Optical sensors based on the NiPc–CoPc composite films deposited by drop casting and under the action of centrifugal force*

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In this study, solution processed composite films of nickel phthalocyanine (NiPc) and cobalt phthalocyanine (CoPc) are deposited by drop casting and under centrifugal force. The films are deposited on surface-type inter-digitated silver electrodes on ceramic alumina substrates. The effects of illumination on the impedance and capacitance of the NiPc–CoPc composite samples are investigated. The samples deposited under centrifugal force show better conductivity than the samples deposited by drop casting technique. In terms of impedance and capacitance sensitivities the samples fabricated under centrifugal force are more sensitive than the drop casting samples. The values of impedance sensitivity (S_z) are equal to (-1.83) MΩ·cm^2/mW and (-5.365) MΩ·cm^2/mW for the samples fabricated using drop casting and under centrifugal force, respectively. Similarly, the values of capacitance sensitivity (S_c) are equal to 0.083 pF·cm^2/mW and 0.185 pF·cm^2/mW for the samples fabricated by drop casting and under centrifugal force. The films deposited using the different procedures could potentially be viable for different operational modes (i.e., conductive or capacitive) of the optical sensors. Both experimental and simulated results are discussed.

Keywords: optical sensors, capacitive mode, impedance mode, centrifugal deposition

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1. Introduction

Phthalocyanines (PCs) are a class of organic semiconductors which have received substantial attention due to their potential applications in a variety of fields. Their distinctive characteristics include semi-conductivities, photo-conductivities, chemical stabilities and optical absorptions in the visible regime.[1] Thin films of PCs can be deposited either by vacuum evaporation, or drop-casting, or spin-coating.[2] Among the PCs, nickel phthalocyanine (NiPc) is considered as a promising phthalocyanine for optoelectronic devices and gas sensing applications.[3–5] NiPc has a charge carrier mobility of 0.1 cm^2·V^{-1}·s^{-1} which is 1000 times higher than copper phthalocyanine (CuPc).[6] The energy band gaps of the NiPc are equal to 3.2 eV and 2.24 eV for direct and indirect allowed transitions, respectively.[7] Maximum optical absorption bands (in the visible region) of the NiPc films have been observed at 300 nm and 650 nm. Schottky diodes of the NiPc have been investigated by Ahmad *et al.*[8] and Shah *et al.*[9]

Composite prepared with proper selection of the HOMO–LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) of the two PCs can enable better exciton dissociation and improve the photon-to-current conversion. Most of the research work on the PCs composite films is either mixed with nano materials or with polymer in the matrix of individual component of the PCs. Bulk heterojunction structures of CuPc and H_2Pc under varying illumination conditions have been studied by Farooq *et al.*[10] A comparative analysis of *I–V* characteristics in dark and under illumination showed that the devices are sensitive to visible light. Properties of semiconductor devices depend on fabrication technology. The properties of the electronic devices based on PCs grown by organic molecular beam deposition (OMBD) technique have been investigated by Colesniuc.[11] He reported that the conductivity of the grown film increases exponentially with temperature rising, whereas it decreases exponentially with the thickness of the film increasing. Organic field effect transistors have also been fabricated using PCs with standard vacuum evaporated method.[12] However, no work has been reported on the bulk heterojunction of the two or more PCs deposited under different conditions. It is expected that different deposition conditions will change the sensitivity of the PCs based bulk heterojunction optical sensor.

Previously, the effects of varying light intensity on the electrical parameters of NiPc and CoPc have been investigated

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experimentally.[13–16] and theoretically.[17] NiPc and CoPc have different work functions, 4.0 eV and 4.4 eV, respectively. The optical studies of NiPc and CoPc, based on the combination of the integrated capacitance and impedance, are conducted in this work. This integrated platform that is expected to enhance the conductivity possesses the desired features of an optical sensor, i.e., better linearity, better capacitive sensitivity, and fewer impedance which can be further optimized by film deposition techniques. In this article, the thin NiPc and CoPc heterojunction films are prepared under different gravities and the effects of light on the capacitance and impedance of the samples are investigated.

2. Experiment

Commercially available NiPc ($C_{32}H_{16}N_8Ni$) and CoPc ($C_{32}H_{16}N_8Co$) were purchased from Sigma-Aldrich and directly used without further purification. Figure 1(a) shows the schematic diagrams of the both deposition processes. Whereas, figure 1(b) shows the ceramic alumina substrate with surface-type silver electrodes, which have interdigitated silver electrodes coated on ceramic alumina sheet of size 14 mm by 7 mm with an interelectrode distance of 0.21 mm, fabricated by screen printing and chemical etching technology.[18] Figures 1(c) and 1(d) show the molecular structures of organic semiconductors NiPc and CoPc. Both have the same structure, only the central metal Ni is replaced by the Co. The thin films of NiPc and CoPc composite are deposited from their 5-wt% solution in chloroform by drop-casting and centrifuge HETTICH EBA-20 S. As per our previous optimization, it was determined to fabricate the sensors at 5000 rpm. Film thickness decreases, whith increasing the rpm and vice versa. During the centrifugal process, acceleration (α) is calculated from the expression $a = R\omega^2$, where R is the radius and ω is the angular velocity of the centrifugal machine.For each experiment, there were two symmetrical glass tubes installed and they were filled with an equal volume of solutions (0.5 ml). The solution was allowed to evaporate at room temperature and atmospheric pressure, which is dominant in the centrifugal process. The centrifugation thin film deposition time was ~ 40 min without heating. The average thickness values of the NiPc and CoPc heterojunction thin films were equal to 10 ± 1 μm. NiPc and CoPc individual films were also deposited using spin coating to record the absorptions and thickness values of the films (~ 60 nm–70 nm).

Figure 2 shows the atomic force microscope (AFM) images and roughness values of the NiPc and CoPc composite films deposited by drop casting and centrifugal force. It is seen that the films deposited under centrifugal force have more developed surface structure so these will be more sensitive as compared with drop casted samples. The electrical parameters, such as impedance and capacitance of the sample were measured each as a function of intensity of light by LCR meter Mo-Tech 4090 that was used at a frequency of 1 kHz and voltage level of 1 V. A filament lamp of 100 W was used as a light source.

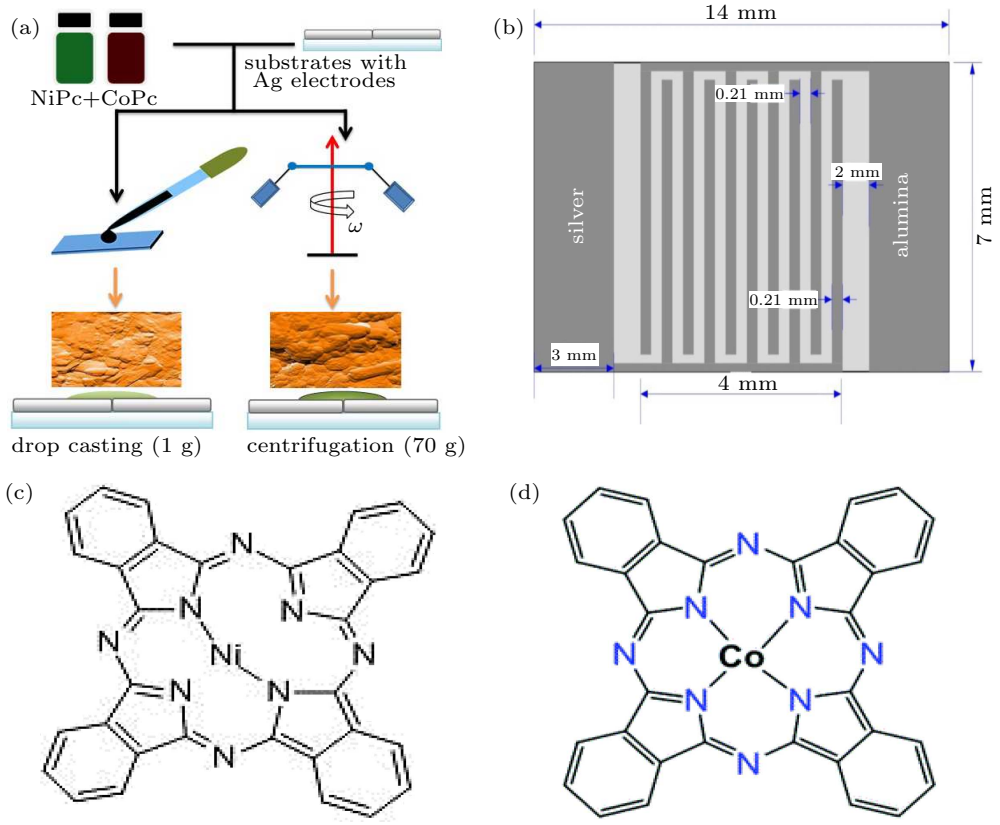


Fig. 1. (color online) (a) Schematic diagram of the drop casting and centrifugal deposition, (b) ceramic alumina substrate with surface type of silver electrodes. Molecular structures of organic semiconductor NiPc (c) and CoPc (d).

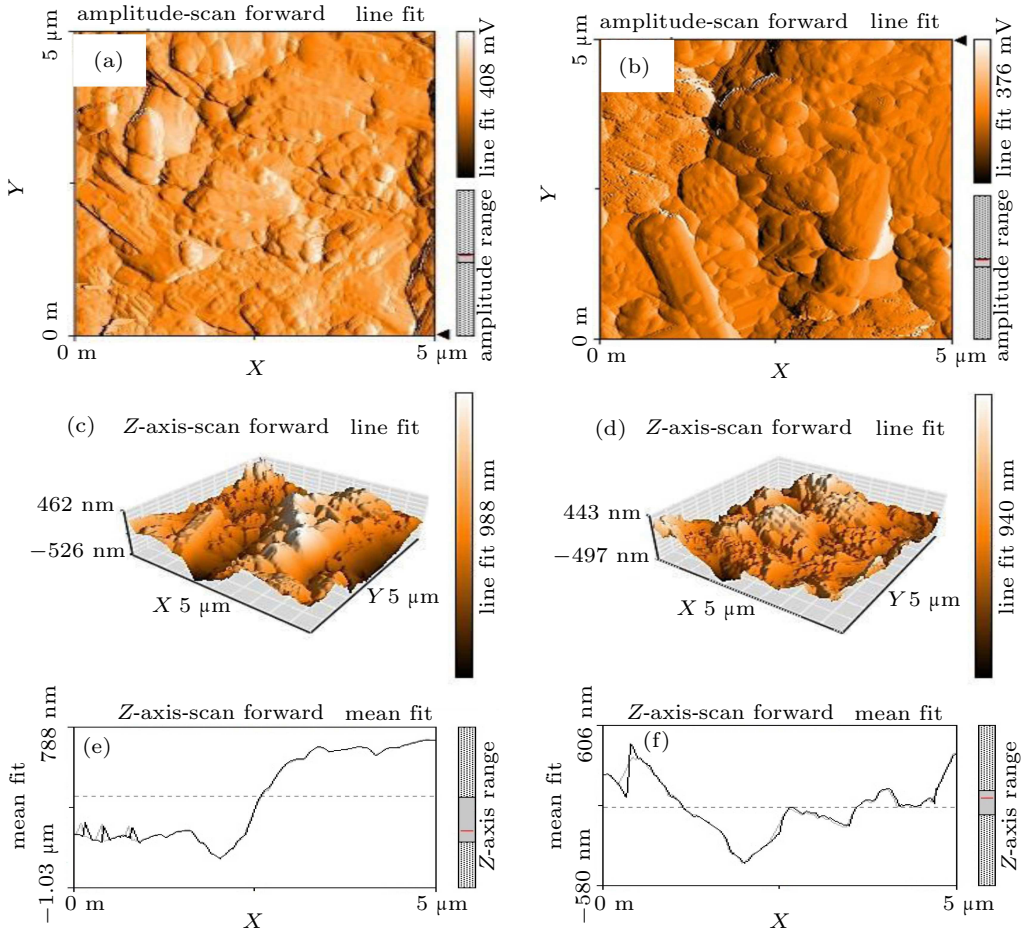


Fig. 2. (color online) Atomic force microscope (AFM) images [two-dimensional (2D) and three-dimensional (3D)] and roughness values of the NiPc and CoPc composite films deposited by drop casting (a), (b), and (c) and centrifugal force (d), (e), and (f), respectively.

3. Results and discussion

From their optical properties, it may follow that NiPc and CoPc are approximately the same as those seen in Fig. 3(a).[16,19] HOMO and LUMO energy diagrams of the NiPc and CoPc bulk heterojunction are shown in Fig. 3(b). In the design of this diagram, it is taken into consideration that the HOMO–LUMO gaps are equal to 1.47 eV and 1.87 eV for NiPc and CoPc, respectively.[20] Their respective work functions are 4.0 eV and 4.4 eV, while the work function of the silver electrode is equal to 4.3 eV. These samples contain bulk heterojunctions at a micro level. As the work function of NiPc is lower than that of CoPc, therefore the transfer of charges takes place from NiPc to CoPc. It means that the molecule of NiPc functions as a donor, whereas the molecule of CoPc acts as an electron acceptor. The transfer of chargesleads to that formation of dipole in the bulk of the sample, which is chaotically oriented in the space between the Ag electrodes, resulting in zero electric field because there is no contribution of electrode potential because both electrodes have the same material. These samples show good responses when used as impedance and capacitance elements.

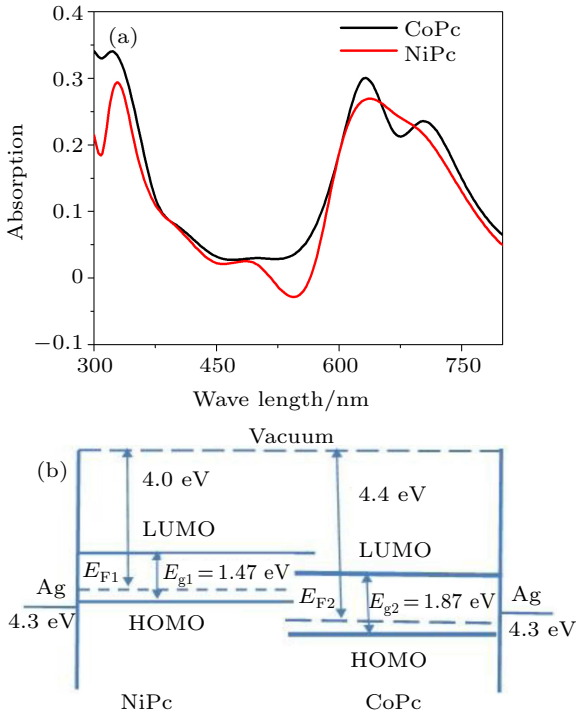


Fig. 3. (color online) (a) Absorption spectra of NiPc and CoPc films. (b) HOMO and LUMO diagrams for the NiPc and CoPc bulk heterojunction.

Figure 4(a) shows impedance–illumination relationships for the NiPc and CoPc heterojunction samples fabricated by drop casting and under centrifugal force. It can be seen that impedance decreases in both cases with the increase of light intensity up to 23 mW/cm^2. It is calculated that impedance decreases 1.4 and 2.1 times for the samples fabricated by drop casting and under centrifugal force, respectively. Figure 4(b) shows the relationships between capacitance and light intensity for the NiPc and CoPc heterojunction samples. It is found that the capacitance values increase 1.3 and 2.1 times with the increase of light intensity , respectively, for the samples made by drop casting and under centrifugal force. The relationships shown in Fig. 4 have the following peculiarities: the samples fabricated under centrifugal force show more changes of the impedance and capacitance under effect of light. The thickness values of the samples are almost the same. It can be considered that the samples grown in different deposition conditions have different structures as shown in AFM images. The samples deposited by centrifugal force are rougher, leading to the increase of sensitivity.

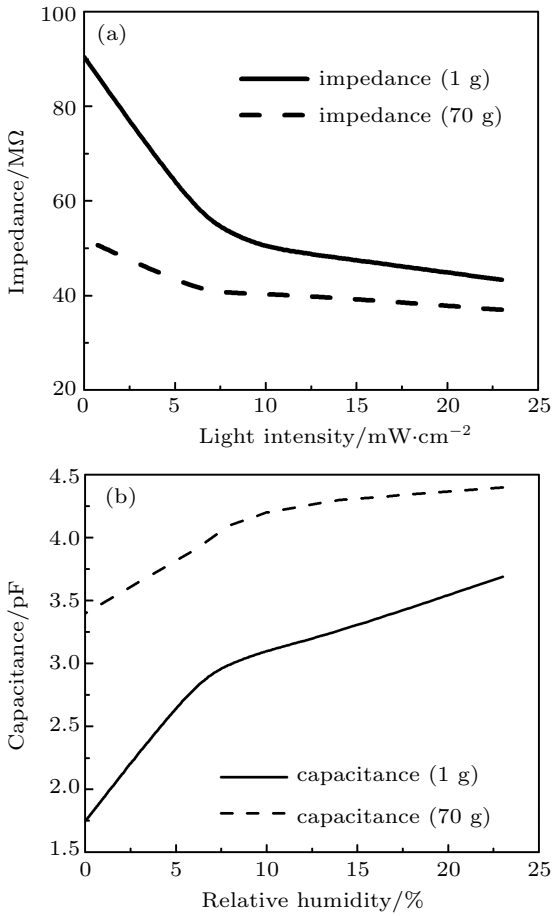


Fig. 4. (a) Relationships between impedance and light intensity and, (b) relationships between capacitance and light intensity for the NiPc-CoPc samples.

By comparing the impedances and capacitances (given in Fig. 5) of the samples fabricated by drop casting and under centrifugal force, it can be assumed that the centrifugal processing could bring to proper rearrangements of the NiPc and CoPc molecules, which leads to making the charges transfer from donor to acceptor more easily. From the electronic point of view, the decrease of impedance (Z) with the increase of light intensity can be described by resistance (R) decrease and the capacitance (C) increase and can be described by $Z = R/((1 + j\omega RC))$,[21,22] where ω is the circular frequency. The decrease of the impedance and increase of the capacitance are due to the increased concentration of charge carriers and change in permittivity, which can be explained by the effect of light.[23,24] The capacitance also relies on material polarizability such as electronic (α_e), dipolar (α_{dip}), and ionic (α_i).[25] Another form of polarizability, that is known, is due to transfer (α_{tr}) of charge carriers (electrons and holes), which depends on concentration of charge carriers and has been reported in Refs. [26] and [27]. It should be different, in that α_e is due to the relative displacement of orbital electrons, whereas the α_{tr} is due to charges participating in conduction process. The Clausius–Mosotti relation,[25] if we take into consideration only polarizability due to transfer of charge carriers, can be expressed as $(\varepsilon - 1/\varepsilon + 2) = (Na_{tr}/3\varepsilon_0)$, where ε is the relative permittivity, N is the total concentration of charge carriers, and ε_0 is the permittivity of free space.

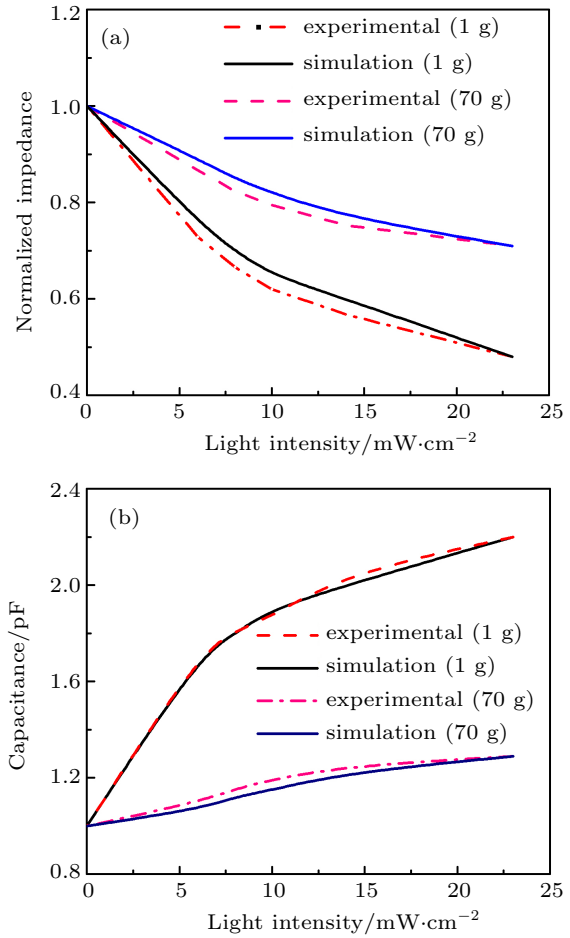


Fig. 5. (color online) (a) Normalized impedance versus light intensity, and (b) normalized capacitance versus light intensity.

The impedance–light intensity relationships for the NiPc and CoPc heterojunction can be described by the equation $y = e^{-x}$. Assuming that $x = ab$, where b is the light intensity and a is the fitting parameter that is calculated to be 0.0319 for sample deposited by drop casting and 0.0149 for the sample deposited under centrifugal force. Figure 5(a) shows that simulated relationships have quasi-exponential behavior. The normalized capacitance-intensity of light relationships for the NiPc and CoPc heterojunction sample can be simulated by the equation $y = \log(x+1) + 1$, (assuming that $x = ab$, where b is the light intensity and a is the fitting parameter). For the sample deposited by drop casting and under centrifugal force, the values of fitting parameter a are calculated to be 0.041 and 0.646, respectively. The effects of light intensity on capacitance and impedance of the NiPc and CoPc heterojunction samples can be predicted through the sensitivities of impedance (S_z) and capacitance (S_c) and be described by the expressions $S(Z) = \Delta Z/\Delta G$ and $S(C) = \Delta C/\Delta G$, respectively,[22] where ΔZ, ΔC, and ΔG are the changes of impedance, capacitance, and light intensity (in units mW/cm^2). The values of $S(Z)$ are (-1.83) MΩ·cm^2/mW and (5.365) MΩ·cm^2/mW for the samples fabricated by drop casting and under centrifugal force, respectively. Similarly, the values of $S(C)$ are equal to 0.083 pF·cm^2/mW and 0.185 pF·cm^2/mW for the samples fabricated by drop casting and under centrifugal force, respectively. The effects of light intensity on capacitance and impedance of NiPc–CoPc samples can be possibly utilized for making the light sensors.

4. Conclusions

In this study, the effects of illumination on the impedance and capacitance of the NiPc–CoPc composite (bulk heterojunction) sensors are investigated. The photo sensors are fabricated by drop casting and under centrifugal force. Samples fabricated under centrifugal force show better sensitivity than by drop casting. The values of impedance sensitivity (S_z) of the samples fabricated by drop casting and under centrifugal force are equal to (-1.83) MΩ·cm^2/mW and (-5.365) MΩ·cm^2/mW, respectively. Likewise, the values of capacitance sensitivity (S_c) are equal to 0.083 pF·cm^2/mW and 0.185 pF·cm^2/mW for the samples fabricated by drop casting and under centrifugal force, respectively.

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