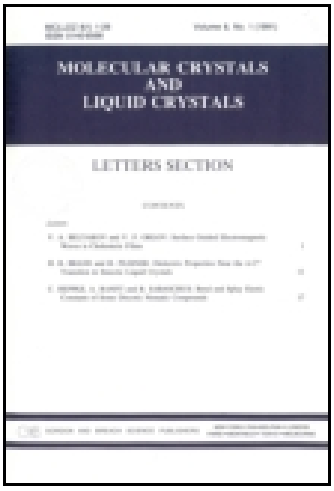

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C_2H_5OH Gas Sensing Based on Poly(3-hexylthiophene)/Nb-Loaded ZnO Nanocomposite Films

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C_2H_5OH Gas Sensing Based on Poly(3-hexylthiophene)/Nb-Loaded ZnO Nanocomposite Films

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The C_2H_5OH gas sensors were developed using flame-made 0.75mol%Nb/ZnO NPs composite with P3HT as the sensing materials. The composite films of P3HT: 0.75mol% Nb/ZnO NPs in the ratio of 4:1, 3:1, 2:1, 1:1 and 1:2 were prepared by drop casting method onto Al_2O_3 substrates interdigitated with Au electrodes. The sensing films were analyzed by XRD, SEM and EDS. The gas sensing of C_2H_5OH was studied at the room temperatures. It was found that the composite films P3HT:0.75mol% Nb/ZnO NPs in the ratio of 2:1 showed the highest sensitivity and fast response time towards C_2H_5OH gas at room temperature.

Keywords P3HT:Nb/ZnO hybrid film; C_2H_5OH; gas sensor; flame spray pyrolysis

Introduction

There is a great approach for the improvement of the mechanical strength and characteristics of oxide semiconductors sensors by combining the conducting polymers (organic) with oxide semiconductors (inorganic) counter parts to form composites. The organic/inorganic composite materials combine the advantages of both materials, flexibility and solution process ability of organic semiconductors, stability and high charge carrier mobility of inorganic semiconductors and simplicity in sensitivity at room temperature. In recent years, many studies of organic/inorganic nanocomposite sensors have been reported by several research groups [1, 2]. The gas sensitivity of the PAni/SnO_2 hybrid to ethanol was studied by Geng L. *et al*. [1]. It was found that the PAni/SnO_2 hybrid material had gas sensitivity only when operated at 60 and 90°C, and it showed the highest sensitive to C_2H_5OH (∼1.36) at 250 ppm and short response time (within 1 min) when operated at 60 °C. Raut B.T. *et al*. [2] found that the camphor sulfonic acid (CSA) doped polyaniline/CdS nanohybrid materials

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showed the sensitivity 3% to 100 ppm C_2H_5OH at room temperature. Saxena V. *et al*. [3] report that P3HT:ZnO-nanowire hybrid sensor was more sensitive and stable to NO_2 and H_2S gas compared to P3HT and ZnO alone at room temperature. Baratto C. *et al*. [4] also proved that composites sensors of P3HT-ZnO had higher response compared to either P3HT or ZnO sensors when exposed towards NO_2 gas at room temperature while virtually no response to CO and ethanol. In order to have a greater understanding of composites materials in sensing performance, nanocomposite sensors of P3HT:0.75mol% Nb-loaded ZnO nanoparticles (Nb/ZnO NP_S) were investigated in this study.

Experimental

Unloaded ZnO and 0.75mol%Nb/ZnO NP_S were synthesized by flame spray pyrolysis (FSP) technique [3]. The precursor solutions were prepared from zinc naphthenate (Aldrich, 8 wt.% Zn) and niobium (V) ethoxide (Aldrich,99.999%) diluted in toluene/methanol in the ratio of 70/30 vol.%. The nanoparticles were characterization by XRD, BET, HR−TEM, EDS.

Composite films were prepared by incorporating regioregular P3HT (Rieke Metals) blends both with and without addition of 0.75mol%Nb/ZnO nanoparticles. The composite sensor had the device configuration (Figure 1) using alumina inter-digitated Cr/Au electrodes on the front side as substrates. In order to make hybrid films of difference composition: 4:1, 3:1, 2:1, 1:1 and 1:2 of P3HT:0.75mol%Nb/ZnO NPs, NPs was dispersed in 0.5 mL of 1-butanol and 15 mg of P3HT was dissolved in 0.5 mL of chlorobenzene. Five sets of P3HT: 0.75mol%Nb/ZnO blend solutions were prepared by adding 0.75mol%Nb/ZnO

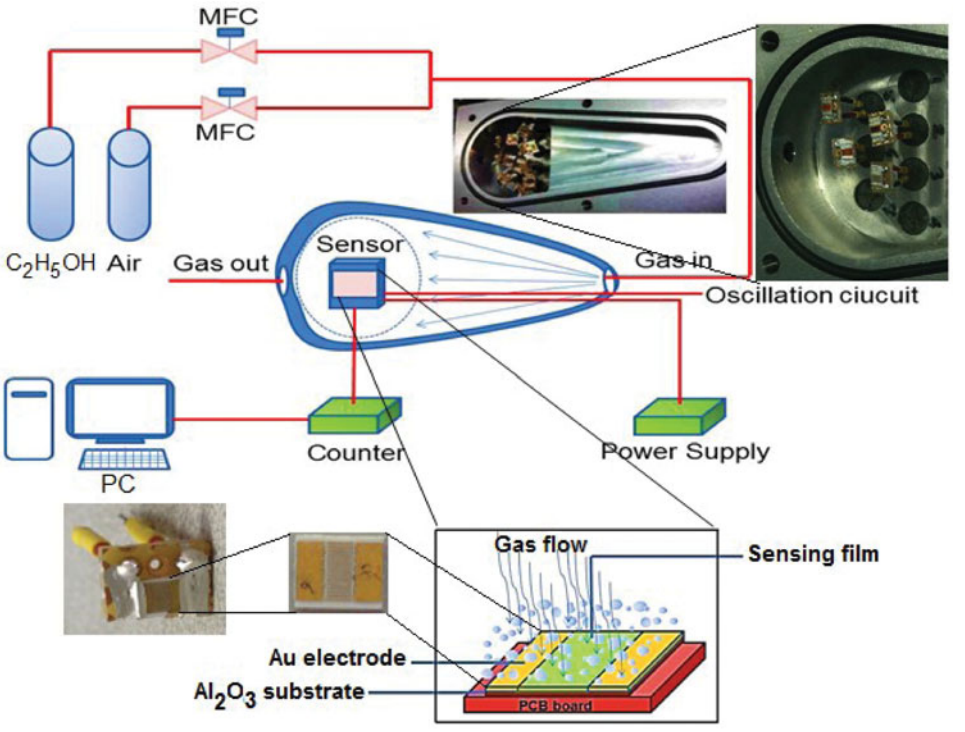

Figure 1. Gas sensing measurement system.

solution to stirred solutions of P3HT. The P3HT:0.75mol%Nb/ZnO blend solutions were drop cast on top of electrode followed by drying in air. In order to make contacts on films for resistance measurements, silver wires were attached using silver paint. After completion, the devices were transferred to a sensor chamber for the sensing tests at room temperature. After the sensing test, the sensing films were analyzed by XRD, FE-SEM and EDS.

The gas sensing tests were performed by the gas sensing measurement system as shown in Fig. 1. In the figure, two mass flow controllers (MFCs) were used to control the flow rate of synthetic air (dry air), the carrier gas and the target gas. The carrier gas and target gas were mixed and introduced to the testing chamber. A PC was connected to the testing circuit to monitor and record the resistance of the sensor. The temperature and humidity of the testing room were controlled by a central air conditioner. The sensing experiments were carried out by measuring the reversible change of resistance of the sensor devices taken under a voltage of 5V dc bias and current measurement through a 6487 Keithley picoammeter. The gas sample exposure time and the clean air restoring time were fixed at 10 min and 10 min, respectively. Ethanol (C_2H_5OH) vapor concentration was varied from 50 to 1000 ppm.

Results and Discussion

The crystalline phase and morphology of the 0.75mol%Nb/ZnO NPs were characterized by X-ray diffraction (XRD). Figure 2 shows that the NPs was highly crystalline and the peak can be confirmed to be the hexagonal structure of ZnO match well with the JCPDS No. 89-1397. Nb peaks was also found in these patterns match well with the JCPDS file No. 34−0370. Figure 3 showed the XRD diffraction patterns of P3HT and P3HT:0.75mol%Nb/ZnO NPs composite sensing films in that the P3HT films can be confirmed to be the monoclinic structure match with the JCPDS No. 48-2040 and the diffraction patterns of (▲) Al_2O_3 (JCPDS file No. 88-0826) and (Δ) Au (JCPDS file No. 89-3697) from the substrates are also visible in these samples. The specific surface area of the NPs was measured by nitrogen adsorption (BET analysis). It was found that the calculated particle size of 0.75mol%Nb/ZnO NPs is 9.12 nm. HR-TEM bright-field image of 0.75mol%Nb/ZnO NPs was presented in our previous work [5]. The ZnO NPs were observed as particles having the clear spherical, hexagonal and rod-like morphologies. The crystallite sizes of ZnO spherical and hexagonal particles were in the range of 5–20 nm. ZnO nanorods were found to be ranging from 5–20 nm in width and 20–40 nm in length.

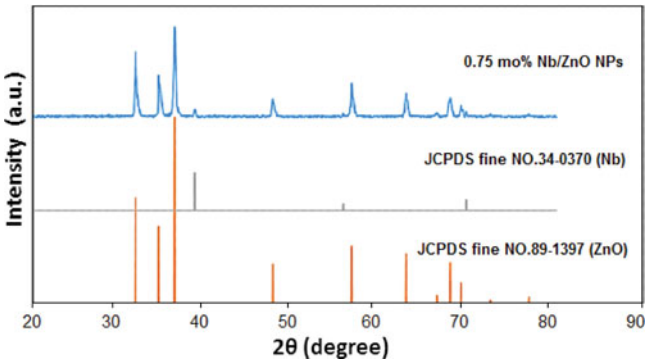

Figure 2. XRD patterns of 0.75 mol% Nb/ZnO NPs.

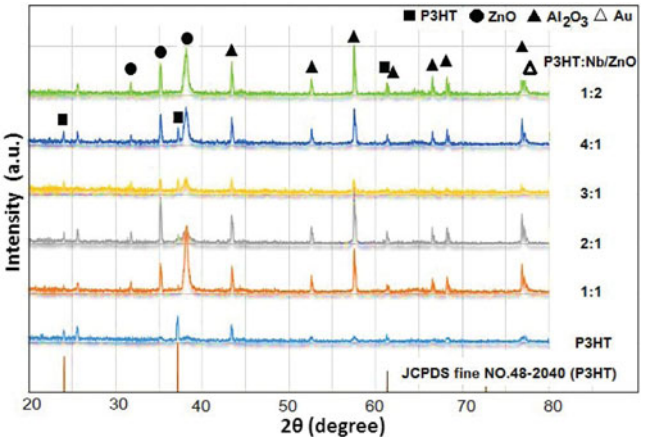

Figure 3. XRD patterns of P3HT sensing films and P3HT:0.75mol%Nb/ZnO NPs composite sensing films.

The surface morphology, cross-section and film thickness of P3HT:0.75mol%Nb/ZnO NPs composite sensing film was observed using SEM analysis as shown in Figs. 4 and 5. The film thickness of sensing film was about 6 μm. This film exhibited porous with good surface homogeneity of P3HT and 0.75mol%Nb/ZnO NPs structures which tremendously

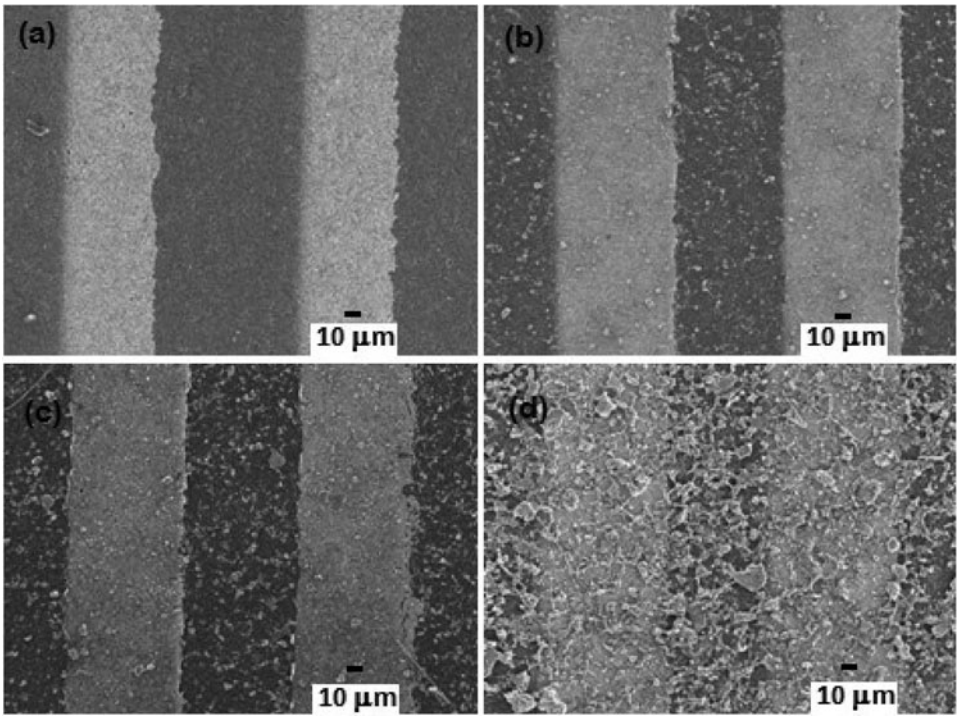

Figure 4. The surface morphology of (a) P3HT (b-d) P3HT:0.75mol%Nb/ZnO NPs composite sensing films in the ratio of 4:1, 2:1 and 1:2 respectively on an Al_2O_3 substrate interdigitated with Au electrodes.

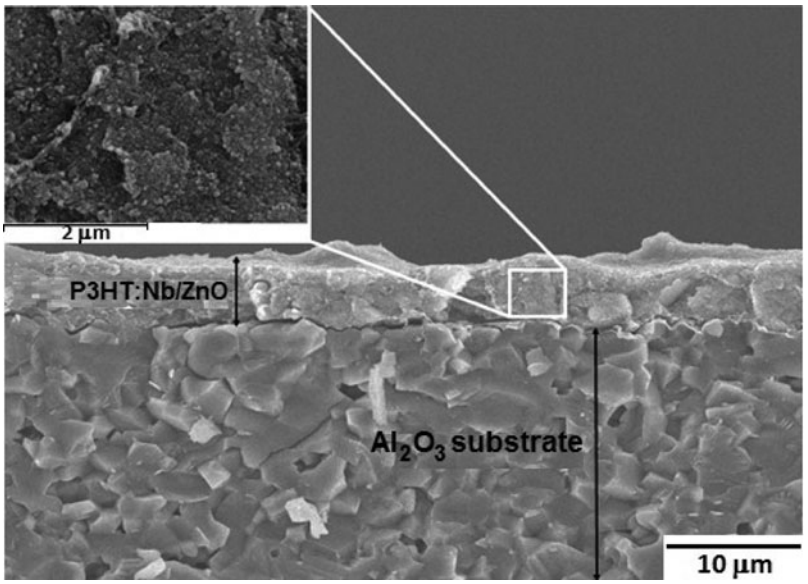

Figure 5. The cross-section and film thickness of P3HT: 0.75mol%Nb/ZnO NPs composite sensing films in the ratio of 2:1 on an Al_2O_3 substrate interdigitated with Au electrodes.

benefited to the C_2H_5OH gas sensing properties. In contrast, the dense film formation due agglomeration of nanoparticles will be decrease the gas absorption at the surface.

In addition, the trends in the elemental composition of the agglomerated composite sensing films formed P3HT:0.75mol%Nb/ZnO NPs was shown by the EDS line scan mode in Figure 6. The elemental-line histograms were shown as signals corresponding to a rich

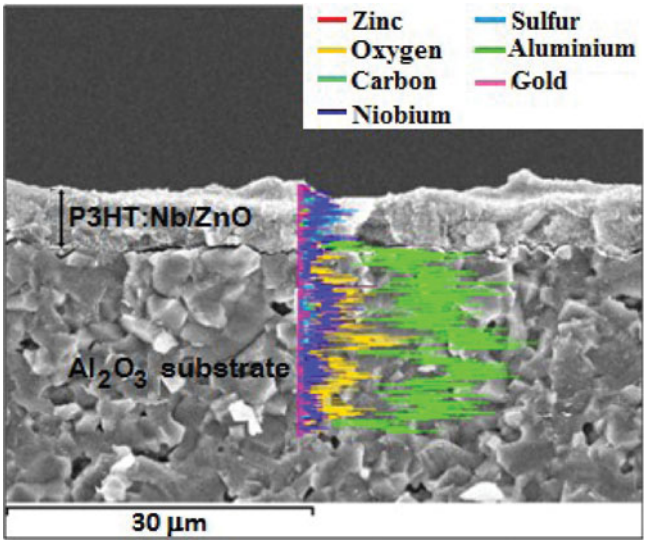

Figure 6. The phase boundaries of microstructures of P3HT:0.75mol%Nb/ZnO NPs (2:1) composite film (up), substrate interdigitated with Au electrodes (down) and EDS elemental-line scan analysis.

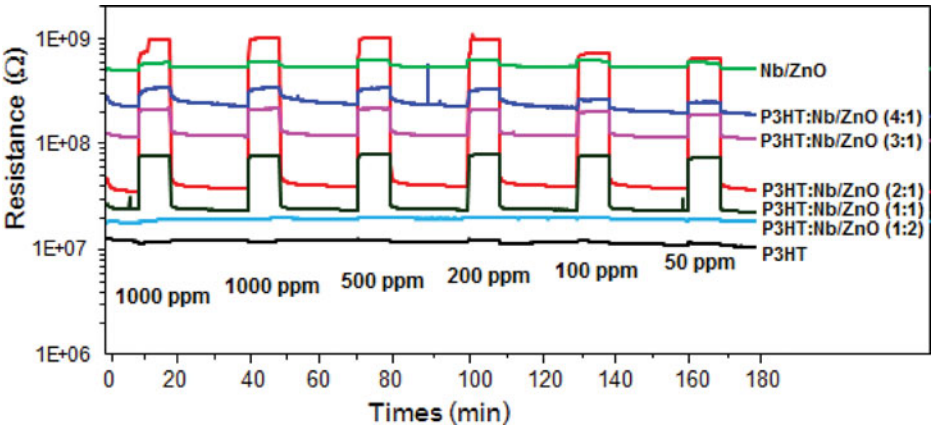

Figure 7. The dynamic response to C_2H_5OH vapor at room temperature of all samples.

in aluminium (Al) caused by the contamination of alumina substrate, zinc (Zn), oxygen (O), carbon (C) and sulfur (S) elements.

The sensing performance was investigated significantly under exposure C_2H_5OH vapor at room temperature with various vapor concentrations (50–1000 ppm) in dry air in terms of the response and response times. For reducing gases including C_2H_5OH, conducting polymer sensor response (S_{rd}) was defined as: $S_{rd} = \frac{R_g}{R_a}$ when Rg and Ra are the electrical resistance when exposed to ethanol and air, respectively. The gas sensing properties of P3HT and P3HT:0.75mol%Nb/ZnO NPs in the ratio of 1:1, 2:1, 3:1, 4:1 and 1:2 sensors at room temperature were tested. Figure 7 shows the dynamic response to 50 to 1000 ppm C_2H_5OH vapor of all samples. It was found that the response to 1000 ppm C_2H_5OH at room temperature of 2:1 P3HT:0.75mol%Nb/ZnO NPs has the highest response (24.8). Figure 8 shows the typical response–response time characteristics of the sensor for 1000 ppm

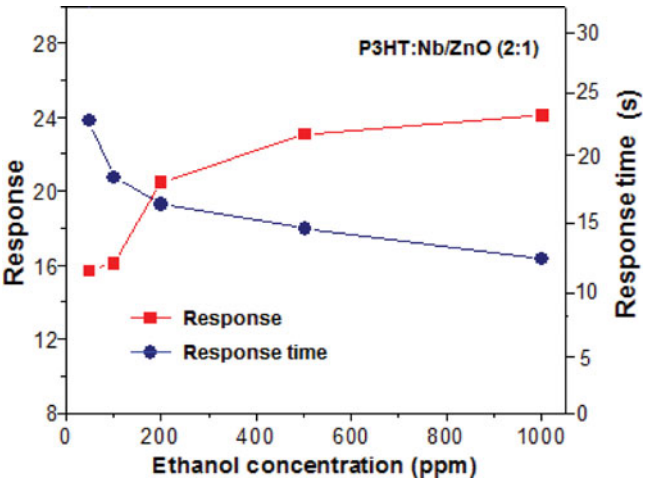

Figure 8. Variation of response (left) with concentration of C_2H_5OH and variation of response times (right) change in resistance at room temperature.

C_2H_5OH at room temperature. The response time is defined as the time taken to reach 90% of the response when gas is introduced. It clearly shows that P3HT:0.75mol%Nb/ZnO NPs sensor in the ratio of 2:1 has the fastest response time (∼11 s).

The possible sensing mechanism for C_2H_5OH detection in these materials is based on reactions that occur at the P3HT: 0.75mol%Nb/ZnO NPs composite sensor surface, resulting in a change in resistance of the P3HT: 0.75mol%Nb/ZnO NPs composite films after adsorption of oxygen [1]. The n-type ZnO formed a hetero-p–n junction to p-type P3HT with a depletion region [4]. When the P3HT:0.75mol%Nb/ZnO NPs composite films were exposed to C_2H_5OH that acted as a acceptance, the depletion region changed, and the resistance of conducting polymer increased continuously. Therefore, the width of the depletion region increased, and the conductivity of the P3HT channel decreased [6].

Conclusions

In conclusion, drop-cast composite thin films consisting of P3HT and 0.75mol%Nb/ZnO NPs (2:1 by weight ratio) exhibited high sensitivity and fast response for C_2H_5OH at room temperature. The results demonstrate that these composite films can be utilized for fabrication of room temperature operating C_2H_5OH gas sensors in the 50–1000 ppm range with high response and very short response time.

Acknowledgments

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