The Photo-Electrical Behavior of *n*-Si and *p*-Si/Orange Dye/ Conductive Glass Cells

M.H. Sayyad[1]*, Kh.S. Karimov[2], A. Ellahi[1], S.A. Moiz[1], Z.M. Karieva[3],

M.A. Turaeva[2] and Kh. Zakaullah[1]

[1]GIK Institute of Engineering Sciences and Technology, To pi, 23460, N.W.F.P., Pakistan

[2]Physical Technical Institute of Academy of Sciences, Dushanbe, 734025, Tajikistan

[3]Tajik Technical University, Dushanbe, 734000, Tajikistan

Abstract

The photo-electrical behavior of *n*-Si/orange dye/conductive glass and *p*-Si/orange dye/conductive glass sandwich type cells were investigated. In these cells crystal silicon of *n*-type and *p*-type and conductive glass (CG) electrodes were employed and the aqueous solution of organic dye (OD) was used as an electrolyte in the distilled water. Under filament lamp illumination, photo-induced open-circuit voltage and short-circuit current exponentially dropped with time for the *n*-Si/orange dye/CG cell. In the *p*-Si/orange dye/CG cell, the photovoltaic effect was not observed. The *n*-Si/OD/CG cell showed high photo-electrical response under illumination. In the light-voltage/current conversion, these cells behaved as a differentiator and exhibited charge-storage properties.

Introduction

More recently, characterization of organic semiconductors and studies of the photo-electric and photo-electrochemical cells based on organic semiconductors have attracted considerable interest [1-16]. This is mainly due to low cost, ease of devices fabrication and interesting electrical and optical properties. Also organic semiconductors are highly promising materials for future cost effective electronic and optoelectronic devices such as light-emitting diodes, lasers, photodetectors, field-effect transistors and integrated circuits [17 and references therein]. Individual semiconducting molecules or molecular complexes are of interest for the fabrication of electronic devices on the molecular scale [18].

Alternative materials and methods of fabrication for all kinds of devices are constantly sought. Organic cells may be fabricated with organic dyes, low molecular weight semiconductors, semiconducting polymers, or on some combination of these materials. Fabrication and investigation of organic photo-electric devices is very promising field due to their high sensitivity in the wide spectral range of wavelengths. The combination of organic and inorganic semiconducting materials provides an alternative for the production of low-cost and high efficiency photovoltaic devices. We reported organic-on-inorganic Ag/*n*-GaAs/*p*-CuPc/Ag photoelectric sensor that was sensitive in UV-visible-IR spectral range (200-1000 nm) [19]. The present paper is one of a series on the characterization of OD and its use as an organic semiconductor which have to date concerned with the investigations of electrical properties of the OD films deposited from aqueous solution at high gravity conditions [20] and a two-layer structure, poly-N-epoxi-propylcarbazole/OD heterojunction, that has shown a rectification behavior [21]. This paper presents the results of investigation of photo-electric properties of *n*-Si/orange dye/conductive glass and *p*-Si/orange dye/conductive glass photoelectrochemical cells. The study of these cells may represent an interesting alternative for all-inorganic and all-organic photovoltaic devices [22]. These cells not only convert solar energy to electrical but also has the ability to store energy [23]. Studies of the properties of organic semiconductors have been exploited in producing diodes, field effect transistors and electroluminescent devices

---

*corresponding authors. E-mail: sayyad@giki.edu.pk

of these materials [24]. Therefore, the investigations carried out in this work may be utilized for the production of organic electronic devices.

Experimental

Commercially produced organic semiconductor orange dye (OD), $C_{17}H_{17}N_5O_2$ (Fig. 1) with molecular weight of 323 g/mole and density of 0.9 g/cm^3 was used for the fabrication of photo-electrical cell. In the cell, the crystal silicon electrodes of *n*- and *p*-type with concentration of dopants of 10^{22} m^{-3} and conductive glass (In$_2$O$_3$) were used. The 5 wt.% aqueous solution of the OD was used as an electrolyte in distilled water. Figure 2 shows schematic diagram of the fabricated sandwich type *n*-Si (or *p*-Si)/OD/CG cell. The *n*-Si and *p*-Si electrodes dimensions were equal to 4×5×0.5 mm. The separation between the *n*-Si (or *p*-Si) electrode and conductive glass layer was equal to 1 mm. The terminal contacts to *n*-Si and *p*-Si were made by metallic clips that had no connections with the solution.

For the investigation of photo-electric properties of the cell the conventional digital volt-ampere-meters, an oscilloscope, an intensity-meter and a lux-meter were used. All experiments were carried out at room temperature conditions. Filament lamp was used as a light source.
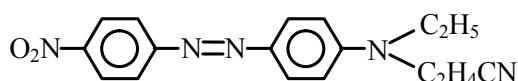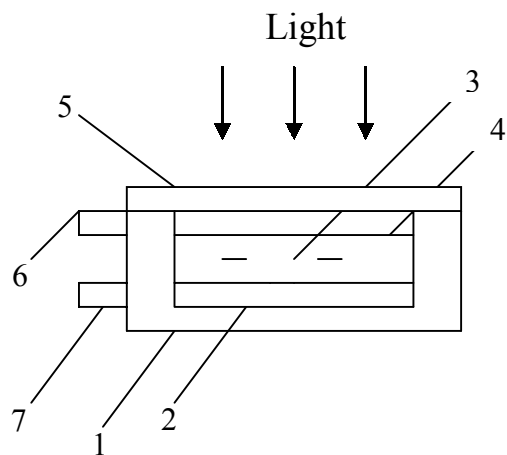

Fig. 1. Molecular structure of orange dye (OD).

Fig. 2. Cross-sectional view of the *n*-Si (or *p*-Si)/OD/CG cells: 1 – cell's body, 2 – *n*-Si (or *p*-Si), 3 – aqueous solution of orange dye, 4 – conductive glass, 5 – glass, 6 and 7 – terminals.

Results and Discussion

The semiconductor-electrolyte interface at equilibrium is described in [25,26]. When semiconductor is immersed in redox electrolyte the Fermi level E_F of semiconductor equilibrates with the Fermi level in electrolyte $E_{F,redox}$ that is related with redox potential E_{redox} of the electrolyte by the following expression [26]:

$$E_{F,redox} = -4.5 \text{ eV} - q \cdot E_{redox} \qquad (1)$$

where q is electronic charge. The E_{redox} is defined with reference to standard hydrogen electrode (SHE).

In order to identify the electronic energy levels at the interface between the semiconductor and the electrolyte, we investigated visible absorption spectrum of orange dye aqueous solution (Fig. 3). It is seen that absorption starts in the wavelength range 550-850 nm and covers 350-550 nm as well. This absorption is equivalent to the charges excitation in the energy band of 1.5-2.3 eV and 2.3-3.5 eV, respectively.
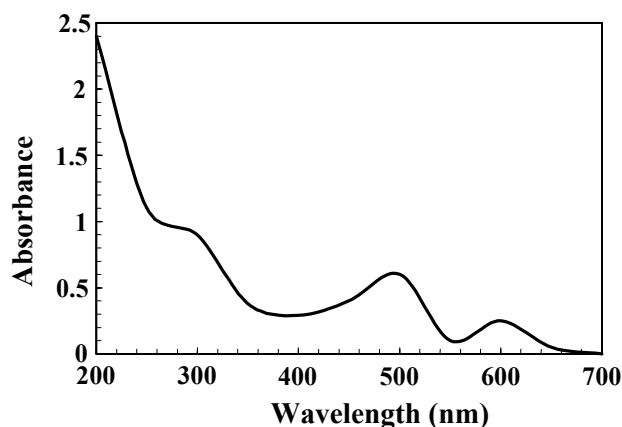

Fig. 3. Absorption *vs.* wavelength for an orange dye aqueous solution.

Figures 4a and 4b show energy levels in semiconductor-electrolyte interface for the *n*-Si/OD/CG and *p*-Si/OD/CG cells respectively. Here, V_{se} and V_{ce} are potential barriers between the *n*-Si semiconductor-electrolyte and conductive glass-electrolyte interfaces, respectively. Here, we assume that the V_{se} value may be large and approximately comparable with Si band gap (1.1 eV). For the case of *p*-Si semiconductor-electrolyte, the V_{se} may be negligible because the orange dye is also a *p*-type organic semiconductor [20,21]. The excitation energy levels in OD solution are the larger ones of the energy gap of the Si. Therefore, we can assume that on illumi-

nation of the cells at energies lower than 1.5 eV and above 1.1 eV photons of incident light are transmitted through OD solution and absorbed by *n*-Si (or *p*-Si). Photons with the larger energy of 1.5 eV are absorbed 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 [25]: *n*-Si semiconductor can receive electrons from the photo-excited dye as well. In the case of *p*-Si/OD/CG cell photo-induced charges may be not separated because of negligible built-in of electric field in the semiconductor surface.
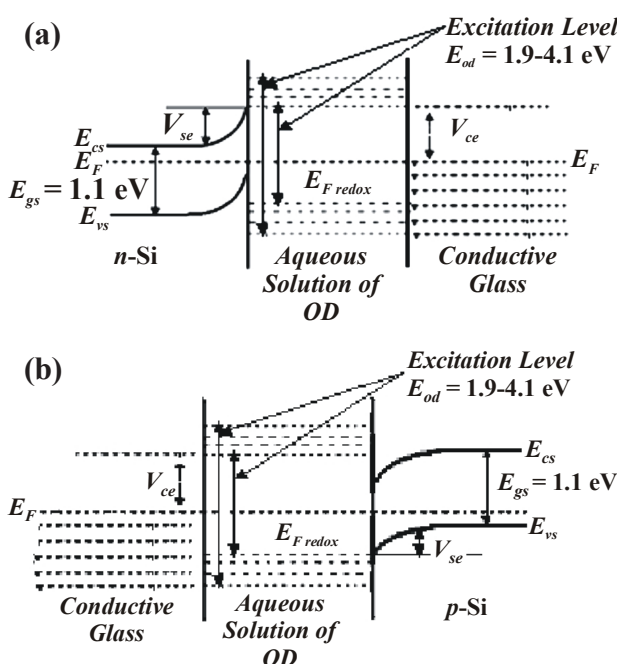

$$\frac{Q_{on}}{Q_{off}} = \frac{\int\limits_{0}^{t_1} i(t)dt}{\int\limits_{t_2}^{t_1} i(t)dt} \qquad (2)$$

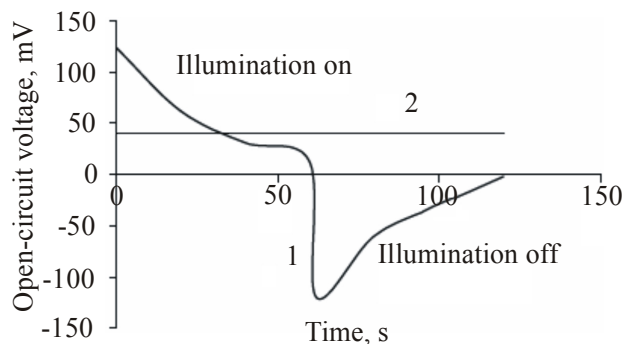where $t_1 = 6$ s , $t_2 = 12$ s (Fig. 6).

Fig. 5. The open-circuit voltage and time relationship for the *n*-Si/OD/CG (1) and *p*-Si/OD/CG (2) cells.
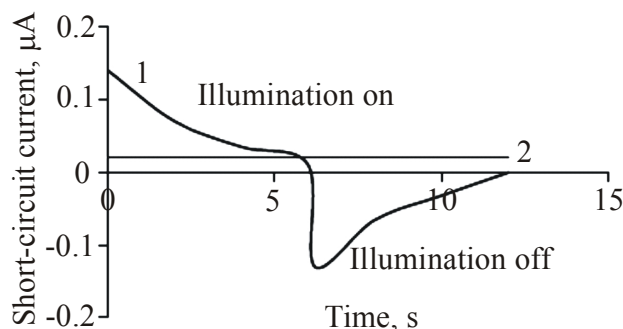

Fig. 6. The short-circuit current and time relationship for the *n*-Si/OD/CG (1) and *p*-Si/OD/CG (2) cells.

Fig. 4. Energy levels in semiconductor-electrolyte interface for the *n*-Si/orange dye/CG cell (a) and p-Si/orange dye/CG cell (b).

Figures 5 and 6 show the open-circuit voltage-time and short-circuit current-time relationships respectively for the *n*-Si/OD/CG and *p*-Si/OD/CG cells at illumination of 15000 Lx. It is seen that in the *p*-Si/OD/CG cell photovoltaic effect is not observed really. In the *n*-Si/OD/CG cell, photo-induced open-circuit voltage and short-circuit current decay exponentially with time constants of the processes being equal to 40 s and 4 s, respectively. On the other hand, the storage of electric energy takes place and its efficiency is equal to 98% for the current-time waveforms. It was found as a Q_{on}/Q_{off} ratio of charges stored at illumination "on" and supplied at illumination "off":

The photo-voltage/current decay with time when the illumination is "on". It may be due to electric charge of the capacitance comprised by *n*-Si electrode - OD solution - conductive glass electrode system. When the illumination is off, the capacitance is discharged providing voltage and current of opposite polarity (Figs. 5 and 6). Actually the open-circuit voltage and short-circuit current waveforms (Figs. 5 and 6) show that the cell performs like the differentiator circuit and properties of this cell are like to transient processes in conventional *RC*-circuit. Taking into account the results presented in Figures 2-6, it is possible to develop the equivalent circuit of the photoelectric sensor [19]. The modified equivalent circuit that reflects the properties of the *n*-Si/OD/CG cell is shown in Fig. 7. Conventional elements of the photoelectric cell equivalent circuit [27] as a

current source (I_{PH}), diode (D), shunt resistance (R_{sh1}) and series resistance (R_s) are concerned to *n*-Si semiconductor. The C and R_{lkg} represent the inter-electrode (*n*-Si-OD solution-CG) effective capacitance and leakage resistance of the C, respectively. The R_{sh2} is a total inter-electrode resistance of the electrolyte. The two resistances R_{lkg} and R_{sh2} are rather non-linear, like varistors, because of electric field dependence of the ionic conduction [28].
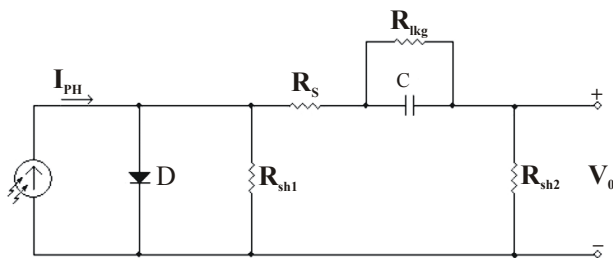

Fig. 7. Equivalent circuit of the *n*-Si/OD/CG cell: I_{PH} – photo-current source, R_S – series resistance, R_{sh1} and R_{sh2} – shunt resistances, C – effective capacitance, R_{lkg} – leakage resistance, D – represents electrode-electrolyte junction.

It is known [26] that on electrolyte side of electrode-electrolyte interface there is 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 effective capacitance C (Fig. 7) incorporates the C_H and C_E (electrolyte capacitance) connected in series. The effective capacitance C may be determined from experimental data obtained above using conventional relationship:

$$C = Q/U = \int idt / U \qquad (3)$$

where Q is charge and U is voltage across capacitor and $T = 6$ s. The U and charge $q = \int idt$ we can obtain from Fig. 5 and Fig. 6, respectively, and determine the value of C that is equal to 3.4 μF. From the following expression for the energy (W_c) of charged capacitance:

$$W_c = CU^2/2 \qquad (4)$$

and we can also calculate the power conversion efficiency (η) which is given by:

$$\eta = \frac{W_c}{W_l} \times 100\% \qquad (5)$$

where W_l is energy of light.

$$W_l = J \cdot S \cdot T \qquad (6)$$

where J is intensity of irradiation (30 mW/cm²), S is area of *n*-Si electrode (20 mm²) and T is time of illumination ($T = 6$ s, Fig. 6), respectively. Finally from eq. 4, it was determined the efficiency, that is equal to 1×10^{-4}%. As the value of the η is small, the *n*-Si/OD/CG cell may be interesting, first of all, as a photoelectric sensor that has signal storage behavior as well, rather than solar cell.

Assuming that depletion layer is formed in *n*-Si semiconductor electrode surface and the potential barrier V_{se} is comparable with gap in electronic states of Si semiconductor ($E_g = 1.1$ eV), the width (d) of the depletion layer may be determined from the following expression [29]:

$$V_{SN} = qN_D \cdot d^2/2\mu\mu_o \qquad (7)$$

where q is electronic charge, N_D is concentration of donors, $\varepsilon = 12$ is dielectric constant of Si and ε_o is permittivity of free space. Using the eq. 7, the value of d was determined being equal to 360 nm. This value is in the range of nominal dimensions (10-1000 nm) of the depletion region's width [29].

Conclusions

The *n*-Si/OD/CG and *p*-Si/OD/CG cells were fabricated with the aqueous solution of the orange dye (OD) as electrolyte and its properties were investigated. Under filament lamp illumination, photo-induced open-circuit voltage and short-circuit current increased with illumination and exponentially dropped with a time. At light-voltage/current conversion the cell performs as a differentiator. It has been found that the *n*-Si/OD/CG cell shows charge-storage behavior when the illumination is off. The charge-storage efficiency was equal to 98% for the current-time wave-forms. The width of the depletion layer was estimated as 360 nm in the *n*-Si semiconductor surface. The energy conversion efficiency of the cell was equal to 1×10^{-4}%. In *p*-Si/OD/CG cell the photovoltaic effect was not observed. In this case the photo-induced charges in *p*-Si may be not separated rather because of negligible built-in electric field in the semiconductor surface.

Acknowledgements

References

1. Lesiak, B., Kosinski, A., Krawczyk, M., Zommer, L., Jablonski, A., Kövér, L., Tóth, J., Verga, D., Scerny, I., Zemek, J., and Jiricek, P., Polish J. Chem. 74:847 (2000).

2. Brabec, C.J., and Sariciftci, S.N., Monatshefte für Chemie 132:421 (2001).

3. Gebeyehu, D., Brabec, C.J., and Sariciftci, N.S., Thin Solid Films 403-404:271 (2002).

4. Y.J. Ahn, Y.J., Kang, G.W., and Lee, C.H., Mol. Cryst. 377:301 (2002).

5. Ray, A.K., Tracey, S.M. Hassan, A.K., Shishiyanu, S.T., and Shishiyanu, T.S., Moldavian Journal of the Physical Sciences N2:5 (2002).

6. Hanyz, I., and Wróbel, D., Cryst. Res. Technol. 38:325 (2003).

7. Peumans, P., Yakimov, A., and Forrest, S.R., Appl. Phys. 93:3693 (2003).

8. Boguta1, A., Wróbel, D., Hoffmann, T.J., and Mazurkiewicz, P., Cryst. Res. Technol. 38:267 (2003).

9. Senthilarasu, S., Velumani, S., Sathyamoorthy, R., Subbarayan, A., Ascencio, J.A., Canizal, G., Sebastian, P.J., Chavez, J.A., and Perez, R., Appl. Phys. A 77:383 (2003).

10. Roman, L.S., Arias, A.C., Theander, M., Andersson, M.R., and Inganäs, O., Braz. J. Phys. 33:376 (2003).

11. Kwong, C.Y., Djurišic, A.B., Chui, P.C., L.S. Lam, L.S.M., and Chan, W.K., Appl. Phys. A 77:555 (2003).

12. Zaban, A., Zhang, J., Diament, Y., Melemed, O., and Bisquert, J., J. Phys. Chem. B m107:6022 (2003).

13. Longo, C., and De Paoli, M.A., J. Braz. Chem. Soc. 14:889 (2003).

14. Dyakonov, V., Appl. Phys. A 79:21 (2004).

15. Slooff, L.H., Wienk, M.M., and Kroon, J.M., Thin Solid Films 451-452:634 (2004).

16. Possamai, G., Maggini, M., Menna, E., Scorrano, G., Franco, L., M. Ruzzi, M., C. Corvaja, C., Ridolfi, G., Smaorì, P., Geri, A., and Camaioni, N., Appl. Phys. A 79:51 (2004).

17. K. Hannewald, K., Stojanovi, V.M., Schellekens, J.M.T., Bobbert, P.A., Kresse, G., and Hafner, J., Phys. Rev. B 69:75211 (2004).

18. Gao, H.J., Sohlberg, K., Xue, Z.Q., Chen, H.Y., Hou, S.M., Ma, L.P., Fang, X.W., Pang, S.J., and Pennycook, S.J., Phys. Rev. Lett. 84:1780 (2000).

19. Karimov, Kh.S., Akhmedov, Kh.M., Dzhuraev, A.A., Khan, M.N., Abrarov, S., and Fiodrove, M.I., Eurasian ChemTech Journal 2:181 (2000).

20. Karimov, Kh.S., Ahmed, M.M., Moiz, S.A., Babadzhanov, P., Marupov, R., and Turaeva, M. A., Eurasian Chem.Tech. Journal 5:109 (2003).

21. Karimov, Kh.S., Ahmed, M.M., Gul, R.M., Mujahid, M., and Akhmedov, Kh.M., J. Valiev, in: Proc. Advanced Materials-2001, (Dr. A.Q. Khan Research Laboratories, Rawalpindi, Pakistan, 2002) 329-333.

22. F. Garnier, J. Opt. A: Pure Appl. Opt. 4:S247 (2002).

23. Licht, S. Ramakrishnan, P.A., Faiman, D., Katz, E.A., Shames, A., and Goren, S., Solar Energy Materials and Solar Cells 56:45 (1998).

24. Faria, R.M., and Oliveira Jr, O.N., Braz. J. Phys. 29:360 (1999).

25. Gratzel, M., Nature 414:338 (2001).

26. Rajeshwar, K., in: Semiconductor Electrodes and Photoelectrochemistry, Vol. 6 "Encyclopedia on Electrochemistry", WILEY-VCH, Weinheim, GRM, 2002, p. 1.

27. Twidell, J.W., and Weir, T.D., Renewable Energy Resources, E & FN Spon, Cambridge, 1986, p. 158.

28. Blythe, A.R., in: Electric Properties of Polymers, Cambridge University Press, USA, 1979, p. 91.

29. Bar-Lev, A., in: Semiconductors and electronic devices, 2nd Edition, Prentice-Hall International Inc., Englewood Cliffts, NJ, London,1984, p. 459.