron sputtering [3], pyrolysis by sputtering [4], ultrasonic sputtering [5, 6], sol-gel technology [7], spin coating method. In comparison with the above methods, the spin coating method has many advantages: simplicity of technology, low cost of reagents and equipment, the use of low-temperature deposition, which allows the production of high-quality films of various shapes and sizes.

It is known that the annealing temperature affects oxygen vacancies and the defectiveness of In_2O_3 films, as a result is observed of change in the structural and electrical properties of the films [8, 9]. Hence, to increase the efficiency of electronic transport, it is necessary to establish the effect of thermal annealing on the surface structure, absorption, and electrophysical and photovoltaic characteristics in In_2O_3 films. In this regard, in this paper, has been studied the influence of the annealing temperature of In_2O_3 films obtained by spin coating on the morphology, optical and electrical properties of the electron transport layer (ETL) in organic solar cells (OSCs).

1. Experimental methods

The Fluorinated Tin Oxide (FTO) -based substrates were prepared according to the methodology [10]. Indium oxide films were obtained on the FTO/glass substrates surface as follows: indium nitrate hydrate [$\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$] weighing $m=190\text{mg}$ (Borun New Material Technology Ltd.) was dissolved in a volume of ethylene glycol $V = 1\text{ ml}$. The solution was stirred at room temperature for 16 hours and then kept for 24 hours at room temperature. In_2O_3 films were obtained by spin-coating (SPIN150i, Semiconductor Production System) at a substrate rotation speed of 2000 rpm. After that, the films were annealed in an air atmosphere at temperatures of $200^\circ\text{C} - 500^\circ\text{C}$ for an hour.

The surface topography of the In_2O_3 films was studied by scanning electron microscopy (SEM, MIRA 3LMU, TESCAN). The absorption and reflection spectra the studied samples were recorded using the AvaSpec-ULS2048CL-EVO (Avantes) spectrometer. The impedance spectra were measured using a potentiostat-galvanostat P45X in the impedance mode. The voltage-current characteristics of photosensitive cells was determined by the Sol3A Class AAA Solar Simulators (Newport) with PVIV-1A I-V Test Station.

To obtain organic solar cells, a photoactive P3HT:ICMA layer was applied to the surface of the In_2O_3 film by spin-coating (3000 rpm) (Figure 1) (P3HT 95%, ICMA 98%, Sigma-Aldrich) at a concentration of 1:0.8. After that, the film of the photoactive layer was annealed in an air atmosphere at a temperature of 140°C for 10 minutes, then an hole transport layer (HTL) of PEDOT:PSS ($d \sim 30\text{ nm}$) was applied to the surface by spin-coating (3000 rpm), and then a current-removing electrode (Ag, $d \sim 120\text{ nm}$) was sprayed by thermal deposition on the CY-1700x-spc-2 installation (Zhengzhou CY Scientific Instruments Co., Ltd).

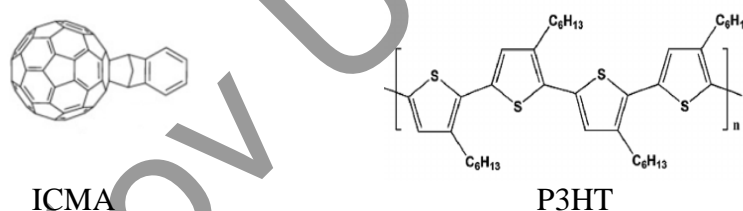


Fig.1. Structural formulas of compounds of donor-acceptor pairs P3HT: ICMA

2. Results and discussion

Figure 2 shows SEM images of the surface of the studied films annealed at different temperatures. It can be seen from the figure that the surface of the film is a porous structure. The annealing temperature of the films affects the morphology of the surface. Thus, the pore sizes begin to decrease with an increase in the annealing temperature of the films.

To determine the effect of the annealing temperature on the optical properties of In_2O_3 , the absorption and reflection spectra of films annealed at different temperatures were measured (Figure 3). The characteristics of the absorption spectra of In_2O_3 films at different annealing temperatures are given in Table 1. Measurement of absorption spectra showed that the absorption of films increases with increasing annealing temperature (Figure 3, a). The annealing temperature does not affect the shape of the absorption spectrum [8].

The inset of Figure 3, a illustrates the dependences of the band gap In_2O_3 at different annealing temperatures. The graph shows that at an annealing temperature at 200°C , the optical band gap is 4.68 eV [11, 12]. An increase in the annealing temperature from 300°C to 500°C leads to an increase in the optical band gap from 3.21 eV to 3.41 eV . The increase in E_g is associated with a decrease in the oxygen vacancy density in the film with an increase in the annealing temperature.

Figure 3, b demonstrates the reflection spectra of thin films In_2O_3 . That can be found from the figure that the film annealed at $T = 200^\circ\text{C}$ reflects light very weakly in the short-wavelength region of the spectrum. When the annealing temperature rises to 300°C and above, the shape of the absorption spectrum changes.

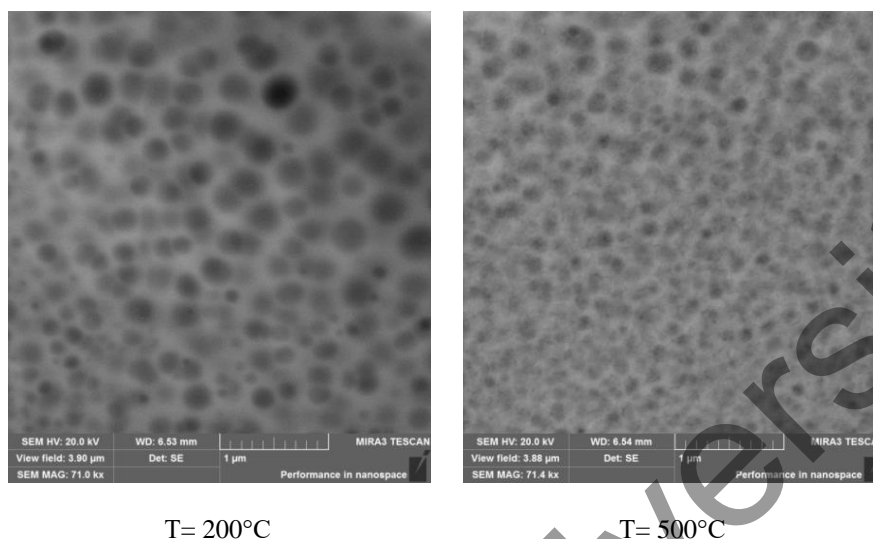


Fig.2. SEM images of the surface of In_2O_3 films annealed at different temperatures

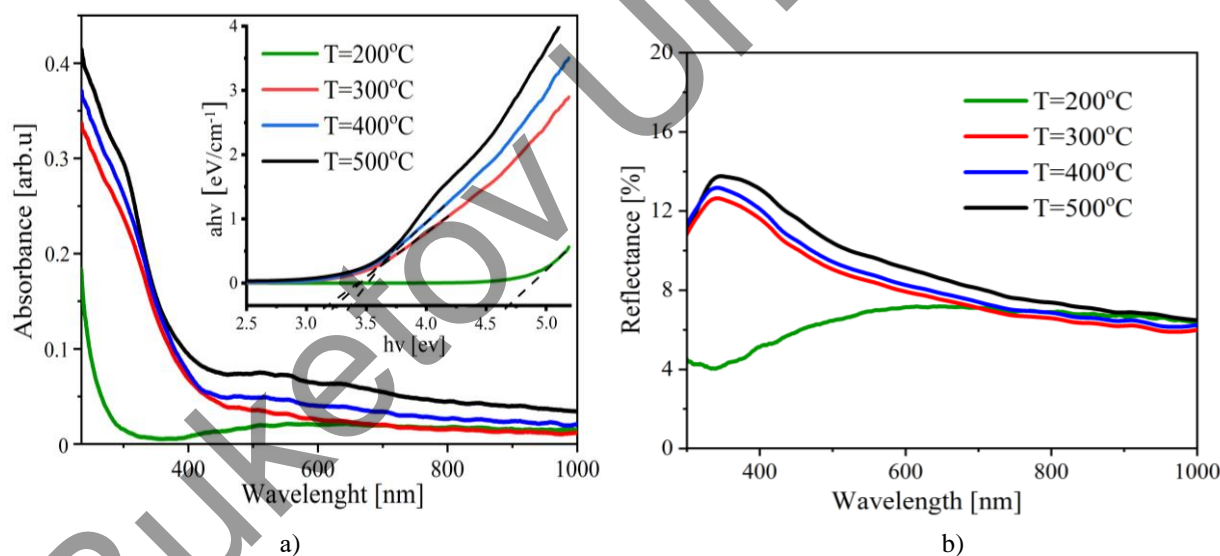


Fig.3. Absorption (a) and reflection (b) spectra of In_2O_3 films

Table 1. Parameters of optical absorption spectra of In_2O_3 films at different annealing temperatures

No.	Annealing temperature, $^\circ\text{C}$	Absorption, arb.u. ($\lambda = 235 \text{ nm}$)	Band gap, eV	Reflection, % ($\lambda = 345 \text{ nm}$)
1	200	0.18	4.68	4.1
2	300	0.33	3.21	12.6
3	400	0.36	3.32	13.2
4	500	0.41	3.41	13.8

The reflection of light by the film in the short-wave region of the spectrum is higher than in the long-wave region. An increase in the annealing temperature above 300°C slightly affects the reflection of the films. To determine the effect of the annealing temperature of In_2O_3 films on electronic transport, an $\text{In}_2\text{O}_3/\text{P3HT}:\text{ICMA}/\text{PEDOT}:\text{PSS}/\text{Ag}$ cell was assembled in a polymer solar cell (Figure 4).

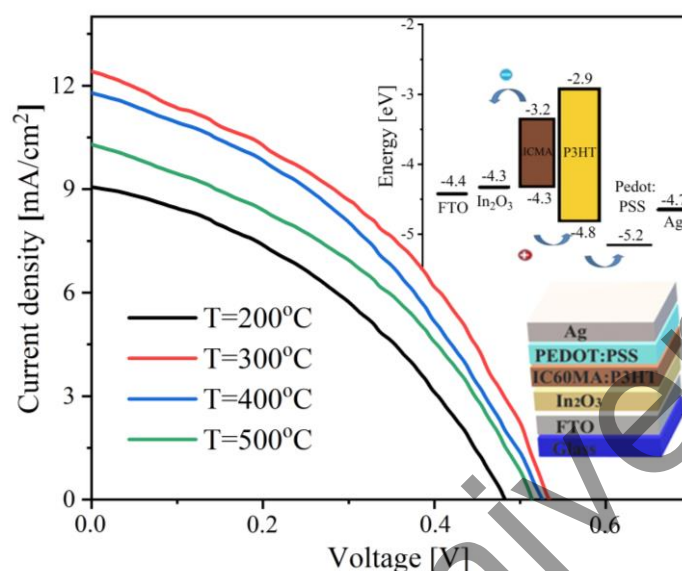


Fig.4. The voltage-current characteristics of FTO/ In_2O_3 /P3HT:ICMA/ PEDOT:PSS/Ag OSCs

When the P3HT:ICMA layer is photoexcited forms an electron-hole pair, which then forms at the interface $\text{In}_2\text{O}_3/\text{P3HT}:\text{ICMA}$ and P3HT:ICMA/PEDOT:PSS decays into a free electron and a hole (Figure 4). Electrons are injected into the In_2O_3 layer, and a hole is injected into the PEDOT:PSS layer. The volt-ampere characteristics of a polymer solar cell are shown in Figure 4.

Table 2 shows the photovoltaic parameters of the cell calculated on the basis of the voltage-current characteristics. As can be seen from Figure 4 and Table 2, the voltage-current characteristics parameters depend on the annealing temperature In_2O_3 . At the annealing temperature $T = 200^\circ\text{C}$, the efficiency of the cell was 1.7%. When the annealing temperature rises to $T = 300^\circ\text{C}$, there is an increase in the values of currents, voltage and power conversion efficiency (PCE) of the cell. With an increase in the annealing temperature of In_2O_3 films above 300°C , a decrease in the values of the voltage-current characteristics parameters is observed.

Table 2. Parameters of the voltage-current characteristics solar cells

Annealing temperature, °C	V_{oc} , (V)	J_{sc} , (mA/cm^2)	V_{max} , (V)	J_{max} , (mA/cm^2)	Fill factor	PCE, %
200	0.48	9.06	0.30	5.72	0.4	1.7
300	0.53	12.41	0.34	7.91	0.41	2.7
400	0.52	11.76	0.33	7.34	0.4	2.4
500	0.51	10.24	0.32	6.51	0.4	2.0

The observed changes in the voltage-current characteristics are related to the structural changes of indium oxide observed with an increase in the annealing temperature, which affect the transfer of charge carriers to OSCs. To study in detail the effect of indium oxide structure on the dynamics of charge carrier transport in OSCs, the impedance spectra of OSCs were measured. Figure 5 illustrates the impedance spectra of organic cells with indium oxide as an ETL layer annealed at different temperatures and the electrical circuit that was used to fit the impedance spectra.

Table 3 shows the electric transport parameters of cells calculated using the EIS-analyzer software package, where (R_w) is the equivalent resistance of the In_2O_3 film; (R_{rec}) is the resistance characterizing the recombination of localized electrons with holes; (k_{eff}) is the effective recombination rate of charge carriers; (τ_{eff}) is the effective lifetime of charge carriers. Table 3 shows that at the annealing temperature of 200°C of the In_2O_3 film, the resistance of the R_w film shows the highest value compared to other films, while the recombination resistance of R_{rec} is the lowest value. This leads to a deterioration in the transport of injected electrons into the FTO electrode. When the annealing temperature of the In_2O_3 film increases to 300°C , the resistance R_w decreases to the lowest value compared to other films, while the resistance R_{rec} increases and reaches the highest value among all. As a result, the electric transport characteristics of the film are improved, this leads to an increase in efficiency (2.7%).

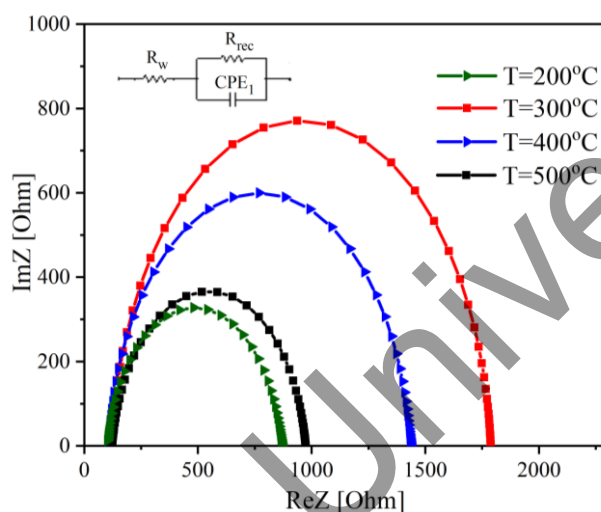


Fig.5. Impact of annealing temperature of In_2O films on the impedance spectra of OSCs

Table 3. The value of electrophysical parameters of films.

Annealing temperature, $^\circ\text{C}$	R_w , (Ohm)	R_{rec} , (Ohm)	R_{rec}/R_w , (Ohm)	τ_{eff} , (ms)	k_{eff} , (s^{-1})
200	121	769	6.35	1.1	948
300	99	1667	16.84	2.1	476
400	102	1331	13.05	1.7	561
500	105	952	9.07	1.3	782

The analysis of the cell impedance spectra shows that the In_2O_3 film at an annealing temperature of 300°C is optimal for OSCs, at which an increase in the efficiency of charge carrier transport is observed. In this case, the electrons in the photoactive layer have the maximum lifetime of charge carriers and a low probability of recombination.

Conclusion

In this paper has been studied, the influence of the In_2O_3 annealing temperature on morphology, structure and optical properties. It is established that with increasing annealing temperature, the porosity of the film begins to decrease. It is shown that an increase in the annealing temperature leads to an increase in the optical band gap by 0.2 eV. It is shown that the parameters of the voltage-current characteristics depend on the annealing temperature In_2O_3 . It is established that the annealing temperature of 300°C of In_2O_3 films is optimal for OSCs. At this temperature,

observed an increase in efficiency up to 2.7%, the maximum lifetime of charge carriers and a low probability of recombination in the OSCs. The obtained experimental data will have a perspective for the creation of electron transport layers of an organic photoconverter, providing a high conversion rate of light energy into electrical energy. This will help in the development of lightweight, technologically advanced and inexpensive in mass production, autonomous power supply sources for a wide range of electronic appliances and devices.

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