An inkjet printed NO_2 sensor operating under room temperature and low humidity environment

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ABSTRACT

In this paper, a room temperature operation NO_2 sensor based on polypyrrole (PPy) /AZO (5% Al-doped ZnO)/Fe_2O_3 sensing material was developed. For the environmental monitoring, the ambient factor effect for NO_2 detection was discussed. Based on the results, oxygen plays anessential role for NO_2 sensing, which can enhance the reaction between NO_2 and PPy. The sensor shows linear response to NO_2 in range of 3-15 ppm at room temperature. It was reveal that the blending of AZO and Fe_2O_3 can improve the stability of sensor and the response to NO_2, separately. Furthermore, PPy/AZO/Fe_2O_3 based sensor performed good performance till RH 30%, which is verified the capability of environment monitoring. In summary, the blending of AZO and Fe_2O_3 nanoparticles in PPy sensing material is a promising NO_2 sensor for environmental monitoring.

Keywords: inkjet-printing, NO_2 sensor, polypyrrole

1. INTRODUCTION

Air pollution has become a serious problem in recent years. NO_2, this reddish-brown toxic gas has a characteristic sharp, biting odor and is a prominent air pollutant in large cities and the atmosphere. Therefore, many researchers developed various sensing materials for NO_2 sensing, such as SnO_2[1],Fe_2O_3[2]and ZnO[3] etc. However, most of metal oxide materials need to operate at high temperature and leads to the high power consumption sensors. To fabricate a low cost and room temperature operation sensor, polymer material based sensors were developed[4]. In traditional electrochemical sensor, the fabrication is bulky and relatively expensive, which limited the application for environment monitoring.

To resolve these problems, many research were developed a room temperature operation, and simple fabrication sensors. Sarfraz et al. [5] published printed chemical resistive of H_2S sensor on paper substrates, which can operate at room temperature. In addition, F. Molina-Lopez et al. [6] developed humidity sensor by the simple and low cost technology, inkjet-printing process. By these methods, the sensor has the advantage of low cost and low operating temperature.

In this paper, an inkjet-printed chemical sensor based on PPy/AZO/Fe_2O_3 was used for NO_2 detection. The effect of oxygen and humidity for NO_2 detection were also discussed. This sensor provides a room temperature operation and low humidity environmental monitoring capability.

2. EXPERIMENTAL

2.1.Sensor fabrication

A p-type wafer with 300 nm oxide on the top of surface was used as the device substrate. The substrate was cleaned by acetone and isopropyl alcohol. After drying the substrate by N_2 gas, the substrate was heated to remove humidity. Followed by the photolithography, the electrode was defined with W/L in the ratio of 800um/40um. Then the sensing electrode, i.e. 20nm/200nm of Cr/Au electrodes, was achieved by e-gun evaporation and lift-off process.

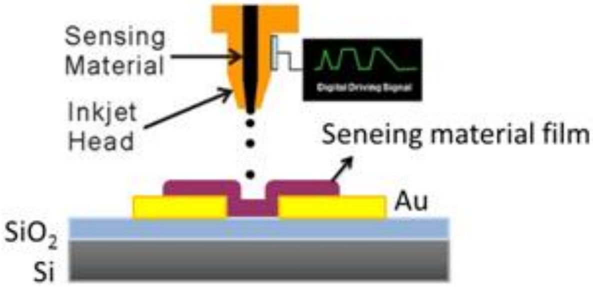

Fig. 1: the inkjet-printing process and device structure

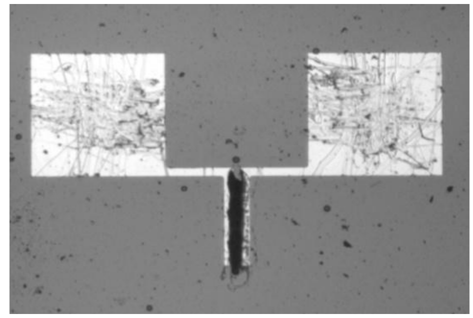

Fig. 2: the optical image of humidity sensor

This process prepared the substrate for the inkjet-printable sensing material.

Polypyrrole (PPy) was synthesized by chemical oxidative polymerization technique using monomer pyrrole. Since PPy is unsolvable in water or some common organic solvent, the sensing film takes two steps of printing process for the in-situ synthesis of PPy.

First, the oxidant solution, 11.47 wt% of $FeCl_3$ was dissolved in de-ionized (DI) water and then printed. The ratio of the $FeCl_3$/pyrrole is studied by [7]. When printing the $FeCl_3$ solution, the humidity should kept in RH20%~RH30%. Later, 4.7 wt% of pyrrole monomer was dissolved in ethanol and then blended with 0.0125 wt% AZO nanoparticle and 0.025 wt% Fe_2O_3 nanoparticle. After adding materials into solutions, the blended solution was put in a sonicator with hot water shaking for 1 hour to improve mixing. Finally, the disperse solution was printed on the oxidant and synthesized to form PPy/AZO/Fe_2O_3 film. To improve the synthesis of PPy, sensor was heated at 100°C for 5 minutes. Finally, sensor was soaked in the methanol solution for 24 hours to rinse off the excess oxidant and the solvent then dry in the ambient environment. The optical image of the fabricated humidity sensor was shown in Fig. 2. Chemical structure of thin film was examined by FTIR technique to ensure the polypyrrole was polymerized successfully.

2.2.Measurement

To measure the response of the developed sensing material, the LCR meter, Agilent E4980A, provides AC 1V to measure the impendence of sensing film with the frequency of 1 kHz. Fig. 3 shows the measure system, the gas sensing was operated in the measure chamber. The NO_2 detection in dry air and N_2 environment was measured to discuss the effect of oxygen. Before gas sensing, the chamber was vacuumed by a mechanical pump for 10 minutes to remove the ambient gases. Followed the dry air (79% N_2 and 21% O_2) or N_2 flushing as the initial condition. After removing dry air or N_2 by vacuuming for 10 minutes, NO_2 with dry air or N_2 was then flow into the chamber and wait for 5 minutes.

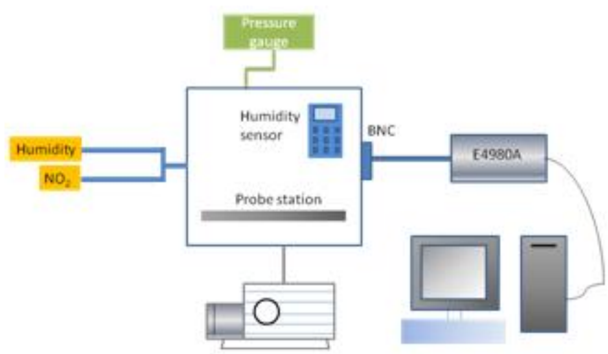

Fig.3: The schematic diagram for gas sensor measurement

Furthermore, NO_2 detected in humidity environment was also tested. For NO_2 detection with various relative humidity conditions, DI water was inkjet and flowed with air and NO_2, separately. Which is in order to make the water fully vaporize. The relative humidity concentration was detected from a commercial humidity meter. All the sensor measurements were carried out at room temperature.

3. RESULTS ANDDISCUSSION

3.1. Gas sensing properties

The sensor was tested for NO_2 and humidity. All the measurement operate at room temperature. For oxidizing gas like NO_2, the independence should decrease on exposure to NO_2. The sensitivity is defined as

$$\text{Sensitivity (\%)} = \frac{R_0 - R_{NO2}}{R_0} \times 100\%$$

Where R_0 represents the sensor in the initial condition. Since the resistance decreased with the rising of NO_2 concentration, the sensitivity can be defined. The reaction time is around 50 seconds, which is relative lower than other polymer sensing material. The fast respond time is due to thin film made by inkjet printing.

Fig.4 shows when the measure chamber flushed by different concentration of NO_2, the impedance decrease. The more concentration of NO_2 is flushed, the more the sensitivity is. Adeel Afzal et al. [8] reported NO_2 sensing mechanism. When PPy thin film is putting in the ambient environment, the oxygen molecules extract electron from PPy causing the formation of oxygen ions O^{2-}, O^- and O_2^- adsorbed at surface. NO_2, the strongly oxidizing gas with high electron affinity 2.28 eV, is much higher than oxygen's 0.43 eV. Hence, the redox reaction take place at the surface. PPy is a P-type material. The more NO_2 molecules interact with the surface, the more electron is absorbed, the hole is accumulated and the impedance decrease. In Fig. 5, we can find when NO_2 flushing to the chamber by air, the PPy thin film shows higher sensitivity. On the other side, NO_2 flushing to the chamber by N_2 shows no sensitivity. This result shows oxygen plays an important role in NO_2 sensing.

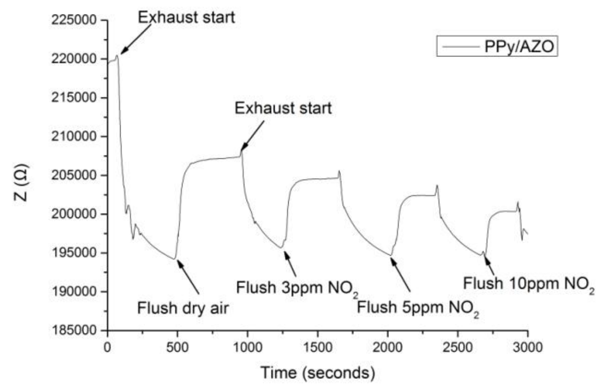

Fig.4: NO_2 response curve of PPy sensor in dry environment

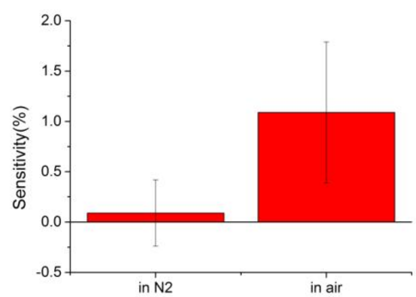

Fig. 5 : The sensitivity to a) 5ppm NO_2+ N_2 and b) 5ppm NO_2+ dry air in room temperature

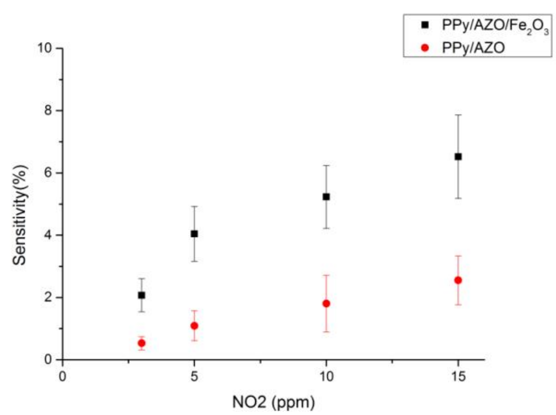

Fig. 6: Response of PPy/AZO and PPy/AZO/Fe_2O_3 film with NO_2 in dry air and room temperature

Fig. 6 shows the sensor doping Fe_2O_3 show higher response. In 3ppm NO_2, 2.07% with Fe_2O_3 relative to 0.53% without Fe_2O_3.In 5 ppm NO_2, 4.04% with Fe_2O_3 relative to 1.09%

without Fe_2O_3.

3.2. Humidity effect

Humidity plays an important role in PPy sensing. Humidity can oxidize PPy, which increase the impedance of PPy thin film [9], [10]. Also, the impedance variation by considering the dipole effect on this polar polymer [11].

As previously discuss, the sensor response to humidity and NO_2 are in opposite direction. It's difficult to distinguish these 2 target gas in high humidity. Fig. 7 shows the sensor still work in RH 20% and RH 30%. However, in high humidity (RH 50% and RH 60%), it's difficult to distinguish the NO_2 concentration. It may cause by the saturation of the PPy surface.

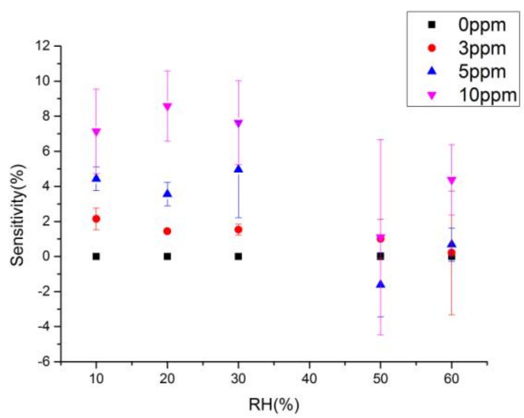

Fig. 7: PPy doped Fe_2O_3 sensor's sensitivity toward NO_2 concentration in different RH% in room temperature

4. CONCLUSION

In this paper, we made a NO_2 gas sensor by PPy. PPy thin film prepared by inkjet printing method can reduce its material waste and easy fabrication. For understanding the nanocomposite, the sensitivity between doping Fe_2O_3 or not is also studied. After adding Fe_2O_3, the sensor shows higher response. This sensor can detect down to 3ppm NO_2. In summary, the in-situ polymerized PPy sensing material by inkjet-printing technology is a promising NO_2 sensor for environmental monitoring.

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