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Temperature Variation Effects on I-V Characteristics of Cu-Phthalocyanine based OFET

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Abstract**—**In this study we present the effect of elevated temperatures from 300K to 400K on the electrical properties of copper Phthalocyanine (CuPc) based organic field effect transistors (OFET). Thin films of organic semiconductor CuPc (40nm) and semitransparent Al (20nm) were deposited in sequence, by vacuum evaporation on a glass substrate with previously deposited Ag source and drain electrodes with a gap of 40 μm. Under resistive mode of operation, where gate was suspended it was observed that drain current of this organic field effect transistor (OFET) show an increase with temperature. While in grounded gate condition metal (aluminum) – semiconductor (Copper Phthalocyanine) Schottky junction dominated the output characteristics and device showed switching effect from low to high conduction states like Zener diode at higher bias voltages. This threshold voltage for switching effect has been found to be inversely proportional to temperature and shows an abrupt decrease after knee temperature of 360K. Change in dynamic resistance (R_d = dV/dI) with respect to temperature was observed to be -1%/K.

Keywords**—**Copper Phthalocyanine, Metal-Semiconductor Schottky Junction, Organic Field Effect Transistor, Switching effect, Temperature Sensor

I. Introduction

DURING the past decade, field effect transistors based on conjugated polymers, oligomers and low molecular weight organic semiconductors have been investigated widely. Lower material and fabrication cost of organic field-effect transistors (OFETs) are attracting extensive interest for their potential applications in organic electronic devices [1]-[5]. Noh et al. fabricated highly photosensitive organic phototransistor (OPT) based on a biphenyl end-capped fused bithiophene oligomer [6]. The device showed a photocurrent response similar to the absorption spectrum of the organic semiconductor under 380 nm UV light. It is expected that the OPT may be used in highly sensitive UV sensors. Similar to the previous case in [7] the effect of ultraviolet light irradiation on the characteristics of OPTs containing sexithiophene (6-T) and pentacene was examined.

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The transistors showed two distinguishable responses, i.e., fast and slow responses from photoconductive and photovoltaic effects, respectively. It suggests the possibility of its application in light-addressable field-effect transistor memory devices. The most widely used organic semiconductors as pentacene, thiophene oligomers and regioregular polythiophene showed good performance for use in OFET, but further improvements seem to be needed [1].

Park et al. demonstrated the non-volatile and non-destructive photomemory operation of organic copper phthalocyanine/inorganic ferroelectric $PbZr_{0.2}Ti_{0.8}O_3$ heterojunction gate and $La_{0.87}Ba_{0.13}MnO_3$ ferromagnetic semiconductor oxide channel [8]. 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.

For detection of gas species the FET with a floating gate was fabricated [9]. Nanoscale organic and polymeric FETs as chemical sensors showed high sensitivity [10]. Gas sensors were also fabricated based on conducting polymers [11].

Among Organic semiconductors phthalocyanines [12] copper phthalocyanine (CuPc) is specially well-studied organic photosensitive semiconductors with molecular structure shown in Fig. 1 (a). It has high absorption coefficient in wide spectrum and high photo-electromagnetic sensitivity at low intensities of radiation. The deposition of thin CuPc films by vacuum sublimation is easy. Purification of CuPc is simple and economical as the sublimation occurs at relatively low temperatures (673.15 - 873.15 K). In [13]-[14], we reported the fabrication of organic-on-inorganic Ag/p-CuPc/n-GaAs/Ag photoelectric sensors. Properties of the sensor were investigated at room and elevated temperatures in photovoltaic and photoconduction mode of operation under filament lamp illumination. Photocurrent and photo-voltage spectra showed that cell is sensitive in the large spectral range of wavelengths 200-1000 nm from UV to visible and NIR spectrum.

Some of the OFETs show sensitivity not only to applied voltage but to electric field of molecules as well. Recently Bartic et al. fabricated OFET that was able to detect charged/uncharged chemical species in aqueous media via field effect; the chemical sensitivity of the transistor was illustrated for protons and glucose [15]. In ion-sensitive field effect transistor (ISFET) the gate oxide was covered by Si_3N_4 or Al_2O_3 to improve stability and Nernstian behavior [16]. Conductivity of Phthalocyanine based Langmuir-Blodgett film's was highly sensitive to NO and NO_2 gases [17]. Copper phthalocyanine films were found sensitive to chlorine (Cl_2) [18]. The CuPc based FET with suspended gate showed high sensitivity to NO_2 gas [19].

Phthalocyanines have been used for humidity sensing resistors [20] only. In this paper the temperature sensitive OFET (TSOFET) with CuPc and Schottky junction (Al-CuPc) are reported that have the structure of MESFET. The effect of temperature on output characteristics of phthalocyanine based OFET has been studied in order to investigate potentialities of transistor to use it as temperature sensor, and, secondly, to know the interval of temperature where the transistor's parameters will be stable for practical application of the devices as the active elements of the electronic circuits.

(a)

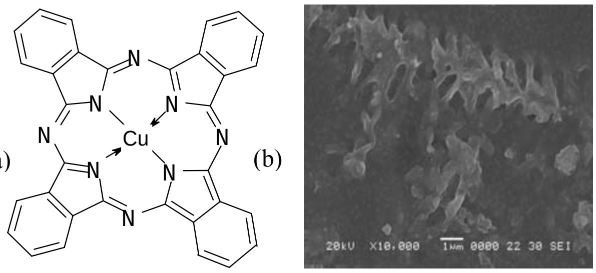

Fig. 1 (a) Molecular structure of copper phthalocyanine (CuPc). (b) SEM image of the CuPc film.

II. FABRICATION

In this study high purity CuPc, obtained from Sigma Aldrich, was used for fabrication of device. The α and β-forms are most frequently encountered states of CuPc. X-ray diffraction data showed that the deposited CuPc films were in β-form [21]. Examination of scanning electron micrographs denies the existence of any particular crystal orientations in the CuPc film [21]. Band gap of CuPc is equal to (1.6-2.0) eV and conductivity is equal to ($1.2x10^{-8}$–$5x10^{-13}$) $\Omega^{-1}cm^{-1}$ at T=300 K [12], [22] and [23]. The sublimation temperature varies from 673.15 K at a pressure of 10^{-4} Pa to 853.15 K at 10^{-4} Pa [12].

Thin films of CuPc were thermally sublimed onto glass substrate (with pre deposited 50 nm thick silver electrodes) at 673.15 - 723.15 K and ~10^{-4} Pa in Edwards AUTO 306 vacuum coater with diffusion pumping system. The deposition rate was equal to 0.2 nm/s.

The substrate's temperature in this process was held at ~313.15 K. Thickness of the CuPc film was obtained by Edwards FTM5 film thickness monitor and was found to be 40nm. SEM image of the CuPc film has been depicted in Fig. 1(b). On CuPc film the semi-transparent 20 nm Al film (transparency being equal to 10-15%) was deposited. Earlier investigations showed that CuPc forms ohmic contacts with Ag and Schottky type rectifying contacts with Al [13]. Usually the CuPc films show p-type conductivity [12], [22] and [23].

Fig. 2 shows cross-sectional view of the fabricated OFET: source and drain electrodes connected with Ag films and gate electrode with Al film. The geometrical length, width and thickness of the CuPc channel were equal to 40 μm, 20 mm and 60 nm.

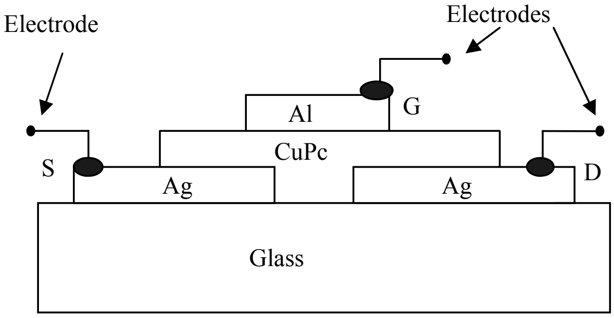

Fig. 2 Cross sectional view of the organic FET

III. EXPERIMENTAL

Electrical characteristics of TSOFET were evaluated for temperature range 300K-400K, by using Computer interfaced Keithley SMU 236 employing Labview 2009 software. For temperature dependent characterization, Janis cryogenic system was used with the Lakeshore 331 Temperature controller. The optical responses were measured using optical window and for dark conditions windows were covered by aluminum foil. Facility of in situ Illumination levels measurement by illumination measuring device was also present in the chamber. However in this paper we only present OFET's multi-temperature I-V response under dark condition. The results for optical response have been presented somewhere else [24]. Temperature level was prone to measurement error of ±0.5^{o}C. The repeatability of the observed values were checked and found within ±5%.

IV. RESULTS AND DISCUSSION

Fig. 3 shows the output drain current (I_D)-drain source voltage (V_{DS}) characteristics of the CuPc based OFET at different temperatures, when Gate of the OFET was suspended. It is seen that the output characteristics of the OFET show quasi-linear behavior at low temperatures and slightly super linear deviation at elevated temperatures. Actually these characteristics don't cover saturation region. With increase of the temperature the current increases at a particular voltage, for example at 5 V current increases approximately 1.5 times.

Fig. 4(b) shows the output drain current (I_D)-drain source voltage (V_{DS}) characteristics of the CuPc based OFET at different temperatures, when Gate and Drain of the OFET were grounded. It is seen that the output characteristics of the OFET show non-linear behavior. With increase of the temperature the current increases at a particular voltage, for example at 5 V current increases approximately 7.5 times. Ratio of the resistances at T=400K measured at 1 V and 5 V is equal approximately to 10. This behavior is like switching effect from low conductance to high conductance state that was observed in some inorganic semiconductor films [25], organic films of poly-N-epoxypropylcarbazole (PEPC) [26]. This behavior is well-known for Zener diodes, which observed at reverse bias [27]. In the case of this OFET it is observed at forward bias.

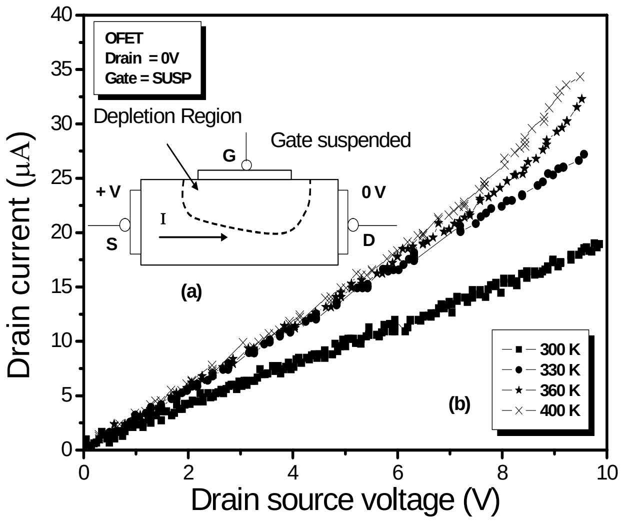

Fig. 3 (a) Schematic diagram of the OFET at suspended Gate. (b) The output (drain current-drain source voltage) characteristics of the CuPc based OFET at different temperatures, when Gate of the OFET was suspended.

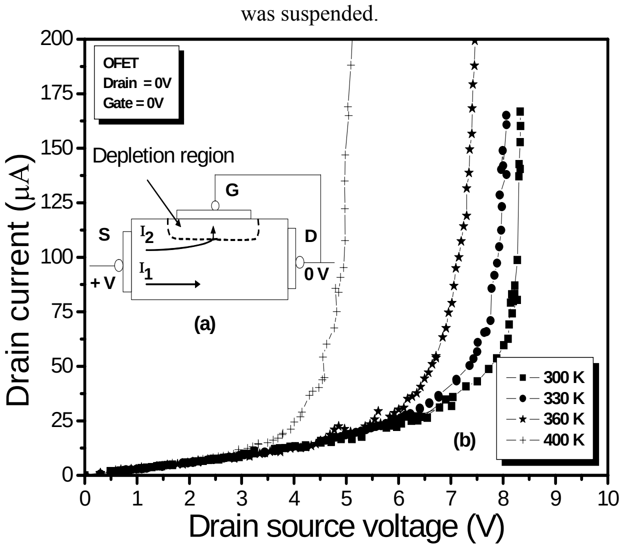

Fig. 4 (a) (inset) Schematic diagram of the OFET with grounded Drain and Gate. (b)The output (drain current-drain source voltage) characteristics of the CuPc based OFET at different temperatures, when Gate and Drain of the OFET were grounded.

Fig. 5 shows the threshold voltage (V_{th}) versus temperature relationship obtained by use of the data presented in Fig. 4(b). It is seen that the V_{th} decreases with increase of the temperature. It may be due to decrease in the effective width of the depletion region at Al-CuPc Schottky junction that have the character of the avalanche process of intensive generation of charge carriers due to collisions of charge carriers with CuPc molecules at higher temperature.

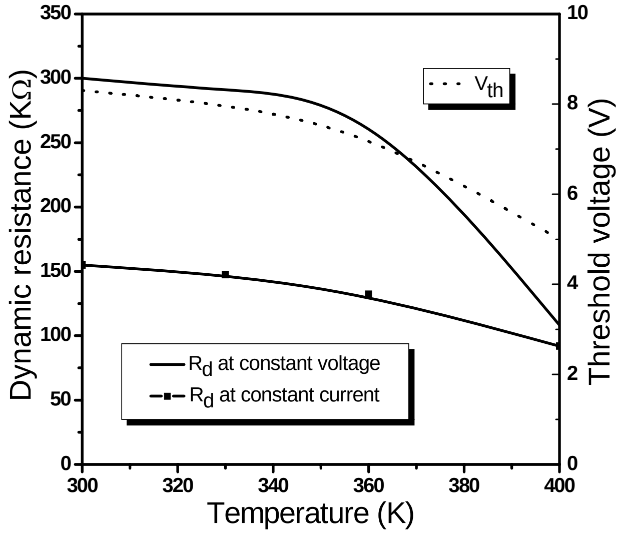

Fig. 5 a)-dashed line represents the threshold voltage-temperature relationship [from Fig. 4(b)]. b)-solid lines show dynamic resistance–temperature relationships [from Fig. 4(b)] at constant voltage (V = 4.5 V) and constant current (I = 150μA).

For some practical applications of the OFET as temperature sensitive FET (TSOFET) it would be reasonable to estimate temperature sensitivity of the drain-source resistance (R_d=V_{DS}/I_D). Fig. 5 shows this relationships obtained by use of data presented in Fig. 4(b) at constant voltage (V = 5V) and constant current (I = 150μA). It is seen that in both cases resistance decreases with temperature approximately 9.4 and 1.7 times respectively.

The average temperature sensitivity (S) of the TSOFET can be evaluated as [28]:

$$S = \frac{\Delta R}{R \Delta T} \quad (1)$$

Where ΔR and ΔT are changes in resistance and temperature respectively.It was found that S = -1%/K at constant voltage measurement. Conventional semiconductor thermistors made of metal oxides have sensitivity in the interval of – (3-4)%/K [28]. The advantage of TSOFET over conventional temperature sensor is firstly their ease of fabrication and secondly, TSOFET is multifunctional device that can be used potentially for measurement not only temperature but humidity and light as well [24], [29]. Meanwhile Fig. 4(b) shows that TSOFET can be used for stabilization of the voltage as Zener diodes and the value of threshold voltage can be controlled by temperature. Fig. 3(a) (inset) and Fig. 4(a) (inset) show the schematic diagrams of the OFET at suspended Gate and grounded Gate and Drain conditions respectively. In Fig. 3(a) the current pass only through channel, whereas in Fig. 4(a) currents I_1 and I_2 pass through forward biased junction and channel respectively. This is the reason why we get different output (drain current-drain voltage) characteristics in linear region of Fig. 3 (b) and Fig. 4 (b).

The simplified conduction mechanism in the organic semiconductors can be explained by the following approaches. In multicrystalline thin films as in disordered system, mostly hopping mechanism of conduction was observed [22]-[23], due to phonon assisted hopping of carriers from one localized state to another. As a rule the mobility increases with temperature, but it depends on actual contribution from scattering phenomenon: it was found that the mobility may increase, decrease or be independent of temperature in different organic semiconductors [22]-[23]. Usually a value of mobility around 1 $cm^2 V^{-1}s^{-1}$ is a boundary between band transport and hopping mechanisms.

Tunneling effect actually is most universal phenomenon, but it may contribute mostly at very low temperatures where band and hopping mechanism have less contribution. It is believed that in tunneling mechanism mobility shows temperature independent behavior and has low value i.e. ($\mu << 1 cm^2V^{-1}s^{-1}$).

The mechanism of conductivity in CuPc can be considered as thermally assisted hopping transitions between spatially separated sites of molecules which can be attributed to the Percolation theory [30]. According to Percolation theory, the average conductivity (σ) can be calculated as:

$$\sigma = \frac{1}{LZ} \qquad (2)$$

Where L is a characteristic length, depending on the concentration of the sites, Z is the resistance of the path with the lowest average resistance.

The structure and properties of organic semiconductors and, in particular, thin films depend not only on molecular structure or concentration of impurities but also on technology of deposition [22], [23] and [31]. Therefore further improvement in properties of OFET would be expected. The simulation and OFET's parameters optimization would be the matter of the future work.

V. Conclusion

The electrical characteristics, of Copper Pthalocyanine (CuPc) based temperature sensitive organic FET, were investigated in the temperature interval of 300K – 400K. It was observed that drain current of this organic field effect transistor (OFET) showed an increase with temperature. Examination of I-V characteristics under grounded gate condition confirmed presence of switching effect from low to high conduction states at high bias voltages. This threshold voltage of the switching effect showed inverse relation with temperature. The average temperature sensitivity of the resistance of the FET was equal to -1%/K. Further improvements in TSOFET's performance may be made by optimizing thickness of gate (Al) and semiconductor (CuPc) thin films as well as by miniaturizing semiconducting channel gap width and length. Owing to its sensitivity to temperature, light and humidity CuPc has been proposed to be used in industry as multifunctional sensor.

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