

Copper phthalocyanine and metal free phthalocyanine bulk heterojunction for temperature sensing

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This study presents the fabrication and temperature sensing properties of the sensors based on copper phthalocyanine (CuPc) and metal free phthalocyanine (H₂Pc) bulk heterojunction. To fabricate the sensors on conductive glass, indium tin oxide (ITO) layer was deposited on glass substrate and the bulk heterojunction thin films of CuPc and α -Pc with 100-200 nm thickness were deposited by thermal evaporation. As a top electrode Al thin film was deposited by thermal evaporation as well. The resistance of the sensors decreases with temperature in the interval from 30 °C to 90 °C. Resistance temperature coefficients (S) at 30 °C was in the range from (-4 %/°C) to (-6 %/°C) depending on the technological parameters of the samples. Simulation was carried out and results were in good agreement with experimental data. The obtained results show that the investigated heterojunction's temperature sensitivity is in the range of sensitivity of best semiconductor temperature sensors.

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1. Introduction

Bulk heterojunction solar cells (BHSC) are under intensive investigations due to their good performance, simplicity of technology and potential utilization for solar energy conversion in the future [1-4]. Investigations of the properties of bulk heterojunction structures are important, firstly, due to effect of temperature to the properties of BHSCs and, secondly, for fabrication of temperature sensors.

Temperature measurement is important first of all for the comfort of human being. At the same time, temperature sensors are also used in different areas of technology. Temperature sensors are normally categorized as contact and non-contact type sensors. The former type includes resistance temperature detectors (RTDs), thermistors and thermocouples [5]. For the fabrication of the RTDs the commonly used sensing materials are the platinum and gold, which are very expensive [6], and in some cases copper. For the fabrication of thermistors usually semiconductor, in particular, oxide of metals are used. Organic materials are considered potentially very promising [7, 8] for use in temperature sensors with high sensitivity and relatively low cost.

The metal phthalocyanines (MPcs) are the nontoxic p-type organic materials with good thermal and chemical stability. These materials are extremely attractive for use in optical and electronic devices. Recently, the temperature sensing properties of the organic semiconductor aluminium phthalocyanine chloride (AlPcCl) that is the

low molecular weight and low density (1.0 g/cm³) material having band-gap energy of 1.56 eV, were tested and they were lower than the ones presented here [9].

Copper phthalocyanine (CuPc) is one of the well investigated organic semiconductors that was used for fabrication of solar cells [10], light and humidity sensors [11]. CuPc and metal free phthalocyanine (H₂Pc) have different work functions, 3.87 eV and 4.04 eV accordingly, that potentially allow the fabrication of bulk heterojunctions. The energy gap of the CuPc and H₂Pc are equal to 1.6 eV [12, 13] and 2.2 eV accordingly. The energy gaps of CuPc and H₂Pc are sufficiently large that justifies to fabricate the temperature sensors on the base of these materials. In this work the fabrication and temperature sensing properties of copper phthalocyanine and metal free phthalocyanine bulk heterojunction are described.

2. Experimental

For the fabrication of bulk heterojunction samples, CuPc and H₂Pc have been used, which are commercially available by Sigma Aldrich, U.S.A. CuPc and H₂Pc have chemical formula C₃₂H₁₆CuN₈ and C₃₂H₁₈N₈ respectively. Molecular structures of the CuPc and H₂Pc are shown in Fig.1 (a and b).

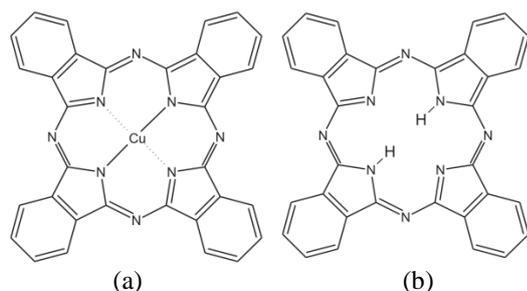
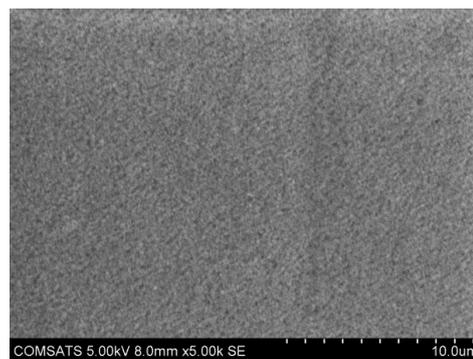


Fig.1. Molecular structures of the CuPc (a) and H₂Pc (b).

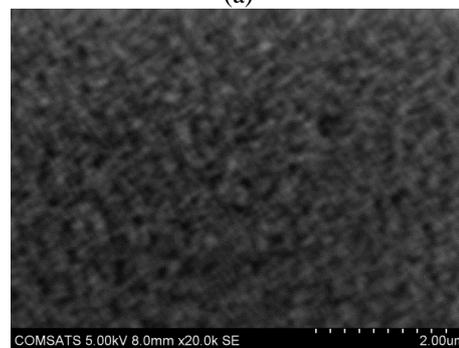
The CuPc is a *p*-type organic semiconductor [10, 12]. It is known that, at least, seven crystalline polymorph states of CuPc exist: α , β , γ , R , δ , ε etc. [13]. The α -CuPc form is a metastable one at $T = 165$ °C and can be converted thermally or with solution to the β -form. The α and β forms are the most frequently encountered states of CuPc. The fabrication of CuPc films were in β -form because thermal sublimation was used for film deposition. The structure that characterizes the β -form is a monoclinic crystal P_{21}/a with $a = 19.407$ Å, $b = 4.79$ Å, $c = 14.628$ Å and $\beta = 120.93$ Å [13]. It has a conductivity of $5 \times 10^{-13} \Omega^{-1} \text{cm}^{-1}$ at $T = 300$ K [14, 15]. The molecular weight of the CuPc molecule is 576 a.m.u. Sublimation temperatures vary from 400 °C at a pressure of 10^{-4} Pa to 580 °C at 10^{-4} Pa [16]. The molecular weight of the H₂Pc molecule is 576 a.m.u. and their sublimation temperatures vary from 400 °C at a pressure of 10^{-4} Pa to 580 °C at 10^{-4} Pa.

To fabricate the samples, the 50 wt. % CuPc and H₂Pc pallet was used to sublime and deposit on conductive glass (ITO) substrate by using EDWARD 306 vacuum thermal evaporator. Sizes of the ITO substrates, organic heterojunction films and aluminum films were equal to $2.5 \times 2.5 \text{ cm}^2$, $2.5 \times 1.8 \text{ cm}^2$ and $1 \times 0.8 \text{ cm}^2$ respectively. Sublimation temperatures of organic semiconductors and the measured vacuum were equal to 460 °C and 10^{-4} Pa. Evaporation temperature for Al electrode was equal to 660 °C. Thickness of the CuPc-H₂Pc heterojunction thin films measured by thickness monitor was equal to 100 nm and 200 nm. The rate of deposition is maintained to be equal to 0.1-0.2 nm/sec.

For the surface morphology of the film, the SEM and AFM images are shown in Fig. 2 and Fig. 3 respectively. The uniformly distributed black and white spots in SEM images (Fig. 2(a and b)) show the uniform mixing of the constituent materials. AFM images (Fig. 3) also confirm the uniform mixing of both materials in BHJ film while the 3-D AFM image (Fig. 3(b)) shows the morphology and surface structure of the thin film.

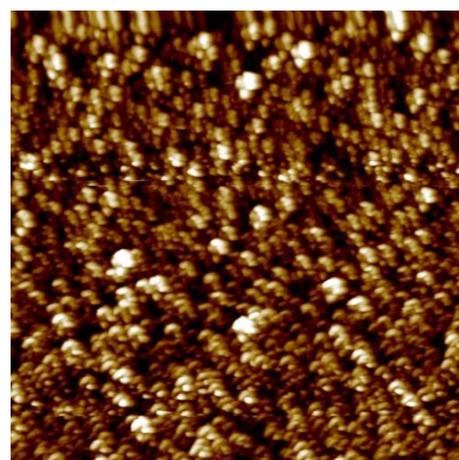


(a)

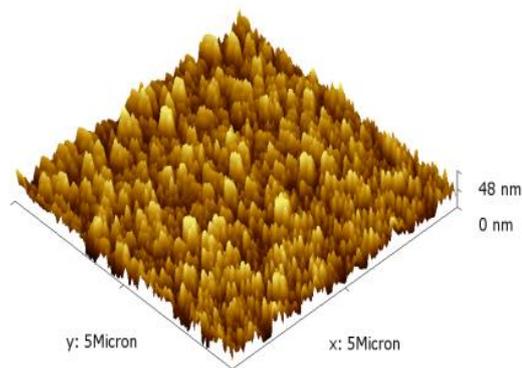


(b)

Fig.2. (a and b) SEM image of the CuPc and H₂Pc bulk heterojunction film.



(a)



(b)

Fig.3. (a and b) AFM images of the CuPc and H₂Pc bulk heterojunction film.

On the organic semiconductors film the aluminium thin film of the thickness of 100 nm was deposited as well. Fig.4 shows schematic diagram of the CuPc and H₂Pc bulk heterojunction sample.

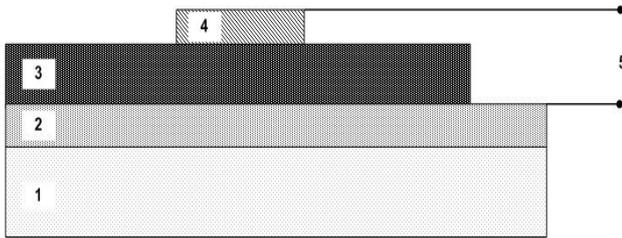


Fig.4. Schematic diagram of the CuPc and H₂Pc bulk heterojunction sample: glass substrate (1), conductive glass (2), CuPc-H₂Pc thin film (3), aluminium film (4), terminals (5).

Experiments were carried out in the special chamber. For the measurement of resistance HIOKI 3256 digital HiTester was used. To confirm the repeatability of the results, testing was carried out four times.

3. Results and discussion

Fig. 5 shows the resistance-temperature relationship of copper phthalocyanine and metal free phthalocyanine bulk heterojunction sample with thickness of film equal to 100 nm and 200 nm at DC. It is seen from the Fig. 5 that the change in temperature from 30 °C to 90 °C causes 5.3 times decrease in the resistances of the sample.

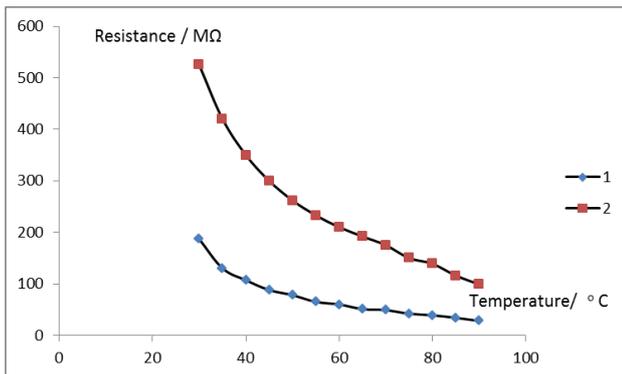


Fig.5. Resistance-temperature relationships of copper phthalocyanine and metal free phthalocyanine bulk heterojunction samples with thickness of film of 100 nm (1) and 200 nm (2) at DC.

It is seen that the resistances exponentially decrease with increase in temperature.

The resistance (R) of the samples can be determined by the following expression:

$$R = \frac{d\rho}{A} = \frac{d}{\sigma A} \quad (1)$$

Where d is the inter-electrode distance, ρ is resistivity, σ is conductivity and A is the cross-sectional area of the bulk heterojunction sample. The increase in the conductivity of the samples with increase in temperature is regarded, in particular for organic semiconductors, to the increase in the concentration and mobility of the charge carriers [14, 15]. The resistance temperature coefficient of the samples may be calculated as [5, 17]:

$$S = \frac{\Delta R}{R_o \Delta T} \quad (2)$$

where S is the resistance temperature coefficient, R_o is the initial resistance, ΔR is the change in resistance and ΔT is the change in temperature. The values of S for the data shown in Fig. 5 were in the range of (-4 %/°C) – (-6 %/°C) at $T=30$ °C.

The conduction mechanism in the CuPc and H₂Pc bulk heterojunction samples may also be considered as transitions between spatially separated molecules or sites, which may be credited to the percolation theory [1, 18]. Keeping in view the percolation theory, the following relationship can be used for the calculation of effective conductivity (σ):

$$\sigma = \frac{1}{LZ} \quad (3)$$

where L represents the characteristic percolation length, which depends on the concentration of sites, while Z is the resistance of a path with lowest average resistance. The increase in temperature causes to generate charge carriers, which results in reduction of L and Z .

The simulation of resistance temperature relationship has been carried out for the samples. For this purposes resistance-temperature relationships (Fig.5) are represented in Fig. 6 as relative change of the resistance (R/R_o) with temperature, where R and R_o are the values of the resistance at T and initial resistance at $T=30$ °C. The mathematical function given in Eq. (4) [19]:

$$f(x) = e^{-x} \quad (4)$$

can be used for the simulation of the experimental result shown in Fig. 5:

$$\frac{R}{R_o} = e^{-k(T-T_o)} \quad (5)$$

where k is fitting parameter ($k= 0.03361/^\circ\text{C}$). The comparison of simulated and experimental (using Eq. (5)) results are given in Fig.6. It is seen that experimental and simulated results are close to each other.

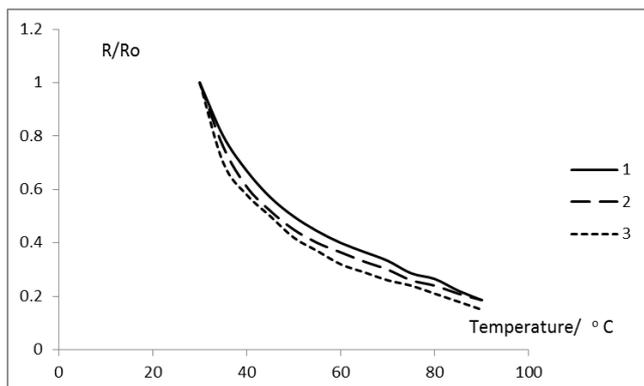


Fig.6. Experimental (1 and 3) and simulated (2) relative resistance-temperature relationships of copper phthalocyanine and metal free phthalocyanine bulk heterojunction sample with thickness of film of 100 nm and 200 nm at DC.

As it's known that resistance temperature coefficient (S) of thermistors are proportional to energy gap of semiconductors [17]. The high temperature sensitivity of the copper phthalocyanine and metal free phthalocyanine bulk heterojunction samples may be, first of all, due to sufficiently large energy gap of the CuPc and H₂Pc, presence of hopping mechanism of conduction and especially donor-acceptor transfer of charges between CuPc and H₂Pc. Fig.7 shows energy band diagram of copper phthalocyanine and metal free phthalocyanine bulk heterojunction in thermal equilibrium. Comparison of valence band-conduction band transitions in CuPc and in H₂Pc with intermolecular band transitions (Fig.7) shows that unlike to former case in the latter case the value of energy gap is larger that may be responsible for the greater resistance temperature coefficient of the bulk heterojunction with respect to the separate CuPc or H₂Pc samples.

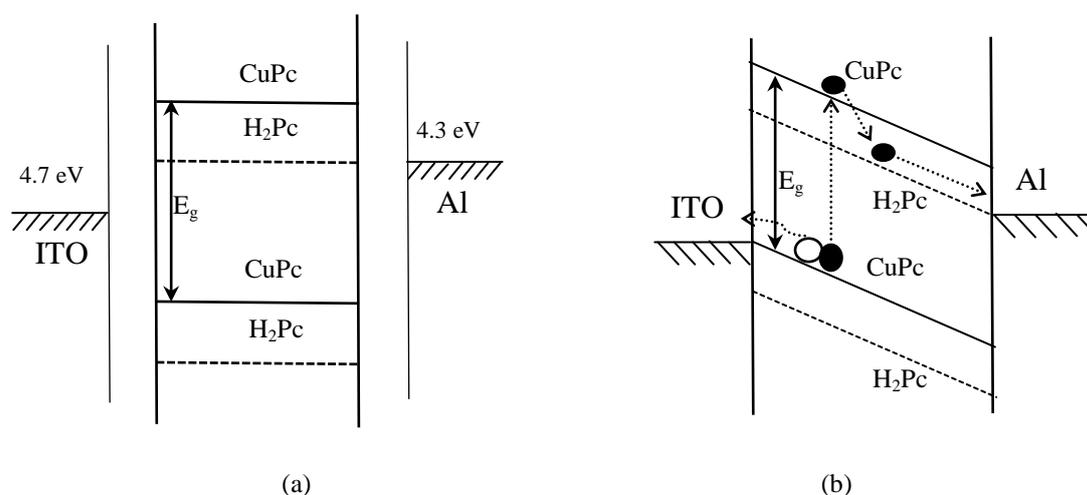


Fig.7. (a and b). Band diagram of ITO/CuPc-H₂Pc/Al heterojunction for flat band conditions (a) and under short circuit conditions along with electron-hole pair dissociation and transportation of charges to the corresponding electrodes (b). Not taking into account possible interfacial layers at metal-semiconductor (ITO/CuPc-H₂Pc/Al) interface.

Practically nonlinear, exponential resistance-temperature relationship of the CuPc-H₂Pc heterojunction can be realized by use of operational amplifiers [20].

The performance analysis of the organic semiconductor based nano-electronic devices is being done now a day because the organic semiconductors are more vulnerable to oxidation and hence degrading the device performance. Considering the time degradation of the device performance for such sensors, there are not any previous examples in literature which show the effect of time on the device performance.

The resistance-temperature behavior of the device after 3 months is given in fig. 8(a and b). The device performance degrades with passage of time and the sensitivity decreases for the whole range of temperature. The fresh samples are more sensitive for lower temperatures but this high sensitivity for lower temperatures decreases with time as well.

The degradation in device performance with time mainly depends on the rate of corrosion of Al electrode and the degradation of organic material due to oxidation. The device performance degrades gradually with time due to oxidation of organic material via microscopic pinholes in the top electrode as well as the oxidation of metal electrode which is Aluminum in most cases.

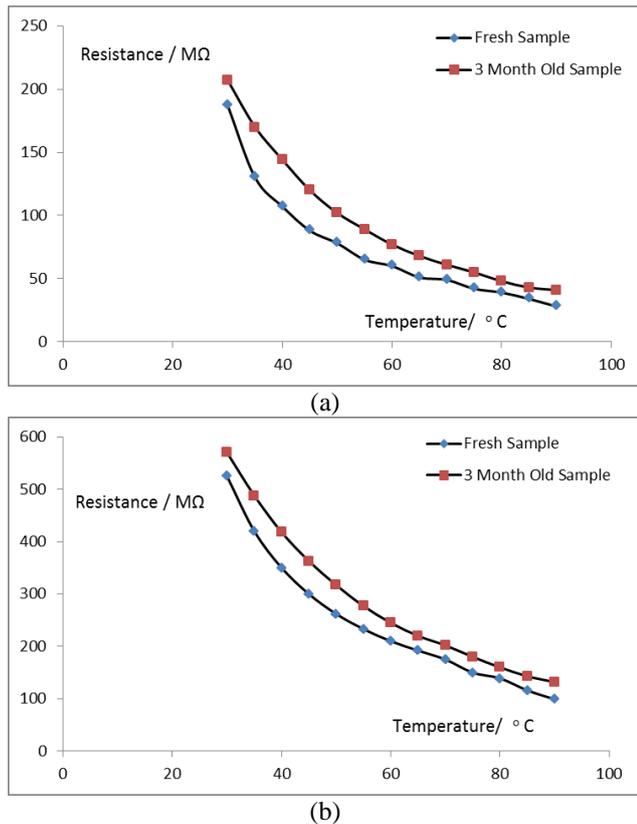


Fig. 8. Effect of time on Resistance-Temperature relationship for 100 nm thick sample (a) and 200 nm thick sample (b).

4. Conclusions

Fabrication and investigation of the properties of copper phthalocyanine (CuPc) and metal free phthalocyanine (H₂Pc) bulk heterojunction based temperature sensors showed that the resistance temperature coefficients at 30 °C was in the range of (-4%/°C) – (-6%/°C) depending on the technological parameters of the samples. Simulation was carried out and results were in agreement with experimental data. The obtained results show that the investigated heterojunction's temperature sensitivity is in the range of sensitivity of best semiconductor temperature sensors. The resistance-temperature sensors may be used in the instruments for environmental monitoring and assessment of temperature.

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