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Microstuctural and Ethanol Sensing Variations of TiO_2-PSS Multi Layered Thin Films

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Abstract: The aim of this paper is to investigate the effect of films layers on microstructures and ethanol sensing behavior of TiO_2-PSS (Poly(styrenesulfonate)) composites thin films. The composites solution was prepared by direct addition of PSS liquid into TiO_2 solution. The TiO_2-PSS films were deposited onto SiO_2 coated silicon substrate followed by Al electrode deposition for device fabrication. Three different layers of TiO_2-PSS films were prepared for this experiment. SEM characterization revealed that the thickness and surface morphology of the films were influeneced by the number of deposited layer. It was observed that film with porous microstructure exhibit the best sensing pattern.

Key words: TiO_2 · PSS · Nanocomposite · Thin film · Ethanol · Gas sensor

INTRODUCTION

Metal oxide as inorganic materials such as SnO_2, TiO_2 and ZnO have been well studied for gases detection and considered attractive for their low cost and simple sensing method. However, the high temperature operation of the sensor make the lifetime of the sensor become shorter and required more electricity. Other problems associated with metal oxide thin films were their sensitivity, stability and selectivity at low concentration of the gases [1-3]. For organic materials, conducting polymer were finding a growing number of applications in various electronics device including gas sensors. While most commercially available sensors based on metal oxide gas sensor, these conducting polymers have improved many characteristics especially low operating temperature (< 30 °C). Conducting polymers are easy to synthesize through chemical or electrochemical processes. In addition, their molecular chain structure can be modified by copolymerization or structural derivations. However, pure conducting polimers have low conductivity, chemically sensitive and have poor mechanical properties [4,5].

Complementary behaviours obtained from inorganic/polymer composites are thought could improve the disadvantages of both pure materials. In recent years, many studies on hybridization of conducting polymer and metal oxides as gas sensor have been reported [6-11]. Sieviro *et al.* (2007) reported that TiO_2-CuPc sensor is more sensitive and stable compared to TiO_2 alone as methanol sensor [6]. Savage (2009) also proved that composites sensors of PPy and MoO_3 has higher response compared to either PPy or MoO_3 sensors when exposed towards ethanol vapour at room temperature [7]. The PANi/TiO_2 and SnO_2/PANi composites sensors were reported to exhibit faster response, shorter recovery time and higher sensitivity when exposed towards NH_3 at room temperature [8,9]. Besides, potential usage of p-polyaniline/n-TiO_2 heterojunction thin film as LPG gas sensor at room temperature had also been reported [10]. In addition TiO_2-PANi as ethanol sensor at room temperature has been investigated in our previous report [11]. These findings proved that composite between these two materials produced better gas sensor especially at lowering the operating temperature.

Based on these reported findings, microstructure, surface morphology and surface roughness were among the identified factors that greatly influence the sensing performance of the films. In order to have a greater understanding of composites materials in sensing performance, hybridization of TiO_2 and PSS was done in this experiment. TiO_2 was chosen due to its unique physical and chemical properties such as large energy gap, good dielectric constant, environmental-friendliness

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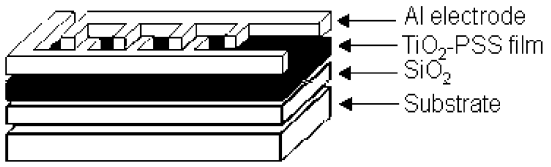

Fig. 1: Device structure

and easy to synthesis. PSS was chosen as hybrid materials because of some advantages in comparison with other regular conducting polymers used in gas sensors, such as higher conductivity, higher stability, more availability and lower cost compared to other conducting polymers regularly used as gas sensor [12].

MATERIALS AND METHODS

TiO_2 solution was prepared via sol gel method. The precursors of the solution were potassium chloride (KCl), titanium (IV) ethoxide (TEOT) and ethanol. KCl was first dissolved in 5 mL deionized water. Then 0.02 mL of dissolved KCl were added into 3 mL ethanol and stirred for 60 minutes. Finally, 0.051 mL TEOT was dropped wisely into the precursor solution. Small amount of acetylacetone was added to stabilize the TiO_2 solution.

The hybridization was done by direct addition of Poly(styrenesulfonate) or PSS solution into TiO_2 sol with volume ratio of TiO_2: PSS fixed at 1vol%. Then TiO_2-PSS solution were deposited onto SiO_2 coated silicon substrate using spin coating technique to form three different thickness of composite films namely 3, 4 and 5 layers. These films were labeled as S_1, S_2 and S_3 respectively. For device fabrication, top of each film was deposited with Al electrode comb shaped by e-gun technique. The structure of the device is shown in Figure 1. SEM was used for morphological characterization of the film surface.

Gas detection system was designed based on variation in conductivity of the sensing material resulted from alternate interaction with nitrogen and ethanol gas. The device was put in an airtight chamber and electrically connected to a power supply with constant voltage of 3V before exposed to test gas. The electrical response (current) during experiment was monitored using Keithley multimeter as a sensor responded towards environmental variation.

RESULTS AND DISCUSSION

Microstructural Investigation: Figure 2 shows the SEM micrographs for all films. It can be seen that dramatic variation in surface morphology as the number of layers increases. Since the roughness and porosity level increased with the number of layer, it was obvious that the surface morphology of the upper most layer influenced by the roughness of the previous layer. This can be attributed by the increment of resistance on the surface which hindered the distribution/movement of TiO_2-PSS solution on subsequent layer. As can be seen in Fig. 2a, films S_1 showed smooth surface with agglomerated particles at the outer surface. As the films become thicker (effect of layer addition), the surface roughness also increased due to the formation of big agglomerated particles distributed on the films surface (Figure 2b and 2c). Agglomerated particles that overlapped each other formed porous structure of the film (Figure 2c) and give better surface area which were significant for gas responded.

Gas Sensing Test: Figure 3 shows the time dependence plot of the sensor voltage during ethanol sensing for all films at room temperature. The results were expressed in terms of relative change in current in the circuit as a function of time. Films S_1 and S_2 showed no systematic pattern when exposed towards nitrogen and ethanol which confirmed that these films were not responsive towards the test gas. By comparison, film S_3 able to differentiate the analyte and thus exhibited a systematic pattern. The current in the circuit increased in the ethanol ambience, indicating a reduction in the total resistance in the circuit. In general, when the film was exposed to ethanol vapour, the current of the film increased and decreased when replaced with nitrogen.

Despite same materials used as active layer for detection of ethanol, only sensor with 5 layers displayed systematic sensing capability. This variations in detecting ethanol proved that the surface morphology significantly influenced effect the sensing properties of the TiO_2-PSS layer. Agglomerated structure relatively gives large specific area for sample S_3 compared to S_1 and S_2. The agglomerated structure and pores formed also offers location for entrapment of the gas molecules. The entrapment of the gas molecules enable the active sensing materials and gas molecules to touch and interact each other and allowed physisorption process between gas molecules and film took place. Sufficient period of physisorption process lead to chemisorption process. When chemisorptions process take over the film conduction considered changed. The mechanism explained the changes of the film conduction.

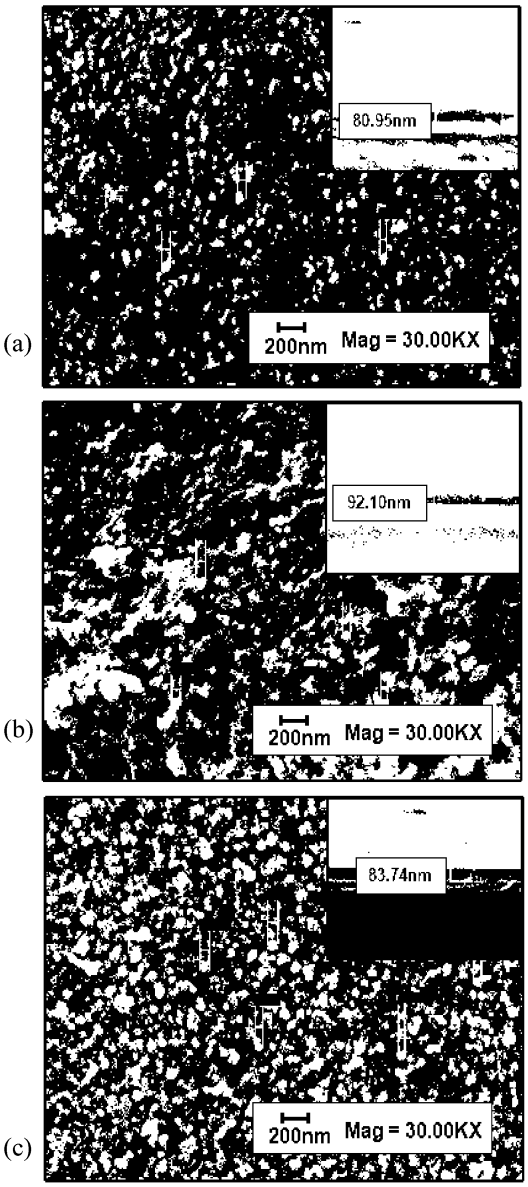

Fig. 2: SEM images of (a) S_1, (b) S_2 and (c) S_3

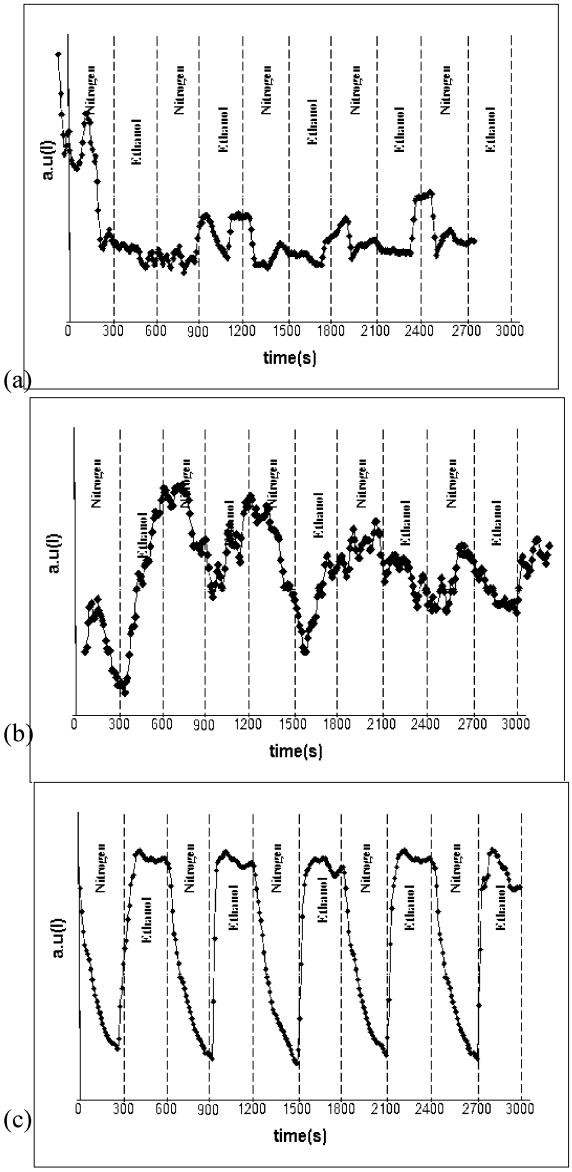

Fig. 3: Sensor response of (a) S_1, (b) S_2 and (c) S_3 towards ethanol vapor at room temperature

Although the sensing mechanism of TiO_2-PSS has not been clear, a plausible explanation on variation in current produced is due to the reduction and oxidation gasses. As a reducing gas, etanol function as a reducing agent. When the ethanol vapour was exposed to the film it will transfer the electrons to the film. Electron transferring decreased the resistance cause the current to increase and work function of the sensing material. For recovery process N_2 gas were restore after the gas test and decreasing the current value because N_2 was oxidising gas function as reduction agent.

CONCLUSION

In conclusion, numbers of deposited layer affect the surface morphology of TiO_2-PSS films. The formation of rough surface morphology improve the interaction and entrapment of the analyte and thus effect the sensing capacity of the active layer.

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