Solid State Science and Technology, Vol. 17, No 1 (2009) 126-131
ISSN 0128-7389

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 Nanoelectronic (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 polypyrole, polythiopenes 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 ($< 10^{-5}$ S cm^{-1}), chemically sensitive and have poor mechanical properties. For that, hybridization of

Corresponding Author: hafizhj@ukm.my

Solid State Science and Technology, Vol. 17, No 1 (2009) 126-131
ISSN 0128-7389

metal oxide and conducting polymer are believed can improve the properties of pure materials for gas sensing detection.

The hybridization between titanium dioxide (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 ^oC and 90 ^oC 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.

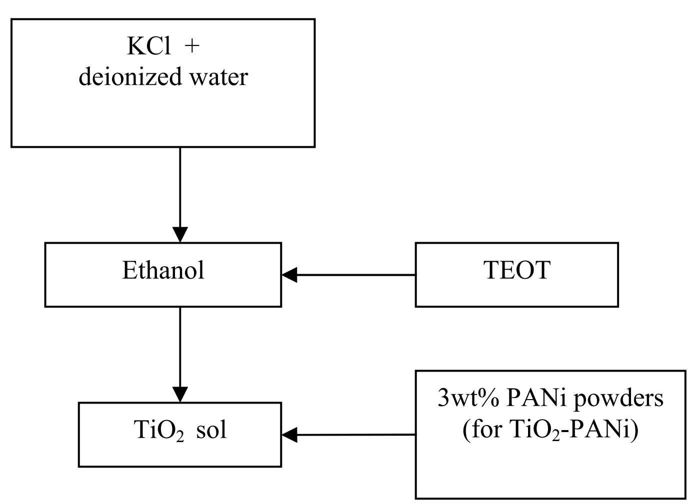

Figure 1: Flow chart of synthesis process for TiO_2 and TiO_2-PANi solution

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.

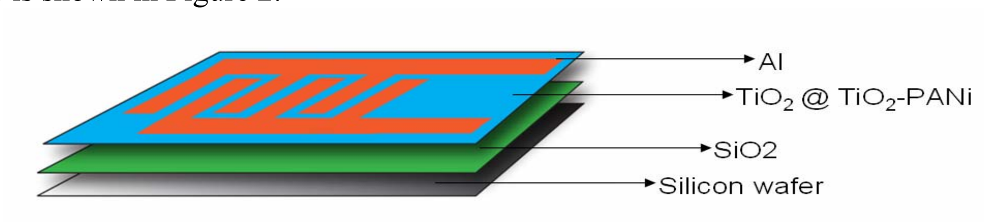

Figure 2: Fabrication of sensor device

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 (λ=1.5406Å), 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).

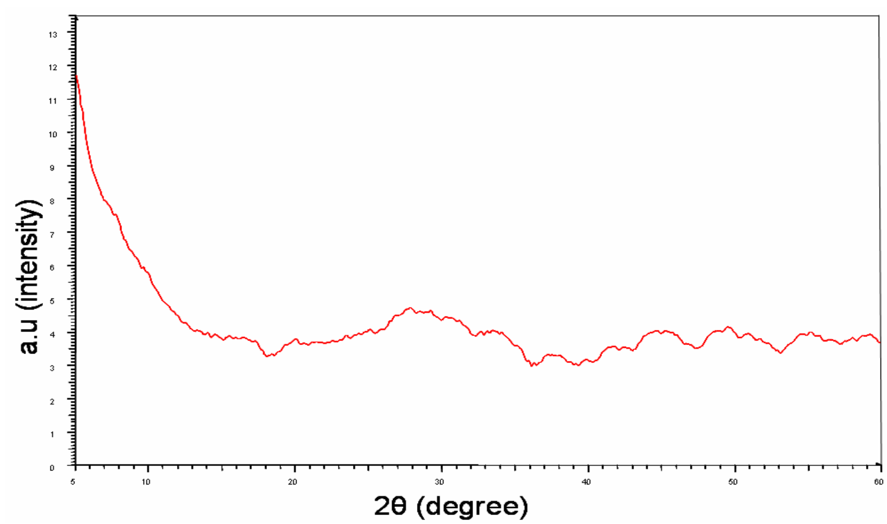

Figure 3: Typical XRD spectrum of amorphous TiO_2 and TiO_2-PANi thin film

Corresponding Author: hafizhj@ukm.my

Solid State Science and Technology, Vol. 17, No 1 (2009) 126-131
ISSN 0128-7389

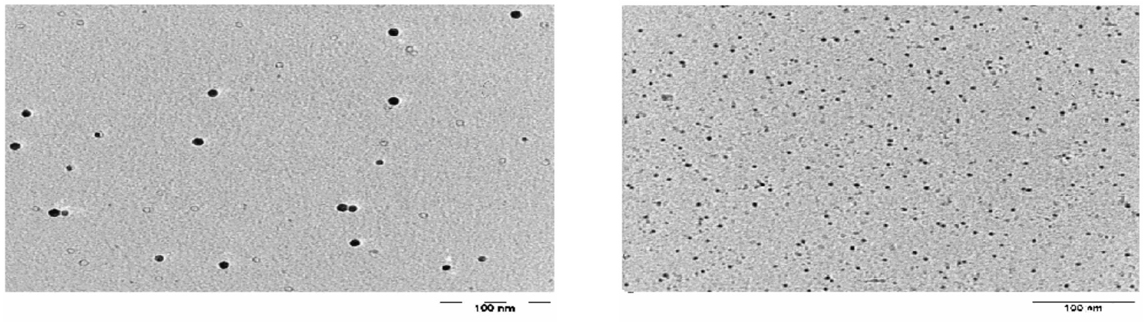

Figure 4 : TEM images of (a) TiO_2 (b) TiO_2-PANi dried sol- gel

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.

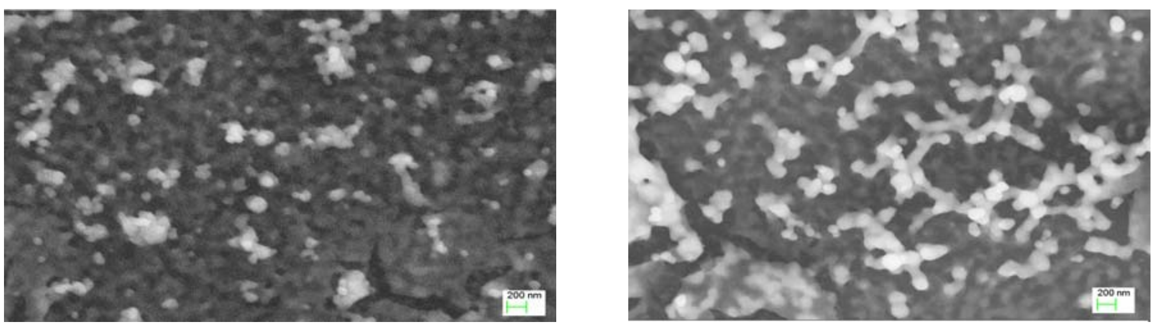

Figure 5: SEM images of (a) TiO_2 (b) TiO_2-PANi thin film

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 ^{0}C [7,8].

Corresponding Author: hafizhj@ukm.my

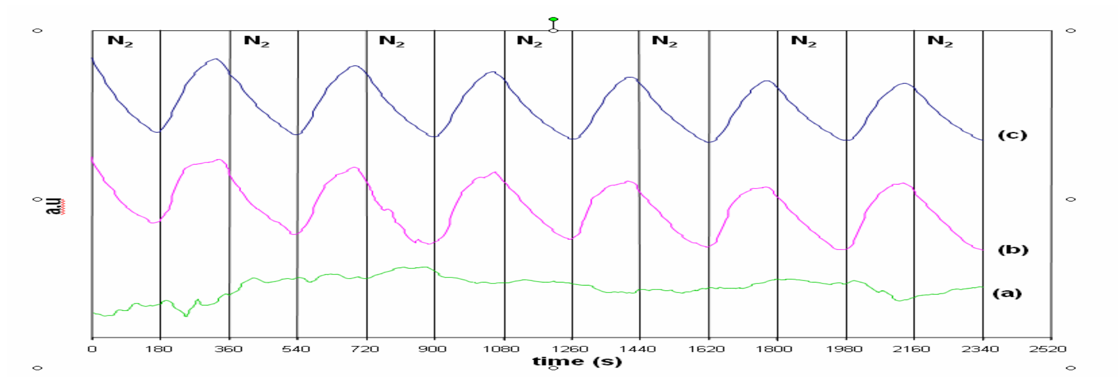

Figure 6 : Response of (a) TiO_2 thin film towards ethanol vapour (b) TiO_2-PANi thin film towards ethanol vapour and (c) TiO_2-PANi thin film towards methanol vapor

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

[1]. Dhawale, D.S., Salunkhe, R.R., Patil, U.m., Gurav, K.V., More, A.M., Lokhande, C.D. 2008. Room temperature liquefied petroleum gas (LPG) sensor based on p-polyaniline/n-TiO_2 heterojunction. *Journals of Sensors and Actuators*.

[2]. Bai, H. & Shi, G. 2007. Review gas sensors based on conducting polymers.

Corresponding Author: hafizhj@ukm.my

Journal of Sensors. **7**: 267-307

[3]. Tai, H., Jiang Y., Xie, G., Yu, J., Chen, X. & Yu, Z. 2007. Influence of polymerization temperature on NH_3 response of Pani/TiO_2 thin film gas sensor. *Journal of Sensors and Actuators B*. **129**:319-326

[4]. Shi Jian, S. & Kuramoto, N. 2000. Processable polyaniline-titanium dioxide nanocomposites: effect of titanium dioxide on the conductivity. *Journal of Synthetic Metals*. **114**: 147-153

[5]. Geng L., Zhao, Y., Huang, X., Wang, S., Zhang, S. & Wu, S. 2007. Characterization and gas sensitivity study of Polyaniline/SnO_2 hybrid material prepared by hydrothermal route. *Journal of Sensors and Actuators B*. **120**: 568-572

[6]. Arshad, S., Mat Salleh, M. & Yahaya, M. 2008. The performance of quartz crystal microbalance gas sensor using titanium dioxide nanoparticles coated with porphyrin thin films. *Journal of Sensor Letter*. **6**: 1-5

[7]. Hieu, N. V., Duy, N. V., Huy, P. T. & Chien, N. D. 2008. Inclusion of SWCNTs in Nb/Pt co-doped TiO_2 thin film sensor for ethanol vapour detection. *Journal of Physica E*. **40**: 2950-2958

[8]. Tang, H., Prasad, K., Sanjines R. & Levy, F. 1995. TiO_2 anatase thin films as gas sensors. *Journal of Sensors and* Actuators. **26-27**: 71-75

[9]. Xu, J. C., Liu, W. M., & Li, H. L. 2005. Titanium Dioxide Doped Polyaniline. *Journals of Materials Science & Engineering*. **25** : 444-447

[10]. Zheng, J., Li, G., Ma, X., Wang, Y., Wu, G., & Cheng, Y. 2008. Polyaniline-TiO_2 nano-composite-based trimethylamine QCM sensor and its thermal behavior studies. *Journal of Sensors and Actuators B*.

[11]. Ram, M. K., Yavuz, O., Lahsangah, V. & Aldissi, M. 2005. CO gas sensing ultrathin nanokomposit conducting polimer. *Journal of Sensors and Actuators B*. **106**: 750-757

[12]. Teleki, A., Bjelobrk, N. & Pratsinis, S. E. 2008. Flame-made Nb- and Cu-doped TiO_2 sensors for CO and ethanol. *Journal of Sensors and Actuators B*. **130**: 449-457

[13]. Somani, P. R., Marimuthu, P. R., Mulik, U. P., Sankar, S. R. & Amalnerkar, D. P. 1999. High piezoresistivityand its origin in conducting polyaniline/TiO_2 composites. *Journal of Synthetic Metals*. **106**: 45-52

Corresponding Author: hafizhj@ukm.my