

ХИМИЧЕСКИЕ НАУКИ

UDK 662.997

Altantsetseg Delgerjargal

Department of Chemical and Biological Engineering
School of Engineering and Applied Sciences

National University of Mongolia
Mongolia, Ulaanbaatar

Khayankhyarvaa Sarangerel

Department of Electrotechnics
School of Power Engineering

Mongolian University of Science and Technology
Mongolia, Ulaanbaatar

Byambasuren Delgertsetseg

Faculty of Engineering

New Mongol Institute of Technology
Mongolia, Ulaanbaatar

Chimed Ganzorig

Faculty of Engineering

New Mongol Institute of Technology
Mongolia, Ulaanbaatar

INFLUENCE OF VARIOUS SURFACE-ACTIVE ORGANIC MONOLAYERS ON WORK FUNCTION OF INDIUM-TIN-OXIDE AND DEVICE PERFORMANCE

The device performance of organic photovoltaics (OPVs) deposited on ITO electrodes were reported. For a typical device configuration of ITO/ZnPc/C₆₀/Al with and without BCP as an exciton

blocking layer, the device performances, including J_{sc} , V_{oc} , FF , and η_p have been examined. In addition, the correlation between the change in the work function by the chemical modification of ITO and the device performances, including J_{sc} , V_{oc} , FF , and η_p is examined and the PV characteristics before and after the chemical modification of ITO electrodes were compared. Effective conversion of solar energy into electricity issues are considered. Formation of molecular self-assembled monolayer (SAM) at electrode surfaces and how to bind molecules on electrode surfaces were reported.

Key words: ORGANIC MONOLAYERS, INDIUM-TIN-OXIDE, ITO electrodes, self-assembled monolayer (SAM), transparent conducting oxide (TCO).

Introduction

Research field on OPVs is focused on the characterization of new organic materials and interfacial layers for the effective conversion of solar energy into electricity. The most essential properties that a material must meet before it can be used for solar cell applications include (a) strong light absorption over a broad spectral range, (b) good charge collection properties, (c) low cost of production, (d) stability over time when subjected to illumination, (e) high abundance of source materials and (f) environmentally friendly technology. OPVs have seen significant improvement in the last two decades, but more progress such as increasing power conversion efficiency, improving stability, and improving device reproducibility must still be made before they are ready for commercial applications.

Power conversion efficiency (PCE) of OPVs determined the area of the solar cell, the number of photons, the spectrum of the incident light, the optical properties of the solar cell and the energy level offset between the highest occupied molecular orbital (HOMO) of the donor, lowest unoccupied molecular orbital (LUMO) of the acceptor.

In this paper, the improvement of the device performance of OPVs by controlling the work function of anode electrodes to enhance charge collection and to fine-tune the energy level alignment at the interface between electrodes and active organic layers was described. In addition, the further improvement of built-in potential, which is defined by the energy difference between the work functions of anode and cathode electrodes to enhance the device performance, was investigated. For that, the work function of ITO anode should be increased using molecular self-assembly, and the work function of cathode electrode have to be decreased by insertion of the ultra-thin buffer layer between the organic layer and cathode.

In recent years, a formation of molecular self-assembled monolayer (SAM) at electrode surfaces has been widely used for organic optoelectronic devices. How to bind molecules on electrode surfaces has been studied extensively among electrochemists since 1970s and was called as chemical modification of electrode surfaces [14]. Studies for formation of various organic monolayers with carboxylic and phosphonic acids as well as organosilanes on *n*-type transparent oxide electrode surfaces with wide band gap were reviewed and discussed comprehensively [13].

Most of the useful transparent conducting oxide (TCO) with a wide bandgap (≥ 3 eV) studied up to now have been chemically inert conductive oxides, such as TiO_2 , SnO_2 , In_2O_3 and ZnO . The bandgaps of these *n*-type semiconductors correspond to the energy photons in the UV region. Schematic band diagram of these oxides is shown in Figure 1 [14].

ITO is commonly used as an essential bottom contact electrode material in PV cells, due to its low resistivity, high transparency in visible region, possibility of patterning and relatively high conductivity. However, the properties of the ITO surface make it incompatible with organic layers. Furthermore, resistance in device through low hole mobility in ITO is caused by relatively low work function of ITO.

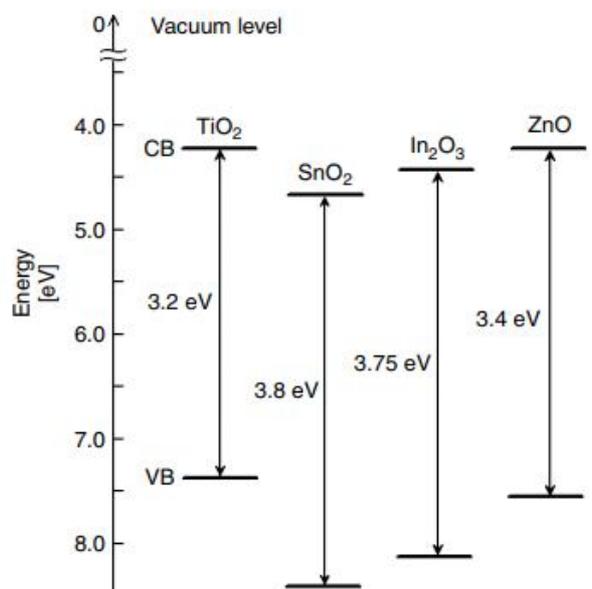


Figure 1. Schematic diagram illustrating the energy levels of conduction band (CB) and valence band (VB) of some n-type undoped semiconductor oxides such as TiO₂, SnO₂, In₂O₃, and ZnO

Various treatments such as self-assembling monolayer of dipolar molecules [10; 11], UV-ozone [8], forming a thin layer of conjugated polymers [6] on the surface of ITO electrodes have been used to improve the work function of ITO electrodes.

Armstrong *et al.* used ferrocene dicarboxylic acid (Fc(COOH)₂) and 3-thiophene acetic acid (3-TAA) to modify ITO films before they further modified these interfaces by electrochemically growing a thin layer of poly(3,4-ethylenedioxythiophene)/poly(styrene sulfonic acid) (PEDOT:PSS) [12]. The higher short-circuit currents observed in organic PV cells [9] using these chemically modified interfaces was attributed to better wettability of the organic layers compared to the polar ITO surface, and also enhanced transfer between the ITO electrode and CuPc layers by means of the charge intermediate PEDOT:PSS layer.

Experimental section

The substrates used in this study were 160-nm-thick ITO coated glass plates with resistance of ca. 15 Ω/square supplied by Sanyo Vacuum Industries. The substrates were cut into 10×12 mm² sample slides, and the ITO layers were etched by an aqua regia solution to form 2-mm-wide stripes for use as anodes.

Patterned ITO substrates were cleaned and rinsed by two detergent solutions (Extran MA 03, pH 6.8, MERCK and Kontaminon O, pH 10, WAKO) and deionized water and then stored under isopropanol until being required. Prior to use, the ITO substrates were further cleaned and ultra-sonicated successively in acetone and in isopropanol, and then transferred to boiled isopropanol for 30 minutes each. This cleaned ITO will be called hereafter “as-cleaned ITO”.

After cleaning, the substrates were immersed for 15 min in dichloromethane solutions containing 1 mM of para-benzene sulfonyl chlorides with C₆H₅-, Cl-, CF₃-, NO₂- and H- terminal groups to form the SAM on the surface of ITO.

The modified ITO electrodes were rinsed in pure dichloromethane to remove excess unbound molecules and then dried in glove box. The dip time required to form the complete monolayer was done for 10 min. SAMs are ordered molecular assemblies formed by the adsorption of molecules with a surface-active binding group on a solid surface (see Figure 2) [14].

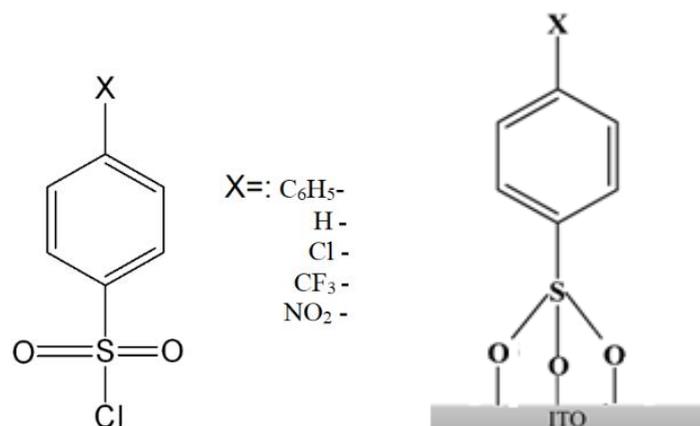


Figure 2. Chemical structure and schematic drawing of formation SAMs

The value of CPD of chemically modified ITOs was measured by Kelvin probe force microscopy (KPFM). Then work function of ITO was calculated from the CPD value.

Chemically modified ITOs were used as some anode electrodes to prepare PV cells of configurations with ITO(modified)/ZnPc/C₆₀/BCP/Al (Figure 3). ZnPc was used as donor materials in these devices. Vacuum evaporation system “Showa Shinku” was used for deposition of materials with pressure of $5-7 \times 10^{-4}$ Pa at rates of 1-1.5 Å/s for organic materials and 3-4 Å/s for Al electrode. The shadow mask was used to determine the size of active area in all devices as 5×5 mm².

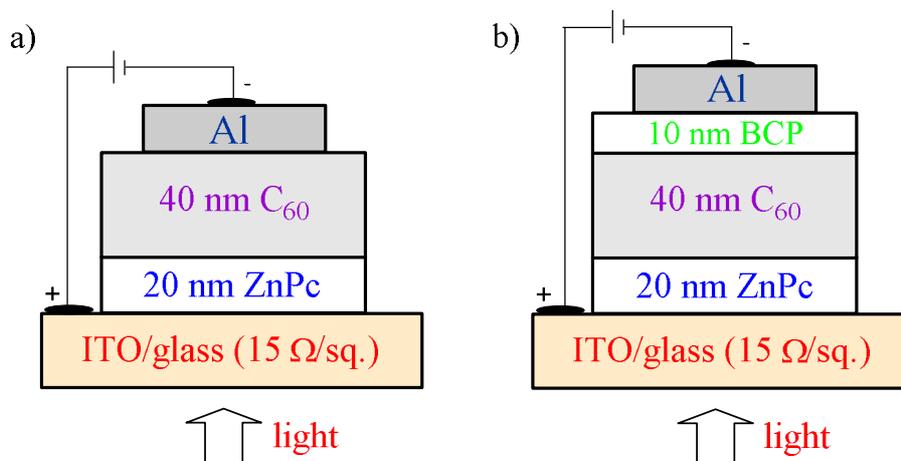


Figure 3. Device structures of (a) ITO/ZnPc(20 nm)/C₆₀(40 nm)/Al two-layer and (b) ITO/ZnPc(40 nm)/C₆₀(40 nm)/BCP(10 nm)/Al three-layer OPVs

Results and Discussion

Proposed energy level diagrams for the OPVs used this study are shown in Figure 4 [1]. The effective work functions of variously modified ITO were estimated from the CPD values calculated above together with the assumption that the work function of ITO treated at 120°C after cleaning agrees with the consistent value of 4.5 ± 0.1 eV for the work function of as-received bare ITO [6; 7].

Five kinds of self-assembly molecules, C₆H₅-, H-, Cl-, NO₂-, and CF₃-, terminated benzenesulfonyl chlorides have a high electron affinity for -OH groups due to chemisorption of the molecule onto the ITO substrate. The molecules also show varying degrees of electron-withdrawing character, resulting in different magnitude of dipole moment. In this case, the result is a large dipole moment, μ , pointing towards the ITO surface and it has been shown to result in an increased work

function of the ITO surface [2]. The effective work functions of ITO were calculated from the CPD values for the chemically modified ITOs as well as 4.87 eV for C₆H₅, 4.99 eV for H-, 5.11 eV for Cl-, 5.17 eV for CF₃ and 5.28 eV for NO₂-terminated benzenesulfonyl chlorides [3; 5].

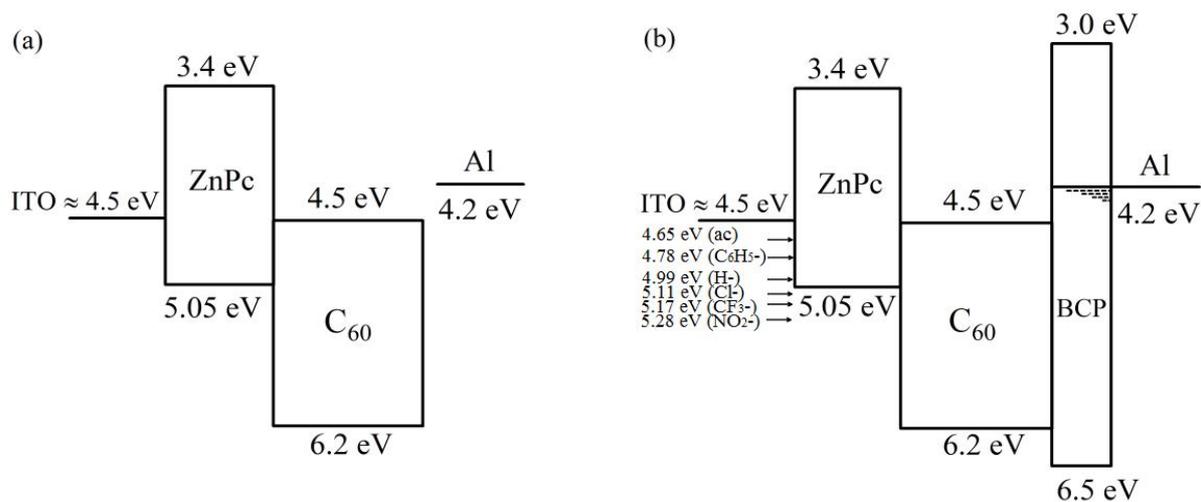


Figure 4. Schematic energy diagrams for a) two-layer and b) with BCP layer OPVs

Figure 5 shows the $J - V_{\text{bias}}$ characteristics of ITO(as-cleaned)/ZnPc(20 nm)/C₆₀ (40 nm) cells under white light illumination of 100 mW/cm² in OPVs with and without BCP.

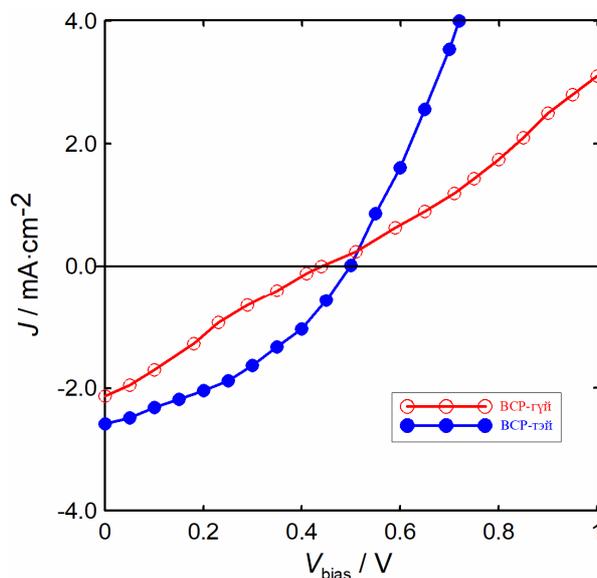


Figure 5. $J - V_{\text{bias}}$ characteristics of OPVs on “as-cleaned” ITO with and without BCP as an exciton blocking layer under 100 mW/cm² illumination

The PV characteristics are obtained in a two-layer cell with 20 nm and 40 nm layer thickness for ZnPc and C₆₀, respectively, under illumination the V_{oc} was 0.30 V, $J_{\text{sc}} = 1.96 \text{ mA/cm}^2$, $FF = 0.22$ and $\eta_p = 0.13 \%$. The V_{oc} of a three-layer cell was 0.49 V higher than for two-layer cell, although both J_{sc} and FF were improved, resulting in an increased PCE.

In this case, FF (0.38) of the cell with BCP was 1.7 times higher than that of the cell without BCP (0.22), accompanied by a nearly 30% increase in J_{sc} . Generally, the cells with BCP show a much better behavior with respect to the two-layer structure cells. The $J - V_{\text{bias}}$ characteristics of

ITO/ZnPc (20 nm)/C₆₀ (40 nm)/BCP (10 nm)/Al cells with variously treated ITO electrodes as well as chemically modified ITO by C₆H₅-, H-, Cl-, NO₂-, and CF₃- terminated benzenesulfonyl chlorides and “as-cleaned” ITO are shown in Figure 6. The PV characteristics of the cells are summarized in Table 1.

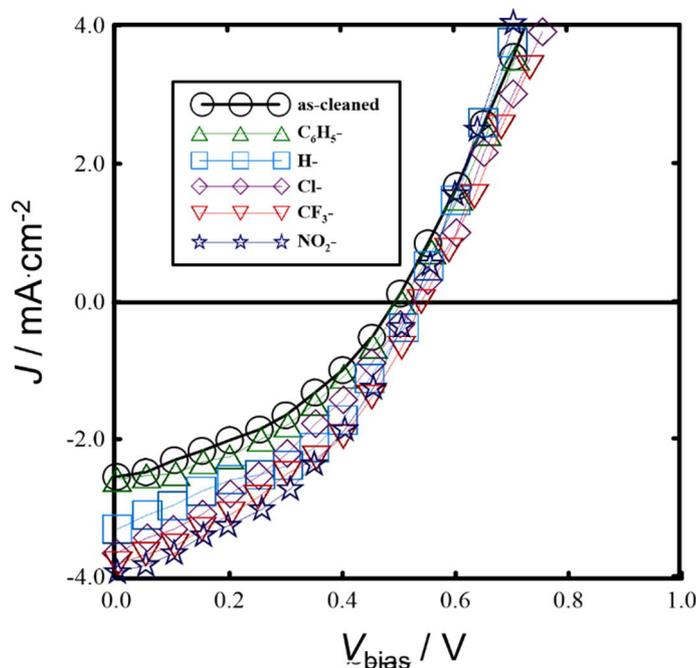


Figure 6. The J-Vbias characteristics of ITO/ZnPc (20 nm)/C₆₀(40 nm)/BCP (10 nm)/Al cells with variously treated ITO and “as-cleaned ITO” under 100 mW/cm² illumination

The results show that the ITO modified by NO₂- and CF₃- terminated benzenesulfonyl chlorides should be better improved the PV characteristics by providing a good contact with ZnPc. In fact, the chemical modification of ITO by molecular self-assembly with a dipole moment of appropriate direction and magnitude was an effective way to change the work function of ITO and to decrease the injection barrier between ITO and the HOMO level of ZnPc as electron-donor in OPVs.

In the cell with chemically modified with NO₂- terminated benzenesulfonyl chlorides, the PV performance improve significantly, such as the J_{sc} , V_{oc} , FF and η_p were measured as 3.93 mA/cm², 0.54 V, 0.41, and 0.86 %, respectively, as shown in Table 1. This result suggested that the work function of ITO modified by C₆H₅-, H-, Cl-, NO₂-, and CF₃- terminated benzenesulfonyl chlorides shifted down to the HOMO level of ZnPc resulting in formation of Ohmic contact at the ITO/ZnPc. interface.

The cell with “as-cleaned” ITO shows relatively poorer performance to compare with ITO modified with C₆H₅-, H-, Cl-, NO₂-, and CF₃- terminated benzenesulfonyl chlorides. Khodabakhsh and co-workers examined the chemical modification of ITO using self-assembled monolayers of molecules with permanent dipole moments. The chemically modified ITOs have been used to control the anode work function and device performance in molecular solar cells based on CuPc:C₆₀ HJ [3; 4].

Photovoltaic characteristics for the OPVs using ITO chemically modified with H– and Cl–terminated benzenesulfonyl chlorides under 100 mw/cm² illumination

	Modified ITO	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η_p (%)
Without BCP	(as-cleaned)	1.96	0.30	0.22	0.13
	(as-cleaned)	2.56	0.49	0.38	0.48
With BCP	C ₆ H ₅ –	2.58	0.50	0.40	0.52
	H–I	3.31	0.51	0.42	0.71
	Cl–	3.65	0.52	0.37	0.70
	CF ₃ –	3.81	0.53	0.42	0.85
	NO ₂ –	3.93	0.54	0.41	0.86

The PV characteristics of the OPVs using the ZnPc/C₆₀ heterojunction layer under 100 mW/cm² illumination of white light source was examined. Two types of device structures have fabricated to see the effect of BCP as the exciton blocking layer; one is ITO/ZnPc/C₆₀/Al and the other is ITO/ZnPc/C₆₀/BCP/Al. The OPVs with BCP have more than 1.7 times the FF as compared to typical two-layer devices without BCP, resulting in a more than 3.6 times of the PCE. Moreover, PV performance was increased significantly by using chemically modified ITO electrodes.

In the cell with chemically modified ITO with NO₂⁻, the J_{sc} , V_{oc} , FF and η_p were measured as 3.93 mA cm⁻², 0.54 V, 0.41, and 0.86%. It has been shown that ITO electrodes modified with organic molecules such as benzenesulfonyl chloride may improve the PV device efficiency by providing a good contact with ZnPc as an electron donor material. In our case, the cell with as-cleaned ITO anode showed relatively poor performance.

This study supports the device performance that change in work function of ITO and introduction of BCP thin layer between C₆₀ and Al interface are dominate factors in improving PV characteristics in OPVs.

Conclusions

Dependence of the work function of ITO electrode on dipole moments of terminal groups of the SAM molecules was investigated. In the case of modification of anode electrode with benzene sulfonyl chloride with NO₂⁻ terminal group, photovoltaic performance of OPVs with structure of ITO(NO₂⁻)(160 nm)/ZnPc(20 nm)/C₆₀(40 nm)/BCP (10 nm)/Al was obtained as V_{oc} =0.54 B, J_{sc} =3.93 mA·cm⁻², FF =0.41 and η_p =0.86.

The efficiency of this device was 4 times higher than that of standard OPVs. It has a trend to increase OPV performance as increasing negative value of dipole moments of the terminal groups of SAM molecules, which are used chemical modification of ITO electrode, was increased.

LIST OF REFERENCES

1. Murray R.W. Electroanal. Chem. – 1984. – 15, 191.
2. Ganzorig C., Fujihira M. Encyclopedia of Electrochemistry. – 2007. – 261.
3. Appleyard S.F., Day S.R. J. Mat. Chem. – 2000. – 10, 1, 169.
4. Ganzorig C., Kwak K.J. App. Phys. Lett. – 2001. – 79, 272.
5. Arias A., Roman L. Thin Solid Films. – 2000. – 371, 201.
6. Brown T., Kim J., Friend R. [et al.]. Synthetic metals. – 2000. – 111, 285.
7. Donley C. [et al.]. Langmuir. – 2002. – 18, 2.

8. Kallmann H., Pope M. J. Chem. Phys. – 1959. – 30, 585.
9. Deibel C., Dyakonov V. Rep. Prog. Phys. – 2010. – 73, 9, 096401.
10. Kim J. J. Appl. Phys. – 1998. – 84, 6859.
11. Sugiyama K. J. Appl. Phys. – 2000. – 87, 295.
12. Brabec C.J. Chem. Phys. Lett. – 2001. – 340, 3.
13. Sarangerel K., Ganzorig C., Fujihira M. Chem. Lett. – 2008. – 37, 778.
14. Raus H.C. Solar Cell Array. Design Handbook. – 1980. – New York. – 86.

Алтанцецег Делгеряргал

Кафедра химической и биологической инженерии
Школа инженерных и прикладных наук
Национальный университет Монголии
Монголия, г. Улан-Батор

Хаянхярваа Сарангерел

Кафедра электротехники
Школа Энергетики
Монгольский университет науки и техники
Монголия, г. Улан-Батор

Бямбасурен Делгерцецег

Инженерный факультет
Новый Монгольский технологический институт
Монголия, г. Улан-Батор

Чимед Ганзориг

Инженерный факультет
Новый Монгольский технологический институт
Монголия, г. Улан-Батор

ВЛИЯНИЕ РАЗЛИЧНЫХ ПОВЕРХНОСТНО-АКТИВНЫХ ОРГАНИЧЕСКИХ МОНОСЛОЕВ НА ФУНКЦИОНИРОВАНИЕ ОКСИДА ИНДИЯ-ОЛОВА И УСТРОЙСТВО ЕГО РАБОТЫ

Сообщается о рабочих характеристиках органических фотоэлектрических элементов (ОПВ), нанесенных на электроды окиси индия олова (ITO). Для типичной конфигурации устройства ITO / ZnPc / C₆₀ / Al с и без БСП в качестве слоя блокировки экситона были рассмотрены рабочие характеристики устройства, включая J_{sc} , V_{oc} , FF и η_p . Кроме того, изучалась корреляция между изменением работы выхода в результате химической модификации ITO и характеристик устройства, включая J_{sc} , V_{oc} , FF и η_p , и сравнивались характеристики PV до и после химической модификации электродов ITO. Были рассмотрены вопросы эффективного преобразования солнечной энергии в электричество. Описано формирование молекулярного самоорганизующегося монослоя (SAM) на поверхностях электродов и способы связывания молекул на поверхностях электродов.

Ключевые слова: органические монослои, оксид индия-олова, электроды ITO, молекулярный самоорганизующийся монослой (SAM), прозрачный проводящий оксид (TCO).