Effect of Heating on the Impedance of NiPc Based Organic Field Effect Transistor

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Abstract**—**Nickel phthalocyanine (NiPc) is one of the most promising organic semiconductor having potential applications in photovoltaic and gas sensing technologies due to their higher absorption spectrum coefficient in wide range and higher photo magnetic sensitivity at low radiation intensities. In this study we have fabricated NiPc based field effect transistors (FETs) of varying channel thickness and investigated the effects of heating on their electrical characteristics. NiPc and semi-transparent aluminum (Al) thin films were layered by vacuum evaporator in sequence over a pre-deposited silver (Ag) electrodes (drain-source). The current flow was controlled using Schottky junction defined by metal (Al) semiconductor (NiPc) interface. At 100 Hz operational frequency, it is observed that by increasing the ambient temperature from 26-62 ^{0}C, the impedance of the transistors decreases. It was observed that for 100 nm, 200 nm and 300 nm thick films FETs, the reduction in the impedance was 2.3, 1.5 and 1.3 times, respectively. Temperature coefficients for impedance change were also evaluated and found to be -2.35%$^{\circ}$C^{-1}, -1.39%$^{\circ}$C^{-1} and -1.18%$^{\circ}$C^{-1} for 100 nm, 200 nm and 300 nm thick films FETs, respectively. Moreover, impedance-temperature relationships obtained for NiPc based FETs were also simulated and discussed.

***Keywords—Organic field effect transistor, Nickel phthalocyanine, Metal semiconductor Schottky junction, Phototransistor, Temperature sensors*.**

I. INTRODUCTION

To fulfill the serious demand for lower-cost, lighter-weight, flexible, and small sized devices with wide utility in electronics, carbon-based field effect transistors (FETs) have gained a lot attention during recent past. Majority of organic semiconductors phthalocyanines are known for their photosensitive behavior. They also offer a wide absorption spectrum coefficient and high photo magnetic sensitivity at low radiation intensities.

Nickel phthalocyanine (NiPc) is one of the most promising phthalocyanines organic semiconductors. Recently, NiPc has got an increased interest in organic electronic industry because of its wide applications in photovoltaic and gas sensing [1-10]. NiPc has energy band gap of 2.24 eV and 3.2 eV for indirect and direct transitions, respectively [10]. Further, NiPc is also a preferred phthalocyanine because; it has higher charge carriers mobility compared to copper phthalocyanine (CuPc) [9]: 0.1 cm^2/Vs in NiPc and 10^{-4} cm^2/Vs in CuPc. Most of the organic transistors reported have FETs structures [11-15]. Properties of CuPc based FET, CuPc-NiPc and CuPc-GaAs hetero-junctions were investigated and reported in [1, 12]. Moreover, electrical response of organic semiconductors based FETs are sensitive not only to light but also to heating. CuPc and metal free phthalocyanine bulk heterojunctions for temperature sensing applications were investigated and reported in [16]. In 2015, Chani *et al.* fabricated and investigated temperature sensors fabricated using carbon nano tubes (CNT) [17] and demonstrated their potential use in the industry.

Properties of FETs can be affected by the heating process in particular, heating will change concentration of charges inside the channel as well as their mobility. This phenomenon is commonly employed to fabricate temperature sensors based on organic semiconductor materials. It is important to mention here that at metal-semiconductor interface, there is an interfacial layer with interface states [18], which can potentially act as traps for free carriers. Thus, affecting the response of the device. Moreover, there is a commonly observed process in semiconductor devices known as— device degradation process. The degradation of organic semiconductor devices, usually, takes place due to the degradation of the contact resistances. This type of degradation creates an additional difficulty to assess the resistance of the device with reasonable accuracy. Therefore, unlike the conventional approach it would be appropriate to measure the impedance instead of the resistance of the samples, because in this case the effects of the traps in the metal-semiconductor contact will probably be minimized.

Recently, we have fabricated NiPc based field effect phototransistor (OFET) with Al-NiPc Schottky junctions and investigated their *I-V* characteristics under dark and illuminated conditions [19]. It was found that for the transistors having 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 of 34.4 mW/cm^2, at drain-source voltage of 3V which is comparable with the response of the FET described by Park *et al.* [20]. Moreover, we also studied the effects of humidity to the electrical properties of NiPc FETs [21, 22]. In this article, the effects of heating on the impedance of NiPc FETs are investigated and reported.

II. Experimental

Analytical grade NiPc was arranged from Sigma-Aldricha and was used without any further purification. Fig. 1 shows its molecular structure. A thin layer of it was sublimed on the glass substrate at 500 ˚C and ~10^{-4} Pa using Edwards AUTO 306 vacuum coater with diffusion pumping system and thickness monitor. The substrate had 100 nm thick surface-type silver film electrodes also deposited by vacuum evaporation technique. The substrate temperature was maintained at ~40˚C during deposition. The surface-type Ag electrodes serve as drain and source for OFET. The gap between source and drain was 40 μm.

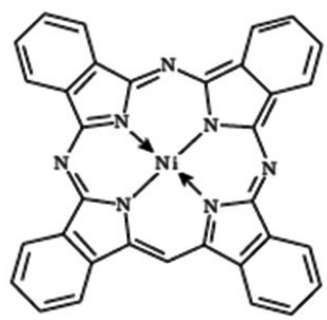

Fig. 1. Molecular structure of P-type NiPc organic semiconductor.

NiPc layer was then covered by a semi-transparent, 22 nm thick Al film of dimension 2 x 10 mm^2. The transparency of Al film was 10-15%. The deposition rate of Ag, Al films were 8 nm/min whereas it was 5 nm/min for NiPc. Fig. 2 presents 2D and 3D AFM micrographs of NiPc thin films obtained by Agilent's Pico Plus, under ambient condition, with a scan size area of 2 μm. 2D micrograph is helpful to find the grain size whereas; 3D AFM image is used to understand the orientation of the grains. As measured from film thickness monitor, the deposited film was 300 nm. However, from AFM 3D image the evaluated thickness of the grown film was 280 nm.

The width and length of NiPc FET channel was 10 mm and 40 μm, respectively. FETs with varying channel thickness: 100 nm, 200 nm and 300 nm were fabricated as shown in Fig. 3. Finished devices were characterized in a chamber wherein temperature and impedance were assessed by FLUKE 87 and MT 4090 LCR meter, respectively, at operating frequency of 100 Hz.

In Fig. 4 impedance-temperature relationships of NiPc organic semiconductor FETs are shown. In [19] it is established that FET with thinner NiPc have larger resistance. Here similar results are obtained in Fig. 4 by measuring the impedance at 100Hz. In Fig. 5 normalized impedance-temperature relationships are shown. It is seen that as temperature increases, impedance decreases for all transistors, especially, for those transistors having thinner NiPc films. It is obvious that as thickness of the NiPc film is decreased, depletion region contribution, which is more sensitive to the heating effect, in the total crossection of the films, is increased. Thus, devices with thinner films exhibited pronounced heating effects.

Relative impedance-temperature relationships for the NiPc film based FET were approximated by exponential function:

$$y = e^{-x} \quad (1)$$

where,

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$$x = (T - 26)b \qquad (2)$$

In Equation (2), 26˚C is initial temperature, T is temperature in ˚C, and b is fitting parameter. Here T ≥ 26˚C. It was observed that simulation complies reasonably well with experimental data at T = 62˚C, as shown in Fig. 5. It was determined that b = 0.0231˚C^{-1}, 0.0121˚C^{-1} and 0.008˚C^{-1} for the simulated graphs related to the NiPc transistors (Fig. 5) for NiPc thickness of 100 nm , 200 nm and 300 nm, respectively.

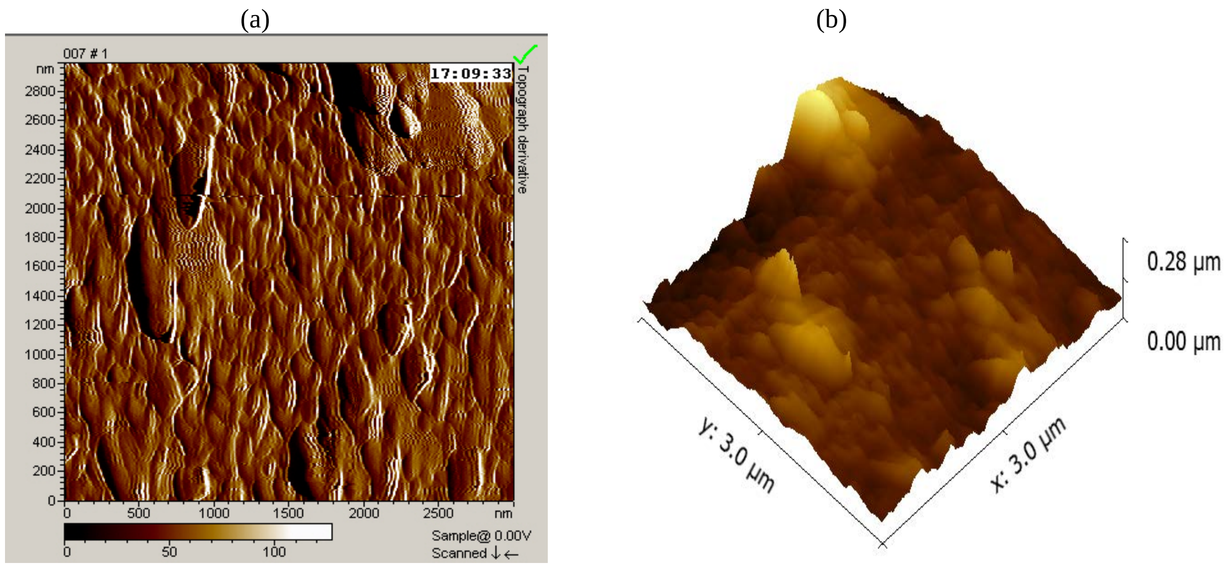

Fig. 2. (a) 2D and (b) 3D AFM micrographs of NiPc thin film

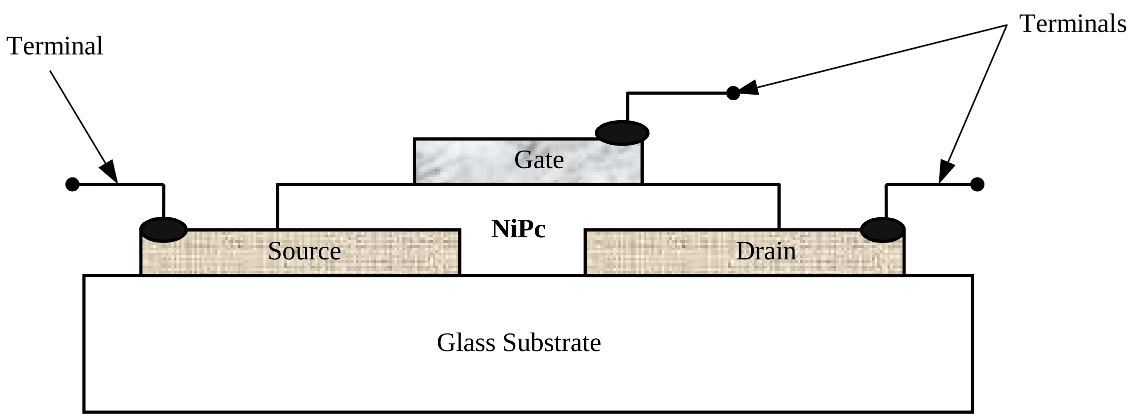

Fig. 3. Cross-sectional view of the fabricated field effect transistors

III. RESULTS AND DISCUSSION

Assuming that FET in this case is a two-terminal temperature sensor then the following equation shows the sensitivity relationship of the sample [23]:

$$S = \frac{\Delta R}{R_0\, \Delta T} * 100\% \qquad (3)$$

Where, R_o, ΔR and ΔT represent the initial resistance, change in resistance and change in temperature, respectively. For each sample average temperature sensitivity was calculated and found to be -2.35%$^{\circ}C^{-1}$ (100 nm thick NiPc film), -1.39%$^{\circ}C^{-1}$ (200 nm thick NiPc film) and -1.18 %$^{\circ}C^{-1}$ (300 nm thick NiPc film) at 100 Hz.

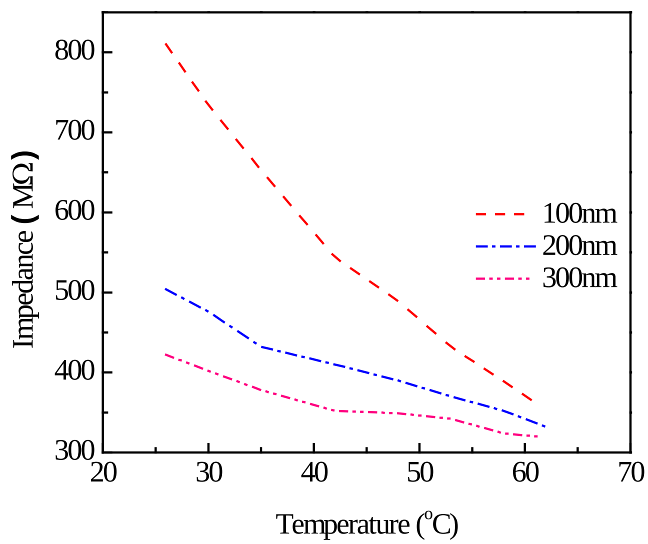

Fig. 4. Impedance-temperature relationships for the NiPc based FETs: thickness of NiPc films were 100 nm, 200 nm and 300(3) nm.

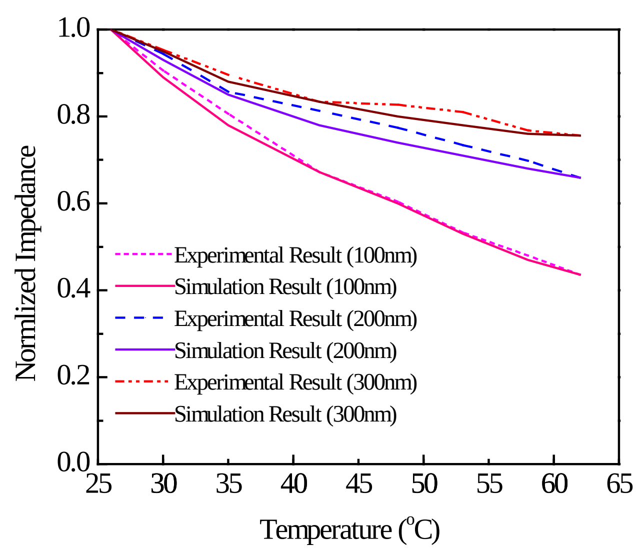

Fig. 5. Simulated and experimental relative impedance-temperature relationships for NiPc film based FETs having varying film thickness.

Temperature sensors which are produced commercially (thermistors), usually offer DC sensitivity ranging from -3%$^{\circ}C^{-1}$ to -5%$^{\circ}C^{-1}$ [23]. In our case observed sensitivities are based on AC measurements which are normally lower than DC sensitivities. However, AC sensitivities have the advantage, especially, for the devices based on organic semiconductor, because fluctuation in contact resistance and accordingly in the current, causes less effect in AC measurements. This may be explained by the fact that the value of impedance, associated with the capacitive component, allows to by-pass the current as shown in Fig. 6 by the equivalent circuit of a contact.

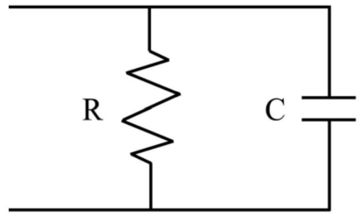

Fig. 6. Equivalent circuit of the contact impedance of NiPc sample.

This circuit shown in Fig. 6 can be used not only as an equivalent circuit of contact impedance, but also as a simplified equivalent circuit of an OFET. If an OFET is used as a two terminal temperature sensor, its response is quasi-exponential (Fig. 5) and for practical applications, its impedance-temperature relationship can easily be linearized by using a linearization circuit as shown in Fig. 6 [24]. For the equivalent circuit shown in Fig. 6, the impedance (Z) can be obtained as

$$Z = \frac{R}{1 + j\omega RC} \qquad (4)$$

where ω is circular frequency, R is resistance and C is capacitance.

The decrease in impedance by the increase in temperature is associated with two main parameters: a) increase in the capacitance of the sample and b) decrease in its resistance value. Reduction in the sample resistance can be explained as: with increased temperature, there will be more bonds breaking causing increased carrier concentration (n_i) in NiPc film, which can be expressed as [25-27]:

$$n_i = N_o exp(\frac{-E_g}{2kT}) \qquad (5)$$

where N_o is pre-exponential factor, E_g is energy gap, k is the Boltzmann constant.

On the other hand, there are a number of factors which affect the capacitance of the samples. They are: a) relative dielectric constant of the thin film material; b) area of electrodes and c) gap between electrodes. Capacitance relies upon material's polarizability (α), sources of which are electronic (α_e), dipolar (α_{dip}) and ionic (α_i) [26]. Another form of polarizability, that is well known, is due to transfer (α_{tr}) of charge carriers (electrons and holes) as reported in [28]. It is worth mentioning that α_e is due to relative displacement of orbital electrons of atoms, whereas the α_{tr} is due to charges participating in conduction process which can be trapped in the semiconductor-electrode interface. The Clausius-Mosotti relationship, if we take into consideration only polarizability due to transfer of charge carriers, can be represented by the following equation [26]:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N a_{tr}}{3\varepsilon_{\circ}} \qquad (6)$$

where ε is relative permittivity and $N \sim n_i$ is total concentration of charge carriers [18]. Here ε_o is permittivity of free space.

Moreover, in organic semiconductors, mobility (μ) has also got temperature dependence and it increases with increasing temperature thus, contributing to the increase in conductivity as given below [27]

$$\mu(F,T) \approx \frac{exp(\frac{-\Delta E}{kT})}{exp(\beta\sqrt{\frac{F}{kT}})} \qquad (7)$$

where F, ΔE and β are electric field, activation energy and exponential factor, respectively.

Temperature dependent increase in mobility is usually associated with hopping mechanism [25, 27]. On the other hand, mobility decreases in those materials wherein conduction is primarily related to the energy bands [18]. If mobility of a sample is less than 1 cm^2/Vs, it is considered that the hopping mechanism of charges transfer is a dominating one. And for mobility greater than 1 cm^2/Vs the energy band related conduction would be a prevailing mechanism [25, 27].

As shown above (Eq. 4 and Fig. 6), the parallel combination of capacitance and resistance can be used to model impedance. The resistance decreases as temperature increases, and capacitance increases, due to increase of permittivity, that definitely shows decrement in impedance because of the dominating fact of the resistor.

Fig. 7 shows the simplified schematic diagram of an OFET: flow of currents and depletion region at low and high temperatures as well. In particular, the figure demonstrates the effect of heating on OFET channel area: depletion region at lower (1) and higher (2) temperatures, space charge (3 and 4), I_{ch} and I_j are the channel current and the junction current, respectively. The diagram illustrates that as temperature increases, width of the depletion region decreases thus, increasing the cross-section of the conductive channel of the OFET. It definitely decreases the resistor and accordingly impedance of the transistor which was observed experimentally (Fig. 4 and Fig. 5).

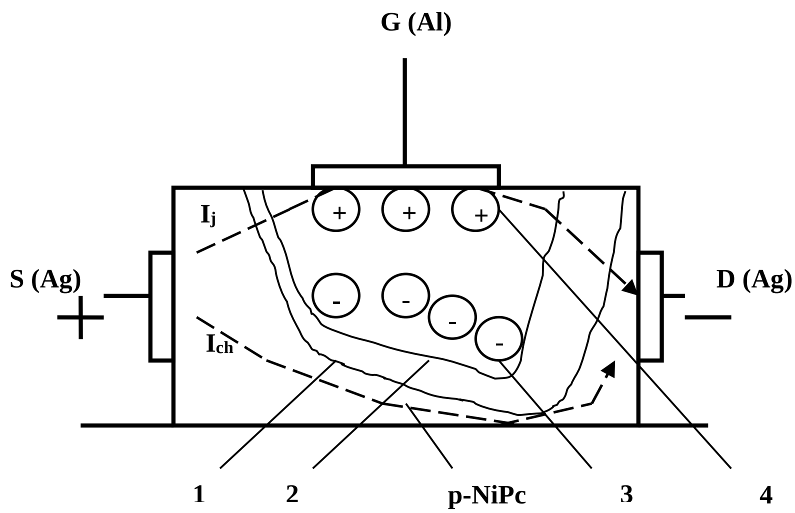

Fig. 7. Effects of heating on junction depletion region and source-drain current of an OFET: depletion region at low (1) and high (2) temperatures, space charge (3 and 4), I_{ch} and I_j are the channel current and the junction current respectively.

TABLE I. Temperature-impedance effect of Nickel Phthalocyanine based field effect transistor measured at 100 Hz.

Potential Application — NiPc films as temperature sensors			
Sample No.	Thickness (nm)	Initial Impedance (kΩ)	Temperature Sensitivity (%^{o}C^{-1})
1.	100	810	- 2.35
2.	200	504	- 1.39
3.	300	422	- 1.18

The obtained results show that one of the applications of NiPc based transistors could be the multi-functional sensors, i.e., temperature, light and humidity sensors. For temperature sensing applications, the sensor should be placed in sealed nontransparent box, made from high thermal conductance materials. Likewise for light sensing applications, the sensor should have transparent and non-porous window. Whereas, for humidity sensing, the sensor should be placed in a box having porous nontransparent window. Moreover, for a complete system, the measuring sensors as active device should be connected to the arms of a Whetstone bridge along with of a dummy sensor in order to compensate or reduce experimental errors especially when a couple of parameters are to be assessed [23]. These multi-functional sensors can potentially be used for humidity, temperature and light intensity measurements or, in general, for environmental monitoring.

CONCLUSION

Effects of heating on the impedance of NiPc based organic field effect transistors (OFETs) were investigated and it was observed that the transistors showed high temperature dependent responses. As NiPc is known to be a good light and humidity sensing material, it was demonstrated that the transistors fabricated using NiPc films can be used as multi-functional sensors to evaluate light, humidity and temperature variations. It was further established that NiPc based OFET can potentially be used in environmental monitoring equipment to assess light, humidity and temperature changes.

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