Sensors and Materials, Vol. 15, No. 4 (2003) 177–190 MYU Tokyo

S & M 0519

Examining the Gas-Sensing Behaviors of Carbon Nanotubes Using a Piezoelectric Quartz Crystal Microbalance

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(Received November 1, 2002; accepted June 25, 2003)

Key words: carbon nanotubes, piezoelectric quartz crystal microbalance (PQCM), gas sensors, frequency change, adsorption, sensitivity

Carbon nanotube bundles absorb gases very well since they have many adsorption sites. A gas sensor is demonstrated by deposition of carbon nanotube bundles on a piezoelectric quartz crystal. The sensor is utilized to detect the concentration of a flowing mixture of gases, determined from alterations in oscillation frequency. The detected gases included carbon monoxide, nitrogen dioxide, hydrogen, and nitrogen in air and the operation temperature varied from 25°C to 200°C. The prepared sensor is more sensitive at higher temperatures. The gas response is very low below 100°C. The preferred operating temperature is suggested to be 200°C. The oscillation frequency of the sensor increases when the gas sensor is exposed to the detected gases. An increase in frequency indicates a weight loss of the carbon nanotube, suggesting that the mechanism of detection is desorption, which is proposed to be caused by oxygen adsorption followed by desorption due to chemical reactions of the detected gase.

1. Introduction

Iijima discovered carbon nanotubes (CNTs) in 1991.⁽¹⁾ Since his discovery, much effort has been made to elucidate their novel mechanical and electronic properties and to find applications.⁽²⁻⁶⁾ CNTs exhibit very good adsorption properties because they have a large specific surface area and a nanoscale structure that provides a large amount of sites where gases can react.⁽⁷⁻¹¹⁾ Adsorption of a gaseous molecule on the surface of a CNT changes its

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electric properties, enabling the CNT to act as a gas sensor.⁽¹²⁻¹³⁾ For example, J. Kong *et al.*⁽¹⁴⁾ demonstrated a gas sensor based on individual single-walled carbon nanotubes (SWCNTs), whose electric conductance responds quickly and sensitively when the nanotubes are exposed to gaseous molecules, such as NO₂ and NH₃.

Besides electrical changes, changes in adsorbed mass can also be used to sense gases. Coating gas-adsorbing materials onto the surface of a piezoelectric quartz crystal microbalance (PQCM) is a well known method for detecting gases.^(15–18) J. Wei *et al.*⁽¹⁹⁾ developed an in-line sensor for trance moisture monitoring based on a PQCM coated with a reactive metal thin film. PQCM is compact and can accurately measure very small mass changes. It is increasingly becoming recognized as a powerful tool for studying nano-mass changes. However, insufficient information is available on the feasibility of applying PQCMs to CNTs to sense gases. In this investigation, PQCM gas sensors are fabricated by deposition of SWCNT bundles on the surface of a quartz crystal (SWCNT-coated PQCM). The adsorption behaviors of SWCNT bundles are investigated using various gases including carbon monoxide (CO), nitrogen dioxide (NO₂), hydrogen (H₂), and nitrogen (N₂), all diluted in pure air. The surface reaction of these gases on SWCNT bundles can be studied by a frequency change of the SWCNT-coated PQCM.

2. Experiments

An AT-cut type PQCM is used to measure the variation of adsorbed molecules in SWCNTs. The PQCM is composed of a thin quartz disk with two gold electrodes, one on each side, as schematically illustrated in Fig. 1. The SWCNT materials are obtained from CarboLex. Inc. and consist of >90 vol% SWCNTs that are produced by the arc discharge method using a Ni-Y catalyst.⁽²⁰⁾ CP grade and CPann grade types of SWCNTs are used and denoted as types A and B, respectively. Both kinds of SWCNTs are paper-like samples. The CP grade material is purified by nitric acid reflux to remove residual catalyst particles, followed by close-flow filtration in a surfactant (sodium lauryl sulfate). The CPann-grade is further annealed at 800 K in vacuum; this post-treatment step removes



Fig. 1. Schematic of piezoelectric quartz crystal (a) side view, (b) front view.

most of the residues left by the purification process.⁽²¹⁾ Figures 2(a) and 2(b) are transmission electron microscopy (TEM) images of types A and B, respectively, showing that the tubes are present in bundles, with bundle diameters in the range of 10-40 nm, i.c., containing ~ 100-500 tubes. TEM specimens are prepared by dropping the ethanol-dissolving suspension of CNTs on an amorphous carbon film, which is covered on a 1000 mesh copper grid.

The SWCNT bundles are also dispersed in acetone by ultrasonic vibration for 20 min. Afterwards, the SWCNT suspensions are dropped onto the surfaces of the gold electrodes of PQCMs. The SWCNT-coated PQCMs are heated in a furnace at 300°C for 1 h in air, and then air-cooled.

Figure 3 illustrates the experimental apparatus used. The piezoelectric apparatus includes an oscillator powered by a regulated power supply, ensuring that the applied voltage remains constant. In this experiment, pure air is used as a carrier gas, and its flow rate is kept constant at 500 sccm. Here, the pure air consists of 20 at% O_2 and 80 at% N_2 with total impurities less than 100 ppm. Four test gases, CO, NO₂, H₂, and N₂ gases, are used to evaluate the adsorption behaviors of SWCNT bundles. The air and the test gases flow through a mixer to a closed glass chamber. The diameter of the glass chamber is 12 cm and the height is 8 cm. Different concentrations of these test gases are produced by modulating their flow rates. A heating tape controls the heating of the glass chamber, which is shielded by a thermally insulating material. The glass chamber is also vacuumed by connecting a vacuum pump to the outlet of the chamber.

In each test, two SWCNT-coated PQCM samples, type A and type B, and one PQCM sample without SWCNT bundles, are simultaneously placed in the glass chamber for measurement. The PQCM sample without SWCNT bundles is used to eliminate the effects of the thermal environment and the intrinsic properties of quartz crystal. The frequencies of the three samples are simultaneously recorded by a computer, which shows time versus frequency curves.



Fig. 2. Transmission electron micrograph of (a) type A and (b) type B single-wall carbon nanotube bundles.





3. Results and Discussion

3.1 Stability test

A stability test is first performed to ensure that the deposited SWCNT bundles are firmly attached to the surface of the gold electrode. The frequency of SWCNT-coated PQCMs will then remain stable. The frequency of the as-deposited SWCNT-coated PQCM is continuously monitored for 76 h. The frequency of the SWCNT-coated PQCM is gradually increased and becomes stable after about 24 h. This observation suggests that the SWCNT bundles can be fixed stably on the surface of PQCMs by appropriate heat treatment. The stability of the frequency of the SWCNT-coated PQCMs also suggests that the frequency change in the following tests is dominated by the adsorption effect of gases onto the SWCNT bundles.

3.2 Adsorption weight analysis using PQCMs

The mechanism of the PQCM must be understood before the adsorbed mass on the surface of the quartz plate can be calculated. When an external AC electrical potential is applied to the electrodes of a PQCM, it will produce a cyclical electric field across the PQCM, inducing an oscillation in the quartz disk. The oscillation frequency of a PQCM depends on the total mass of the crystal and on any coating layers on the surface. When a coating layer is deposited on the surface of a PQCM, the oscillation frequency changes slightly, by Δf (Hz). Sauerbrey determined a relation for AT-cut PQCM.⁽²²⁾

$$-\Delta f = \frac{2.3 \times 10^6 f^2 \Delta M}{Ac} \tag{1}$$

where Ac (cm²) is the area of the gold electrode on the PQCM; f (MHz) is the oscillation frequency of the PQCM, and ΔM (g) is the increase in the total mass on the PQCM. In this experiment, Ac is approximately 0.1 cm². For a SWCNT-coated PQCM type A, the original oscillation and the post-deposition frequencies are 9037928 Hz and 9037429 Hz, respectively. The corresponding values for the type B PQCM are 9039860 Hz and 9039030 Hz. From eq. (1), the deposited mass of SWCNT bundles is approximately 2.7×10^{-7} g in type A and 4.5×10^{-7} g in type B.

3.3 Frequency versus time evolution curve

Figure 4 plots the typical responses of SWCNT-coated PQCMs as a function of time and gas concentration. The values of difference in frequency shown in Fig. 4 are calculated by subtracting the frequency of the type A or B from the frequency of the PQCM sample without SWCNT bundles. Thus, the intrinsic effects of PQCM can be ignored, and the reactions between SWCNT bundles and the CO gas determine the change of frequencies.



Fig. 4. Typical difference in frequency as a function of time in different concentrations of CO gas at $200 \,^{\circ}$ C in (a) type A, (b) type B SWCNT-coated PQCMs.

Figure 4(a) and 4(b) reveal the frequency response of type A and type B SWCNT-coated PQCMs, respectively, in CO-containing air at 200°C.

The values of difference in frequency increase when the concentration of CO gas increases to 1700 ppm, in Fig 4(a), indicating that the mass of the SWCNT-coated PQCM decreased. However, when the concentration of CO gas further increases to 2900 ppm, the value decreases, indicating that the mass of SWCNT-coated PQCM increased. Thus, Fig. 4(a) implies that when exposed to the CO-containing air at 200°C, type A SWCNTs desorbed at the beginning of the increased concentration of CO gas and then adsorbed when the concentration increased further. For type B SWCNTs (Fig. 4 (b)), however, no adsorption is observed, even when the concentration increased to 2900 ppm.

When the flow of CO gas into the chamber finally stopped, the frequency of the SWCNT-coated PQCMs recovered to the original value, as shown in Fig. 4. Similar results were observed in different gases and testing temperatures. The recovery of the frequency demonstrated the reliability of the gas sensor assembly used in this experiment.

3.4 Response of SWCNT-coated PQCM sensors in various gaseous atmospheres

Response time, recovery time, working temperature, kinds of detected gas and sensitivity are normally used to characterize the performance of a gas sensor. Dimension-dependent partial sensitivity, $S_i = (\partial x'/\partial p_i)^{(23)}$ is used here to assess the sensitivity of the SWCNT-coated PQCMs, where x' is the measuring signal and p_i is the partial pressure or concentration of detected gas *i*. In this study, the response curve is the relationship between the measured signal and the concentration of detected gas. A simple linear relationship for a PQCM detector has been proposed as follows:^(24,25)

$$\Delta f = -k_c \Delta C_0 \tag{2}$$

where Δf is the value of frequency change after exposure to detected gas, ΔC_0 is the concentration of the detected gas, and $-k_c$ is the slope of the response curve and may represent the sensitivity of a SWCNT-coated PQCM at a given temperature.

The response curves of the SWCNT-coated PQCM sensors can be obtained from a series of curves like that in Fig. 4, but at different testing temperatures and atmospheres. Here, the response curves are presented by a set of values of frequency change (Δf). The Δf shown in these figures represent the increase between the frequencies when exposed to pure air and that when exposed to the detected gases at the same temperature. For example, the value of "difference in frequency" of the SWCNT coated-PQCM type A in pure air at 200°C is about 35200 Hz, as shown in Fig. 4(a). When 500 ppm of CO gas in air continuously flowed into the test chamber at 200°C the value of "difference in frequency" increased to 35260 Hz. Therefore, the Δf is 60 Hz. A larger positive Δf represents a more vigorous desorption reaction. The frequency changes Δf can be normalized by the deposited mass of CNTs calculated in Section 3.2, and are around 2.7×10^{-7} g and 4.5×10^{-7} g for PQCMs of types A and B, respectively. Tables 1 and 2 list the normalized Δf of the SWCNT-coated PQCMs of types A and B, respectively, as a function of temperature and concentration of detected gases.

Table 1.

Frequency changes (10 MHz/g) of type A SWCNT-coated PQCMs as a function of temperature and concentrations of CO, NO_2 , H_2 , and N_2 gases in air.

Temp. (°C)		CO (ppm)			NO ₂ (ppm)					H ₂ (%)					N ₂ (%)				
	500	900	1700 2	2900	500	900	1700	2900		5	9	17	29	5	9	17	29		
25	0	0	0	0	0	4	6	3		-3	0	1	2	-2	-1	-2	-2		
100	0	0	0	0	9	11	12	6		-1	-2	-4	-6	3	4	3	-5		
150	11	21	32	9	9	20	31	39		1	6	6	3	6	9	12	11		
200	23	42	61	38	56	58	38	27		35	54	65	96	26	41	56	32		

Note: negative value indicates the adsorption of gas and positive value indicates the desorption of gas.

Table 2.

Frequency changes (10 MHz/g) of type B SWCNT-coated PQCMs as a function of temperature and concentrations of CO, NO₂, H_{2} , and N_2 gases in air.

Temp (°C)). CO (ppm)				NO ₂ (ppm)					H ₂ (%)					N ₂ (%)				
	500	900	1700	2900	500	900	1700	2900		5	9	17	29	5	9	17	29		
25	0	0	0	0	-1	-6	-1	-4		1	6	6	6	-1	-1	-1	-1		
100	0	0	0	0	0	0	0	-3		3	3	2	3	1	2	2	2		
150	2	6	8	12	4	7	9	4		4	4	4	4	2	3	6	8		
200	3	6	11	10	3	14	23	28		-2	-3	4	34	0	3	7	11		

Note: negative value indicates the adsorption of gas and positive value indicates the desorption of gas.

The linear relationship of eq. (2) between the frequency change and the gas concentrations is an advantage of the piezoelectric technique.⁽²⁶⁾ However, here, the response curves did not follow a linear relation completely. The result of nonlinear relation is explained by complex adsorption-desorption and chemical reaction processes during gas detection in this study. Since the carrier gas is pure air, at least two gaseous species, O₂ and N₂ are present in the experimental system, which results in the complex reaction process. Figure 5(a) and 5(b) are the response curves of type A SWCNT-coated PQCM for detecting CO and N₂ gases, respectively, showing the representative response curves in this study. It is noted in Fig. 5 that the Δf decreases at high gas concentrations at temperatures of 150°C and 200°C.

Three important features of these SWCNT-coated PQCM gas sensors revealed by Tables 1 and 2 can be summarized. The first is that the SWCNT-coated PQCM sensor, of either type A or B, is more sensitive at temperatures of 150°C and 200°C, than at temperatures below 100°C. This result suggests that the suitable operating temperature of the SWCNT-coated PQCM gas sensors is around 200°C. The second feature is that almost all of the sensitivities in these Tables are positive at the initial concentration, implying that



Fig. 5. Frequency changes of type A SWCNT-coated PQCMs as a function of temperature and concentration for (a) CO and (b) N_2 gases in air.

the SWCNT-coated PQCM gas sensors underwent a desorption reaction when exposed to the atmosphere detected in the experiments. The third is that the type A SWCNT-coated PQCM is more sensitive than the type B PQCM under any given conditions. This desorption behavior could be explained by the fact that many gaseous molecules have been previously adsorbed onto the surfaces of exposed SWCNTs before the detecting experiments began.⁽¹²⁾ A vacuum test experiment, exposing the SWCNT-coated PQCM gas sensors in an evacuating chamber, was carried out to verify this hypothesis. Figure 6 plots the values of difference in frequency as a function of time and vacuum pressure for both types (A and B) of SWCNT-coated PQCM. As shown in Fig. 6, the frequency increases when the pressure declines. This suggests that some materials are removed from the SWCNTs while the test chamber is being evacuated. When the chamber is subsequently exposed to pure air at a pressure of 1 atm, the frequency returned to the basic frequency before evacuation. The recovery of the frequency suggests that the adsorption and desorption of gases onto the SWCNT-coated PQCM is reversible. This reversible result is consistent with results obtained by several other researchers(12-14) who reported that CNTs possess a strong ability to adsorb gaseous molecules such as oxygen (O_2) , NO_2 , H_2 and others. Figure 7 plots frequency change (not the previous Δf) against vacuum pressure to compare quantitatively the amounts of desorption of types A and B SWCNTs. A frequency at 80 torr is taken as a reference. Figure 7 clearly shows that type A SWCNTs desorb much more than type B SWCNTs under the same evacuation conditions. Restated, type A SWCNTs adsorb more gaseous molecules than type B SWCNTs in the same atmosphere, perhaps because the annealing treatment undergone by type B SWCNTs resulted in the elimination of defect-adsorption sites,⁽¹²⁾ reducing the sites of adsorption of SWCNTs.

The results of the vacuum tests described above suggest that many gaseous molecules are adsorbed on SWCNTs for different ambient gas pressures. Although the pre-adsorbed gases are of various species, we suggest that the previous adsorption of O_2 is primarily responsible for the desorption reaction of SWCNT-coated PQCM, as shown by the chemical reactions that describe the possible mechanisms of desorption of O_2 from the surfaces of CNTs.



Fig. 6. Difference in frequency as a function of time and air pressure in vacuum for both type A and B SWCNT-coated PQCMs.



Fig. 7. Frequency change as a function of time and air pressure in vacuum for both type A and type B SWCNT-coated PQCMs

Until now, studies on the adsorption of oxygen on surfaces of SWCNTs have mainly focused on its effect on electrical properties.^(12–13) According to some studies of oxygen species on metal oxide semiconductors, involving electron paramagnetic resonance measurements^(27–29) at temperatures up to around 150°C, the principal chemisorbed ion formed on the surface of oxides is O_2^- . At temperatures of 150–200°C, the principal chemisorbed ion formed on the surface of oxides is reported to be O⁻. For simplicity, the ion formed on the surfaces of CNTs is assumed to be O⁻ at high temperatures:

$$O_{2 (gas)} + 2e^{-}_{(CNTs)} \leftrightarrow 2O^{-}_{(CNTs)}$$
(3)

When the SWCNTs are in vacuum, the partial pressure of $O_2(P_{Oa(gas)})$ declines and causes O_2 to dissociate from the SWCNTs' surfaces, increasing the frequency of SWCNT-coated PQCM.

If CO is introduced into the test chamber, it may cause O_2 desorption in the following two ways. The first is by reacting with $O_{2(gas)}$ in air:

$$CO_{(gas)} + \frac{1}{2}O_{2(gas)} \leftrightarrow CO_{2(gas)}$$
(4)

This path is not considered to be the main mechanism of desorption of O_2 from the SWCNTs' surfaces, because the concentration of CO is much smaller than that of O_2 in air. Therefore, $P_{O_2(aas)}$ does not decrease much in reaction (3).

The second proposed mechanism is that CO directly reacts with the O_2 adsorbed on the SWCNTs' surfaces. This mechanism is similar to the accepted CO reaction mechanism with SnO_2 .⁽³⁰⁾

$$CO_{(gas)} + O_{(CNTs)} \leftrightarrow CO_{2(gas)} + e^{-}$$
 (5)

This latter path should be the one by which the desorption of O^- from the SWCNTs' surface proceeds. In such a case, thermodynamic balancing yields the following equilibrium equation.

$$\Delta G^{o} = -RT \ln \frac{n P_{CO_{2}(g\omega)}}{P_{CO_{2}(g\omega)}} \alpha_{O^{-}(CVT_{2})}$$
(6)

where ΔG^o is the Gibbs free energy change of reaction (5) at equilibrium, $P_{CO:(gas)}$ and $P_{CO(gas)}$ are the partial pressures of $CO_{2(gas)}$ and $CO_{(gas)}$, respectively, *n* is the electron concentration, and $\alpha_{O^-(CNT_s)}$ is the activity of O⁻ adsorbed on SWCNTs, which is related to the saturation adsorption concentration $C_{O^-(CNT_s)}$ by a factor activity coefficient $\gamma_{O^-(CNT_s)}$.

In this experiment, $P_{COt(gas)}$ can be considered to be constant at low CO concentration because $P_{COt(gas)}$ may be determined by the concentration of $P_{COt(gas)}$ in the carrier gas, air. Then, the activity of O⁻ ($\alpha_{O^-(covr_i)}$) or the saturation concentration of the adsorbed O⁻ is inversely proportional to $P_{COt(gas)}$, which is substantially consistent with the results that show that Δf increases as CO concentration declines, as shown in Tables 1 and 2. However, the Δf decrease with CO concentration increase in Tables 1 and 2 is unexpected in this situation. The first cause of the result may be that reaction (4) contributes to the reaction in the chamber, increasing $P_{COt(gas)}$, suppressing reaction (5) and driving this reaction to the left side of the equation. As reaction (5) shifts to the left, adsorption of O⁻_(CNTs) occurs again, causing the Δf in Tables 1 and 2 to decrease as the concentration of CO increases. The result may also follow from a second mechanism of CO adsorption-desorption as follows:

$$CO_{(gas)} \leftrightarrow CO_{(CNTs)}$$
 (7)

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At higher $CO_{(gas)}$ concentration, the adsorption of CO gas on SWCNTs becomes more significant because of the availability of more adsorption sites via reaction (5). The increasing adsorption rate of $CO_{(gas)}$ on SWCNTs at higher CO concentrations may cause the Δf in Tables 1 and 2 to decrease.

It can be seen in Tables 1 and 2 that the SWCNT-coated PQCM sensors respond apparently when exposed to traces of CO and NO₂ gases at 200°C. The mechanism is believed to not only involve the saturation of adsorption-desorption in a detected gas. As explained for the response to CO, the mechanisms by which SWCNTs respond to NO₂ are as follows:

$$NO_{2(gas)} + O_{(CNTs)} \leftrightarrow NO_{(CNTs)} + O_{2(gas)}$$
(8)

$$NO_{(CNT_s)} + O_{(CNT_s)} \leftrightarrow NO_{2(gas)} + 2e_{(CNT_s)}$$
(9)

NO₂ might react with O⁻_(CNTs) on the surface of SWCNTs and form NO⁻_(CNTs) and O_{2(gas)} (reaction (8)) at 100°C to 200°C. The $NO^{-}_{(CNTs)}$ is then fast-reacted with O⁻_(CNTs) (reaction (9)) to remove O_{2(gas)} from the SWCNTs. This may explain the increase in frequency of SWCNTs-coated PQCM.

Responses to H_2 are observed only at 200°C and Δf increases with the concentration of H_2 , as shown in Tables 1 and 2. This result is explained by first considering the possible reactions in the gaseous system. H_2 gas can be adsorbed on SWCNT bundles:

$$H_{2(gas)} \leftrightarrow H_{2(CNTs)}$$
 (10)

Also, H_2 gas may react with O_2 in air:

$$H_{2(gas)} + \frac{1}{2}O_{2(gas)} \leftrightarrow H_2O_{(gas)}$$
(11)

The other reaction is of H_2 gas with adsorbed $O_{(CNTs)}$, as in the case involving CO gas, because H_2 is also a reductant. This surface reaction is expressed as:

$$H_{2(gas)} + O_{(CNTs)} \leftrightarrow H_2 O_{(gas)} + e_{(CNTs)}$$
(12)

Reaction (10) results in the adsorption of H_2 as the concentration of H_2 increases. However, this result is not consistent with the desorption results. Reaction (11) decreases $P_{Or(gas)}$, activating reaction (3) and causing O_2 to be desorbed from SWCNT bundles. Reaction (12) also causes O_2 to be desorbed. This assumption is consistent with the results of this study. Tables 1 and 2 show that the sensors work only at 200°C for H_2 detection, indicating the gas-sensing reaction requires an activation energy. We then propose that reaction (12) is most probable to explain the desorption phenomenon of the CNTs for H_2 detection.

As shown in Fig. 5(b), the Δf response of type A in N₂ detection at 200°C increases with increasing N₂ concentration up to 17%, but decreases with increasing N₂ concentration up

to 29%. The response to N_2 is similar to that of CO, shown in Fig. 5(a). The only possible reaction is the competition of adsorption-desorption between O_2 and N_2 :

$$N_{2(gas)} \leftrightarrow N_{2(CNTs)}$$
 (13)

Increasing the concentration of N₂ in air decreases $P_{Or(gas)}$. For example, $P_{Or(gas)}$ is around 0.2 atm in pure air, and as low as 0.14 atm in a mixture of 29% N₂ in air. Decreasing $P_{Or(gas)}$ causes desorption of O⁻ from SWCNT bundles, according to reaction (3). As N₂ concentration increases, reaction (13) may become more significant than desorption of oxygen. N₂ is adsorbed onto the CNTs, reducing the frequency of SWCNT-coated PQCMs, as shown in Fig. 5(b).

Tables 1 and 2 show that the SWCNT-coated PQCMs have almost no sensitivity to CO, NO₂, H₂, and N₂ in air at 25°C and at 100°C. The temperature effect is explained with reference to some studies of the adsorption of oxygen on the oxide's surfaces.^(26–28) At temperatures of up to around 150°C, the main chemisorbed ions are O₂⁻ and O⁻. These species are sufficiently strongly bound to withstand evacuation and heating to 550°C. Although the form of oxygen adsorption on the SWCNTs' surfaces remains unclear, the strong bonding force of O₂⁻ and O⁻ may correspond to the temperature effect displayed in Tables 1 and 2.

Comparing the normalized frequency changes in Tables 1 and 2 revealed that type B is less sensitive than type A to CO, NO_2 , H_2 and N_2 in air. This result is consistent with the results from the vacuum test, presented in Fig. 6. The frequency change in the y-coordinate is normalized in the same way as in the vacuum test. It reveals that SWCNT-coated PQCMs type A adsorb more gaseous molecules than SWCNT-coated PQCMs type B, because type B SWCNTs have more regular structures and less amorphous species than type A SWCNTs after being purified by heat treatment in a vacuum. The irregular structures and amorphous species are considered to be good sites of adsorption of gaseous ions, atoms or molecules. Therefore, more oxygen species can be expected to be preadsorbed in SWCNT-coated PQCMs type B in ambient air, causing more desorption by evacuation and reaction with detected gases.

4. Conclusion

A SWCNT-coated PQCM gas sensor that consists of SWCNT bundles and PQCM is demonstrated. The properties of the gas sensor concerning the detection of CO, NO₂, H₂ and N₂ are investigated by monitoring Δf in a quartz plate. The frequency of PQCM typically increases with the concentration of the detected gas, indicating mass loss or desorption from the surface of the PQCM. Desorption mechanisms of various gases on SWCNTs are proposed in this study. In detecting CO, NO₂ and H₂, the detected gas chemically reacts with O₂ which is previously adsorbed on the SWCNTs' surface. However, in N₂ detection, an increase in N₂ concentration causes a decrease in O₂ concentration in pure air, leading to desorption of O₂ on the SWCNTs' surface.

The detection response of SWCNT-coated PQCM type B sensor is smaller than that of type A. This is because the SWCNTs are vacuum-annealed in type B, which may decrease

the irregular structures and amorphous species of SWCNTs. Therefore, type B provides less adsorption sites for detecting gas.

The temperature at which the SWCNT-coated PQCMs best detects these gases is approximately 200 °C. These results reveal that SWCNT-coated PQCM can be feasibly used to study the gas-sensing properties of SWCNTs, because of their stability and sensitivity.

Acknowledgments

The authors would like to thank the National Science Council of the Republic of China, Taiwan for financially supporting this research under Contract No. NSC89-2216-E-036-010. Dr. Leszek Stobinski at the Institute of Atomic and Molecular Sciences, Thin Film Processing Laboratory, Academia Sinica, Taipei, Taiwan, R.O.C. is also appreciated for valuable discussions.

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