1. Introduction

Gas sensors are generally defined as devices to detect or measure concentration of (bio-)chemicals in gaseous state. The demands of highly sensitive gas sensors for industry, environmental monitoring, safety, biomedicine, and pharmaceutics have provoked the intensive research interests in micro-electromechanical systems (MEMS) and nanotechnology. The nanotechnology in conjunction with MEMS has created huge potential to build highly sensitive, low cost, compact gas sensors with low power consumption. (Graf et al., 2006; Panchanpakesan et al., 2006; Udrea et al., 2007; Maeng et al., 2008-b)

Fig. 1. An example of MEMS sensor system integrated with nanostructured sensing materials. The darkish areas are covered with multi-walled CNTs.

There exist various types of MEMS gas sensors: two terminal resistance type, field-effect transistor (FET) type, capacitance type, and surface acoustic wave (SAW) type, etc. Among them, the two terminal resistance type gas sensors are most widely used and investigated as the manufacturing process is very cost effective. In the manufacturing of two terminal resistance type gas sensors, semiconducting materials such as SnO$_2$, ZnO and WO$_3$ are used as sensing elements. Among them, nanocrystalline SnO$_2$ has been
focused in gas sensor applications as this material was first commercialized for industrial resistance type gas sensors. (Göpel & Schierbaum, 1995; Cheng et al., 2004) As the demand for sensors both highly sensitive and very compact increases, however, the problems of this material have been revealed. The conventional semiconducting materials need high temperature operation for enhancement of the sensitivity. If the grain size of the sensing elements becomes very small, the coalescence of the grains is inevitable and this leads to the change of the base-line resistance of the sensors. (Shukla et al., 2003) Another problem is the thickness and uniformity control of the semiconducting sensing materials. The conventional sensors adopt thick layer of sensing materials and the control of the thickness uniformity is not difficult. In the MEMS gas sensors, ultrathin layer of nanostructured sensing materials is needed as this facilitates both the high sensitive detection of gases and the low power operation of the sensors. (Udrea et al., 2009) The thickness uniformity control of extremely thin films is not as easy as the thick film cases. Recent development of metal oxide semiconducting nanowires, nanobelts, and nanosheets overcomes the problem of coalescence of materials by thermal heating and accelerates the progress of MEMS gas sensors. (Park et al., 2010; Moon et al., 2010; Maeng et al., 2011) However, the thickness uniformity control problem still remains. The use of semiconducting CNTs as gas sensing elements instead of metal oxide nanomaterials proposed couple of decades before and have been studied intensively due to their inherent properties such as high strength, high electrical and thermal conductivity and high surface-to-volume ratio. In this chapter, the recent development of two terminal resistance type single-walled carbon nanotube (SWCNT) network gas sensors will be reviewed.

2. Individual SWCNT gas sensor

The early work by Kong et al. showed that the electrical resistance of individual semiconducting SWCNTs dramatically changes when exposed to gaseous molecules such as nitrogen dioxide, ammonia, and oxygen under applied gate voltages. These FET type SWCNT gas sensors exhibited very good sensitivity and fast response time at room temperature. The electrical properties of individual metallic SWCNTs in various chemical environments were also investigated under gate modulation. The resulting electrical conductance changes turned out to be negligible compared to the semiconducting counterparts. (Kong, J. et al. (2000))

It is difficult to pick up an individual semiconducting SWCNT from as-grown samples, which are mixtures of both metallic and semiconducting SWCNTs. Furthermore, the alignment of an individual semiconducting SWCNT between pre-patterned electrodes is very complicated process. Therefore, the individual semiconducting FET type SWCNT gas sensor is impractical. More practical way of making semiconducting SWCNT sensors is to use mat or network of SWCNTs, which consist of both metallic and semiconducting SWCNTs, as sensing elements.

3. SWCNT network gas sensor fabricated by direct CVD

Direct growth of SWCNTs network from selectively arranged catalyst by chemical vapor deposition (CVD) has been attempted by various authors. (Qi et al., 2003; Stardermann, et al., 2004; Wongwiriyapan et al., 2006)
Qi et al. fabricated SWCNT FET sensors by using direct CVD growth technique at 900°C and reported that all the devices showed highly sensitive chemical gatings, which indicates that the charge transfer is predominantly through semiconducting SWCNTs. This cannot be easily understood. The nanotubes formed at the devices are mixture of both semiconducting and metallic SWCNTs as the chirality control of SWCNTs is impossible for present day CVD technology. Since the average conductance of a metallic SWCNT is about two orders of magnitude higher than that of semiconducting counterpart (Liang et al., 2007), the main charge transfer would be through metallic SWCNTs for many of the devices.

Fig. 2. (a) Optical image of an array of SWCNT network devices. (b) Optical image of one device. The black regions contain catalyst patterned on top of opposing Mo source and drain electrodes. (c) Scanning electron microscopy (SEM) image of a SWCNT network bridging two opposing Mo electrodes in a device. Excepted from Qi et al., 2003. © American Chemical Society
Stadermann et al. grew SWCNT networks directly onto silicon dioxide substrates using CVD. Gold was deposited onto the surface and patterned to form the electrodes. The devices were tested as FETs by applying sufficient back gate voltage (10V) to show conductance changes between 1% and 50%. These data demonstrate that, in a network of SWCNT between two electrodes, a large part of the current is carried by a small number of highly conductive metallic connections, and the connections involving semiconducting tubes, even though much more numerous, carry a comparable or smaller portion of the current.

Wongwiriyapan et al. synthesized SWCNT film directly on a substrate by thermal CVD. Vertically aligned SWCNTs with a high density were grown at 750 °C, while horizontally lying SWCNT networks with a low density were grown in the temperature range 800–950 °C. Figure 3 shows the varieties of SWCNT networks depending on the growth temperatures. Figure 5. in conjunction with Figure 4. shows the relationship between the surface coverage of SWCNTs and the normalized sensor response: the SWCNT networks with the lowest density exhibited the highest normalized sensor response. Here the normalized sensor response is defined as \( \Delta G/G_0 \), where \( G_0 \) and \( G \) represent the conductance values of the junction before and after the exposure to target gas respectively and \( \Delta G \equiv G - G_0 \). The sensitivity of a sensor at certain concentration values of target gas is defined as the maximum achievable normalized sensor response. The poor sensitivities for high density SWCNT network sensor can be attribute to the conduction of carriers through predominately metallic pathways in the network.

Fig. 3. SEM image of SWCNT network synthesized at different temperatures: (a) 750°C, (b) 850°C, (c) 900°C and (d) 950°C. Excepted from Wongwiriyapan et al., 2006. © IOP Publishing Ltd
This direct growth of SWCNT networks by CVD exhibits complexity with low yield in manufacturing point of view. Furthermore, the SWCNT network sensors can be fabricated on conventional bulky sensor platforms only. The maximum temperature achieved by MEMS gas sensor platform is limited below 700°C at present. (Haque et al., 2008-a, 2008-b)
4. Drop-deposited SWCNT network gas sensor

The most widely reported SWCNT gas sensor is drop-deposited SWCNT network sensor. (Li, et al., 2003; Lu et al., 2006) In this case, the purified SWCNTs are generally dispersed in solutions (surfactants) and then drop-deposited onto interdigitated area of electrodes pre-patterned on the insulating substrate. Figure 6 shows the SEM image of a SWCNT network device fabricated by the drop-deposition method. Figure 7 shows the normalized sensing response of a SWCNT network sensor for various concentrations of NO₂ gas at room temperature. Here 10 minute UV light illumination was introduced to accelerate NO₂ desorption.

Fig. 6. SEM image of SWCNT network bridging two gold electrodes. Excepted from Li et al., 2003. © American Chemical Society

Fig. 7. Normalized sensor response of a drop-deposited SWCNT network sensor upon exposure to various concentration of NO₂ gas. Excepted from Li et al., 2003. © American Chemical Society
This type of fabrication of network sensor is preferred at the research level as it is very simple. But, as shown in Figure 6 the deposited SWCNT network exhibits non-uniformity, which leads to poor reproducibility of the sensor. Thus, this method is not adequate for mass-production.

5. Vacuum filtered SWCNT network gas sensor

In order to enhance non-local uniformity of the SWCNT network sensors, Cho et al. used vacuum filtration method. In this process, 30 nm average pore size AAO filter membrane was installed inside the vacuum filtration system. Then, vacuum filtration of SWCNT solution containing 1% surfactant (SDS) was achieved as shown in Figure 8(a). The SWCNT network deposited on the AAO, then were transferred onto sensor platform as shown in Figure 8(b). By changing the weight of SWCNTs added to the solution, the thickness of the SWCNT network was controlled. As shown in Figure 9, it was revealed that the lower the SWCNT density, the higher the sensitivity of the SWCNT network sensor. The study by Cho et al. gives important information: The SWCNT network sensors must be very thin in order to get high sensitivity. (Cho et al., 2006) Hu et al. reported ultrathin uniform SWCNT network deposition by vacuum filtration method. However, no gas sensors have ever reported by them. (Hu et al., 2004)

Fig. 8. Schematic illustration of (a) the vacuum filtration method using AAO filter membrane and (b) PDMS mold transfer of SWCNT network. Excepted from Cho et al.,2006. © Materials Research Society
Fig. 9. SEM images of the SWCNT network formed on the filter membrane. The initial SWCNT densities used to form each of the thin film were (a) 0.04mg/ml, (b) 0.08mg/ml, (c) 0.12mg/ml, and (d) 0.16mg/ml. The tool bar all indicate 2 μm. Excepted from Cho et al., 2006. © Materials Research Society

Fig. 10. Normalized sensor responses to the 50% NH₃ gas diluted in N₂ for various sensors with different nanotube densities. Excepted from Cho et al., 2006. © Materials Research Society

6. AC dielectrophoretically assembled SWCNT network gas sensor

To form very uniform and thin SWCNT network, AC dielectrophoresis technique was introduced. (Suehiro et al., 2005; Lee et al., 2006) By using the technique, FET and resistance type sensors were fabricated and tested for various gases.
Single-Walled Carbon Nanotube Network Gas Sensor

Fig. 11. (a) Optical image of a SWCNT network sensor. (b) AFM image of SWCNT network deposited between the Au gap by ac dielectrophoresis. Excepted from Lee et al., 2006. © American Chemical Society

Fig. 12. Dependence of channel current upon gate bias of a SWCNT network FET fabricated by ac dielectrophoresis. The FET characteristics were measured at different SOCl₂ concentrations. Small on/of ratio (~1) and vertical shift confirms that the charge transfer between SWCNT network and SOCl₂ occurs mainly through metallic pathways. Excepted from Lee et al., 2006. © American Chemical Society

Figure 11. exhibits a SWCNT network FET device fabricated by Lee et al. and Figure 12. shows its performance under both gate modulation and gas adsorption. From the observation that gate voltage does not modulate the drain current Lee et al. reached a conclusion that the semiconducting nanotubes do not mainly contribute to the signal. They attributed this to the high density of the nanotube network. If the nanotube density is too high, the signal transduction occurs through metallic pathways, which leads to poor sensitivity.
Fig. 13. SEM image of SWCNT network device fabricated by ac dielectrophresis for 3 hours. The inset is magnified image near an electrode corner. Excepted from Suehiro et al., 2005. © Elsevier B.V.

Figure 13. exhibits a SWCNT network device fabricated by Suehiro et al.. By monitoring impedance of the devices during the ac dielectrophresis Suehiro et al. controlled the assembly of SWCNT and reached a conclusion that the semiconducting SWCNT do contribute to the sensing. Figure 14 exhibits normalized sensor response of a SWCNT network sensor fabricated by Suehiro et al..

Fig. 14. The dependence of NO\textsubscript{2} gas concentration upon the normalized sensor response of a SWCNT network gas sensor fabricated by ac dielectrophresis. Excepted from Suehiro et al., 2005. © Elsevier B.V.
7. SWCNT network gas sensor fabricated by surface-programmed assembly technique

Recently, ultra uniform and thin SWCNT network sensors fabricated by ‘surface-programmed assembly’ technique were reported by several authors. (Wang et al., 2009; Tran et al., 2008; Maeng et al., 2008-a) As this technique enables very precise control of nanotube density, it is expected that semiconducting nanotubes contribute to the sensing mechanism as is predicted by percolation theory which leads to high sensitivity. In addition, this technique is expected to facilitate wafer scale production of SWCNT sensor. Wang et al. reported SWCNT sensors fabricated by using self-assembled monolayer (SAM) of hydrophilic 3-aminopropyltrimethoxysilane (APS) as shown in Figure 15. In this process very thin SWCNT network patterns were selectively formed on the functionalized region. From the DMMP detection experiments, they revealed that the sensitivity reaches a maximum when networks of overlapped nanotubes disappear, i.e. the nanotubes are assembled to form a monolayer network. This conclusion supports the observations by Cho et al. that the thinner the SWCNT network the higher the sensitivity of the sensor. (Cho et al., 2006) It is further revealed that SWCNT monolayer with maximum connectivity is ideal for making highest sensitivity gas sensors.

Fig. 15. (a) Optical image of the electrode arrays, where deposited SWCNT networks are separated by Au electrodes. (b) SEM image of SWCNT networks bridging Au electrodes deposited on Si/SiO2 substrate. (c) An enlarged SEM image of (b). Excepted from Wang et al., 2006. © IOP Publishing Ltd
Tran et al. fabricated SWCNT sensors on both functionalized substrate with hydrophilic monolayer of 3-aminoprophilethoxysilane (APTES) and bare substrate as shown in Figure 16.

![SEM image of (a) the sensor device which consist of interdigitate electrodes and SWCNTs (b) the SWCNT networks formed on bare surface (c) the SWCNT networks formed on the APTES-treated surface.](image)

Then, they tried to compare NO\textsubscript{2} detection response of the two sensors as shown in Figure 17. The response time of the functionalized substrate-based gas sensor is very fast (a few seconds), while that of the bare substrate-based one is very slow (hundreds of seconds). It is conjectured that the interaction between APTES and sidewall of SWCNTs gives easier accessibility to the gas molecules. The sensitivity of the sensor on APTES-treated substrate is also shown to be higher than that on bare substrate.
Maeng et al. reported highly uniform SWCNT monolayer sensors fabricated by using hydrophobic octadecyltrichlorosiline (OST) surface functionalization. This time, SWCNTs are selectively assembled on non-functionalized or bare surface regions of the substrates. The atomic force microscopy (AFM) image of a SWCNT junction shows a low-density monolayer of SWCNT network between the Au/Ti electrodes. (Figure 18)
Figure 19 shows the normalized responses of typical SWCNT monolayer network sensor fabricated on bare surface to various NO\textsubscript{2} gas concentrations at room temperature. If we compare Figure 19 with Figure 17, it seems that SWCNT monolayer sensor formed on bare substrate exhibits higher sensitivity than that formed on APTES-functionalized substrate for the same concentration of NO\textsubscript{2}. This is contradictory to the observation by Tran et al.. It is likely that Tran et al. could not optimize the sensor fabrication conditions and further researches are necessary to determine whether or not SWCNT monolayer sensor formed on bare substrate assumes higher sensitivity than that formed on APTES-functionalized substrate. Considerably high sensitivity of the sensor indicates that semiconducting SWCNTs are involved in the sensing as percolation theory describes.

In order to construct a conduction model of the SWCNT network sensor, Suehiro et al. assumed that the base-line conductance $G_0 = N_t g_0$, where $N_t$ is the total number of SWCNTs and $g_0$ is the average conductance of one SWCNT. It was implicitly assumed that all SWCNT had the same electrical property. After NO\textsubscript{2} adsorption, the conductance of individual SWCNT is further assumed to be increases by $\Delta g$ on average, which leads to the total increase of sensor conductance $\Delta G = N_t \Delta g$. From this relations, they further derived the relation that normalized sensor response $\Delta G/G_0 = \Delta g/ g_0$. However, they gave no thought to the fact that the random network both follows percolation theory and consists of very different types of SWCNTs. According to the percolation theory, $G_0 \propto (N_t - N_c)^\nu$ when all the nanotubes have the similar electrical conductance. Here
The critical number corresponding to percolation threshold, and \( \nu \sim 1.94 \) is the critical exponent. (Stauffer, 1985) If some of the constituents have totally different electrical conductances as was the case of SWCNT network, the calculation becomes a bit complicated.

Fig. 20. (a) Normalized sensor response \( \Delta G/G_0 \) of SWCNT network sensor to 500 ppb NO\(_2\) gas. (b) Sensitivity \( R_s \) vs base-line conductance \( G_0 \) graph. (Inset) Sensitivity \( R_s \) linearly proportional to the inverse of the base-line conductance. Excepted from Maeng et al., 2008-a. © American Institute of Physics

8. **Theoretical explanation of the inverse proportionality of sensitivity to the base-line conductance of SWCNT network sensor based on the percolation theory**

The sensing characteristics shown in Figure 20 can be attributed to both the mixing nature of metallic and semiconducting SWCNTs and the randomly assembled network. Even though the SWCNT monolayer network is so uniformly deposited that each devices have equal number of SWCNTs and fixed ratio of metallic SWCNT/semiconducting SWCNT, the fluctuations of the base-line conductance can occur depending on the numbers of metallic SWCNTs which contact with electrodes. If the width of the electrode is comparable to the size of nanotubes as was in the case of the work by Maeng et al. the numbers may differ from device to device. Now, it should be explained how the difference of base-line conductance of devices influence the sensitivity of the devices. \( G(c) \), the sheet conductance of a device at a gas concentration \( c \), can be described as:

\[
G(c) = \frac{1}{\pi} \left( \frac{4.236}{L_{\text{tube}}} \right)^2
\]

is the critical number corresponding to percolation threshold, and \( \nu \sim 1.94 \) is the critical exponent.
\[ G(c) = g_s(c)P_s + g_m(c)P_m \tag{1} \]

where \( g_m(c) \) and \( g_s(c) \) are average conductance per a metallic-only pathway and that including semiconducting nanotubes at a gas concentration \( c \), respectively. While the SWCNTs treated by ac dielectrophoresis are aligned with preferential directions, those by surface programmed assembly method are randomly oriented. This enables the application of the percolation theory in estimating possible conduction pathways in a SWCNT monolayer network.

By using the percolation theory, \( P_t = P_0(N_t - N_c) \nu \), \( P_m = P_0(N_m - N_c) \nu \), the relation \( \Delta g_m / \Delta g_s \ll 1 \), and the relation \( g_s(0) / g_m(0) \ll 1 \), where \( P_t \) is the total conduction paths, \( P_m \) is the number of metallic-only paths, \( P_0 \) is a constant, \( N_m \) is the number of metallic SWCNTs in the network, \( \Delta g_m = g_m(c) - g_m(0) \), and \( \Delta g_s = g_s(c) - g_s(0) \), it is obtained

\[ \frac{\Delta G}{G_0} = \frac{\Delta g_s P_t}{G_0} - \frac{\Delta g_s}{g_m(0)} \times \left[ 1 - \frac{g_s(0)}{g_m(0)} \left( \frac{\epsilon - \delta}{1 - \delta} \right) \right] \]

\[ \approx \frac{\Delta g_s P_t}{G_0} - \frac{\Delta g_s}{g_m(0)} \tag{2} \]

where \( \epsilon \equiv N_t / N_m = 1.5 - 3 \) and \( \delta \equiv N_c / N_m \).

For a specific gas concentration, the achievable maximum value of \( \Delta g_s \equiv \Delta g_{s,max} \) is a constant. Furthermore, if it is assumed that the SWCNTs are dispersed so uniformly that the total number \( P_t \) of all conduction paths is a constant, the sensitivity for the specific gas concentration can have the form

\[ \text{Sensitivity} R_s \approx \frac{\Delta g_s}{G_0} - \beta \tag{3} \]

where \( a \equiv \Delta g_{s,max} \) \( P_t \) = constant and \( \beta \equiv \Delta g_{s,max} / g_m(0) = \text{constant} \). (Maeng et al., 2008-a) This result explains the linear proportionality of sensitivity to the inverse of the initial conductance \( G_0 \).

9. Future prospects of SWCNT network gas sensor

To secure the reproducibility of the SWCNT monolayer network sensor, the size of the electrodes must be large enough so that the numbers of metallic SWCNTs contacting with electrodes are averaged out. The SWCNT monolayer sensor is very promising not only in the perspective of sensitivity but also in the perspective of sensor operation. Even though the response time of semiconducting SWCNT sensor is about one order of magnitude faster than conventional metal oxide sensors, the recovery time of the sensor is about one order of magnitude slower than the metal oxide counterparts. This slow recovery time of the SWCNT sensors is due to irreversible binding of gas molecules on the SWCNT surface and is a primary hurdle for most SWCNT sensors that have appeared in the literature to date. MEMS-based metal oxide sensors usually adopt microheaters to enhance gas adsorption rate at moderate temperature range (200 ~ 400ºC) and the desorption rate at higher temperature range. The integration of microheater with SWCNT network sensor will be also very useful for acceleration of desorption rate of adsorbed species even though some
authors suggest to use UV source for the same purpose. (Li et al., 2003; Karthigeyan, et al., 2008; Maeng, et al., 2008-a) The use of microheaters is highly recommendable as the characteristics of SWCNT devices are affected by humidity. (Sung et al, 2006) Carbon nanotubes are also known to exhibit higher sensitivity at moderately elevated temperature range.(Valentini, et al.,2003) It is, thus, desirable for SWCNTs network to become monolayer so that the temperature of microheater and the nanotubes coincides during the operation. In this regards, the attempt to fabricate mass-production scale SWCNT sensors by depositing SWCNT monolayer onto microheaters of the MEMS sensor platforms is much needed and to be explored in the future.

10. Conclusion

In this chapter, an attempt has been made to provide overview of resistance and FET type SWCNT network gas sensors. In the thick SWCNT network sensor, the conduction of charge carriers occurs primarily through metallic-only pathways and the sensor sensitivity is poor. As the thickness of the sensor is reduced, the sensitivity tends to be enhanced. There exist a critical point where main conduction begin to occur through semiconducting-metallic mixed pathways. The critical point is determined by the density of SWCNT network. When the network becomes non-overlapping monolayer, the semiconducting nanotubes contribute to the electrical conduction so significantly that sensitivity reaches a maximum value. The behavior of the sensor sensitivity can be explained satisfactorily by the percolation theory at this condition.

11. Acknowledgment

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12. References


Carbon Nanotubes are among the strongest, toughest, and most stiff materials found on earth. Moreover, they have remarkable electrical and thermal properties, which make them suitable for many applications including nanocomposites, electronics, and chemical detection devices. This book is the effort of many scientists and researchers all over the world to bring an anthology of recent developments in the field of nanotechnology and more specifically CNTs. In this book you will find:
- Recent developments in the growth of CNTs
- Methods to modify the surfaces of CNTs and decorate their surfaces for specific applications
- Applications of CNTs in biocomposites such as in orthopedic bone cement
- Application of CNTs as chemical sensors
- CNTs for fuelcells
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