An MWCNT-doped SnO_2 thin film NO_2 gas sensor by RF reactive magnetron sputtering*

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Abstract: An MWCNT-doped (multi-walled carbon nanotube) SnO_2 thin film NO_2 gas sensor, prepared by radio frequency reactive magnetron sputtering, showed a high sensitivity to ultra-low concentrations of NO_2 in the parts per billion range. X-ray diffraction, X-ray photoelectron spectroscopy, and scanning electron microscopy (SEM) characterizations indicated that the MWCNTs were affected by the morphology of the SnO_2 thin film and the particle size. The properties of the MWCNT-doped SnO_2 sensor, such as sensitivity, selectivity, and response-recovery time, were investigated. Experimental results revealed that the MWCNT-doped SnO_2 thin film sensor response to NO_2 gas depended on the operating temperature, NO_2 gas concentration, thermal treatment conditions, film thickness, and so on. The mechanism of the gas-sensing property of the MWCNT-doped SnO_2 thin film sensor was investigated and showed that the improved gas-sensing performance should be attributed to the effects between MWCNTs (p-type) and SnO_2 (n-type) semiconductors.

Key words: SnO_2; multi-walled carbon nanotube; RF reactive magnetron sputtering; NO_2 sensor
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1. Introduction

There are various types of sensors that can be used to detect small concentrations of combustible or toxic gases in air. Among these sensors, semiconductor gas sensors are particularly interesting because of their structural simplicity and low price.

Carbon nanotubes (CNTs) are promising materials with unique properties, such as high electrical conductivity, mechanical strength, nanometer-scale sizes, and high aspect ratio. Their adsorption ability and wide surface area make them attractive as gas-sensing materials, which have been intensively studied as molecular-scale device elements and components for nanomachines. Recently, it has been reported that a CNT sensor, based either on single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs), can be used to detect H_2, CO, NH_3, SO_2, NO_2, and so on[1−7]. For example, an SWCNT coated with Pd nanoparticles as a sensor has a high sensitivity to H_2[8], whereas a SnO_2/SWCNT hybrid material shows an enhanced sensitivity to NO_2[9]. Peng and Cho have demonstrated the high sensitivity of boron-doped SWCNTs (B-doped SWCNTs) for carbon monoxide and water[10], and Santos *et al.* have found the highest sensitivity of NO_2 sensors that can detect 5 ports per billion (ppb) NO_2[11]. However, there is almost no report regarding the use of radio frequency reactive magnetron sputtering to study MWCNT-doped SnO_2 NO_2 gas sensors.

Over the past years, interest in air pollutants and their monitoring has been growing in our lives. Nitrogen oxides, such as nitrogen dioxide (NO_2), are typical air pollutants that cause environmental problems. NO_2 coming from combustion processes using fossil fuels or automobiles is a very hazardous and harmful air pollutant. Therefore, the exhaust of this material is strictly regulated. In Japan, the short-term (10 min) exposure limit for NO_2 is 5 parts per million (ppm), and the environmental standard value (mean value for a day) is as low as 0.04 to 0.06 ppm[12]. The exact detection of ultra-low concentrations of NO_2 is very important. Various approaches have been used to detect low concentrations of NO_2; however, conventional commercial devices based on spectroscopic (infrared) analysis and chemiluminescence are too large to use. From this point of view, it is necessary to develop practical, small, highly sensitive and inexpensive NO_2 gas sensors to detect low NO_2 concentrations.

In this paper, the mechanism and properties of an MWCNT-doped SnO_2 thin film NO_2 gas sensor prepared by radio frequency (RF) reactive magnetron sputtering are shown, and experimental results reveal that the sensor shows a high sensitivity to ultra-low NO_2 concentrations.

2. Experimental

The sensors were prepared by depositing thin film polycrystalline MWCNT-doped SnO_2 onto 2×4 mm^2 polished silicon substrates with a Pt interdigitated electrode and a heater, using RF reactive magnetron sputtering with a Sn target (99.99% purity). The substrate temperature was maintained at room temperature. The total pressure of the plasma was kept at 1.2 Pa and the sputter gas was made of Ar (80 vol.%) and oxygen (20 vol.%). The accelerating voltage was 900 V and the total forward RF power was 150 W. The deposition rate was

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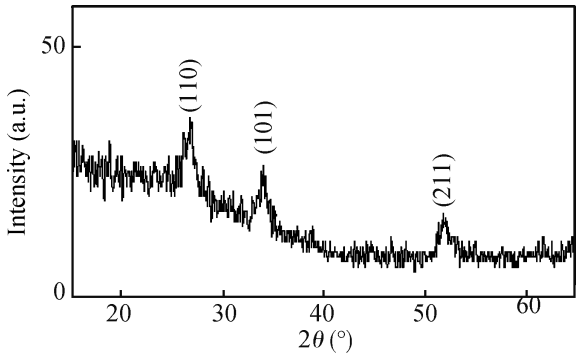

Fig. 1. XRD patterns of SnO_2/MWCNT material.

about 4 nm/min. From 5 to 100 nm, different MWCNT-doped SnO_2 thin film thicknesses were considered. After deposition, the samples underwent thermal treatment for a period of 1 h at 500 °C to stabilize the defect concentration and distribution.

The MWCNTs (Chengdu Organic Chemicals Co., Ltd., Chinese Academy of Sciences; diameter: 10–30 nm, length: 5–15 μm, purity: > 95 %) were treated with acid using a method reported previously[13]. At the beginning of the hybrid gas sensor fabrication, the MWCNT bundles were added and dispersed in the organometallic solutions by ultrasonic vibration for about 2 h to obtain well-mixed suspensions, and then spin-coated to the Sn target. MWCNTs were deposited in substrates with SnO_2 which was produced a chemical reaction between Sn and O_2 at the same time.

3. Results and discussion

3.1. Microstructure characterizations

The structure and crystal of the film were observed by Philips X'Pert Pro MPD. The X-ray diffraction (XRD) patterns of MWCNT-doped SnO_2 are shown in Fig. 1. Only SnO_2 in the crystalline phase, including (110), (101) and (101) diffraction peaks, could be indexed from the patterns for the composite. Note that the characteristic peaks of MWCNTs could hardly be identified from the patterns of the composite. This observation could be explained by the concentration of MWCNTs being far lower than that of SnO_2 matrices. Such a low MWCNT concentration could not easily be detected by X-ray diffraction[14].

The material surface element and chemistry conditions were observed by X-ray photoelectron spectroscopy (XPS), which modeled ESCALAB 250, and the XPS patterns of the MWCNT-doped SnO_2 thin film material are shown in Fig. 2. Furthermore, because the MWCNT diffraction peak was not observed in the XRD, the XPS experiment determined the existence of MWCNTs. The C1s and $Sn3d_{5/2}$ characteristic peaks were respectively the most prominent spectrum peaks when we studied the C and Sn elements by XPS[15]. After sample surface cleaning by Ar ions, the XPS patterns of the MWCNT-doped SnO_2 material were obtained and are shown in Fig. 2. The C1s spectrum characteristic peak was located at 284.6 eV, and the $Sn3d_{5/2}$ characteristic prominent peak was located at 486.6 eV, in good agreement with the standard database.

In Fig. 2(c), the MWCNT typical C1s line shape was fitted using asymmetry, which is a well-known phenomenon occurring in conductive materials[16]. Deconvolution of the C1s

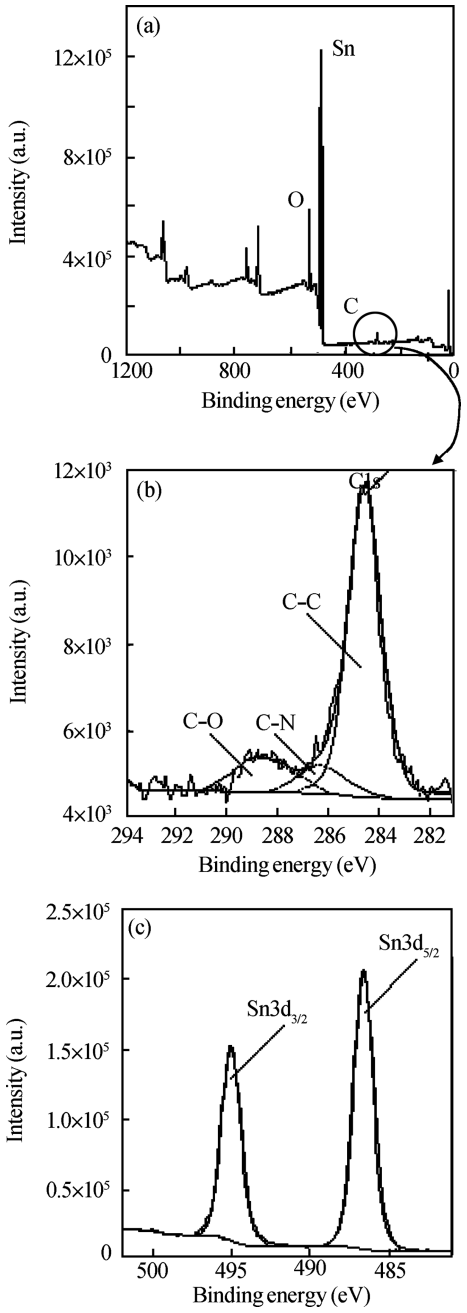

Fig. 2. XPS patterns of MWCNT-doped SnO_2 thin film material of (a) survey, (b) C1s, and (c) Sn3d.

spectra resulted in three contributions, the first one at 284.6 eV, assigned to a C–C peak, the second one at 287.1 eV, associated to C–N surface groups and the third broad one at 289.2 eV, probably corresponding to a C–O peak, resulting from an average MWCNT with an extended p-electron conduction band system[17].

The morphology of the MWCNT-doped SnO_2 thin film was observed using a Hitachi S-3000N scanning electron microscope (SEM) with an accelerating voltage of 20 keV. The SEM images of MWCNT-doped SnO_2 composite film samples after heat treatment at 500 °C are shown in Fig. 3. As in the composite, it was found that the MWCNTs dispersed well and separated from each other clearly (see, Fig. 3(a)) and that they were well embedded by spherical tin oxide nanoparticles.

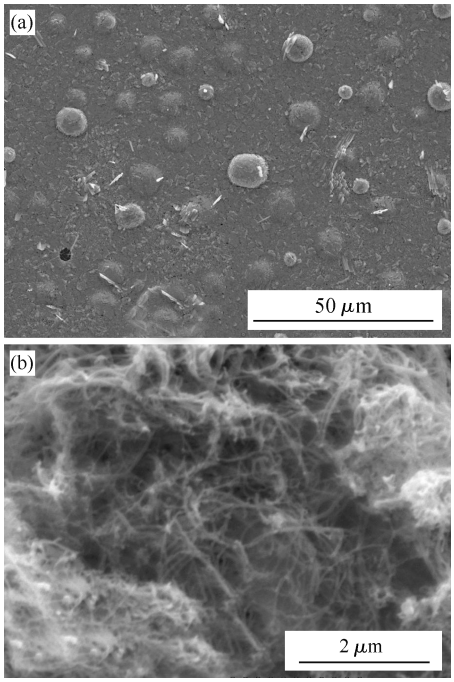

Fig. 3. SEM image of MWCNT-doped SnO_2 and enlarged partial image.

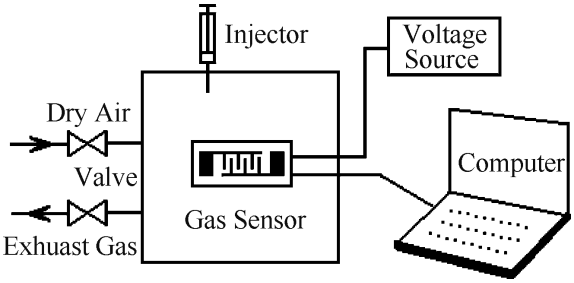

Fig. 4. Schematic diagram of apparatus for measuring gas sensor property.

The protruding surface structure was observed to be suitable for gas sensors. It was observed that there were many fiber-like protrusions emerging from the SnO_2 matrix, which might indicate that the MWCNTs were most embedded in the SnO_2. The MWCNTs on the surface of the composite thin film were also coated by SnO_2 nanoparticles as indicated in Fig. 3(b).

3.2. Gas sensor characteristics

The gas-sensitive characteristics of the sensor exposed alternately to NO_2 and purified air were investigated by online electrical response recording (shown in Fig. 4), using a reference, purging gas, and an electrical circuit. The electrical voltage of the sensor was collected by a GDM8045 AD/DA data acquisition card and transported into a computer. The testing chamber had a volume of 20 L and was always under normal pressure during the measurements. The desired NO_2 gas concentrations were obtained by mixing NO_2 gas with dry and clean air in the chamber using an injector and a valve, and the experiment was repeated for three time cycles.

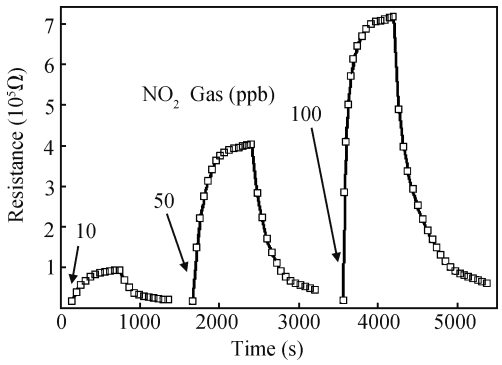

Fig. 5. Resistance changes of sensor as a function of time for three cycles of a sequence of NO_2 concentrations ranging from 10 to 100 ppb.

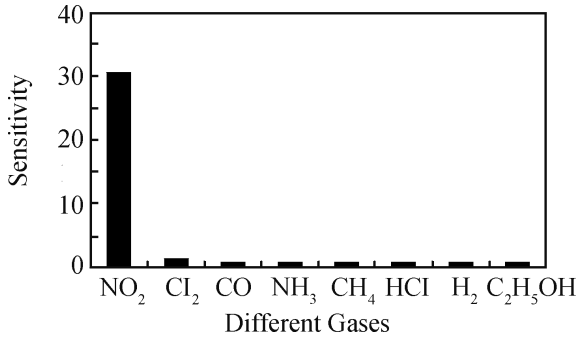

Fig. 6. Selectivity property of sensor and its sensitivity to100 ppb NO_2 versus another gas of 100 ppm.

3.2.1. Sensor sensitivity

The response sensitivity (S) of the sensor, which is defined as the sensor response versus concentration, is shown as Eq. (1)[18]

$$S = \frac{R_{NO_2}}{R_{air}}. \quad (1)$$

Here, R_{air} and R_{NO_2} are the resistances of the sensor in air and in NO_2, respectively. The response and recovery times were defined as the times required to reach 90% of the total resistance change. The response sensitivity of the sensor is shown in Fig. 5. The data show that the response to NO_2 was approximately linear up to 100 ppb NO_2. In the current study on the MWCNT-doped SnO_2 thin film sensor, the sensor resistance increased by a factor of 0.3 per ppb increase in NO_2 concentration. The experimental results revealed that the MWCNT-doped SnO_2 sensor showed a high sensitivity to ultra-low concentrations of NO_2 gas.

3.2.2. Sensor selectivity

The sensor had a very good selectivity and its sensitivity was more than 30 on 100 ppb NO_2. However, it exhibited a very low sensitivity to other disturbance gases at a concentration of 100 ppm (shown in Fig. 6).

3.2.3. Operating temperature of sensors

The SnO_2 doped MWCNTs thin film responded to NO_2 gas depending on the operating temperature. With increasing film temperature, the response time of the sensor decreased rapidly,

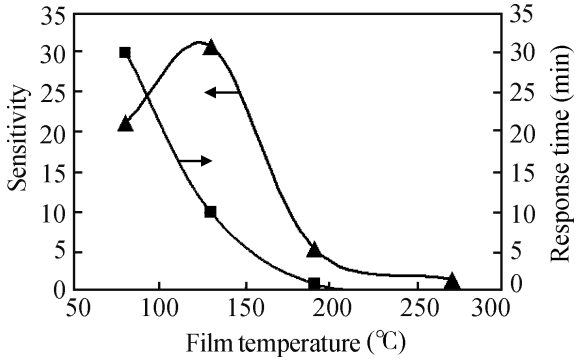

Fig. 7. NO_2 sensitivity (100 ppb) and response time versus temperature of film of sensor.

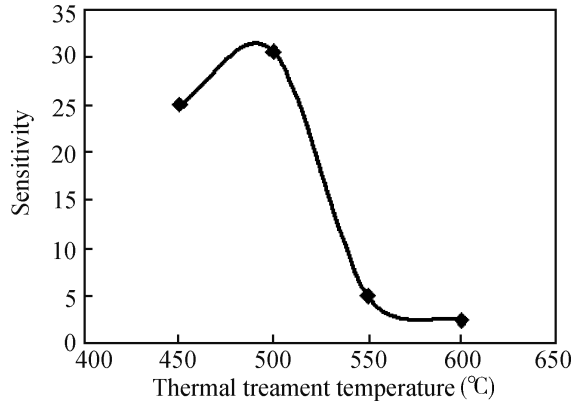

Fig. 8. Relationship between sensitivity of sensor versus temperature of thermal treatment on 100 ppb NO_2.

and its sensitivity showed the best operating point of about 130 °C. Therefore, all SnO_2/MWCNT sensors could operate with high sensitivity and stability at a relatively low operating temperature (about 130 °C) with a relatively higher sensitivity and a faster response time (shown in Fig. 7).

3.2.4. Effect of thermal treatment conditions

The calcination from 450 to 600 °C was carried out at a vacuum of 10^{-2} Torr to avoid the burning of CNTs because a thermal gravimetric analysis characterization pointed out that the MWCNTs in the composites started to burn out at a temperature of 548 °C in air[19].

It was obvious that increasing the annealing temperature might result in the improvement in the contact between the SnO2 nanoparticles and MWCNTs; on the other hand, the higher calcination temperature might also result in the burning of MWCNTs by residual oxygen or the damaging of the MWCNT structure. However, the low calcination temperature induced complete crystallization of the material and affected the stability of the sensor. Thus, the appropriate calcination temperature was about 500 °C (shown in Fig. 8).

3.2.5. Effect of film thickness

It is well known that the thickness of a sensitive layer markedly affects the gas-sensing performance of thin film sensors, which provide a very suitable film thickness to produce high-performance gas sensors[20−24]. The best operating point and highest sensitivity were observed for the sensor with 30 nm

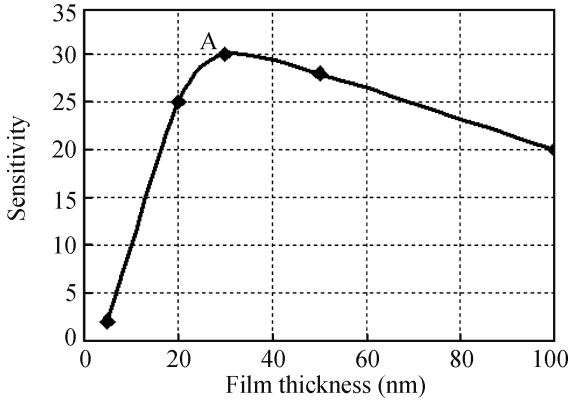

Fig. 9. Effect of film thickness of gas sensor versus sensitivity on 100 ppb NO_2.

film thickness (point A in Fig. 9). On the left-hand side of point A in Fig. 9, the sensitivity of the sensor increased with film thickness, resulting in much greater NO_2 contact with the MWCNT-doped SnO_2material, and on the right-hand side of point A of Fig. 9, a increase in the thickness of the thin film composite sensors resulted in a decrease in response due to the increase in the diffusion length of the gas.

3.2.6. Mechanism of MWCNT-doped SnO_2 thin film sensor

The mechanism of the MWCNT-doped SnO_2 thin film sensor is very complex. The exact mechanism of the MWCNT-doped SnO_2 composite as a sensing material has not yet been clarified.

As is well known, it is mainly the physical adsorption (Eq. (2)) or chemical adsorption (Eqs. (3)–(5)) of oxygen on the thin film surface of the sensor. When exposed to NO_2 gas, the electrons of the thin film material can be captured by the oxidation of NO_2 (Eq. (6) and (7)). The decomposition of NO_{ads} will further produce NO(g) gas (Eq. (8)). Therefore, physical or chemical adsorption can change the conductivity of the MWCNT-doped SnO_2 composite material during its exposure to NO_2 gas.

$$O_2(g) \leftrightarrow O_{2ads}, \tag{2}$$

$$O_{2ads} + e \leftrightarrow O^-_{2ads}, \tag{3}$$

$$O^-_{2ads} + e \leftrightarrow 2O^-_{ads}, \tag{4}$$

$$O^-_{ads} + e \leftrightarrow O^{2-}_{ads}, \tag{5}$$

$$NO_2(g) \rightarrow NO_{2(ads)}, \tag{6}$$

$$NO_{2(ads)} + 2e \leftrightarrow NO_{ads} + O^{2-}_{ads}, \tag{7}$$

$$NO_{ads} \leftrightarrow NO(g) \uparrow . \tag{8}$$

The material of SnO_2 behaves similarly to an n-type semiconductor, and the majority carriers of SnO_2 are electrons; however, MWCNTs are consider as p-type semiconductors, their majority carriers are holes, and p–n junctions are fabricated between SnO_2 and MWCNTs[25−27]. The changes in

the barrier height and the depletion layer of the SnO_2 sensitive layer were modulated by p-MWCNTs/n-SnO_2 junctions. The number of electrons in MWCNT-doped SnO_2 is reduced, and the resistance of the sensor is increased in a contrasting manner by adsorbing strongly oxidative NO_2. The effects between MWCNTs (p-type) and SnO_2 (n-type) semiconductors may improve the performance of the gas sensor at ultra-low concentrations of NO_2 in the ppb range[28−30]. The experimental results, particularly the sensitivity of the MWCNT-doped SnO_2 NO_2 sensor being higher than that of the pure SnO_2 sensor, imply that the response of the MWCNT-doped SnO_2 sensor is mainly contributed by MWCNTs. The working principle of selectivity- modified MWCNT-doped SnO_2 materials is still not well understood.

O^{2-}_{ads} owing to the chemical adsorption on the material surface, the desorption of is difficult at high chemical energy and the recovery of the SnO_2-WMNT material requires more time (Eq. (9)). Previous reports have shown that a CNT-based sensor can detect various gases at room temperature, but its response and recovery times are long, even more than 1 h[31].

$$O^{2-}_{ads} \rightarrow \frac{1}{2}O_2(g) + 2e. \quad (9)$$

4. Conclusions

An MWCNT-doped SnO_2 thin film NO_2 gas sensor, prepared by RF reactive magnetron sputtering, shows a higher sensitivity than a pure SnO_2 thin film NO_2 gas sensor, and a high sensitivity to ultra-low concentrations of NO_2 in the ppb range. The response of the MWCNT-doped SnO_2 composite thin film gas sensor strongly depends on the process of preparing the sensitive film. The optimum conditions of the MWCNT-doped SnO_2 composite thin film are 500 °C calcination temperature, 30 nm film thickness, and 130 °C work temperature. However, the obtained results generally imply that these conditions should be optimized for practical applications of the composites of MWCNT-doped SnO_2 as NO_2 gas sensors. Observations of the thin film morphology revealed that the MWCNT bundles are embedded in the SnO_2 nanoparticle materials. From a physical and chemical point of view, the changes in the barrier height and conductivity of the SnO_2/MWCNT sensitive layer may modulate the depletion layer at the p–n junction consisting of MWCNTs (p-type) and SnO_2 (n-type) semiconductors, and may improve the performance of the gas sensor at ultra-low concentrations of NO_2 in the ppb range. The device response to NO_2 gas was observed to agree favorably with that predicted by multispecies adsorption theory. However, the exact mechanism of the MWCNT-doped SnO_2 composite as a sensing material has not yet been clarified. Thus, more experiments are required to determine such a mechanism.

References

[1] Collins P G, Bradley K, Ishigami M, et al. Extreme oxygen sensitivity of electronic properties of carbon nanotubes. Science, 2000, 287: 1801

[2] Kong J, Franklin N R, Zhou C, et al. Nanotube molecular wires as chemical sensors. Science, 2000, 287: 622

[3] Zhao J, Buldum A, Han J, et al. Gas molecule adsorption in carbon nanotubes and nanotubes bundles. Nanotechnology, 2002, 13: 195

[4] Goldoni A, Larciprete R, Petaccia L, et al. Single-wall carbon nanotube interaction with gases. Chem Soc, 2003, 125: 11329

[5] Kotsikau D, Ivanovskaya M, Orlik D, et al. Gas-sensitive properties of thin and thick film sensors based on Fe_2O_3–SnO_2 nanocomposites. Sensors and Actuators B, 2004, 101: 199

[6] Ivanoc P, Llobet E, Vilanova X, et al. Development of high sensitivity ethanol gas sensors based on Pt-doped SnO_2 surfaces. Sensors and Actuators B, 2004, 99: 201

[7] Teeramongkonrasmee A, Sriyudthsak M. Methanol and ammonia sensing characteristics of sol–gel derived thin film gas sensor. Sensors and Actuators B, 2000, 66: 256

[8] Kong J, Chapline M G, Dai H. Functionalized carbon nanotubes for molecular hydrogen sensors. Adv Mater, 2001, 13: 1384

[9] Wei B Y, Hsu M C, Su P G, et al. A novel SnO_2 gas sensor doped with carbon nanotubes operating at room temperature. Sensors and Actuators B, 2004, 101: 81

[10] Peng S, Cho K. Ab initio study of doped carbon nanotube sensors. Nano Lett, 2003, 3: 513

[11] Santos J, Serrini P, Beirn B O, et al. A thin film SnO_2 gas sensor selective to ultra-low NO_2 concentrations in air. Sensors and Actuators B, 1997, 43: 154

[12] Tanaka S, Esaka T. High NO_x sensitivity of oxide thin films prepared by RF sputtering. Mater Res Bull, 2000, 35: 2491

[13] Chen Y S, Li Y, Wang H C, et al. Gas sensitivity of a composite of multi-walled carbon nanotubes and polypyrrole prepared by vapor phase polymerization. Carbon, 2007, 45: 357

[14] Wei B Y, Hsu M C, Suet P G, e al. A novel SnO_2 gas sensor doped with carbon nanotubes operating at room temperature. Sensors and Actuators B, 2004, 101: 81

[15] Xie H M, Zhou D F, Zhou D. Synthesis and characterize of the tin-graphite intercalation compound. Funct Mater, 2004, 2: 106

[16] Rousseau B, Estrade-Szwarckopf H, Bonnamy S, et al. Optical and scanning electron microscopies cross-fertilization: application to worn carbon/carbon composite surface studies. Carbon, 2005, 43: 1331

[17] Okpalugo T, Papakonstantinou P, Murphy H. High resolution XPS characterization of chemical functionalized MWCNTs and SWCNTs. Carbon, 2005, 43: 153

[18] Babaei F H, Orvatinia M. Analysis of thickness dependence of the sensitivity in thin film resistive gas sensors. Sensors and Actuators B, 2003, 89: 256

[19] Hieu N V, Thuy L T B, Chien N D. Highly sensitive thin film NH_3 gas sensor operating at room temperature based on SnO_2/MWCNTs composite. Sensors and Actuators B, 2008, 129: 888

[20] Galdikas A, Kaiulis S, Mattogno G, et al. Thickness effect of constituent layers on gas sensitivity in SnO_2/[metal]/metal multilayers. Sensors and Actuators B, 1999, 58: 478

[21] Montmeat P, Lalauze R, Viricelle J P, et al. Model of the thickness effect of SnO_2 thick film on the detection properties. Sensors and Actuators B, 2004, 103: 84

[22] Sakai G, Baik N S, Miura N, et al. Gas sensing properties of tin oxide thin films fabricated from hydrothermally treated nanoparticles dependence of CO and H_2 response on film thickness. Sensors and Actuators B, 2001, 77: 116

[23] Zahab A, Spina L, Poncharal P. Water-vapor effect on the electrical conductivity of a single-walled carbon nanotube mat. Phys Rev B, 2000, 63: 1000

[24] Sakai G, Matsunaga N, Shimanoe K, et al. Theory of gas diffusion controlled sensitivity for thin film semiconductor gas sensor. Sensors and Actuators B, 2001, 80: 125

[25] Modi A, Koratkar N, Lass E, et al. Miniaturized gas ionization sensors using carbon nanotubes. Nature, 2003, 424: 171

[26] Someya T, Small J, Kim P, et al. Alcohol vapor sensors based on single-walled carbon nanotube field effect transistors. Nano Lett, 2003, 3: 877

[27] Li J, Lu Y, Ye Q, et al. Carbon nanotube sensors for gas and organic vapor detection. Nano Lett, 2003, 3: 929
[28] Zhang W, Vasconcelos E A, Uchida H, et al. A study of silicon Schottky diode structures for NO_x gas detection. Sensors and Actuators B, 2000, 65: 154
[29] Zhang W, Uchida H, Katsube T, et al. A study of silicon Schottky diode structures for NO_x gas detection. Sensors and Actuators B, 1998, 49: 58
[30] Savage N, Chwieroth B, Ginwalla A, et al. Composite n–p semiconducting titanium oxides as gas sensors. Sensors and Actuators B, 2001, 79: 17
[31] Wanga S G, Zhang Q, Yang D J, et al. Multi-walled carbon nanotube-based gas sensors for NH_3 detection. Diamond Relat Mater, 2004, 13: 1327