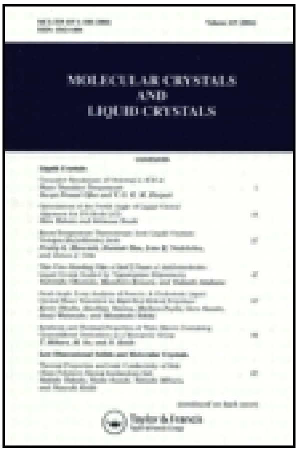

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Investigation of Optical and Humidity-Sensing Properties of Vanadyl Phthalocyanine-Derivative Thin Films

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Investigation of Optical and Humidity-Sensing Properties of Vanadyl Phthalocyanine-Derivative Thin Films

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In this study an active layer of Vanadyl 2,9,16,23-tetraphenoxy-29H,31H-phthalocyanine (VOPcPhO) has been employed in surface type humidity sensor. On top of preliminary deposited asymmetric metal electrodes, a VOPcPhO thin film was spun cast to obtain a surface type Al/VOPcPhO/Au sensor. The gap between the electrodes was 40 um. A solution of 30 mg/ml was deposited at 3000 rpm. The thickness of the VOPcPhO film was 150 nm. The capacitive effect of the sample was evaluated in the relative humidity range 0–87%RH, at room temperature. It was observed that the capacitance of the sensor increases 10 times under the effect of entire humidity range in the relative humidity level. The optical properties of VOPcPhO thin film were also investigated. The humidity-dependent capacitive properties make the sensor suitable for the application in the instruments used for environmental monitoring of humidity.

Keywords Vanadyl 2,9,16,23-tetraphenoxy-29H,31H-phthalocyanine; humidity sensor; UV/Vis spectroscopy

1. Introduction

Water vapors are present everywhere in the atmosphere and can be easily adsorbed on any surface. Therefore, much attention is being paid, in the recent years, to measure and control the humidity in order to improve life quality and enhance industrial processes. A humidity sensor, to be employed in a wide range of applications, must possess good sensitivity, short response time, negligible hysteresis, good durability and low manufacturing cost. Humidity sensors are widely used in many applications, such as process control, meteorology, agriculture and medical equipment. Commercially available sensors make use of metal oxides such as Al_2O_3 and TiO_2 [1, 2]. With the advancement in research for materials,

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organic semiconductors make good candidates for sensor applications due to low cost, high sensitivity, fast response, flexibility, easy fabrication etc [3–6]. The electrical properties, either resistance or capacitance, of the sensing device are enormously changed with the adsorption of water molecules. Thus there exist basically two types of humidity sensors; capacitive-type [5–8] and resistive-type [9–14]. Some of the organic compounds used in the capacitive-type humidity sensors are cellulose acetate butyrate [15], porphyrin [16], polyimide [17], polymethyl methacrylate PMMA [18] and methyl-red [19]. Sensors based on capacitive technique can be employed in extreme environments e.g. swimming pools and livestock facilities. The capacitive-type sensors are more costly as compared to the resistive-type sensors, however, the former type of sensors require less sophisticated and simple electronics [5].

Metal phthalocyanines are used in a variety of applications such as solar cells [20], field-effect transistors [21] and sensors [22–25] etc. due to their thermal and chemically stability [25]. Like most of the metal phthalocyanines, VOPcPhO is also a p-type semiconducting material [26, 27]. VOPcPhO shows changes in its electrical properties on the exposure to the humid environment [28]. The conductivity of the p-type metal phthalocyanines is enhanced due to the generation of carriers induced by the formation of charge transfer complexes at phthalocyanine surfaces [22].

Although gas sensing properties of metal phthalocyanines are well studied, a few studies have been undertaken to explore the humidity sensing properties using metal phthalocyanines. This study is based on the investigation of humidity sensing properties of VOPcPhO thin film spin coated on asymmetric metal electrodes prepared by photolithography technique. It is demonstrated that the surface-type capacitive humidity sensor developed in this research work, has the potential for being applied in the measurement of relative humidity present in the surrounding atmosphere.

2. Experimental Methods

2.1 Material Preparation and Sensor Fabrication

Vanadyl 2,9,16,23-tetraphenoxy-29H,31H-phthalocyanine, a soluble derivative of VOPc, with chemical formula $C_{56}H_{32}N_8O_5V$, was obtained from Sigma Aldrich and used without purification for the fabrication of the Al/VOPcPhO/Au surface-type capacitive humidity sensor. The chemical structure of VOPcPhO is presented in Figure 1. The VOPcPhO was easily dissolved in chloroform in order to obtain 30 mg/ml (3% weight) solution. Prior to the deposition of thin film of VOPcPhO by spin coating technique, asymmetric metal electrodes were patterned on cleaned glass substrate using photolithography. The glass substrate was cleaned using standard cleaning procedures. Conventional photolithography and lift-off techniques were employed for the pattern transfer on glass substrate. The processing steps for patterning asymmetric metal electrodes are illustrated in Figure 2. As a first step the photoresist was spin coated on the cleaned substrate employing Clarient AZ 4620 spin coater. After the exposure to UV and development of photoresist, the first metal electrode with a thickness around 275 nm was sputtered. Later the photoresist was stripped off using acetone and isopropyl alcohol. Then, on the patterned Al-electrode a photoresist layer was deposited again through the spin coating method. The exposure/development steps were applied to define the Au-electrode (2nd metal-electrode). Afterwards, a 270 nm thick film of gold was deposited through sputtering which was followed by a photoresist lift-off process. The gap between the electrodes was 40 um. Eventually, a thin film of VOPcPhO, with a

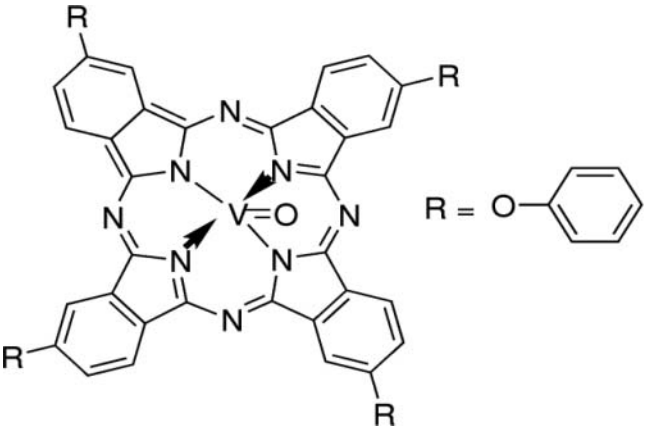

Figure 1. A molecular structure of Vanadyl 2,9,16,23-tetraphenoxy-29H,31H-phthalocyanine (VOPcPhO).

nominal thickness of 150 nm was incorporated into the gap between the two asymmetric metal-electrodes by spin casting using a WS-400B-6NPP-Lite spin coater in the presence of nitrogen flow. The thin film of VOPcPhO serves as the dielectric for the Al/VOPcPhO/Au surface-type capacitive humidity sensor. The spin speed was maintained at 3000 rpm to acquire a thin film of required thickness. The device structure is illustrated in Figure 3.

2.2 Measurements

The absorption spectra of VOPcPhO films were obtained by Jasco V-570 UV/Vis/NIR spectrometer. The in situ capacitance versus relative humidity measurements of Al/VOPcPhO/Au sensor were carried out in a local made hermetically sealed humidity chamber. The chamber can provide a humidity range of 0–95% RH. The capacitive measurements were carried out using commercial digital humidity and LCR meters. The capacitive measurements were performed at a frequency of 1 KHz with an ESCORT ELC-133A LCR meter. The relative humidity (RH) inside the chamber was varied between 0% and 87% RH, with a step size of 5% RH, using dry and wet air. The test chamber provides different humidity levels for the sensor and the capacitance of the humidity sensor increases as the humidity rises. The device is fixed in the humidity chamber and is exposed to humid ambience.

3. Results and Discussion

3.1 Characterization of VOPcPhO Thin Film

The UV/Vis/NIR absorption spectrum of the VOPcPhO thin film spin-coated on glass substrate is presented in Figure 4. Two well known bands, a Q-band and a Soret-band, of the metal-phthalocyanines are observed in the spectrum. The Soret band, often called B-band, appears in the near UV spectral region, which lies between 270 nm and 410 nm. Two prominent high energy peaks appear at 346 nm and 290 nm. The Soret band also possesses a shoulder peak at 408 nm[29–31]. A close inspection of the absorption spectrum in Figure 4 reveals that the Q-band splits out in two distinct peaks and lies in the range of

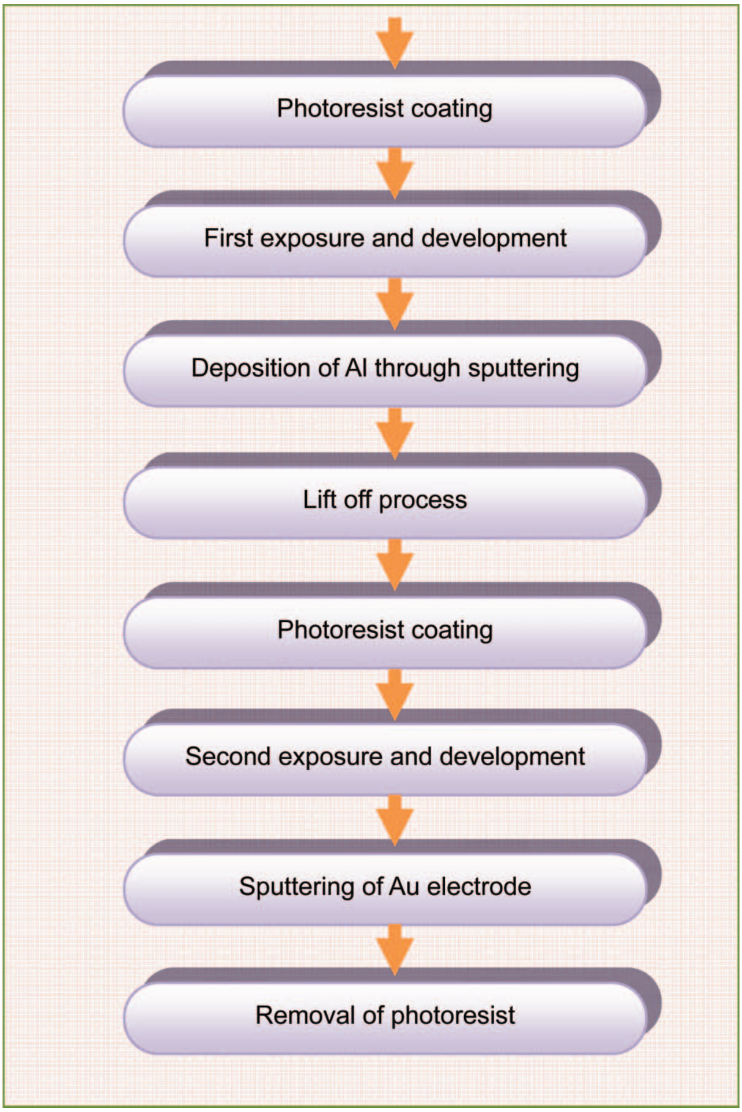

Figure 2. The steps employed in the photolithography for the fabrication of the asymmetric sputtered metal-electrodes for humidity sensors.

660 nm to 715 nm. The Q-band, with a strong peak appearing at 664 nm and a shoulder at 710 nm, exists in the visible region of the spectrum.

We attribute both Q-band and Soret-band to the two lowest singlet–singlet electronic transitions of the conjugated system, labeled as $a_{1u} \leftarrow e_g$ and $a_{2u} \leftarrow e_g$, transitions respectively [32, 33]. The strong π- π^* transitions in the Q-band might be due to the excitations between bonding and antibonding molecular orbitals [29]. The strong peak in this region is associated with the first π- π^* transition on the phthalocyanine macrocycle, while the shoulder may be attributed to excitonic transition or vibrational interval [34, 35]. The Davydov splitting is observed in the Q-band region. The energy separation value due to the Davydov splitting is of the order of 0.15 eV.

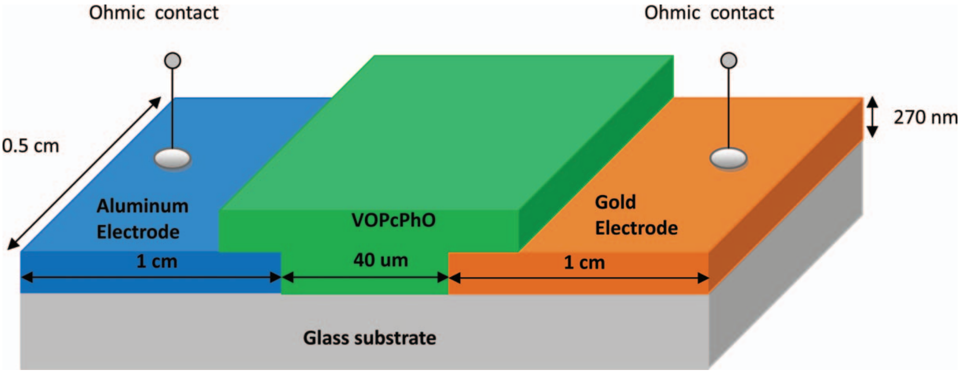

Figure 3. A device structure of a co-planar humidity sensor.

The absorption spectra play an important role in the measurement of the energy band gap of semiconducting materials, nanomaterial and solar industries. The absorption coefficient for the VOPcPhO thin film has been calculated by the following equation [36]:

$$\alpha = 2.303A/d \tag{1}$$

where ‘A’ is the measured absorbance and ‘d’ is the thickness of the VOPcPhO thin film.

The energy band structure and the type of optical transition can be assessed from the correlation between absorption coefficient and the photon energy given below [37]:

$$\alpha^r \sim (h\nu - E_g) \tag{2}$$

Here E_g is the energy gap and $h\nu$ is the photon energy. The constant r determines the type of transition. For the direct allowed transitions the value of $r = 2$ while for indirect allowed transition r has a value of 1/2. By manipulating Eq. (2), a graph was plotted to find the value of r. In our case r turned out to be equal to 2, which indicates direct allowed

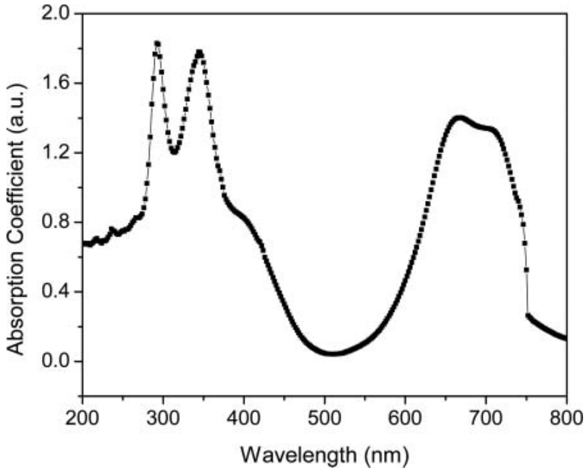

Figure 4. Absorption spectra of spin coated VOPcPhO thin film on glass.

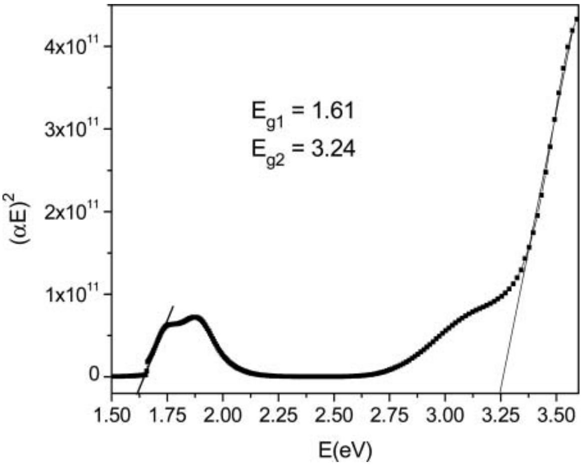

Figure 5. The variation of the absorption coefficient (α) as a function of photon for VOPcPhO thin film.

transition. The optical energy gaps were obtained by plotting α^2 versus hν and extrapolating to zero absorption, as shown in Figure 5. For the VOPcPhO thin film, the E_{g1}, in the visible spectral region, is obtained as 1.61 eV and E_{g2} is evaluated as 3.24 eV in the ultra violet region.

3.2 Humidity Measurements

The amount of water vapours present in the atmosphere is used to define humidity. The following relation [38] can be employed to describe the relative humidity:

$$RH = \frac{P_w}{P_s} \times 100\% \tag{3}$$

where Pw and Ps are the pressure of water vapors and the saturated pressure, respectively.

The capacitance helps investigating the dielectric property of a material as the permittivity of the material and the capacitance are directly proportional to each other. The capacitive sensors typically exhibit non-linear behavior as a function of relative humidity which can be described by the following equation [38]:

$$\frac{C_h}{C_0} = \left(\frac{\varepsilon_w}{\varepsilon_d}\right)^n \tag{4}$$

where ε_w the dielectric constant in wet state, ε_d the permittivity of the dielectric in a dry state and n is the morphological factor of the dielectric material.

In this study, a surface-type humidity sensor Al/VOPcPhO/Au was tested under humidity level ranging from 0% to 87% RH. The response-recovery time and capacitance versus relative humidity characteristics were investigated. Figure 6 shows capacitance (C) versus relative humidity (% RH) for the Al/VOPcPhO/Au surface-type capacitive sensor. The capacitive response of the sensor has been investigated over a range of 0–87% RH. The relative humidity was increased in steps of 5% RH providing sufficient time to allow the sensor to respond fully and stabilize. The sample was placed in a humidity chamber with

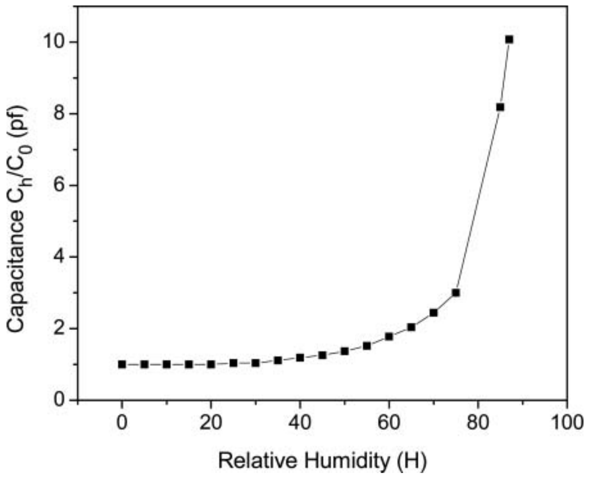

Figure 6. Capacitance versus relative humidity relationship for the Al/VOPcPhO/Au capacitive sensor based on VOPcPhO.

controlled temperature and relative humidity for humidity measurements. The capacitance versus relative humidity measurements were carried out at room temperature under dark conditions.

It can be observed from Figure 6 that the capacitance shows an exponential increase with elevating levels of humidity. The capacitance of the sensor increases 10 times over increasing relative humidity. The surface type capacitive sensor Al/VOPcPhO/Au is sensitive between 55% RH and 75% RH and insensitive below 55% RH. The exponential increase in the capacitance of the device may be inferred to the fact that only a few molecules are adsorbed because the water vapors do not cover the surface continuously. However, the capacitance increases significantly when one or more layers of water are formed [19]. The single layer physisorption changes to multilayer physisorption for the range 55–75% RH which is considered as the transition humidity range [39].

The organic sensing layer, used as a dielectric, absorbs or releases water vapors proportional to the relative humidity present in the atmosphere and consequently changing the resistance or capacitance of the sensor. Capacitive-type humidity sensors depend on the change in the permittivity of the dielectric material used between the electrodes respectively with corresponding change in the relative humidity levels. The capacitive-type sensors respond well over a wide range of relative humidity. The sensing material, VOPcPhO in our case, can absorb moisture and tends to change the dielectric constant in response to the changes in the humidity environment. The amount of adsorbed water molecules at the surface of the active layer significantly alters the dielectric constant of the sensor element. The phenomenon working behind is that the dielectric constant of water (~80) is much greater than that of the organic compound and when the sensor is exposed to moisture, the dielectric constant of the active material increases with rising humidity levels and consequently enhances the capacitance. The charge transfer complexes and water vapors adsorbed in the pores of VOPcPhO film might be responsible for exponential increase in the capacitance [16, 19, 40].

Several other possible reasons such as gap between the electrodes, area, relative permittivity and polarizability of organic material seem responsible for the observed change in the capacitance with relative humidity [6].

With the help of various probabilities, the increase in capacitance with increasing relative humidity can be best explained. The polarization and polarizability are co-related by the following relation [41].

$$P = N\alpha E \tag{5}$$

where P, α and E are the polarization, polarizability and electric field, respectively.

The polarization in the capacitance of the dielectric material can be caused by various types of polarizabilities such as electronic polarizability (α_e), ionic polarizability (α_i) and dipolar polarizability (α_{dip}). The electronic polarization has a negligible effect and it occurs due to relative displacement of the electron cloud. The ionic polarization arises when the positive and negative ions of a dipole change their distance. This type of polarization is present, universally, in all materials. Dipolar polarization or orientational polarization arises due to change in the orientation of the permanent dipoles present in the material.

It may be assumed that there are some internal charge transfer complexes [8, 16, 40] present in VOPcPhO, which give rise to ionic and electronic polarization. The water molecules comprise of dipoles, which are responsible for the dipolar polarization. It has been reported by a research group that in normal and humid environment, the polarizability occurs due to transfer of charge carriers [42].

In the light of previous discussion the net polarizabilty (α_n), under normal conditions, can be written as:

$$\alpha_n = \alpha_i + \alpha_e + \alpha_{dip} + \alpha_{tn} \tag{6}$$

when the device is exposed to humidity, the total polarizability (α_h) may take the form as shown below:

$$\alpha_h = \alpha_i + \alpha_e + \alpha_{dip} + \alpha_{th} \tag{7}$$

where α_{th} is polarizability due to the transfer of electron/holes in humid ambience. It can be considered that the humidity affects the concentration of charge carriers and total polarizability (α_h).

The Clausius-Mossotti equation gives relation among relative dielectric constant ε_r, polarizability of material α and concentration of molecules N, (or N_d as concentration of the charges in dry air) in the material [41].

$$\frac{\varepsilon_d - 1}{\varepsilon_d + 2} = \frac{N_d\alpha_d}{3\varepsilon_0} \tag{8}$$

where ε_d is the relative permittivity and ε_0 is permittivity of free space.

On the basis of this equation, the following expression has been derived [43, 44]:

$$\frac{C_h}{C_0} = \frac{1 + 2N_d\alpha_d\left(1 + K(RH)^n\right)/3\varepsilon_0}{\left[1 - N_d\alpha_d\left(1 + K(RH)^n\right)/3\varepsilon_0\right]\varepsilon_d} \tag{9}$$

where C_h is capacitance in humid conditions, C_0 is capacitance in dry air, k is humidity capacitive factor and RH is the relative humidity level. In this case the value of k is 1.209×10^{-4} $(\mathrm{RH})^{-1}$. The value of relative permittivity, ε_d of the material is taken as 4 and that of a morphological factor n is 2. This relation has been used for simulation of capacitance-humidity relationship. Figure 7 shows comparison between the experimental and simulated relative capacitance-humidity results for the Al/VOPcPhO/Au capacitive

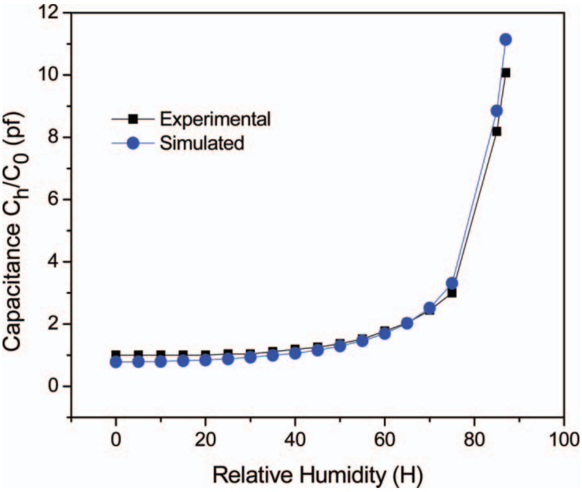

Figure 7. Capacitance-relative humidity relationship for Al/VOPcPhO/Au capacitive sensor: (1) experimental (2) Simulated.

type humidity sensor. The simulated results are found well in agreement with experimental ones.

The response or recovery time can be explained as the time required by the device to achieve 90% of the total capacitance change [45]. The measured response and recovery characteristics of the Al/VOPcPhO/Au surface-type humidity sensor corresponding to humidification are presented in Figure 8. The response and recovery time for the sensor were measured by increasing the humidity from 30% RH to 90% RH (absorption) and decreasing the humidity from 90% RH back to 30% RH (desorption). For evaluating sensor response time the variation of capacitance at a fixed value of relative humidity (90% RH) is noted

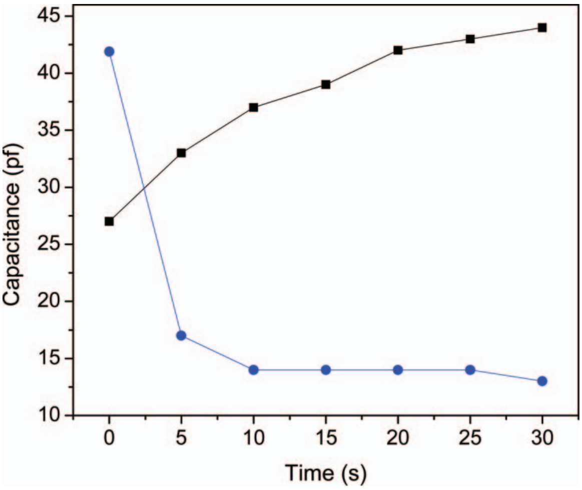

Figure 8. Response recovery versus time relationship for the Al/VOPcPhO/Au surface-type humidity sensor.

with time and is plotted in Figure 8. For recovery time similar observations are taken during desorption and is shown in Figure 8. The response time and recovery time of the sensing material are found to be 20 s and 10 s respectively.

4. Conclusion

This study has successfully fabricated surface-type Al/VOPcPhO/Au capacitive humidity sensor. The investigation made on the sample leads to the fact that the capacitance of the sensor increases with increasing humidity levels. The polarization due to adsorption of water vapors and transfer of charge carriers is generally the main cause of such capacitance response. The absorption spectrum has been utilized to determine optical energy gap. Considerable features of the surface-type humidity sensors are economical cost, simplicity and ease of fabrication. It may be possible to exploit high sensitivity and better stability of the sensor in commercial applications.

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