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A New Active Organic Component for Flexible Ammonia Gas Sensors

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Abstract

The objective of this study was to realize flexible gas sensors using low cost solution processing such as drop casting. As active sensor material, a p-type organic semiconductor, α-ω-hexyl-distyrylbithiophene (DH-DS2T), was used. DH-DS2T based transistors exhibit high mobility together with a good air stability. As a chemical compound, DH-DS2T presents a good solubility in common organic solvent, which means thin films could also processed by solution fabrication. Sensor responses were studied by measuring the current through the semiconductor organic film as an ammonia gas concentration function (NH_3: 25, 50, and 100 ppm). We demonstrate here that DH-DS2T has efficient sensor responses and leads to an efficient fully solution processed gas sensor on flexible substrate.

Keywords : flexible gas sensor, oligomers, organic semiconductors, ammonia detection.

1. Introduction

Flexible electronic structures with the potential to bend, expand and manipulate electronic devices are wide-open and rapidly developing field of academic and industrial research. Low-cost, ruggedness, light weight and ease of manufacturability are just some of the important advantages over their conventional rigid-substrate counterparts. Flexible electronics development began with the first flexible solar cell arrays on a plastic substrate in 1967 to provide flexibility [1, 2]. Afterwards, flexible electronics was driven by solar cell research, then by other applications as organic light emitting diodes, thin film transistors, photovoltaic cells and sensors [3, 4, 5]. Nowadays, sensor fabrication on flexible substrates, including robustness and low cost, is a research field of increasing industry demands [6]. Such novel sensor generation is aimed to open new applications in environmental monitoring, or food and medical industry such as detection directly on food surface or as flexible plasters on the skin [7]. In order to produce flexible low cost sensors, solution processing, soluble

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electronic materials and plastic substrate have to be combined to drastically lower the device fabrication cost, compared to conventional silicon processing [8, 9]. Fabrication of these devices on flexible substrates, particularly on plastic, brings with it new challenges. One way is to use soluble small-molecules, so called oligomers, which were developed as semiconductors providing higher electronic performances than polymers. Such oligomers can be dissolved in common organic solvents and be processed from liquid solution at room temperature. Based on previous work [10], we proposed flexible sensor process based on distyrylbithiophene oligomeres. Oligomer layers used are discussed in terms of their properties, as well as their sensitivity towards the detection of NH_3.

2. Experiment details

Several series of simple structurally and readily available oligothiophene derivatives end-capped with styryl units, DS*n*Ts (*n* = 2-4) were synthesised. Due to their low solubility in common organic solvents, we applied substitution of hexyl chains on α-ω-end positions of DS2T (Figure 1a) as simple approach to increase their solubility (α-ω-hexyl-distyrylbithiophene: DH-DS2T) [11]. Thus, DH-DS2T oligomers can be processed from liquid solution at room temperature. In order to realize fully solution-processed gas sensor, DH-DS2T films were realized by solution drop casting on a polymer flexible substrate bearing printing metal electrodes. Polyethylene terephthalate (PET) sheets were used as flexible substrate. We use a solution containing DH-DS2T in chlorobenzene at $1{,}5\times10^{-3}$ mol/l. Finally, DH-DS2T was drop casted on a PET substrate where metallic ink, purchased from CABOT was prior printed by inkjet printing methods to performed Silver (Ag) interdigitated electrode arrays (Figure 1b). Then, gas sensing experiments were performed by measuring the sensor electrical resistance upon exposing to four controlled gas concentrations (ammonia NH_3, ozone O_3, nitrogen dioxide NO_2, carbon monoxide CO). At room temperature, sensors were exposed to the desired ammonia concentrations which are obtained by mixing a standard gas known volume with dry air.

(a) (b)

Figure 1: (a) Molecular structures of distyryl-bithiophene (DS2T) and α,ω-hexyl-distyryl-bithiophene (DH-DS2T).
(b) Optical microscopy images of DH-DS2T based thin films deposited by drop-casting on Si/SiO2 substrates.

3. Results and discussion

First, sensors were exposed at room temperature to four gases separately (NH_3, O_3, NO_2, CO) at the same concentration level. DH-DS2T sensors showed a visible response only to NH_3, suggesting its sensitivity and potential application in monitoring NH_3.Therefore, our discussion will concern sensor response to ammonia which it is one of the most important industrial chemicals, used as precursor of various nitrogen compounds, including fertilizers, and as refrigerant gas. Sensors were exposed during two minutes to NH_3 concentrations between 25 and 100 ppm at room temperature. Figure 2 represents the sensor response over time of the DH-DS2T device at three ammonia concentrations [11]. DH-DS2T is a p-type semiconductor and the stake in touch with electron gas donors (NH_3) is increasing the resistance due to the holes recombination with electrons gas donors. Thus, we observed sensor resistance increase in ammonia gas presence for all gas concentration and a relatively fast decrease when cutting off NH_3. The changes upon gas exposure are reversible and proportional to ammonia concentrations. The normalized response R_{gas}/R_{air} defined as the sensor resistance ratio at various ammonia concentrations (R_{gas}) to that in synthetic dry air (R_{air}) at 25 ppm shows value of 3.2 which indicate the high potential of DH-DS2T sensors for gas detection below this threshold. Indeed, as a consequence of its large toxicity, the acceptable ammonia concentration at the working place is very low, only 25 ppm for 8 h exposure.

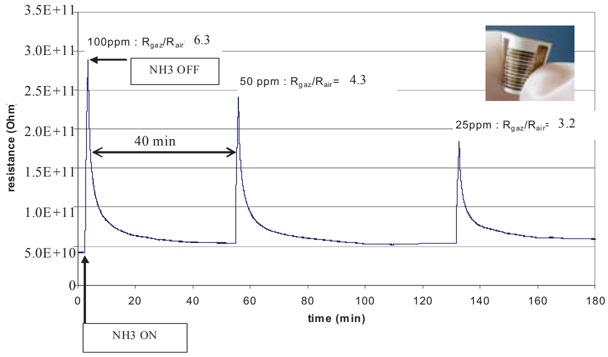

Figure 2: Ammonia sensor response of a sensor based on DH-DS2T drop casted layer on flexible PET substrate (NH_3 exposition time = 2 min). R_{gaz}/R_{air} : normalised response defined as the sensor resistance ratio (R_{gas}) to that in synthetic dry air (R_{air}).

A relevant ammonia chemical gas sensor must therefore detect ammonia concentrations below these thresholds. Moreover, four gas cycles produced similar responses (Figure 3a). Some results have also indicated that the solution concentration influences the sensitivity which is calculated from the following expression:

$$S = R_{gas} / R_{air} \qquad (1)$$

where R_{gas} is the sensor resistance during vapor exposure, and R_{air} the initial resistance. To check the mass concentration effect on the sensor response, various DH-DS2T solutions were exposed to ammonia. The sensitivity variations as function of four mass concentrations under three NH_3 concentrations are presented on figure 3b. This could be explaining by better sensitive layer conduction due to the higher oligomer crystal numbers. Therefore, in dilute DH-DS2T solution, less charge remained on the previously grown layer, and so less NH_3 molecule is adsorbed on the DH-DS2T layer, causing a lower sensitivity.

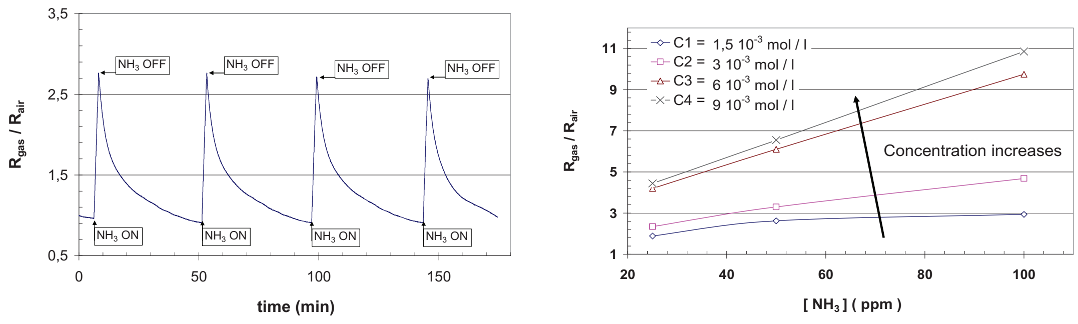

Figure 3: (a) Repetitive sensor response unnder100 ppm NH_3. (b) Sensitivity Evolution according to four concentrations of DH-DS2T solution.

4. Conclusion

A simple and effective method to fabricate flexible gas sensors based on DH-DS2T for ammonia gas detection has been demonstrated. These sensors are simply realized, fairly cheap and operate at room temperature with very low power consumption. This work reports electrical resistance measurements for sensors fabricated from an organic compound and tested at room temperature against ammonia at several concentration level. The sensors, obtained by drop coating on interdigitated electrodes, exhibited potential applications for sensitivity ammonia measurements.

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