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# Copper Phthalocyanine Surface-type Photocapacitive Sensor

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## Abstract

In this study the photocapacitive behavior of organic semiconductor, photosensitive material copper phthalocyanine (CuPc) were investigated. Thin film of the copper phthalocyanine was deposited by vacuum evaporation on glass substrate with silver surface-type electrodes and Ag/CuPc/Ag photo capacitive sensor was fabricated. It was shown that under filament lamp illumination up to 1000 lx the capacitance of the Ag/CuPc/Ag photo capacitive sensor increased continuously up to 20% with respect of dark condition. It is assumed that photo capacitive response of the sensor is associated with polarization due to the transfer of photo-generated electrons and holes.

## Introduction

At present organic semiconductors and devices have attracted much due to their interesting properties and potential applications for solar cells, light emitting diodes, field effect transistors and different kinds of detectors [1-4]. In [5] it was fabricated and investigated self-charging photocapacitor for direct conversion and storage of solar energy. The photocapacitor was constructed on a multilayered photoelectrode comprising dye-sensitized semiconductor ($TiO_2$) nanoparticules/hole-trapping layer/activated carbon particles in contact with an organic electrolyte solution, in which photogenerated charges are stored at the electric double layer. A high-voltage photo-rechargeable photocapacitor of three-electrode configuration, comprising a dye-sensitized mesoporous $TiO_2$ electrode, two-carbon coated electrodes, and two-liquid electrolytes was investigated in [6]. As far as capacitive sensors are concerned it was investigated piezocapacitive sensor with poly-O-phthalanthracenate under uniaxial compression [7].

In [8,9] it was synthesized photocapacitive organic semiconductor material with PEPC doped by oligomeric salt of perily (OSP). It was shown that this material may be used for fabrication of the photocapacitors sensitive in visible spectrum.

Copper phthalocyanine is one of the well-studied organic photosensitive semiconductor [10,11]. It has high absorption coefficient in a wide spectrum and high photo-electromagnetic sensitivity at low intensities of radiation. It is possible simply to deposit thin CuPc films by vacuum sublimation. Purification of CuPc is simple and technology is economical as the sublimation occurs at relatively low temperatures (400-600°C). Recrystallization of CuPc is attained from organic solutions at room temperature. The CuPc is very stable organic dye. In this paper we report on investigation of photo capacitive sensor with CuPc.

## Experimental

Figure 1 shows the molecular structures of CuPc. For the photocapacitive sensor commercially produced CuPc (Sigma-Aldrich) was used. It is known that, at least, seven crystalline polymorph states of CuPc exist: $\alpha$, $\beta$, $\gamma$, $R$, $\delta$, $\varepsilon$ *etc*. The fabrication of CuPc films were in $\beta$ form. The structure that characterizes the $\beta$ form is a monoclinic crystal $P2_1/a$ with $a = 19.407$ Å, $b = 4.79$ Å, $c = 14.628$ Å and $\beta = 120.93$ Å [12]. It has band gap of about 1.6 eV and a conductivity at $T = 300$ K of $5\times10^{-13}\ \Omega^{-1}\cdot$cm [12]. The mo-

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lecular weight of the CuPc is 576 a.m.u. Sublimation temperatures varies from 400°C at $10^{-4}$ Pa to 580°C at $10^{-4}$ Pa [12].

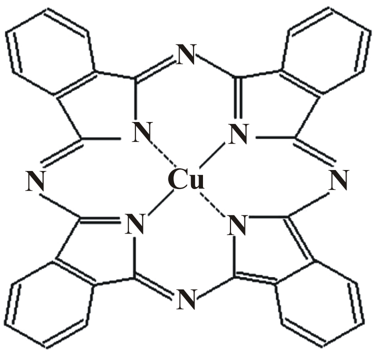

Fig. 1. Molecular structure of copper phthalocyanine.

Thin films of CuPc, of thickness 20-40 nm, were thermally sublimed on glass substrate (of sizes of $25\times25\times1$ mm$^3$) with silver surface-type electrodes (gap between electrodes was equal to 0.2 mm, the length of the gap was 20 mm) at 400-450°C at $10^{-4}$ Pa. and Ag/CuPc/Ag photocapacitive sensor was fabricated. Silver electrodes were also deposited by vacuum evaporation technique. Earlier investigations showed that the Ag forms ohmic contacts with CuPc.Thickness of the CuPc films was measured by crystal-controlled thickness monitor [13].

Figure 2 shows absorption spectrum of the CuPc film deposited by vacuum evaporation on the glass substrate.

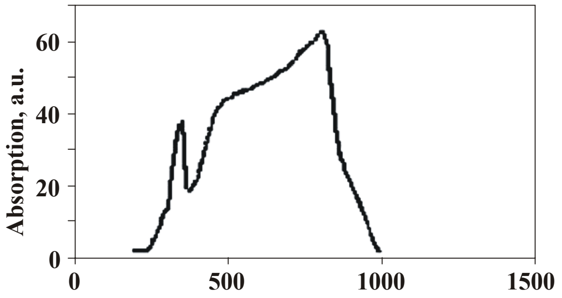

Fig. 2. Absorption spectrum of the CuPc film deposited by vacuum evaporation on the glass substrate.

Figure 3 shows cross-sectional view of the fabricated Ag/CuPc/Ag photocapacitive sensor. Measurement of the capacitance was done by conventional instruments at the frequency of 1 kHz, at room temperature (25±0.5°C). The capacitive sensors were illuminated by filament lamp.

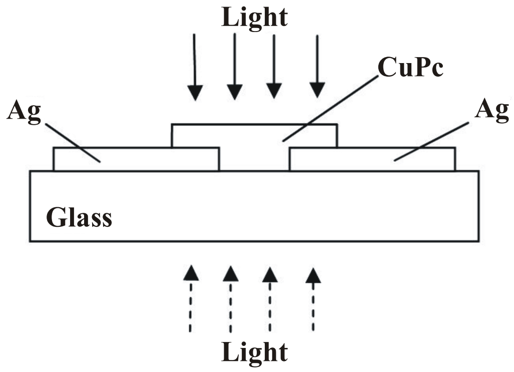

Fig. 3. Schematic diagram of Ag/CuPc/Ag photocapacitive sensor.

## Results and Discussion

Figure 4 shows relative capacitance – illumination relationship for the Ag/CuPc/Ag surface-type photocapacitive sensor at low level of illumination (up to 1000 lx). Here dark capacitance $C_d$ = 17 pF. It is seen from Figure 4 that photocapacitance increases with increase of illumination to 20%. The response of the sensor at illumination from the face and back sides approximately is the same. For calculation of the relative dielectric constant $\varepsilon_d$ at dark conditions, we can consider, in the first approximation, the silver electrodes and gap with deposited CuPc (Fig. 3) as a plane capacitor. For the plane capacitor [14]:

$$C_d = \varepsilon_d \varepsilon_0 A/d \qquad (1)$$

where $\varepsilon_0$ is permittivity of free space, $d$ is distance between plates of the capacitor, area of capacitor's plates $A = 6\times10^{-4}$ mm$^2$, $d$ = 0.2 mm. In the result of calculation it was found from eq. 1 that $\varepsilon_d = 4$.

Figure 5 shows relative capacitance – illumination relationship for the Ag/CuPc/Ag surface-type photocapacitive sensor at high level of illumination (up

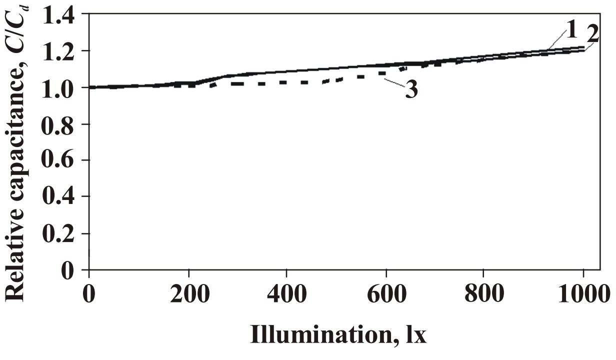

Fig. 4. Relative capacitance – illumination relationships for the Ag/CuPc/Ag surface-type photocapacitive sensor: 1, 2 illuminated from back and face sides, 3 is calculated result.

to 10000 lx). It is seen that the response of the detector is complicated: with increase of the illumination photocapacitance increases, it is saturated and finally decreases a few. The $C/C_d$ – illumination curve's character may be simply explained by the following approach. In the effect of light concentration of charge carriers may increase exponentially. Therefore the polarizability due to the transfer of charge carriers as electrons and holes may increase as well. At the same time filament lamp illumination may heat the sample that in turn may decrease the polarizability.

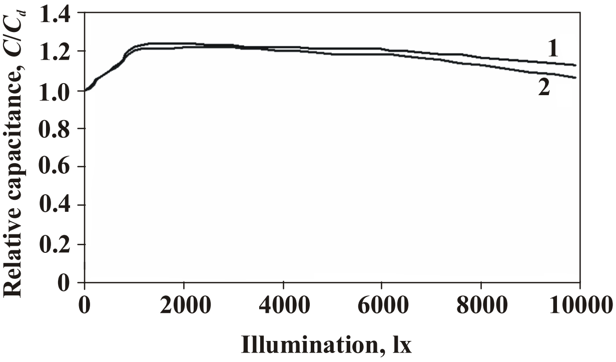

Fig. 5. Relative capacitance – illumination relationship for the Ag/CuPc/Ag surface-type photocapacitive sensor at high levels of illumination (up to 10000 lx): 1 and 2 under illumination from back and face sides.

As is known [15] the capacitance value depends on polarizability of the material and basically there are several sources of it as dipolar $\alpha_{dip}$, ionic $\alpha_i$ and electronic $\alpha_e$ polarizability. In this case we assume that dipolar ($\alpha_{dip}$) polarizability due to absence of visible dipoles in, molecular structures of the investigated materials may be neglected. Electronic polarizability is most universal and arises due to relative displacement of the orbital electrons. As the CuPc may comprise internal charge-transfer complex we can assume that ionic polarization takes place. The ionic and electronic polarizability probably affect to dark capacitance at low frequency (1 kHz) measurements of capacitance. In [16-18] it was investigated the polarizability due to the transfer ($\alpha_{td}$) of charge carriers as electrons and holes that are present at normal, including at dark conditions. Therefore we may write for the total polarizability at dark conditions ($\alpha_d$)

$$\alpha_d = \alpha_i + \alpha_e + \alpha_{td} \tag{2}$$

For the illuminated samples conditions the total polarizability ($\alpha$) may be the following:

$$\alpha = \alpha_i + \alpha_e + \alpha_t \tag{3}$$

where $\alpha_t$ is polarizability under illumination due to the transfer of excess, induced by light, electron/holes charge carriers. Here we take into consideration that concentration of charge carriers and total polarizability ($\alpha$) are illumination dependent.

In general form the relationship between the relative dielectric constant and molecular concentration, $N$, (or $N_d$ as concentration of the electron/holes at dark conditions) and polarizability of the molecule is determined by Clausius-Mosotti relation [15]:

$$\frac{(\varepsilon_d - 1)}{(\varepsilon_d + 2)} = \frac{N_d \alpha_d}{3\varepsilon_0} \tag{4}$$

From this equation it may be found relative dielectric constant as:

$$\varepsilon_d = \frac{1 + \frac{2N_d\alpha_d}{3\varepsilon_0}}{1 - \frac{N_d\alpha_d}{3\varepsilon_0}} \tag{5}$$

and similarly for dielectric constant under illumination ($\varepsilon$):

$$\varepsilon = \frac{1 + \frac{2N\alpha}{3\varepsilon_0}}{1 - \frac{N\alpha}{3\varepsilon_0}} \tag{6}$$

if

$$\frac{C}{C_d} = \frac{\varepsilon}{\varepsilon_d} = \frac{1 + \frac{2N\alpha}{3\varepsilon_0}}{\left(1 - \frac{N\alpha}{3\varepsilon_0}\right)\varepsilon_d} \tag{7}$$

Actually in the eq. 6 the $N$ may be considered as concentration of electrons/holes under llumination. The product ($N\alpha$) depends on intensity of illumination ($J$) of light, *i.e.* with increase of illumination concentration of electrons/holes and, probably, mobility of charge carriers will change as well. If we assume that

$$N\alpha = N_d\alpha_d(1 + kJ) \tag{8}$$

where $k$, we may call, photocapacitive factor. The eq. 7 may be rewritten as the following empiric expression that may be used for simulation of relative capacitance-illumination intensity relationships of photocapacitive sensor:

$$\frac{C}{C_d} = \frac{1 + \dfrac{2N_d\alpha_d(1+kJ)}{3\varepsilon_0}}{\left(1 - \dfrac{N_d\alpha_d(1+kJ)}{3\varepsilon_0}\right)\varepsilon_d} \qquad (9)$$

From eq. 9 it may be calculated the product $N_d\alpha_d = 1.3\times10^{-11}$ F/m in the case of dark conditions for the Ag/CuPc/Ag sensor ($J = 0$, $\varepsilon_d = 4$ and $C_d = 17$ pF).

Figure 4 shows simulated relative capacitance-illumination relationship compared with results obtained in experiment for the Ag/CuPc/Ag sensor: it is seen that both graphs show reasonable agreement. In this case $k = 3.5\times10^{-5}$ (1/lx).

Figure 6 shows detailed (a) and simple (b) equivalent circuits of the surface-type photocapacitive sensor. Detailed circuit contains actually three basic capacitances with three kinds of dielectric: $C_a$ capacitance with air, $C_d$ is capacitance with CuPc at dark condition, $C_{ph}$ is CuPc capacitance at illumination and $C_g$ is glass capacitance. Where $G_d$ is dark conductance of CuPC, $G_{ph}$ is the conductance of CuPc under luminance and $G_g$ is the glass conductance. Simple circuit Figure 6b shows $C_d$ is capacitance with CuPc at dark condition, and $C_{ph}$ is CuPc capacitance at luminance, $G_d$ is dark conductance of CuPC, $G_{ph}$ is the conductance of CuPc under luminance. Assuming that properties of the surface-type capacitive detector, first of all, depend on properties of photosensitive organic semiconductor copper phthalocyanine, we developed simplified equivalent circuit Fig. 6b as well. The equivalent circuit reflects the point that photocapacitance and photoconductivity phenomena have a common physical reason as photogeneration of electron/holes under illumination.

## Conclusions

The properties of the surface-type Ag/CuPc/Ag photocapacitive sensor was investigated. It was found that under filament lamp illumination up to 1000 lx the capacitance of the Ag/CuPc/Ag sensor increased to 20% with respect of dark condition. At further increase of illumination the photocapacitance increased a few and even decreased at 6000-10000 lx. It means the sensor show higher sensitivity at low illumination. The capacitive sensor can detect from two sides: face and back sides. It is assumed that in general the photocapacitive response of the sensor is associated with polarization due to the transfer of photo-generated electrons and holes. Calculated results reasonably matched with experimental. Equivalent circuits of the sensor were developed.

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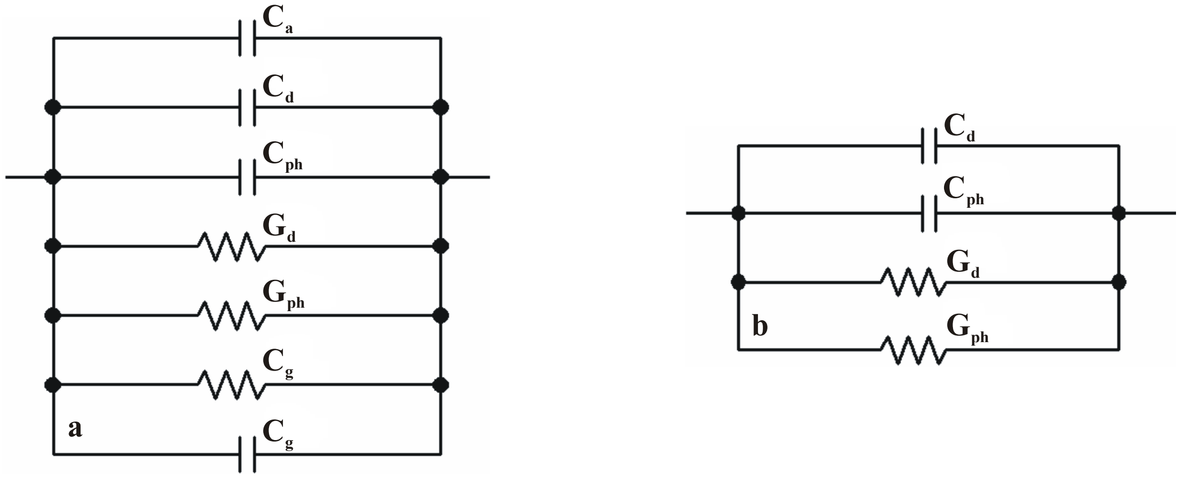

Fig. 6 Detailed (a) and simple (b) equivalent circuits of the Ag/CuPc/Ag surface-type photocapacitive sensor.

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