Gas Sensing Characterization of Branched SnO_2 Nanowires

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Abstract

Rutile-type SnO_2 nanowires have been synthesized by a thermal chemical vapor deposition, using a mixture of SnO and graphite powders as tin source. Branched nanowires with an uniform diameter of 50–80 nm, a length of several to ten micrometers, and a definite included angle of ~68° are observed from scanning electron spectroscope and high-resolution transmission electron spectroscope. The branched SnO_2 network was inferred through a vapor-liquid-solid growth mechanism. For a trace level (20–60 ppm) CO gas detection, a guasi-step function was employed for describing the behavior of gas sensors. The analyzed results demonstrated that the SnO_2 nanowires-based nanosensor not only represents a greater sensitivity (~1.6 times) but also a shorter time constant (~0.75 times), compared with the thin-film sensor.

本研究利用化學氣相沉積法合成金紅石結晶狀之二氧化錫奈米線，並探討其一氧化碳之氣體感測性能。研究中使用氧化錫和石墨粉體做為錫的前趨物來源，並經由掃描式電子顯微鏡和高解析穿透式電子顯微鏡可觀察出二氧化錫奈米線分支狀奈米結構，其奈米線直徑約 50 到 80 nm、長度約幾微米至十微米、分支夾角約為 68 度。而二氧化錫的分支網狀結構可推斷是經由氣液固(Vapor-liquid-solid)成長機制所生成。針對一氧化碳氣體於二氧化錫奈米線之感測行為，本研究以擬階級函數來描述此氣體感測行為，並且得到良好的套適結果(correlation)。由分析結果顯示，若以薄膜感測器與二氧化錫奈米線為奈米感測器比較，二氧化錫奈米線為基準的奈米感測器不僅表現出良好的敏感度且有較短的時間常數。

Keywords: **Tin oxide, Nanowires, CO sensor, Gas detection**

INTRODUCTION

Conductometric metal-oxide-semiconductor nanomaterials are widely recognized as the key compounds in nanofabrication. They act critical roles in nanotechnology due to

their nanometer-sized geometry, unique properties, and high compatibility with microelectronic processing [1]. Among the nanomaterials, semiconductor nanowires and nanobelts are promising candidates for the fabrication of nanodevices using the integrity of individual nanowire or nanobelt [2,3]. Considering a wide band semiconductor (E_g = 3.6 eV at 300 K), SnO_2 is a crucial functional material that has been extensively used for gas sensor, transparent conductor, and nanoelectronic device [4]. Based on the deduction above, it is reasonable to infer that small crystalline SnO_2 size, such as SnO_2 nanowires or nanostructires, would probably promote the gas sensitivity of sensors.

In the present work, an attempt to fabricate a novel gas sensor by using SnO_2 nanowires is investigated. The as-grown SnO_2 nanowires has a purely single crystalline. Compared with thin-film sensor, the gas sensor fabricated with the nanomaterials may enhance the sensitivity and shorten the responding time. A step function for describing the CO sensing properties employed here would shed some lights on how morphology affecting the gas sensing properties.

EXPERIMENTAL

SnO_2 nanowires were synthesized by thermal evaporation of SnO powders under controlled conditions with the presence of nanosized gold catalysts. In brief, a plasma sputtering was used to deposit the nano-Au particles or thin films onto Si wafer. The prepared Si wafer with gold thin film was carefully cut into 2 × 2 cm^2, and then put in a quartz tube (65 mm inner diameter) that was inserted in a horizontal electronic resistance furnace. Prior to heating, the furnace was rapidly heated up to 900 °C at a linearly heating rate of 10 °C/min, and kept at this temperature for 1 h. After the growth system was cooled down to room temperature, a transparent wool-like product grown on Si wafer was thus obtained.

For the fabrication of gas sensors, a gold comb-type electrode structure was made using a metal deposition technique with shadow masking on an alumina substrate. A ruthenium heater was deposited on the back side of the electrode in order to control the working temperature of the sensor. After that, a bunch of nanowires was placed onto the electrodes for measuring their electric conductance, and *I-V* measurements confirmed that the contact is ohmic. In comparison, a SnO_2 thin film prepared by using sol-gel technique was employed to examine its sensing properties. The detailed processing for preparing SnO_2 thin film has been reported elsewhere [5]. After heat treatment at 450 °C, the polycrystalline SnO_2 thin film can be coated onto the electrode. A closed system is used to determine the gas sensing properties of the sensors. A bell-type chamber with a constant volume of 10 L was applied to control the sensing environment, and an inlet located on the top of the chamber can be injected different

concentrations of gases. In the present study, CO gas was chosen as detecting gas and its concentrations were ranged from 20 to 60 ppm.

Sensitivity characteristics were measured in the temperature range from 150 to 450 °C. At each temperature, the sensor was stabilized in air to a steady resistance value (R_{air}), and the reduction in sensor resistance (R_t) at any time in the presence of CO atmosphere was recorded.

RESULTS AND DISCUSSION

Figures 1 show a series of typical TEM analyses for the individual SnO_2 nanowire. The HRTEM image of the single SnO_2 nanowire clearly shows the wire has a shape of a prism with unique facet. The tip of the multilayered SnO_2 nanowire consists of about 100 atomic layers, and the lattice spacing is 0.26 nm, which is consistent with the lattice parameter for *d* space (101) plane in a SnO_2 rutile structure. A SAD of the single nanowire, as shown in the inset of Figure 1(c), also indicates that it is monocrystalline with a rutile structure. The spots in the pattern confirm that the SnO_2 nanowire, synthesized with the thermal evaporation, possesses an excellent crystallinity. This confirms a fact that the included angle is exactly 68° between [$\bar{1}$01] and [101] crystalline orientations.

Figure 2 shows that the temperature dependence of the sensitivity (R_{air}/R_t) to 20 ppm CO gas for both gas sensors fabricated with SnO_2 thin film and nanowires. Both the sensors exhibit the maximum sensitivity at 350 °C. Taking account into a semiconductor-type sensor, the principle of the sensor has been well established in the literatures [7,8]. Oxygen molecule interacts with *n*-type SnO_2 semiconductor after diffusive transfer from the gas to the surface:

$$O_{2,\,gas} \rightarrow O_{2,\,surf} \qquad +- \qquad \text{(R1)}$$

Then the adsorbed oxygen molecules at heated tin-oxide surfaces would form surface oxygen ions by trapping two electrons from the tin-oxide conduction band:

$$O_{2,\,gas} + 2\,e^- \leftrightarrow 2\,O^-_{surf} \qquad \text{(R2)}$$

After sufficiently long-time reaction, the molecular ionization (R2) establishes an equilibrium between the partial pressure of oxygen in the surrounding gas phase and the density of surface oxygen ions.

A particularly well-established detection reaction is CO on tin-oxide surfaces. The CO molecules, in general, of electron-donor, can be chemically adsorbed onto the tin-oxide surfaces filled with oxygen ions, thus interacting with the ion-adsorbed species following the reaction:

$$CO_{gas} + O^-_{surf} \rightarrow CO_2 + e^- \qquad \text{(R3)}$$

The injection of electrons (R3) results in a decrease of the electrical resistance at the tin-oxide surface.

This result of Figure 2 demonstrates that in the cases of the crystalline structure, the increase of sensitivity is remarkably affected by the dimension or grain-size effect. This result can be inferred by a fact that in the novel sensor based on the single crystalline of the SnO_2 nanowires, almost all of the adsorbed species are active in producing a surface depletion layer. This facilitates that free carriers cross the wire's bulk along the axis in a channel-like way [1], thus followed by increasing the sensitivity of the sensor.

To investigate the sensing behavior of the SnO_2 materials, a dynamic responding experiment for both sensors is performed in a concentration range of 20 to 60 ppm at 350 °C. The schematic diagram of gas detection circuit and the CO sensitivity varied with time for the gas sensors fabricated with SnO_2 nanowires and thin film are illustrated in Figures 3. To describe with the kinetic of the sensors, a quasi-step function is employed to identify the time-dependent responses of the sensors. Here suggesting that signal output, R_{air}/R_t, is equal to y, and a quasi-step function describing sensing characteristics can be expressed as follows

$$y(t) = y_0 + y' [1 - \exp(-t/\tau)] \quad (1)$$

where $y(t)$ and y_0 are signal outputs corresponding to any time t and the initial stage, respectively, y' is the constant of the maximum signal output at ultimate time, τ is the time constant, which is used to evaluate the responding rate. These parameters varied with concentrations ranged from 20 to 60 ppm CO for both sensors are listed in Table 1. The results form this table reflect that both the y' and τ values is an increasing function of CO concentration for both sensors. This is beneficial to assist us in designing a real-time CO sensor. In addition, a fairly good prediction for both sensors is achieved by using the parameters determined from the quasi-step function, also illustrated in Figure 3(b).

CONCLUSIONS

We have fabricated gas sensors based on the SnO_2 nanowires and the branched nanowires synthesized by thermal evaporation of SnO and graphite powders under controlled conditions. The morphology and microstructure of the single crystalline SnO_2 nanowires and the branched nanowires were characterized by means of SEM, HRTEM, and SAD. Each nanowire had a uniform diameter of 50–80 nm and a length of several to ten micrometers. A quasi-step function was also employed for describing the behavior of the gas sensors. The results also indicated that the SnO_2 nanosensor not only presents a greater sensitivity (~1.6 times), but also a shorter time constant (~0.75 times), compared with the thin-film sensor. According the above sensing properties, this demonstrates the potential of fabricating nanostructured sensor using the integrity of branched SnO_2 nanowires with a great sensitivity.

REFERENCES

1 Comini E, Faglia G, and Sberveglieri G, *Appl. Phys. Lett.* **81:** 1869 (2002).

2 Calestani D, Zhaa M, Salviati G, Lazzarini L, Zanotti L, Comini E, and Sberveglieri G, *J. Cryst. Growth* **275**: e2083 (2005).

3 Peng XS, Zhang LD, Meng GW, Tian YT, Lin Y, Geng BY, and Sun SH, *J. Appl. Phys*. **93**: 1760 (2003).

4 Ma YJ, Zhou F, Lu Li, and Zhang Z, *Solid State Commun*. **130:** 313 (2004).

5 Li N, and Martin CR, *J. Electrochem. Soc*. **148**: A164 (2001).

6 Wang JX, Liu DF, Yan XQ, Yuan HJ, Ci LJ, Zhou ZP, Gao Y, Song L, Liu LF, Zhou WY, Wang G, and Xie SS, *Solid State Commun*. **130**: 89 (2004).

7 Barbi GB, Santos JP, Serrini P, Gibson PN, Horrillo MC, and Manes L, *Sensor and Actuators B* **24-25**: 559 (1995).

8 Becker T, S. Mühlberger. C. B. Braunmühl, Müller G, Ziemann T, and Hechtenberg KV, *Sensor and Actuators B* **69**: 108 (2000).

Table 1. Parameters for CO detection on different gas sensors determined from the quasi-step function, Eq. (1).

Sensor	C_{CO}= 20 (ppm)		C_{CO}= 40 (ppm)		C_{CO}= 60 (ppm)	
type	y'	τ (sec)	y'	τ (sec)	y'	τ (sec)
Thin film	0.60	136	0.64	121	0.75	111
Nanowires	1.01	101	1.25	95.6	1.33	80.6

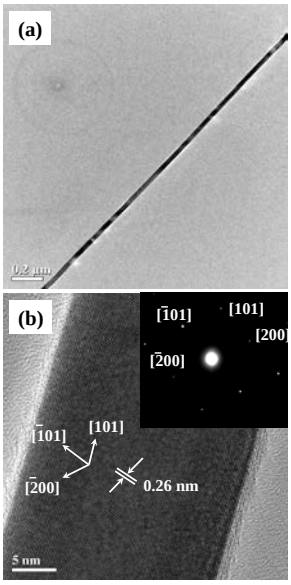

Figure 1. (a) TEM and (b) HRTEM images of the SnO_2 nanowires prepared

using graphite and SnO powder. The inset of Figure 2(b) shows the SAD pattern of the individual SnO_2 nanowire.

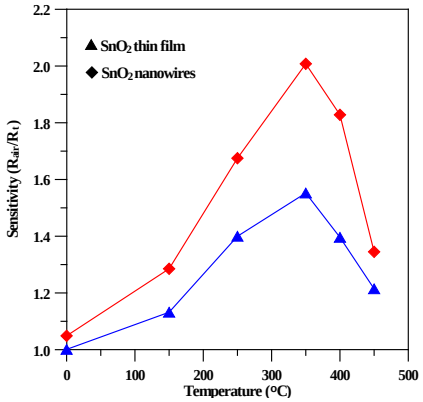

Figure 2. CO sensitivity dependence on detection temperature for the gas sensors fabricated with SnO_2 nanowires and thin film.

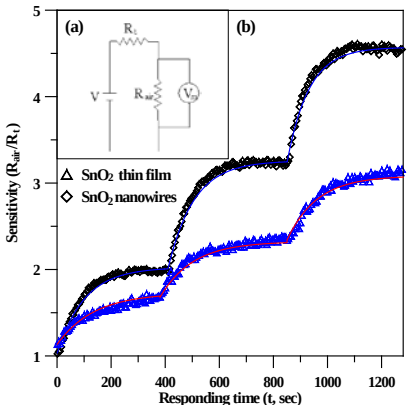

Figure 3. (a) Schematic diagram of gas detection circuit. (b) CO sensitivity dependence on detection time for the gas sensors fabricated with SnO_2 nanowires and thin film, in which the symbols are experimental data, and the solid curves are predicted by the quasi-step function.