Layered Surface Acoustic Wave Hydrogen Sensor Based on Polyethylaniline Nanofibers

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Abstract

Here we report on a layered Surface Acoustic Wave (SAW) gas sensor featuring polyethylaniline nanofibers as the active layer. A rapidly-mixed reaction was employed to synthesize polyethylaniline nanofibers. The product was deposited on a microfabricated ZnO/36° YX LiTaO\textsubscript{3} SAW transducer. Scanning Electron Microscopy (SEM) and Ultraviolet-visible spectroscopy (UV-vis) were utilized to characterize the nanomaterials. The novel sensor was tested towards different concentrations of hydrogen at room temperature. It was observed that the sensor maintained a stable baseline with good repeatability. Hence, the sensor is expected to be potentially attractive for industrial applications.

Keywords: SAW sensors; Polyethylaniline nanofibers; Substituted polyaniline; Hydrogen sensors.

1. Introduction

Conducting polymer gas sensors offer many desirable features including high sensitivities, fast response times and room temperature operation [1]. Due to their rich chemistry and ease of synthesis, conducting polymers can be tailored to accommodate particular device needs.

Polyaniline is one of the most studied conducting polymers for gas sensing applications. Gas sensors based on nanostructured forms of polyaniline offer higher sensitivities towards target gases than those with conventional films due to the higher surface to volume ratios of the nanostructured films compared to conventional ones [2]. The sensitivities of nanostructured polyaniline films towards target gases have been demonstrated to be independent of film thickness due to the highly porous nature of these films [3].

In contrast to the parent polymer polyaniline, the gas sensing properties of alkyl-substituted polyanilines have so far received little attention. Substituted polyanilines are known to have higher dispersibilities in various solvents than that of the parent polymer and some of them possess higher resistance to microbial degradation compared to unsubstituted polyaniline [4].

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In the present report, polyethylaniline nanofibers were utilized as the chemical sensing element of a hydrogen gas sensor. The molecular structure of polyethylaniline used in this study is shown in (Fig 1). It can be seen that the substituent is in the meta position with respect to the benzene ring.

Despite the diversity of methods that have been reported in the literature for the synthesis of the parent polymer (polyaniline) nanofibers, until now there has been little success in synthesizing 1-D nanostructures of alkyl-substituted polyanilines [5]. Recently a template-free general synthetic route has emerged and deployed to the synthesis of substituted polyanilines and other conducting polymers [6-7]. This route provides a facile method to synthesize high quality nanofibers suspended in solutions that can be easily employed in the development of chemical sensors as we have shown in earlier reports, where we fabricated and tested a number of conductometric and layered SAW gas sensors based on polypyrrole, polythiophene and polyanisidine nanofibers [8-11].

For the purpose of this study a layered surface acoustic wave transducer with a zinc oxide intermediate layer was developed. SAW sensors are known for their high sensitivities toward changes in the conductivity or mass of the sensing layer due to the interaction with gas molecules. However, using a layered structure with an intermediate piezoelectric layer help to confine the acoustic energy to the surface, increasing the sensitivity and decreasing the insertion loss [12].

Due to its room temperature operation, this sensor offers less power consumption than metal oxides based sensors that usually operate at elevated temperatures of ~300°C.

2. Experimental

2.1. Microfabrication of layered SAW transducer:

An electron beam evaporator was used to deposit 20 nm of titanium and 80 nm of gold on a 36° YX LiTaO₃ substrate. Etching using a positive photoresist was employed to pattern a two-port resonator with 38 electrode pairs for the input and output interdigital transducers (IDTs) and 160 electrodes in each reflective grating. The aperture width was 700 µm with a periodicity of 40 µm. The centre-to-centre distance between the IDTs was 1920 µm.

A radio frequency (RF) magnetron sputterer was used to deposit the intermediate piezoelectric layer which was a 1.2 µm of ZnO from a 99.99% pure ZnO target with RF power of 120 W. The sputtering gas was 40% O₂ in Ar with a pressure of 1×10⁻² torr, the substrate temperature was 260°C and the deposition time was 60 minutes.

2.2. Synthesis and deposition of polyethylaniline nanofibers:

The chemical synthesis of polyethylaniline nanofibers was conducted in a 20 mL scintillation vial. Ethylaniline (0.39 g, 3.2 mmol) was dissolved in 10 mL of 1 M HCl along with p-phenylenediamine (5.2 mg, 0.05 mmol) which was predissolved in a minimal amount of methanol. A separate solution of 10 mL of 1M HCl containing dissolved ammonium peroxydisulfate (0.18 g, 0.8 mmol) was rapidly mixed with the solution containing the monomer and initiator. The mixture was vigorously shaken for 15 seconds and left unagitated for 1 day after which time the crude product was purified by dialysis against deionized water. The pure polymer was collected and adjusted to a concentration of 2 g/L. In order to conduct UV-Vis spectroscopy, the doped polymer was washed with 0.1 M NH₄OH, dried, and dissolved in N-methyl-2-pyrrolidone (NMP).

Subsequently, the polymer solution was airbrushed onto the surface of the layered SAW transducer using nitrogen gas with a pressure of 200 kPa. A distance of 10 cm between the airbrush tip and the transducer surface was...
maintained during the coating process. The deposition was conducted on a hot-plate with a fixed transducer temperature of 60ºC. As a result a uniform layer of polyethylaniline nanofibers of ~ 500 nm in thickness was deposited on the active region of the layered SAW transducer.

A network analyzer was employed to determine the centre frequency and the insertion loss of the SAW sensor.

3. Results and Discussion

3.1. Characterization of polyethylaniline nanofibers:

A representative SEM image (Fig 2a) shows a nanofibrous mat of polyethylaniline nanofibers with an average nanofiber diameter of 50 nm. Fig 2b is an UV-vis spectrum of polyethylaniline nanofibers that shows two adsorption peaks at 270 nm and 619 nm wavenumbers. There is a noticeable shift in the excitonic transition ($\lambda_{\text{max}}$) to 619 nm compared to that of the parent polymer, polyaniline, found at 630 nm. This observation confirms that polyethylaniline has a slightly higher oxidation state than that of the ideal emeraldine oxidation state [13].

![SEM image of polyethylaniline nanofibers](image1)

![UV-vis spectrum of polyethylaniline nanofibers](image2)

Fig. 2. (a) SEM image of polyethylaniline nanofibers; (b) UV-vis spectrum of polyethylaniline nanofibers.

3.2. Gas sensing results:

The sensor was tested towards different concentrations of hydrogen gas at room temperature. The washing gas was pure dry synthetic air. Fig 3 presents the dynamic response of the sensor. Testing the sensor revealed that it has a stable baseline of 83.95 MHz and good repeatability as shown in Fig 3.

![Dynamic response of polyethylaniline/ ZnO/LiTaO$_3$ SAW hydrogen sensor at room temperature](image3)

Fig. 3. The dynamic response of a polyethylaniline/ ZnO/LiTaO$_3$ SAW hydrogen sensor at room temperature.
The frequency shifts of 9.1 kHz, 14.3 kHz, 20.5 kHz, 26.1 kHz and 30.4 kHz were recorded towards 0.06%, 0.125%, 0.25%, 0.5% and 1% of hydrogen balanced in synthetic air respectively. The 90% response time was 54 seconds for 1% H₂ and the recovery time was 3 minutes. It is expected that during interaction with hydrogen a reduction of the imine sites on the polymer backbone to amine occurs, which decreases the amount of conjugation resulting in a decreased conductivity of the sensing layer causing a decline in the velocity of particle displacement on the surface of the SAW device. This perturbation to the propagating acoustic wave can be measured by recording the shifts of the sensor operational frequency from the centre frequency (baseline) as shown in Fig 3.

4. Conclusions

A novel layered surface acoustic wave gas sensor based on polyethylaniline nanofibers has been fabricated and tested towards various concentrations of hydrogen at room temperature. The synthesis of polyethylaniline nanofibers was conducted through a rapidly mix reaction with the introduction of an initiator to promote homogeneous nucleation of macromolecules. Characterization of the nanomaterial was undertaken using SEM and UV-vis techniques. Testing the sensor concluded that it has a stable baseline and good sensitivity with an operational frequency shift of 30.4 kHz towards 1% of hydrogen gas balanced in synthetic air.

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References