

Photoelectric studies of n-InP/Orange dye/ITO cell

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The photoelectrical behavior of n-InP/Orange dye/ITO sandwich type cell was investigated. In this cell the n-type indium phosphide and indium tin oxide (ITO) coated glass electrodes were employed and as electrolyte 0.5 wt.% solution of orange dye (OD) in distilled water was used. The inter-electrode distance in the n-InP/OD/ITO cell was 40 mm. Dark current-voltage characteristics of the cell showed rectification behavior with rectification ratio (RR) 3.97 at ± 0.9 V. A zero offset voltage of 0.8 V was also observed, i.e. the presence of electrochemical effect. Photo-induced open-circuit voltage and short-circuit current, under modulated (in frequency range of 0–50 kHz) and unmodulated IR, Red, Green Yellow and Blue LEDs illuminations, were investigated and it was found that the cell is sensitive in the wavelength range of 475 nm – 750 nm. It was observed that open circuit voltage decreases and short-circuit current increases with concentration of OD in the solution. Investigation of directivity characteristics showed that the cell is sensitive in wide range of angles ($\pm 180^\circ$). By investigations of optical absorption spectra of the OD solution, band diagram in the n-InP/OD/ITO interfaces was identified. Equivalent circuit of the cell was developed. Variations of voltage/current with time were recorded.

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1. Introduction

Organic photoelectric and photoelectrochemical cells are a subject of increasing interest because of simplicity of the device fabrication and interesting electrical and optical properties. Advantage of photoelectrochemical cell is its ability to generate not only photoelectric power, but also electrochemical energy. Rapid preparation and completeness of the liquid/solid junction is another advantage compared to solid/solid junctions in the conventional photovoltaic cells.

Licht *et al.* [1], studied the photoelectrochemistry of single crystal C_{60} and properties of fullerene photoelectrochemical solar cells. An improvement in photocurrent is reported by utilization of a photoelectrochemical solid/liquid junction, rather than a solid-state photovoltaic junction. A photoelectrochemical cell consisting of a set of organic thin films as electrodes is fabricated in Ref. [2]. The polythiophene film containing 5,10,15,20-tetraphenylporphyrin (TPP) and fullerene (C_{60}) generate anodic photocurrents in the presence of ferrocene, while TPP alone generated cathodic photocurrents. Photoelectrochemical behavior of n-GaAs and n- $Al_xGa_{1-x}As$ in CH_3CH was investigated by Casagrande *et al.* [3], and reported open-circuit voltage of 0.83 V, short-circuit current density of 20 $mAcm^{-2}$ and energy conversion efficiency of greater than 10% at 88 $mWcm^{-2}$ of simulated AM 1.5 solar illumination. Historical background, present status and development prospects for the new generation of photoelectrochemical cells and their applications were reviewed in Ref. [4,5].

Fabrication and investigation of organic photoelectric sensors is also a very promising field due to their high

sensitivity in the wide spectral range of wavelengths. Organic-on-inorganic Ag/n-GaAs/p-CuPc/Ag photoelectric sensor, sensitive in UV-visible-NIR region (200-1000 nm), was investigated by Karimov *et al.* [6]. The photoelectrical behavior of n-Si/orange dye, vinyl-ethynyl-trimethyl-piperidole/ITO sensor was investigated in Ref. [7]. The sensor was sensitive in the range of 500–850 nm. In the light-voltage/current conversion, this sensor behaved as a photoelectric differentiator.

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 [8] and a two-layer structure, poly-N-epoxypropylcarbazole/OD heterojunction, that has shown a rectification behavior [9]. The photoelectrical behavior of n-Si and p-Si/orange dye/ITO was investigated in Ref. [10]. Under filament lamp illumination, the n-Si/OD/ITO showed high photoelectrical response. Electrical properties of Zn/Orange dye aqueous solution/Carbon cell were studied in Ref. [11]. The open-circuit voltage and short-circuit current of the fully charged cell was 1.5V and 0.45 mA, respectively. The cell was rechargeable and efficiency of current discharge/charge was 67%. In Ref. [12], the n-GaAs/OD-VETP/ITO sensor was fabricated and its electrical and photoelectrical properties were investigated. As an electrolyte, the 0.5 wt.% solution of orange dye (OD) and vinyl-ethynyl-trimethyl-piperidole (VETP) in a mixture of distilled water (80%) and methanol (20%), was used. The device shows properties of electrochemical source and photoelectric source as well.

This paper presents the results of investigation of photoelectric properties of n-InP/OD/ITO cell. The possibility of liquid and liquid/solid phase corrosion is common disadvantage in photoelectrochemical analysis. Stability of InP against photoanodic corrosion is much higher with semiconducting oxides [13]. For this reason, InP is one of the most important n-type semiconductors for electrodes.

2. Experimental

Commercially produced p-type organic semiconductor orange dye (OD), $C_{17}H_{17}N_5O_2$ (Figure 1) with molecular weight of 323 g/mole, and density of 0.9 g/cm^3 was used for fabrication of the photoelectric cell. Indium tin oxide coated glass and n-type indium phosphide wafer, of orientation (100), with concentration of dopants $3 \times 10^{18} \text{ cm}^{-3}$, doped by Tellurium were used as electrodes in the cell. As an electrolyte, 0.5 wt.% solution of orange dye (OD) in distilled water was used.

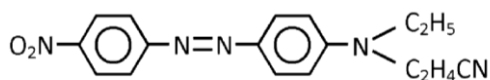


Fig. 1. Molecular structures of the Orange Dye (OD).

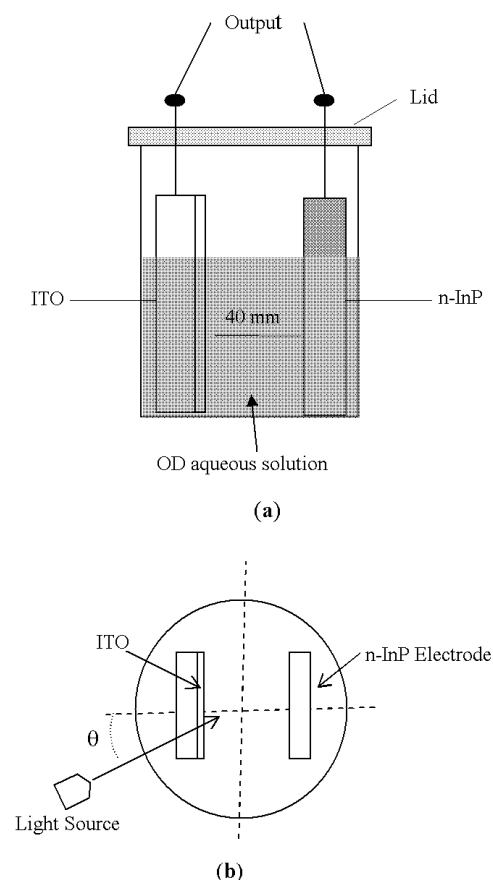


Fig. 2. Cross-sectional view of the n-InP/OD/ITO Cell along with experimental arrangement. (a) Cross-sectional view of an n-InP/OD/ITO Cell (b) Irradiation Mechanism.

Fig. 2 shows schematic diagram of the fabricated n-InP/OD/ITO cell. The n-InP wafer's diameter was 20 mm and the size of ITO electrode was $50 \text{ mm} \times 25 \text{ mm}$. The separation between the n-InP and ITO electrodes were equal to 40 mm, while the volume of electrolyte was 55 ml. For investigation of photoelectric properties of the cell, measurement of open-circuit voltages and short-circuit currents, the conventional digital volt-ampere meters and an intensity-meter were used. All the measurements were carried out at room temperature. As a light source the IR, Red, Green, Yellow and Blue LEDs with central wavelength 850 nm, 660 nm, 590 nm, 565 nm and 430 nm, respectively, were used. The effective diameter of the light beam was equal to 1.0 cm. The LEDs were modulated by square wave oscillator voltage in the frequency range of 0–50 kHz.

3. Results and discussions

Measured dark I-V characteristics of the n-InP/OD/ITO cell are exhibited in Fig. 3 a zero offset voltage of 0.8 V is observed, which indicates the presence of electrochemical effect in the cell [14]: n-InP electrode's polarity was "positive" with respect to conductive glass electrode. It is seen that the I-V characteristic are nonlinear, showing rectification behavior (rectification ratio, as ratio of forward bias current to reverse bias one at $V = \pm 0.9 \text{ V}$ is equal to 3.97 if we deduct the effect of zero offset current). At the estimations of the photo voltages/currents of the cell the dark voltages/currents zero offsets were, respectively, deducted. Forward bias behavior of the I-V characteristics was observed when the polarity of the voltage applied to ITO was "negative".

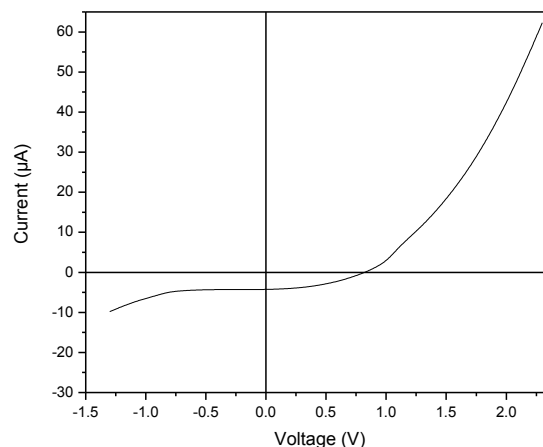


Fig. 3. Dark current-voltage characteristics of the n-InP/OD/ITO Cell.

A set of I-V characteristics measured at different illuminations are shown in Fig. 4(a). It is observed that the I-V characteristics have the behavior of commercially available photo-diodes: reverse bias currents increase and are strongly dependent on illumination unlike to forward

bias currents. Fig. 4(b) shows I-V characteristics of the cell in photovoltaic mode of operation. In these characteristics, the maximum power points are shown. From these characteristics the fill factors (FF) and energy conversion efficiencies (η) are estimated using expressions:

$$FF = \frac{P_m}{V_{OC} \times I_{SC}} \quad (1)$$

$$\eta = \frac{P_m}{E \times A_c} \quad (2)$$

where P_m is maximum power point, V_{OC} is open circuit voltage, I_{SC} is short circuit current, E is irradiance and A_c is surface area of the cell.

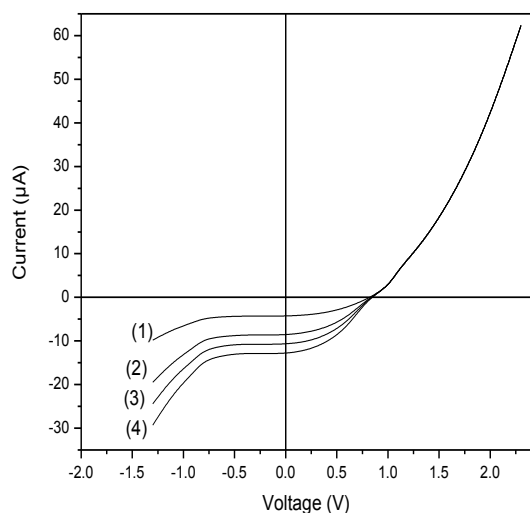


Fig. 4(a). I-V characteristics of the n-InP/OD/ITO Cell under dark and light conditions, using Red light: (1) dark, (2) 600 lux, (3) 810 lux, and (4) 1160 lux

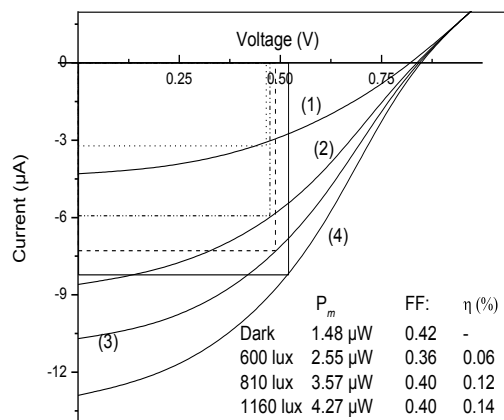


Fig. 4(b). The maximum r (fill factor, FF) for illuminated n-InP/OD/ITO Cell

FF values were equal to 0.36, 0.40 and 0.40 at illuminations of 600, 810 and 1160 lux, respectively. The photoelectrical energy conversion efficiency values were equal to 0.06, 0.12 and 0.14 %, respectively, at these illuminations. Although the efficiencies are low but efficiency is not principle parameter if device is used as a sensor.

Fig. 5 shows orange dye concentration effects on open circuit voltage and short circuit current. It is seen that voltage decreases and current increases with concentration that may be, firstly, due to the decrease of junction barrier in the solid-liquid interface, and, secondly, due to the increase of concentration of ions in the solution and accordingly increase of solution's conductivity, respectively.

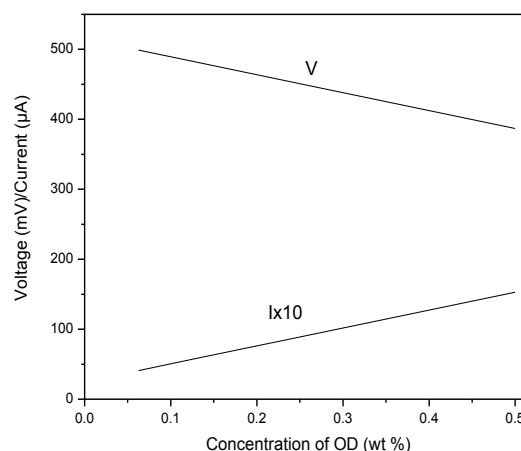


Fig. 5. Orange dye concentration effects on open circuit voltage and short circuit current of the n-InP/OD/ITO Cell

Fig. 6(a) describes photo voltage/current-intensity of light (Red LED was used) relationships at modulating signal frequency of 100 Hz. The voltage and current characteristics are non-linear and quasi-linear, respectively, that, in principle, is like to conventional photo-diode characteristics [15]. Polarity of photo-induced voltage was positive on n-InP electrode. DC components of the voltages and currents prevail a little over the AC components. Fig. 6(b) shows photo voltage/current-spectral sensitivity of the n-InP/OD/ITO cell. It is seen that the cell is sensitive in the wavelength ranges of 475-750 nm, the maximum is around of 600-625 nm, i.e. the cell is selective and it is sensitive mostly to red light. In Fig. 6(c) photo voltages/currents-modulation frequency relationships of the cell are shown. It is seen that currents are practically independent of frequency in the range of 0-50 kHz, whereas voltages decay exponentially, that may be due to the presence of built-in capacitances in the cell.

Fig. 7 shows directivity characteristics of the n-InP/OD/ITO cell: voltages/currents-illumination angle (Fig. 2) relationships. The cell is sensitive in wide range of

angles ($\pm 180^\circ$) that is essentially wider than in some conventional photo-diodes ($\pm 90^\circ$ in the case of PN303). Though sensitivity of the sensor is maximum at the illumination from the side of conductive glass electrode, the n-InP/OD/ITO cell can receive signal from backside as well, i.e. at the illumination of n-InP.

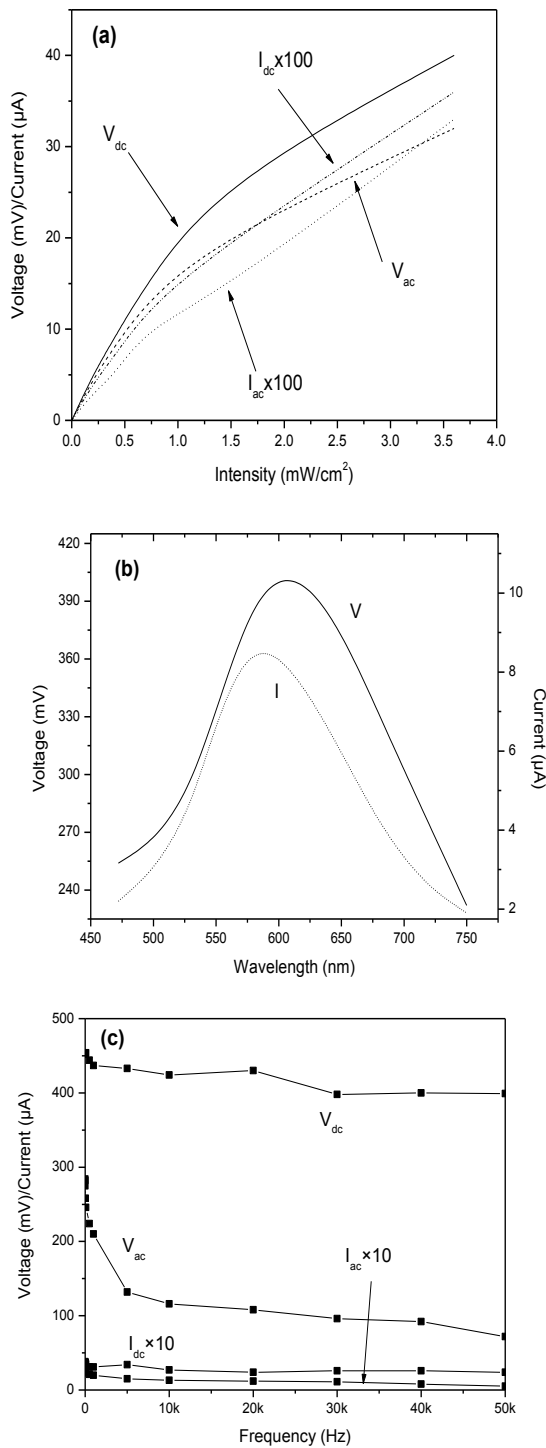


Fig. 6. Electrical response of an n-InP/OD/ITO Cell (a) as a function of incident light intensity, (b) at varying wavelength of incident light and (c) as a function of incident light modulated at different frequencies.

The semiconductor-electrolyte interface at equilibrium is described in Ref. [4,14]. 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 solution (Fig. 8). It is seen that absorption actually starts in the wavelength range of 625 nm and increases sharply at 475 nm and covers 550–280 nm wavelength range as well. This absorption is equivalent to the charges excitation in the energy band of 1.98–2.61 eV and 2.61–4.43 eV, respectively. Fig. 8 show absorption of n-InP and voltage sensitivity of the cell as well. The cell is sensitive in the spectral range where absorption of OD solution is small but absorption of the n-InP is large. It means that OD solution from some point plays the role of filter, making the cell selective, i.e. sensitive in the narrow wavelength range to the red light.

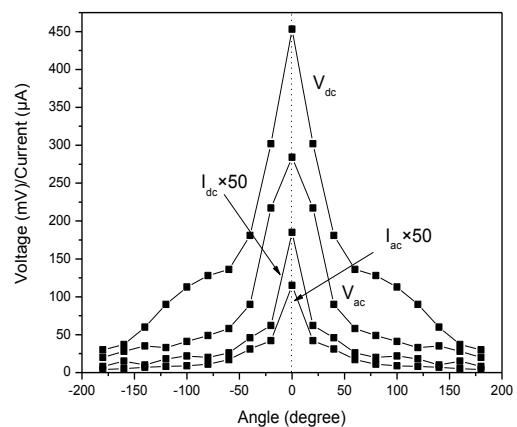


Fig. 7. Directivity characteristics of the n-InP/OD/ITO Cell: voltage/current – illuminating light beam angle relationships.

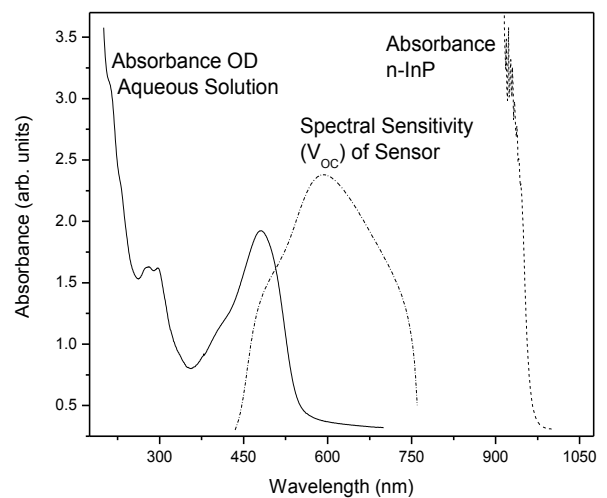


Fig. 8. Absorbance vs wavelength of the OD solution, n-InP, and voltage spectral sensitivity of the n-InP/OD/ITO Cell.

The excitation energy levels in OD solution are larger than the energy gap (1.35 eV) of the n-InP. Therefore, we can assume that at illumination of the cells by photons of energy lower than 1.98 eV and above 4.43 eV, the incident light is transmitted through OD solution and absorbed by n-InP. Photons with energy greater than 1.98 eV are

In general form, the variety of the semiconductor-electrolyte energy band diagrams are described in Ref. [4]. Taking into account the absorption spectrum of OD solution and n-InP, we may draw schematic energy band diagram of the n-InP/OD/ITO cell in the semiconductor-

absorbed partly by OD solution. Photo-induced charges in n-InP 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 [16]: n-InP semiconductor can receive electrons from the photo-excited orange dye as well.

electrolyte-conductive glass interfaces for the equilibrium case (Fig. 9a). Here V_{se} and V_{ce} are potential barriers between the n-InP semiconductor-electrolyte and ITO-electrolyte interfaces, respectively. Now we can design the band diagram for the non-equilibrium case (Fig. 9b), if we

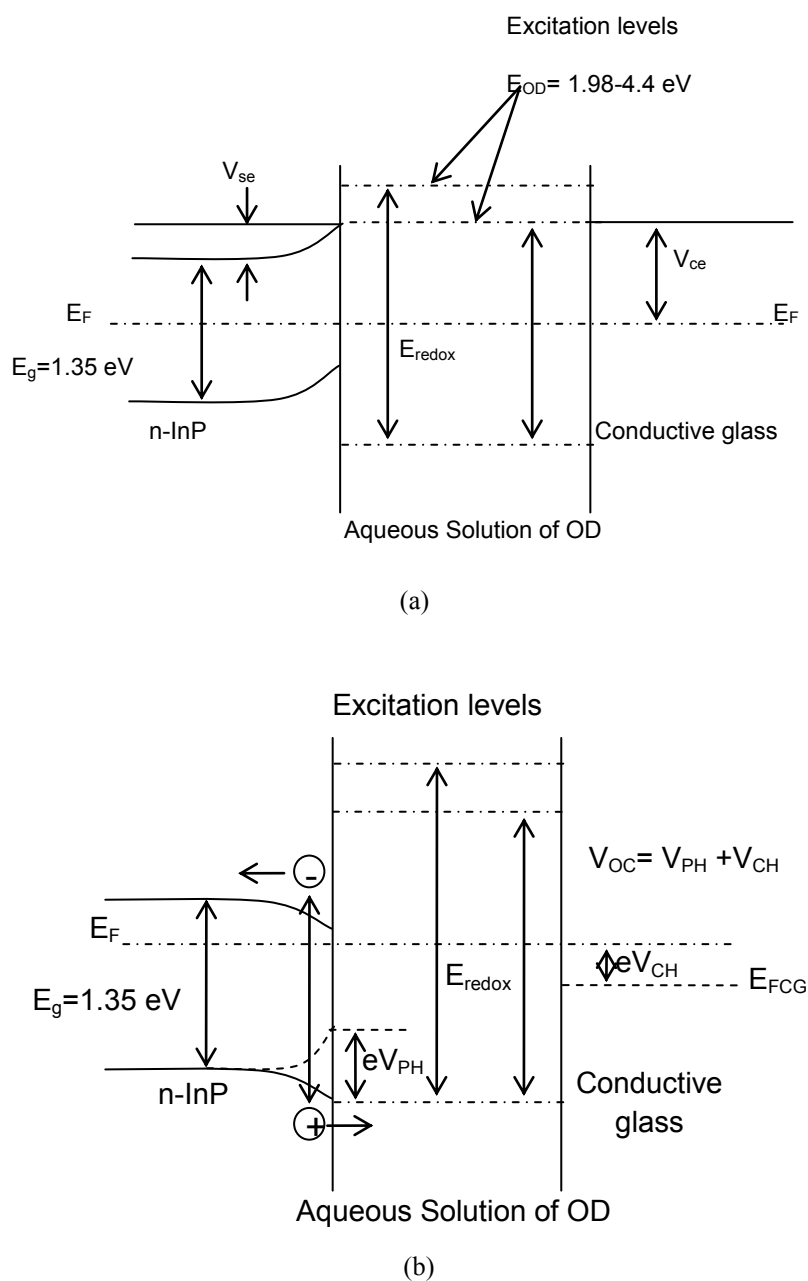


Fig. 9. Equilibrium (a) and under optical excitation (b) energy band diagrams of the n-InP/OD/ITO Cell.

take into consideration that polarities of photo-induced voltage (V_{ph}) and developed due to the electrochemical effect voltage (V_{ch}) were coincided and summed to the total output voltage of the cell. The V_{ch} is the open-circuit voltage at dark condition (it is equal to zero offset voltage in Fig. 3). In the case of non-equilibrium conditions, i.e. at presence of photo-induced voltage and voltage developed due to electrochemical reactions, the band bending probably changed as shown in Fig. 9(b) due to the effect of positive charges in the n-InP-electrolyte interface.

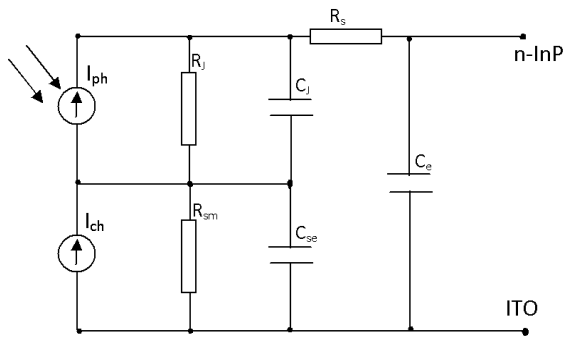


Fig. 10. Equivalent circuit of the n-InP/OD/ITO Cell under optical excitation.

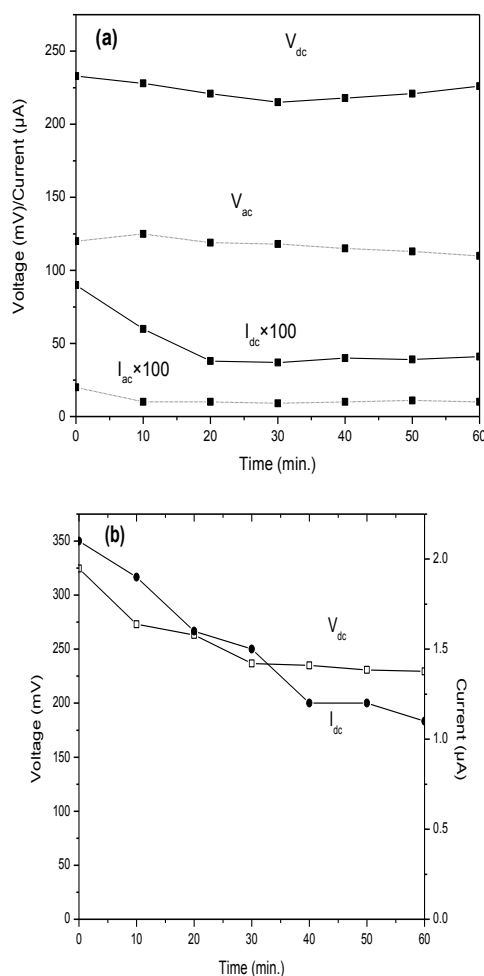


Fig. 11. Voltage/current-time relationships at the illumination of the n-InP/OD/ITO Cell by (a) modulated light at 100 Hz (b) non-modulated light.

Taking into account the experimental results presented above, it is possible to develop the equivalent circuit of the photoelectric cell [17]. The modified equivalent circuit that reflects the properties of the n-InP/OD/ITO cell is shown in Fig. 10. Conventional elements of the photoelectric cell equivalent circuit as a photo-induced current source (I_{PH}), junction resistance (R_j), junction capacitance (C_j) and series resistance (R_s) are concerned to n-InP semiconductor. The current source (I_{ch}) represents the electrochemical source, semiconductor-electrolyte-ITO resistance (R_{sm}) and semiconductor-electrolyte and electrolyte-ITO effective capacitance (C_{se}) concerned to the source. The capacitance C_e is the external inter-electrode capacitance of the cell. On the electrolyte side of electrode-electrolyte interface, there is double layer (Helmholtz layer) of negative and positive ions [4, 14]. The width of this layer is equal to 0.4–0.6 nm. The Helmholtz layer is characterized by the Helmholtz capacitance C_H . The capacitance C_{se} (Fig. 10) actually may be equal to C_H .

Fig. 11(a) shows voltage/current–time relationships at the illumination of the n-InP/OD/ITO cell by modulated light ($f = 100$ Hz) and Fig. 11(b) shows the same relationship at the illumination of the cell by un-modulated light. In the case of Fig. 11(a) variations of AC voltage and AC current with time are in the range of $\pm 6\%$ and $\pm 37\%$, respectively. DC voltage/current show exponential decay. In the Fig. 11(b), exponential decay of the DC voltage and current are seen, as well. The observed phenomena may be the results of photochemical and electrochemical reactions that take place in the electrodes-electrolyte interfaces.

4. Conclusions

The n-InP/OD/ITO cell was fabricated. As an electrolyte the 0.5 wt.% solution of orange dye (OD) in distilled water was used. Electric and photoelectric properties of the cell were investigated. The cell shows properties of electrochemical source and photoelectric source as well. The voltages of the effects were added and total voltage was equal to 840 mV at 3.6 mWcm⁻² intensity of light radiation. The cell has wide directivity characteristics and shows narrow wavelength selectivity (its sensitivity is maximum to red light). Equivalent circuit of the cell was developed and the energy band diagrams of it at equilibrium and non-equilibrium conditions were designed. The cell may be used as teaching aid for demonstrative purposes, in optical communication, in instrumentation laboratories and for registration of the atmospheric lightning as well. Development of the cell may result to the fabrication of electrolysis based hydrogen generator that works on splitting of water under the effect of electric field.

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