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Thin film transistors gas sensors based on reduced graphene oxide poly(3-hexylthiophene) bilayer film for nitrogen dioxide detection

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ABSTRACT

Reduced graphene oxide (RGO)/poly(3-hexylthiophene) (P3HT) bilayer films were firstly utilized as active layers in OTFT gas sensors for nitrogen dioxide (NO_2) detection. The OTFT with RGO/P3HT bilayer film exhibited the typical transistor characteristics and better gas sensing properties at room temperature. The electrical parameters of OTFTs based on pure P3HT film and RGO/P3HT bilayer film were calculated. The threshold voltage of OTFT was positively shifted due to the high concentration carriers in RGO. The sensing properties of the sensor with RGO/P3HT bilayer film were also investigated. Moreover, the sensing mechanism was analyzed as well.

1. Introduction

As a toxic gas, NO_2 is produced and released into the environment by internal combustion engines and fuel combustion, especially diesel engines. So far, a lot of researches on NO_2 gas sensors have been reported, including different sensing materials such as inorganic semiconductor oxide [1–3], conducting polymer [4–6], graphene [7–12] and single-walled nanotubes (SWNT) [13], and different types of sensors such as resistance [6–8], quartz crystal microbalance (QCM) [14], OTFT [5,7] and surface acoustic wave (SAW) [15]. Recently, organic thin film transistor (OTFT) gas sensors have attracted great attention, although it was proposed for the first time several years ago [16]. It is peculiar in OTFT gas sensors that the transistor channel materials were also acting as sensitive materials. Graphene, a two dimensional (2D) monolayer of sp^2-bonded carbon atoms, is an ideal sensing material for field effect transistors (FETs) because of its outstanding electrical properties and high surface-to-volume ratio [9,11,12]. Sensors based on graphene were fabricated for detection of such gases as H_2, NO_2, NH_3, H_2O and NO [17,18]. The intrinsic graphene suffers from no dangling bonds on its surface which could enhance the chemisorptions of target molecules [19], therefore, gas sensors based on the graphene functionalized with polymers or other suitable modifiers can improve their gas-sensing properties [20,21]. Among polymers, poly(3-hexylthiophene) (P3HT), a typical p-type conductive polymer, belongs to the class of dissoluble semiconducting polymer, and its mobility was also found to be very high [22]. The good semiconductor performance and good solubility in a variety of organic solvents enabled the material to be widely applied in the OTFT sensors [23–26]. Furthermore, RGO was found to be colloids in organic solvent [27], which made it hard to form RGO-polymer composite solution. And RGO/P3HT bilayer film applied in OTFT gas sensor to detect NO_2 was firstly reported to our knowledge.

In this work, both pure P3HT film and RGO/P3HT bilayer film were fabricated by airbrushing process as active layers of OTFT gas sensors. Their electronic characteristics and gas-sensing properties were characterized and discussed. The sensitivity of bilayer film was improved because of RGO deposited as the bottom layer. Meanwhile, the OTFT gas sensors exhibited outstanding selectivity. Moreover, the sensing mechanisms were analyzed as well.

2. Experimental

2.1. Sensor fabrication

OTFTs with a bottom contact configuration were fabricated on a n+-type (0.02 Ω cm) Czochralski (CZ)-grown silicon wafer. The gate dielectric layer was 195 nm thick thermal SiO_2. The source and drain interdigital electrodes were formed on the top of the gate dielectric by thermal evaporating titanium (Ti) film (20 nm) and gold (Au) film (50 nm). The interdigital electrodes of the source and drain with channel length 50 μm and channel width 8000 μm were realized by photolithography, as shown in Figure 1(a). RGO aqueous dispersion (0.4 wt.%) was purchased from Chengdu Organic

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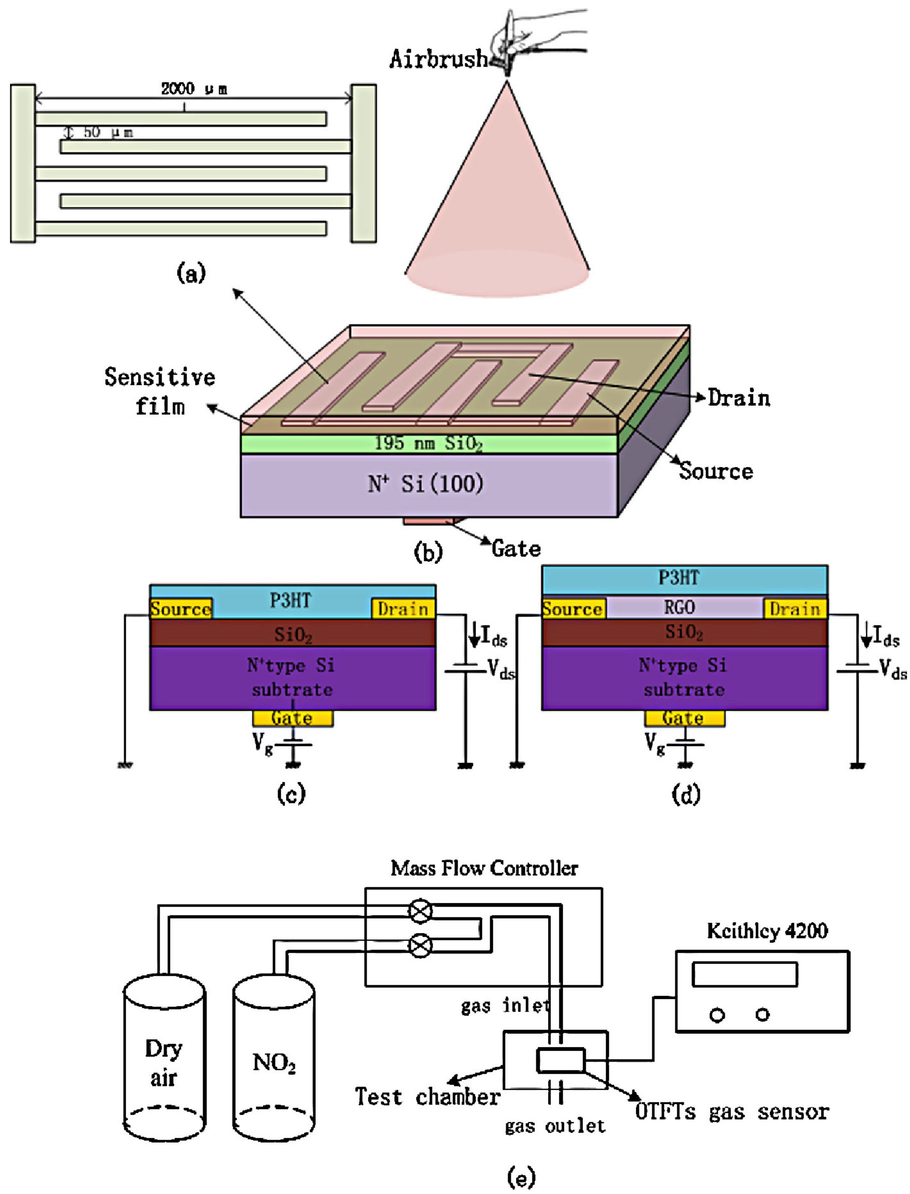

Figure 1. Schematics of (a) interdigital electrodes of the source and drain, (b) OTFT gas sensor and airbrush process, (c) the single layer film as sensitive film, (d) the bilayer film as sensitive film and (e) the schematic of the test system for the gas sensor.

Chemicals Co. Ltd., Chinese Academy of Sciences. 0.1 ml 0.4 wt.% RGO aqueous dispersion was further diluted to 0.004 wt.% by 9.9 ml deionized water. P3HT (purchased from Luminescence Technology Corp.) was dissolved in chloroform with concentration of 67.8 wt.%. The RGO diluted solution was sonicated for 1 h to form uniform solution. In order to decrease the solvent (chloroform) volatilization, the 67.8 wt.% P3HT was only sonicated for 10 min. The active layers of OTFT gas sensors were fabricated by airbrushing the RGO and P3HT solutions in sequence on the source and drain electrodes. The technology of spray-deposited film, a kind of solution process, has been applied in OTFTs [28,29] and sensors [30]. During the process of spray-deposited films, films were formed by depositing small aerosolized droplets, numerous voids were existed. In this case, these voids were thought to be capable of absorption of vapor molecules by weak chemical interactions [31]. In order to remove the organic solvent (chloroform), the devices were heated in a vacuum drying oven at 70 °C all night. The schematic of OTFT gas sensors were given by Figure 1(b). The parameters of OTFT gas sensors were listed in Table 1. The schematics of both sensitive films for these sensors were shown in Figure 1(c) and (d). In this work, three OTFT gas sensors with different airbrushing volume were fabricated, and the thickness of film was proportional to the volume of airbrushing solution.

2.2. Test instrument

The gas chamber made from Teflon for sensor test was 5 cm × 3 cm × 2 cm. The schematic of the test system for the gas sensor was shown in Figure 1(e). To exclude the influence of other

Table 1
Parameters and electronic properties of OTFT gas sensors.

	Device 1	Device 2	Device 3
Sensitive film	Pure P3HT film	RGO/P3HT bilayer film	RGO/P3HT bilayer film
Quantity	1 ml	0.05 ml/1 ml	0.05 ml/1.5 ml
$I_{ds}(V_{ds} = V_{gs} = -50\,V)$ (A)	1.63E−7	6.51E−6	1.46E−6
V_{th} (V)	−8.8	40.9	36.8
I_{on}/I_{off}	3.48	1.55	2.11
μ (cm^2/V s)	8.35E−5	5.56E−4	1.37E−4