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Electron beam evaporated carbon nanotube dispersed SnO_2 thin film gas sensor

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Abstract Carbon nanotube (CNT) is a useful material for gas-sensing applications because of its high surface to volume ratio structure. In this work, multi-wall CNTs are incorporated into tin oxide thin film by means of powder mixing and electron beam evaporation and the enhancement of gas-sensing properties is presented. The CNTs were combined with SnO_2 powder with varying concentration in the range of 0.25–5% by weight and electron beam evaporated onto glass substrates. From AFM and TEM characterization, CNT inclusion in SnO_2 thin film results in the production of circular cone protrusions of CNT clusters or single tube coated with SnO_2 layer. Experimental results indicate that the sensitivity to ethanol of SnO_2 thin film increases by the factors of 3 to 7, and the response time and recovery time were reduced by the factors of 2 or more with CNT inclusion. However, if the CNT concentration is too high, the sensitivity is decreased. Moreover, the CNT doped film can operate with good sensitivity and stability at a relatively low temperature of 250–300°C. The improved gas-sensing properties should be attributed to the increasing of surface adsorption area of metal oxide produced by CNT protrusion.

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1 Introduction

Conductometric thin film semiconductor gas sensors have recently been of much interest for many gas-sensing applications because of microelectronic compatibility, ease of control of processing parameters, reproducibility, fast response, relatively low power consumption/cost, and simple electronic interface. Gas sensors fabricated by different thin film deposition techniques, including sputtering, sol-gel, evaporation, chemical vapour deposition (CVD), have been widely studied [1–10]. Electron-beam evaporation is one of the preferred techniques for thin film gas sensor fabrication because of ability to directly evaporate high quality metal oxide film, flexibility in doping, in-situ multiplayer deposition capability, and reproducibility [6, 7]. However, e-beam evaporation has not been popular for gas sensor fabrication because conventional e-beam evaporated gas sensor tends to suffer from poor gas-sensing sensitivity and selectivity problems due to unfavourable material properties as a results of decomposition at a high evaporation temperature [6]. Several approaches including doping with suitable materials and ion-assisted deposition (IAD) have been applied to improve the sensor performances [8–10].

Carbon nanotube (CNT) is a useful material for gas-sensing applications because of its high surface to volume ratio structure. CNTs have been incorporated into a variety of gas sensors by different means to improve their gas-sensing properties. For example, the sensitivity of metal oxide gas sensor can be enhanced by single-wall CNTs inclusion in sol-gel prepared tin oxide thin film [11]. In this work, multi-wall

CNTs are incorporated into tin oxide thin film by means of powder mixing and electron beam evaporation and the effect of CNTs dispersion in electron-beam evaporated tin oxide thin film is reported. The sensors were tested toward ethanol vapour.

2 Materials and methods

2.1 Materials for gas sensor fabrication

The starting materials are an analytical grade tin oxide (SnO_2) powder (99.9%) and CNT powder. First, multi-wall CNTs were synthesized by chemical vapor deposition (CVD) using acetylene and argon gases with iron catalyst at 600°C [12]. The CNTs were then thoroughly mixed with SnO_2 powder with concentration in the range of 0.25–5% by weight. For electron beam evaporation, CNT-SnO_2 powder was compressed into cylindrical pellets. The substrates for thin film coating were standard BK7 glass slides. NiCr (Ni 80% and Cr 20%) was used as the low cost material for the thin film heater.

2.2 Gas sensor fabrication

The gas sensors were fabricated from a series of thin film deposition using Denton's ion-assisted e-beam evaporator system. This system consists of a high vacuum chamber equipped with electron gun, ion gun, quartz lamp, quartz crystal monitor, and optical monitor. The gas sensor fabrication process started with the deposition of Cr/Au interdigitated electrodes on a glass or alumina substrate. Prior to deposition, the substrates were cleaned by oxygen-ion bombardment in a vacuum pressure of $\sim 10^{-4}$ Torr. This cleaning is to improve adhesion of the film to the substrates by removing moisture and any organic contaminants on the surface. Chromium (Cr) and gold (Au) layers were then successively e-beam evaporated over the glass substrate through electroplated-Ni shadow masks having an interdigitated pattern. The width, spacing, and length of the interdigitated electrode were ~ 100 μm, ~ 100 μm, and ~ 1 mm, respectively. The thickness of Cr and Au layers were ~ 50 nm and ~ 200 nm, respectively. The film thickness was measured by the quartz crystal monitor and calibrated by a Detak profiler.

Next, the compressed CNT-SnO_2 material was electron beam evaporated over interdigitated electrode through another electroplated shadow mask with square window pattern aligned to interdigitated area. For metal oxide deposition, substrates were heated to the desired temperature with quartz lamp radiation. The deposition rate, film thickness, and substrate temperature were approximately 0.2 nm/s, 300 nm, and 130°C, respectively. The evaporated film was then annealed at 500°C for 3 h. After the metal oxide coating, a Cr layer and a NiCr (Ni 80% and Cr 20%) layer were then blanket e-beam evaporated over the backside of substrate. The Cr layer is required as an adhesive layer between the NiCr film and the glass substrate. The thickness of Cr and NiCr layers were ~ 50 nm and 500 nm, respectively. The thickness of NiCr layer was suitably chosen for gas sensor heating up to 350°C.

2.3 Gas sensing measurements

The gas-sensing characteristics of metal oxide thin films were characterized with ethanol (C_2H_5OH) vapour. For electrical testing, the sensor electrodes were gold-ball bonded for electrical connection and the NiCr heaters were bonded to solid wires with silver conductive epoxy. The gas sensors were then mounted in a stainless steel gas-testing chamber. The NiCr-heater was heated by a regulated dc power supply to different operating temperatures. The resistances of various sensors were continuously monitored with a LabView based software from the computer through the measuring circuit. The measuring circuit was a current to voltage converter, which gives the output voltage that is inversely proportional to the resistance of the gas sensor.

For gas testing, purified air (99.99% Air Zero) and ethanol containing gas sample were mixed with different ratios and made to flow through the testing chamber. The gas flow rates were precisely manipulated using a computer controlled multi-channel mass flow controller. Purified air was used at a constant flow rate of 0.100 litres per minute. The ethanol gas source was obtained by passing Air Zero through 99.9% ethanol. The sensor was exposed to the gas sample for ~ 80 s for each gas response tested and the sensor was recovered by exposure to purified air. The operating temperature was varied from 200°C to 350°C.

3 Results and discussion

The surface morphologies of CNT dispersed tin oxide thin films were imaged using an atomic force microscope (AFM). Typical AFM micrographs of CNT-SnO_2 thin film with different CNT concentrations are shown in Fig. 1. It can be seen that CNT inclusion in SnO_2 thin film results in the production of circular cone protrusions on the smooth SnO_2 background. In addition, the density, average base size, and maximum height of circular cone protrusions are increased as the content of CNT increases. As the CNT content increases from 0.25% to 5%, the density, the average base size, and the maximum height of protrusions are increased from ~ 0.02 μm^{-2} to ~ 0.75 μm^{-2}, from ~ 100 nm to 400 nm, and from ~ 85 nm to ~ 280 nm, respectively. The corresponding root mean square (rms) surface roughness of thin film are estimated to be increasing from ~ 5.6 nm to 152 nm as the CNT

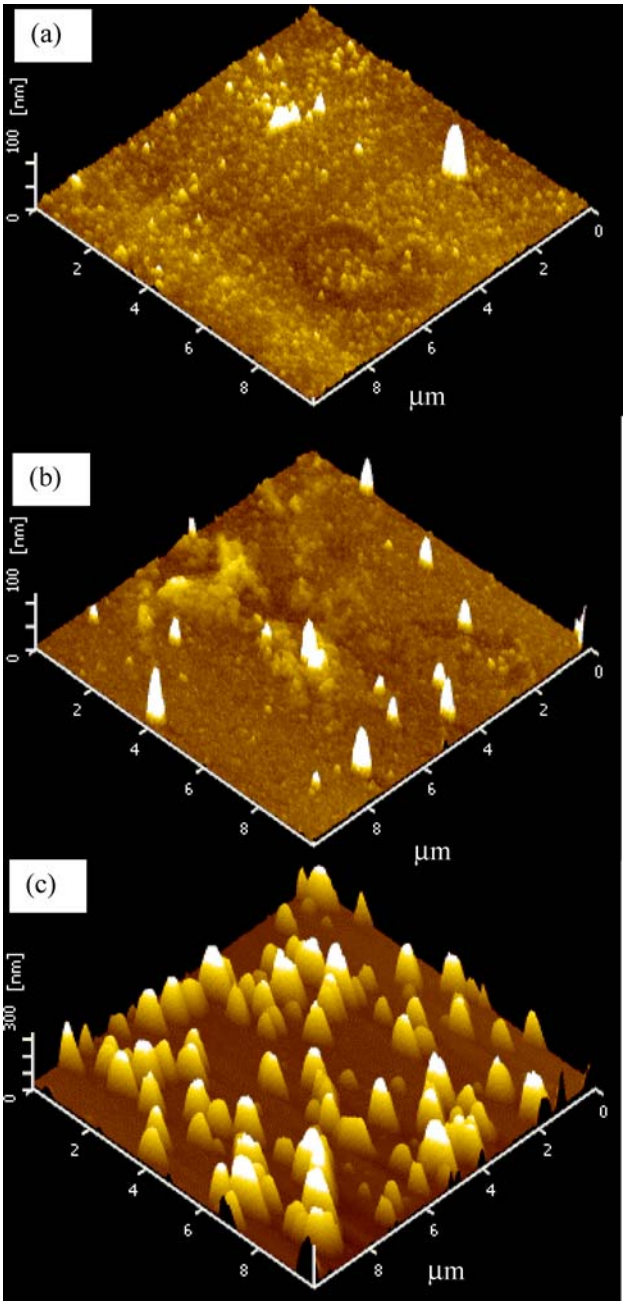

Fig. 1 Typical AFM micrographs of CNT-SnO_2 thin film with different CNT concentrations (a) 0.25% wt, (b) 1% wt, and (c) 5% wt

content increases from 0% to 5%. Thus, an important advantage of CNT inclusion into metal oxide thin film by this technique is the ability to control density, size, and height of the protrusion. It is interesting that CNTs arrange perpendicularly to the substrate rather than randomly lying on the surface. A possible reason for this phenomenon is that CNTs rearrange themselves while they are moving toward substrates in line with the material evaporation trajectory, which is almost perpendicular to the substrate.

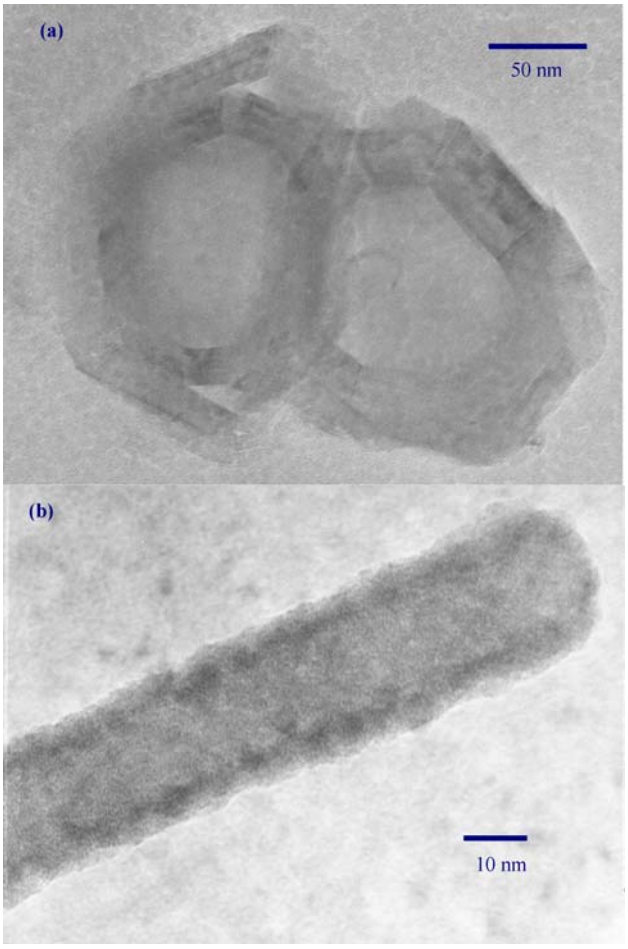

Fig. 2 Typical HRTEM (High Resolution-TEM) top view images of CNT-SnO_2 composite (a) a circular tube cluster and (b) an isolated tube lying at an angle

The detailed structure of CNT-SnO_2 composite was characterized by a transmission electron microscope (TEM). Typical HRTEM (High Resolution-TEM) images of CNT-SnO_2 composite are shown in Fig. 2. From the TEM images, it can be identified that the observed circular cone protrusions are either circular clusters of multi-wall CNTs (Fig. 2(a)) or a single multi-wall CNT lying at an angle (Fig. 2(b)), which are coated by nanocrystal SnO_2 layer. The diameter of CNTs and the crystal size of SnO_2 are estimated to be in the range of ∼10–70 nm and 3–10 nm, respectively. Thus, the result reveals that CNTs can be co-evaporated with SnO_2 material with no significant decomposition at the evaporation temperature of ∼1500°C. Furthermore, the CNTs are self-organized on the substrate with specific configurations, i.e, circular cluster or isolated tube lying at some angle.

The gas-sensing characteristics of oxygen-ion assisted e-beam evaporated metal oxide thin films deposited with different oxygen flow rates at various temperatures were measured. The gas-sensing characteristics of the tin oxide thin film with no CNT dispersion is given as a base line. Typical

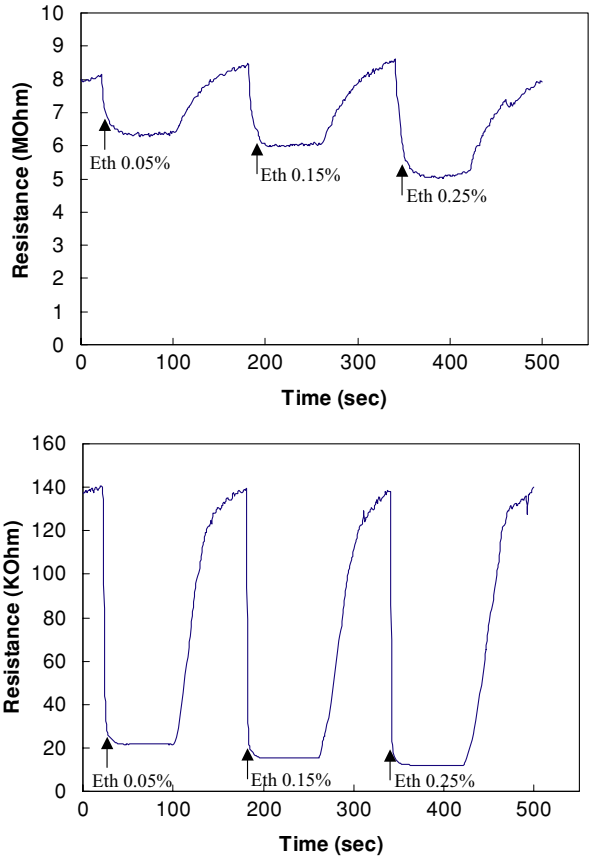

Fig. 3 Typical time responses to ethanol at 250°C of tin oxide thin film with (a) no CNT and (b) 2% CNT

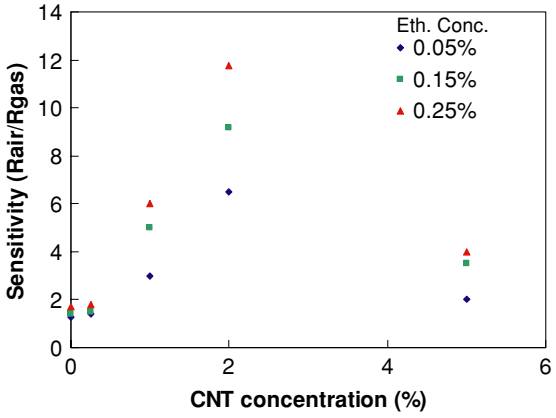

Fig. 4 Typical sensitivity to ethanol vs. CNT concentration of tin oxide thin films at 250°C

time response to ethanol of the tin oxide sensors with no CNT and 2% CNT at 250°C are shown in Fig. 3(a) and (b), respectively. The concentration of the gas sample is indicated in the figures. From the figures, it is clear that there is an abrupt decrease in the sensor's resistance due to gas adsorption after each injection of gas sample. The abrupt decrease in resistance confirms that the adsorption is chemical adsorption with reducing reaction, which results in electron transfer from the gas sample to the semiconductor surface. It is clear that the resistance change of the SnO_2 gas sensor with 2% CNT is considerably more than that of sensor with no CNT. Thus, the sensitivity of the SnO_2sensor can be appreciably improved by CNT inclusion. The typical response and recovery times of the SnO_2 gas sensor with no CNT to ethanol are ∼6 s and ∼100 s, respectively, while the typical response and recovery times of the SnO_2 gas sensor with 2% CNT are ∼3 s and ∼60 s, respectively. Therefore, CNT inclusion in SnO_2 gas sensor also results in a reduction of response and recovery time by about a factor of two in this case.

Gas-sensing sensitivity for a reducing gas of a semiconductor gas sensor is normally defined as the ratio of resistance with no gas sample to that with a gas sample. From the time response data, gas-sensing sensitivity was calculated and plotted versus various parameters including CNT concentration, gas concentration, and temperature. Figure 4 shows the sensitivity to ethanol of tin oxide thin films as a function of CNT concentration at 250°C operating temperature. From Fig. 4, it is clear that the sensitivity to ethanol of SnO_2 gas sensor is increased at first as CNT content increases up to 2% but it is reduced rapidly when CNT concentration is further increased to 5%. The sensitivity to ethanol of SnO_2 thin film increases by the factors of 3 to 7 depending on CNT concentration and the optimum value for CNT concentration is approximately 2%.

The results indicate that the CNT inclusion improves the gas sensing sensitivity of e-beam evaporated metal oxide thin films but if the CNT content is too high the sensitivity decreases. A plausible explanation for the observed effect is that the addition of CNTs considerably increases the surface adsorption area of the tin oxide. The significant increase of metal oxide surface area is evident from the surface and material characterization using AFM and TEM. As discussed above, the CNTs are found to scattered as separated circular clusters or single tube that protrude from the flat surface with SnO_2 coating. However, when CNT content is sufficiently high the CNTs begin to connect together and results in shorter resistance path that shunts gas-sensing current of the metal oxide layer. Thus, the gas sensitivity is reduced for very high CNT concentration.

The effect of operating temperature was also investigated. The operating temperature was varied from 150 to 350°C. Figure 5 shows the effect of temperature on sensitivity to ethanol of tin oxide thin film with no CNT and 2% CNT. For temperatures below 200°C, the tin oxide thin film gave low to negligible response to ethanol and hence the sensitivity is ∼ 1. From Fig. 5, it can be seen that the tin oxide thin films with CNT have high sensitivity at moderate temperatures of 250–300°C while those with no CNT should be operated at higher

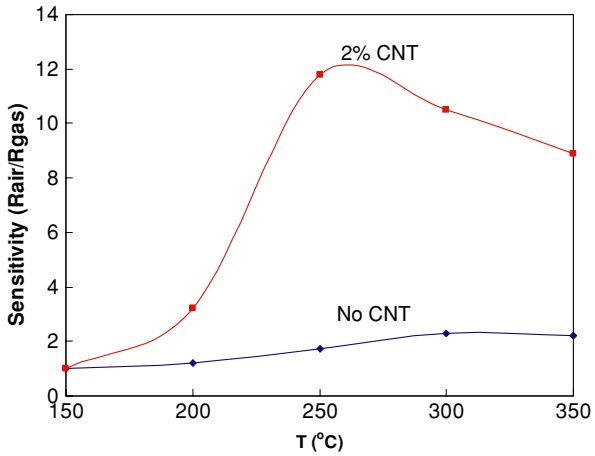

Fig. 5 Typical tin oxide thin film's sensitivity to ethanol vs. temperature with no CNT and 2% CNT at 0.25% ethanol concentration

temperature. Thus, the increased surface adsorption area of metal oxide by CNT inclusion also leads to some reduction of operating temperature. In addition, the sensitivity of CNT doped sample tends to slightly decrease above 300°C. This unexpected characteristic cannot yet be clearly explained. However, we speculate that it may result from the combined effect of the microstructure and composition of the SnO_2-CNTs composite. Furthermore, small amount of iron catalyst in CNTs may also contribute to this behavior.

4 Conclusions

In conclusion, multi-wall CNTs are incorporated into tin oxide thin film by means of powder mixing and electron beam evaporation and the enhancement of gas-sensing properties is reported. The CNTs were combined with SnO_2 powder with varying concentration in the range of 0.25–5% by weight and was electron beam evaporated onto glass substrates with the controlled thickness of 300 nm. From AFM and TEM characterization, CNT inclusion in SnO_2 thin film results in the production of circular cone protrusions of CNT clusters or single tube coated with SnO_2 layer. Experimental results indicate that the sensitivity to ethanol of SnO_2 thin film increases by the factors of 3 to 7 with CNT inclusion up to 2%. In addition, the response time and recovery time were also reduced by the factors of 2 or more with CNT addition. Moreover, the CNT doped film can operate with good sensitivity and stability at a relatively low temperature of 250–300°C. The improved gas-sensing properties should be attributed to the increasing of surface area of metal oxide produced by CNT protrusion. Our results, therefore, suggest that CNT doping in SnO_2 thin film by e-beam evaporation is an effective method to improve gas-sensing performances for metal oxide thin film gas sensor.

References

1. E. Zampiceni, E. Comini, G. Faglia, G. Sberveglieri, S. Kaciulis, L. Pandolfi, and S. Viticoli, *Sensors and Actuators*, **B89**, 225 (2003).
2. I. Jimnez, J. Arbiol, G. Dezanneau, A. Cornet, and J.R. Morante, *Sensors and Actuators*, **B93**, 475 (2003).
3. K. Aguir, C. Lemire, and D.B.B. Lollman, *Sensors and Actuators*, **B84**, 1 (2002).
4. T. Hyodo, N. Nishida, Y. Shimizu, and M. Egashira, *Sensors and Actuators*, **B83**, 209 (2002).
5. T. Oyabu, *J. Appl. Phys.*, **53**, 2785 (1981).
6. H. Madhusudhana and N. Chanodrkar, *Sensors and Actuators*, **B9**, 1 (1992).
7. M. Ivanovskaya, P. Bogdanov, G. Faglia, P. Nelli, G. Sberveglieri, and A. Taroni, *Sensors and Actuators*, **B77**, 268 (2001).
8. S. Shukla, S. Seal, L. Ludwig, and C. Parish, *Sensors and Actuators*, **B97**, 256 (2004).
9. D.E. Morton and A. Dinca, in *Proceeding of the 42nd Annual Technical Conference of the Society of Vacuum Coater* (Chicago, 1999), pp. 16–22.
10. A. Wisitsoraat, A. Tuantranont, V. Patthanasettakul, T. Lomas, and C. Pakabut, in *Proceeding of the 1*st *International Conference on Smart Material* (Chiangmai, Thailand, 2004), pp. 1–3.
11. J. Gong and Q. Chen, in *Technical Proceedings of the 2004 NSTI Nanotechnology Conference and Trade Show*, vol 3, p. 561.
12. S. Thongthem and P. Singjai, in 10th *Joint Vacuum Conference* (Slovenia, 2004).