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Fabrication and study of NiPc thin film based surface type photocapacitors

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In this paper, the study of nickel phthalocyanine (NiPc) as an active material in photocapacitive detectors is reported. The NiPc thin film based Al/NiPc/Al and Ag/NiPc/Ag surface type photocapacitive detectors were fabricated. The devices were prepared by thermal evaporation of NiPc films of different thicknesses on thoroughly cleaned glass substrates with preliminary deposited metallic electrodes. It was observed that photocapacitance of the samples increases with increase in thickness of the NiPc film and illumination as well. Under filament lamp illumination, the relative capacitance of the sample having aluminum electrodes was greater than the silver one. The photocapacitive response of the detectors is associated with polarization, due to the transfer of photo-generated electrons and holes. The equivalent circuit of the photocapacitive detectors is proposed. Data obtained by simulation showed reasonable agreement with the experimental results.

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1. Introduction

In recent years, organic semiconducting materials have attracted much attention in the fabrication of a wide range of electric, electronic and optoelectronic devices [1-5]. The fabrication of most of these devices involves the deposition of thin films of organic semiconductors on substrates of conducting or semiconducting materials. These thin films are deposited using a thermal vacuum evaporator or spin coater [4, 5]. On the top of these thin films metallic electrodes are deposited using thermal vacuum evaporator. These thermally deposited electrode materials often penetrate through the organic thin films and result in the failure of these sandwich type devices. The thin film based devices fabricated in the surface type configuration employing organic semiconductors as active materials are mostly found successful [5, 6]. Also the fabrication of surface type devices is relatively easy to fabricate. Because of these advantages, there is growing interest in the fabrication and study of thin film based surface type devices [7, 8].

Properties of organic semiconductors are highly dependent on ambient conditions and this makes them very promising for the development of various types of sensors such as temperature, strain, light, radiation and humidity etc. [9-12]. The phthalocyanines belong to the class of organic semiconductors and have been extensively employed in the fabrication of organic and organic-inorganic devices [13-15]. Phthalocyanines exhibit good thermal and chemical stability [16-17]. They can be easily deposited as thin films by thermal evaporation without dissociation. Therefore, many studies have been carried out on phthalocyanine based thin film devices [18-20].

As far as we know, a few studies have been reported on photocapacitive detectors fabricated using light sensitive organic materials [21-23]. These devices were made in the sandwich-type structure. A surface type photocapacitive detector was fabricated using organic semiconductor (CuPc) by Karimov *et al.* [6]. This detector showed increase in capacitance up to 20% at 1000 lx relative illumination with respect to the dark. We have very recently reported the synthesis and photocapacitive studies of Cu(II) 5,10,15,20-tetrakis(4′-isopropylphenyl) porphyrin (CuTIPP) [5]. In this work, the Al/CuTIPP/Al and Ag/CuTIPP/Ag surface type photocapacitive detectors were fabricated. Under filament lamp illuminations of up to 4000 lx the capacitance of the Al/CuTIPP/Al and Ag/CuTIPP/Ag photocapacitive detectors was measured and increases in capacitance by 2.6 and 2.2 times, respectively, was observed with respect to the dark conditions.

This paper reports the fabrication and study of surface-type photocapacitive detectors, employing NiPc as light sensitive organic semiconducting material. Effect of NiPc film thickness and illumination is examined and the performances of Al/NiPc/Al and Ag/NiPc/Ag surface-type devices are compared. The equivalent circuit of the devices is presented. A comparison of the measured and computed data is provided.

2. Experimental

Fig.1 shows molecular structure of the NiPc. The NiPc powder was obtained from Sigma Aldrich and used without further purification. Thin films of NiPc of thicknesses 100, 150, 200 nm, were thermally sublimed on glass substrates (25 mm x 25 mm) with preliminary deposited electrodes of silver and aluminum. The length and width of the gap between the electrodes were 45 μm and 17 mm, respectively. During deposition the chamber pressure was kept at 10^{-5} mbar. Deposition rates and film thickness were monitored by using crystal-controlled thickness monitor [24].

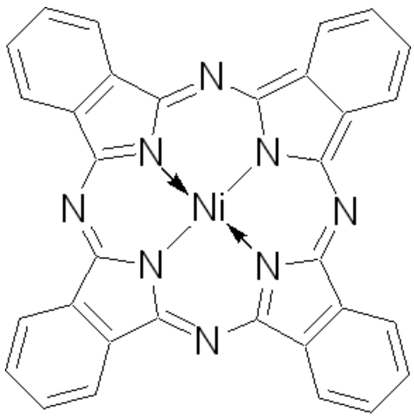


Fig. 1. Molecular structure of NiPc

Cross-sectional view of the fabricated photocapacitive detectors is shown in Fig. 2. The photocapacitance *vs.* illumination measurements were carried out by using conventional instruments at the frequency of 1 kHz, at room temperature. The capacitive detectors were illuminated by tungsten filament lamp.

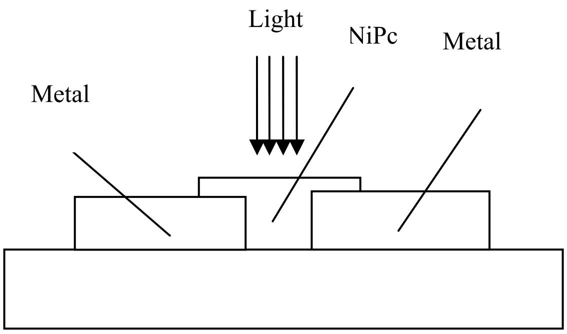


Fig. 2. Cross - sectional view of the metal/NiPc/metal surface type photocapacitive detectors: Metal is Al or Ag

3. Results and discussion

The absorption spectrum of NiPc measured in the region of Q-band between 550 nm and 750 nm is shown in Fig. 3. The spectrum was recorded of NiPc film deposited by thermal evaporation on the glass substrate. The spectrum comprises a high-energy peak at 2.018 eV and a low energy shoulder at 1.85 eV. These excitations generally arise due to the π-π* transitions between bonding and antibonding molecular orbitals [25].

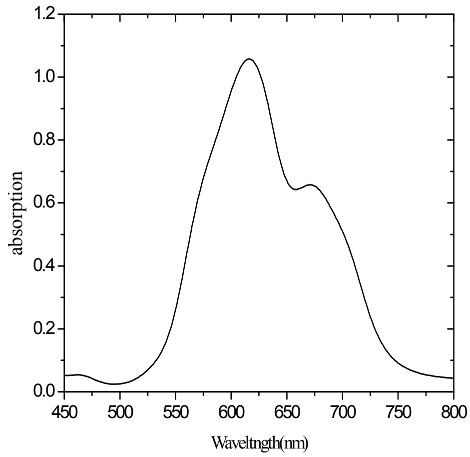


Fig. 3. Absorption spectrum of the NiPc film deposited by thermal evaporator on the glass substrate.

Fig. 4 shows relative capacitance-illumination relationships for the Ag/NiPc/Ag surface-type photocapacitive detectors. Here C_{ph} is photocapacitance (capacitance under illumination), C_d is capacitance under dark conditions. It can be observed from Fig. 4 that photocapacitance of the Ag/NiPc/Ag photodetector increases with increase in illumination. Upto 1800 lx the capacitance increased by 7, 9 and 9.75 times for 100, 150 and 200 nm NiPc thick films with respect to the dark condition, respectively. With increase in illumination, concentration of charge carriers increases logarithmically. Therefore, the polarizability due to the transfer of charge carriers as electrons and holes may increase as well.

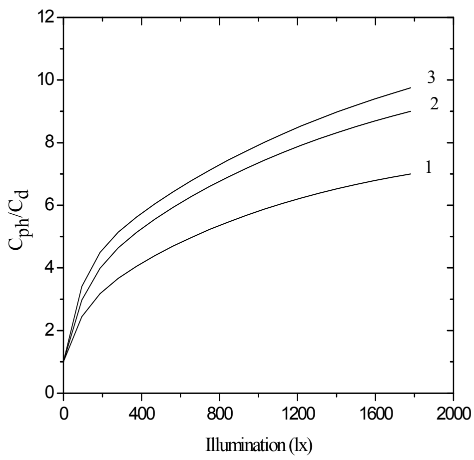


Fig.4. Relative capacitance-illumination relationships for the Ag/NiPc/Ag photocapacitive detector: the NiPc film thickness was equal to 100 nm (1), 150 nm (2), 200 nm (3).

Fig. 5 shows relative capacitance-illumination of the Al/NiPc/Al detectors. The value of the capacitance increases with increasing of illumination up to 1800 lx by 8.5, 9.5 and 10.5 times for 100, 150 and 200 nm thick NiPc films, respectively, with respect to the dark conditions.

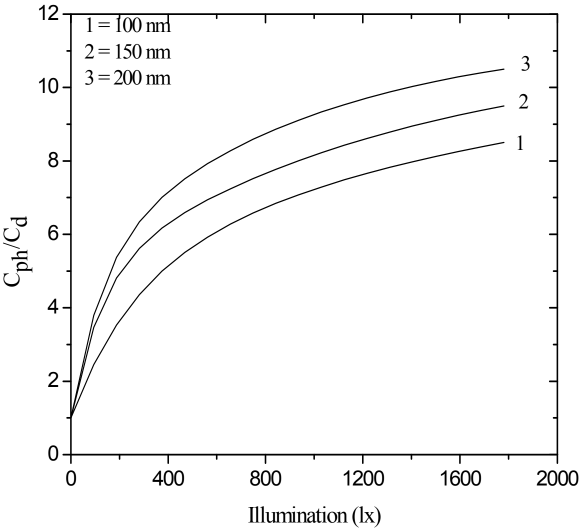


Fig .5. Relative capacitance–illumination relationships for the Al/NiPc/Al photocapacitive detector: the NiPc film thickness was equal to 100 nm (1), 150 nm (2) and 200 nm (3).

It can also be observed that the capacitance of the sensor increases logarithmically with increasing illumination. It can be observed that the device with Al electrode is more sensitive than Ag. This behavior of the photocapacitive type detectors studied in this work is similar as observed in our earlier study [5] of the Al/CuTIPP/Al and Ag/CuTIPP/Ag photocapacitive detectors. However, the NiPc is more photo-sensitive as compared to the CuTIPP. The better performance of the Al/NiPc/Al can be explained on the basis of metal/organic junction, silver forms ohmic contact while the aluminum usually forms Schottky type rectifying contact with organic semiconductors [26-28].

A depletion region is formed in the case of Al electrode at the junction interface. Therefore, the ratio of concentration of photo-induced charges to concentration of charges at dark condition is higher for Al sample. It may be the main reason of better performance of the Al/NiPc/Al detector than the Ag/NiPc/Ag.

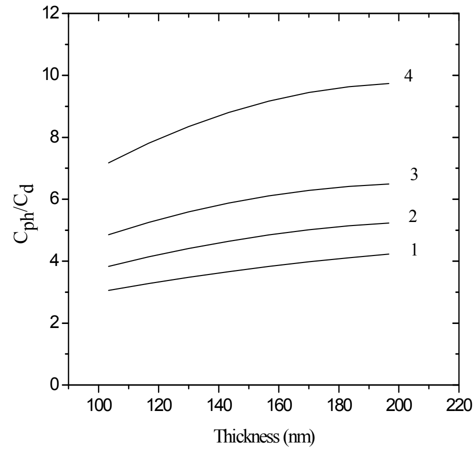


Fig. 6. Relative capacitance-thickness relationships for the Ag/NiPc/Ag photocapacitive photocapacitive detector at illumination 160 lx (1), 300 lx (2), 500 lx (3) and 1780 lx (4).

Relationship between relative capacitance and thickness for both samples is shown in Figs. 6 and 7. It can be seen that the capacitance of the photocapacitor increases with increasing of thickness and intensity of light. The thickness dependence of photosensitivity can be accounted for by considering the concept of Schubweg and light absorption in a photodetector [29]. For thin samples, some of the light impinging on the films is transmitted through it, and hence the utilization of light is comparatively low. For thick samples the transmission is relatively less, therefore, the relative capacitance is greater.

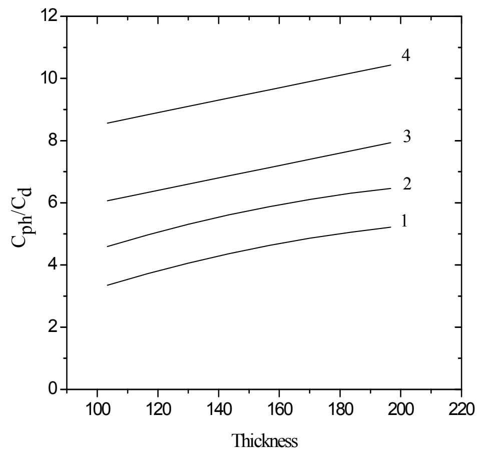


Fig. 7. Relative capacitance-thickness relationships for the Al/NiPc/Al photocapacitive detector at illumination 160 lx (1), 300 lx (2), 500 lx (3) and 1780 lx (4).

The capacitance depends on the polarizability of the material [28,30] and there are several sources of polarizability: dipolar (α_{dip}), ionic (α_i) and electronic (α_e). Dipolar α_{dip} polarizability may be neglected for NiPc due to absence of visible dipoles in molecular structure. As the NiPc may comprise of internal charge-transfer complexes, we can assume that the ionic polarization also takes place in this organic semiconductor. The polarizability due to the transfer of charge carriers (α_{td}), occurs even at dark conditions [31-33]. Thus total polarizability of the material at dark conditions (α_d) may be written as:

$$\alpha_d = \alpha_e + \alpha_i + \alpha_{td} \quad (1)$$

The total polarizability (α) of sample under illumination is given by:

$$\alpha = \alpha_e + \alpha_i + \alpha_t \quad (2)$$

where α_t is polarizability under illumination due to the transfer of electron / holes charge carriers. Total polarizability (α) and concentration of charge carriers are dependent on illumination.

In general form the relationship between relative dielectric constant, charge carrier concentration and polarizability of the molecule is determined by Clausius-Mosotti relation [30]:

$$(\varepsilon_d - 1)/(\varepsilon_d + 2) = N_d \alpha_d / 3\varepsilon_\circ \quad (3)$$

where ε_d is relative permittivity, ε_o is permittivity of free space and N_d is concentration of charge carriers in dark. From above relation, we may derive:

$$\varepsilon_d = (1 + 2N_d \alpha_d / 3\varepsilon_\circ)/(1 - 2N_d \alpha_d / 3\varepsilon_\circ) \quad (4)$$

Similar expression can be written for dielectric constant under illumination:

$$\varepsilon_{ph} = (1 + 2N\alpha / 3\varepsilon_\circ)/(1 - N\alpha / 3\varepsilon_\circ) \quad (5)$$

The value of $N\alpha$ depends upon illumination. Relative capacitance-illumination relationship (Figures 4 & 5) shows logarithmic like behavior. The equation for $N\alpha$ can written as:

$$N\alpha = N_d \alpha_d [1 + \log(1 + kJ)]$$

where k is photocapacitive factor, J is the light intensity. Putting the value of $N\alpha$ in equation (5), we get,

$$\varepsilon_{ph} = [\{1 + 2N_d \alpha_d (1 + \log(1 + kJ)) / 3\varepsilon_\circ\}] \\ /[\{1 - N_d \alpha_d (1 + \log(1 + kJ)) / 3\varepsilon_\circ\}] \quad (6)$$

From equation (4) and (6), we can derive the expression:

$$\varepsilon_{ph/}\varepsilon_d = [\{1 + 2N_d \alpha_d (1 + \log(1 + kJ)) / 3\varepsilon_\circ\} \\ /\{1 - N_d \alpha_d (1 + \log(1 + kJ)) / 3\varepsilon_\circ\}] \\ /[(1 + 2N_d \alpha_d / 3\varepsilon_\circ)/(1 - N_d \alpha_d / 3\varepsilon_\circ)] \quad (7)$$

At lower intensity, we may consider

$$[1 - N_d \alpha_d \{1 + \log(1 + kJ)\} / 3\varepsilon_\circ] = \\ (1 - N_d \alpha_d / 3\varepsilon_\circ)$$

Now Eq. (7) can be written as:

$$\varepsilon_{ph} / \varepsilon_d = [1 + 2N_d \alpha_d \{1 + \log(1 + kJ)\} / 3\varepsilon_\circ] \\ /(1 + 2N_d \alpha_d / 3\varepsilon_\circ) \quad (8)$$

The relation between dielectric constant and capacitance can be described by [34].

$$C_{ph} / C_d = \left(\varepsilon_{ph} / \varepsilon_d\right)^n \quad (9)$$

The factor n is related to dielectric (morphology). So the Eq. (9) can be modified as:

$$C_{ph} / C_d = \begin{pmatrix} [(1 + 2N_d \alpha_d \{1 + \log(1 + kJ)\} \\ / 3\varepsilon_\circ)]/(1 + 2N_d \alpha_d / 3\varepsilon_\circ) \end{pmatrix}^n \quad (10)$$

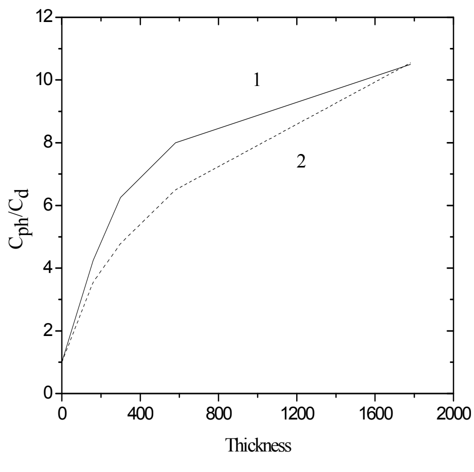
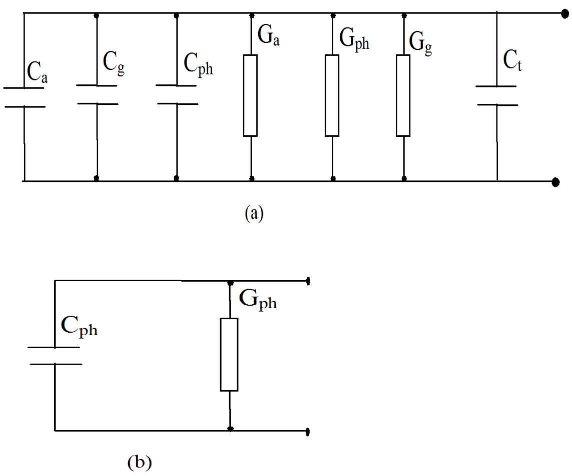


Fig.8. relative capacitan-illumination relationship for Al/NiPc/Al capacitive sensor, the film thickness is 200 nm: experimental (1) and simulated (2).

In dark condition, we can calculate the value of $N_d \alpha_d$. The simulated results obtained by using equation (10) are also shown in Fig. 8. In this case the value of k is 0.0356 lx^{-1} and n = 3.5. Fig. 8 shows comparison of simulated and experimental results of relative capacitance-illumination relationship. Both the graphs show reasonable agreement.

Fig. 9 shows detailed (a) and simplified (b) equivalent circuits of the surface-type photocapacitive detectors investigated in this work. Detailed circuit contains actually three basic capacitances due to three kinds of dielectric: air (C_a), NiPc (C_d and C_{ph}) and glass (C_g). Assuming that properties of the surface-type capacitive detector, first of all, depend on properties of photosensitive organic semiconductor, we developed simplified equivalent circuit (b) as well. The equivalent circuit reflects the point that photocapacitance and photoconductivity phenomena have a common physical reason as photo-generation of electrons / holes under illumination.



9taile) simplified (b) equivalent circuits of the Ag/NiPc/Ag and Al/NiPc/Al surface-type photocapacitive detectors: C_a is capacitance with air dielectric, C_d is capacitance with NiPc dielectric at dark condition, C_{ph} is capacitance with NiPc dielectric due to illumination, C_t is terminal capacitance, G_d is dark conductance of NiPc, C_g and G_g are capacitance and conductance due to glass dielectric (substrate).

4. Conclusion

The Ag/NiPc/Ag and Al/NiPc/Al surface type photocapacitive sensors were fabricated and investigated. It was observed that the sensitivity increases with increasing of NiPc film thickness and illumination. The photosensitive response of the sample having Al electrodes is better than Ag electrodes. Due to high photo sensitivity NiPc can be used as an active material for photodetectors. From the point of technology, fabrication of surface-type photocapacitive detectors is more simple than of sandwich-type ones.

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