Gas sensing characteristics of polycrystalline SnO2 nanowires prepared by polyol method

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1. Introduction

Nanostructured oxide semiconductors offer a cost-effective method for detecting trace concentrations of toxic and dangerous gases [1–3]. For instance, SnO2 1D nanostructures, such as nanowires (NWs) [4–8], nanorods [9,10], nanobelts [8.11–13], and nanotubes [14] are the representative materials for use as gas sensors. Until now, SnO2 1D nanostructures have generally been prepared in a single crystalline form by thermal evaporation at high temperature (1000 °C) [6–8,11–13]. High crystallinity and less-agglomerated configuration are the major advantages. However, the preparation of chemically active NWs on a large scale using a cost-effective route still remains a challenging issue. Recently, Wang et al. [15] suggested that polycrystalline SnO2 NWs can be prepared by a polyol method. It was suggested that the formation mechanism of the NWs involved the production of tin glycolates, followed by oligomerization. It implies that the diameters, extent of aggregation, morphologies, and surface structures of the SnO2 NWs are dependent on the concentrations of the source materials, the reaction temperature, and the reaction time. The morphological properties of the NWs will affect their final gas sensing performance, such as sensitivity and response kinetics.

In this study, polycrystalline SnO2 NWs were prepared by heating ethylene glycol solution containing SnC2O4. The sizes and morphologies of the NWs were manipulated by varying the concentration of SnC2O4 and by using nucleating agents, such as Pd, Ag, and Ru. The main aim of this research was to enhance the gas sensitivity of the NWs by investigating the effects of varying the morphologies of the NWs and the effects of incorporating catalytically active nucleating agents. Another aim was to achieve an understanding of the NW formation mechanism.

2. Experimental

SnC2O4 (Sigma–Aldrich, 98%) and ethylene glycol (JUNSEI Chemical) were used as the source material and the polyol solvent, respectively. Various concentrations of SnC2O4-containing solution were made by adding 0.06, 0.07, or 0.2 mol of SnC2O4 to 100 ml of ethylene glycol. The precursor NWs were heat-treated at 600 °C, which successfully transformed them into SnO2 NWs without undergoing any morphological change. The morphology of the SnO2 NWs could be manipulated either by controlling the SnC2O4 concentration or by adding easily reducible noble metal salts, such as PdCl2, AgNO3, or RuCl3·H2O. The thicker and shorter SnO2 NWs, which resulted from the use of a high SnC2O4 concentration during the preparation, showed lower gas sensitivity due to their decreased gas sensing surface area. The addition of catalytically active Pd, Ag, or Ru not only changed the gas sensitivity but also significantly shortened the gas recovery times. The gas sensing characteristics of the SnO2 NWs were related to the NW morphology and, when applicable, the catalyst used.

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The Sn-precursor NWs, after drying, were prepared into a paste form and applied to an alumina substrate having two Au electrodes. The sensor element was heat-treated at 600 °C for 3 h to convert the Sn-precursor NWs into polycrystalline SnO2 NWs and to decompose the organic content of the paste. The 1D morphology of the NWs did not change as a result of the heat treatment. The sensor was placed in a quartz tube and the temperature of furnace was stabilized at 400 °C. The gas concentration was controlled by changing the mixing ratio of the parent gases (200 ppm C2H5OH, 200 ppm C3H8, and 100 ppm CO, all in air balance) and the dry synthetic air. A parent gas was used at each measurement. A flow-through technique with a constant flow rate of 500 cm3/min was used. The gas response ($R_s/R_g$) was measured at 400 °C by comparing the resistance of the sensor in the high-purity air ($R_s$) and that in the target gases ($R_g$). The dc 2 probe resistance of the sensor was measured using an electrometer interfaced with a computer.

3. Results and discussion

3.1. Preparation of the polycrystalline SnO2 nanowires

Fig. 1 shows the X-ray diffraction patterns of the as-prepared Sn-precursor NWs and the SnO2 NWs after heat-treatment at 600 °C. The small peaks were indexed to SnC2O4. Broad background peaks were also found (Fig. 1(a)). Therefore, the as-prepared Sn precursor was regarded as being amorphous with a minor amount of SnC2O4 phase. Pure SnO2 resulted from the heat treatment at 600 °C for 3 h.

SEM images of the Sn-precursor NWs and the SnO2 NWs are given in Fig. 2. The morphologies and aspect ratios of the Sn-precursor NWs (Fig. 2(a), (c), (e)) were highly dependent on the SnC2O4 concentration, but remained similar after the heat treatment at 600 °C for 3 h (Fig. 2(b), (d), (f)). This suggests that the morphologies and aspect ratios of the SnO2 NWs can be manipulated during the precursor formation stage.

All of the SnO2 NWs were polycrystalline, being composed of fine primary particles approximately 50 nm in size. The diameters of the SnO2 NWs prepared from the solutions containing 0.06, 0.07, and 0.2 mol of SnC2O4 were approximately 250 nm, 350 nm, and 800 nm, respectively. Increasing the SnC2O4 concentration resulted in the SnO2 NWs generally becoming thicker and shorter (i.e. having decreased aspect ratios) (Fig. 2(b), (d), (f)). Note that the S-007 NWs (Fig. 2(b)) showed particularly uniform and smooth surface morphologies.

In order to investigate the NW formation mechanism, a solution containing 0.07 mol of SnC2O4 was injected into hot ethylene glycol solution, as described earlier. Fig. 3 shows the SEM images of the samples prepared by this hot injection method. Uniformly sized secondary particles (~100 nm) were formed by refluxing the reaction mixture for 2 h after the hot injection (Fig. 3(a)). The particles were approximately spherical. Upon increasing the reaction time to 3 h, the particles became rectangular shaped and NWs had started to grow.

A previously suggested mechanism for the formation of SnO2 NWs involves the formation of tin glycolates via the gradual replacement of oxalic groups by ethylene glycol, the oligomerization of the tin glycolates into long chains, and the self-assembly of the chains into ordered bundles [15]. The appearance of the fine powder particles at the initial stage of the reaction and their subsequent transformation into short NWs with rectangular cross-sections (as shown in Fig. 3) indicates that the SnO2 NWs in this study are also formed by the anisotropic polymerization of the precursor materials.

Tin glycolates will be released slowly when the SnC2O4 concentration is low. This provides a feasible environment for the polymerization to occur in an anisotropic manner. By contrast, tin glycolates will be released rapidly when the SnC2O4 concentration is high. This promotes the self-assembly of the polymerized tin glycolate chains rather than the anisotropic growth of the NWs. This leads to the formation of thicker and shorter NWs. This explains the increase in diameter and the decrease in length of the SnO2 NWs with increasing SnC2O4 concentration, as shown in Fig. 2.

In order to study the effect of the noble metal catalyst on the morphology and gas sensitivity of the SnO2 NWs, 100 ppm (wt%) of PdCl2, AgNO3, or RuCl3·H2O were added to ethylene glycol solution containing 0.07 mol of SnC2O4. The catalyst-doped Sn-precursor NWs all showed similar morphologies and consisted of uniform

### Table 1
Sample specifications and surface areas.

<table>
<thead>
<tr>
<th>Precursor NWs</th>
<th>SnO2 NWs</th>
<th>SnC2O4 (mol)</th>
<th>Catalyst</th>
<th>S.S.A. (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-006</td>
<td>S-006</td>
<td>0.06</td>
<td>–</td>
<td>16.6</td>
</tr>
<tr>
<td>P-007</td>
<td>S-007</td>
<td>0.07</td>
<td>–</td>
<td>14.2</td>
</tr>
<tr>
<td>P-007-Pd</td>
<td>S-007-Pd</td>
<td>0.07</td>
<td>PdCl2 100 ppm¹</td>
<td>15.2</td>
</tr>
<tr>
<td>P-007-Ag</td>
<td>S-007-Ag</td>
<td>0.07</td>
<td>AgNO3 100 ppm²</td>
<td>13.7</td>
</tr>
<tr>
<td>P-007-Ru</td>
<td>S-007-Ru</td>
<td>0.07</td>
<td>RuCl3·H2O 100 ppm³</td>
<td>13.8</td>
</tr>
</tbody>
</table>

¹ As-prepared Sn-precursor nanowires.
² SnO2 nanowires prepared by heat treatment of precursors at 600 °C for 3 h.
³ Specific surface area of the SnO2 NWs as determined by BET analysis.
⁴ Catalyst-containing salt/SnC2O4 = 100 ppm by weight during polyol-mediated reaction (catalyst-containing salt = PdCl3, AgNO3, or RuCl3·H2O).
NWs with diameters of \(~250\,\text{nm}\) and lengths of \(~2\,\mu\text{m}\) (Fig. 4(a), (c), (e)). These NWs could be converted into catalyst-loaded SnO₂ NWs by heat treatment at 600 °C for 3 h without a change of morphology (Fig. 4(b), (d), (f)). The catalyst-loaded Sn-precursor NWs and SnO₂ NWs were thicker and shorter than their undoped counterparts (shown in Fig. 2(c) and (d), respectively). Easily reducible precious metals are known to act as nucleating agents during the polyol process. Considering the high standard reduction poten-
Fig. 4. SEM images of the Sn-precursor and SnO2 NWs doped with one of various catalysts: (a) P-007-Pd, (b) S-007-Pd, (c) P-007-Ag, (d) S-007-Ag, (e) P-007-Ru, and (f) S-007-Ru.

Fig. 5. Gas responses \( \frac{R_a}{R_g} \) upon exposure to 100 ppm CO, 200 ppm C\(_3\)H\(_6\), 200 ppm C\(_2\)H\(_5\)OH, and 200 ppm CH\(_3\)COCH\(_3\), respectively. All three sensors showed similar responses (\( S = \frac{R_a}{R_g} \)) to CO and C\(_2\)H\(_5\)OH (4.9–6.9). However, the responses to C\(_2\)H\(_5\)OH and CH\(_3\)COCH\(_3\) were markedly (3.6–16.3 times) higher than those to CO and C\(_3\)H\(_6\). Thus, it is possible to detect C\(_2\)H\(_5\)OH and CH\(_3\)COCH\(_3\) selectively. The responses to CH\(_3\)COCH\(_3\) and C\(_2\)H\(_5\)OH tend to decrease with increasing the initial SnC\(_2\)O\(_4\) concentration. This can be attributed to the decreased surface area for the gas sensing reaction (Table 1), due to the thickening of the NWs (Fig. 2(b), (d), (f)). In addition, the ratios between the responses of S-006, S-007, and S-02 sensors to CH\(_3\)COCH\(_3\) and
C2H5OH (Sacetone/Sethanol) are 1.73, 1.59, and 1.55, respectively. This indicates that the S-006 sensor is advantageous to achieve high selectivity to acetone.

The dynamic response transients are shown in Fig. 6. The 90% response times for the gas exposures (t90%(air-to-gas)) ranged from 2 to 4 s. While the 90% recovery times (t90%(gas-to-air)) from the exposure to CO, C2H5OH, and CH3COCH3 are 144, 97, 441, and 473 s, respectively. The significantly longer t90%(acetone-to-air) and t90%(ethanol-to-air) values compared to the t90%(COs-to-air) and t90%(propanes-to-air) values reflect the difference in the recovery reaction.

The results of studying the effects of catalytically active nucleating agents on the gas sensing characteristics are shown in Fig. 7. Note that the responses to all four gases were enhanced by doping with 100 ppm AgNO3, or RuCl3·H2O. However, the gas responses to C2H5OH and CH3COCH3 were decreased by doping with 100 ppm Pd (Fig. 7(c), (d)). The change in the gas response upon doping with a catalyst was quantified by taking the ratio between the gas responses of the sensors with and without the catalyst (Scatalyst/Spure). Note that Scatalyst/Spure > 1 and Scatalyst/Spure < 1 mean the enhancement and deterioration of the gas response upon doping with the catalyst, respectively. The Scatalyst/Spure values for 100 ppm CO were 1.51, 2.59, and 3.25 for S-007-Pd, S-007-Ag, and S-007-Ru sensors, respectively. Similar tendencies were found for the Scatalyst/Spure values for 200 ppm C2H5OH and S-007-Ru sensors, respectively. These results show that the gas responses to CO and C2H5OH were enhanced by the catalysts; the Ru resulted in the most improved response, while the Pd resulted in the least improved response. On the other hand, the highest enhancements in gas responses upon exposure to 200 ppm C2H5OH and 200 ppm CH3COCH3 were attained by Ag doping (2.63 and 2.98), followed by Ru doping (2.00 and 1.66). In contrast, when doped with Pd, the Scatalyst/Spure values upon exposure to 200 ppm C2H5OH and 200 ppm CH3COCH3 were 0.55 and 0.44, respectively, which means that decreased gas responses resulted.

The BET surface areas of the S-007, S-007-Pd, S-007-Ag, and S-007-Ru NWs are 14.2, 15.2, 13.7, and 13.8 m2/g, respectively (Table 1). The morphologies of catalyst-doped S-007-Pd, S-007-Ag, and S-007-Ru NWs are similar with each other (Fig. 4(b), (d), (f)) but thicker and shorter compared to that of undoped S-007 NWs (Fig. 2(d)). The change of morphology by doping catalyst indicates that the Pd, Ag, and Ru play the role of nucleating agents during polyol-mediated reaction. And the gas responses of S-007-Pd, S-007-Ag, and S-007-Ru sensors to CO, C2H5OH, and CH3COCH3 are different with each other. This can be attributed to the difference in the catalytic promotion of gas sensing reaction. The above illustrates the possibility of controlling the sensor responses to various gases and artificial olfaction using sensor arrays and pattern recognition.

The dynamic response transients of S-007, S-007-Pd, S-007-Ag, and S-007-Ru upon exposure to 200 ppm C2H5OH are shown in Fig. 8 and the t90%(air-to-gas) and t90%(gas-to-air) values to CO, C2H5OH, and CH3COCH3 are summarized in Fig. 9. The t90%(air-to-gas) values were as short as 1–3 s (Fig. 9). This indicates that both the diffusion of the reducing gases onto the sensing surface and the subsequent oxidation reaction occur rapidly, probably due to the less agglomerated network structures of the SnO2 NWs. However, the t90%(gas-to-air) values of the S-007 sensor ranged from 372 to 585 s (Fig. 9). These significantly longer recovery times indicate that the series of reactions (consisting of (1) the diffusion of the oxygen gas onto the sensor surface, (2) the dissociation of the oxygen molecules into oxygen atoms, and (3) the formation of negatively charged surface oxygen) are relatively slow. Considering the very short t90%(air-to-gas) values of 1–3 s, the gas diffusion step is unlikely to be significantly contributing to the slow recovery process.
Among the series of reactions, the surface reactions (2) and (3) seem to be rate determining. The doping with 100 ppm Pd, Ag, or Ru decreased the $t_{90\%\text{ethanol-to-air}}$ values down to 87, 161, 300 s, respectively (Figs. 8 and 9(c)). In addition, the recovery times from the exposure to CO, C$_2$H$_5$OH, and CH$_3$COCH$_3$ were also shortened significantly by the doping with Pd, Ag, or Ru (Fig. 9(a), (b), (d)).

It has been reported that doping WO$_3$ thin films with Pd, Pt, or Au [17,18] and SnO$_2$ thin films with Pd [19] shortens the recovery times significantly. Recently, Helwig et al. [20] measured the intrinsic gas response and recovery time using a so-called ‘moving gas outlet technique’, and suggested that the activation energy for adsorption and desorption on the SnO$_2$ film are lowered by doping the film with a Pt catalyst. With this in mind, the shortening of the recovery time in the present study can be attributed to the effect of the catalytic activation. Note that the $t_{90\%\text{gas-to-air}}$ values are significantly shortened by the catalyst in the order of Pd, Ag, and Ru. This indicates that oxidation catalysts, such as Pd and Ag, are more advantageous for recovering the surface with an adsorbed oxygen layer.

4. Conclusion

Polycrystalline SnO$_2$ nanowires (NWs) were prepared by a polyol-mediated reaction and subsequent heat treatment. The NWs tended to become thicker and shorter upon increasing the SnC$_2$O$_4$ concentration or the addition of nucleating agents, such as PdCl$_3$, AgNO$_3$, and RuCl$_3$·H$_2$O. This is thought to be due to the promotion of the self-assembly reaction between the polymerized tin glycolate chains rather than the anisotropic polymerization of the Sn-precursor materials. The addition of nucleating agents, such as Pd, Ag, and Ru, changed the gas response ($R_a/R_g$) values and shortened the recovery times significantly. This suggests that the Pd, Ag, and Ru play dual roles; they act as nucleating agents and as catalysts. By varying the SnC$_2$O$_4$ concentration and catalyst materials,
the polyol-mediated preparation of SnO$_2$ NWs allows the gas sensitivity, the detectable gas types, and the response time of a gas sensor to be tailored.

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References


Biographies

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