

# Humidity effect on organic semiconductor NiPc films deposited at different gravity conditions

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**Abstract.** In this study, thin films of Nickel Phthalocyanine (NiPc) were deposited by centrifugation at high gravity (70g), and also at normal gravity (1g) conditions to fabricate humidity sensors. Ceramic alumina sheet, coated with silver electrodes, having interelectrode distance of 0.21 mm were used to assess the electrical properties of the sensors. Room temperature capacitance and impedance variations were measured as a function of relative humidity ranging from 25 % ~ 95 % at 1 kHz frequency. It was observed that sensors fabricated at 70g were more sensitive compared to sensors fabricated at 1g. Sensors fabricated at 70g exhibited 1.8 times decrease in their impedance and 1.5 times increase in their capacitance at peak ambient humidity. SEM images showed more roughness for the films deposited at 70g compared to films deposited at 1g. It was assumed that surface irregularities might have increased active surface area of 70g sensors hence changed the electrical response. Impedance-humidity and capacitance-humidity relationships were modeled and a good agreement was observed between experimental and modeled data. Experimental data showed that NiPc films could be useful for instrumentation industry to fabricate organic humidity sensors.

## 1. Introduction

Humidity sensors play an important role in today hi-tech era, especially in the field of metrology and environmental assessment [1-6]. On the basis of their measuring standards, humidity sensors are categorized as resistive, capacitive, gravimetric, or hydrometric [7]. To fabricate a humidity sensor, diverse methodologies and materials have been reported in the literature [8]. A plainer construction of capacitive humidity sensors, using copper phthalocyanine (CuPc) films, was reported in [9]. Humidity effects on electrical conductivity of carbon nanotubes (CNTs) were studied by many researchers, and it has been reported that the water molecules act as a donor and modify the electrical properties of single-walled carbon nanotubes (SWNTs) [10]. Whereas, investigation pertaining to the electrical transportation of double-walled carbon nanotubes (DWNTs) showed that water molecules act as an acceptor in DWNTs [11]. Humidity sensors, based on Ce-doped nanoporous ZnO, Fe<sub>2</sub>O<sub>3</sub> and polyaniline were also investigated and reported in [12-14]. As a result of these investigations, it can be said that different materials with different compositions have a useful potential for humidity sensing applications.

Nickel phthalocyanine (NiPc) is an organic semiconductor that was considered a promising phthalocyanine for optoelectronic devices and gas sensing applications [15-24]. NiPc has a charge carrier mobility of  $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , which is 1000 times greater than copper phthalocyanine (CuPc) [24].



Its energy band gap is 2.24 eV and 3.2 eV for indirect and direct allowed transitions, respectively [25]. Zubair [26] and Shah [27] fabricated and investigated NiPc based Schottky barrier diodes, and their studies confirmed the potential of NiPc as an organic semiconductor material to be used in electronic devices and sensors technology.

It is an established fact that the performance of organic semiconductor devices is heavily dependent on the chosen technology. Thin films of organic semiconductors, which usually act as a conducting channel, can be deposited by: a) vacuum evaporation; b) drop-casting; or c) spin-coating. At the same time, in the recent past, organic semiconductor thin films deposition by centrifugation at high gravity was also reported [28]. In [28], heterojunctions of silicon and thin layer of poly-N-epoxypropylcarbazole with tetracyanoquinodimethane (TCNQ) impurities were fabricated. The poly-N-epoxypropylcarbazole films on silicon wafers were deposited at normal temperature, but at various gravity conditions: 1g, 123g, 277g, and also at 1107g. A smooth layer and strong adhesiveness was obtained by this process of deposition. Current-voltage characteristics of the deposited heterostructures, as a function of temperature ranging from 20–60 °C, were assessed. It was observed that almost every sample exhibited p-p isotype heterojunctions. Temperature dependent junction's parameters such as reverse saturation current, rectification ratio, junction resistance and threshold voltage were measured.

In 2009, Tahiret *et al.* manufactured many organometallic vanadium complexes such as VO<sub>2</sub>(3-fl), VO(PBO)<sub>2</sub> and VO(DBM), and deposited the thin films by centrifugation process at 183g, 733g and 1650g [29]. As a result, sandwich type samples were fabricated based on Al/VO<sub>2</sub>(3-fl)/Ga, Cu/VO<sub>2</sub>(3-fl)/Ga, Al/Vanadyl(acac)/Ga, Cu/Vanadyl(acac)/Ga, Al/VO(PBO)<sub>2</sub>/Ga, Cu/VO(PBO)<sub>2</sub>/Ga, Al/VO(DBM)/Ga, Cu/VO(DBM)/Ga, Al/Vanadyl(acac)/TiO<sub>2</sub>/Ga, and Cu/VO<sub>2</sub>(3-fl)/TiO<sub>2</sub>/Ga. Current voltage characteristics of the finished devices showed non-linear rectification behavior. Samples fabricated using VO<sub>2</sub>(3-fl) and Vanadyl(acac) showed switching effect. These samples also exhibited two distinct conductance states referred to as low and high conductance states. Such behavior is typically known as memory cell characteristics of the type called as write-once-read-many-times (WORM). It is worth mentioning that memory cell characteristics were observed only in those devices which were fabricated using Cu electrodes.

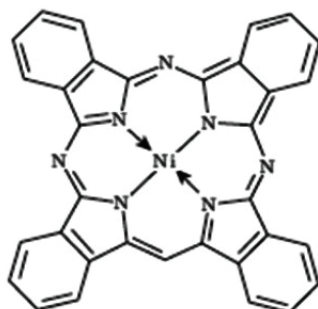
This article deals with fabrication and characterization of NiPc based humidity sensors and their optimization as a function of fabrication parameters. Finished devices were characterized using a humidity chamber fitted with LCR meter to assess the change in the device impedance and capacitance by varying ambient humidity. The composition of the rest of the article is that Section-2 deals with experimental techniques used to fabricate NiPc thin films sensors at 1g and also at 70g. Section-3 describes experimental results and their plausible explanation followed by the conclusions drawn from this study.

## 2. Experimental

Figure 1 illustrates molecular structure of NiPc organic semiconductor. For thin films deposition commercially available NiPc (C<sub>32</sub>H<sub>16</sub>N<sub>8</sub>Ni) of Sigma-Aldrich was used. NiPc films were deposited at 1g and 70g by drop costing and centrifugation respectively from 5wt. % solution prepared in chloroform. A table-top centrifuge commercially known as HETT ICH EBA-20S was used. Acceleration (*a*) was calculated using Equation (1):

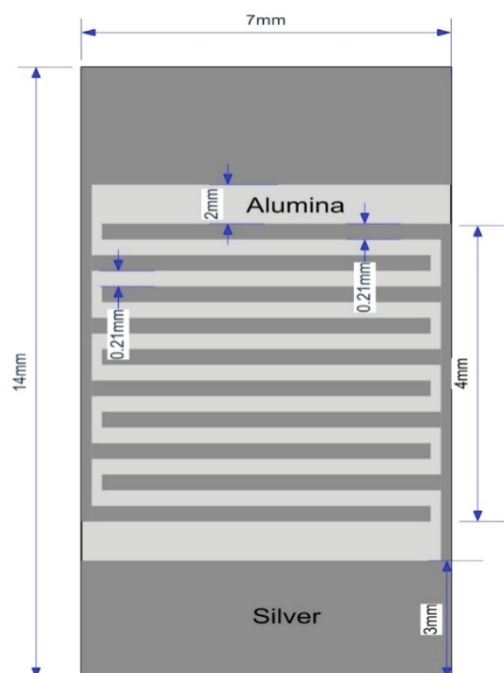
$$a = R\omega^2 \quad (1)$$

where *R* is radius and  $\omega$  is angular frequency.



**Figure 1.** Molecular structure of Nickel phthalocyanine (NiPc)

Figure 2 shows schematic diagram of the substrate used for the deposition of NiPc thin films. It is made of ceramic alumina sheet having 14 mm length and 7 mm width. It contains surface-type interdigitated silver electrodes having 0.21 mm interelectrode distance, fabricated by screen printing and followed by chemical etching [12].



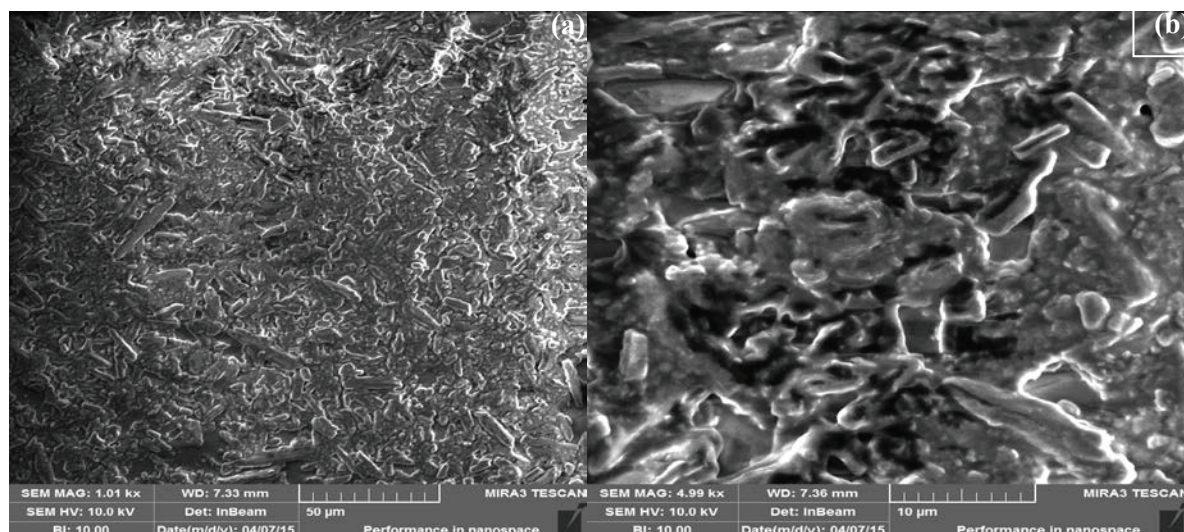
**Figure 2.** Ceramic alumina substrate with surface type silver electrodes

During centrifugation process, each experiment was performed using two symmetrically installed glass tubes filled with equal volume of solution (0.5 ml). The tube had internal diameter of 12 mm and length of 95 mm. The centrifuge's rotation speed was set at 5000 rpm. The achieved thickness of NiPc grown films were 7–10  $\mu\text{m}$ . It was observed that the layers achieved at 1g were usually thicker compared to those grown at 70g, which means that the acceleration and thickness have an inverse relationship. The same behaviour was observed by us earlier and was reported in [28, 29].

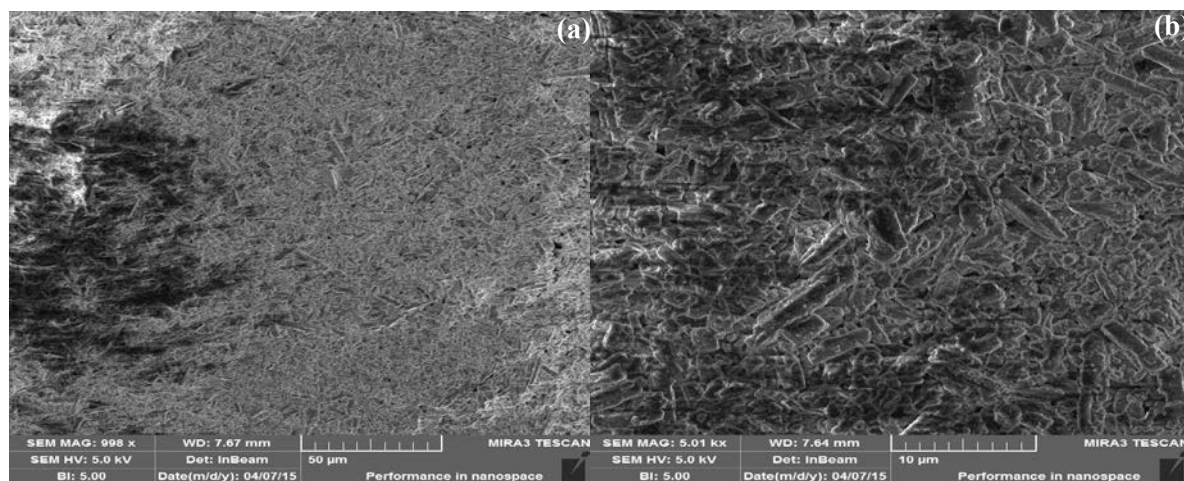
As a norm during centrifugal procedure, solution evaporation was carried out at room temperature and at atmospheric pressure. It was noted that during centrifugation process, 10–15 min were required to get films deposited on the substrates. Figure 3 shows SEM images of NiPc films deposited at 1g. Moreover, Figure 4 represents SEM micrographs of NiPc films deposited at 70g from solution prepared in chloroform.



The obtained SEM images of NiPc films showed that the films deposited at 1g appeared to be more uniform and smooth but with larger grain size. On the other hand, SEM micrographs of the films deposited at 70g showed relatively rough surface morphology, but with smaller grain size. The impact of roughness of the films and unit grain size on the humidity sensing characteristics is discussed in Section 3. Electrical properties of the sensors were investigated in a humidity chamber. Impedance and capacitance variation were assessed by using LCR meter MT 4090 by setting frequency at 1 kHz and voltage level at 1 V.



**Figure 3.** SEM images of NiPc films deposited at 1 g (a) 50  $\mu\text{m}$  and (b) 10  $\mu\text{m}$

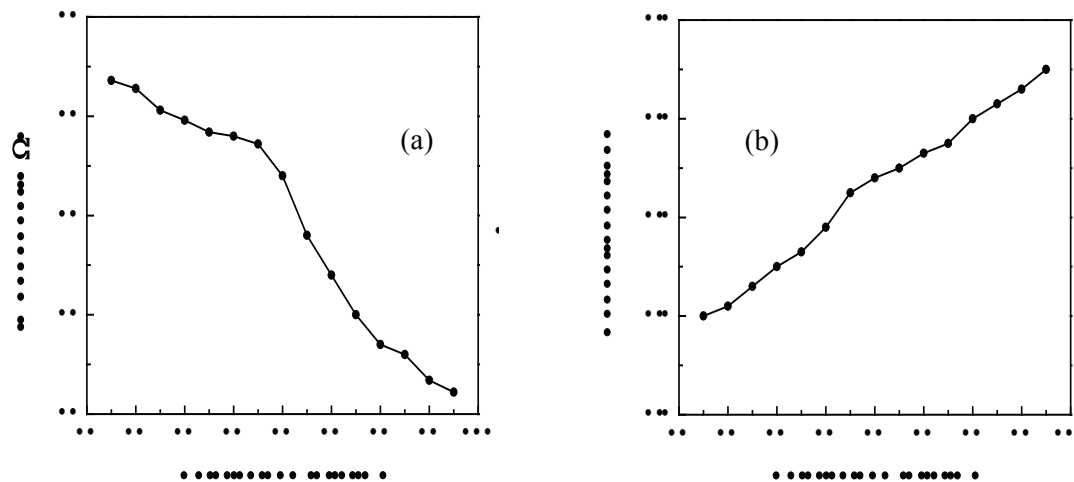


**Figure 4.** SEM images of NiPc films deposited at 70 g (a) 50  $\mu\text{m}$  and (b) 10  $\mu\text{m}$

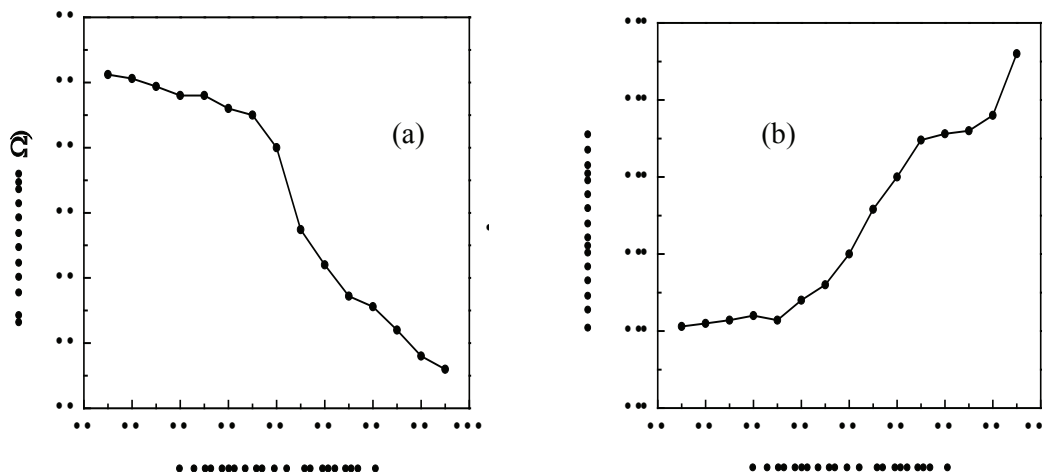
### 3. Results and discussion

Figure 5 (a) and (b) show impedance-humidity and capacitance-humidity relationships for NiPc samples deposited at 1g by drop-casting method, respectively. It can be seen that the impedance decreased 1.5 times; whereas, the capacitance exhibits an increase of 1.1 times in its magnitude while changing the ambient humidity from 25% to 95%.

In Figure 6 (a) and (b) impedance-humidity and capacitance-humidity profiles are shown for NiPc samples deposited at 70g by a centrifugation process, respectively. In the figure, the impedance of the sample shows 1.8 times decrease in its magnitude while changing the humidity from 25 % to 95 %; whereas, for the same change in humidity the capacitance exhibited an increase of 1.5 times with respect to its initial values.



**Figure 5.** Experimental data showing (a) impedance-humidity and (b) capacitance-humidity relationships for NiPc samples deposited at 1g.



**Figure 6.** Experimental data representing (a) impedance-humidity and (b) capacitance-humidity relationships for NiPc samples deposited at 70g.

The impedance-humidity and capacitance-humidity relationships shown in Figures 5-6 can be modeled by placing a resistance ( $R$ ) and a capacitance ( $C$ ) in parallel [30, 31]. From circuit point of view, decrease in impedance ( $Z$ ) with incremental increase in humidity can be explained by using an expression involving  $R$  and  $C$  as given below [30, 32, 33]:

$$Z = \frac{R}{(1 + j\omega RC)} \quad (2)$$

Equation (2) describes that the observed change in the magnitude of  $Z$  because of the changing value of ambient humidity can be associated with the collective response generated by both  $R$  and  $C$ , but with dominating  $R$  contribution.

It is an established fact that capacitance of a material is dependent on its polarizability which has got numerous basic constituents like dipolar ( $\alpha_{dip}$ ), ionic ( $\alpha_i$ ) and electronic ( $\alpha_e$ ) polarizability [32]. In NiPc,  $\alpha_{dip}$  could be associated with H<sub>2</sub>O dipoles absorbed by the films, and appear to be a dominating factor in determining the characteristics of NiPc. On the other hand,  $\alpha_e$  is common and arises due to the relative displacement of the orbital electrons. There is a good possibility that organic molecules may

interact with water molecules to define charge-transfer complexes and as a result, the presence of  $\alpha_i$  in NiPc can safely be assumed. Furthermore, it can be assumed, that  $\alpha_{dip}$  and  $\alpha_i$  polarizabilities affect the capacitive properties at lower frequencies (120 Hz-1 kHz), where  $\alpha_e$  dominates at high frequencies. In [34], it was discussed that the transfer of charge carriers, i.e., electrons and holes, can originate another type of polarizability referred to as charge transfer polarizability,  $\alpha_m$ . Hence, we can possibly write the total polarizability,  $\alpha_n$  for NiPc film:

$$\alpha_n = \alpha_{dip} + \alpha_i + \alpha_e + \alpha_{tn} \quad (3)$$

According to Clausius-Mosotti, the relative permittivity,  $\varepsilon$  and electrons/holes concentration,  $N_n$  under normal conditions, can be associated with  $\alpha_n$  as [34, 35]:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N_n \alpha_n}{3\varepsilon_0} \quad (4)$$

where  $\varepsilon_0$  is permittivity of free space. Considering that capacitance is proportional to permittivity on the basis of equation (4), one can write [36]:

$$\frac{C_H}{C_n} = \frac{[1 + 2N_n \alpha_n (1 + k\Delta RH)/3\varepsilon_0]}{[1 - N_n \alpha_n (1 + k\Delta RH)/3\varepsilon_0]\varepsilon} \quad (5)$$

In Equation (5),  $C_H$  and  $C_n$  are capacitances at  $RH > 25\%$  and  $RH = 25\%$  respectively  $k$  is a constant defining humidity based capacitive factor (or fitting parameter) of the sample, and  $\Delta RH = RH - RH_0$  is the percentage increase of relative humidity with respect to initial value  $RH_0 = 25\%$ . Assuming relative permittivity of NiPc equal to 4, one can evaluate the value of  $N_n \alpha_n$  by employing Equation (4). The evaluated value  $N_n \alpha_n$  can then be used in Equation (5) and assuming  $C_H/C_n = 1.13$  at  $RH = 95\%$ , the value of  $k$  was found to be  $0.013 (\%)^{-1}$ . Thus, Equation (5) can be used as first approximation to simulate capacitance-humidity response of NiPc samples. As  $Z$  includes both capacitance and resistance (equation-2), the simulation of the capacitance thus allows us to simulate impedance as well.

Change in capacitance due to the change in humidity can possibly be associated with the increase in dielectric permittivity due to the absorption of water molecules by the surface of the NiPc, which in turn increases its capacitance. Further, absorbed water molecules also generate more displacement current, which, in turn, reduces resistance of the sample. Another plausible explanation of increased capacitance and reduced resistance at higher humidity could be associated with the doping of NiPc film by the absorbed water molecules. This, in turn, increases the polarizability and also the concentration of charges which inherently increases capacitance and reduces resistance of the sample [36].

Sensitivity of a humidity sensor can be evaluated using incremental change in  $Z$  and  $C$  ( $S_z$  and  $S_c$ ) as a function of changed humidity conditions and can be estimated as [30]:

$$S_z = \frac{\Delta Z}{\Delta RH} \quad (6)$$

$$S_c = \frac{\Delta C}{\Delta RH} \quad (7)$$

where  $\Delta Z$ ,  $\Delta C$  and  $\Delta RH$  are increments of impedance, capacitance and relative humidity (in %). It can be shown that in average  $S_z = -0.32 \text{ M}\Omega/\%$ ,  $S_c = 0.025 \text{ pF}/\%$  for samples deposited at 70g, and  $S_z = -0.22 \text{ M}\Omega/\%$ ,  $S_c = 0.007 \text{ pF}/\%$  for samples deposited at 1g at 1 kHz frequency. Thus, NiPc samples can potentially be used to fabricate humidity sensors for environmental monitoring and assessment.



To evaluate the dynamics of the water vapor absorption and desorption processes of NiPc samples, the average response and recovery time were evaluated by impedance-time measurements at the change of humidity from 25 % to 95 % and from 95 % to 25 % which were found to be 1.0 min and 2.5 min, respectively. The response and recovery times were measured accordingly, at the change of impedance from 90 % to 10 % and vice versa.

#### 4. Conclusion

To fabricate humidity sensors, Nickel phthalocyanine's (NiPc) thin films were deposited by centrifugation at high gravity (70g), and also by drop-casting at normal gravity (1g) on surface-type ceramic substrate having interdigitated silver electrodes. The sensitivity of the sensors was then assessed by evaluating impedance and capacitance variations as a function of ambient humidity. It was found that NiPc sensors fabricated at 70g showed larger response to the humidity than 1g devices. It was also observed that by varying ambient humidity impedance of the samples decreases whilst the capacitance increases, which could be associated with the diffusion of water molecules into NiPc films which presumably had increased charge concentration, and also the permittivity of the NiPc films. This effect was higher for devices fabricated at high gravity condition, contrary to those made at 1g, due to increased surface area as evident from SEM micrographs. It has been demonstrated that NiPc films can potentially be used in organic semiconductor industry especially, in instrumentation technology.

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