Polyvinylpyrrolidone/Polyaniline Composite Based 36° YX LiTaO$_3$ Surface Acoustic Wave H$_2$ Gas Sensor

(Pengesan Gas Hidrogen: Komposit Polivinilpirrolidon/polianilin di Atas 36° YX LiTaO$_3$ Gelombang Akustik Permukaan)

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ABSTRACT

Poly-vinyl-pyrrolidone (PVP)/polyaniline based surface acoustic wave (SAW) sensors were fabricated and characterized and their performances towards hydrogen gas were investigated. The PVP/polyaniline fibers composite were prepared by electrospinning of the composite aqueous solution deposited directly onto the active area of SAW transducers. Via scanning electron microscopy (SEM), the morphology of the deposited nanostructure material was observed. From the dynamic response, frequency shifts of 6.243 kHz (1% H$_2$) and 8.051 kHz (1% H$_2$) were recorded for the sensors deposited with PVP/ES and PVP/EB, respectively.

Keywords: Gas sensor; polyvinylpyrrolidone/polyaniline composite; surface acoustic wave

ABSTRAK

Lapisan pengesan polivinilpirrolidon (PVP)/polianilin yang dimendap secara terus di atas kawasan aktif pengesan gelombang akustik permukaan (SAW) telah berjaya dihasilkan. Permukaan bahan komposit yang dihasilkan melalui kaedah elektroputaran ini dicirikan menggunakan mikroscop elektron imbasan (SEM). Prestasi pengesan bahan komposit/ SAW terhadap gas hidrogen telah dianalisis. Anjakan frequensi sebanyak 6.243 kHz (1% H$_2$) dan 8.051 kHz (1% H$_2$) bagi pengesan yang dimendapkan dengan PVP/ES dan PVP/EB telah direkodkan.

Kata kunci: Komposit polivinilpirrolidon/polianilin; pengesan gas; gelombang akustik permukaan (SAW)

INTRODUCTION

Generally, non-conducting polymers such as poly-vinyl-pyrrolidone (PVP) are defined as the polymers with high resistivity (Yuqing et al. 2004). Although these types of polymers are useful for a variety of chemical sensor types, the use of PVP as the sensing layer has been rarely reported. Recently, He et al. (2010) has electrospin-coated the PVP fibers onto the surface acoustic wave (SAW) device and successfully functions as H$_2$ gas sensor. The work was then extended by Chee et al. (2010) by adding multiwall carbon nanotube (MWNT) to produce the composite of PVP/ MWNTs fibers as H$_2$ gas sensor. By modifying the previous research, this work shows the gas sensing properties of PVP/ polyaniline composite/36° YX LiTaO$_3$ SAW device.

In the literature, PVP has been used in sensing applications. The ability of thin film PVP based sensors (De Queiroz et al. 2001; Du et al. 2007; Iwaki et al. 2007; Mirmohseni & Oladegaragoze 2003; Tang et al. 2005; Yang et al. 1999) to sense gas molecules have attracted the authors to explore the potential of nanoscale structure of PVP as gas sensing layers compared with the conventional PVP thin film.

Electrospinning has grown from a small niche process to a widely used fibre formation technique. It only requires a relatively simple set-up, which consist of three major parts; a spinneret (a metallic needle), a collector (this experiment used SAW transducer) and a high voltage power supply.

Recently, the authors have successfully developed electrospin-coated PVP fibers based 36° LiTaO$_3$ surface acoustic wave (SAW) sensors (Chee et al. 2010; He et al. 2010). Motivated from the results, the authors investigated the gas sensing performance of PVP/polyaniline composite based SAW sensor. Polyaniline was selected due to its promising feature for gas sensing (Arsat et al. 2009). Besides, having several oxidation states may give an advantage to the composite as the conductivity of the material varies in each state. In addition to that, by adding polyaniline as composite material of sensing layer, sensor devices able to sense target gas at low operating temperature (Jumali et al. 2009, 2011). This therefore, makes the polyaniline an interesting material as a composite for gas sensing application.

EXPERIMENTAL DETAILS

Through photolithography method, SAW devices were fabricated on 36° YX LiTaO$_3$ substrates, patterning to have 16 electrode pairs in the input and output interdigital

transducer (IDT). These transducers also have 140 reflectors in each side, periodicity of 20 μm, centre-to-centre distance of 200 μm and a 350 μm aperture width. The IDTs and reflectors were formed from the metallization double layer of titanium (Ti) and gold (Au). Au with a thickness of 80 nm was chosen as IDTs patterns as it is highly inert to most analytes and provides high conductivity. In order to promote the adhesion of the Au to the surface 20 nm thick of Ti was deposited in between the Au and the substrate. The centre frequency of the SAW transducer is 200 MHz.

In this work, two types of commercial polyaniline (emeraldine salt (ES) and emeraldine base (EB)) were used as PVP composites. The commercial ES (Molecular weight, $M_w = 15,000$) and EB ($M_w = 10,000$) are used without further purification. Due to the hydrophobic nature of polyaniline, either chloroform (ChCl$_3$) or N-methl-2-pyrrolidone (NMP) were commonly used to dissolved the particles. Further investigation was conducted to observe the effect of ES/ChCl$_3$ and ES/NMP towards gas sensing properties. The results showed that the conductivity of polyaniline was reduced by adding NMP. Therefore ChCl$_3$ was chosen for dissolving polyaniline to maintain the conductivity.

The solutions then were filtered using 0.2 μm filters to remove any undissolve particles. Then, 0.9 g of PVP powder were mixed with 2 mL of filtered ES. However, due to the lower M_w of EB compared with ES, 1.0 g of PVP was added in the prepared solution. Both mixtures then were stirred continuously for few hours. Similar to the preparation of pure PVP, both solutions were then left unstirred until all bubbles disappeared before it is electrospin-coated onto the active area of SAW device.

Results and Discussion

The surface morphology of the electrospin-coated PVP/ES and PVP/EB composites were investigated via scanning electron microscopy (SEM) and are shown in Figures 1(a) and 1(b), respectively. It is observed that both composites similar surface morphologies, which are fibers and beads. For PVP/ES, the widths of the fibers are measured to be in the range of 50 to 650 nm. It is also observed that the electrospin-coated fibers are in random direction in plane parallel to the substrate. Whereas for PVP/EB, the width of the fibers is bigger than that of PVP/ES. The width were between 322 and 1000 nm.

The sensing performance of the PVP/ES and PVP/EB composites based SAW sensors were investigated by placing the sensors in the gas chamber. This chamber is connected to the computerized mass flow controller, which was then utilized to vary the concentration of H$_2$ gas. The total constant flow air of this system was controlled at 200 sccm. Both types of sensors were exposed to hydrogen pulse sequences of 0.06%, 0.12%, 0.25%, 0.50%, 1.00% and 0.12% concentrations in dry synthetic air at room temperature. The output of this sensor was measured via Fluke high-resolution frequency counter (PM66860B). In Figure 2, the measured response for the device that contains ES as the composite was 6.243 kHz towards 1% H$_2$, whereas the response of PVP/EB (Figure 3) was 8.051 kHz towards 1% H$_2$ gas. However, it is observed that the frequency shift for 0.06% and 0.12% of PVP/EB based sensors were small and insignificant. Therefore, it shows that PVP/EB based SAW sensor was not suitable to measure H$_2$ concentrations lower than 0.25%.

The frequency shift versus different concentrations of H$_2$ gas is curve shown in Figure 4. It can be seen that frequency shift for both devices increases almost linearly with H$_2$ concentrations. Fast response of 24 s towards 1% H$_2$ concentration was observed for both PVP/ES and PVP/EB based SAW gas sensors. Figure 5 shows the response sequence for different H$_2$ gas concentrations. It is also observed from Figures 2 and 3 that the baseline of the PVP/ES based SAW gas sensor is more stable than that of the PVP/EB based SAW gas sensor.
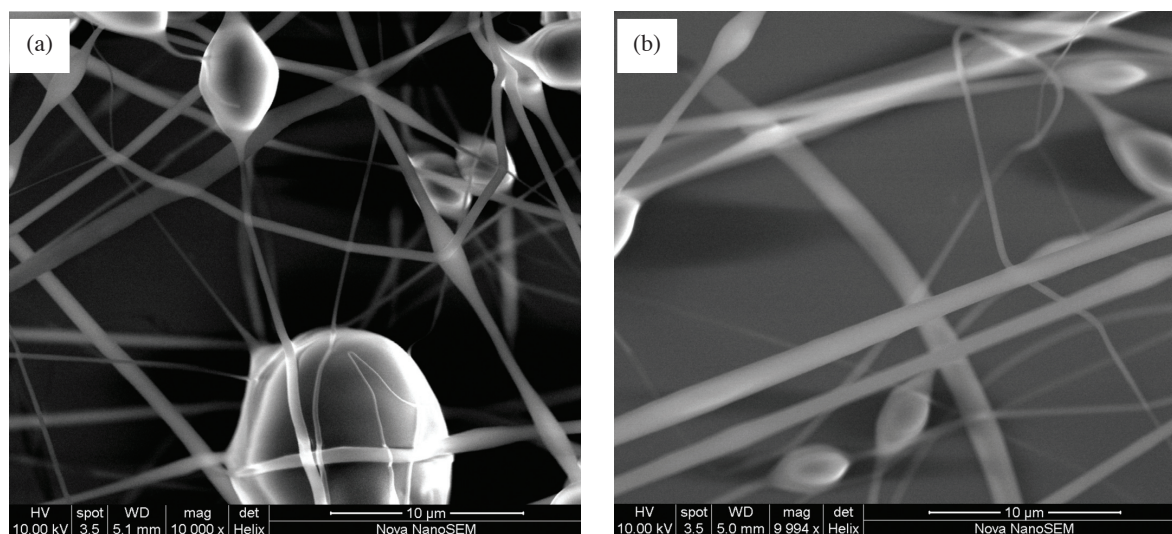

FIGURE 1. SEM images of electrospun PVP composite with (a) polyaniline emeraldine salt and (b) polyaniline emeraldine base
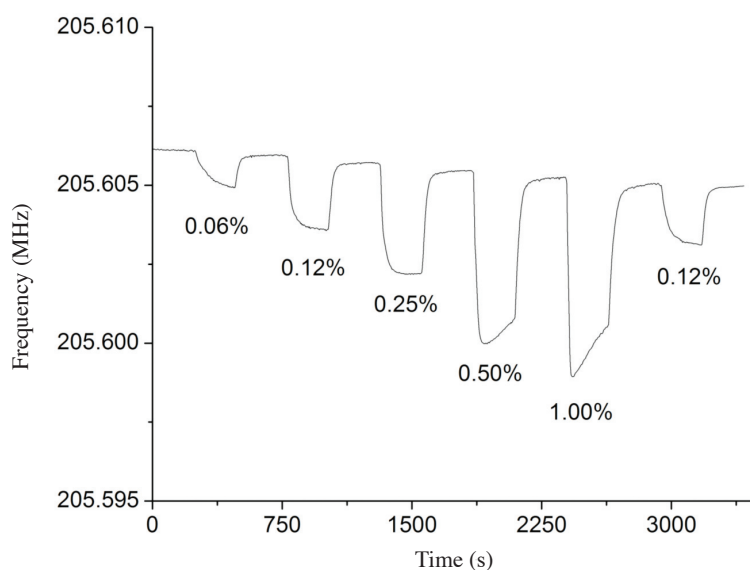
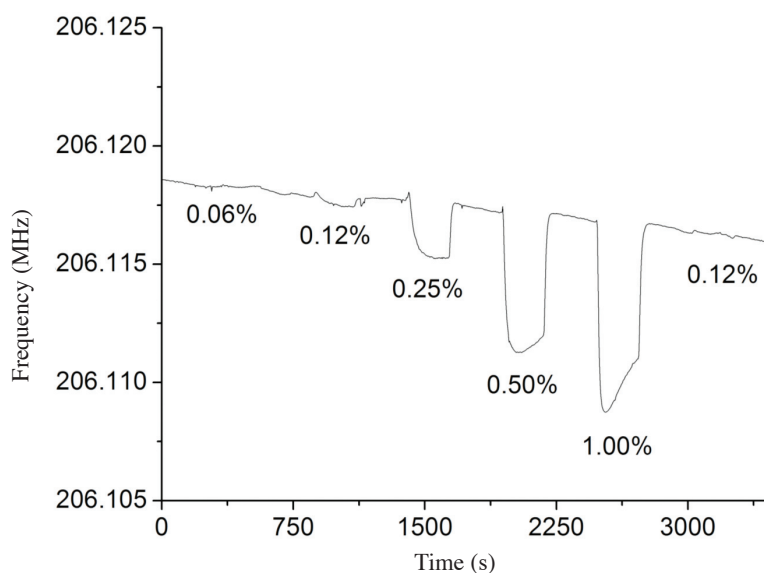FIGURE 2. Dynamic response of PVP/ES based SAW sensor towards H_2 gas

FIGURE 3. Dynamic response of PVP/EB based SAW sensor towards H_2 gas

For the PVP/ES, it is believed that the conductivity of the composite increases upon exposure to H_2 gas. This results in a decrease in the acoustic velocity and therefore, a decrease at the resonant frequency. However for the PVP/EB, it is believed the adsorption of H_2 gas causes the mass of the sensing film to change, which contributes to the decrease in acoustic wave velocity and subsequently the resonant frequency. The adsorption of H_2 gas into PVP/ES and PVP/EB appeared to involve the penetration of the gas accompanied by swelling of the polymer (Hosseini & Entezami 2001).

CONCLUSION

PVP in the presence of polyaniline ES and EB was successfully employed on SAW transducers via electrospinning process.

The SAW sensors then were exposed to H_2 gas to investigate the sensing performance. PVP/EB sensor was observed to show high sensitivity, however the device detection limit of H_2 at room temperature was 0.25%. Whereas for PVP/ES based SAW sensors, the device was able to measure as low as 0.06% H_2 gas concentrations with good baseline stability.

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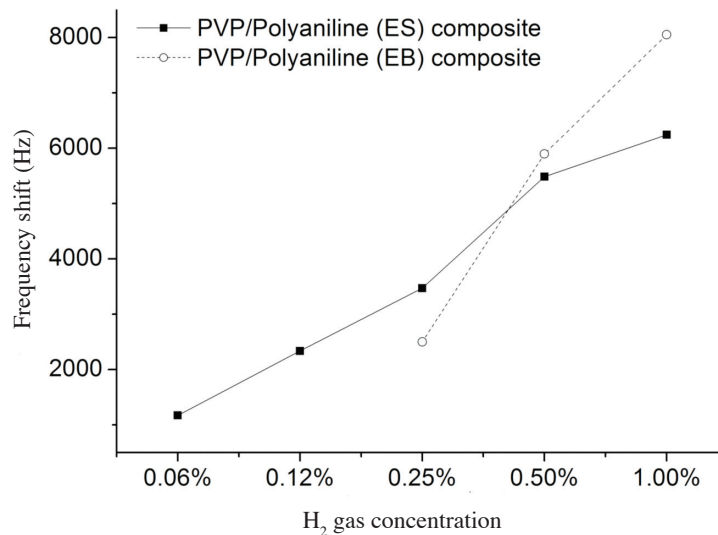
FIGURE 4. Frequency shift of PVP/Polyaniline based SAW sensors versus H_2 gas concentration
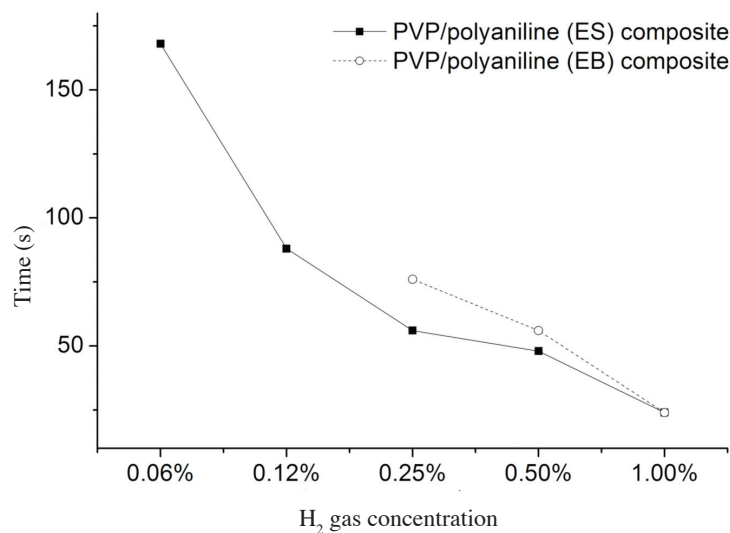

FIGURE 5. Response time of PVP/Polyaniline based SAW sensors versus H_2 gas concentration

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