The photo-electrical behavior of n-Si/orange dye, vinyl-ethynyl-trimethyl-piperidole/conductive glass electrochemical sensor

A. ELAHI, M. H. SAYYAD*, Kh. S. KARIMOV[a], Kh. ZAKAULLAH, M. SALEEM
GIK Institute of Engineering Sciences and Technology, Topi, N.W.F.P, 23460, Pakistan
[a]*Physical Technical Institute of Academy of Sciences, Dushanbe, 734025, Tajikistan*

The photo-electrical behavior of n-Si/orange dye, vinyl-ethynyl-trimethyl-piperidole/conductive glass sandwich type sensor is investigated. In this sensor the crystalline silicon of n-type and conductive glass (CG) electrodes are employed and as electrolyte the 0.5 and 1 wt.% solutions of organic dye (OD) and vinyl-ethynyl-trimethyl-piperidole (VETP) in a mixture of distilled water (80%) and spirit is used. Properties of the n-Si/OD-VETP/CG sensor are investigated at the inter-electrode distances of 3 mm, 15 mm, and 30 mm. Photo-induced under IR, Red, Green and Blue LEDs illuminations, open-circuit voltage and short-circuit current are investigated and it is found that the sensor is sensitive in the range of 500 nm – 850 nm. It is observed that with increase of the inter-electrode distance the current increases and voltage remains constant. Increase of concentration of the OD and VETP in the solution results to increase of the voltage and decrease of the current. In the light-voltage/current conversion this sensor behaved as a photoelectric differentiator.

(Received April 5, 2007; after revision May 1, 2007; accepted June 26, 2007)

Keywords: Photoelectric sensor, Orange dye, Organic semiconductor, Vinyl-ethynyl-trimethyl-piperidole

1. Introduction

An increasing number of papers deal with the properties of organic photo-electric and photo-electrochemical cells. This is mainly due to low cost, simplicity of device fabrication and interesting electrical, electrochemical and optical properties, and environmentally harmless or friendly technology. The properties of dye-sensitized solar cells with a one-facial monolithic set-up were investigated in [1]. This cell was produced for the first time by screen printing. The conversion of light to electricity by cis-X_2 Bis (2,2'-bipyridyl-4,4'-dicarboxylate) ruthenium (II) complexes on nanocrystalline TiO_2 electrodes was studied in [2]. A solar-to-electric energy conversion efficiency of 10 % was attained with this system. The photo-electrochemistry of single crystal C_{60} and fullerene photo-electrochemical solar cells was studied by Sinke *et. al.* [3]. The properties of solid state organic solar cells were investigated in [4]. This study had shown record efficiency of 11% at 0.25 cm^2 and 6.5% at 1.6 cm^2 cells' area. Photoelectric behavior of n-GaAs and n-$Al_xGa_{1-x}As$ in CH_3CN was investigated in [5] and it was shown that open-circuit voltage was equal to 0.83 V, short-circuit current density was 20 mA cm^{-2} and energy conversion efficiency greater than 10 % at 88 mW cm^{-2} simulated AM 1.5 solar illumination was determined. Historical background, present status and development prospects for the new generation of photo-electrochemical cells, including dye–sensitized nanocrystalline TiO_2 film, were reviewed in [6].

At the same time, unlike to solar cells for the photo-electric sensors, the efficiency is not the main parameter. Therefore, fabrication and investigation of organic photo-electric sensors is very promising field due to their high sensitivity in a wide spectral range of wavelengths. The electrical and photoelectrical properties of the organic photovoltaic devices based on the organic thin layers were summarized in [7]. We investigated organic-on-inorganic Ag/n-GaAs/p-CuPc/Ag photoelectric sensor that was sensitive in UV-visible-IR spectra (200-1000 nm) [8].

The present paper is one of a series on the characterization of OD and its use as an organic conductor, which have to date concerned with the investigations of electrical properties of the OD films deposited from aqueous solution [9,10] and a two-layer structure, PEPC/OD heterojunction, that exhibited a rectification behavior [11], the Photo-Electrical Behavior of n-Si and p-Si/Orange Dye/Conductive Glass Cells [15] This paper presents the results of investigation of Photo-Electric Properties of n-Si/Orange dye, Vinyl-Ethynyl-Trimethyl-Piperidole/ Conductive Glass Sensor.

2. Experimental

Commercially produced organic semiconductor orange dye ($C_{17}H_{17}N_5O_2$) and vinyl-ethynyl-trimethyl-piperidole ($C_{12}H_{19}NO$) with molecular weight of 323 g/mole and 218 g/mole, and density of 0.9 g/cm^3 and 0.6 g/cm^3 were used for fabrication of photo-electrical sensor. In the cell as electrodes the crystalline silicon of n-type with concentration of dopants of 10^{22} m^{-3} and conductive glass (In_2O_3) were used. As an electrolyte the 0.5 and 1 wt.% solutions of organic dye (OD) and vinyl-ethynyl-trimethyl-piperidole (VETP) in mixture with distilled water (80%) and spirit were used. The VETP has gel and complex forming behavior and it is used here to increase viscosity of the solution to minimize leakage.

Fig. 1 shows the schematic diagram of the fabricated n-Si/OD-VETP/CG sensor.

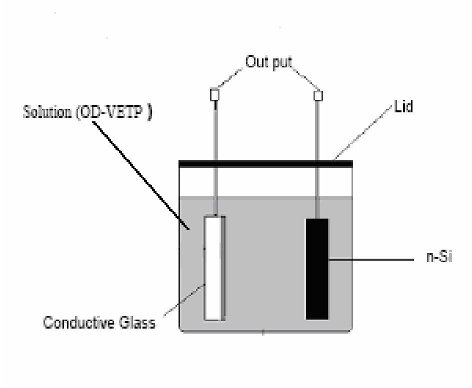

Fig. 1. Schematic diagram of the n-Si/OD-VETP/CG sensor.

The n-Si and CG electrode dimensions were to $40 \times 20 \times 0.5$ mm^3. The distances between the n-Si and conductive glass electrodes were equal to 3 mm, 15 mm, and 30 mm, respectively. For investigation of photo-electric properties of the sensor the digital volt–ampere meters, an oscilloscope, and an intensity meter were used. All experiments were carried out at room temperature conditions. As a light source the IR, Red, Green and Blue LEDs with effective diameter of the light beam of 1 cm were used. In some measurements filament lamp was also used.

3. Results and discussion

Fig. 2 shows dark current-voltage characteristics of the n-Si/OD-VETP/CG sensor at concentration of solution that was equal to 1 wt.% and inter-electrode distance of 30 mm.

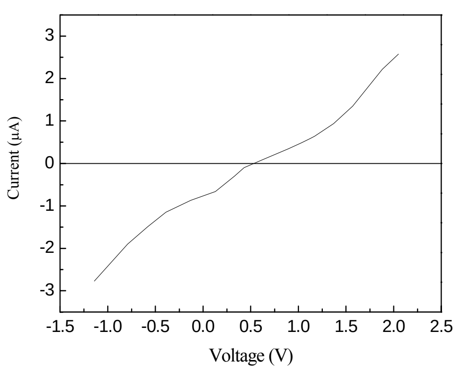

Fig. 2. Dark current-voltage characteristics of the n-Si/OD-VETP/CG sensor at concentration of solution that was equal to 1 wt.% and inter-electrode distance of 3 mm.

It is seen that there is a zero offset voltage: current is equal to zero at 0.5 V applied to n-Si electrode. The zero offset current was equal to -1.0 μA. It indicates the presence of electrochemical effect in the sensor [12]. The polarity of n-Si electrode was "positive" with respect of conductive glass electrode. It is seen that the I-V characteristic is quasi-linear. At the estimations of the photo voltages/currents of the sensor the dark voltages/currents zero offsets were respectively deducted.

Fig. 3 shows photo voltage/current-light intensity (Filament lamp modulated by square wave voltage of frequency of 0.1 Hz was used) relationships of the sensor (concentration of solution that was equal to 1 wt.% and inter-electrode distance of 30 mm). The voltage and current characteristics are non-linear and quasi-linear, respectively, that is, in principle, is similar to conventional photo-diode characteristics [13].

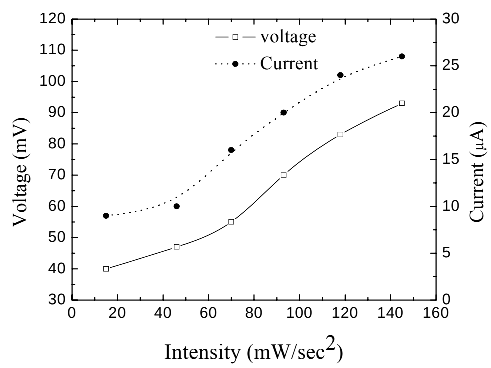

Fig. 3. Photo voltage/current-intensity of light relationships of the sensor (concentration of solution that was equal to 1 wt.% and inter-electrode distance of 30 mm). Filament lamp was modulated by square wave voltage of frequency of 0.1 Hz.

Fig. 4 shows peak photo voltage/current – spectral sensitivity of the n-Si/OD-VETP/CG sensor (concentration of solution that was equal to 1 wt.% and inter-electrode distance of 30 mm).

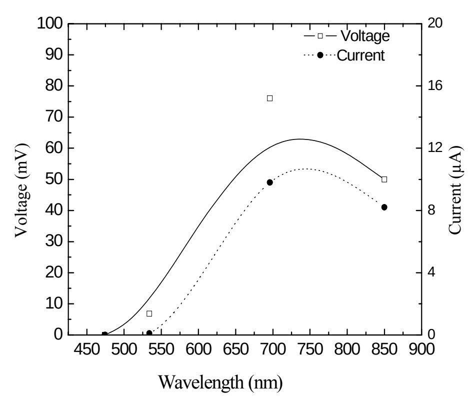

Fig. 4. Photo voltage/current – spectral sensitivity of the n-Si/OD-VETP/CG sensor (concentration of solution that was equal to 1 wt.% and inter-electrode distance of 30 mm).

It is seen that the sensor is sensitive in the wavelength range of 530 nm – 850 nm, i.e. the sensor is selective, it is sensitive mostly to IR, red and green lights.

Fig. 5 shows photo voltage/current–modulation frequency relationships of the sensor (concentration of solution that was equal to 1 wt.% and inter-electrode distance of 15 mm).

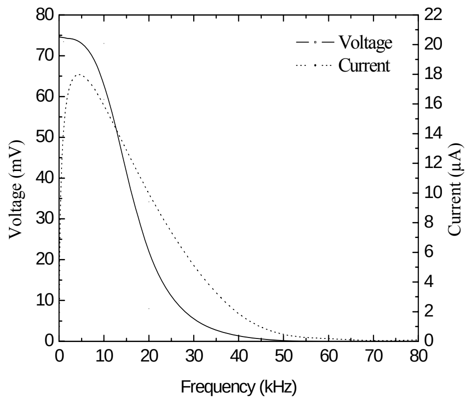

Fig. 5. Photo voltage/current–modulation frequency relationships of the sensor (concentration of solution that was equal to 1 wt.% and inter-electrode distance of 15 mm.)

It is seen that photo voltage/current practically are constant up to the frequencies of 1 kHz and then decaying exponentially to about 13 kHz and 20 kHz for voltage and current, respectively, that may be due to the presence of built-in capacitances in the sensor.

Fig. 6 shows directivity characteristics of the n-Si/OD-VETP/CG sensor: voltages/currents –illumination angle relationships (concentration of solution was equal to 1 wt.% and inter- electrode distance to 30 mm).

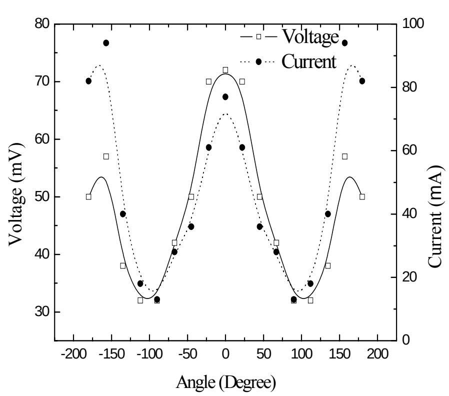

Fig. 6. Directivity characteristics of the n-Si/OD-VETP/CG sensor: voltages/currents illumination angle relationships (concentration of solution was equal to 1 wt.% and inter-electrode distance to 30 mm).

The sensor is sensitive in wide range of angles ($\pm180^o$) that essentially is wider than in some conventional photo-diodes ($\pm90^o$ in the case of PN303). The sensitivity of the sensor is maximum at the illumination from the side of conductive glass electrode and from backside (of Si electrode) as well.

Fig. 7 shows photo voltage/current dependences on inter-electrode distances for the sensor (concentration of solution was equal to 1 wt.%): it is seen that voltage practically is constant but current increases with distance. This is unusual behavior and in the first approximation may be explained by increase of ions concentration in the inter-electrode space of the sensor with increase of inter-electrode distance.

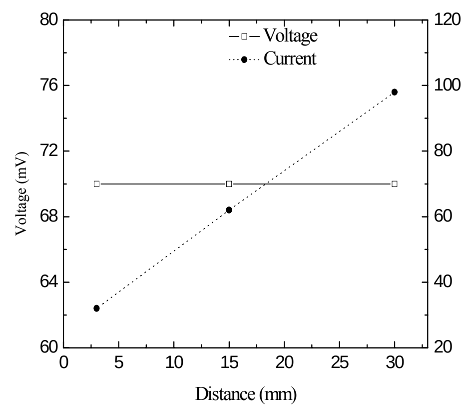

Fig. 7. Photo voltage/current dependences on inter-electrode distances for the sensor (concentration of solution was equal to 15 mm).

Fig. 8 shows photo-voltage/current – solution concentration relationship of the n-Si/OD-VETP/CG sensor (inter-electrode distance was equal to 15 mm).

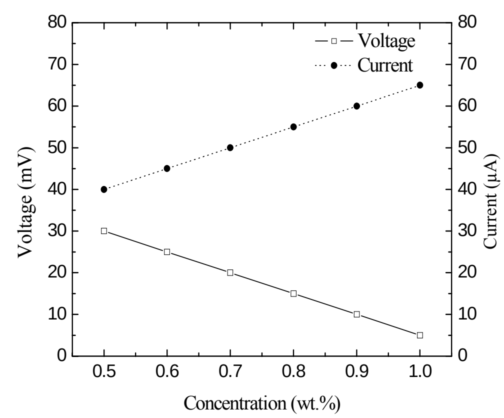

Fig. 8. Photo-voltage/current – solution concentration relationship of the n-Si/OD-VETP/CG sensor (inter-electrode distance was equal to 15 mm).

From above figure it is clear that voltage increases and current decreases with the concentration. In the case of voltage it may be due to increase of the chemical reaction rates in the electrode-electrolyte interface, whereas the decrease of the current may be connected with the decrease of the ions mobility in the solution.

Fig. 9 shows the photo voltage/current – time relationship in the case of illumination of the sensor (concentration of solution was equal to 1 wt.% and inter-electrode distance to 30 mm) by filament lamp modulated light of frequency of 0.1 Hz and intensity of radiation of 100 mW/cm^2. It is seen that actually the sensor works as photo electrical converter.

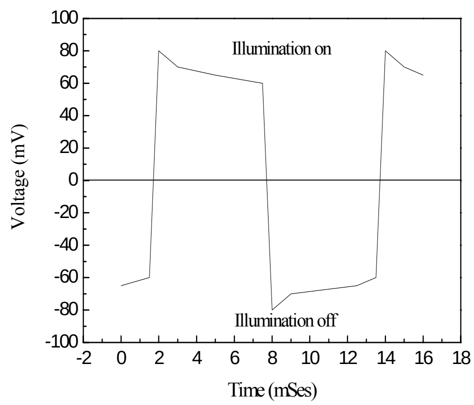

Fig. 9. Photo voltage/current –time relationship in the case of illumination of the sensor (concentration of solution was equal to 1 wt.% and inter-electrode distance to 30 mm.) by filament lamp modulated light of frequency of 0.1 Hz . and intensity of radiation of 100 mW/cm^2.

Photo voltage – time relationship for the case of modulation by red LED with frequency of 100 Hz is shown in Fig. 10. This waveform shows the differentiation properties of the sensor.

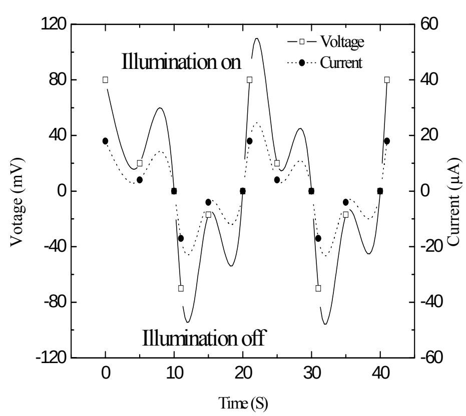

Fig. 10. Photo voltage – time relationship for the case of modulation by red LED with frequency of 100 Hz.

The semiconductor-electrolyte interface at equilibrium is described in [6,12]. When semiconductor is immersed in redox electrolyte the Fermi level (E_F) of semiconductor equilibrates with redox potential of the electrolyte (E_{redox}). In order to identify the electronic energy levels at the electrolyte we investigated visible absorption spectrum of orange dye and vinyl-ethynyl-trimethyl-piperidole solution (Fig. 11).

It is seen that absorption actually starts in the wavelength range of 850 nm and increases sharply at 550 nm and covers the range 550 nm – 250 nm as well. This absorption is equivalent to the charge excitation in the energy band of 1.46 eV- 2.25 eV and 2.25 eV – 4.77 eV, respectively. The absorption of Si and voltage sensitivity of the sensor are shown in Fig. 11. The sensor is sensitive in the spectral range where absorption of OD-VETP solution is small but absorption of the Si is large. It means that OD-VETP solution from some point plays the role of filter, making the sensor selective, i.e. sensitive in the range of wavelength of green-red-IR lights.

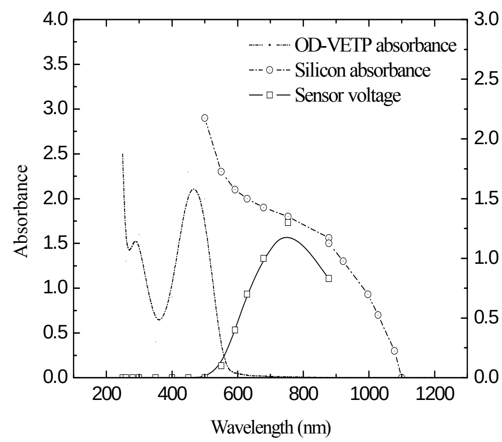

Fig. 11. Visible absorption spectra of orange dye and vinyl-ethynyl-trimethyl-piperidole solution, Si and voltage sensitivity of the -Si / OD-VETP / CG sensor.

The excitation energy levels in OD solution are larger than the energy gap of Si. Therefore, we can assume that at illumination of the cell by lower than 1.46 eV and above 1.1 eV the incident photons are transmitted through OD solution and absorbed by n-Si . Photons with energy larger than 1.46 eV are absorbed partly by OD solution. Photo-induced charges in n-Si may contribute to the cell's photocurrent. On the other hand, it may be visible contribution of orange dye solution in photoelectric effect as in dye-sensitized cells [6]: n-Si semiconductor can receive electrons from the photo-excited orange dye as well.

In their general form the variety of the semiconductor-electrolyte energy band diagrams were described in [6]. Taking into account the absorption spectra of OD-VETP solution and Si, we may draw schematically the energy band diagram of the n-Si/OD-VETP/CG sensor in the semiconductor-electrolyte-conductive glass interfaces for the equilibrium case (Fig. 12a). Here V_{se} and V_{ce} are potential barriers between the n-Si semiconductor-electrolyte and conductive glass-electrolyte interfaces, respectively. The band diagram for the non-equilibrium case is shown in Fig. 12b. We took into consideration that polarities of photo induced voltage (V_{ph}) and that developed due to the electrochemical effect voltage (V_{ch}) coincide and are summed to the total output voltage of the sensor. The V_{ch} is the open-circuit voltage at dark condition (it is equal to zero offset voltage in Fig. 2).

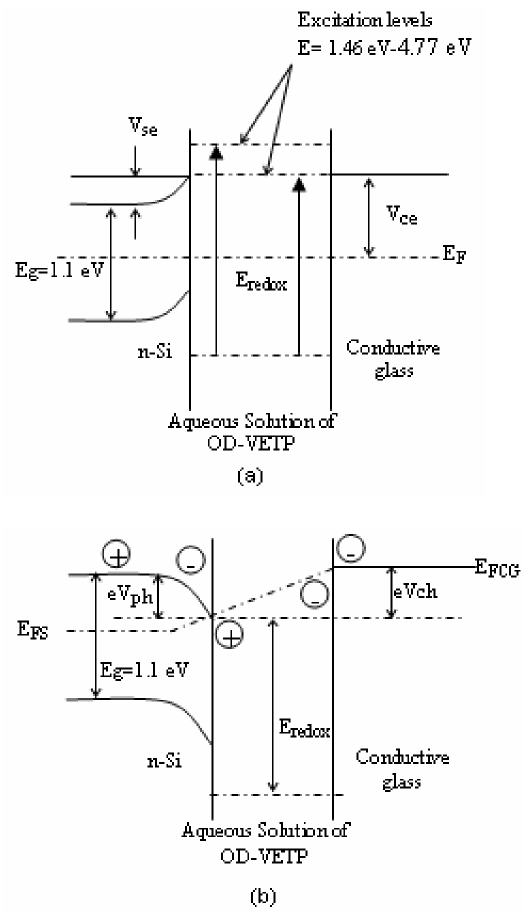

Fig. 12. Schematic energy band diagram of the n-Si/OD-VETP/CG sensor in the semiconductor-electrolyte-conductive glass interfaces for the equilibrium (a) and non-equilibrium cases (b).

In the case of non-equilibrium conditions, i.e. in the presence of photo induced voltage and voltage developed due to electrochemical reactions the band bending is probably changed (Fig. 12b) due to the effect of positive charges in the n-Si – electrolyte interface.

Taking into account the experimental results presented above it is possible to develop the equivalent circuit of the photoelectric sensor [14]. The modified equivalent circuit that reflects the properties of the n-Si /OD-VETP/CG sensor is shown in Fig. 13.

Conventional elements of the photoelectric sensor equivalent circuit comprising photo induced current source (I_{ph}), junction capacitance (C_j) and series resistance (R_s) are concerned to n-Si semiconductor. The current source (I_{ch}) represents the electrochemical source. The semiconductor-electrolyte-conductive glass resistance (R_{sm}) and semiconductor-electrolyte and electrolyte-conductive glass effective capacitance (C_{se}) are related to this source. The capacitance C_e is the external inter-electrode capacitance of the sensor. It is known [6,10] that on the electrolyte side of electrode-electrolyte interface there is a double layer (Helmholtz layer) of negative and positive ions. The width of this layer is equal 0.4-0.6 nm. The Helmholtz layer is characterized by the Helmholtz capacitance C_H. The capacitance C_{se} (Fig. 13) actually may be equal to C_H.

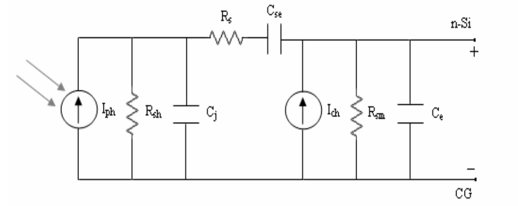

Fig. 13. Equivalent circuit of the n-Si /OD-VETP / CG sensor.

4. Conclusions

The n-Si/OD-VETP/CG electrochemical sensor was fabricated. As an electrolyte, the 0.5 wt.% and 1.0 wt.% solutions of orange dye (OD) and vinyl-ethynyl-trimethyl-piperidole (VETP) in a mixture of distilled water (80%) and spirit was used. Electric and photoelectric properties of the sensor were investigated. The sensor shows properties of electrochemical source and photoelectric source as well. The voltages of the effects were summed and the total voltage was equal to 0.5-0.6 V at an intensity of light radiation equal to 1-2 mW/cm^2. The sensor has wide direct analityc characteristics and shows wavelength selectivity in the range of green-red and IR lights. Equivalent circuit of the sensor was developed and the energy band diagrams of it at equilibrium and non-equilibrium conditions were drawn. In the light-voltage/current conversion this sensor behaves as a photoelectric differentiator. The sensor may be used in optical communication and instrumentation laboratories and for registration of the atmospheric lightning as well.

Acknowlegements

The authors are grateful to the GIK Institute of Engineering Sciences and Technology for supporting to this work and providing the necessary research facilities.

References

[1] A. Hinsch, R. Kinderman, M. Spath, E. Rijnberg, J. A. M. van Roosmalen, Proc. 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion, Vienna, 1998, p.1-4.
[2] M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos, M. Grätzel, J. Am. Chem. Soc. **115**, 6382 (1993).
[3] W. C. Sinke, M. M. Wienk, Photochemistry: Solid-state organic solar cells, Nature, **395**, 544 (1998).
[4] S. Licht, O. Khaselev, P.A. Ramakrishnan, D. Faiman, E. A. Katz, A. Shames, S. Goren, Fullerene Photoelectrochemical Solar Cells, Solar Energy Materials and Solar Cells **51**, 9 (1998).
[5] L. G. Casagrande, A. Juang, N. S. Lewis, J. Phys. Chem. B **104**, 5436 (2000).

[6] M. Grätzel, Photoelectrochemical Cells, Nature **414**, 338 (2001).
[7] S. Antohe, J. Optoelectron. Adv. Mater. **2**(5), 498 (2000).
[8] Kh. S. Karimov, Kh. M. Akhmedov, A. A. Dzhuraev, M. N. Khan, S. M. Abrarov, M. I. Fiodorov, Eurasian Chem. Tech. Journal **2**, 251 (2000).
[9] Effect of Temperature and Humidity on Electrical Properties of Organic Orange Dye Complex Films Eurasian Chem. Tech J. **6**,145 (2004).
[10] Kh. S. Karimov, M. M. Ahmed, S. A. Moiz, P. Babadzhanov, R. Marupov, M. A. Turaeva, Eurasian Chem. Tech. J. **5**, 109 (2003).
[11] Kh. S. Karimov, M. M. Ahmed, R. M. Gul, M. Mujahid, Kh. M. Akhmedov, J. Valiev, Proceedings of the Advanced Materials-2001, Published by Dr. A. Q. Khan, Research Laboratories, Rawalpindi, Pakistan, 2002, p. 329.
[12] K. Rajeshwar, in: S. Licht (Ed.), Semiconductor Electrodes and Photoelectrochemistry, vol. 6 "Encyclopedia on Electrochemistry," A. Bard, Series Ed) WILEY-VCH, Weinheim, GRM (2002).
[13] A. Bar-Lev, Semiconductors and electronic devices, 2nd Ed., Prentice-Hall International Inc., Englewood Cliffts, NJ, London (1984).
[14] Kh. S. Karimov, M. M. Ahmed, S. A. Moiz, M. I. Fedorov, Solar Energy Materials & Solar Cells, **87**, 61 (2005).
[15] M. H. Sayyad, Kh. S. Karimov, A. Ellahi, S. A. Moiz, Z. M. Karieva, M. A. Turaeva, Kh. Zakaullah, Eurasian Chem.Tech. J. **7**(2), 133 (2005).

*Corresponding author: sayyad@giki.edu.pk ; hsayyad62@hotmail.com