Nickel phthalocynanine based organic transistor

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A semitransparent Al film of 15 nm, thin films of p-type organic semiconductor nickel phthalocynanine (NiPc) and Al film of 100 nm were deposited in sequence by vacuum evaporation on indium tin oxide (ITO) coated glass substrates. Organic transistors (OTs) were fabricated with two, metal (aluminum)–semiconductor (nickel phthalocyanine) Schottky junctions. The effect of light irradiation on their resistance was investigated. It was found that the resistance of the OTs was decreased with increase of irradiance. The energy band diagram of the transistor with two Al-NiPc junctions was developed.

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1. Introduction

Field-effect transistors (FETs) based on organic materials such as conjugated polymers, oligomers and low molecular weight materials have been investigated widely [1, 2]. Lower material and fabrication cost of organic field effect transistors (OFETs) is attracting extensive interest of the researchers for their potential applications in several devices [3-7]. A review of the properties of organic semiconductor FET fabricated during 1983 to 2000 is presented in Ref. [3]. It was shown that the highest mobility of 1.5 $cm^2V^{-1}s^{-1}$ was observed in the pentacene based FETs. Some of the OFETs show sensitivity not only to applied voltage itself but to electric field of molecules as well. Bartic et al described an OFET that was able to detect charged/uncharged chemical species in aqueous media via the field effect; the chemical sensitivity of the organic transistor was illustrated for protons and glucose [8].

In the past years, organic phototransistors (OPT) were fabricated and investigated as well. Noh et al fabricated and investigated an OPT based on a biphenyl end-capped fused bithiophene oligomer [9]. Under 380 nm UV light, the OPTs showed a photocurrent response similar to the absorption spectrum of the organic semiconductor. It is expected that the OPTs may be used in highly sensitive UV sensors. Similar to the previous case, the effect of ultraviolet light irradiation on the characteristics of organic phototransistor containing sexithiophene (6-T) and pentacene was examined [10]. The transistors showed two distinguishable responses i.e. fast and slow. The slow response was observed in several weeks. It suggests the possibility of application of this OPT in the light-addressable field-effect transistor memory devices. The most widely used organic semiconductors as pentacene, thiophene oligomers and regioregular polythiophene showed good performance in OFETs, but further improvements seem face saturation [3].

In Ref. [11], copper phthalocyanine (CuPc)/inorganic ferroelectric $PbZr_{0.2}Ti_{0.8}O_3$ heterojunction gate and a ferromagnetic oxide semiconductor $La_{0.87}Ba_{0.13}$ MnO_3 channel photomemory was described. The device demonstrated the non-volatile and non-destructive photomemory operation. The device could write the light information with the combination of the light irradiation and the negative gate bias and delete only with the positive gate bias.

Majority of the phthalocyanines are well-studied organic photosensitive semiconductors [12]. They have high absorption coefficient in wide spectrum and high photo-electromagnetic sensitivity at low intensities of radiation. The deposition of thin films of phthalocyanines by vacuum sublimation is easy. Purification of the phthalocyanines is simple and economical as the sublimation occurs at relatively low temperatures (400–600 ^oC). NiPc is one of the promising phthalocyanines. In recent years, nickel phthalocyanine (NiPc) has received increasing attention due to its potential applications in the area of photovoltaics and gas sensing [13-24]. One of the major advantages of NiPc over CuPc is its higher mobility of charge carriers (0.1 cm^2/Vs and 10^{-4} cm^2/Vs, respectively) [24]. The energy band gap of the NiPc is equal to 2.24 eV and 3.2 eV for indirect and direct allowed transitions [16]. The properties of CuPc based FET structured phototransistor were investigated by Karimov et al [25]. At the same time, the fabrication and investigation of the organic semiconductor based bipolar junction transistor (BJT) structure would be interesting due to some advantages of BJTs over FETs such as higher gain [26]. Less information is available about organic transistors that have non-FETs structures [1, 2]. In this paper, the photoconduction properties of the two Schottky junction

(Al-NiPc) phototransistors are reported at frequency of 120 Hz.

2. Experimental

The research grade NiPc was purchased from Sigma-Aldrich and used as it is without further purification. Fig. 1 shows the molecular structure of the NiPc used as a p-type organic semiconductor.

Aluminum films of 10-15% transparent and 15 nm thick were thermally sublimed onto the ITO coated glass substrates at 500 ^oC and ~10^{-4} Pa in Edwards AUTO 306 vacuum coater with diffusion pumping system and thickness monitor. The substrates' temperature in this process was held at ~40 ^oC. On the semitransparent Al films, the thin films of NiPc of thickness of 100 nm, 200 nm and 300 nm were deposited by thermal evaporation. Fig. 2 shows UV-VIS transmission spectra of NiPC thin film (100 nm thickness), obtained from Lambda 950, Perkin Elmer UV-VIS Spectrophotometer. A transmission peak was observed at 495 nm in the visible region.

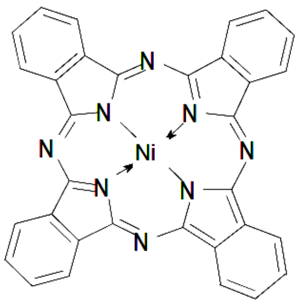

Fig. 1. Molecular structure of the nickel phthalocyanine used as a p-type organic semiconductor

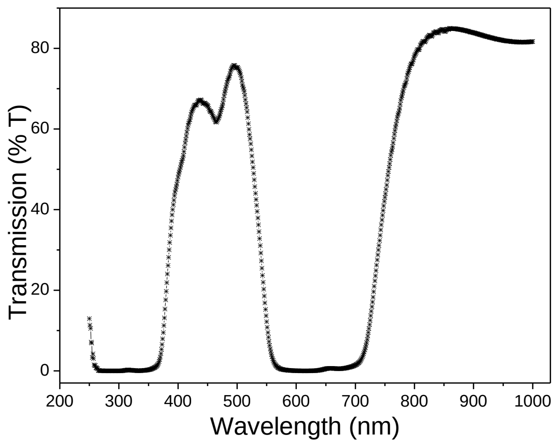

Fig. 2. UV-VIS transmission spectrum of the nickel phthalocyanine thin film (300 nm thickness)

On the top of NiPc films, the Al films of thickness of 100 nm were deposited. The deposition rate of Al and NiPc films were 8 nm/min and 5 nm/min, respectively. Fig. 3 shows cross-sectional view of the fabricated transistor. The area of the transistor was 20 mm x 15 mm. The tungsten filament lamp was used as a source of light. The measurements of resistance at 120 Hz were carried out by U1732A LCR meter at room temperature.

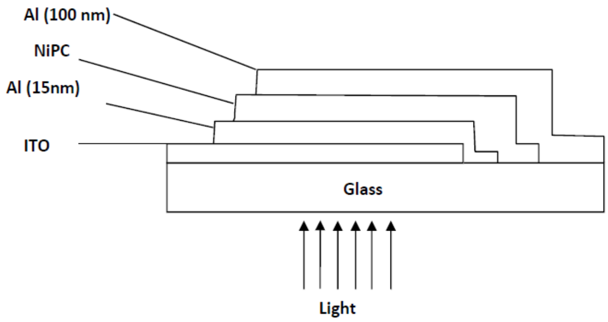

Fig. 3. Cross-sectional view of the fabricated organic transistor

3. Results and discussion

Fig. 4 shows the resistance-irradiance relationships of the organic phototransistor, based on NiPc films with different thickness of (a) 100 nm, (b) 200 nm and (c) 300 nm. For the samples of thickness 100 nm, 200 nm and 300 nm, the resistance decreases up to 1.66, 4.50 and 4.49 times, respectively as irradiance increases up to 40 mW/cm^2. The generation of charge carriers take place in the samples which are under light irradiance and a decrease of the resistance is observed. When NiPc film thickness is lesser, the sample is saturated by charges under illumination and recombination take place. Hence change in resistance is lower in these samples under effect of light. In thick film samples, the decrease of the resistance under the effect of light is larger as compared to thin film samples due to nonuniform illumination of the volume of the samples. According to Fig. 2, light transmit through NiPc film in the interval of 370-560 nm and above of 700 nm. In the other parts of the transmission spectrum, absorption of light take place which results to the generation of charge carriers. This effect decreases the length of the two Schottky junctions which are formed in Al-NiPc interfaces and therefore decreases total resistance of the samples as well. Fig. 5 shows relative resistance (R_{off}/R_{on})-irradiance relationships. It is seen that the performance of these transistors depends on the thickness of the NiPc films. The OFF/ON resistance ratio is maximum at NiPc thickness of 200 nm and 300 nm that, firstly, probably related with the complete absorption of the light, secondly, with optimal ratio of depletion region width and thickness of the film. Fig. 6 shows resistance-thickness relationships at different irradiances (0, 10, 20, 30 and 40 mW/cm^2). It is observed that the resistance increases with thickness. The behavior is linear under dark conditions and non-linear under illumination which can be linearized by linear circuits. Non-linear behavior of the characteristics may be due to nonlinear dependence of the photoresistance of the samples due to the behavior under illumination of the bulk resistance and two Schottky junction resistances as well.

Taking into account the data presented in Fig. 2 and Ref. [16, 24], an energy-band diagram of the Al/*p*-NiPc metal-semiconductor junction (Fig. 7) was developed. In this diagram E_c, E_v and E_g are bottom of conduction band, top of valence band and band gap, respectively.

The two mechanisms, namely, photoconductive behavior and photovoltaic behavior are seem to be responsible for the photoresponse of the OPT as discussed in Ref. [7, 8, 25]. Photoconductive behavior (the increase of conductance due to increase in light irradiance) occurs due to generation of excitons by absorbed photons, and splitting of the excitons into electrons and holes pairs by the electric field of the two depletion regions, by the effect of voltage (between two depletion regions) and by the defects of structure in the bulk of NiPc. Photovoltaic behavior (generation of voltage due to light irradiance) takes place due to the presence of the two rectifying metal-semiconductor Schottky junctions. Due to the effect of light, metal-semiconductor potential barriers and electric fields as well, decrease which result to increase the conductivity of the depletion region of NiPc.

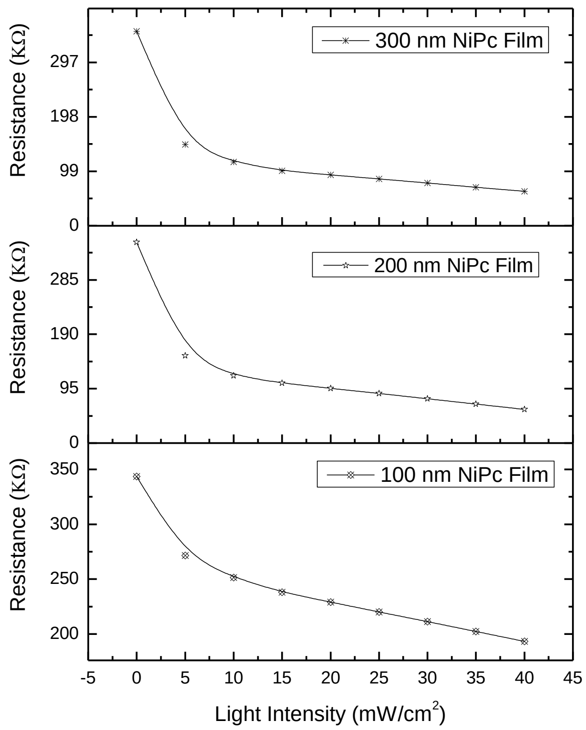

Fig. 4. AC resistance-irradiance relationships for OPTs based on nickel phthalocyanine with NiPc thickness of 100 nm, 200 nm and 300 nm

The expressions for the photocurrent caused by the photovoltaic effect and photocurrent induced by a photoconductive effect are presented by Noh et al [9, 10]. At the same time, the properties of the OPT may be simulated by using equivalent circuit [26] as well, that would be the matter of the future work.

The photo-bipolar junction transistor (PBJT), actually can be used as a high gain photodetector [26] due to transistor action and usually operated at open-base condition, one of the transistor junctions (collector-base) is in the reverse another one (emitter-base) is in the forward bias. In the present research work, AC voltage (120 Hz) was applied to the samples for the measurement of resistance. Therefore at different polarity of the applied voltage, one of the junctions was in forward and another one was in the reverse bias. Unlike to DC measurements of *I-V* characteristics of the phototransistor at different irradiances, the measurements of the resistance at AC allows to get information about the frequency response as well that is important for practical applications. If it is considered that transistor's total delay time (τ) [26] is equal to transit time (τ_t) in NiPc (analogous of the base of BJT), the delay time can be found by the following as:

$$\tau = \frac{L}{v} \quad (1)$$

where 'L' is the thickness of the NiPc films 'v' is the drift velocity of the charges (holes) in NiPc.

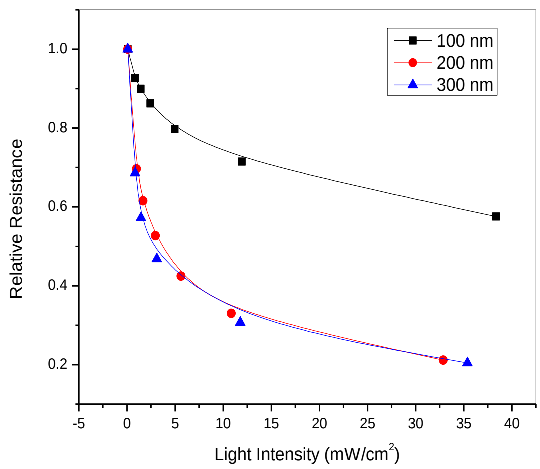

Fig. 5. Relative resistance-irradiance relationships for the nickel phthalocyanine based OPTs where NiPc thickness was 100 nm, 200 nm and 300 nm

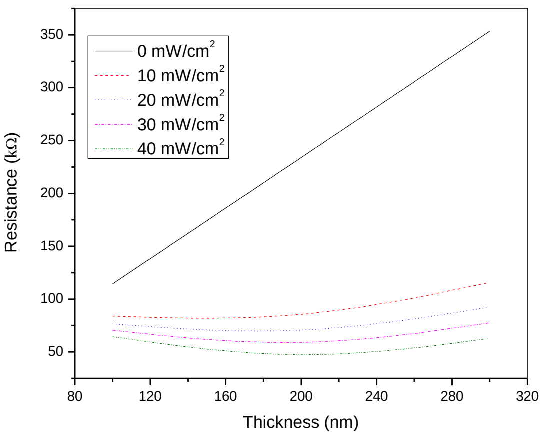

Fig. 6. AC resistance-thickness responses for the nickel phthalocyanine based OPTs at different irradiances

The drift velocity is given as:

$$v = \mu E \tag{2}$$

where ‘μ’ is the mobility of holes and ‘E’ is the electric field due to applied voltage for the measurement of the resistance.

From Eq. 1 and Eq. 2, the delay time (τ) can be expressed as:

$$\tau = \frac{L}{\mu E} \tag{3}$$

Taking into account that L = 200 nm (it is thickness of one of the samples), $\mu = 0.1\ cm^2/V\ s$ [24] and E = U/L = 0.6 V / 200 nm = 30 kV/cm (where U is voltage), one can obtain τ = 6.67 ns. The cutoff frequency (f_T) is determined by [26]:

$$f_T = \frac{1}{2\pi\tau} \tag{4}$$

It was found that f_T = 24 MHz. This value seems larger than actual value of the cutoff frequency because in reality $\tau_t >> \tau$. The frequency response of the CuPc based photoelectric sensor was investigated in the frequency range of 10-100 Hz by Karimov et al and found that f_T was 20 KHz [27]. By substituting Eq. 3 into Eq. 4, it can be shown that f_T is proportional to the mobility of charge curriers:

$$f_T = \frac{\mu E}{2\pi L} \tag{5}$$

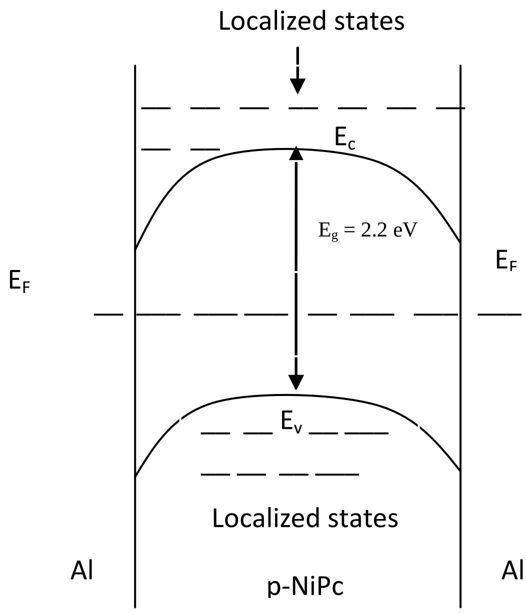

Fig. 7. An energy-band diagram of nickel phthalocyanine based transistor with two Al/p-NiPc metal-semiconductor Schottky junctions

As the mobility of the NiPc (0.1 cm^2/Vs) is 1000 times larger than the mobility of the CuPc [24], so it can be expected that f_T of the NiPc is about of 24 MHz. As the resistance measuring frequency (120 Hz) for the investigation of the NiPc based phototransistor was below the cut-off frequency, it can be considered that it had no effect on the frequency limitation in these experiments that was confirmed by high photo response shown by the transistor.

4. Conclusion

NiPc based bi-junction phototransistors with two Schottky junctions (Al-NiPc) were fabricated and the AC resistance-irradiance response, under filament light irradiation was investigated. It was found that for the transistors with NiPc thickness of 100 nm, 200 nm and 300 nm, the resistance decreases up to 1.66, 4.50 and 4.49 times as irradiance increases up to 40 mW/cm^2, i.e. the performance of these transistors increases with increase of the thickness of the NiPc films. By use of the NiPc absorption spectra and data obtained by the investigation of electric properties of the OPTs, the energy band diagram of the transistor with two Al-NiPc Schottky junctions was designed. The frequency response of the transistor is discussed.

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