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Effects of Additives on the DMMP Sensing Behavior of SnO_2 Nanoparticles Synthesized by Hydrothermal Method

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Abstract

SnO_2 nanoparticles were synthesized by a hydrothermal method and gas sensors were fabricated using nanoparticles to detect dimethyl methylphosphonate(DMMP) gas. The prepared SnO_2 nanoparticles exhibited a high response(72 at 500 °C) to 5 ppm DMMP gas compared to commercial SnO_2 nanopowders, but their recovery was relatively poor. Various metals(Ni, Sb, Nb) were added to the SnO_2 nanoparticles to improve their recovery properties. The focus of this study was to investigate the effects of metal oxide additives on DMMP sensing behavior in SnO_2 nanoparticles.

Keywords : SnO_2, Sensor, DMMP, Recovery, Additive

1. INTRODUCTION

Among the various kinds of oxide semiconductor materials for gas sensors, SnO_2 has attracted much attention for its ability to detect hydrogen gas and other environmental gases such as CO, H_2S, NOx, and VOCs[1-6]. Recently, semiconductor metal oxides including SnO_2 and WO_3 have also been used in detection of chemical warfare agents(CWAs) or simulant gases[7, 8]. There are many well-known organophosphorus(OP) compounds such as tabun(GA), distilled mustard(HD), sarin(GB). Sarin is a representative nerve agent and Dimethyl methylphosphonate(DMMP) can be used as a good substitute for sarin gas because it has a similar functional group to sarin. To date, much research on the detection of DMMP have been published[9-11].

Semiconductor metal oxide gas sensors for detecting DMMP simulant gas have many advantages, such as their cost, small size, and high sensitivity, when compared to other type sensors including quartz crystal micro-balance(QCM)[12, 13], microcantilever(MCL)[14, 15], surface acoustic wave(SAW)[16, 17]. However, semiconductor metal oxide sensors for DMMP exhibit a poisoning effect due to the irreversible reaction between surface atoms of the metal oxides and phosphorus atom of the DMMP molecules[18, 19]. To solve this problem, various metal oxides have been added to the SnO_2 particles[20, 21].

In this study, we synthesized crystalline SnO_2 nanoparticles using a simple hydrothermal method. The prepared SnO_2 nanoparticles exhibited a high response to DMMP gas compared to commercial SnO_2 nanopowders, but response time was very slow and their recovery was poor. To compensate for this poor recovery, the SnO_2 nanoparticles were doped with various metals(M: Ni, Sb, Nb) and their DMMP sensing behaviors were investigated.

2. EXPERIMENTAL

2.1 Preparation of SnO_2 nanoparticles with additives

SnO_2 nanoparticles and M (M: Ni, Sb, Nb)-doped SnO_2 nanoparticles were synthesized using a hydrothermal method. 3.47 g of tin chloride pentahydrate($SnCl_4 \cdot 5H_2O$, GR, Kanto Chemical Co., Inc., Japan) was first dissolved in 10 mL distilled water, and the solution was mixed with 1 M of ammonium bicarbonate(NH_4HCO_3, ≥ 95 %, Junsei Chemical Co., Ltd., Japan) aqueous solution under vigorous magnetic stirring. The resulting white precipitates were washed by centrifuge 5 times with distilled water. The precipitates were dispersed in 55 mL ammonia solution(pH 10.5) and transferred to Teflon-lined

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autoclaves and hydrothermally treated at 200 °C for 3 h. This hydrothermal treatment resulted in a clear and homogeneous SnO_2 sol. In addition, 5 wt% of nickel (II) chloride hexahydrate($NiCl_2 \cdot 6H_2O$, 98 %, Kanto Chemical Co., Inc., Japan), antimony(III) chloride($SbCl_3$, cica-reagent, Kanto Chemical Co., Inc., Japan), and niobium (V) chloride($NbCl_5$, 99 %, Sigma-Aldrich Co., Germany) was mixed with the prepared SnO_2 sol to obtain Ni-, Sb-, and Nb-doped SnO_2 nanoparticles, respectively. After heat-treatment at 600 °C for 1 h, each sol was transformed into undoped-, Ni-, Sb-, and Nb-doped SnO_2 nanoparticles, respectively.

2.2. Characterization of SnO_2 nanoparticles with additives

The prepared SnO_2 nanoparticles were examined by X-ray diffraction(XRD, D8- Advance, BRUKER MILLER Co.) for phase identification and field emission scanning electron microscopy(SEM, JSM-7401F, JEOL) for morphology. The added elements and their chemical states were confirmed by XPS analysis(AXIS-His, KRATOS).

2.3. Measurements of DMMP sensing performance

To prepare the gas sensors, SiO_2/Si wafers were used as substrates and they were cleaned successively with acetone, ethanol, and deionized water. Platinum interdigitated electrodes were deposited on the cleaned SiO_2/Si substrates, and they were annealed at 600 °C for 1 h. SnO_2 nanoparticles were deposited on the platinum interdigitated SiO_2/Si substrates by dropping the prepared SnO_2 sols on the surface. After drying, the SnO_2 nanoparticle sensors were annealed at 600 °C for 1 h.

The SnO_2 nanoparticle sensors were loaded into a quartz tube located in an electrical furnace to investigate their gas sensing properties. Au lead wires were attached to the platinum electrode pairs using silver paste in order to measure the resistance of the SnO_2 nanoparticle films. The resistance of the sensing films was recorded using a Keithley Multimeter 2002.

For measuring their DMMP sensing properties, DMMP vapor was prepared using the bubbling method. Liquid DMMP was kept in a canister at 30 °C, and dry air gas was passed through the canister. Vapor concentrations were calculated using the Antoine Equation, and the concentrated DMMP vapor was diluted by additional air to obtain a 5 ppm DMMP gas/air mixture. The DMMP vapor and dry air gases were alternatively injected into the gas sensors. The DMMP sensing performance of the synthesized SnO_2 nanoparticles and the M (M: Ni, Sb, Nb)-doped SnO_2 nanoparticles were examined at various operating temperatures for 5 ppm DMMP gas. The DMMP response was defined as the ratio of the resistance in air(R_{air}) to that in the target gas(R_{gas}). In addition, the DMMP sensing behavior of commercial SnO_2 nanopowders was also measured for comparison with that of the synthesized SnO_2 nanoparticles.

3. RESULTS AND DISCUSSION

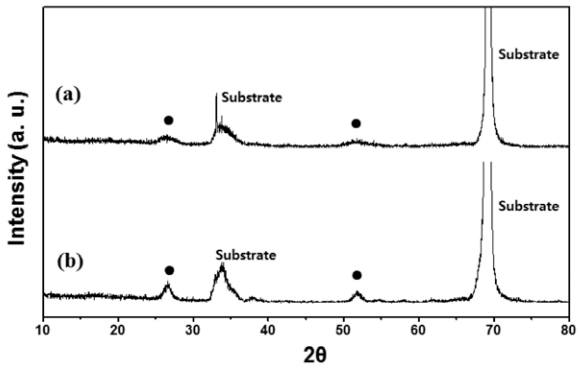

Fig. 1. XRD patterns of synthesized SnO_2 nanoparticles (a) as-prepared (b) after annealing at 600 °C.

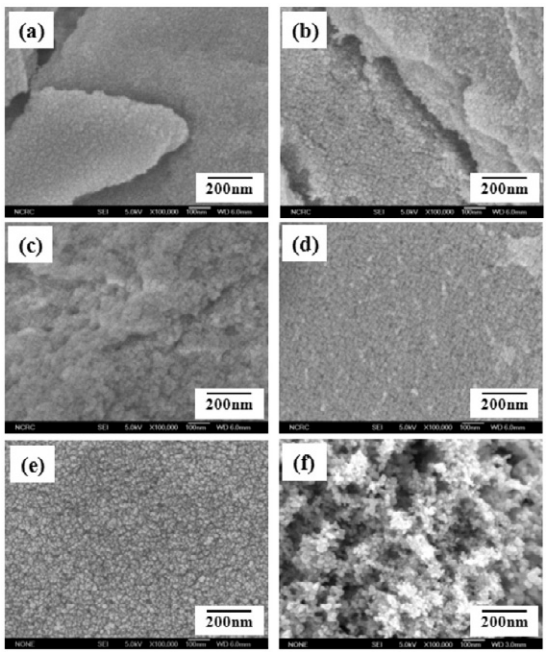

Fig. 2. SEM images of undoped SnO_2 nanoparticles (a) as-prepared (b) after annealing at 600 °C, (c) Ni- (d) Sb- (e) Nb-doped SnO_2 nanoparticles, and (f) commercial SnO_2 nanopowder.

3.1 Characteristics of SnO_2 nanoparticles

X-ray diffraction patterns of the prepared SnO_2 nanoparticles are shown in Fig. 1. Two peaks, ignoring the substrate peaks, were indexed to the SnO_2 cassiterite phase and the intensitiy of these peaks increased after annealing at 600 °C for 1 h. The prepared SnO_2 nanoparticles and M (M: Ni, Sb, Nb)-doped SnO_2 nanoparticles were loaded onto a SiO_2/Si substrate for observation of their morphology by SEM(Fig. 2(a)-(e)). The primary particle size of the as-prepared SnO_2 nanoparticles was about 10 nm, and they were shown to be agglomerated and densely packed. The samples' morphology was maintained even after annealing treatment at 600 °C for 1 h, and no significant grain growth was observed. The morphologies of the M (M: Ni, Sb, Nb)-doped SnO_2 nanoparticles were also observed by SEM. No change of morphology and particle size was found. Commercial SnO_2 nanopowders were also analyzed by SEM, and it was found that several tens of a nanometer sized primary particles were agglomerated (Fig. 2(f)).

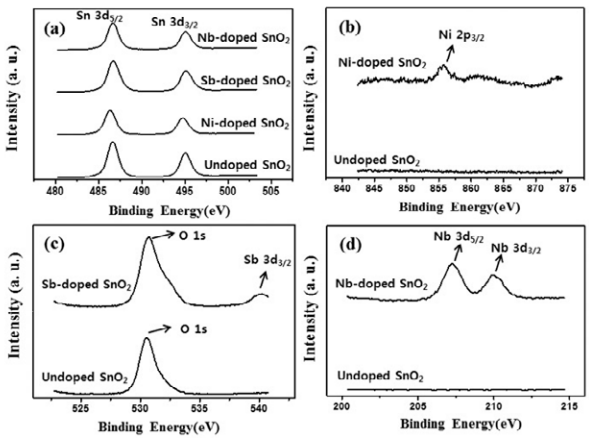

Fig. 3. Core level XPS spectra of SnO_2 nanoparticles (a) Sn3d, (b) Ni2p, (c) Sb3d, and Nb3d.

The presence of the doped elements and their chemical states were investigated using XPS analysis. Fig. 3 shows the XPS profiles of the undoped SnO_2 nanoparticles, Ni-, Sb-, and Nb-doped SnO_2 nanoparticles. The expected peaks for the added elements were observed in all M (M: Ni, Sb, Nb)-doped SnO_2 nanoparticle samples. The chemical states of each added element were identified by the position of their binding energy. A Sn 3d doublet feature at 486.7 and 495.0 eV was observed in all specimens except the Ni-doped SnO_2 nanoparticles, and the main peak(486.7 eV) corresponds well with $3d_{5/2}$(486.6 eV) of SnO_2. The Sn 3d doublet feature of the Ni-doped SnO_2 nanoparticles was observed at 486.3 and 494.8 eV, and the main peak was slightly shifted to a lower energy closer to that of SnO (485.9 eV)[22]. A single peak at 855.7 eV was observed in the Ni-doped SnO_2 nanoparticles, and this is closer to Ni $2p_{3/2}$(855.8 eV) of Ni_2O_3 than Ni $2p_{3/2}$(854.5 eV) of NiO[23]. A single peak at 540.2 eV was observed in the Sb-doped SnO_2 nanoparticles and the doublet peaks at 207.3 eV and 210.0 eV observed in the Nb-doped SnO_2 nanoparticles were similar to those previously reported Sb $3d_{3/2}$(540.4 eV) of Sb_2O_5 and Nb $3d_{5/2}$, $3d_{3/2}$(207.3 eV, 210.1 eV) of Sb_2O_5[24, 25]. Based on this XPS analysis, it was confirmed that the doped metal elements were transformed into their respective metal oxides Ni_2O_3, Sb_2O_5, and Sb_2O_5.

3.2. DMMP sensing performance

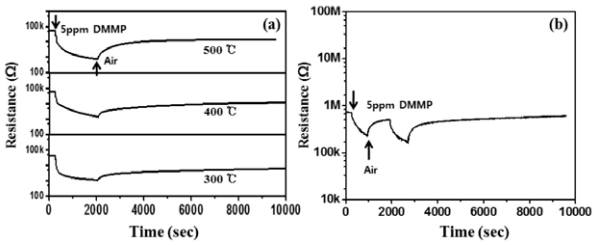

Fig. 4. Response profiles of (a) SnO_2 nanoparticles at 300~500 °C and (b) commercial SnO_2 nanopowder at 400 °C toward 5 ppm DMMP gas.

The response behavior of the SnO_2 nanoparticles measured at 300 °C ~500 °C for 5 ppm DMMP gas is shown in Fig. 4(a). The resistance of the sensor specimens was drastically decreased by injecting DMMP gas, and continuously decreased for 30 min before the switch to pure air gas. SnO_2 nanoparticles synthesized by the hydrothermal method exhibited a high response (39, 42, 72 at 300 °C, 400 °C, 500 °C, respectively) for 5 ppm DMMP gas, whereas the commercial SnO_2 nanopowders exhibited a relatively low response(3.1 at 400 °C)(Fig. 4(b)). The high response of the synthesized SnO_2 nanoparticles can be attributed to the higher surface area of these nanoparticles. However, the synthesized SnO_2 nanoparticles showed a very long response time, so that the resistance of the SnO_2 nanoparticles did not become saturated during the 30 min DMMP injection time at all operating temperatures. Also, only very small portions of

the decreased resistance were recovered after switching to pure air gas at all operating temperatures. This incomplete resistance recovery behavior, or so called poisoning effect, is attributed to the irreversible interaction between the metal oxide and P=O bonding of the DMMP molecules[19].

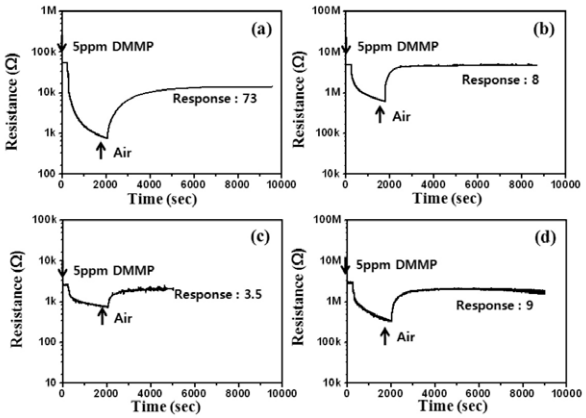

Fig. 5. Response profiles of (a) undoped SnO_2 nanoparticles and (b) Ni- (c) Sb- (d) Nb-doped SnO_2 nanoparticles toward 5 ppm DMMP gas at 500 °C.

Fig. 5 shows the DMMP response behaviors of the undoped SnO_2 nanoparticles and Ni-, Sb-, Nb-doped SnO_2 nanoparticles. The ratio of additives was fixed to 5 wt% based on the previous report in all samples[20]. The addition of additives decreased the magnitude of the gas response, but the recovery behavior was significantly improved. In particular, the Ni-doped SnO_2 nanoparticle sensor showed complete recovery. According to previous reports[19, 26], the decomposition of the DMMP molecules occurs at active sites which exist on the surface of the catalyst materials. However, the irreversible interaction between the surface of the metal oxides and DMMP molecules causes the loss of these active sites, resulting in deactivation of the catalyst materials. Similarly, the DMMP sensing mechanism of the SnO_2 nanoparticles is based on the interaction between surface of the SnO_2 nanoparticles and DMMP molecules. The active site interaction causes the resistance change of the sensing material, but the resistance is not fully recovered because of the poisoning of these active sites. It is speculated that the presence of additives decreases the active sites at the surface of the SnO_2 nanoparticles, which results in a decrease of the DMMP sensing signal, but at the same time greatly improving the recovery behavior by reducing the poisoning effect.

4. CONCLUSION

10 nm-sized SnO_2 nanoparticles were successfully synthesized by a hydrothermal method, and their DMMP sensing performance was examined. The prepared SnO_2 nanoparticles exhibited a higher response(72 at 500 °C) toward 5 ppm DMMP gas than commercial SnO_2 nanopowders, but their resistance was not fully recovered even after injecting pure air gas. For the improvement of their recovery properties, the synthesized SnO_2 nanoparticles were doped with three kinds of metals(M: Ni, Sb, Nb), each with a doping concentration of 5 wt%. These additives affected the response and recovery performance of the SnO_2 nanoparticles similarly for DMMP gas. Especially, Ni-doped SnO_2 nanoparticles exhibited the greatest improvement in recovery.

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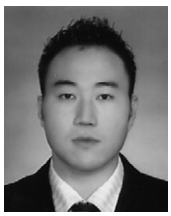

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