Response speed of SnO₂-based H₂S gas sensors with CuO nanoparticles

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The importance of copper oxide (CuO) catalyst and its dispersal in semiconducting tin oxide (SnO₂) is gaining a lot of importance for trace level detection of hydrogen sulfide (H₂S). Maekawa et al., first reported the enhanced sensitivity of SnO₂ with CuO dopant for H₂S gas detection. Subsequently, several studies based on the CuO-SnO₂ system have been reported using thick sintered pastes, Cu/SnO₂ bilayers, CuO-SnO₂ heterocontacts, and chemically fixed CuO on spin-coated SnO₂ films. In general, the response speeds of the investigated material systems have been slow, and in instances where a high sensitivity has been reported, the response speed is often found to be slow (2–175 min). A fast response time (15 to 180 s) has been observed mostly at a higher H₂S concentration, and a slow recovery time has been commonly observed.

In our earlier published work, we reported a significant improvement in the sensor response speed using a structure consisting of uniformly distributed CuO clusters on the SnO₂ film surface, as shown in Fig. 1. In this initial experiment, although the distribution and dimension of the CuO clusters (0.6 mm diam and 10 nm thick) were very coarse, a high sensitivity (~7 × 10³) and a fast response speed (14 s) were observed, but the recovery time of the sensor was slow (~8 min). CuO and SnO₂₋ₓ, which are p- and n-type semiconductors, respectively, have a strong electronic interaction. A vital contribution due to spillover mechanism besides the Fermi level type of interaction was identified with the use of CuO clusters, as shown in Fig. 1. The modulation of the depletion region at the interface due to the conversion of CuO to CuS in the presence of H₂S gas, and the spillover effect of H₂ from the dissociated H₂S onto the uncovered SnO₂, were made possible by the distribution of CuO clusters on the SnO₂ surface. A Secondary ion mass spectroscopy study carried out on an annealed SnO₂ layer loaded with CuO catalyst indicated the presence of a strong Cu concentration on the surface and a small amount in the SnO₂ film bulk as a result of diffusion. In this letter, we report further improvements by optimizing the thickness of the CuO clusters, and a significant reduction in the recovery time is observed with CuO nanoparticles.

SnO₂ films (90 nm) were deposited by a rf reactive sputtering process on borosilicate glass substrates, and platinum (Pt) interdigital electrodes underneath the SnO₂ film were used to measure the change in the electrical conductivity. The sample preparation details are described elsewhere. A mixed SnO₂-CuO composite layer was obtained by oxidizing a sputtered Sn-Cu alloy film, and a CuO-SnO₂ bilayer was formed, by post-annealing in air at 300 °C a thin Cu layer deposited onto SnO₂. The CuO clusters on SnO₂ were obtained by evaporating Cu through a mesh and post-oxidation, as in the previous case. Finally, Cu nanoparticles were chemically derived using a reverse-nanoparticle method involving the reduction of Cu(NO₃)₂ by NaBH₄. The Cu nanoparticles were dispersed in distilled water, and after brief sonication, the nanoparticles were loaded onto the sputtered SnO₂ film. Annealing at 300 °C in air evaporated the water and converted the Cu nanoparticles to CuO. Sensitivity characteristics were measured in the temperature range from 60 to 250 °C. At each temperature, the sensor was stabilized in air to a steady resistance value (Rₐ), and the reduction in

![Depletion region due to adsorbed oxygen](link) Spilled-over hydrogen to adsorbed oxygen

FIG. 1. Schematic showing interaction of H₂S gas with the SnO₂ sensor dotted with CuO clusters.

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Byrd Johnson

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the sensor resistance ($R_s$) in the presence of H$_2$S (20 ppm) was recorded. The sensitivity factor ($S$) is defined as $S = R_a/R_s$, and the response speed was studied at the temperature at which the sensor exhibited a maximum sensitivity.

Figure 2 compares sensitivity and the response speed characteristics for trace level (20 ppm) H$_2$S gas detection for the first four sensors: simple SnO$_2$ film, mixed SnO$_2$-CuO composite layer, CuO/SnO$_2$ continuous bilayer, and evaporated CuO clusters on the SnO$_2$ structure. The SnO$_2$ film sensor with CuO clusters (0.6 mm diam and 10 nm thick) exhibited a high sensitivity of $7.3 \times 10^3$ at a low operating temperature of 150 °C, and a fast response speed of 14 s.

In view of the enhanced sensitivity of the SnO$_2$ film with CuO clusters, the effect of CuO cluster thickness in the range from 2.5 to 20 nm was studied in detail, while maintaining a constant diameter (0.6 mm). A maximum sensitivity was observed with 8-nm-thick CuO clusters, as shown in Fig. 3. To further understand this result, the variation in the resistance values of the sensor $R_a$ (in air) and $R_g$ in the presence of H$_2$S as a function of temperature and CuO thickness was studied. An increasing CuO cluster thickness exhibited increasing values of $R_a$ [Fig. 4(a)] in the entire temperature range (60 to 250 °C). This is attributed to the increased penetration of the depletion region into the SnO$_2$ layer at the CuO/SnO$_2$ interface (Fig. 1) and effectively decreases the cross-sectional area of the conducting channel available for the charge carriers in the SnO$_2$ film.

The change in resistance $R_a$ with temperature [Fig. 4(a)] exhibited a characteristic plateau region at higher values of CuO thickness (>8 nm), and pointed towards the enhanced catalytic activity of CuO for the adsorption of oxygen in the temperature range from 130 to 160 °C. Activity for enhanced oxygen adsorption is known to be high for CuO catalyst at $(T > 130 °C)$.[5] In contrast, the variation in resistance $R_g$ exhibited a minimum at 150 °C, for all values of CuO thickness [Fig. 4(b)], and surprisingly, the lowest $R_g$ value was observed for the 8-nm-thick CuO catalyst clusters. A decrease in $R_g$ (in the presence of H$_2$S gas) depends mainly on two factors: (i) conversion of CuO to CuS and (ii) the spillover of hydrogen dissociated from the H$_2$S gas molecule, which further removes the adsorbed oxygen from the uncovered SnO$_2$ surface. At a higher thickness of CuO (>8 nm), a complete conversion of CuO to CuS does not seem to occur with 20 ppm of H$_2$S, and the modulation in the depletion region is limited, resulting in a relatively higher value of $R_g$ [Fig. 4(b)]. With CuO thickness (<10 nm) in the range from 2.5 to 8 nm, there is probably a complete conversion of CuO to CuS. Specifically at a thickness of 8 nm, there is a maximum contribution from the spillover of dissociated hydrogen, yielding the lowest value of $R_g$. However, with 2.5- to 5-nm-thick CuO, the spillover effect is inadequate due to the limited CuO island thickness. A comparison of the response characteristics in Table I show that the response speed improves with decreasing thickness of the CuO dotted islands, but the sensitivity and the recovery time exhibit a competing effect. Although an optimum thickness of 8 nm of CuO catalyst exhibited the highest sensitivity, the improvements in the response speed (12 s) and recovery time (366 s) were marked.

![FIG. 2. Sensitivity and response speed variation with dispersal of the CuO catalyst.](image)

![FIG. 3. Sensitivity dependence on thickness of CuO clusters at the operating temperature.](image)

![FIG. 4. Resistance values: (a) $R_a$ variation and (b) $R_g$ variation with thickness of CuO clusters.](image)
micrometer-sized grains observed on the virgin SnO$_2$ film of an average size of 15 nm, in contrast to the elongated CuO nanoparticles as seen with an atomic force microscope.

A reverse-micellar Cu(NO$_3$)$_2$ solution, another reverse-micellar solution of NaBH$_4$ solution was added dropwise to a reverse-micellar Cu(NO$_3$)$_2$ solution, another reverse-micellar solution of NaBH$_4$ solution was added dropwise with constant stirring. In the presence of inert nitrogen, the solution was allowed to stand for 4 h, and Cu nanoparticles were extracted by adding dry acetone and centrifugation. The Cu nanoparticles were dispersed in distilled water and evenly spread onto the SnO$_2$ film surface using a micropipette. By varying the water content parameter $w_w$ (defined as the molar ratio of water to surfactant concentration $w_s = [H_2O]/[AOT]$), the size of the nanoparticle could be controlled. Figure 5 shows the surface of the SnO$_2$ film loaded with CuO nanoparticles as seen with an atomic force microscope (AFM). The nanoparticles are round in shape, with an average size of 15 nm, in contrast to the elongated micrometer-sized grains observed on the virgin SnO$_2$ film.

In summary, a SnO$_2$ sensor loaded with CuO nanoparticles exhibits a fast response speed with a high sensitivity and quick recovery time. The origin for the quick recovery is due primarily to the efficient dispersal of the CuO catalyst, and its presence in the form of nanoparticles proffers a greater surface area on the SnO$_2$ film surface. A post-deposition annealing treatment of the Cu nanoparticles (300 °C in air) was considered sufficient to transform them to CuO, and the dispersal also allowed exposure of the underlying SnO$_2$.

The response speed and the recovery characteristics of the SnO$_2$ sensor with CuO nanoparticles is shown in Fig. 6, and is compared with the earlier data obtained with the coarse distribution of large diameter (0.6 mm) CuO clusters having an optimum thickness of 8 nm. It is interesting to note that the recovery time of the sensor with CuO nanoparticles reduced to 61 s, the sensor is able to completely recover to its initial high-resistance value $R_g$ from the low value $R_a$ (after interaction with the H$_2$S gas), and the reproducibility of the sensor was good for consecutive back-to-back runs, as shown in insert of Fig. 6.

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**TABLE I. Variation in response speed and recovery times of the SnO$_2$ as a function of CuO cluster thickness.**

<table>
<thead>
<tr>
<th>CuO thickness (nm)</th>
<th>Sensitivity</th>
<th>Response time (s)</th>
<th>Recovery time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>7.3$\times$10$^3$</td>
<td>14</td>
<td>481*</td>
</tr>
<tr>
<td>2.5</td>
<td>1.2$\times$10$^3$</td>
<td>8</td>
<td>279</td>
</tr>
<tr>
<td>5</td>
<td>4.1$\times$10$^3$</td>
<td>9</td>
<td>302</td>
</tr>
<tr>
<td>8</td>
<td>8.1$\times$10$^3$</td>
<td>12</td>
<td>366</td>
</tr>
<tr>
<td>10</td>
<td>6.2$\times$10$^3$</td>
<td>18</td>
<td>347</td>
</tr>
<tr>
<td>15</td>
<td>1.1$\times$10$^3$</td>
<td>29</td>
<td>313</td>
</tr>
<tr>
<td>20</td>
<td>78.229</td>
<td>42</td>
<td>294</td>
</tr>
</tbody>
</table>

*See Ref. 6.

**FIG. 5.** AFM image of SnO$_2$ film surface loaded with CuO nanoparticles.

**FIG. 6.** Response and recovery characteristics of the SnO$_2$ sensor loaded with CuO nanoparticles and 8-nm-thick CuO clusters.