Enhanced Gas Sensing Properties of Pt-Loaded TeO₂ Nanorods

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The NO₂ gas sensing properties of multiple-networked, Pt-loaded TeO₂ nanorod sensors were examined. Scanning electron microscopy revealed nanowires with diameters of 50-100 nm and lengths of a few micrometers. Transmission electron microscopy and X-ray diffraction showed that the nanorods were tetragonal-structured, single crystal TeO₂. The Pt-loaded TeO₂ nanorod sensors exhibited sensitivities of 11.00, 10.26, 11.23 and 11.97% at NO₂ concentrations of 10, 50, 100 and 200 ppm, respectively, at 300 °C. These sensitivities were more than 10 times higher than those of bare-TeO₂ nanorod sensors. The response times of the sensors were 310, 260, 270 and 230 sec at NO₂ concentrations of 10, 50, 100 and 200 ppm, respectively. The recovery times of the Pt-loaded TeO₂ nanorods were 390, 330, 335, and 330 sec at NO₂ concentrations of 10, 50, 100 and 200 ppm, respectively. The origin of the enhanced sensing properties of the TeO₂ nanorods by Pt loading is discussed.

Key Words : Nanorods, TeO₂, Pt-doping, Gas sensor, NO₂

Introduction

One-dimensional (1D) nanostructure-based metal oxide sensors have attracted considerable attention because of their higher sensitivity, superior spatial resolution and rapid response due to the high surface-to-volume ratios than thin film-type gas sensors.¹⁻⁵ On the other hand, they have several problems to overcome, such as a lack of sensitivity and very low sensitivity to low gas concentrations at room temperature. The development of highly selective and controllably-sensitized devices remains a challenge.

Tellurium dioxide (TeO₂) is an attractive semiconductor oxide material with unique physical and chemical properties suitable for a wide range of technological applications, such as deflectors,¹ modulators,² dosimeters,³⁻⁴ optical storage material,⁵ laser devices⁶ and gas sensors.⁷⁻⁸ TeO₂ nanorods have been synthesized by the thermal evaporation of Te powders,⁹ laser ablation of Te,¹⁰ and direct thermal oxidation of Te at ambient pressure in a flow of O₂ without the presence of a catalyst.¹¹ Microcrystals of TeO₂ have been synthesized by the hydrolysis of tellurium isopropoxide in the presence of a tetra alkyl ammonium bromide solution.¹¹

Regarding TeO₂ nanostructure sensors, the gas sensing properties of the TeO₂ nanowires synthesized by the thermal evaporation of Te metal in air were reported for the first time.¹² Their report demonstrated the possibility of making low power consumption gas sensors sensitive to toxic gases, such as NO₂, NH₃ and H₂S using TeO₂ nanowires. Several techniques have been developed to enhance the sensitivity, selectivity, or lower the operational temperature of 1D nanostructure sensors. These include surface functionalization,¹³⁻¹⁵ doping,¹⁶⁻¹⁸ and heterostructure formation.¹⁹⁻²¹ On the other hand, there are few reports on the application of these techniques to TeO₂ 1D nanostructure sensors. This study examined the effect of Pt-doping on the NO₂ gas sensing properties of networked TeO₂ nanorods.

Experimental

TeO₂ nanorods were synthesized on p-type Si (100) substrates in a quartz tube furnace by the thermal evaporation of Te powders at 400 °C in air without the use of metal catalysts. Thermal evaporation was carried out for 1 h and the furnace was cooled to room temperature. The weight of the TeO₂ nanorods dispersed on a substrate was approximately 0.5 mg and the area of the sensing element was 7 mm × 10 mm. For platinum doping, a 40-μL ethanol solution of platinic chloride (H₂PtCl₆·H₂O) at a concentration of 1.25 × 10⁻³ mol/L was poured onto the TeO₂ nanorod sensors. After annealing at 350 °C for 30 min under a flow of Ar gas (100 standard cubic centimeters per min (sccm)), two different types of gas sensors were fabricated: undoped and 2 wt% Pt-loaded TeO₂ nanorod sensors. The Pt concentration in the Pt-doped sensors was estimated by calculating the weight ratio of Pt in the ethanol solution of platinic chloride to the TeO₂ nanorods. The collected nanorod samples were characterized by scanning electron microscopy (SEM, Hitachi S-4200) equipped with an energy dispersive X-ray spectrometer (EDXS), transmission electron microscopy (TEM, Philips CM-200) and X-ray diffraction (XRD, Philips X’pert MRD diffractometer).

For the sensing measurements, Ni (~200 nm in thickness) and Au (~50 nm) thin films were deposited sequentially by sputtering to form electrodes with ohmic contact using an interdigital electrode mask. Figure 1 shows a schematic diagram of the multiple-networked TeO₂ nanorod sensors. The electrical and gas sensing properties of the bare and Pt-loaded TeO₂ nanorods were measured at room temperature.
using a home-made gas sensing measurement system. During the measurements, the nanorod gas sensors were placed in a sealed quartz tube with an electrical feed through. A given amount of NO$_2$ (> 99.99%) gas was injected into the testing tube through a microsyringe to obtain the given NO$_2$ concentration and the electrical resistance of the nanowires was monitored at the same time. The sensitivity of the p-type TeO$_2$ nanorod sensors was defined as $\frac{R_a - R_g}{R_g}$ for oxidizing gas NO$_2$, where $R_a$ and $R_g$ are the electrical resistances of the sensors in air and target gas, respectively. The response time is defined as the time needed for the change in electrical resistance to reach 90% of the equilibrium value after injecting the gas. The recovery time is defined as the time needed for the sensor to return to 90% above the original resistance in air after removing the gas.

Results and Discussion

Figure 2(a) shows FESEM images of the Pt-loaded TeO$_2$ nanorods prepared by the thermal evaporation of Te powders in air followed by Pt loading. Scanning electron microscopy revealed Pt-loaded TeO$_2$ nanorods with diameters of a few hundreds of nanometers and lengths of a few tens of micrometers. An enlarged SEM image (Fig. 2(b)) showed that the some of the Pt into the nanorods had precipitated as particles on the surface of the TeO$_2$ nanorods during the annealing process. Therefore, it might be a more appropriate to say that the surfaces of the TeO$_2$ nanorods are functionalized with Pt and the nanorods are loaded with Pt. EDX analysis of the nanorod (Fig. 2(c)) provided some evidence of Pt loading of TeO$_2$ nanorods.

Figure 3 shows a XRD pattern of the as-synthesized Pt-loaded TeO$_2$ nanorods. The main diffraction peaks in the pattern of the as-synthesized nanorods (Fig. 3) were indexed to a tetragonal structured, single crystal TeO$_2$, indicating that the nanomaterial is TeO$_2$. In addition to the reflections from TeO$_2$, two small sharp reflection peaks from Pt were identified. The low-magnification TEM image shows a typical Pt-loaded TeO$_2$ nanorod with a thickness of approximately 120 nm (Fig. 4(a)). Pt particles were distributed randomly over

Figure 2. (a) SEM image of the Pt-loaded TeO$_2$ nanorods, Inset, enlarged SEM image of a typical TeO$_2$ nanowires. (b) Enlarged SEM image and (c) EDX spectrum of Pt-loaded TeO$_2$ nanorods.

Figure 3. XRD pattern of the Pt-loaded TeO$_2$ nanorods.
the surface of the TeO$_2$ nanorod. The HRTEM image of the interfacial region of the Pt-particle and TeO$_2$ nanorod (Fig. 4(b)) revealed a Pt particle size of approximately 20 nm. The resolved spacing between the two neighboring parallel fringes in the particle and nanorod were approximately 0.22 and 0.24 nm, respectively, which are in good agreement with the interplanar spacings of the (111) plane of face-centered cubic-structured Pt (JCPDS No. 01-1190, $a = 0.3912$ nm) and the (200) plane of simple tetragonal-structured TeO$_2$ (JCPDS No. 78-1713, $a = 0.481$ nm and $c = 0.7613$ nm), respectively. The corresponding selected area electron diffraction (SAED) patterns recorded perpendicular to the long axis (Fig. 4(c)) that were indexed to the [201] zone axis of TeO$_2$. Two sets of spotty diffraction patterns were observed: a set of strong reflection spots and another set of dim ones. The strong reflection spots in the corre-

Figure 4. (a) Low-magnification TEM image of a typical Pt-loaded TeO$_2$ nanorod and (b) HRTEM image of a typical Pt-loaded TeO$_2$ nanorod at the TeO$_2$-Pt interface region. (c) corresponding SAED pattern.

Figure 5. (a) Dynamic responses of the bare- and Pt-loaded TeO$_2$ nanorod sensors to NO$_2$ gas at 300 °C. (b) Enlarged part of the dynamic response of the bare-TeO$_2$ nanorod sensor in (a) at a NO$_2$ gas concentration of 200 ppm. (c) Enlarged part of the dynamic response of the Pt-loaded TeO$_2$ nanorod sensor in (a) at a NO$_2$ gas concentration of 200 ppm.
Table 1. Relative sensitivity measured at different NO₂ concentrations, for bare and Pt-loaded TeO₂ nanorod sensors

<table>
<thead>
<tr>
<th>NO₂ Conc.</th>
<th>Sensitivity (%)</th>
<th>Response time (sec)</th>
<th>Recovery time (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200 ppm</td>
<td>Bare-TeO₂ 0.92</td>
<td>Pt-TeO₂ 11.97</td>
<td>Bare-TeO₂ 170</td>
</tr>
<tr>
<td>100 ppm</td>
<td>Bare-TeO₂ 0.92</td>
<td>Pt-TeO₂ 11.23</td>
<td>Bare-TeO₂ 185</td>
</tr>
<tr>
<td>50 ppm</td>
<td>Bare-TeO₂ 0.90</td>
<td>Pt-TeO₂ 11.12</td>
<td>Bare-TeO₂ 200</td>
</tr>
<tr>
<td>10 ppm</td>
<td>Bare-TeO₂ 0.88</td>
<td>Pt-TeO₂ 11.00</td>
<td>Bare-TeO₂ 200</td>
</tr>
</tbody>
</table>

The holes combine with the electrons released from the surface reaction on the material, resulting in a decrease in electrical resistance. In the case of Pt-loaded TeO₂ nanorods, the adsorption of NO₂ gas and the formation of free holes by NO₂ gas were enhanced on the Pt nanoparticle surface because of the following two reasons:

(1) The TeO₂ nanorod surface is enriched with chemisorbed oxygen species due to the presence of the Pt clusters and the NO₂ gas is spilt over the TeO₂ nanorod surface by the Pt nanoparticles, so that one observes the enhanced sensing effect.

(2) As indicated by SEM (Fig. 2(b)) and TEM (Fig. 3(a)), the Pt nanoparticles have a larger surface to volume ratio than the TeO₂ nanorods owing to their particle-like shape and very irregular surface morphology as well as the high catalytic or conductive nature of Pt, which can lead to the enhanced adsorption of NO₂ gas. NO₂ molecules dissociate on catalytic Pt particles and then diffuse to the substrate, probably across and/or through the particles, where NO₂ molecules can interact with semiconducting TeO₂ nanorods to increase the conductance. Therefore, NO₂ molecules dissociate and generate chemisorbed oxygen species much more rapidly due to the enhanced interaction by Pt.

Consequently, the number of holes released from the gas species increases. In short, combination of the spillover effect and the enhancement of chemisorption and dissociation of gas enhances the electrical response of the Pt-loaded TeO₂ nanorod sensor to NO₂ gas.

Conclusions

Multiple-networked Pt-loaded TeO₂ nanorod sensors exhibited sensitivities more than 10 times higher than those of bare-TeO₂ nanorod sensors. The response and recovery times of Pt-loaded TeO₂ nanorods were somewhat longer than those of bare-TeO₂ nanorods, but less than 7 min. These results are comparable to the NO₂ gas sensing data of other material sensors reported. The TeO₂ nanorod surface is enriched with chemisorbed oxygen species due to the presence of the Pt clusters and the NO₂ gas is spilt over the TeO₂ nanorod surface by the Pt nanoparticles, so that one observes the enhanced sensing effect. Another possible explanation is that the Pt nanoparticles have a larger surface to volume ratio than the TeO₂ nanorods owing to their
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particle-like shape and very irregular surface morphology as well as the high catalytic or conductive nature of Pt, which can lead to the enhanced adsorption of NO\textsubscript{2} gas. NO\textsubscript{2} molecules dissociate on catalytic Pt particles and then diffuse to the substrate, probably across and/or through the particles, where NO\textsubscript{2} molecules can interact with semiconducting TeO\textsubscript{2} nanorods to increase the conductance. Therefore, NO\textsubscript{2} molecules dissociate and generate chemisorbed oxygen species much more rapidly due to the enhanced interaction by Pt. In short, the enhanced chemisorption of NO\textsubscript{2} gas molecules and the formation of holes by them enhances the electrical response of the Pt-loaded TeO\textsubscript{2} nanorod sensor to NO\textsubscript{2} gas.

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References