

PSSA Doped Polyaniline Nanofiber Based ZnO/64° YX LiNbO₃ SAW H₂ Gas Sensor

A. Z. Sadek*, K. Kalantar-zadeh*, W. Wlodarski*, C. Baker[†] and R. B. Kaner[†]

*School of Electrical and Computer Engineering
RMIT University, Melbourne, Australia
Email: sadek@ieee.org

[†]Dept. of Chem. and Centre on Functional Engineered Nano Architectonics (FENA),
University of California, Los Angeles, California 90095, USA

Abstract— A polyaniline (PANI) nanofiber based Surface Acoustic Wave (SAW) gas sensor has been developed and investigated towards hydrogen (H₂) gas. A template-free, rapidly-mixed reaction approach was employed to synthesize polyaniline nanofibers, which utilized chemical oxidative polymerization of aniline. Hydrochloric acid (HCl) was used as the dopant acid in the synthesis of the polyaniline nanofibers. Polystyrene sulfonic acid (PSSA) was used to re-dope PANI nanofibers after dialyzing with ammonium hydroxide. Then PSSA doped nanofibers were deposited onto a ZnO/64° YX LiNbO₃ SAW transducer. The sensor was exposed to various concentrations of H₂ gas in an ambient of synthetic air, and operated at room temperature.

Keywords-polyaniline; nanofiber; hydrogen; gas sensor

I. INTRODUCTION

Gas sensors based on semi-conducting metal oxide thin films have been widely used for environmental, industrial and domestic applications. However such sensors suffer from lack of selectivity, long-term stability and high (200-500°C) operating temperatures [1]. Room temperature operation of a sensor is highly desirable, as elevated temperature operation causes long-term instability due to gradual change of the semiconducting metal oxide's structure. With continuous demand for miniaturization, energy saving and long-term stability, there is need to develop a new type of sensors which are highly sensitive and selective, have fast response and recovery and operate at room temperature. As an alternative to metal oxide semiconductors, conducting polymers have received increased interest for use in gas sensing. This is due to their room temperature operation, low production cost, ease of deposition onto a wide variety of substrates [2] and their rich chemistry for structural modifications [3]. Among the family of conducting polymers, polyaniline is one of the most studied materials because of its simple synthesis, good environmental stability and simple non-redox acid doping/base de-doping process to control conductivity [4]. By changing the doping level, the conductivity of polyaniline can be tuned for specific applications such as sensors, actuators, rechargeable battery electrodes, anticorrosion coatings, gas-separation membranes, display devices and field effect transistors [5]. Depending on the extent of the redox reaction, polyaniline can exist in a range of oxidation states: fully reduced leucoemeraldine, half

oxidized emeraldine, and fully oxidized pernigraniline. Polyaniline in the emeraldine oxidation state can be reversibly switched between electrically insulating and conducting forms. The polyemeraldine form consists of amine (-NH-) and imine (=N-) sites in equal proportions. The imine sites are protonated in preference to achieve an intermediate bipolaron form (Fig. 1-middle) which further undergoes a dissociation to form delocalized polaron lattice. A polaron can be considered a type of electronic defect that occurs within the π orbitals of the polymer backbone and is the charge carrier responsible for the high conductivity of doped polyaniline [6]. By controlling the pH of the dopant acid solution, any desired quantity of dopants can be added until all imine nitrogens are doped. Dopants can be removed by a reversible reaction with any common base such as ammonium hydroxide.

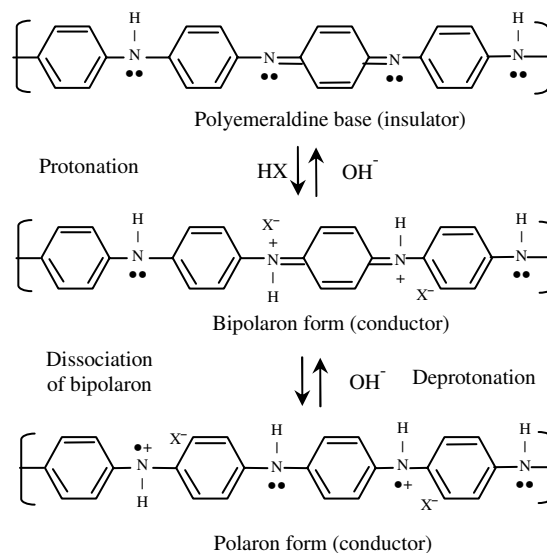


Figure 1. Polyaniline undoped form (top), intermediate bipolaron form (middle) and the fully doped polaron form (bottom) [7].

The conductivity of polyaniline depends on both the degree of protonic acid doping of the imine sites and the redox doping of the main polymer chain [4]. Any interaction with polyaniline that alters either of these processes will affect its conductivity.

As a result, redox active chemicals and gases can affect the conductivity of polyaniline by changing its inherent oxidation state.

However, traditional polyaniline is not as sensitive as metal oxides towards gas species. There have been several reports on improving polyaniline's sensitivity and selectivity by methods such as synthesis of nanostructured forms [8-9], addition of metal catalysts [10-11] and combining with metal oxides [12] and other polymers [13]. Among these options, the synthesis of nanostructured forms appears to be the most promising approach. The effects of sensitive layer morphology, such as grain size, structural formation, surface to volume ratio and film thickness on the sensor sensitivity are well recognized [14]. Gas sensors based on nanostructured materials have been shown to have greater sensitivity due to high surface to volume ratios. Moreover, due to porosity of the film, the entire sensitive layer can be affected by the interactions with the gas species rather than only the surface.

When used as a sensitive layer in gas sensors, polyaniline nanofibers can greatly improve carrier diffusion due to their high surface to volume ratio, and have a large penetration depth for gas molecules [8]. The sensitivity of the conventional polyaniline thin film sensors depends on the film thickness [9]. Generally, sensor sensitivity increases with a reduction of film thickness. Polyaniline nanofibers have a cylindrical morphology and form porous structures when deposited as thin films. Due to this porosity, polyaniline nanofiber based sensor sensitivity is independent of layer thickness. This allows the fabrication of sensors with reproducible responses that have a large tolerance in thickness variation [8].

The hydrogen storage properties of conducting polymers have been actively studied. Cho et al. [15] suggested that 6-8 wt% hydrogen storage in HCl doped polyaniline and polypyrrole at room temperature is possible. The authors attributed this unusual phenomenon to the combined effects of molecular sieving and metallic properties of the conducting polymer. Panella et al. [16] could not reproduce this result and Huang et al. [17] observed a much lower hydrogen storage capacity of 1.44 wt%.

In this work, we present a layered SAW device which is used as the transducing platform. The layered structure consists of a substrate, which is 64° YX LiNbO₃ and an intermediate ZnO protective layer. The ZnO layer protects inter digital transducers from being short-circuited by doped polyaniline nanofibers. Shear-horizontal (SH) leaky surface acoustic wave is the dominant mode in this layered device. For gas sensing, polyaniline nanofibers can be deposited onto the active area of a SAW device as a sensing layer. In a SAW device, the change in electrical conductivity of the sensing layer perturbs the velocity of the propagating acoustic wave due to piezoelectric effects. The center frequency of a SAW device is given by the equation, $v = fp$, where v is the surface wave velocity, f is the center frequency, and p is the interdigitated transducer period. Therefore the variation in velocity can be monitored by measuring the changes in resonant frequency of the SAW device. This change in frequency is proportional to the concentration of analyte present in the environment.

In this paper, polyaniline nanofibers were synthesized from chemical oxidative polymerization of aniline using a template-free, rapidly-mixed reaction approach. PSSA doped polyaniline nanofiber sensitive layer was formed on the layered SAW transducer for H₂ gas sensing. Finally, the responses of the sensor to different H₂ gas concentrations were determined.

II. EXPERIMENTAL

The SAW transducer pattern was formed on a 64° YX LiNbO₃ substrate. The device consists of a two-port resonator with 38 electrode pairs in input and output inter-digital transducers (IDTs), 160 electrodes in each reflective array, 700 μm aperture width and a periodicity of 40 μm. A two-port resonator structure was chosen over a delay line as its higher phase slope increases oscillation stability. The IDTs and reflectors were formed by patterning an 80 nm Au layer by photolithography. The Au layer was deposited on top of a 20 nm Ti layer, for improved adhesion to the substrate. A 1.2 μm thick layer of ZnO was deposited on the surface of the 64° YX LiNbO₃ substrate by radio frequency (RF) magnetron sputtering. ZnO was sputtered deposited 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 10⁻² Torr, the substrate temperature was 260°C and the deposition time was for a periods of 60 minutes.

Previous approaches for making polyaniline nanostructures often require structure-directing templates, which must be removed at the end of the reaction. Recently, a template-free, rapidly-mixed reaction approach was introduced to synthesize polyaniline nanofibers using rapid chemical oxidative polymerisation of aniline [18]. The polymerisation is performed in an aqueous solution where aniline is rapidly polymerized in 1 M HCl acid by the quick addition of the oxidant (ammonium peroxydisulfate ((NH₄)₂S₂O₈)). The ratio of aniline to oxidant is approximately 4 to 1 and the aniline concentration is 0.5 M. Due to the immediate interaction between the monomer and the oxidant, the primary reaction product, nanofibers, is the main morphology present. After completion of the reaction, the product is collected for purification. Filtration, centrifugation or dialysis with water gives pure HCl doped polyaniline. This can be de-doped by washing or dialyzing with aqueous ammonia or sodium hydroxide. For this study, HCl doped solution was dialyzed against 0.1 M ammonium hydroxide (NH₄OH) to obtain dedoped polyaniline nanofibers which then re-doped by mixing 1 M PSSA to the solution. To obtain highly pure polyaniline nanofiber, the solution is cleaned in a five-step centrifugation process. Centrifugation is carried out until a dense pellet forms. Resuspension is done with water on the first centrifugation, then the doping acid. Water is used for the remaining resuspension steps with the final pellet re-suspended to 2 g/L polyaniline nanofibers.

Doped polyaniline nanofiber dispersions were drop cast onto the active area of the ZnO/64° YX LiNbO₃ SAW transducer using a micropipette. It was then left to dry in a clean, dry environment for one day. The gas sensor is made up of two important physical components: the sensitive polyaniline nanofiber layer, which interacts with the gas media

by changing conductivity, and the SAW transducer, which changes its operating frequency with any conductivity change. Using the layered SAW device as a positive feedback element in a closed loop circuit with an amplifier, an oscillator was formed. A frequency counter was used to measure the operational frequency of the transducer upon exposure to the H_2 gas. The operational frequency of the sensor was found to be approximately 109.9 MHz in dry synthetic air at room temperature.

The sensor was mounted inside an enclosed environmental cell. Four mass flow controllers (MFCs) were connected to form a single output that supplied gas to the cell. The gas mixture was delivered at a constant flow rate of 0.2 liters per minute. A computerized gas calibration system was used to vary the concentration of H_2 gas in synthetic air. The sensor responses were displayed in real-time and saved for off-line processing and analysis. Gas exposure time was fixed for each pulse of H_2 gas and the cell was purged with synthetic air between each pulse to allow the surface of the sensor to regain atmospheric conditions. The sensor was exposed to a hydrogen gas pulse sequence of 0.06%, 0.125%, 0.25%, 0.50%, 1%, and 0.06% concentrations in synthetic air at room temperature. A Fluke high-resolution counter (PM66860B) was used to measure the frequency.

III. RESULTS

A scanning electron microscope (SEM) image of the polyaniline nanostructures on the $ZnO/64^\circ YX LiNbO_3$ substrate is shown in Fig. 2. The SEM result indicates that the polyaniline layer deposited on the SAW substrate consists of a large quantity of nanofibers. The average diameter of the polyaniline nanofibers is about 30 nm with lengths up to several microns.

The dynamic response of the sensor to a sequence of different H_2 gas concentrations in synthetic air is shown in Fig. 3. The sensor response, defined as the variation in operating frequency of oscillation due to the introduction of the gas, was 28 kHz towards 1% of H_2 in synthetic air. A relatively fast response time of 1 min and a recovery time of 4 min with good repeatability were observed at room temperature. Fig. 4 shows the frequency shift as a function of H_2 concentrations. It was observed that the PSSA doped polyaniline nanofiber based sensor has higher sensitivity towards H_2 in comparing to the HCl doped [7].

It was observed that the frequency of oscillation of the sensor decrease with the H_2 exposure. It means that the conductivity of PSSA doped polyaniline nanofiber sensitive layer increases after exposure to H_2 gas. The mechanism of polyaniline and hydrogen interactions is not fully understood yet. The SAW sensor results and a separate test of just conductivity show us that resistance decreases in doped polyaniline on exposure to H_2 . The hydrogen may form a bridge between nitrogen atoms on two adjacent chains or there may be partial protonation of some of the imine nitrogens [19]. It has also been suggested that the resistance change is caused by the formation of water [12].

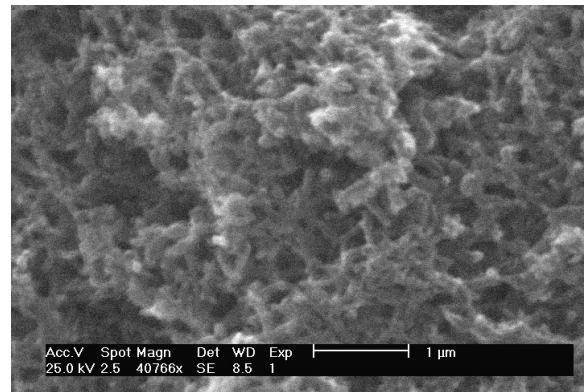


Figure 2. SEM image of PSSA doped polyaniline nanofibers

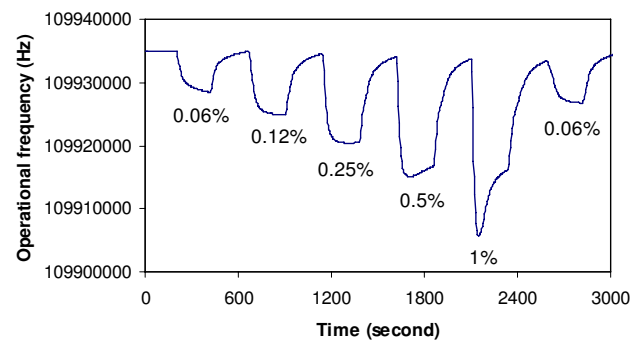


Figure 3. Dynamic response of a PSSA doped PANI nanofiber based 64° YX LiNbO₃ SAW sensor towards H₂ at room temperature.

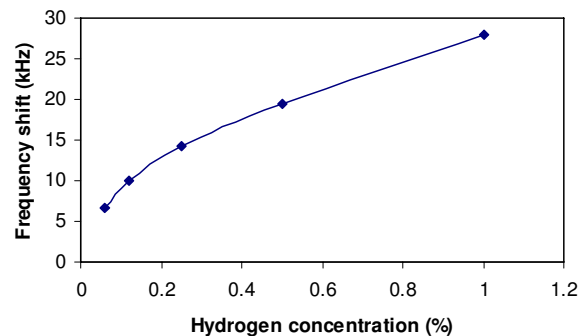


Figure 4. Frequency shift (kHz) versus H₂ concentration (%) at room temperature.

IV. CONCLUSIONS

A SAW gas sensor has been developed based on polyaniline nanofibers synthesized by template-free, rapidly-mixed reaction polymerization of aniline using HCl as the dopant acid. PSSA acid was then used to re-dope the nanofiber for stable response. The SAW gas sensor based on these nanofibers has been exposed to different concentrations of H_2 gas at room temperature. The sensor response, defined as the variation in resonant frequency, was 28 kHz towards 1% of H_2 at room temperature. A relatively fast response and recovery time with good repeatability and base-line stability were observed. Such interesting sensing results, obtained at room

temperature, show promise for fabricating portable and stable sensors using inexpensive polyaniline based nanofibers.

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