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Flexible organic thin-film transistors NO_2 sensors based on poly(3-hexylthiophene)/graphene composite films

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Abstract:
Flexible organic thin-film transistors (OTFTs) based on nitrogen dioxide gas sensors were developed using spin-coated Poly methyl methacrylate (PMMA) as gate dielectric layer and sprayed-coated poly(3-hexylthiophene) (P3HT)/graphene composite materials as active layer. Different mass ratio and film thickness of composite films of OTFTs were fabricated to optimize performance. Optimized flexible OTFT gas sensor exhibited typical transistor characteristics and higher sensitivity at room temperature. Besides, it can undertake 500 cycles mechanical distortion without big change of gas sensitive response under tensile stress (ε=0.23%), gas sensing response is only reduced by 30%. In this work, flexible OTFT gas sensors have excellent mechanical flexibility, and will broaden the range of flexible electronic devices.

Key words: flexible OTFT, NO_2 gas sensor, P3HT, graphene, composite film

Introduction

Graphene, a two dimensional (2D) monolayer of sp^2-bonded carbon atoms, has outstanding electrical properties and high surface-to-volume ratio [1]. In recent years, graphene involved field effect transistors (FETs) and gas sensor have been investigated to improve their performance. In this work, flexible OTFT gas sensors based on sprayed-coated P3HT/graphene composite film were fabricated on15 mm×15 mm ITO (60 nm) coated PEN substrates (0.125 mm). The composite film is also a sensitive film.

Experiments

PMMA was deposited by spin-coating method and annealed at 100℃ in air for 1 hour. Then gold S/D electrodes (60 nm,W/L=33) were evaporated. Finally P3HT and graphene mixed solution was spray deposited to form composite film and drying at 60 ℃. The schematic of the flexible OTFT gas sensor is shown in Fig.1. Devices were measured with a gas sensing test system and a semiconductor characterization system (Keithley SCS-4200).

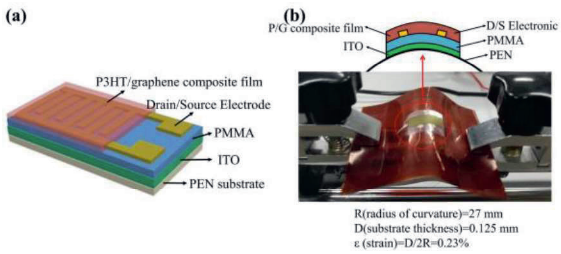

Fig.1. (a) The schematic of flexible OTFT gas sensor on a PEN substrate. (b) The schematic diagram of bending.

Results and discussion

Response (R) and sensitivity are defined based on Eq. (1) and Eq. (2), respectively:

$$R = (I_{gas} - I_0)/I_0 \quad (1)$$

$$S = \Delta R/\Delta C \quad (2)$$

where I_0 is the initial I_{ds}, it's a steady-state value after exposed in dry air for enough time, and I_{gas} is the real-time I_{ds} under different concentrations of NO_2. C is the gas concentration, so the sensitivity (S) is the slope of concentration-response fitting line.

The mass ratio of P3HT and graphene are changed, OTFTs of different mass ratio are respectively marked as PG-1, PG-2 and PG-3 (M_{P3HT}:$M_{graphene}$=60:1, 150:1, 240:1). Graphene functionalized film can enhance the chemisorptions of gas molecules because of no dangling bonds on the surface of intrinsic graphene. As shown in Fig.2 (a), the gas-sensing properties of OTFT gas sensors containing graphene have been improved. PG-2 has largest sensitivity according to Fig.2 (b), but worst repeatability (Fig. 3(a)). Take all things into account, PG-3 is considered to be the best performance device, and is bended outward under tensile stress (ε=0.23%). The bending direction is aligned vertical to the channel direction.

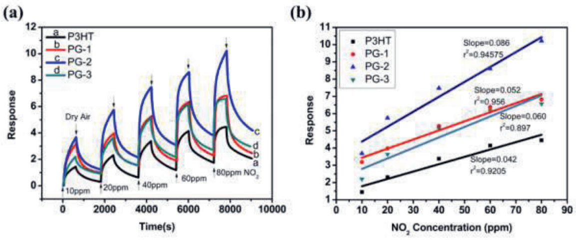

Fig. 2. (a) Real-time NO_2 responses of OTFT gas sensors of different film mass ratio. (b) Linear fitting curves of response and concentration.

The response after bending is exibited inFig.3 (b). It can be found that the response of PG-3 has decreased by 30% (from 6.02 to 4.20) after 500 bending cycles. Incompletely desorbed NO_2 molecules , H_2O and O_2 molecules in air react with the film, which is called doping effect [2], so the response dropped.

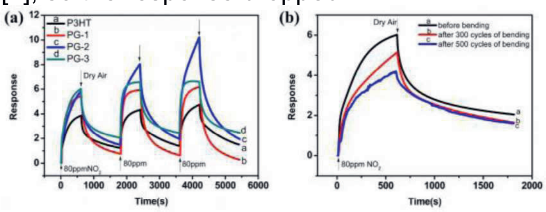

Fig. 3. (a)The repeatability to 80 ppm NO2. (b) Real-time responses of PG-3 before and after bending.

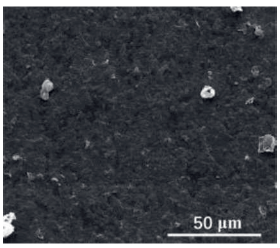

Fig. 4. SEM image of P3HT/graphene composite film

As shown in Fig.4, the P3HT/graphene composite film is rough and graphene is clearly visible on its surface. Fig.5(a) exhibits UV–Vis absorption spectra of composite films. There are two absorption peaks at 535 nm,563 nm, which are attributed to the π-π* conjugate electron transition in P3HT, and one peak at 610nm because of strong inter-chain interactions, respectively [3]. The inset figure describes the influence of solvent on P3HT film, peaks show a red-shift because of the addition of ethanol, indicating the longer conjugation length. Fig.5 (b) and (c) exhibits Raman spectra of films. Two strong peaks at 1379 and 1448 cm^{-1} can be observed, corresponding to C–C and C=C of a thiophene ring, respectively [4]. The Raman spectra of composite films contain peaks at 1345 and1588 cm^{-1}, they are the D and G characteristic peaks of graphene.

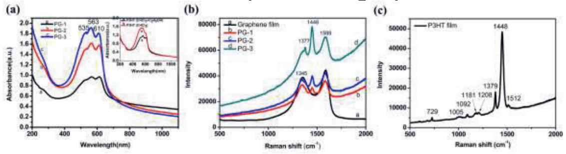

Fig. 5. (a) UV–Vis absorption spectra. (b)(c) Raman spectra.

Conclusions

Flexible organic thin-film transistor gas sensors based on sprayed-coated P3HT semiconductor layer were fabricated on PEN substrates to detect nitrogen dioxide. Mass ratio optimized device exhibites high sensitivity and stable repeatability. In addition, it has excellent mechanical flexibility and could understand 500 cycles of mechanical distortion.

Acknowledgment

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