COMPARATIVE STUDIES ON MICROSTRUCTURAL AND GAS SENSING PERFORMANCE OF TiO$_2$ AND TiO$_2$-PANI NANOCOMPOSITE THIN FILMS.

Mohammad Hafizuddin Haji Jumali$^1$, Izura Izzuddin$^1$, Norhashimah Ramli$^1$, Muhamad Mat Salleh$^2$ and Muhammad Yahaya$^1$.

$^1$School of Applied Physics, Faculty of Science and Technology, $^2$Institute of Microengineering and Nanoelectronc (IMEN), Universiti Kebangsaan Malaysia (UKM), 43600 Bangi, Selangor, MALAYSIA

ABSTRACT

In recent years, the development of inorganic-organic hybrid materials has grown due to better properties and wide range of potential use. The aim of this research is to investigate the effect of PANi addition on VOC gas sensing properties and microstructures of TiO$_2$ based thin films. TiO$_2$ ceramics were prepared via sol-gel technique. PANi, in amount of 3wt% was added to TiO$_2$ sol to produce TiO$_2$-PANI solution. Then TiO$_2$ and TiO$_2$-PANI solutions were deposited onto SiO$_2$ coated silicon substrate using spin coating technique for fabrication of gas sensing device. XRD investigation showed that the thin films were amorphous. TEM study of the TiO$_2$ and TiO$_2$-PANI powders revealed a significant reduction of TiO$_2$ particles size from 10nm to 2nm with the addition of PANi. SEM micrographs showed that both films exhibit an open porous structure with TiO$_2$ rich grain particles well distributed on the substrate. The gas sensing devices were exposed towards VOCs vapours. It was found that the device with addition 3wt% of PANi exhibit a systematic response towards ethanol and methanol vapour exposure at room temperature. In contrast TiO$_2$ thin film did not show any response due to low operating temperature.

INTRODUCTION

Research on sensing materials has been focused on the design of higher performance and elevated efficiency gas sensing elements with suitable sensing materials. Generally, gas sensor can be classified mainly into two main categories i.e. organic and inorganic materials. ZnO and SnO$_2$ have been well studied for gases detection and considered attractive for their low cost and simple sensing method [1]. However, the high temperature operation of the sensor make the lifetime of the sensor become shorter, increasing resistance and thus required more electricity for operation. Other problems related to metal oxide thin films are their poor performance regarding the sensitivity, stability and selectivity at certain low concentration of the gas. For organic materials category, conducting polymers such as polypyrrole, polyiopenes and polyanilines experience a growing number of applications in various electronics device. It was included gas sensors device which explored since early 1980 [2]. Although most commercially available sensors are based on metal oxide gas sensor, the conducting polymers offer few interesting characteristics especially low operating temperature. Nevertheless, pure conducting polymers have low conductivity ($< 10^{-5} \text{ S cm}^{-1}$), chemically sensitive and have poor mechanical properties. For that, hybridization of
metal oxide and conducting polymer are believed can improve the properties of pure materials for gas sensing detection. The hybridization between titanium dioxide (\(\text{TiO}_2\)) and polyaniline (PANi) were investigated in this experiment. TiO\(_2\) was chosen due to its unique physical and chemical properties such as large energy gap, dielectric constant, environmental-friendliness and easy to synthesis. Among various conducting polymers, polyaniline was found to be a better choice for gas sensing materials due to its chemical stability, inexpensive monomer and comparatively stable in air. Tai et al. (2007) reported that the PANi/TiO\(_2\) thin film sensor exhibit faster response, shorter recovery time and higher sensitivity when exposed towards NH\(_3\) at room temperature compared to Pani thin film [3]. The conductivity of the nanocomposite films increase slightly with increasing TiO\(_2\) into PANi content and decreases with excess TiO\(_2\) content as reported by Su et al. (2000) [4]. Dhawale et al. (2008) have succeeded in fabricating p-polyaniline/n-TiO\(_2\) heterojunction thin film for LPG gas sensor [1]. For PANi-SnO\(_2\) gas sensor, Geng et al. (2007) found that the sensor showed optimum sensitivity at 60 °C and 90 °C in detecting ethanol and methanol [5]. Performance of PANi addition towards TiO\(_2\) thin film in detecting volatile organic compound (VOC) gas namely ethanol and methanol were studied in this paper.

**EXPERIMENTAL**

TiO\(_2\) solution was prepared using sol gel method as reported by Syariena et al. (2008) [6]. 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 5 mL ethanol and stirred for 60 minutes. Finally, 0.085 mL TEOt were dropped into the precursor solution. Small amount of acetylacetone was added to stabilize the TiO\(_2\) solution. For fabrication of composite films, 3wt% of Polyaniline (PANi) in form of powder was directly added into 5mL TiO\(_2\) sol and keep stirred for about 18 hours. The whole process to synthesis the precursor solution is shown in Figure 1.

**Figure 1: Flow chart of synthesis process for TiO\(_2\) and TiO\(_2\)-PANi solution**

Corresponding Author: hafizhj@ukm.my
The TiO$_2$ and TiO$_2$/Pani thin films were then deposited onto Si/SiO$_2$ substrate using spin coating technique. The spinning rate was fixed at 3000rpm for 30 seconds. Then, the films were left to dry at room temperature. The procedure was repeated 2 times in order to get 3 layers of thin film. Finally, the comb shape of Al electrode was deposited on the surface of the film by e-gun technique to fabricate sensor device. The structure of the device is shown in Figure 2.

![Figure 2: Fabrication of sensor device](image)

For gas sensing test, the device was exposed towards ethanol and methanol vapour at room temperature. N$_2$ was purged for recovery process. A constant voltage of 3 volt was applied to the sensor. The gas sensor measurement system was completed with data acquisition system. Structure characterization were done using Bruker D8 Advance XRD with Cu Kα ($\lambda=1.5406\text{Å}$), Zeiss (Gemini) FE-SEM unit employed for surface morphology and Philips TEM used for particles observation.

RESULT AND DISCUSSION

**Microstructural investigation**

X-ray diffractograms for both TiO$_2$ and TiO$_2$-PANi thin films showed that both films were in amorphous states (Figure 3).

![Figure 3: Typical XRD spectrum of amorphous TiO$_2$ and TiO$_2$-PANi thin film](image)
TEM micrographs (Figure 4) revealed that dark TiO$_2$-rich particles in TiO$_2$ and TiO$_2$-PANi compositions exist as round particles with size of 10nm and 5nm respectively. Additionally, TiO$_2$-rich particles were uniformly distributed in PANi, which offer an interesting microstructures for gas sensing device.

SEM investigation showed that the nature of the surface structure of the films. The TiO$_2$ rich films exhibited an open porous structure. The similar porous structure was also observed in TiO$_2$-PANi films with white TiO$_2$-rich particles well distributed over the surface (Figure 5).

**Gas sensing test**

For gas sensing test, the device and measurement system was designed using the concept of conductivity variation in the sensing materials. Figure 6 (a) shows the response of TiO2 thin films towards ethanol. It was observed that TiO$_2$ was not responsive and failed to differentiate between the vapour and N$_2$. This behaviour was expected since the measurement was conducted at low operating temperature. Tang et al. (1995) and Hieu et al. (2008) suggested that operating temperature for TiO$_2$ thin film in detecting ethanol vapor exceeding 300 $^\circ$C [7,8].
In contrast, TiO$_2$-PANi thin films exhibited a systematic response when exposed towards ethanol vapor. Being the reduction agent, the introduction of ethanol vapor towards the composite thin film injected electrons to the film, and thus significantly increase the number of charge carrier in the film. As a result, more electrons flowed in the film and at the same time reduced the resistance of the film. During recovery process, the film was exposed towards N$_2$ gas. As can be seen from the Figure 6 (b), the film exhibited a reduction in voltage, a consequence of oxidizing process by the N$_2$ gas. The suitability of TiO$_2$-PANi as methanol vapor sensor was also investigated. Similar pattern was observed as shown in Figure 6 (c). Over long exposure it was observed that TiO$_2$-PANi sensor exhibited a good stability and repeatability as gas sensor with consistent pattern and response magnitude.

**CONCLUSION**

In conclusion, the addition of PANi improved the gas sensing properties of TiO$_2$ thin films at room temperature. The nanocomposite TiO$_2$ thin film exhibit a satisfactory response towards ethanol and methanol vapor. However, the ability to select different type of gas remain the main issue as the detection pattern for both gases are similar.

**ACKNOWLEDGEMENT**

The authors would like to thank the Malaysia Ministry of Science, Technology and Innovation for the grant of eScience Fund 03-01-02-SF0079.

**REFERENCES**


Journal of Sensors. 7: 267-307


Corresponding Author: hafizhj@ukm.my