Humidity sensitive organic field effect transistor

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Abstract: This paper reports the experimental results for the humidity dependent properties of an organic field effect transistor. The organic field effect transistor was fabricated on thoroughly cleaned glass substrate, in which the junction between the metal gate and the organic channel plays the role of gate dielectric. Thin films of organic semiconductor copper phthalocynanine (CuPc) and semitransparent Al were deposited in sequence by vacuum thermal evaporation on the glass substrate with preliminarily deposited Ag source and drain electrodes. The output and transfer characteristics of the fabricated device were performed. The effect of humidity on the drain current, drain current-drain voltage relationship, and threshold voltage was investigated. It was observed that humidity has a strong effect on the characteristics of the organic field effect transistor.

Key words: organic field effect transistor; CuPc; metal–semiconductor Schottky junction; humidity sensor
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1. Introduction

During the past decade, field effect transistors based on conjugated polymers, oligomers and low molecular weight organic semiconductors have been investigated widely. The lower material and fabrication costs of organic field effect transistors (OFETs) are attracting extensive interest for their potential applications in organic devices[1−5]. Noh *et al*.[6] fabricated a highly photosensitive organic phototransistor (OPT) based on a biphenyl end-capped fused bithiophene oligomer. 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. Similarly, the effect of ultraviolet light irradiation on the characteristics of OPTs containing sexithiophene (6-T) and pentacene was examined[7]. The transistors showed two distinguishable responses, i.e., fast and slow responses from photoconductive and photovoltaic effects, respectively. This suggests a possible application in light-addressable field effect transistor memory devices. The most widely used organic semiconductors of pentacene, thiophene oligomers and regioregular polythiophene show good performance for use in OFETs, but further improvements are needed[1].

Park *et al*.[8] demonstrated the non-volatile and non-destructive photomemory operation of an organic copper phthalocyanine/inorganic ferroelectric $PbZr_{0.2}Ti_{0.8}O_3$ heterojunction gate and a $La_{0.87}Ba_{0.13}MnO_3$ ferromagnetic semiconductor oxide channel. The device could write light information with a combination of light irradiation and the negative gate bias, and delete only with the positive gate bias.

For detection of a gas an FET with a floating gate has been fabricated[9]. Nanoscale organic and polymeric FETs used in chemical sensors show high sensitivity[10]. Gas sensors based on conducting polymers have also been fabricated[11].

Organic semiconductors phthalocyanines[12] and especially CuPc are well-studied organic photosensitive semiconductors. It has a 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 (400–600 °C). The current authors reported the fabrication of organic-on-inorganic Ag/p-CuPc/n-GaAs/Ag photoelectric sensors[13, 14]. The properties of the sensor were investigated at room and elevated temperatures in photovoltaic and photoconduction modes of operation under filament lamp illumination. Photocurrent and photo-voltage spectra showed that the cell is sensitive in a large spectral range of wavelengths 200–1000 nm from UV to visible and NIR spectra.

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

It was found that humidity affects the properties of gas sensitive gateless FETs[20]. A pentacene FET was exposed to humidity and it was found that its saturation current and mobility decreased[21, 22]. The sensitivity of this FET decreases when the thickness of the pentacene increases and humidity is above 30%. Below 30% humidity, it was observed that thicker films were more sensitive but with a memory effect.

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Table 1. X-ray diffraction results for CuPc film deposited by vacuum evaporation.

Parameter	Value
d_1	12.9694 Å
d_2	11.7992 Å
d_1/d_2	1.0993
$2\theta_1$	6.8100
$2\theta_2$	7.4875
I_1	236.00
I_2	230.5
I_1/I_2	1.0238

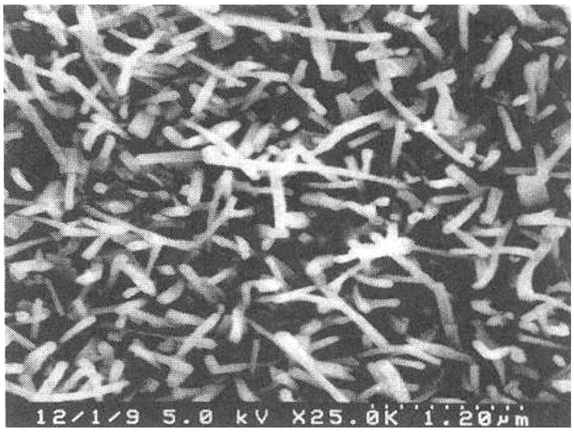

Fig. 1. Scanning electron micrographs of thermally deposited CuPc film.

Phthalocyanines have been used for humidity sensing resistors only. As it is known that transistors have several advantages over resistors[21], for example, due to presence of the gate, very thin films (20–50 nm) may be used, and the value and polarity of gate potential can control the absorption process of the species on the sensor's surface. Therefore it is reasonable to investigate the effect of humidity on phthalocyanine-based FETs. In this paper a humidity sensitive FET (HSFET) with a Schottky junction (Al–CuPc) is reported that has the structure of a MESFET.

2. Experimental

CuPc was obtained from Sigma Aldrich. The molecular structure of CuPc is well-known[23, 24]. At least seven crystalline polymorph states of CuPc exist: α, β, γ, etc.[25]. Table 1 shows X-ray diffraction data for CuPc film[26]. The distance d between molecular planes was calculated using Bragg's law, $2d\sin v = n\lambda$, where n is the order, λ the wavelength and θ the glancing angle of the X-ray beam. The glancing angles of the two peaks with wavelengths of 600 and 700 nm are indicated by θ_1 and θ_2, with intensity I_1 and I_2. The presence of these two peaks suggests that the α form of CuPc was obtained. The estimated values, from Ref. [25], for the distance between two crystal planes for this form of CuPc is $d_1 = 12.96$ Å and $d_2 = 11.96$ Å, while the β form has $d_1 = 9.703$ Å and $d_2 = 7.314$ Å.

Scanning electron micrographs, SEM, (Fig. 1) showed that no particular crystal orientations in the CuPc films exist[26].

The α-CuPc form is a metastable one at $T = 165$ °C and can be converted thermally or with solution to the β-form. The α and β-forms are the most frequently encountered states of CuPc. X-ray diffraction data showed that the deposited CuPc films were in the β-form[26]. Scanning electron micrographs showed that no particular crystal orientations in the CuPc films exist[26]. The band gap of CuPc is equal to 1.6–2.0 eV and its conductivity is equal to 1.2×10^{-8}–5×10^{-13} $\Omega^{-1}\cdot$cm^{-1} at $T = 300$ K[12, 23, 24]. The sublimation temperature varies from 400 °C at a pressure of 10^{-4} Pa to 580 °C at 10^{-4} Pa[12].

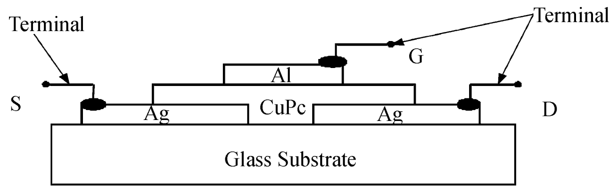

Fig. 2. Cross sectional view of the organic field effect transistor.

Thin films of CuPc were thermally sublimed onto glass substrate (with pre deposited 50 nm thick silver electrodes) at 400–450 °C and $\sim 10^{-4}$ Pa in an Edwards AUTO 306 vacuum coater with a diffusion pumping system. The deposition rate was equal to 0.2 nm/s. The substrate's temperature in this process was held at ~40 °C. The thickness of the CuPc film was measured by an Edwards FTM5 film thickness monitor. On CuPc film a semi-transparent 20 nm Al film (whose transparency was 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, 23, 24].

Figure 2 shows a cross-sectional view of the fabricated OFETs: source and drain terminals connected with Ag films and the gate terminal with Al film. The geometrical length, width and thickness of the CuPc channel for sample #1 were equal to 100 μm, 20 mm and 60 nm and for sample #2 100 μm, 1 mm and 100 nm respectively. The measurements of voltage, current and humidity were conducted with digital meters at room temperature. The sample was placed in a special chamber where the relative humidity could be changed in the range of 40%–90%.

3. Results and discussion

Figure 3 shows the output and transfer characteristics of the CuPc-based OFET (sample #1). It is seen that in principle the characteristics are like that of an organic FET based on thiophene and NiPc[1, 21]. The value of drain current I_D of the OFET (Fig. 3) is increased by an increase in negative gate–source voltage V_{GS} and a decrease in positive V_{GS}. It means that the OFET is working in enhancement and in depletion mode of operations respectively. In a saturation regime (Fig. 3(a)) for the MESFET structure I_D is determined from the following equation[27]:

$$I_D = k(V_{GS} - V_{Th})^2, \quad (1)$$

where V_{Th} is the threshold voltage, and k is a conduction parameter:

$$k = \mu \varepsilon_s W / 2aL, \quad (2)$$

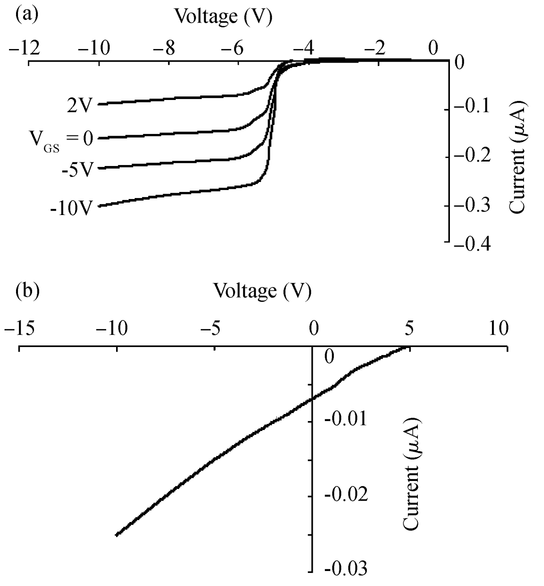

Fig. 3. (a) Output and (b) transfer characteristics of the CuPc-based OFET. The thickness of the CuPc film was equal to 60 nm; the geometrical length and width of the channel were equal to 100 μm and 20 mm respectively (sample #1).

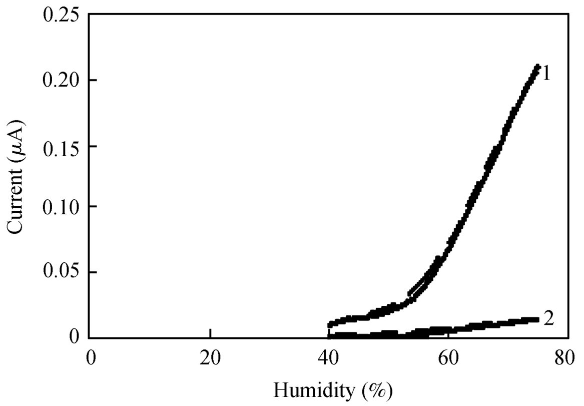

Fig. 4. Drain current–relative humidity relationship at drain–source voltage equal to 5 V for the OFET. (Geometrical length, width and thickness of the CuPc channel for different samples (#1 and #2) were equal to 100 μm, 20 mm and 60 nm, and 100 μm, 1 mm and 100 nm respectively.) Solid and dashed lines show increase and decrease of humidity respectively.

where L is channel length, W is channel width, ε_s is the permittivity of the semiconductor material ($\varepsilon_s = 4 - 8.85 \times 10^{-14}$ F/cm), a is channel thickness (60 nm) and μ is the field effect mobility. The transconductance (g_m) of the enhancement mode device operating in the saturation region[28] is:

$$g_m = (\partial I_D / \partial V_{GS}) = 2k(V_{GS} - V_{Th}). \quad (3)$$

It is seen that transconductance increases with V_{GS}.

The mobility can be calculated in the saturation regime by using Eqs. (1) and (2). It was found that $\mu = 1 \times 10^{-6}$ cm^2/(V·s) for the $V_{GS} = -10$ V, $V_{DS} = -8$ V, $V_{Th} = 5$ V, and $I_D = 2.75 \times 10^{-8}$ A. The attained value of mobility is close to that determined by the SCLC approach ($\mu = 2 \times 10^{-5}$ cm^2/(V·s))[12].

In the molecular FET the total current I_t is equal to the sum of the channel current I_D and the bulk current I_b [1]. The I_{on}/I_{off} ratio at saturation may be calculated by the following expression[1]:

$$I_{on}/I_{off} = I_{Dsat}/I_b. \quad (4)$$

Experimentally I_{on}/I_{off} was found from Fig. 3(a) to be equal to 25.

Figure 4 shows the drain current versus relative humidity relationship of the OFET measured at room temperature. It is seen that as relative humidity increases from 40 to 75% the drain current increases 20 and 15 times at a drain–source voltage of 5 V for samples #1 and #2 respectively and the graphs show good reversibility with increase and decrease in humidity values.

Figure 5 shows the drain current versus drain–source voltage relationship (sample #1) for the OFET at different values of humidity ranging from 40 to 75%. It is seen that the drain current increases with an increase in relative humidity. Based on Fig. 5 the threshold voltage versus humidity was obtained as shown in Fig. 6.

Figure 7 shows the drain current versus drain voltage relationship for the OFET (sample #1) at high values of relative hu-

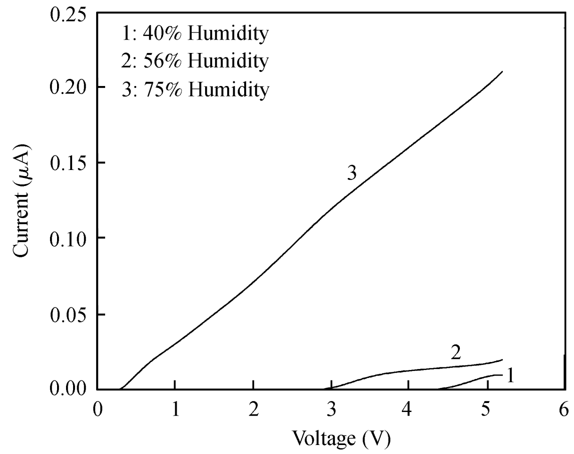

Fig. 5. Drain current–drain voltage relationship for the OFET: humidity was equal to (1) 40%, (2) 56% and (3) 75%. Geometrical length, width and thickness of the CuPc channel were equal to 100 μm, 20 mm and 60 nm (sample # 1).

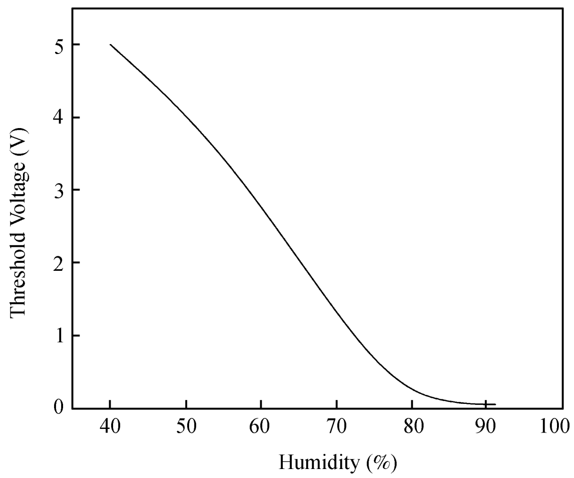

Fig. 6. Threshold voltage versus relative humidity relationship for the OFET at drain–source voltage equal to 5 V (sample #1).

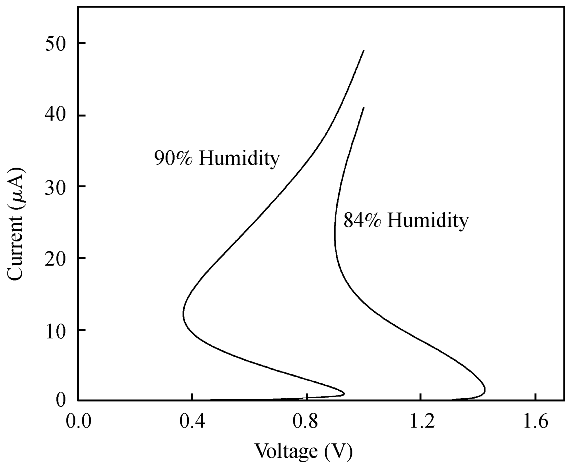

Fig. 7. Drain current versus drain voltage relationship for the OFET (sample #1).

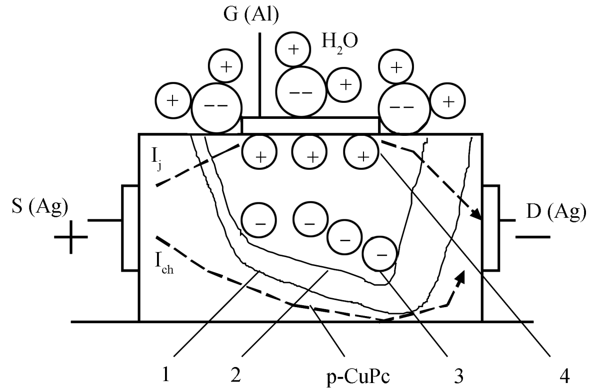

Fig. 8. Effect of polar water molecules on the width of the junction depletion region and source–drain current: depletion region at (1) low and (2) higher humidity, (3 and 4) space charge, I_{ch} and I_j are the channel current and the junction current respectively.

midity in the range of 84%–90%. It is seen that these curves are unlike the curves shown in Fig. 5. The curves show abrupt increase of the current up to 256 and 350 times at relative humidity of 84% and 90% respectively, with negative differential resistance. This kind of phenomenon has been observed in a number of electronic devices, including tunnel diodes[28], and may be used for the fabrication of oscillators. Practically, JFETs show avalanche breakdown of the gate-to-channel diode. With an increase in the drain voltage, the breakdown occurs at the drain end of the channel where there is a reverse voltage[27]. Generally speaking, the gas-sensing properties of the devices depend on two processes: surface absorption and diffusion[21]. The first process may be physical or chemical in nature, i.e. physisorption and chemisorption respectively. In physical absorption, van der Waals electrostatic forces usually play a primary role, whereas in chemical absorption the formation of chemical bonds between, for example, water molecules and substrate may be observed. As a rule, the chemical absorption process is a slow process and sometimes irreversible. But physical absorption is faster and reversible. The latter case probably takes place in the currently investigated humidity sensitive OFET: response and recovery times were approximately in the range of 1–2 s and 3–5 s respectively.

In particular, by increasing the concentration of water molecules, the electric field of H_2O dipoles increases which results in a decrease of the length and width of the depletion region as shown in Fig. 8. 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 the gate) increase due to a decrease in the length and width of the depletion region. The decrease of the initial built-in junction electric field due to the electric field of the H_2O molecules is probably one reason behind this phenomenon. If the channel current monotonously increases with humidity, the junction current may grow fast (Fig. 7) due to breakdown of the gate–drain junction that is in reverse bias, as the source–gate junction is in forward bias. The breakdown of the gate–drain junction may be due to an avalanche mechanism or a tunneling mechanism (Zener breakdown)[27]. Actually, the effect of the H_2O dipole's electric field is like an applied forward bias voltage (negative) to the gate–source terminals of this OFET.

The structure and properties of organic semiconductors and, in particular, thin films depend strongly not only on molecular structure and concentration of impurities but also on the technology used for deposition[23, 25, 29]. Therefore further improvement of the OFET properties would be expected in this area. The parameter optimization of the HSOFET and circuit simulation will be studied in future work.

4. Conclusions

The electrical characteristics of a CuPc-based humidity sensitive organic FET were investigated. It was found that the drain current of this OFET increases with humidity. Drain current increased 15–20 times as relative humidity increased from 40% to 75%. At higher values of relative humidity the drain current increased abruptly by 256 and 350 times at a relative humidity of 84% and 90% respectively, and shows negative differential resistance in the I–V characteristics. The latter phenomenon may be due to breakdown of the drain–gate junction. This behavior of the HSFET is explained by decrease of the depletion region's length and width, due to the electric field of H_2O molecules.

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