

Mechanism of the Enhanced Sensitivity of SnO₂-based Gas Sensors Modified with Surface Sulfate Species

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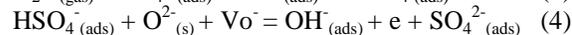
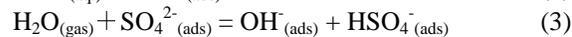
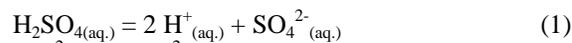
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We have developed a novel surface modification method for stannic oxide-based CO gas sensors.¹⁻⁶ This method is simply accomplished by dipping the sensor element in an aqueous solution containing a surface modifier followed by heating. For example, the sensor element consisting of sintered SnO₂-Al₂O₃ is dipped into a low concentration of sulfuric acid solution for 2 sec. and heated at 873 K for 5 min.¹ This simple treatment induces the enhancement of CO sensitivity and completely suppresses the drift of the sensor resistance in a long-term operation. When a thiourea solution is substituted for a sulfuric acid solution, the same effects are obtained.² The surface modification using a platinum group metal chloride solution also gives an advantage that the effects of ambient temperature and humidity on sensor resistance drastically are reduced.³⁻⁶ These results suggest a new concept of sensor modification: that the sensing characteristics could be drastically changed by the surface treatment of the sintered sensor element using the simple procedure, and that the use of a very small amount of modifier would be sufficient to improve the sensing properties. However, the mechanism of the surface modification has not yet been clarified. In this paper, we concentrated the surface modification mechanism by sulfuric acid and thiourea. The sensor surfaces modified with sulfuric acid or thiourea are analyzed by X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (IR). From the results, the role of surface sulfate species as a surface modifier is discussed. A possible mechanism of the surface modification with sulfate species, by which the sensor resistances in air or CO decrease and the CO sensitivity is enhanced, is proposed.

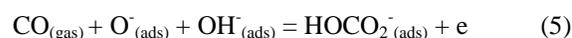
A SnO₂ powder containing 2 wt% Pd was prepared in the same manner as previously described.¹⁻⁶ The SnO₂ powder was pressed to form a disk and heated at 873 K for 5 min. The surface modification of the SnO₂ disk was carried out by dipping the disk into sulfuric acid or thiourea solutions for 2 sec. and heating at 873 K for 1 min. The modified and unmodified disks were used as samples for XPS and FTIR measurements.

XPS measurements for the samples modified with sulfuric acid revealed that surface sulfate species existed on the modified SnO₂ disk. FTIR spectra of the samples also showed the absorption peaks corresponding to surface sulfate species. Moreover, a comparison of FTIR spectra for the samples modified and unmodified with sulfuric acid indicated a significant variation in the absorption peak corresponding to surface hydroxyl groups: the absorption peak of surface hydroxyl groups

increased by the surface modification with sulfuric acid. On the other hand, the sensor resistances in air and CO are reduced by the surface modification with sulfuric acid compared to those for the unmodified sensor.^{1,7} From these results, we hypothesized the following reactions for the surface modification with sulfuric acid.



The reactions indicate that surface sulfate species produced in the surface modification process encourages the adsorption of H₂O resulting in the generation of surface hydroxyl groups, in which a negatively charged surface oxygen and an oxygen vacancy are consumed with the release of an electron to SnO₂. With the hypothesis, the sensor resistance in air would decrease by the surface modification compared to that without the modification. We also made a possible mechanism for the enhancement of CO sensitivity by the surface modification on the basis of the above reactions. The CO adsorption reaction on SnO₂ at room temperature is proposed as follows.⁸



This reaction suggests that the number of the active site for CO adsorption depends on that of the site where negatively charged oxygen species and surface hydroxyl groups are located closely. Therefore, if surface hydroxyl groups increase by the surface modification with sulfuric acid, the active site for CO adsorption is expected to increase, resulting in the enhancement in CO sensitivity. In this case, the sensor resistance in CO is reduced by the surface modification, since by the surface modification the sensor resistance in air decreases and the number of CO adsorbed on SnO₂ (and that of electrons released to SnO₂) increases.

XPS and FTIR spectra of the samples modified with thiourea also indicated the existence of surface sulfate species and the increase in surface hydroxyl groups on the modified SnO₂ surface. In addition, the surface modification with thiourea reduces the sensor resistances in air and CO, and enhances the CO sensitivity.² Therefore, the same mechanisms described above are expected for the sensor resistance change and the enhancement in CO sensitivity induced by the modification.

References

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