Nanomaterial Based Room Temperature Hydrogen Gas Sensors

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Abstract- Polyaniline (PANI) nanofiber and PANI/semiconducting metal oxide nanofiber composites based layered surface acoustic wave (SAW) and conductometric sensors have been developed and investigated towards hydrogen (H_2) gas. Chemical oxidative polymerization of aniline was employed to synthesize pure PANI nanofibers as well as PANI/semiconducting metal oxide composites. The nano-materials were deposited onto layered $ZnO/64°$ YX $LiNbO_3$ SAW and conductometric transducers. The novel sensors were exposed to H_2 gas. Fast response and recovery with good repeatability were observed at room temperature.

I. INTRODUCTION

Much attention has, and is, being paid to the sensing of hydrogen, largely due to its potential for use as a clean source of energy. Hydrogen burns cleanly, requires no fuel processor in fuel cells, and is producible from renewable energy resources, e.g. electricity from solar cells [1]. It is the most attractive future energy source.

In addition, hydrogen is a major cause of corrosion whereby it weakens metals internally. This is especially significant at elevated temperatures where it is termed High Temperature Hydrogen Attack (HTHA). Due to its small size, hydrogen molecules can penetrate into metals and affect properties such as strength and durability, resulting in embrittlement. For example, HTHA in petrochemical plants is caused when the hydrogen from the steam seeps into carbon and low alloy steels at high temperatures. The hydrogen reacts with the carbides in the steel, decarburising it and forming methane gas bubbles. These bubbles grow with time and result in micro cracking. The combination of micro cracking and decarburisation weakens the steel leading to major failures [2]. This process is initiated by the formation of hydrogen gas in boiler tubes caused by a corrosive reaction between steam and steel tubing as follows:

$$Fe + H_2O = Fe_3O_4 + H_2 \qquad (1.1)$$

The hydrogen available from the above reaction scheme reacts with carbides to decarburise the steel and forms methane gas based on the following:

$$Fe_3C + 2H_2 = 3Fe \text{ (decarburisation)} + CH_4 \qquad (1.2)$$
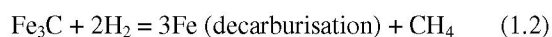
Corrosion caused by hydrogen can have a great impact on steel, especially in gas pipelines or in aircraft. Other important applications for hydrogen sensors include: fire warning systems; leakage detection and monitoring of process control systems in industries such as glass, and petroleum industries; hydrogen driven vehicles; and even in biomedical applications, where the presence of hydrogen gas can indicate certain types of bacterial infection.

Further to these abovementioned hydrogen sensing applications, there is the question of storage and transportation. There are inherent difficulties in transporting and storing it in large amounts, and safety concerns add to these difficulties. Manipulation and storage of hydrogen are associated with danger of leakage, which leads to an explosive atmosphere if the hydrogen volume concentration exceeds 4%.

The most relevant application pertaining to this research is hydrogen sensing for environmental and industrial process control and combustion monitoring. Hence the need for monitoring hydrogen in both: room and high temperature.

In the past few years, intense research activities have been devoted to the synthesis, structural characterization and investigation of physical properties of nanostructured materials. Due to size effects, nano-materials often exhibit novel physical properties and are of great interest for fundamental studies and for device applications [3]. Electrical, magnetic, optical and mechanical properties have all been observed to change at the nanoscale. Potential applications of nanostructured materials include: highly efficient catalysts, highly sensitive gas sensors, high frequency resonators, photo detectors, nano-sensors, nanoscale biological sensors, etc [4-7].

Gas sensors are increasingly required for industrial health and safety, environmental monitoring and process control. To meet these demands, the performance of conventional devices, such as sensitivity, selectivity and stability can be enhanced through nano-technology [8]. Recent advances in the development of nanostructured oxides, polymers and carbon [9-11] provide the opportunity to greatly increase the gas response of these materials, as their performance is directly related to granularity, porosity and ratio of surface area to

volume. For gas sensing application, new generation of gas sensors is being developed based on nano-structured polymers, semiconducting oxides as well as polymer/semiconducting oxide composites. They have an increased surface to volume ratio when compared to conventional thin film based sensors.

Conducting polymers have received increasing interest as smart sensors due to their room temperature sensitivity, low production cost, ease of deposition onto a wide variety of substrates [12-13] and their rich chemistry for structural modifications [14-15]. Polyaniline is unique among the family of conducting polymers since its doping level can be controlled through a non-redox acid doping/base dedoping process [16]. By changing the doping level, the conductivity of polyaniline can be modified for specific applications. Polyaniline can exist in a range of oxidation states. The one that can be doped with an acid to a highly conductive state is called polyemeraldine (Figure 1: top). It consists of amine (-NH-) and imine (=N-) sites in equal proportions. The imine sites can be protonated to achieve an intermediate bipolaron form (Figure 1: middle) and finally by dissociation to a polaron lattice (Figure 1: bottom), resulting in high conductivity [17]. It is widely believed that polarons are the charge carriers responsible for the high conductivity of doped polyaniline. 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.
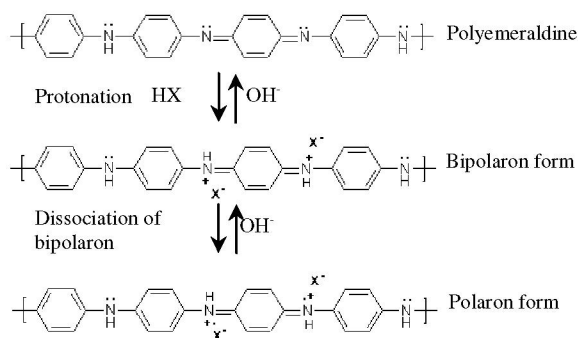

Figure 1. Polyaniline undoped form (top), intermediate bipolaron form (middle), and the fully doped acid form (bottom).

Since the conductivity of polyaniline depends on both the oxidation state of the main polymer chain and the degree of protonation of the imine sites [18], any interaction with PANI that alters either of these processes will affect its conductivity. Unlike acids and bases, redox active chemicals and gases can affect the conductivity of polyaniline by changing its inherent oxidation state. Depending on the extent of the redox reaction three different forms of polyaniline can be made: fully reduced leucoemeraldine, half oxidized emeraldine, and fully oxidized pernigraniline. The emeraldine form of polyaniline can be doped with a protonic acid to produce electrical conductivity [19]. Neutral, non-redox organic compounds, such as chloroform or toluene, are able to change the conductance of

doped polyaniline films through swelling effects [20]. Adding functional guests into the polyaniline structural matrix, such as metals or enzymes could change polyaniline's electrical conductivity characteristics, leading to a broader scope for the design and development of polyaniline based sensors [21].

Nanostructured polyaniline, in the form of nanowires, nanotubes, nanofibers or nanorods can greatly improve carrier diffusion due to their high surface to volume ratio and large penetration depth for gas molecules [22-23]. Deposition of polyaniline on porous supports can also increase the surface area but extra care needs to be considered due to structural complexities [24-25].

Polyaniline nanofibers with a cylindrical morphology form a porous structure when deposited as a thin film. The nanofibers possess higher surface to volume ratios than ultra-thin polyaniline films of the same thickness [26]. The three-dimensional porous structure of a PANI nanofiber film allows for easy diffusion of gases into and out of the selective layer and the nano scale fiber diameters lead to rapid diffusion of gases into the polyaniline, resulting in fast sensor response and recovery times upon exposure to a number of gases [22-23].

The gas sensitivity of the conventional polyaniline thin film sensors depends on the deposited film thickness [27]. Generally, sensor sensitivity increases with a reduction of film thickness as a thicker film has more inactive materials that do not react with gas species in a short period of time. However, thin film sensors are generally less robust than thick film sensors. On the other hand, sensitivity of a nanofiber polyaniline sensor is independent of layer thickness, due to the porous structure of the film. This advantage results in the capability of fabricating sensors with reproducible responses that have a large tolerance in thickness variation [22].

Conducting polymers are not as sensitive as metal oxides towards gas species and there is a growing interest to combine both organic and inorganic materials for applications in electronics and optics [15]. Combinations of nanosized metal oxides and polyaniline could be the one the most promising methods for increasing the sensitivity and selectivity of the conducting polymer. This composite can operate at room temperature and the selectivity towards different gas species can be controlled by the volume ratio of nanosized metal oxides. In addition, the composite may have better long term stability. The nanocomposite organic/inorganic materials are considered as bi-phase materials where the organic and inorganic phases are mixed at the nanometer scale. Nonetheless, the properties of nanocomposite materials depend not only on the properties of their constituents but also on their combined morphology and interfacial characteristics [28].

Conn, et al. [29] developed a polyaniline/PtO$_2$ based selective H$_2$ sensor and reported that conductivity of

2173

polyaniline increases with H_2 exposure which is due to formation of water. It is known that water present in the polymer takes part in charge transfer leading to an increase in the conductivity of polyaniline which is reversible [30-31]. Wang, et al. [32] developed polyaniline intercalated MoO_3 thin film sensors and reported that the conductivity change is due to a reversible absorption of analyte. Parvatikar, et al. [33] developed polyaniline/WO_3 composite based sensors and reported that conductivity of the film increases with increasing humidity. Ram, et al. [34] developed conducting polymer/SnO_2 and TiO_2 nanocomposite thin film based sensors and found that conductivity of the film increases with NO_2 exposure. Geng, et al. [35] synthesized polyaniline/SnO_2 hybrid materials by a hydrothermal process for gas sensing applications. They found that hybrid materials are sensitive to ethanol and acetone vapor at 60 to 90°C. In this paper, we report the development of pure PANI nanofiber as well as PANI/In_2O_3, PANI/MoO_3 and PANI/WO_3 nanofiber composite based hydrogen gas sensors. To the best of our knowledge, this is the first attempt to study these nanocomposites for H_2 gas sensing applications.

In our work, layered SAW devices were used as the transducing platform. Layered SAW transducers have attracted significant attention in recent years for sensing applications due to their higher sensitivity than their non-layered counterparts. The deposition of a ZnO layer onto 64° YX $LiNbO_3$ substrate forms a layered SAW structure with higher electromechanical coupling. Shear-horizontal (SH) leaky SAW propagation is the dominant mode in this layered substrate. We have also employed conductometric transducers.

II. EXPERIMENTAL

The gas sensor is made up of two important physical components: the sensitive PANI or PANI/metal oxides nanofiber composite layer, which interacts with the gas media by changing conductivity, and the transducer, which converts the chemical signal to an electrical signal

A. Transducer fabrication:

The SAW transducer pattern was formed on a 64° YX $LiNbO_3$ 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. The Au layer was deposited upon 20 nm Ti for improved adhesion to the substrate. The ZnO layer was deposited by RF magnetron sputtering. The sputtering gas was 40% O_2 in Ar at 1×10^{-2} Torr, the substrate temperature was 220°C, giving a deposition rate of ~1.2 μm/hr. The ZnO thin film was employed as the acoustic wave-guiding layer on the 64° YX

$LiNbO_3$ substrate, with a thickness of 1.2 μm. A fabricated dual delay line SAW transducer is shown in Fig. 2.
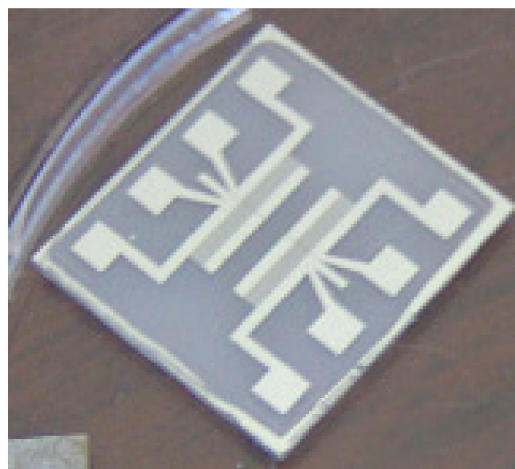

Figure 2: A typical SAW sensor showing two sets of identical resonators.

Hydrogen gas conductometric sensors were also designed and fabricated. Platinum (Pt) sputtered inter digital electrodes and heater were fabricated on 3x3 mm^2 sapphire substrate to form a transducer.

B. Sensitive thin film fabrication:

There are two major polymerization approaches to synthesize polyaniline nanofibers: electro-polymerization and chemical polymerization. Template-free, interfacial polymerisation was employed to synthesize polyaniline nanofibers using chemical oxidative polymerisation of aniline [22-23]. The polymerisation is performed in an aqueous solution where aniline is rapidly polymerised in 1M acid by the quick addition of the oxidant. 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. Washing or dialyzing with water gives pure doped polyaniline that can be dedoped by washing or dializing with ammonia. The average diameter of the polyaniline nanofibers is about 50 nm with a length of several microns.

In this paper, the chemical polymerization technique has also been employed to synthesize PANI/In_2O_3, PANI/MoO_3 and PANI/WO_3 nanocomposites. At first, aniline monomer was added into the 1.0 M camphorsulfonic acid (CSA) solution of In_2O_3, MoO_3 and WO_3 nanoparticles, respectively. The concentration of aniline monomer to semiconducting metal oxide is 17 to 5 in the solution. Next, ammonium persulfate was added to the mixture and allowed to further react overnight. The product was dedoped with 1.0 M NaOH and further purified by four cycles of washing with distilled water-centrifugation.

2174

Doped and dedoped PANI as well as composite nanofiber dispersions were drop cast onto the surface of both conductometric and SAW transducers. They were then left to dry in a clean, dry environment for one day. In a SAW device, the change in electrical conductivity perturbs the velocity of the propagating acoustic wave due to piezoelectric effects. The deviations in velocity are monitored by measuring the changes in frequency of the sensing device. This change in frequency is directly proportional to the amount of a specific gas present in the environment, resulting in a quantitative determination of the presence of gas and its concentration.

III. RESULTS

A. Characterization:

A Scanning Electron Microscope (SEM) image of the pure PANI nanostructures on the sapphire substrate is shown in Fig. 3. The SEM result indicates that the polyaniline layer deposited on the sapphire substrate consists of nanofibers.
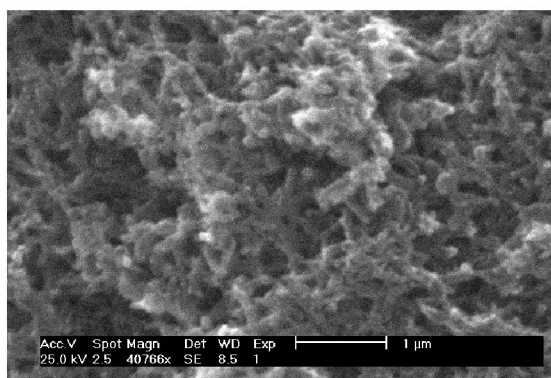

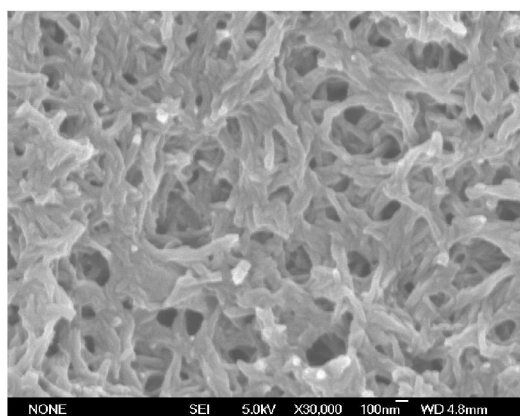Figure 3. SEM image of polyaniline nanofibers on the sapphire substrate.

Figure 4: Close-up SEM image of a PANI/In$_2$O$_3$ nanofiber matt. The scale bar is 100 nm.

SEM and transmission electron microscope (TEM) images of the nanocomposite on 64° YX LiNbO$_3$ substrate are shown in Fig. 4 and Fig. 5, respectively. A layer of 0.4 μm thickness consists of polyaniline/In$_2$O$_3$ nanofibers with average diameters of 90 nm. The nanofibers are connected together in a network. An X-ray diffraction (XRD) pattern is shown in Fig. 6 in which the sharp peaks are due to In$_2$O$_3$ and the broader peaks at $2\theta \sim 26°$ are due to polyaniline. The diffraction peaks from the nanocomposite sample are well matched to the sharp lines from the pure standard In$_2$O$_3$ (shown below the polyaniline/In$_2$O$_3$ diffraction pattern) indicating that the sample contains In$_2$O$_3$ particles.
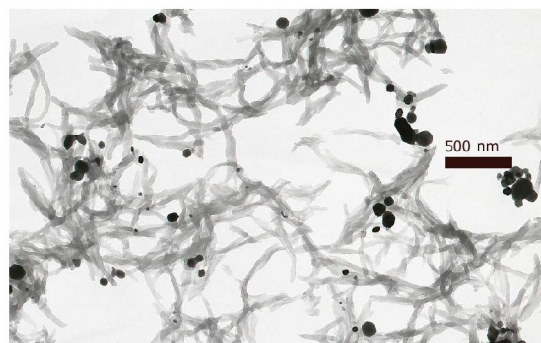

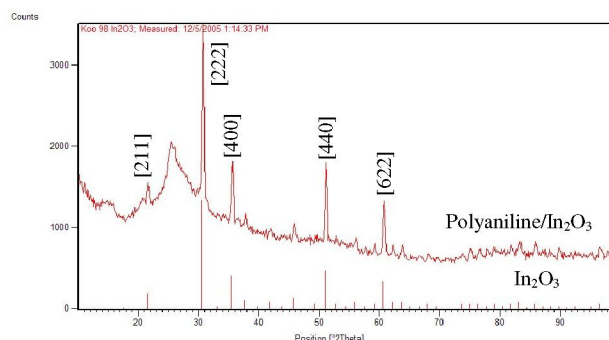Figure 5: TEM image of a PANI/In$_2$O$_3$ nanofiber

Figure 6: X-ray diffraction pattern of a polyaniline/In$_2$O$_3$ nanofiber composite (top) and a bar graph for pure In$_2$O$_3$ from the JC-PDS database (bottom).

B. TEST RESULTS

The sensor was placed in a multi-channel gas calibration system and exposed to various concentrations of H$_2$ gas. Dynamic responses of the dedoped and doped polyaniline nanofiber sensors to H$_2$ gas at room temperature are shown in Fig. 7 and 8, respectively. It was observed that the conductivity of both doped and dedoped sensitive layers increase after exposure to H$_2$ gas.

The hydrogen sensing mechanism for pure PANI is still not fully understood. The hydrogen may form a bridge between nitrogen atoms on two adjacent chains or there may be partial protonation of some imine nitrogen atoms. The sensitivity of the conductometric sensors is defined as: $S = R_{air}/R_{gas}$, where

2175

R_{air} is the resistance of the sensor in air, R_{gas} is the resistance of the sensor in presence of gas. The sensitivity of the sensors was calculated to be 111% for doped and 107% for dedoped polyaniline nanofiber sensors upon exposure to 1% of H_2 at room temperature. Fast response times of 32 seconds and 28 seconds were observed towards 1% H_2 for doped and dedoped sensors, respectively. Two significant observations were obtained from the tests. Firstly, the response curves show that the doped polyaniline nanofiber sensor is more sensitive than the dedoped sensor. Secondly, the baseline of the dedoped nanofiber sensor was more stable than the doped sensor. Additionally, the dedoped nanofiber sensor has better repeatability than the doped sensor.
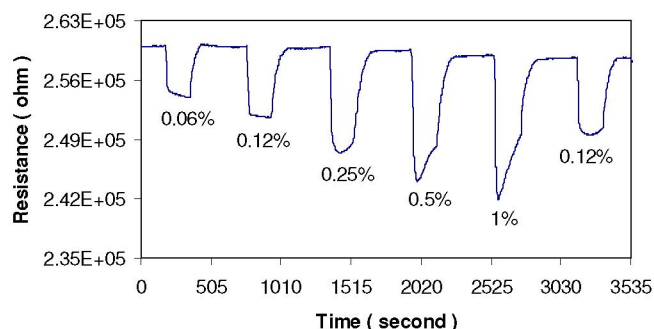

Figure 7. Dynamic response of the dedoped polyaniline nanofiber based conductometric sensor to different H_2 gas concentrations in synthetic air.
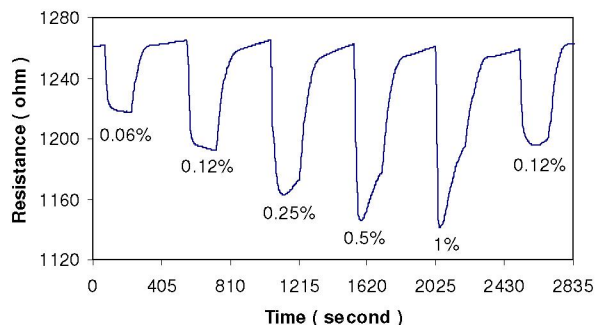

Figure 8. Dynamic response of the doped polyaniline nanofiber based conductometric sensor to different H_2 gas concentrations in synthetic air.

The dynamic response of a PANI/In_2O_3 composite nanofiber based sensor to a sequence of different H_2 gas concentrations in synthetic air is shown in Fig. 9. The sensor response is defined as the variation in operating frequency of oscillation due to the interaction with the target gas. Measured sensor responses were approximately 11 kHz towards 1% of H_2 in synthetic air, respectively. Fast response times of 30 sec and recovery time of 40 sec with good repeatability were observed at room temperature for H_2.

The H_2 sensing performance for a PANI/MoO_3 and PANI/WO_3 nanocomposites based sensors was also examined. The sensors show a repeatable and large response towards H_2; however the PANI/In_2O_3 nanocomposite seems to be the most promising.
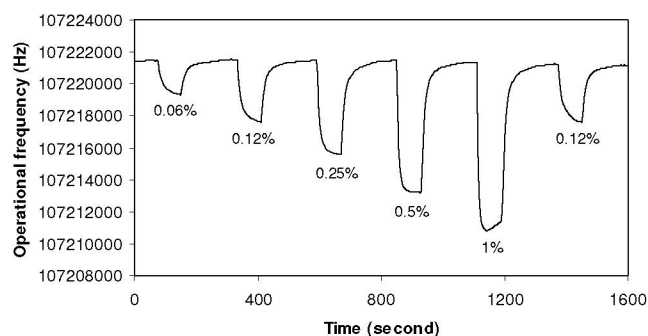

Figure 9: Dynamic response of a polyaniline/In_2O_3 nanofiber based ZnO/64° YX LiNbO$_3$ SAW sensor towards different concentrations of H_2 at room temperature.

There are two possible sensing mechanisms for the H_2 gas with PANI/In_2O_3. The first one is activation of the hydrogen by In_2O_3 due to formation of indium-dihydrogen complexes. The second one is an interaction with the polyaniline backbone possibly facilitated by In_2O_3 which may induce dissociation of the hydrogen leading to either a doping type response or chain alignment.

IV. CONCLUSIONS

SAW and conductometric hydrogen gas sensors operating at room temperature have been developed based on PANI nanofiber as well as PANI/semi-conducting metal oxide nanocomposites. Chemical oxidative polymerization of aniline was employed to synthesize pure PANI nanofibers as well as PANI/semi-conducting metal oxide composites. The sensors show a repeatable and large response towards H_2. Due to room temperature operation, these sensors may prove to be useful for environmental and industrial applications.

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