

MODIFICATION OF STAINLESS STEEL SURFACE FOR MWCNT INKJET PRINTED GAS SENSOR

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Received: May 2, 2018; Revised: August 23, 2018; Accepted: August 27, 2018

Abstract

Austenitic stainless steel foils (304 SS) were used as catalytic substrates for the growth of multi-walled carbon nanotubes (MWCNTs) by using thermal chemical vapor deposition (CVD) technique. Before the MWCNT growth, the surface of substrate was modified using polishing and oxidation treatments. To understand the effect of this modification on the growth of MWCNTs, the as-received 304 SS was also investigated as a comparison. Scanning electron microscopy (SEM), Raman spectroscopy and energy dispersive X-ray spectroscopy (EDS) were employed to study the morphology of MWCNTs and elemental compositions of their substrates. Furthermore, the synthesized MWCNTs associated with dimethyl sulfoxide (DMSO) compound were prepared as the conductive ink used for the fabrication of room temperature ammonia (NH₃) gas sensor. The inkjet printing technique was considered for the deposition of MWCNT sensing films on the silver electrodes. The experimental results reveal that the ink obtained from MWCNTs grown on the modified 304 SS exhibits the high sensitivity and fast response to NH₃ at room temperature.

Keywords: Multi-walled carbon nanotubes, Stainless steel, Inkjet-printed gas sensor

Introduction

Ammonia (NH₃) as high toxic gas has been widely used in various manufacturing industries. However, the leakage of NH₃ is often reported as a serious accident for affecting the lives and assets of employees and

entrepreneurs. Although the gas leak detectors are used, the high price of them is a main problem for small enterprises. Recently, printed electronics have been widely known as the new technique for industrial revolution of

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electronic devices. Because of the advantages of lightweight, flexible characteristics and low-cost fabrication, the printed electronics have recently attracted as candidates in new technological devices such as flexible display screen (Ersman *et al.*, 2013), solar cell (Galagan *et al.*, 2011) and gas sensing detections (Seekaew *et al.*, 2014). For the gas sensor, inkjet printing technique was considered for the effective deposition of sensing films on the interdigitated electrodes (Huang *et al.*, 2014). Multi-walled carbon nanotube (MWCNT) is one of the materials that are applied in gas sensor applications. The NH_3 molecules can be exactly attached on the surface of them at room temperature. The adhesion and distribution of the MWCNT sensing materials in the inkjet inks were reported to affect the gas detective performance (Abdullah *et al.*, 2017). However, The van der Waals forces between the MWCNTs and the neighbor causes the poor dispersion of MWCNTs within various solvents.

In this work, the MWCNTs were grown directly on the 304 SS catalytic substrates. The novel modified process on 304 SS was represented for the effective growth of MWCNTs. Furthermore, the synthesized MWCNTs with dimethyl sulfoxide (DMSO) compound as the good dispersive conductive ink for fabrication of highly sensitive NH_3 inkjet-printed gas sensor at room temperature are highlighted.

A $1 \times 1 \text{ cm}^2$ 304 SS foil with a thickness of 0.1 mm was polished using a silicon carbide (SiC) grinding paper (grit 3,000). This polishing treatment was conducted for eliminating the chromium (Cr) protective layers. The polished 304 SS was then placed into the furnace for oxidation treatment at the temperature of 550°C (45 sec). The iron oxide content (Fe_2O_3) was formed on the top surface of modified 304 SS. This oxide content was used as the catalysts for MWCNT growth during thermal chemical vapor deposition (CVD) process. For the CVD process, acetylene (C_2H_2), hydrogen (H_2) and argon (Ar) were conducted as source gases. The MWCNTs grown on 304 SS using a home-built thermal CVD system were explained in

the previous work of first author (Pakdee *et al.*, 2017). The morphology of MWCNTs and elemental compositions of their substrates were characterized by using scanning electron microscopy (SEM), Raman spectroscopy and energy dispersive X-ray spectroscopy (EDS). For gas sensor preparation, the MWCNTs was dissolved in dimethyl sulfoxide (DMSO) solvent with a weight ratio of 10% MWCNTs to 90% DMSO solvent. The HP deskjet 2000 j210 printer was applied for printing the sensing film on the top layer of gas sensor. The original ink in the printer was removed from a cartridge. The blank cartridge was refilled with the prepared MWCNT conductive ink. The schematic diagram of structure for NH_3 sensor is shown in Figure 1(a). Before the printing, the silver interdigitated electrode with 1 mm interdigit gap was coated on the plastic substrate using screen printing. The MWCNT sensing film was reprinted five times on the substrate. The thickness of sensing film in this work is approximately $1.2 \mu\text{m}$. The photograph of prepared gas sensor is displayed in Figure 1(b). Finally, the sensors were tested under NH_3 gas using a standard flow-through system.

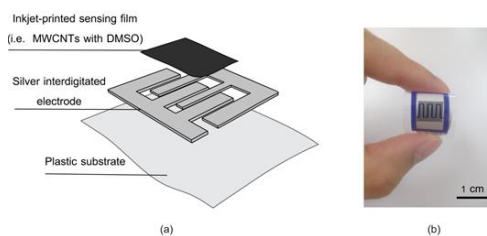


Figure 1. (a) Schematic diagram and (b) photograph of inkjet-printed gas sensor

Materials and Methods

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Results and Discussion

As explained in the first section, the mechanical polishing procedure followed by the oxidation treatment was considered as a modified process for 304 SS. Figure 2 shows SEM images of (a) as-received 304 SS and (b) modified 304 SS. As can be seen that the surface of both conditions reveal the obvious different topologies. For the modified condition, the particle islands and the other with dome-

like structures of 304 SS were observed. By contrast, a smooth and shiny surface can be observed for the as-received 304 SS. There has been a paper reported that the substrate surface is the interested parameter as it is directly involved in CNT growth author (Atthipalli *et al.*, 2013). The smooth and shiny protective chromium oxide layer of the SS can be destroyed by using oxidation treatment at high temperature. The catalyst surface roughness progressively increased the reactivity of gaseous hydrocarbons on SS surface (Zhuo *et al.*, 2014).

Before the MWCNT growth, the creation of thin oxide layers on the top surface of metal substrate has been demonstrated to increase the number of catalysts (Zhuo *et al.*, 2014; Silva *et al.*, 2015). To illustrate this creation, a bare cross-sectional substrate obtained from modified process was mounted with epoxy resin. The cross-sectional SEM image with elemental line scan profiles of modified 304 SS was displayed in Figure 3. The various elemental profiles in the range of 3.5 μm are shown by an arrow in Figure 3(a). The profiles of Fe, Cr, Ni, and oxygen as a function of the distance are further shown in Figure 3(b). It is seen that the concentrations of Fe and oxygen showed a clearly increase after modified

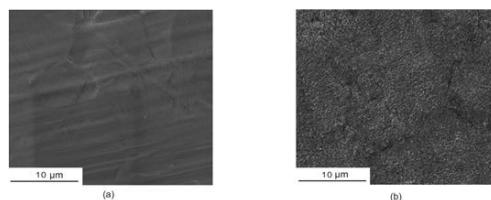


Figure 2. SEM images of (a) as-received 304 SS and (b) modified 304 SS

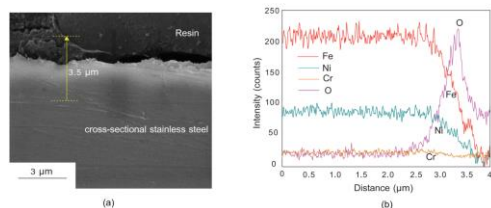


Figure 3. (a) Cross-sectional SEM image and (b) EDS line scan of modified 304 SS

substrate process. Therefore, the oxidation treatment can be promoted for increasing the number of catalysts on metal alloy substrate. After the MWCNT growth, the morphology of MWCNTs can be observed in Figure 4. The dense MWCNTs were grown on the modified 304 SS (Figure. 4(b)) while the lower dense MWCNTs were grown on the as-received 304 SS (Figure 4(a)).

Figure 5 shows the Raman spectra of MWCNTs grown on as-received 304 SS (Figure 5(a)) and modified 304 SS (Figure 5(b)). Raman measurements have been popularly employed for identifying the defect of MWCNTs using the intensity ratio of

D band to G band (I_D/I_G). The values of I_D/I_G ratio for MWCNTs grown on as-received 304 SS and modified 304 SS are found to be 1.41 and 1.23, respectively. Recently, there has been a paper reported that the graphitic defect of carbon strongly interacted with CO, NO, and NO₂ but weakly with NH₃ (Kim *et al.*, 2016). Therefore, the low defective MWCNTs obtained from modified 304 SS condition can be used as a good candidate for fabrication of NH₃ gas sensing devices.

The sensing performance of NH₃ inkjet-printed gas sensor under an air flow rate of 1,000 sccm is shown in Figure 6(a). Upon exposure to NH₃, the resistance of the sensor increases rapidly and then recovers after restoration of pure air. The time to reach 90% of the maximum change for sensor resistance was defined as the response time. The time of NH₃ response for MWCNTs grown on as-received and modified 304 SS substrates are approximately 7 min and 5 min, respectively. While comparing the recovery time, the sensor obtained from as-received 304 SS condition was found to be almost perfectly to the initial state under pure air within 8 min but did not recover for the sensor obtained from modified 304 SS condition. This result may be due to the highly strong bonding between NH₃ molecules and oxygen containing groups on high surface area of MWCNTs at room temperature. To understand the sensitivity of the fabricated sensor, the sensing response (S) of the sensor is defined as $S (\%) = [(R_{\text{gas}} - R_{\text{air}}) \times 100] / R_{\text{air}}$, where R_{gas} and R_{air} are the resistance of the gas sensor in test gas and pure air, respectively. The calculated values of gas response in the NH₃ concentration of 200 ppm for as-received and modified 304 SS conditions are 1.6 % and 9.6%, respectively. In addition, the linear sensitivities of the gas response for the MWCNTs grown on as-received and modified 304 SS substrates in the NH₃ concentration range of 200-1,000 ppm are shown in Figure 6b. It is seen that the MWCNT sensor obtained from modified 304 SS shows higher response compared with the sensor obtained from as-received 304 SS. Accordingly, the MWCNTs grown on modified 304 SS can give the highly sensitive room temperature NH₃ gas sensor.

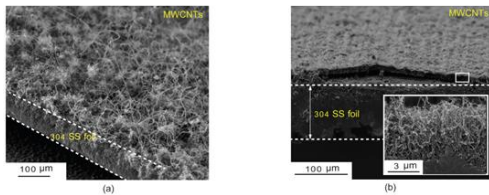


Figure 4. SEM images of MWCNTs grown on (a) as-received 304 SS and (b) modified 304 SS

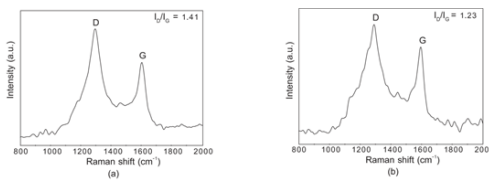


Figure 5. Raman spectra of MWCNTs grown on (a) as-received 304 SS and (b) modified 304 SS

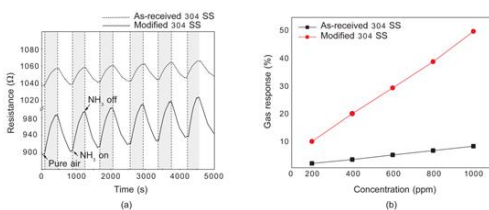


Figure 6. (a) Sensing performance and (b) sensing response of prepared NH₃ gas sensors

The stability of fabricated gas sensors has been also considered. Again, it can be seen in Figure 6(a) that the both sensors show a good reproducibility over six cycles. Therefore, the fabricated sensors are stable during gas measurement process. Moreover, the measurements were also repeated every week for 2 months. It can be found that the all sensors show the good performance of stability with only ~5% of letdown from its initial response up to 1 month under room temperature preservation.

Conclusions

The MWCNT gas sensor has been successfully fabricated by inkjet printing technique. The sensing performances for two sensors from using MWCNTs grown on 304 SS with different conditions of as-received and modified substrates were compared. For the modified 304 SS condition, the sensor exhibits the high sensitivity and fast response to NH_3 at room temperature. It is expected that this finding will be useful for a good selection of materials in an applied gas sensing technology such as flexible and wearable electronic gas sensors.

Acknowledgements

This work was supported by Research and Development Institute, Rajamangala University of Technology Krungthep, Thailand.

References

- Abdullah, S.A., Mohammad, R., Alenezi, K.T.L., and Silva, S.R.P. (2017). Inkjet printing of polymer functionalized cnt gas sensor with enhanced sensing properties. *Mat. Lett.*, 189:299-302.
- Atthipalli, G., Wang, H., and Gray, J.L. (2013). Catalyst-assisted vertical growth of carbon nanotubes on inconel coated commercial copper foil substrates versus sputtered copper films. *Applied Surface Sci.*, 273:515-519.
- Ersman, P.A., Kawahara, J., and Berggren, M., (2013). Printed passive matrix addressed electrochromic displays. *Organic Electronics.*, 14(12):3,371-3,378.
- Galagan, Y., Rubingh, Jan-Eric J.M., Andriessen, R., Fan, C.C., Blom Paul, W.M., Veenstra, S.C., and Kroon, J.M. (2011). Ito-free flexible organic solar cells with printed current collecting grids. *Solar Ener. Mat. Solar Cells*, 95(5):1,339-1,343.
- Huanga, L., Jiang, P., Wang, D., Luo, Y., Li, M., Lee, H., and Gerhardt, A. (2014). A novel paper-based flexible ammonia gas sensor via silver and swnt-pabs inkjet printing. *Sensors Actuators B.*, 197:308-313.
- Kim, J., Choi, S.W., Le, J.H, Chung, Y., and Byun, Y.T. (2016). Gas sensing properties of defect-induced single-walled carbon nanotubes. *Sensors and Actuators B.*, 228:688-692.
- Pakdee, U., Chiangga, S., Suwannatus, S., and Limsuwan, P. (2017). Growth of mwcnts on flexible stainless steels without additional catalysts. *J. Nanomater.*, p. 5672728.
- Seekaew, Y., Lokavee, S., Phokharatkul, D., Wisitsoraat, A., Kerdcharoen, T., and Wongchoosuk, C. (2014). Low-cost and flexible printed graphene-pedot:pss gas sensor for ammonia detection. *Organic Electronics*, 15(11):2,971-2,981.
- Silva, R.M., Bastos, A.C., Oliveira, F.J., Cont, D.E., Fan, Y., Pinna, N., and Silva, R.F. (2015). Catalyst-free Growth of Carbon Nanotube Arrays Directly on Inconel® Substrates for Electrochemical Carbon-based Electrodes. *J. Mat. Chem. A.*, 3(34):17,804-17,810.
- Zhuo, C., Wang, X., Nowak, W., and Levendis, Y.A. (2014). Oxidative heat treatment of 316l stainless steel for effective catalytic growth of carbon nanotubes. *Appl. Surface Sci.*, 313:227-236.