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Capacitance and Resistivity Measurements of Polythiophene /Metallic Nanoparticles-based Humidity Sensors

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Abstract

Capacitive–resistive humidity sensors based on polythiophene (P3HT) organic semiconductor as an active material hybrid with three types of metallic nanoparticles (NP) (Ag, Al, and Cu) were synthesized by pulsed laser ablation (PLA). The hybrid P3HT/metallic nanoparticles were deposited on indium-tin-oxide (ITO) substrate at room temperature. The surface morphology of theses samples was studied by using field emission scanning electron micrographs (FE-SEM), which indicated the formation of nanoparticles with grain size of about 50nm. The electrical characteristics of the sensors were examined as a function of the relative humidity levels. The sensors showed an increase in the capacitance with variation in the humidity level. While the resistivity While the resistivity decrease nonlinearity in the variation of humidity level from 10% to 100%.. The results show that the recovery and response times were higher for the Al/P3HT/Cu/Al sensor compared with those of the other nanoparticles.

Keywords: P3HT, metallic nanoparticles, humidity sensor.

قياسات مقاومة السعوية لأجهزة استشعار الرطوبة من البوليثيوفين / الجسيمات النانوية المعدنية

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الخلاصه

تم تصنيع متحسس الرطوبة المقاومة– السعوية القائم على أشباه الموصلات العضوية من البوليثيوفين (P3HT)كماده فعالة مهجنة مع ثلاثة أنواع من الجسيمات النانوية المعدنية (المنيوم ،فضه ونحاس) بطريقة الاستئصال بالليزر النبضي. ترسب الأغشية الرقيقة الهجينة للبوليمر /الدقائق المعدنية النانوية على ركيزة من أوكسيد قصدير الإنديوم في درجة حرارة الغرفة. تمت دراسة التشكل السطحي للعينات باستخدام صورة مجهرية إلكترونية لمسح انبعاث الحقل والتي توضح تكوين الجسيمات النانوية وكان الحجم الحبيبي حوالي 50 نانومتر. تمت دراسة الخصائص الكهربائية لجهاز الاستشعار كدالة لمستويات الرطوبة النسبية. أظهر المتحسس زيادة في السعة مع تباين في مستوى الرطوبة. بينما أظهرت المقاومة انخفاضًا غير خطيا في تباين مستوى الرطوبة من 10% الى 100%. أظهرت النتائج أن وقت الاسترداد والاستجابة كان أعلى بالنسبة لمستشعر Al / Al / Cu / P3HTمقارنة بالجسيمات النانوية الأخرى

Introduction

For many years, metal oxide semiconductors were essential to fabricate sensors and used in many applications such as industrial process control, toxic and chemical material detection, and environmental monitoring [1, 2]. Nowadays, the nanostructure semiconductors are composed in

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sensors to provide better sensitivities for different gases [3, 4]. Their high sensitivities came from their high surface to volume ratio. Despite that, some limitation were recorded, such as high working temperature [5]. In the last decades, the inorganic semiconductors, especially porous silicon have been used extensively for humidity sensing applications,. Nevertheless, the main problems of high cost and high temperature fabrication procedures urged the scientists to search for better materials. Organic semiconductors are a new class of π-conjugated backbones of macromolecules, where the electrons can move via an π-electron cloud. They are distinguished by their low cost and easy fabrication. Many mechanisms are involved in controlling the conduction, hopping, tunneling, and mobility gaps of organic semiconductors [6, 7]. Polythiopene (P3HT) was used extensively in transistors, solar cells, and sensors applications due to its elevated hole mobility, good stability, and good electrical conductivity [8, 9].

For environmental monitoring and industrial applications, humidity sensors are very important [10]. Humidity sensors can be classified depending on the measuring principle into capacitive, gravimetric, optical, resistive, and integrated types [11]. With a simple comparison between capacitive with resistive humidity sensor, the former show good linearity and greater stability at higher humidity levels. The operation mode of capacitive sensors involves the change in the dielectric constant for the used thin film as humidity sensing occurs with varying humidity levels [12, 13]. The aim of this work was to increase the sensitivity for humidity by using P3HT with different metallic nanoparticles as an active material in manufacturing Al/ P3HT / metallic nanoparticles/Al. The effects of varying capacitance and resistance to various humidity levels are tested at different frequencies.

Experimental Part

Poly(3-hexylthiophene-2, 5-diyl) Regioregular polymer was used as an active material with a molecular weight of 28000Da, supplied by American Dye Source, Inc. Canada. The molecular structure of P3HT is shown in Figure-1. Three metals of high purity were used (Al, Cu, Ag), supplied by the same manufacturer. Chloroform (CHCl3) with high purity was used as a solvent. The vacuum chamber was maintained at a pressure of 2×10^{-5} mbar throughout the evaporating process. The nanoparticles were synthesized in P3HT solution by laser ablation. Briefly, 0.21g of P3HT was dissolved in 3ml of chloroform solvent and left overnight to complete the solvation. Metal slices of $1cm^2$ dimension were cleaned in ethanol and dried, then placed in 3 ml of P3HT solution and irradiated with a pulsed (6 ns) Nd:YAG laser at 532 nm, with 10 Hz repetition rate, 1000Watt, and 20 min irradiation time . To ensure well homogeneous films, spin coating was used with 2500 rpm for 60s. The films were annealed at 60°C to remove any remaining solvent. As a substrate, indium-tin-oxide (ITO) glass was used in order to manufacture organic semiconductors' surface type capacitor. The ITO substrates with dimensions of 25 × 25 mm were washed with acetone and ethanol and ultrasonically placed in deionized water for 20 minutes. After drying, aluminum electrodes with thickness of 150 nm were thermally deposited on the entire back-side of the substrate, with 50 ± 5 μm gap between them via a shadow mask. The evaporation rate for the deposition was adopted to be 0.3 nm/s. Then the solution was spin-coated on the ITO substrate with deposited aluminum electrodes with a surface area of $15 \times 5mm^2$. After spin-coating, these thin films covered homogeneously the gap between the aluminum electrodes. These samples left to dry for 24h at room temperature to form the humidity sensor Al/P3HT/metallic NP/Al.

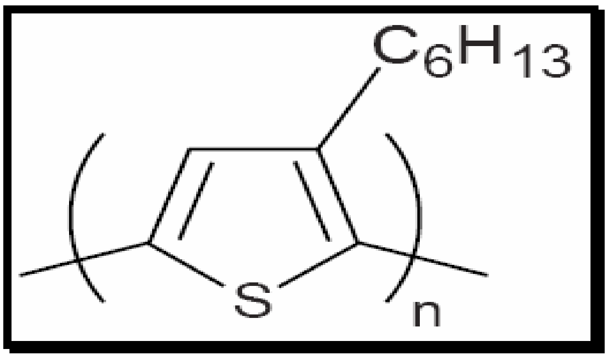

Figure 1-Molecular structure of P3HT [14].

Calculation of Humidity Sensor Parameters

Many parameters affect the capacitance, such as glass substrate area, thickness of the films, and dielectric constant of the materials. Generally, Clausius-Mosotti relation solves the relation between the dielectric constant and polarization [15, 16].

$$\frac{\varepsilon_{dry}-1}{\varepsilon_{dry}+1} = \frac{N_{dry}\alpha_{dry}}{3\varepsilon^{\circ}} \quad \text{................(1)}$$

where ε_{dry} and ε° represents the relative permittivity and the permittivity of free space, respectively, N is the total number of molecules per unit volume, and α is the molecular polarizability. The relative permittivity can be expressed as:

$$\varepsilon_{dry} = \frac{(1+2N_{dry}\alpha_{dry})}{(1-2N_{dry}\alpha_{dry})} \quad \text{..............(2)}$$

Also, the same relation can be given for dielectric constant at high humidity

$$\varepsilon_H = \frac{(1+2N_H\alpha_H/3\varepsilon^{\circ})}{(1-2N_H\alpha_H/3\varepsilon^{\circ})} \quad \text{................(3)}$$

N_H and α_H represents the number of molecules per unit volume and the molecular polarizability in humidity, respectively, and can be expressed as

$$N_H\alpha_H = N_H\alpha_H(1+KH) \quad \text{................(4)}$$

where H and K represent the relative humidity and humidity capacitive factor, respectively. As it is obvious, the value of $N_H\alpha_H$ depends on the relative humidity level.

The relationship between the dielectric constant and capacitance for humidity is given as:

$$\frac{C_H}{C_{dry}} = \left(\frac{\varepsilon_H}{\varepsilon_{dry}}\right)^n \quad \text{............... (5)}$$

Now, the humidity sensor can be written as

$$\frac{C_H}{C_{dry}} = \left(\frac{(1+N_{dry}\alpha_{dry}(1+KH)/3\varepsilon^{\circ})}{(1+N_{dry}\alpha_{dry}(1+KH)/3\varepsilon^{\circ})/\varepsilon_{dry}}\right)^n \quad \text{.............(6)}$$

Results and Discussion

Figure-2 shows FE-SEM images of the P3HT/metallic NPs from our previous work [14]. Figure-2(a) shows the surface morphology of P3HT NPs which are distributed almost homogeneously on the semiconductor surface. In Figure-2(b, c) shows that the nucleation of the nanoparticles is already formed. During the PLA, the heating process will lead to the release of electrons from the materials in the medium and the formation of more NP atoms. The NPs tend to agglomerate in order to form larger NPs. The NPs surrounded by conduction electrons will lead to a repulsion force that will prevent them from further agglomerating. This result agrees with that of Nayel *et al*. [11] and Mustafa *et al*. [14]. The particle size was limited between 20 and 30 nm. This explanation is true for all metallic nanoparticles. For P3HT-Al Np, it was also noted that they are featureless and form strong agglomeration (Figure-2(b). The FESEM images showed clearly that the particles were bound by a surface of amorphous organic residues collected from the polymer decomposition.

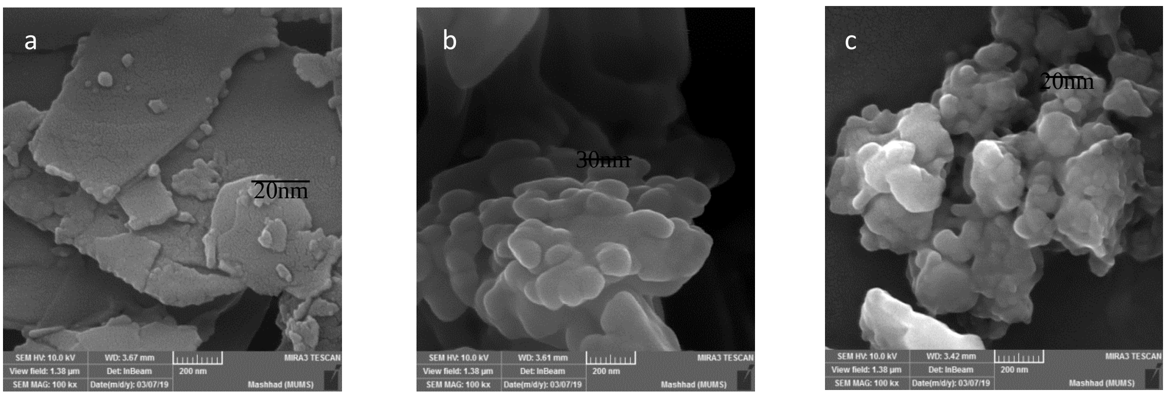

Figure 2-SEM images of P3HT/metallic nanoparticles with size of 200 nm for (a) Ag, (b) Al, and (c) Cu.

Figures-3 and 4 illustrate the normalized capacitance (C/C_0) and normalize resistance (R/R_0) values as a function of relative humidity (RH) for frequency=10KHz and T= 16.2°C. It is clear that the capacitance shows nonlinearity increase in its value for an increase in relative humidity from 10% to 100%. Such behavior can be attributed to two main factors, which are the absorption of water vapor by the porous medium and the dielectric constant of the organic active material. The absorption is affected by surface roughness and porosity. The rougher and more porous surfaces allow for more absorption sites of water molecules. Increasing humidity level leads to an increase in the absorption of water molecules by the organic active material (P3HT/NP) that finally leads to an increase in capacitance. The dielectric constant of the organic active material is used as a dielectric which adsorbs or desorbs water molecules proportional to the relative humidity, which leads to the increase in the capacitance of the sensor [17]. From Figure-3, the differences in capacitance values for each NP can be observed. This is because of the different dielectric constant values for the different NPs, which are equal to 1.8eV for Al, 6.2 eV for Cu, and 12.2eV for Ag. This behavior is illustrated by eq.5. Figure-4, which shows the resistivity as a function of relative humidity of the fabricated humidity sensor, where the resistivity is decreased nonlinearly with increasing relative humidity level

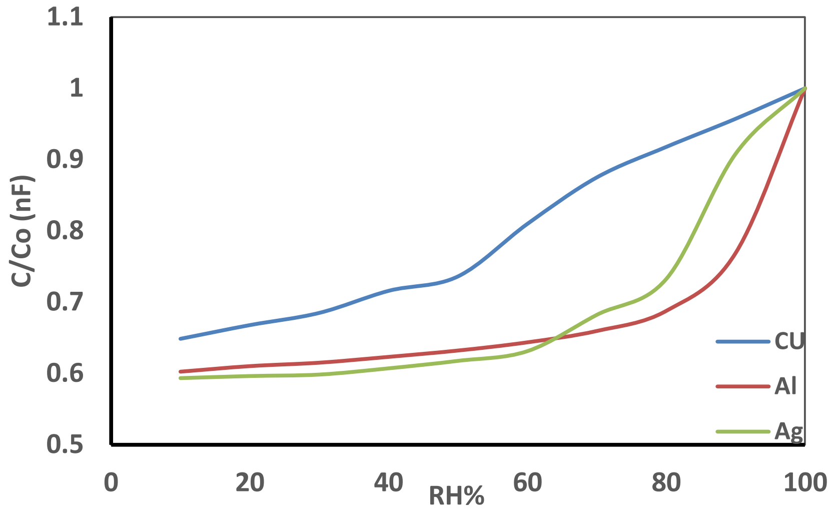

Figure 3-The normalized capacitance (C/Co) versus relative humidity (RH %) for Al/P3HT-metalic NP/Al humidity sensor.

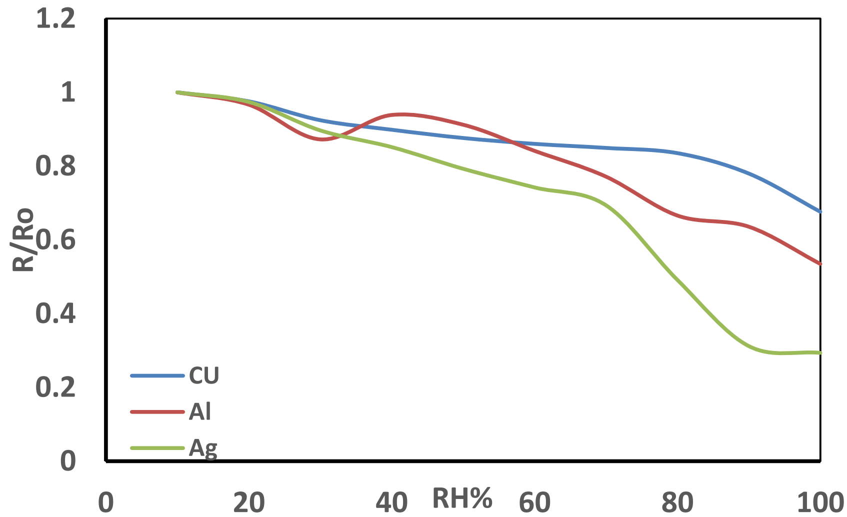

Figure 4-The normalized resistivity (R/Ro) versus relative humidity (RH %) for Al/P3HT-metalic NP/Al humidity sensor.

The response and recover time values are essential parameters which determine the use of sensors for different applications. The response time of humidity sensor is the relation between capacitance and time when changing humidity concentration. In general, response time can be determined by measuring the differences in capacitance after realizing the sensor from a maximum to minimum temperature, which is observed by progression in time. For recovery time, it determines when the sensor is suddenly releases from a minimum to maximum temperature.

The response time can be defined as the time required for a sensor output to adjust to 90% of its final settled value from its previous state. The sensor's recovery time is defined as the time required for the sensor output to decrease to 10% of the final settled value [18]. The values of response and recovery time for each sensor are illustrated in Table-1. Depending on the experimental results, the Al/ P3HT / AlNP /Al shows a fast response and reasonable recovery time.

Table 1-The response and recovery time values for the used sensors

Sensor	Response Time(s)	Recovery Time(s)
Al/ P3HT / CuNP /Al	37	58
Al/ P3HT / AgNP /Al	28	49
Al/ P3HT / AlNP /Al	26	42

Conclusions

In this work, an organic semiconductor of poly(3-hexylthiophene) (P3HT)- inorganic (three metallic nanoparticles ; Al, Ag, and Cu) was produced by pulsed laser ablation (PLA). Drop-casting technique on glass substrates was applied to synthesize the humidity sensor. The performance of this humidity sensor was experimentally studied. The surface morphology shows nanoparticles with a particle size of 50nm. The capacitance increased while the resistance decreased with increasing humidity level, which is caused by increasing the concentration of water vapor molecules. Al/ P3HT /CuNP /Al sensor shows good stability at higher humidity, compared with resistance humidity sensors. The Al/ P3HT / AlNP /Al shows fast response and reasonable recovery times.

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