

Short Communication

Integrated Capacitive and Resistive Humidity Transduction via Surface Type Nickel Phthalocyanine Based Sensor

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This paper reports the study of an organic semiconductor nickel phthalocyanine (NiPc) based thin film surface-type integrated capacitive and resistive type humidity sensor. The capacitance and resistance of the fabricated devices were evaluated at room temperature in the relative humidity (RH) range of 35-95% and 35-75% RH, respectively. In general, an increase in capacitance and decrease in resistance of the Ag/NiPc/Ag sensor was observed with the rise in humidity level. Humidity dependent capacitance and resistance properties of this sensor make it attractive for use in humidity sensors. The response and recovery characteristic of the humidity sensor were also investigated.

Keywords: surface-type humidity sensor, capacitance, resistance, nickel phthalocyanine, environmental monitoring, humidity, organic semiconductor.

1. INTRODUCTION

Organic semiconductors have attracted significant research interest for environment assessment owing to their interesting air quality, barometric pressure, light and temperature dependent electrical properties. These sensors offer potential benefits of the economical, eco-benign and simple device fabrication procedures. Currently, there is an increasing interest to elucidate the potential of the organic semiconductors as sensing element in humidity sensors as well. Transduction of ambient relative humidity (RH) into an electrical signal by the organic sensing layer is a two-step process: (a) physical adsorption/condensation of water vapors on sensing layer and (b) measurement of a key electrical property of the organic film that changes due to its interaction with water vapor [1].

Various humidity sensors exhibiting diverse transduction procedures including capacitive, resistive, hydrometric, gravimetric and optical have been reported in literature [2-4]. The operation mechanism of capacitive type humidity sensor is based on the linear shift in dielectric constant of the sensing layer with the change in ambient humidity. Typically, the change of capacitance to humidity follows a direct exponential association [5]. Capacitive-type sensors offer advantages such as low power consumption, linearity in response and condensation tolerance [6]. Resistive type sensors in turn, quantify the change in electrical conductivity of sensing film in relation to the humidity in the atmosphere. Conductance of high resistive organic thin films usually shows huge increase upon water absorption [7]. Resistive type sensors exhibit high sensitivity, cost-effective fabrication, fast response and easy operation. M. Saleem et. al. previously reported that organic semiconductor based humidity sensors are sensitive for resistance at lower RH (up to 60%), with least change in capacitance, however at higher order of RH, capacitance increases sharply while resistance remains saturated [8]. Therefore, a widespread approach is to utilize integrated capacitive and resistive type sensor with the motive of improving the operation range of hygrometers.

Admittedly, the performance of humidity sensors is determined primarily by the design of the electrode and properties of the hygroscopic material used to fabricate the humidity sensor [12]. For greater exposure of humidity to the active layer and to avoid device shortening issues, sensors with surface type electrodes geometry are usually preferred over sandwich type [9]. Moiz et. al. previously reported highly sensitive orange dye (OD) based resistive hygrometer [10]. However, since OD is water soluble therefore the hygrometer showed poor stability at higher humidity levels. Phthalocyanines and related small organic molecules, for example porphyrins and naphthalocyanines are amongst the most promising materials for humidity sensing applications [11, 12]. These molecules are water insoluble and exhibit low dielectric constant and high resistance which show huge change with change in humidity [13, 14]. Metal phthalocyanines (MPcs) in particular are quite stable (both chemically and thermally) therefore, their thin films can be easily deposited without decomposition [12]. The effect of different parameters such as substrate temperature, evaporation rate and different evaporation technique on the electrical, optical and structural properties of phthalocyanine thin film devices were investigated and reported previously [15-19]. Prior to this study, a surface-type capacitive type humidity sensor based on copper phthalocyanine (CuPc) was fabricated by Karimov et. al. [20], which showed continuous increase in capacitance by 200 times with the increase in humidity.

Primary focus of the present work is to investigate the combined capacitive and resistive humidity transduction. The choice of NiPc as humidity sensing platform is dictated by its favorable eco-friendly and hydrophobic nature. A surface-type humidity sensor (Ag/NiPc/Ag) has been fabricated and variation of capacitance and resistance as a function of relative humidity has been investigated.

2. EXPERIMENTAL

Fig.1 shows molecular structure of nickel phthalocyanine (NiPc) and schematic diagram of the fabrication process of the spincoated sensor. The NiPc powder used in this study was obtained from Sigma Aldrich and was used without further purification. Silver electrodes of thickness ~ 200 nm were

deposited by vacuum evaporation technique on thoroughly cleaned glass substrates. Thin films of NiPc of thickness 100, 150, and 200 nm were thermally sublimed on glass substrates of dimension $25 \times 25 \times 1 \text{ mm}^3$ with preliminary deposited silver electrodes. As the chamber pressure approached a value of approximately 10^{-4} Pa , deposition was initiated. The deposition rates were maintained to be at 0.3 and 0.2 nm/s for Ag and NiPc, respectively. The gap between electrodes and length of the gap was equal to $40 \mu\text{m}$ and 16 mm, respectively. The thickness of each layer was monitored by a crystal-controlled thickness monitor [21]. Integrated capacitive and resistive humidity sensors were fabricated in the planar, surface type Ag/NiPc/Ag geometry as shown in Fig. 1. Capacitance/humidity, resistance-humidity, the capacitance-film thickness relationships as well as a capacitance-temperature ($0 \text{ }^\circ\text{C}$ to $95 \text{ }^\circ\text{C}$) relationship has been investigated. Capacitance and resistance measurements of the fabricated devices were carried out using LCR meter MT 4090 configured at 1 kHz and 1 V. The in-situ humidity was measured using Humidity/Temperature meter TECPEL 322.

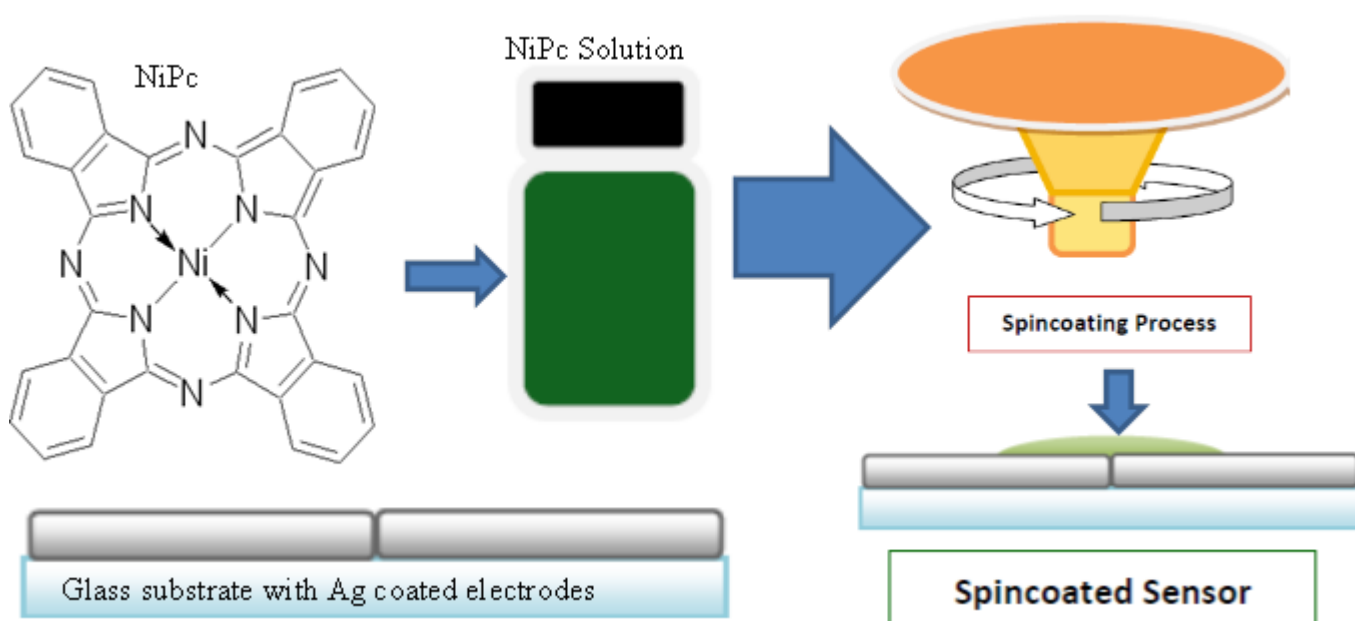


Figure 1. (a) Molecular structure of nickel phthalocyanine (NiPc) and schematic diagram of the fabrication process of the spincoated sensor.

3. RESULTS AND DISCUSSION

The results of the measured capacitance (C) versus relative humidity (RH) relationships for the surface-type capacitive sensors are exhibited in Fig. 2. In these measurements the capacitive response of the sensors was studied over the range of 35-95% RH. Initially the sensors were subjected to 35% RH and allowed to stabilize then the humidity was increased in steps of 5% RH. Each step in humidity was held for sufficient time to allow the sensors to respond fully and stabilize. It can be seen from Fig. 2 that capacitances of the three sample increase from 19 pF to 10191 pF, when the relative humidity is

varied over the 35-95% range. This indicates the decrease of sensitivity with increasing thickness in the range studied and is in agreement with a study of capacitance versus RH for the polyimide films reported by Harrey et. al. [22]. This can be explained as a result of water absorption at the surface of the NiPc thin films, and film morphology. It can be that the capacitances of the sensor increases with increasing humidity levels. This phenomenon might be caused by absorption of the water vapor in the pores of thin films and formation of charge transfer complexes. The dielectric constant changes with the increase of absorption of water vapors, hence the capacitance of the sensor increases. Inset in Fig. 2, shows the effect of NiPc thin films thicknesses on the relative capacitance of the sensors for the fixed values of humidity. Fig. 2, also shows the variation of capacitance with temperature for the surface type capacitive sensor fabricated with NiPc thin film of thickness 100 nm. The increase of capacitance in the higher temperature range is probably due to polarization by transfer of free charges. Conduction of charges may increase due to band-to-band excitation and formation of charge transfer complexes.

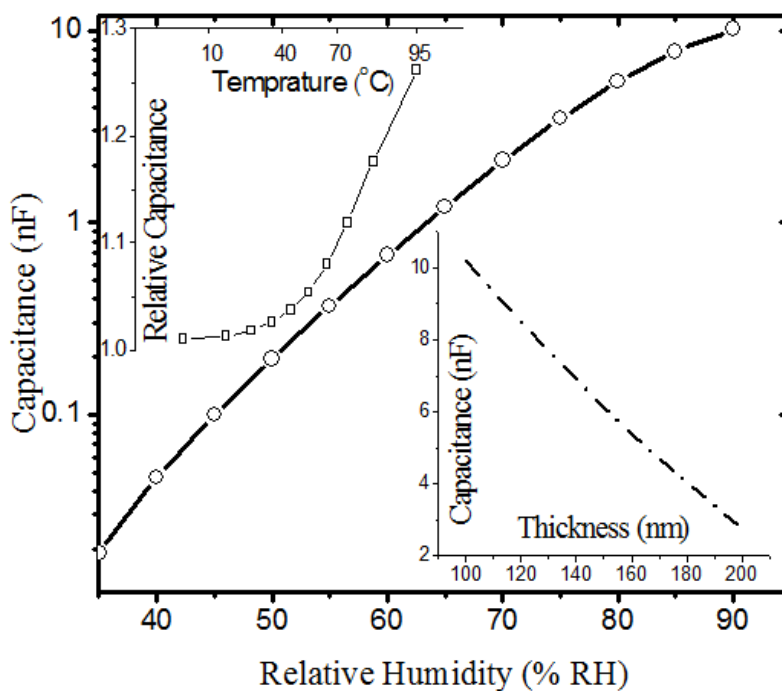


Figure 2. Capacitance/humidity relationship for Ag/NiPc(100 nm)/Ag capacitive sensor. Inset shows the capacitance-NiPc film thickness relationships as well as a capacitance-temperature relationship for Ag/NiPc/Ag capacitive sensor.

The rise in relative capacitance with the increase of humidity can be described by taking into account the various kinds of polarizabilities. As it is well-known [23, 24] that the capacitance value depends on polarizability of the material. There are several sources of polarizability such as dipolar α_{dip} , ionic α_i , electronic α_e and charge transfer (under normal condition) α_{tn} . The total polarizability at normal conditions (α_n) can be given as, $\alpha_n = \alpha_i + \alpha_e + \alpha_{tn} + \alpha_{dip}$. When the sensor was placed in humid environment, then the total polarizability (α_h) may be the following: $\alpha_h = \alpha_i + \alpha_e + \alpha_t + \alpha_{dip}$. Where α_t is polarizability under effect of humidity due to the transfer of electron/holes as charge carriers. In

general, the relationship between dielectric constant and molecular concentration, N and polarizability of the molecules can be determined by Clausius-Mosotti relation [24]: $(\epsilon_d - 1) / (\epsilon_d + 2) = N_d \alpha_d / 3 \epsilon_o$, where ϵ_d is the relative permittivity, and ϵ_o is permittivity of free space. On the basis of this equation, the following expression has been derived [25, 26]:

$$C_h / C_d = [1 + 2 N_d \alpha_d (1 + k H) / 3 \epsilon_o] / [1 - N_d \alpha_d (1 + k H) / 3 \epsilon_o] \epsilon_d \quad (1)$$

where, C_h and C_d represent the capacitance under humid and dry condition, respectively. k is a humidity capacitive factor and H is the relative humidity level. In this case the value of k is $1.6 \times 10^{-2} (\text{RH})^{-1}$. This relation can be used for simulation of the capacitance-humidity relationship.

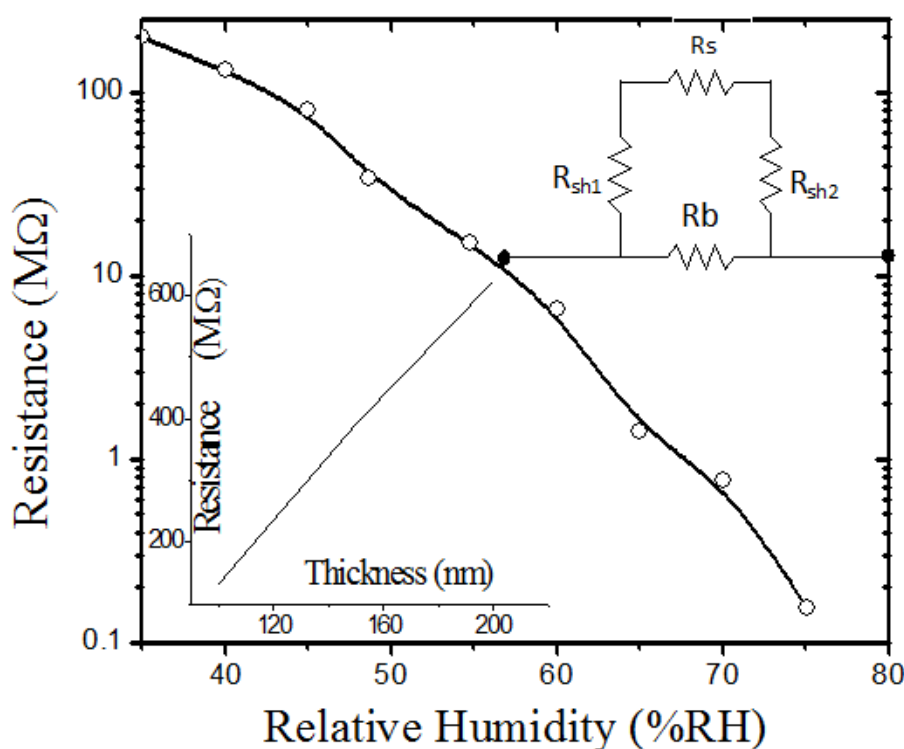


Figure 3. Resistance-humidity relationships for the Ag/NiPc/Ag resistive-type humidity sensor. Inset shows the resistance-thickness relationships for the Ag/NiPc/Ag resistive-type humidity sensor. Equivalent circuit of Ag/NiPc/Ag resistive type humidity sensors is also presented, where; R_s is surface resistor, R_{sh1} and R_{sh2} are shunt resistors, R_b is bulk resistor.

Fig. 3, shows the variation of resistance as a function of relative humidity for the Ag/NiPc/Ag surface-type resistive humidity sensor for 100nm thick NiPc film. The sensor was characterized by varying the relative humidity from 35 to 75% RH. It was observed that the resistance of the humidity sensor decreases as the level of relative humidity is increased. The resistance decreased from 200 MΩ to 133 KΩ for 100 nm NiPc thick film. The change of resistance to increase of humidity may be due to the adsorption of water in the pores of thin film, which leads to increase the charge carrier

concentration in the sensor because the water molecules may play the role of dopants. On the other hand the absorbed water molecules may dissociate into ions and increase the conductivity of the material as well. Therefore the change in conductivity with humidity may be due to both of ionic and electronic conduction. Inset (Fig. 3) shows the relation between resistance and thickness for the Ag/NiPc/Ag surface-type resistive humidity. The resistance of the thinner film is lower than the thicker film. Experimental data shown in Figs. 3 may be explained by equivalent circuits for the Ag/NiPc/Ag sensor (shown in Inset). As the resistance of the sensor increases with the thickness of the NiPc film, we may assume that shunt resistances R_{sh1} and R_{sh2} increases due to increase of length (l) as resistance R is equal to $R=(l/ \sigma A)$. Where σ is conductivity and A is the cross sectional area. Due to a large concentration of water molecules in the surface of the NiPc film (under humid condition) with respect to the bottom, probably humidity first of all changes surface resistance (R_s) than bulk resistance (R_b). On the other hand it is obvious that R_{sh1} and $R_{sh2} \gg R_s$, as the concentration of H_2O large on the surface.

Fig. 4, shows the response and recovery times of the humidity sensor when operated in a capacitive type mode. The response and recovery time of the sensor have been measured by placing the sensor into two different chambers at 90% RH and 40% RH. The curve 1 and 2 shows the water absorption and desorption process, respectively. The response time (humidity changed from 40 to 90 %RH) was 8s while the recovery time (humidity changed from 90 to 40 %RH) was 4 Sec. Inset, shows the response and recovery time of the humidity sensor when operated in resistive mode. The response-recovery time has been determined by moving the sensor rapidly from humidity level of 35%RH to a humidity level of 75%RH and from 75%RH to 35%RH, respectively. The comparison of sensing parameters of the fabricated devices is shown in Table 1.

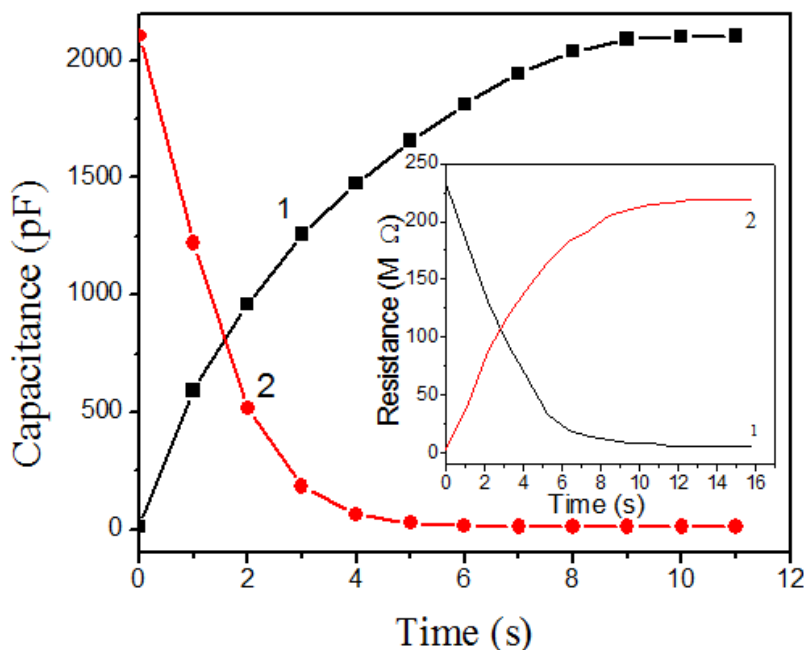


Figure 4. Capacitive response time of the Ag/NiPc 100 (nm)/Ag humidity sensor time. Inset shows the resistive response time of the humidity sensor of Ag/NiPc 100 (nm)/Ag: (1) absorption and (2) desorption.

Table 1. The comparison of sensing parameters of the fabricated devices.

Device	Mode	Bandwidth (%RH)	Change	Response & Recovery
Ag/NiPc 100 (nm)/Ag	Resistive	35 to 75	905M Ω to 9.7M Ω	8s & 4 s
	Capacitive	35 to 95	19pF to 10191 pF	10s & 6 s

4. CONCLUSIONS

An integrated capacitive and resistive humidity sensor using NiPc as sensing material with different film thicknesses was fabricated in planar configuration. The sensor exhibits adequate sensorial properties. In general sensor showed an increase in magnitude of capacitance with rising humidity levels from 35% RH to 95% RH. It is assumed that the capacitive response of the sensor is associated with polarization due to the absorption of water molecules and transfer of charge carriers. The response/recovery times of the sensor in resistive mode were considerably less as compared to capacitive mode.

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