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EFFECT OF HUMIDITY ON THE NiPc BASED ORGANIC PHOTO FIELD EFFECT TRANSISTOR

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Abstract. Thin films of p-type organic semiconducting nickel phthalocynanine (NiPc) and semi-transparent Al were deposited in sequence by vacuum evaporation on a glass substrates with pre-deposited Ag source and drain electrodes. Organic field effect transistors were fabricated with metal (aluminum)–semiconductor (nickel phthalocyanine) Schottky junction. The effect of humidity on the NiPc based organic photo field effect transistors was investigated. It was found that in the relative humidity range of 45% to 93% RH, the resistance of the transistors decreased from 1.37 to 1.25 times depending on the thickness of the NiPc films, accordingly for 100 nm, 200 nm and 300 nm. The utilization of the NiPc based transistor as multi-functional or single-functional sensor is discussed.

Key words: organic field effect transistor, nickel phthalocyanine, metal-semiconductor Schottky junction, phototransistor, humidity.

1. INTRODUCTION

Commonly used inorganic based photo-detectors are photodiodes, phototransistors and photo-conductors [1]. To fulfill the serious demand for low-cost, light-weight, flexible, and large-area electronic applications, the organic field effect transistors (OFET) have gained a lot attention of researcher during past years [2–8]. A biphenyl end-capped fused bithiophene oligomer based organic photo transistor (OPT) showed a photocurrent response at 380 nm UV light similar to the absorption spectrum of the organic semiconductor [9]. It is expected that the OPTs may be used as highly sensitive UV sensors. The effect of UV light irradiation on the characteristics of OPT containing sexithiophene (6-T) and pentacene was examined [10]. The transistors showed both fast and slow responses. The slow response which was observed in several weeks, suggests the possibility of its application in light-addressable field-effect transistor memory devices. OFETs based on most widely used organic semiconductors as pentacene, thiophene oligomers and regioregular polythiophene showed good performance [4].

Low-voltage OPTs seem promising for optoelectronic applications such as photodetectors and memory devices. 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 photo-memory was described by Park *et al.* [10]. The device demonstrated the non-volatile and non-destructive photo-memory 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. Liu *et al.* fabricated pentacene based OFETs in which Ta_2O_5 was used as gate dielectric [11]. As modification layers, the polymer materials as poly(4-vinylphenol) and poly(methyl methacrylate), were spin-coated on the high transparency and high permittivity Ta_2O_5. The effect of the interface modifications in the materials was investigated. The reduction effect of photosensitivity and memory was found as modification layers could block the electron injection process. By modulating of the optical writing process through gate voltages accompanied by light illumination, it was observed that for the modified device, the photo-responsivity, photocurrent/dark current ratio and retention time could be improved. Konstantatos *et al.* demonstrated a hybrid photo-detector that consists of monolayer or bilayer graphene covered with a thin film of colloidal quantum dots, a gain of ~10^8 electrons per photon and a responsivity of ~10^7 AW^{-1} [12].

Majority of organic semiconductors phthalocyanines are well-studied organic photosensitive semiconductors [13]. They have high absorption coefficient in the wide spectrum and high photo-electromagnetic sensitivity at low intensities of radiation. Nickel phthalocyanine (NiPc) is one of the promising phthalocyanines. In recent years, NiPc has received increasing attention due to its potential applications in the area of photovoltaic and gas sensing [14–25]. One of the major advantages of NiPc over CuPc is its higher mobility of charge carriers [25]. The energy band gap of the NiPc is 2.24 eV for indirect and 3.2 eV for direct allowed transitions [17]. The properties of CuPc based OPT, CuPc-NiPc and CuPc-GaAs hetero-junctions were investigated [26–28]. Most of the organic transistors have FETs structures [2–4]. At the same time, the organic bipolar junction transistor (BJT) structures would be interesting for fabrication and investigation. BJTs have higher gain than FETs [1]. Recently, we have fabricated NiPc based field effect phototransistor with Al-NiPc Schottky junctions and investigated the response of the transistor under filament light irradiation [29]. It was found that for the transistors with NiPc thickness of 100 nm, 200 nm and 300 nm, an average increase in drain currents was 7, 13 and 11 times, respectively for light intensity range of 0–34.4 mW/cm^2, at drain-source voltage of 3V which is comparable with the response of the OPT described by Park *et al.* [11]. Properties, of the phototransistors can be affected by the humidity. In this paper, in continuations of our efforts for the fabrication and investigation of the organic phototransistors, the effect of the humidity on the resistance of the NiPc based phototransistors is reported.

2. EXPERIMENTAL

The NiPc was purchased from Sigma-Aldricha and found analytical graded; thus, it was used without any further purification. The band gap of NiPc was 2.22 eV [24]. Figure 1 shows the molecular structure of the NiPc molecule used as a *p*-type organic semiconductor.

Thin films of NiPc were thermally sublimed at 500 °C and ~10^{-4} Pa on glass substrates with preliminary deposited 100 nm thick surface-type silver film electrodes by using Edwards AUTO 306 vacuum coater with diffusion pumping system and thickness monitor. The substrate's temperature in this process was held at ~40 °C. The surface-type Ag electrodes serve as source and drain for the organic photo field effect transistor. The gap between source and drain was 40 μm.

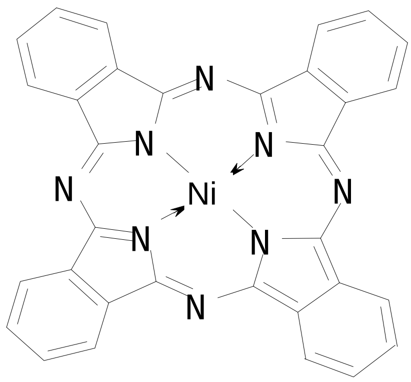

Fig. 1 – Molecular structure of the NiPc molecule used as a *p*-type organic semiconductor.

A semi-transparent, 22 nm thick Al film of dimension 2 × 10 mm^2 was deposited on NiPc film. The transparency of the Al film was 10-15%. The deposition rate of Ag, Al and NiPc films were 8 nm/min, 8 nm/min and 5 nm/min, respectively. Figure 2 shows cross-sectional view of the fabricated OPT: source and drain terminal connected with Ag films and Al film was used as gate terminal. Length and width of the NiPc channel were 40 μm and 10 mm, respectively for each OPT, while thickness of the channel was 100 nm, 200 nm and 300 nm for the three organic phototransistors. Humidity was measured by MS6503. Resistance between source and drain of the transistor was measured by LCR meter, ESCORT ELC-132A at 100 Hz.

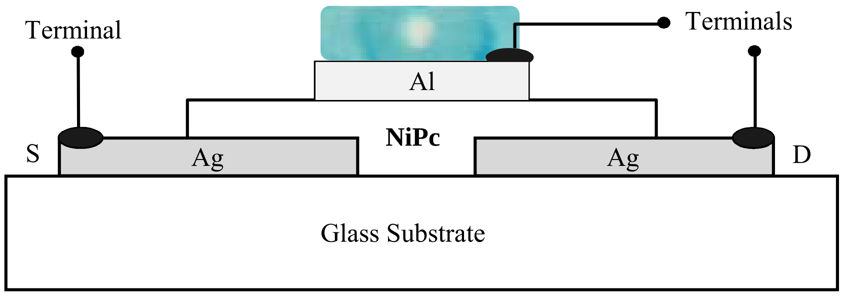

Fig. 2 – Cross-sectional view of the fabricated field effect transistors.

3. RESULTS AND DISCUSSION

Figure 3 shows the source-drain resistance and relative humidity (RH) relationships for the organic field effect transistors based on NiPc films of thickness 100 nm, 200 nm and 300 nm at frequency of 100 Hz for the humidity range of 45–93% RH. It is seen that the resistance of the samples with different thickness (100 nm, 200 nm and 300 nm) of NiPc, decreased by 1.37, 1.27 and 1.25 times, respectively. The resistance humidity coefficient (S) of the NiPc samples can be calculated analogously to resistance temperature coefficients presented in Ref. [30]:

$$S = \frac{\Delta R}{R_o \Delta RH}, \quad (1)$$

where R_o, ΔR and ΔRH are initial value of the transistor's resistance, the changes in the resistance and relative humidity, respectively. It was found that the resistance humidity coefficients of the transistors were –0.90, –0.70 and –0.25 for the samples with thickness of 100 nm, 200 nm and 300 nm, respectively of the NiPc channel.

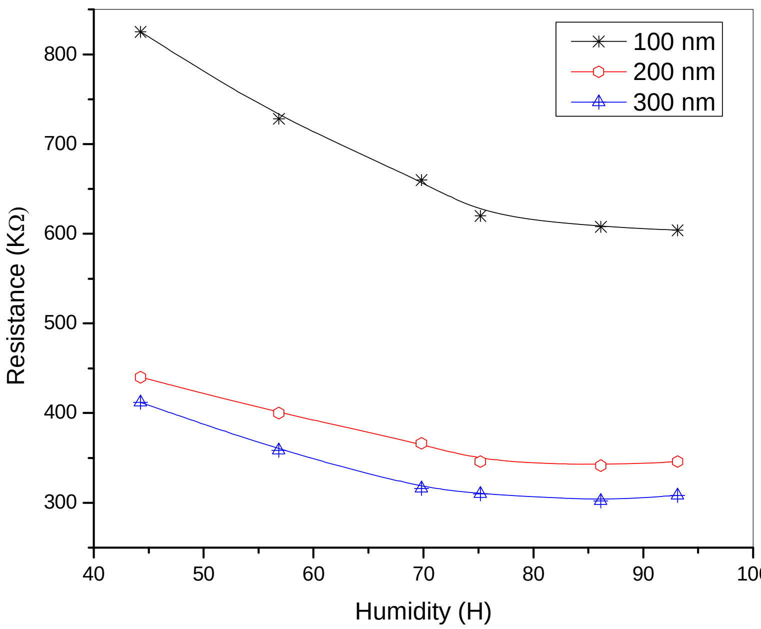

Fig. 3 – The source-drain resistance-humidity relationships for the transistors based on NiPc films of thickness of 100 nm, 200 nm and 300 nm at frequency of 100 Hz.

If we compare the obtained results with organic semiconductors based humidity sensors, for example [31], it would be seen that the resistance of the NiPc based field effect transistors is changing a few under the effect of the humidity. Actually that is due to difference in structures of the devices. In Ref. [31], the structure of the sensor is surface-type, as usually is used for humidity sensors, but in the present case of NiPc based transistors, the active material *i.e.* NiPc is partly covered by Al film (Fig. 2), therefore the water molecules can penetrate at interfaces of the NiPc and Al films only.

The properties of the CuPc based humidity sensitive field effect transistors were investigated [32]. We also represent here some information related to humidity sensing properties described in literature. The gas-sensing properties of the devices depend on two processes: a surface absorption and diffusion [33]. The first process, by nature may be physical or chemical, *i.e.* physisorption and chemisorptions, respectively. In physical absorption, usually van der Waals electrostatic forces play primary role, whereas in chemical absorption, the formation of chemical bonds between water molecules and substrate may be observed. As a rule chemical absorption process is slow process and sometime irreversible. But physical absorption is faster and reversible. The latter case probably takes place in the investigated humidity sensitive OFET.

In particular, by increasing the concentration of water molecules, the electric field of H_2O dipoles increases. As a result, the length and width of depletion region decrease as shown in Fig. 4. Both the channel current I_{ch} (that flows from source to drain) and the junction current I_j (that flows from source to drain through gate) increases due to decrease in the length and width of depletion region. The decrease of initial built-in junction electric field due to electric field of H_2O molecules is probably a reason of this phenomenon.

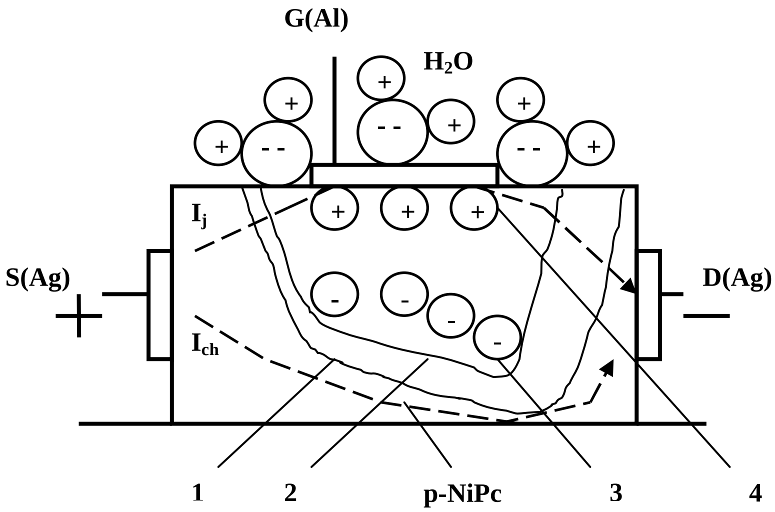

Fig. 4 – The effect of polar water molecules to the width of junction depletion region and source-drain current: depletion region at low (1) and higher (2) humidity, space charge (3 and 4), I_{ch} and I_j are the channel current and the junction current respectively.

Relatively low sensitivity of the NiPc based transistor to humidity allows easier cancelation of the effect of humidity by placing the device in a sealed box. Alternatively, humidity sensitivity of the transistor can be used for the measurement of the humidity, as well in multifunctional sensors. In Table 1, all data about the effect of humidity on the resistance of NiPc based transistors are summarized. For the comparison, the photosensitivity's data is also presented.

Table 1

Effect of humidity on the resistance of the NiPc based field effect transistors

Thickness of NiPc films (nm)	Initial Resistance (kΩ)	Humidity Sensitivity	Light Sensitivity (%/mW cm^{-2})	Potential Application
100	825	– 0.90	– 20	Light and humidity multi-functional sensors
200	440	– 0.70	– 38	
300	425	– 0.25	– 32	

The obtained results show that one of the applications of the NiPc based transistors would be the multi-functional sensors, *i.e.* sensors of light and humidity. For this purpose, the sensor should be placed in sealed box with transparent and non-porous window for the measurement of the light intensity. For the measurement of the humidity, the window should be covered by non-transparent porous lid. These multi-functional sensors potentially can be used for the measurement of light intensity and humidity for environmental monitoring and assessment.

4. CONCLUSIONS

The effect of the humidity on the source-drain resistance of the fabricated NiPc based field effect transistors was investigated. It was found that the transistors can be used as multi-functional sensors for the measurement of light intensity and humidity for environmental monitoring and assessment.

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