Vol. 31, No. 11 Journal of Semiconductors November 2010

Characterization of vanadyl phthalocyanine based surface-type capacitive humidity sensors

Fakhra Aziz[1,2,†], M. H. Sayyad[1], Khassan S. Karimov[1,3], M. Saleem[1],
Zubair Ahmad[1,4], and S. Mahmood Khan[1]

(1 Ghulam Ishaq Khan Institute of Engineering Sciences and Technology, Topi-23640, Pakistan)
(2 Low Dimensional Material Research Center, Department of Physics, University of Malaya, 50603 Kuala Lumpur, Malaysia)
(3 Physical Technical Institute, Aini St-299/1, Dushanbe, 734063, Tajikistan)
(4 Department of Mechanical Engineering, 20 Symonds Street Auckland, University of Auckland, New Zealand)

Abstract: This study presents the fabrication and characterization of novel surface-type capacitive humidity sensors using vanadyl phthalocyanine (VOPc) as the active material. The devices, which comprise three different thicknesses, have been fabricated using the thermal evaporation technique. A thin film of VOPc is deposited on thoroughly cleaned glass substrates with pre-patterned Ag electrodes. The capacitive effect of the samples under humidity has been investigated. Comparison of the samples with different thicknesses shows that the thinnest device seems more sensitive towards humidity. The humidity dependent capacitance properties of the sensor make it beneficial for use in commercial hygrometers.

Key words: surface-type; capacitance; vanadyl phthalocyanine; humidity sensor; organic semiconductor
DOI: 10.1088/1674-4926/31/11/114002 **EEACC:** 2570

1. Introduction

The characterization of organic semiconductors is receiving great attention because of the increased activity in their synthesis and their potential use in a wide range of low cost, large area flexible, nonflexible, disposable electric, electronic and photonic devices, such as rechargeable batteries, junction diodes[1], organic field effect transistors (OFETs)[2], memory, solar cells[3], organic light emitting diodes (OLEDs)[4], optical power limiting[5], displays, RFIDs and sensors[6]. Some of the organic semiconductors have shown high sensitivity to humidity, temperature and different types of gases[7]. Therefore, investigation of the properties of organic semiconductors under different conditions is a very promising field for the development of various sensors. Humidity is one of the most common constituents present in the environment. Therefore, humidity sensors are required for the measurement and control of humidity in many fields, such as industrial production, human comfort, medical and agriculture.

Humidity sensors using organic materials are generally divided into two categories: resistive and capacitive. The capacitive-type humidity sensors are popular due to low power consumption[8]. They show better linearity and good stability at higher temperature and higher humidity as compared to their counterpart resistive-type sensors[9−12]. Organic materials are being extensively studied for the fabrication of capacitive-type sensors[13,14]. Most of these sensors are fabricated in a sandwich configuration, and this structure requires the deposition of organic thin film onto a suitable substrate and a top metallic electrode. This often damages the active material and causes device failure due to shortening[15]. Surface-type devices offer low cost and simple technology for investigating different properties of organic materials, such as charge transport[16], electrolumiscence[17], light sensitivity[18], effect of temperature[13] and effect of humidity[9,13]. Metal phthalocyanines (MPcs) belong to a family of organic semiconductors of great technological importance. These compounds are very stable, both thermally and chemically so their thin films can be deposited without decomposition[18].

Vanadyl phthalocyanine (VOPc) has been reported to have the largest third-order nonlinear optical susceptibility[19−21] and ultrafast optical response (faster than 10 ps)[19,22−24]. It has been used for the fabrication of an organic field effect transistor[25] due to its high mobility (1 cm^2/(V·s)). VOPc is relatively less investigated for its applications in organic electronics. Therefore, we have undertaken its study for its potential use as an active material in the fabrication of organic electric, electronic and photonic devices. As far as we know, VOPc based humidity sensors have not been investigated. In the present study, we report the characterization of Ag/VOPc/Ag surface-type thin film capacitive humidity sensors fabricated using vacuum thermal evaporation on glass substrates. The variation in capacitance as a function of relative humidity (RH) is observed for different thicknesses of VOPc films. The aim of this research is to explore the properties of VOPc as a humidity sensing element and develop a reliable and low cost sensing device for measuring relative humidity of the surrounding environment.

2. Experimental

VOPc with the molecular formula $C_{56}H_{32}N_8O_5V$ was purchased from Sigma Aldrich and used without further purification. The molecular structure of VOPc is given in Fig. 1. The Ag/VOPc/Ag surface-type humidity sensors were fabricated

---

† Corresponding author. Email: fakhra69@yahoo.com

Received 22 May 2010, revised manuscript received 30 June 2010

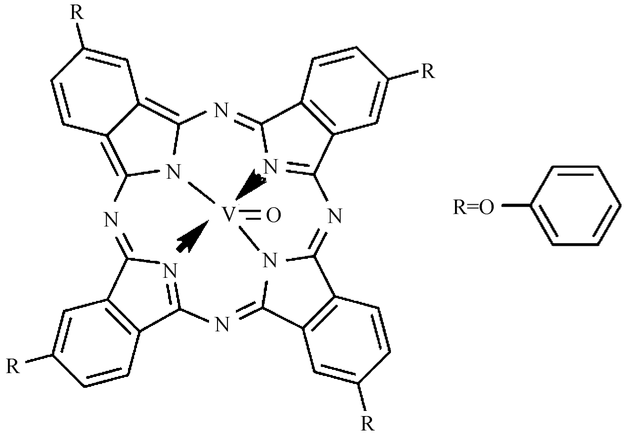

Fig. 1. Molecular structure of vanadyl phthalocyanine (VOPc).

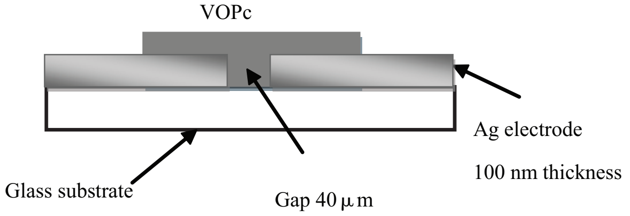

Fig. 2. Cross-sectional view of a Ag/VOPc/Ag capacitive-type humidity sensor.

on plasma cleaned glass substrates with dimensions of 25 × 25 × 1 mm^3. Ag electrodes of thickness 100 nm, with a gap of 40 μm, were thermally deposited on the substrates at the rate of 0.2–0.3 nm/s under a vacuum of 5×10^{-5} mbar. The substrates were plasma cleaned prior to the deposition of electrodes. The deposition was carried out using Edward 306A vacuum evaporator with an FTM5 crystal thickness monitor. The 40 μm gap was achieved by using a shadow mask. Thin films of VOPc were thermally sublimed at the rate of 0.2 nm/s under a vacuum of 5×10^{-5} mbar on the gap between the electrodes. The devices were fabricated for three different thicknesses of the VOPc films, i.e., 50 nm, 100 nm and 150 nm. The cross sectional view of the fabricated capacitive-type humidity sensors is shown in Fig. 2.

The capacitance of a sensor was measured by placing the device in a self made humidity chamber capable of providing a humidity range of 0–95% RH. The commercial digital humidity and capacitance meters were employed for *in situ* capacitance and RH measurements. The capacitive measurements were carried out at a frequency of 1 kHz. The RH inside the chamber was varied between 0 and 95%, with a step size of 5%, 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 AFM image was taken by digital instruments Veeco D3000 microscope with a cantilever provided by APP NANO. The I–V characteristics were obtained using current–voltage source Keithley-228A and Keithley-196 system DMMs.

3. Results and discussion

Humidity is defined as the amount of water vapour present in the atmosphere. To measure the humidity response, it is a common practice to measure the RH at a certain temperature. The RH is defined as[8]

$$\text{RH} = \frac{P_\text{w}}{P_\text{s}} \times 100\%, \tag{1}$$

where P_w is the pressure of water vapour and P_s is the saturated pressure.

The dielectric property of a material can be investigated by means of its capacitance as the permittivity of the material varies proportionally with capacitance. The non-linear behaviour as a function of RH exhibited by capacitive sensors can best be explained by the equation[8]:

$$\frac{C_\text{h}}{C_0} = \left(\frac{\varepsilon_\text{w}}{\varepsilon_\text{d}}\right)^n, \tag{2}$$

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

Essentially, the capacitance variation with RH could be attributed to various aspects: (1) the dielectric constant of water, (2) the porosity of the active thin film, (3) the contact area, gap between the electrodes and relative permittivity of the sensing material, and (4) the polarizability of the organic material[26].

The relative permittivity of water is ~ 80[27, 28], which is quite a bit higher than that of macrocyclic compounds[13]. The water molecules adsorbed by the active layer increase with rising RH, which in turn tends to enhance the capacitance of the sensor. The VOPc based surface type capacitive humidity sensor is enabled to probe humidity variation sensitivity due to a large difference between the relative permittivity of the water and that of the vanadyl phthalocyanine.

The adsorption of the water molecule, which is a kind of polar molecule, onto a solid surface could be categorized as chemisorption and physisorption. The formation of a molecule layer of chemisorptions at a low humidity level and layers of physisorption at increasing humidity levels best describe the adsorption process of water. The water molecules in the chemisorption layer and the first layer of physisorption are doubly bonded and unable to move freely. Molecules present in other physisorption layers are singly bonded, as a result of which they can be polarized easily. Hence the clear increase in relative permittivity and capacitance is inevitable[28].

Another factor responsible for an increase in capacitance with RH may be the porosity of the active film. At higher RH levels and greater film thicknesses, the variation in capacitance becomes less conspicuous because the pores of the film are being filled with water molecules. This results in decreased sensor sensitivity towards humidity[9]. The increased vapour contact area increases the physisorption of water molecules and the dielectric constant of the sensing material[27]. On the other hand, reduced gap play an important role in enhancing the capacitance.

Figure 3 shows the results of measured capacitance (C) versus RH (%) for the surface-type capacitive sensors with different thicknesses of the VOPc thin film. In these measurements, the capacitive response of the sensors was studied over

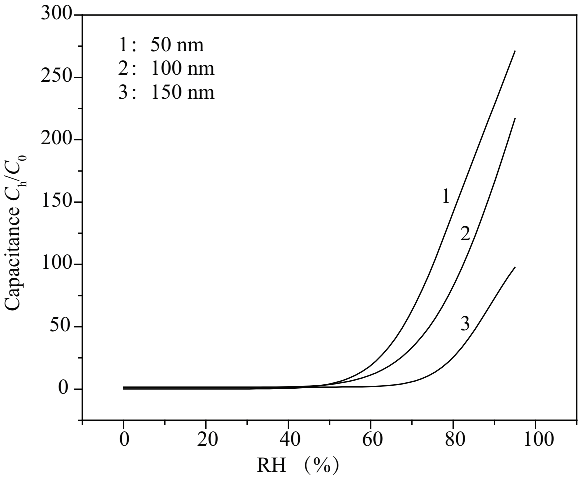

Fig. 3. Capacitance versus RH relationships for the Ag/VOPc/Ag capacitive sensors for the VOPc thicknesses of (1) 50 nm, (2) 100 nm and (3) 150 nm.

a range of 0–95% RH, and the RH was increased in steps of 5%. In each step, the humidity was held for sufficient time to allow the sensors to respond fully and then stabilize.

It is observed that the capacitance of the samples increases to 250, 225 and 110 times for VOPc films having thicknesses of 50 nm, 100 nm and 150 nm, respectively, with the RH being varied over 0–95% range. This indicates a decrease in sensitivity with increasing thickness in the range studied and is in agreement with capacitance versus RH studies for the polyimide films reported by Harrey *et al.*[29].

It can be seen from Fig. 3 that the sensors are insensitive in the range of 0–55% RH, and above 55% RH there is an exponential increase in the capacitance of the devices due to the fact that the coverage of water vapor at the surface is not continuous and only a few molecules are adsorbed. However, when one or several water layers are formed, the increase in the capacitance becomes sharp and linear[9]. This may support the argument that the range 55%–75% RH might be the transition humidity range for which the water molecule adsorption mode changes from single layer physisorption to multilayer physisorption[28]. The phenomenon in Fig. 3 might be caused by the adsorption of water vapor in the pores of thin films and the presence of charge transfer complexes[9, 13]. The dielectric constant changes with increasing adsorption of water vapor, hence the capacitance of the sensor increases.

Figure 4 shows the relative capacitance–thickness relationship for Ag/VOPc/Ag sensors at different levels of humidity, i.e. 70%, 80% and 90% RH. The sensor comprising VOPc thin film of 50 nm gives the best performance. The sensors with thinner VOPc films are more sensitive towards humidity. In the case of a thin film with a thickness of 50 nm, greater capacitance was achieved due to the acquisition of a high concentration of water molecules in the VOPc layer as compared to the other samples of thicknesses100 nm and 150 nm.

The fact that capacitance increases with an increase in RH can be best explained by considering various probabilities. The polarization of the material can describe the state of a dielectric, which is related to the capacitance of the material. The polarization and polarizabilities are co-related by the following relation[30],

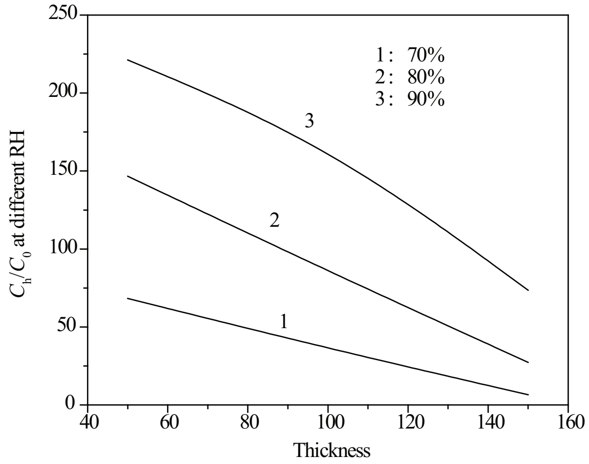

Fig. 4. Capacitance VOPc film thickness relationships for a Ag/VOPc/Ag sensor at RH of (1) 70%, (2) 80%, and (3) 90%.

$$P = N\alpha E, \tag{3}$$

where P is polarization, α is polarizability and E is electric field.

There are several causes of polarizabilities, which are ultimately responsible for the relative change in the capacitance of the dielectric material. The three types of polarizability are electronic polarizability (α_e), ionic polarizability (α_i) and dipolar polarizability (α_{dip}). Electronic polarizability arises due to the displacement of the electron cloud of an atom/ion/molecule with respect to the nucleous. Ionic polarization occurs due to a change in the distance between the positive and negative ions of a dipole. There are certain permanent dipoles also present in a dielectric material that are arranged in a random fashion. These dipoles change their orientation with the application of an electric field, thus giving rise to dipolar polarization or orientational polarization.

The electronic polarization and ionic polarization are induced polarizations. The effect of electronic polarization is very negligible. However, it is universally present in all materials. Ionic polarization occurs in polar materials in which a molecule contains a net positive and a net negative charge[30].

There may be present internal charge transfer complexes[9, 13] in VOPc, therefore it can be assumed that ionic polarization takes place in this organic semiconducting material along with electronic polarization. At low frequency (1 kHz) measurements, the electronic and ionic polarizabilities are probably considered to affect the capacitance of the material. Due to the presence of dipoles of water molecules adsorbed by vanadyl phthalocyanine, dipolar polarization also exists and it seems to play a vital role in humidity-capacitance measurements of the material. In earlier studies, it has been shown that the polarizability due to the transfer of charge carriers as electrons and holes occurs in both normal and humid environments[31].

If we take all the polarizabilities into account, we can write the net polarizabilty (α_n) under normal conditions as

$$\alpha_n = \alpha_i + \alpha_e + \alpha_{dip} + \alpha_{tn}, \tag{4}$$

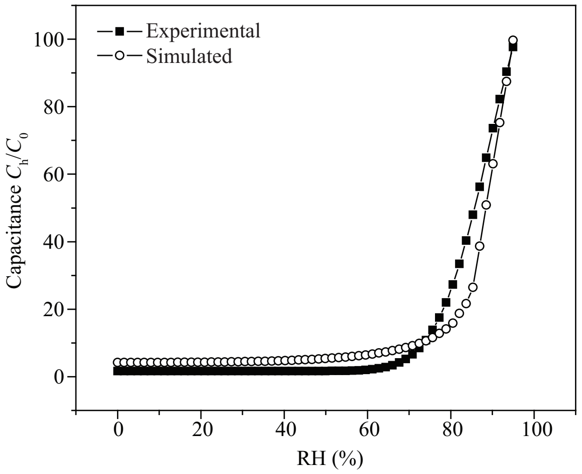

Fig. 5. Capacitance–RH relationship for a Ag/VOPc/Ag capacitive sensor with film thickness of 150 nm.

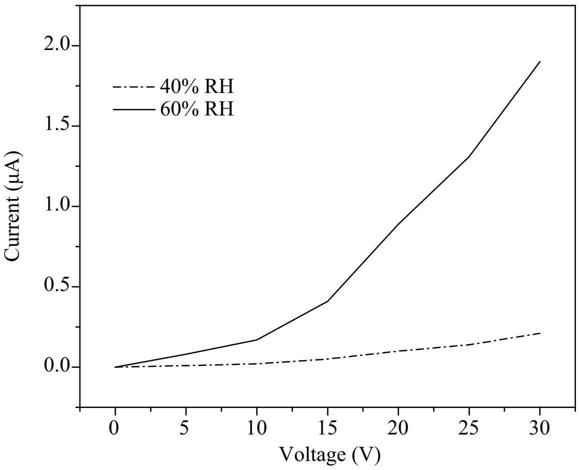

Fig. 6. Current–voltage characteristics of the device under two different humidity levels (40% and 60% RH).

when the sensor is placed in a humid environment. The total polarizability (α_h) may then be

$$\alpha_h = \alpha_i + \alpha_e + \alpha_{dip} + \alpha_{th}, \tag{5}$$

where α_{th} is the polarizability due to the transfer of electron/holes as charge carriers under a humid environment. Here we consider that the concentration of charge carriers and total polarizability (α_h) are humidity variant.

The Clausius–Mossotti equation gives a relation among macroscopic property (relative dielectric constant) ε_r, microscopic property (polarizability of material) α and the concentration of molecules N (or N_d as the concentration of the charges in dry air) in the material[30],

$$\frac{\varepsilon_d - 1}{\varepsilon_d + 2} = \frac{N_d \alpha_d}{3\varepsilon_0}, \tag{6}$$

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[32, 33],

$$\frac{C_h}{C_0} = \frac{1 + 2N_d\alpha_d\left(1 + kH^n\right)/3\alpha_0}{\left[1 - N_d\alpha_d\left(1 + kH^n\right)/3\alpha_0\right]\varepsilon_d}, \tag{7}$$

where C_H is the capacitance in humid conditions, C_0 is the capacitance in dry air, k is the humidity capacitive factor and H is the RH level. In this case, the value of k is 1.099×10^{-4} (RH)$^{-1}$. The value of the relative permittivity, ε_d of the material is taken as 4 and that of a morphological factor n is 2. This relation can be used for the simulation of the capacitance–humidity relationship. Figure 5 shows the comparison between the experimental and simulated relative capacitance–humidity results for the Ag/VOPc/Ag capacitive type sensor. The simulated results are found to be in good agreement with the experimental results.

Figure 6 shows the current versus voltage relationship for the humidity sensor at two different values of humidity (40 % and 60 % RH). It is seen that at any particular voltage, the current increases with an increase in humidity level. This may be due to an increase in the conductivity of the film with increasing humidity level. The drop in resistance with the increase in humidity level can be due to several factors[9, 34]: (1) electronic and ionic conduction; (2) polar molecules of water may increase the conductivity of the thin film due to an increase in proton concentration; (3) there may be some physical phenomena behind all this, such as the effect of an absorbed water molecule as a dipole and impurity.

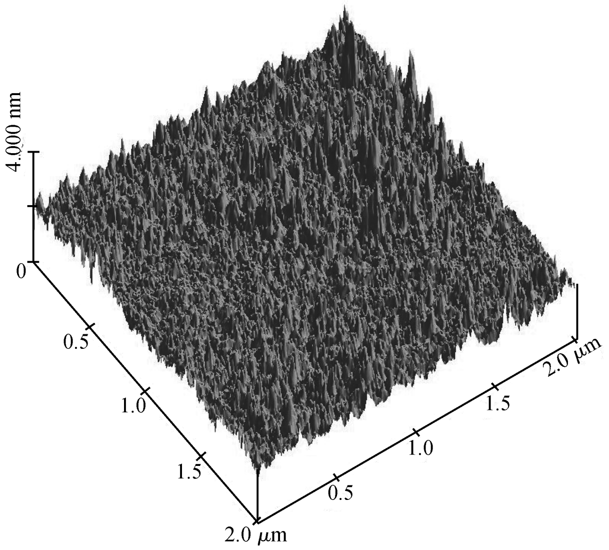

Fig. 7. AFM height image of the surface of the VOPc film deposited on a glass substrate.

The AFM image of the surface of the VOPc active layer on a glass substrate for the capacitive humidity sensor in tapping mode is presented in Fig. 7. The morphology of the film exhibits the non uniform, rough and coarse texture with peak like features. The RMS roughness of the film is 0.233 nm. The film topography suggests that some inter-penetrating VOPc molecular network is formed, which leads to higher absorption[35].

4. Conclusion

In this study we have successfully fabricated surface-type

Ag/VOPc/Ag capacitive humidity sensors. The investigation of the samples of different thicknesses shows that the capacitance of the sensors increases with a rise in humidity levels. In general, such a capacitance response is attributed to polarization due to the adsorption of water molecules and transfer of charge carriers. The sensitivity of the Ag/VOPc/Ag sensor has been found to be dependent on the thickness of the VOPc film. The experimental results show that the thinner the film, the higher the sensitivity. The highest capacitance response was observed for the 50 nm VOPc thick film. It is also observed from the $I-V$ curves that at any certain voltages the current increases with an increase in humidity. This may be attributed to an increase in the conductivity of the film with increasing humidity. The rough and coarse film topography obtained by AFM suggests the formation of an inter-penetrating VOPc molecular network. The key features of the surface-type humidity sensors are their low cost, simplicity and ease of fabrication. It may be possible to exploit the high sensitivity and better stability of these sensors in commercial applications.

Acknowledgement

The extended support of Ghulam Ishaq Khan Institute of Engineering Sciences and Technology is greatly acknowledged. The authors acknowledge the enabling role of the Higher Education Commission, Pakistan, and appreciate the financial support through the Indigenous Fellowship program. The authors are also grateful to the Department of Physics, University of Malaya, Malaysia, for assistance in characterizing thin film of VOPc.

References

[1] Liang G, Cui T, Varahramyan K. Electrical characteristics of diodes fabricated with organic semiconductors. Microelectron Eng, 2003, 65(3): 279

[2] Irimia-Vladu M, Marjanovic N, Bodea M, et al. Small-molecule vacuum processed melamine-C_{60}, organic field-effect transistors. Org Electron, 2009, 10(3): 408

[3] Garcia-Belmonte G, Boix P P, Bisquert J, et al. Simultaneous determination of carrier lifetime and electron density-of-states in P3HT:PCBM organic solar cells under illumination by impedance spectroscopy. Solar Energy Materials and Solar Cells, 2010, 94(2): 366

[4] Ling I M, Chen L H. Organic light-emitting diode performance enhancement via indium tin oxide glass surface modification. Current Applied Physics, 2010, 10(1): 346

[5] Zidan M D, Ajji Z, Allaf A W, et al. Optical limiting behavior of C_{60} doped ethylenepropylenediene polymethylene polymer. Optics & Laser Technology, 2010, 42(4): 600

[6] Muzikante I, Parra V, Dobulans R, et al. A novel gas sensor transducer based on phthalocyanine heterojunction devices. Sensors, 2007, 7: 2984

[7] Saleem M, Sayyad M H, Ahmed Z, et al. Effects of orange dye concentration on electrochemical properties of zinc/orange dye acqueous solution/carbon cells. Kuwait J Sci Eng, 2009, 36(1): 77

[8] Rittersma Z M. Recent achievements in miniaturised humidity sensors—a review of transduction techniques. Sensors and Actuators A: Physical, 2002, 96(2/3): 196

[9] Ahmad Z, Sayyad M H, Saleem M, et al. Humidity dependent characteristics of methyl-red thin film-based Ag/methyl-red/Ag surface-type cell. Physica E, 2008, 41: 18

[10] Operea A, Barsan N, Weimar U, et al. Capacitive humidity sensors on flexible RFID labels. Sensors and Actuators B: Chemical, 2008, 132(2): 404

[11] Li Y, Yang M J, Camaioni N, et al. Humidity sensors based on polymer solid electrolytes: investigation on the capacitive and resistive devices construction. Sensors and Actuators B: Chemical, 2001, 77(3): 625

[12] Yao W, Chen X, Zhang J. A capacitive humidity sensor based on gold–PVA core–shell nanocomposites. Sensors and Actuators B: Chemical, 2010, 145(1): 327

[13] Saleem M, Sayyad M H, Karimov K S, et al. Cu(II) 5,10,15,20-tetrakis(4'-isopropylphenyl) porphyrin based surface-type resistive–capacitive multifunctional sensor. Sensors and Actuators B: Chemical, 2009, 137(2): 442

[14] Adhikari B, Majumdar S. Polymers in sensor applications. Progress in Polymer Science, 2004, 29(7): 699

[15] Shah M, Sayyad M H, Karimov K S, et al. Investigation of the electrical properties of a surface-type Al/NiPc/Ag Schottky diode using $I-V$ and $C-V$ characteristics. Physica B: Condensed Matter, 2010, 405(4): 1188

[16] Agostinelli T, Caironi M, Natali D, et al. Space charge effects on the active region of a planar organic photodetector. J Appl Phys, 2007, 101: 114504

[17] Mauthner G, Landfester K, Köck A, et al. Inkjet printed surface cell light-emitting devices from a water-based polymer dispersion. Org Electron, 2008, 9(2): 164

[18] Sayyad M H, Shah M, Karimov K S, et al. Fabrication and study of NiPc thin film based surface type photocapacitors. J Optoelectron Adv Mater, 2008, 10: 2805

[19] Terasaki A, Hosoda M, Wada T, et al. Femtosecond spectroscopy of vanadyl phthalocyanines in various molecular arrangements. J Phys Chem, 1992, 96(25): 10534

[20] Fang S, Tada H, Mashiko S. Enhancement of the third-order nonlinear optical susceptibility in epitaxial vanadyl-phthalocyanine films grown on KBr. Appl Phys Lett, 1996, 69: 767

[21] Fang S, Kohama K, Hoshi H, et al. Spectral dependence of the anisotrophy of the X3 of epitaxially grown vanadyl phthalocyanine film. Chem Phys Lett, 1995, 234: 343

[22] Si J, Wang Y, Zhao J, et al. Picosecond optical bistability in metallophthalocyanine-doped polymer film waveguides. Opt Lett, 1996, 21: 357

[23] Yuan P, Xia Z, Zou Y H, et al. Ultrafast optical kerr effect of phthalocyanine. Chem Phys Lett, 1994, 224: 101

[24] Yuan P, Xia Z, Zou Y H. Femtosecond time-resolved optical response of phthalocyanine Langmuir-Blodgett film. J Appl Phys, 1994, 75: 4648

[25] Wang H, Song D, Yang J, et al. High mobility vanadyl-phthalocyanine polycrystalline films for organic field-effect transistors. Appl Phys Lett, 2007, 90: 253510

[26] Ahmad Z, Sayyad M H, Karimov K S. Capacitive hygrometers based on natural organic compound. J Optoelectron Adv Mater, 2008, 2: 507

[27] Xiao S H, Xu H J, Hu J, et al. Structure and humidity sensing properties of barium strontium titanate/silicon nanoporous pillar array composite films. Thin Solid Films, 2008, 517(2): 929

[28] Li L Y, Dong Y F, Jiang W F, et al. High-performance capacitive humidity sensor based on silicon nanoporous pillar array. Thin Solid Films, 2008, 517(2): 948

[29] Harrey P M, Ramsey B J, Evans P S A, et al. Capacitive-type humidity sensors fabricated using the offset lithographic printing process. Sensors and Actuators B: Chemical, 2002, 87(2): 226

[30] Barua K C. Introduction to condensed matter physics. Narosa Publishing House Pvt. Ltd, 2007: 196

[31] Saleem M, Sayyad M H, Karimov K S, et al. Synthesis and photocapacitive studies of Cu(II) 5,10,15,20-tetrakis(4'-isopropylphenyl) porphyrin. J Optoelectron Adv Mater, 2008, 10: 1468

[32] Korvink J G, Chandran L, Boltshauser T, et al. Accurate 3D capacitance evaluation in integrated capacitance humidity sensors. Sensors and Materials, 1993, 4: 323

[33] Rittersma Z M, Splinter A, Bodecker A, et al. A novel surface-micromachined capacitive porous silicon humidity sensor. Sensors and Actuators B: Chemical, 2000, 68: 210

[34] Karimov K S, Qazi I, Khan T A, et al. Humidity and illumination organic semiconductor copper phthalocyanine sensor for environmental monitoring. Environ Monit Assess, 2008, 141: 323

[35] Guo T F, Wen T C, Pakhomov G L, et al. Effects of film treatment on the performance of poly (3-hexylthiophene)/soluble fullerene-based organic solar cells. Thin Solid Films, 2008, 516: 3138