

# Effect of Water Vapor on the Gas Sensing Properties for Pd-Loaded SnO<sub>2</sub> Gas Sensors

楠, 馬

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氏 名：馬 楠

論 文 名：Effect of Water Vapor on the Gas Sensing Properties for Pd-Loaded SnO<sub>2</sub> Gas Sensors (Pd 担持 SnO<sub>2</sub> ガスセンサのガス検知特性における水蒸気の影響)

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## 論 文 内 容 の 要 旨

Metal oxide semiconductor gas sensors are attractive to detect inflammable and toxic gases in variety of fields based on the electric resistance change of sensing layer in air and target gas. Tin dioxide (SnO<sub>2</sub>) gas sensors have many obvious advantages such as low cost, long term stability, and high sensitivity. However, their gas sensing performance is seriously affected by the varying humidity in the ambient atmosphere, which greatly hinders their practical application. How to reduce the water vapor interfering effect on the gas sensing properties to keep high stability is the main goal in this research work. Loading noble metal Pd on the SnO<sub>2</sub> surface is one of the most effective methods to enhance the gas sensitivity and suppress the water poisoning effect. To further understand the mechanism of Pd on the sensing process in humid atmosphere is beneficial to designing high performance gas sensors. In this study, the role of Pd and its size effect on the gas sensing process was clarified in different humidity. Moreover, the sensitization effect of Pd was investigated based on SnO<sub>2</sub> MEMS gas sensors and Sb-doped SnO<sub>2</sub> thick-film sensors under humid condition.

Pd-loaded SnO<sub>2</sub> nanoparticles were prepared by loading Pd on the calcined SnO<sub>2</sub> surface. The microstructure of SnO<sub>2</sub> and Pd-loaded SnO<sub>2</sub> nanoparticles was investigated. The oxygen adsorption behavior and sensor response to H<sub>2</sub> and CO for SnO<sub>2</sub> and Pd-loaded SnO<sub>2</sub> sensors were studied in different humidity. Pd-loaded SnO<sub>2</sub> with different Pd particle sizes were prepared, and the influence of the Pd size on the gas sensing properties of Pd-loaded SnO<sub>2</sub> under dry and humid conditions was discussed combining with the TPR measurement. In addition, the Pd sensitization effect in dry and humid atmospheres was examined based on SnO<sub>2</sub> MEMS gas sensors with low power consumption and Sb-doped SnO<sub>2</sub> thick-film sensors with high stability in humid atmosphere.

Chapter 1 introduces the background of SnO<sub>2</sub> gas sensors, including the basic mechanism of semiconductor gas sensors, the methods for improving gas sensing properties, as well as the interfering effect of water vapor on the gas sensing properties. Finally, MEMS gas sensors are introduced.

Chapter 2 studied the role of Pd in the gas sensing process in humid atmosphere by investigating the oxygen adsorption behavior and sensing properties to H<sub>2</sub> and CO in the presence of water vapor. The mainly

adsorbed oxygen species on the SnO<sub>2</sub> surface in humid atmosphere was changed by loading Pd, more specifically, for neat SnO<sub>2</sub> was O<sup>-</sup> but for Pd-SnO<sub>2</sub> was O<sup>2-</sup>. The water vapor poisoning effect on the sensor response was significantly reduced by loading Pd. The TPR results indicated that Pd was existed in PdO form and O<sup>2-</sup> adsorbed on the surface. Therefore, we propose that O<sup>2-</sup> adsorption on PdO enlarged the depletion layer of the interface and prevented OH<sup>-</sup> adsorption on the SnO<sub>2</sub> surface, leading to high sensor response in humid atmosphere for Pd-loaded SnO<sub>2</sub>.

Chapter 3 focuses on the effect of Pd particle sizes on the gas sensing properties in humid atmosphere. Pd-loaded SnO<sub>2</sub> with smaller and larger Pd particle sizes were prepared. The oxygen adsorption behavior and gas sensing properties to H<sub>2</sub> and CO are investigated in dry and humid atmospheres in terms of Pd-loaded SnO<sub>2</sub> with different Pd particle size. The Pd size has no influence on the oxygen adsorption behavior, that the mainly adsorbed oxygen species was O<sup>2-</sup> in both dry and humid atmospheres for Pd-SnO<sub>2</sub>, no matter Pd in smaller or larger sizes. However, different CO sensing behavior was observed for Pd-SnO<sub>2</sub> with different Pd sizes. Pd-SnO<sub>2</sub> with smaller Pd particles was reduced in response by introducing water vapor, while Pd-SnO<sub>2</sub> with large Pd particles showed increased CO response in the presence of water vapor. It was thought that different Pd/PdO distribution states lead to the different sensitization effect to CO oxidation in humid atmosphere.

Chapter 4 investigated the Pd sensitization effect on the gas sensing performance of SnO<sub>2</sub> MEMS sensors. To achieve high sensitivity and low power consumption, MEMS sensors are fabricated by injection method using Pd-loaded SnO<sub>2</sub> nanoparticles. The gas sensing properties to H<sub>2</sub> and CO were investigated under dry and humid conditions by operating the MEMS sensors in constant heating and pulse heating modes. It was demonstrated that Pd-loading greatly enhanced the sensor response to H<sub>2</sub> and CO in low temperature. Pulse heating gave higher sensor response at low temperature in dry atmosphere, while constant heating gave higher sensor response in humid atmosphere.

Chapter 5 reported the gas sensing properties of Pd-loaded/Sb-doped SnO<sub>2</sub>. The role of Pd and its size effect on the Sb-doped SnO<sub>2</sub> sensors is examined by investigating the gas sensing properties to H<sub>2</sub> and CO in dry and humid atmosphere. Pd-loading combined with Sb-doping on SnO<sub>2</sub> greatly reduced the electric resistance and improved the sensor response and stability in humid atmosphere. The Pd size effect on the CO response was also observed in the Sb-doped SnO<sub>2</sub> gas sensor, reflecting by the decreased CO response for Sb-SnO<sub>2</sub> with smaller Pd particles and increased CO response for 0.1Sb-SnO<sub>2</sub> with larger Pd particles in the presence of water vapor.

Chapter 6 summarizes the experimental results with regard to chapter 2, 3, 4 and 5. The role of Pd as well as its size effect on the gas sensing process in humid atmosphere is proposed. The improved gas sensing performance by applying Pd sensitizer is reported based on the SnO<sub>2</sub> MEMS sensors and the Sb-doped SnO<sub>2</sub> thick-film sensors. Finally, some suggestions for the future work are provided.