Humidity sensing properties of Cu_2O-PEPC nanocomposite films

Kh. S. Karimov[1, 2], M. Saleem[3, †], Z. M. Karieva[4], A. Mateen[1], M. Tariq Saeed Chani[1], and Q. Zafar[5]

[1]GIK Institute of Engineering Sciences and Technology, Topi-23640, District Swabi, KPK, Pakistan
[2]Physical Technical Institute of Academy of Sciences, Rudaki Ave. 33, Dushanbe, 734025, Tajikistan
[3]Government College of Science, Wahdat Road, Lahore-54570, Pakistan
[4]Tajik Technical University, Rajabov St. 10, Dushanbe 734000, Tajikistan
[5]COMSATS Institute of Information Technology, Islamabad, Pakistan

Abstract: A blend of copper oxide nanopowder (Cu_2O), 3 wt.%, and poly-N-epoxypropylcarbazole (PEPC), 2 wt.%, in benzol was drop-casted on glass substrates with pre-deposited surface-type silver electrodes for the fabrication of Cu_2O-PEPC nanocomposite thin films. The thicknesses of the Cu_2O-PEPC films were in the range of 10–13 μm. The effect of humidity on the electrical properties of the nanocomposite films was investigated by measuring the capacitance and dissipation of the samples at two different frequencies of the applied voltage: 120 Hz and 1 kHz. The AC resistance of the samples was determined from the dissipation values, and the DC resistance was measured directly. The effect of ageing on the humidity sensing properties of the nanocomposite was observed. After ageing, it was observed that at 120 Hz and 1 kHz, under a humidity of up to 86% RH, the capacitance of the cell increased by 85 and 8 times, and the resistance decreased by 345 and 157 times, accordingly, with respect to 30% RH conditions. It was found that with an increase in frequency, the capacitance and resistance of the samples decreased. It is assumed that the humidity response of the cell is associated with the diffusion of water vapors and doping of the semiconductor nanocomposite by water molecules.

Key words: cuprous oxide; composite; nano-powder; poly-N-epoxypropylcarbazole; humidity; sensor
DOI: 10.1088/1674-4926/33/7/073001 **EEACC:** 2520

1. Introduction

The fabrication of humidity sensors is important for the assessment of environmental conditions in many industrial applications[1−3]. Humidity sensors have several categories based on their measuring principles, which include capacitive, resistive, hydrometric, gravimetric, optical, and integrated types[4−6]. Capacitive-type humidity sensors have various advantages, including low power consumption and large output signals. The performance of such sensors is determined primarily by the properties of the hygroscopic material used for the fabrication of the sensing film and the design of the sensor electrodes[7]. To fabricate the sensors, different techniques and sensing materials have been reported[8−15]. For capacitive-type humidity sensors, surface micromachining[8] and bulk micromachining[9] techniques are used in order to produce a porous silicon-based sensor. A thin-film surface micromachining technique, proposed by Park *et al*.[10], was used for manufacturing humidity and temperature sensors. For the capacitive-type humidity sensor, cellulose acetate butyrate[11, 12] and polyimide[13, 14] are among the most used sensing materials. A surface-type capacitive humidity sensor based on copper phthalocyanine (CuPc) was fabricated by Karimov *et al*.[15]. The capacitance of the detector increased continuously by 200 times with an increase in humidity from 35% to 92% RH.

Complexes of poly-N-epoxypropylcarbazole (PEPC) are known as photosensitive organic semiconductors that have good adhesive properties and are used for the fabrication of solar cells and photocapacitors[16]. Copper oxide (Cu_2O) is a p-type photosensitive semiconductor with a band gap of 2 eV[17, 18]. It is nontoxic and there is an abundance of copper in nature. Nanodots and nanostructure thin films of Cu_2O have been fabricated[19, 20].

Investigations of the effects of humidity on copper oxide composites are important for extending the knowledge about their physical properties, and for the fabrication of humidity sensors with high sensitivity, stability and linearity of response characteristics. It would therefore be reasonable to investigate the effects of humidity on the electric properties of copper oxide nanoparticles and poly-N-epoxypropylcarbazole composites. In this paper, we have investigated the humidity sensing properties of Cu_2O-PEPC nanocomposite films.

2. Experimental methods

Figure 1 shows the molecular structure of PEPC. The PEPC was synthesized in the laboratory[16] and Cu_2O nanopowder was commercially purchased from WINLAB UK. The glass substrates were initially cleaned ultrasonically by acetone for 10 min, followed by plasma cleaning for 5 min. The blend of copper oxide nanopowder (3.0 wt.%) and poly-N-epoxypropylcarbazole (2.0 wt.%) in benzol was drop-casted on glass substrates with pre-deposited surface-type silver electrodes for the fabrication of the Cu_2O-PEPC nanocomposite thin films. The gap between the silver electrodes was 40 μm.

† Corresponding author. Email: msaleem108@hotmail.com, drsaleem@ymail.com
Received 24 December 2011, revised manuscript received 30 January 2012

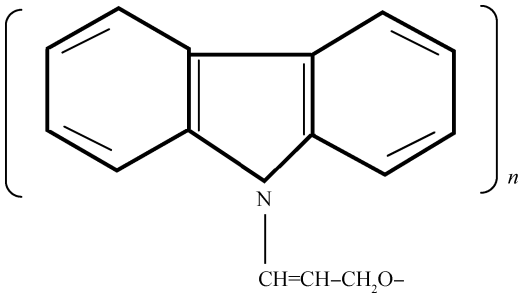

Fig. 1. The molecular structure of poly-N-epoxypropylcarbazole (PEPC), $n = 4$–6.

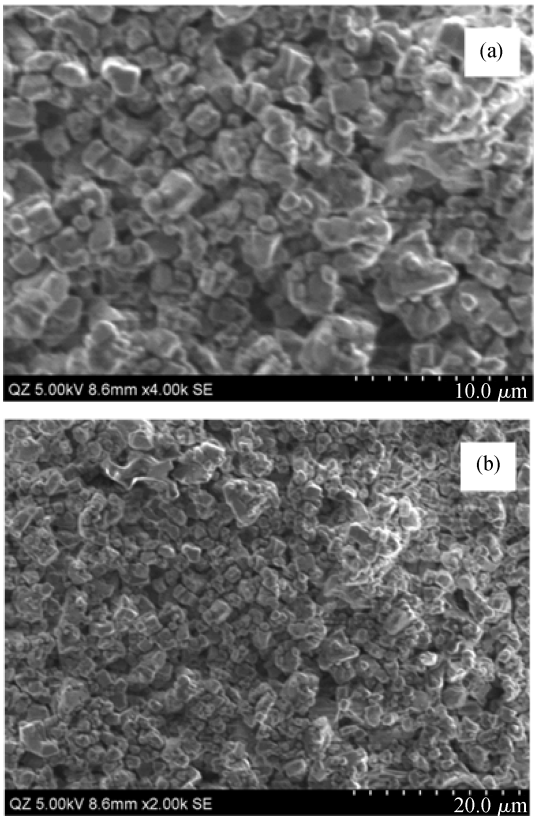

Fig. 2. SEM images of the Cu_2O-PEPC film at different magnifications.

Figures 2(a) and 2(b) show SEM micrographs of the thin film of the Cu_2O-PEPC nanocomposite at different magnifications; obtained from a Hitachi SU-1500 scanning electron microscope. The SEM micrographs clearly suggest porosity in the active thin film, suggesting Cu_2O-PEPC as a possible candidate for humidity sensing applications. Figure 3 shows the X-ray diffraction pattern (XRD) of the Cu_2O-PEPC nanocomposite thin film obtained from the "Panalytical Xpert pro". The indexed peaks of the XRD pattern are in agreement with the ICDD reference card "00-001-1142". Figures 4(a) and 4(b) show two dimensional and three dimensional atomic force microscope (AFM) images obtained by Agilent's Pico Plus under ambient conditions with a scan size area of 5 μm. A two dimensional micrograph is helpful in finding the grain size, whereas the three dimensional AFM image can help in understanding the orientation of the grains.

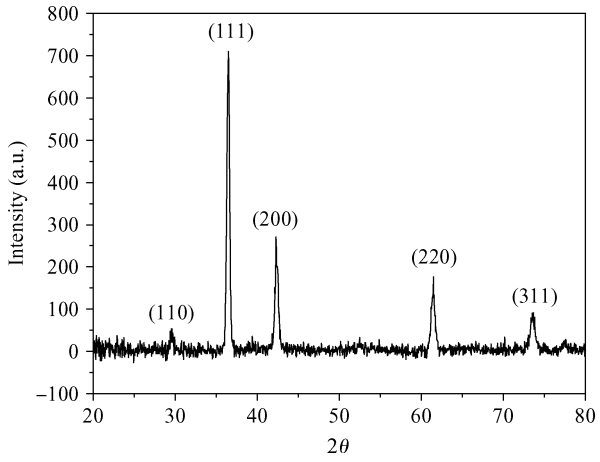

Fig. 3. XRD pattern of the Cu_2O-PEPC nanocomposite thin film.

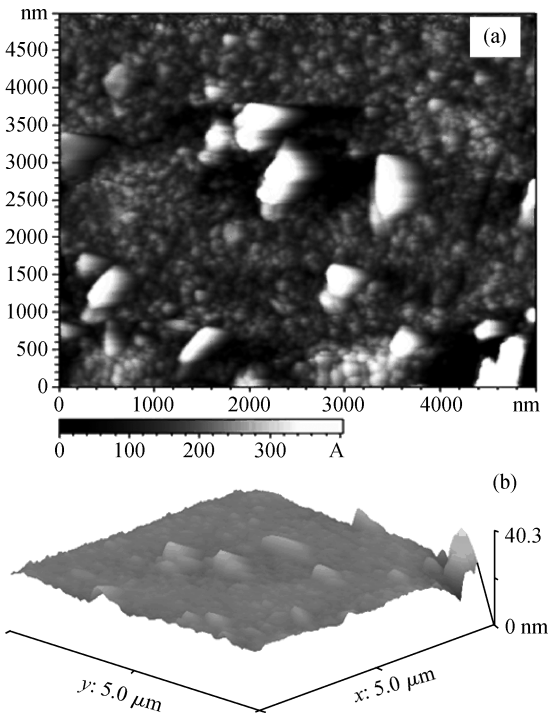

Fig. 4. AFM (a) 2D and (b) 3D micrographs of the Cu_2O-PEPC nanocomposite thin film.

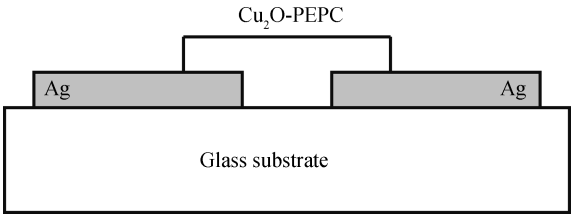

Fig. 5. Schematic diagram of the Ag/Cu_2O-PEPC/Ag humidity sensing device.

The effect of humidity on the electrical properties of the nanocomposite films was investigated by measurement of the capacitance and dissipation of the samples at two different frequencies of the applied voltage: 120 Hz and 1 kHz, at room

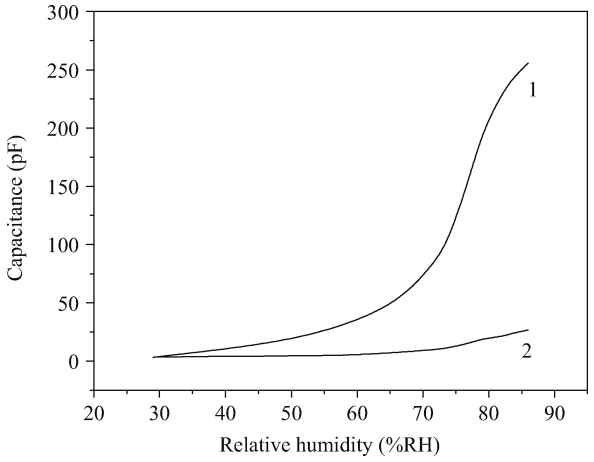

Fig. 6. Capacitance–relative humidity (RH) relationships of the Ag/Cu_2O-PEPC/Ag device measured at (1) 120 Hz and (2) 1 kHz of the applied voltage.

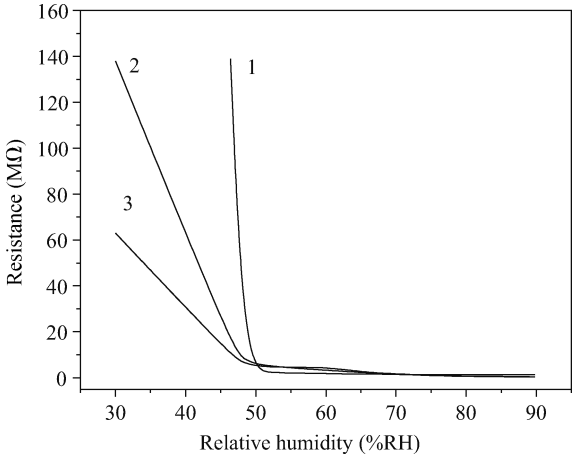

Fig. 7. Resistance–relative humidity (RH) relationships of the Ag/Cu_2O-PEPC/Ag device measured at (1) DC, (2) 120 Hz and (3) 1 kHz of the applied voltage.

temperature. The AC resistance of the samples was determined from the dissipation values, and the DC resistance was measured directly. A cross-sectional view of the fabricated Ag/Cu_2O-PEPC/Ag sensor is shown in Fig. 5.

The resistance (R) of the sample was determined from the values of dissipation (D) from the following expression[21]:

$$R = \frac{1}{2\pi f C D}, \tag{1}$$

where f is the frequency and C is the capacitance.

For the ageing, the capacitance and resistance of the freshly fabricated sample were investigated several times. It was found that on average, the effect of humidity on the capacitance and resistance decreased in the ageing process by approximately 50%–60%.

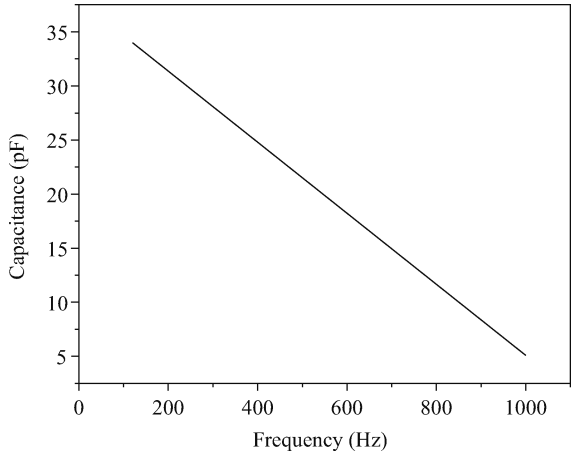

Fig. 8. Capacitance–frequency relationships for the Ag/Cu_2O-PEPC/Ag device measured at a relative humidity of 60%.

3. Results and discussion

Figure 6 shows the capacitance–relative humidity (RH) relationships of the Ag/Cu_2O-PEPC/Ag sample measured at 120 Hz and 1 kHz of the applied voltage. It is seen from Fig. 6 that at 120 Hz and 1 kHz under a humidity of up to 86% RH, the capacitance of the sample increased by 85 and 8 times, accordingly, with respect to 30% RH conditions. Figure 7 shows that at 120 Hz and 1 kHz, the resistance of the sample decreased by 345 and 157 times, accordingly, with respect to 30% RH conditions. The DC resistance–humidity relationships (Fig. 7) of the sample were sharper than the AC resistance relationships. In a humidity range of 46%–52%, the DC resistance decreased by 63 times, whereas the AC resistance at 120 Hz and 1 kHz decreased by 3 and 2.2 times, respectively. The increase in capacitance and decrease in resistance of the sensor might be caused by the absorption of water vapor in the semiconductor thin film, the formation of charge transfer complexes (CTC) and doping of the nanocomposite by H_2O.

The response (in the case of absorption) and recovery (in the case of desorption) time is an important parameter for humidity sensors. The response time of the sensor was measured from 30% to 90% RH at room temperature. The response and recovery times were about 10 s and 30 s, respectively, for capacitive measurements, while 12 s and 34 s for resistive measurements. The response times were shorter than the recovery times. Sensitivity (S) was determined for capacitive and resistance humidity measurements using relations:

$$S_{\mathrm{C}} = \frac{\Delta C}{\Delta(RH)}, \tag{2}$$

and

$$S_{\mathrm{R}} = \frac{\Delta R}{\Delta(RH)}. \tag{3}$$

The sensitivity of the sensor for capacitive measurements (Fig. 6) is 0.83 pF/% and 0.17 pF/% at 120 Hz and 1 kHz, respectively. For resistive measurements (Fig. 7), the sensitivity of the sensor is 65 MΩ/% for DC resistance, and 8 MΩ/% and 3 MΩ/% for AC resistance at 120 Hz and 1 kHz, respectively.

Figures 8 and 9 show the capacitance–frequency and resistance–frequency relationships for the Ag/Cu_2O-PEPC/Ag sample measured at a relative humidity of 60% and 46%, respectively. It is seen that capacitance and resistance decrease with an increase of frequency by 14 and 7 times, respectively.

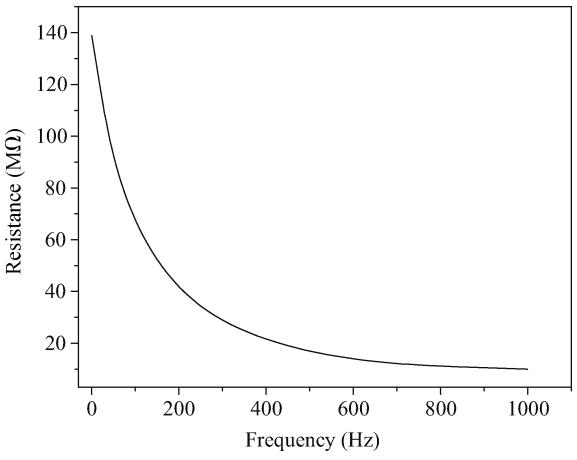

Fig. 9. Resistance–frequency relationships for the Ag/Cu_2O-PEPC/Ag device measured at a relative humidity of 46%.

This may be due to a relatively longer (with respect to the period of applied AC voltage) relaxation time[22], that may result in a decrease in the displacement current due to orientation and deformation of H_2O molecules under the effect of an electric field[23].

The capacitance depends on a number of parameters as the capacitor's plate area, the distance between the plates and the relative dielectric constant of the materials between the plates. The relative capacitance increase with the increase in humidity can be explained by taking into account the different types of polarizabilities. As is known, the capacitance value depends on the polarizability of the material, and basically there are several sources of it as dipolar (α_{dip}), ionic (α_i) and electronic (α_e) polarizability[22].

Electronic polarizability is the most universal and arises due to relative displacement of the orbital electrons. As there is a strong effect of humidity on the capacitance and resistance of the sensor, we assume that the absorption of H_2O increases the dipolar polarizability (α_{dipH}) in the Cu_2O-PEPC nanocomposite with respect to the dipolar polarizabilty (α_{dip}) due to Cu_2O, PEPC and some uncontrolled impurities. The dipolar, ionic and electronic polarizabilities probably affect the capacitance at low frequency (120 Hz, 1 kHz) measurements of the capacitance, whereas electronic polarizability has an influence at higher frequencies. In Refs. [24–26], it has been reported that the polarizability was observed due to the transfer (α_{tn}) of charge carriers as electrons and holes that were present at normal conditions. Therefore, we may write for the total polarizability (α_n) at normal conditions (RH is equal to 30%):

$$\alpha_n = \alpha_{dip} + \alpha_i + \alpha_e + \alpha_{tn}. \quad (4)$$

For the samples affected by humidity conditions (RH is above 40%), the total polarizability (α_h) may be given by the following relationship:

$$\alpha_h = \alpha_{dipH} + \alpha_i + \alpha_e + \alpha_t, \quad (5)$$

where α_t is the polarizability due to the transfer of electron/hole charge carriers produced under the effect of H_2O molecules, which are playing the role of dopants. Here we take into consideration that the concentration of H_2O molecules, charge carriers and total polarizability (α_h) are humidity dependent.

The simulation of the capacitance–humidity relationship based on the Clausius-Mosotti relation[22] was presented in Ref. [16].

As capacitance/resistance–humidity relationships show non-linear behavior, the use of op-amp logarithmic amplifiers[27] allows us to linearize the humidity response of this sample for practical applications in instrumentation.

Figures 6 and 7 indicate that at lower humidity the resistance and at higher humidity the capacitance show high sensitivity. This means that the Cu_2O-PEPC composite may be used for the development of humidity sensors where a combination of resistance and capacitance measurements may be used to cover a wider humidity range.

4. Conclusion

The humidity sensing properties of Cu_2O-PEPC nanocomposite films, deposited from solution by drop-casting, were investigated. It was observed that the capacitance increased and the resistance decreased with an increase in humidity level. It is assumed that in general: (1) the capacitive response of the sensor is associated with dipolar polarization of the absorbed H_2O molecules by nanocomposite films and polarization due to the transfer of charge carriers; and (2) the decrease in resistance is due to the increase in H_2O molecule concentration and displacement currents, and the concentration of charge carriers doped by water molecules.

Acknowledgements

The authors are grateful to the GIK Institute of Engineering Sciences and Technology for its support in this work and the COMSATS Institute of Information Technology, Islamabad, Pakistan, for providing the necessary research facilities.

References

[1] Weng Q, Yang S. Urban air pollution patterns, land use, and thermal landscape: an examination of the linkage using GIS. Environ Monit Assess, 2006, 117: 463
[2] Anjaneyulu Y, Jayakumar I, Bindu V H, et al. Real time remote monitoring of air pollutants and their online transmission to the web using internet protocol. Environ Monit Assess, 2007, 124: 371
[3] Joyce A, Adamson J, Huntley B, et al. Standardisation of temperature observed by automatic weather stations. Environ Monit Assess, 2001, 68: 127
[4] Rittersma Z M. Recent achievements in miniaturized humidity sensors: a review of transduction techniques. Sensors Actuator A, 2002, 96: 196
[5] Lee C Y, Lee G B. Humidity sensors: a review. Sens Lett, 2005, 3: 1
[6] Chen Z, Lu C. Humidity sensors: a review of materials and mechanisms. Sens Lett, 2005, 3: 274
[7] Korvink J G, Chandran L, Boltshauser T. Accurate 3D capacitance evaluation in integrated capacitive humidity sensors. Sens Mater, 1993, 4: 323
[8] Rittersma Z M, Splinter A, Bodecker A, et al. A novel surface-micromachined capacitive porous silicon humidity sensor. Sensors Actuators B, 2000, 68: 210

[9] O'Halloran G M, Sarro P M, Groeneweg J, et al. A bulk micromachined humidity sensor based on porous silicon. Int Conf Solid-State Sens Actuators, 563 Chicago, IL, USA, June 1997
[10] Park S, Kang J H, Park J, et al. One-bodied humidity and temperature sensor having advanced linearity at low and high relative humidity range. Sensors Actuators B, 2001, 76: 322
[11] Carr-Brion K. Moisture sensors in process control. New York: Elsevier, 1986
[12] Grange H, Delapierre G, Seiyama T. Chemical sensor technology. Vol. 2, 154. Tokyo: Kodansha; Amsterdam: Elsevier, 1989
[13] Grange H, Delapierre G, Seiyama T. Chemical sensor technology. Vol. 2, 155. Tokyo: Kodansha; Amsterdam: Elsevier, 1989
[14] Matsugnchi M, Sadaoka Y, Nosaka N, et al. Effect of sorbed water on the dielectric properties of acetylene-terminated polyimide resins and their application to a humidity sensor. J Electrochem Soc, 1993, 140: 825
[15] 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
[16] Karimov K S, Akhmedov K, Qazi I, et al. Poly-N-epoxypropylcarbazole complexes photocapacitive detectors. JOAM, 2007, 9: 2867
[17] Musa A O, Akomolafe T, Carter M J. Production of cuprous oxide, a solar cell material, by thermal oxidation and a study of its physical and electrical properties. Solar Energy Mater Solar Cells, 1998, 51: 305
[18] Nair M T S, Guerrero L, Arenas O L, et al. Chemically deposited copper oxide thin films: structural, optical and electrical characteristics. Appl Surf Sci, 1999, 150: 143
[19] Zhang H, Goodner D M, Bedzyk M J, et al. Formation and kinetics study of cuprous oxide nanodots on $LaAlO_3$ (001). Chem Phys Lett, 2004, 395: 296
[20] Shahid N A M, Khadar M A. Evolution of nanostructure, phase transition and band gap tailoring in oxidized Cu thin films. Thin Solid Films, 2008, 516: 6245
[21] Irwin J D. Basic engineering circuit analysis. 6th ed. New York: John Wiley & Sons, 1999
[22] Omar M A. Elementary solid state physics. Singapore: Pearson Education Inc, 1999
[23] Hibbert D B. Introduction to electrochemistry. Mackays of Chatham PLC Chatham, Kent, UK, 1993
[24] Kargin V A, Nauka. Organic semiconductors. Moscow, 1968
[25] Iwamoto M, Manaka T. Organic films and control of current–voltage characteristics by the surface polarization. Proc Int Symp Super-Functionality Organic Devices, IPAP Conf Series 6, 2005: 63
[26] Amy F, Chan C, Kahn A. Polarization at the gold/pentacene interface. Organic Electronics, 2005, 6: 85
[27] Simpson C D. Industrial electronics. Prentice Hall Inc, USA, 1996