Improving Sensitivity and Selectivity in TiO_2-Based Gas Sensors for High Temperature Applications

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Gas sensors capable of operating at 400-600 ^oC are necessary for combustion process monitoring in automotive an aeronautic applications. Thick film metal oxide semiconductor sensors based on TiO_2 have been shown to be sensitive to carbon monoxide, a gas of interest in combustion processes(2). Improving the sensitivity and selectivity of such sensors is important in developing these sensors as practical devices. In order to increase the sensitivity of TiO_2 sensors to CO, reactively r.f. sputtered thin films have been produced and studied. Minimization of sensor response to interferent gases is also a concern in sensor development. Sensor arrays have recently been explored as a way to differentiate between gases of interest in a mixture(3). In order to detect CO in a changing oxygen background, a sensor array consisting of two differently-doped TiO_2-based sensors has been incorporated.

Reactive r.f. sputtering was used to produce thin film TiO_2 sensors. Electrical measurements, x-ray diffraction and scanning electron microscopy have been used to study the gas sensitivity, structure and morphology of the sensors. The effects of calcination temperature and film thickness on sensor performance have been studied. The Ar/O_2 ratio has also been varied. Increased sensitivity to CO of thin film sensors over thick film anatase TiO_2 sensors has been demonstrated. However, a peak film thickness is necessary to achieve this increased sensitivity. Figure 1 shows the relative responses of thick and thin film TiO_2 sensors to CO.

In order to be able to differentiate between gases in a mixture, responses of multiple sensors have been evaluated using pattern recognition techniques. Two TiO_2 based sensors have been used to determine the concentrations of CO and O_2 in a mixture. Sensors used in the array include anatase TiO_2 doped by mechanical mixing with 10% La_2O_3 and anatase TiO_2 doped by mechanical mixing with 10% La_2O_3 and chemisorption-hydrolysis of 8% CuO (3). Figure 2 a and b show relative responses of the 10% La_2O_3-TiO_2 and 8% CuO-10% La_2O_3-TiO_2 sensor to 0-1000 ppm CO in 2, 5, and 10% O_2/N_2 balance. Differentiation of gases in a mixture is achieved by modeling the sensor responses, generating contour plots of these modeled responses and using these plots to predict unknown mixture compositions. A contour plot generated from the responses of the aforementioned sensors is shown in Figure 3, where each contour line represents constant resistance and the intersection of lines from the 2 sensors give a unique gas composition.

References:

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[2] S. H. Hahn, N. Barsan, U. Weimar, Investigation of CO/CH_4 mixture with differently doped SnO_2 sensors Sens. Actuators B 78 (2001) 64-68.
[3] F. Boccuzzi, A. Chiorino, G. Martra, M. Gargano, N. Ravasio, B. Carrozzini, Preparation, Characterizaion and Activity of Cu/TiO2 Catalysts I. Influence of the Preparation Method on the Dispersion of Copper in Cu/TiO2, J. Catal. 165 (1997) 129-139.

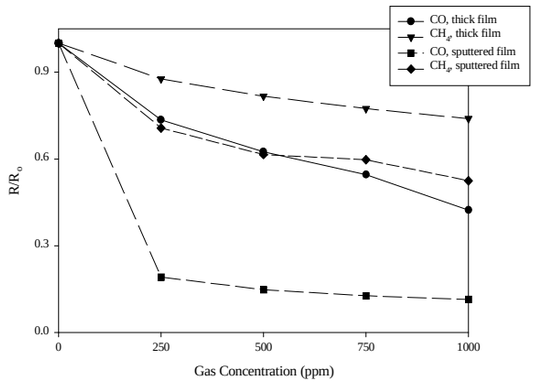

Figure 1. Comparison of sensitivity of thick film anatase TiO_2 sensor and reactively sputtered TiO_2 sensor.

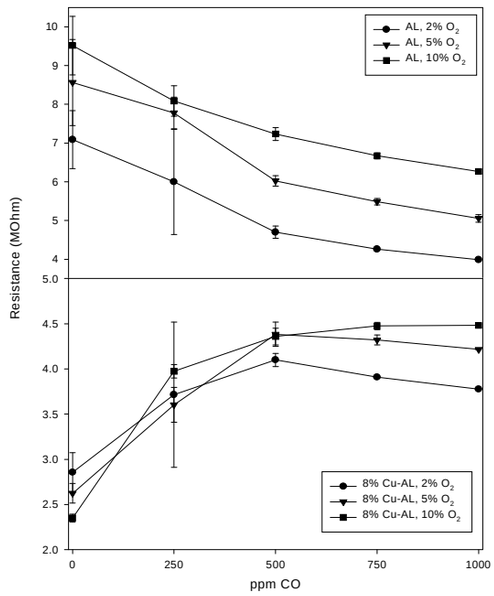

Figure 2. Responses of 10% La_2O_3-TiO_2 and 8% CuO-10% La_2O_3-TiO_2 sensors to 0-1000 ppm CO and 2-10% O_2 at 600 ^oC.

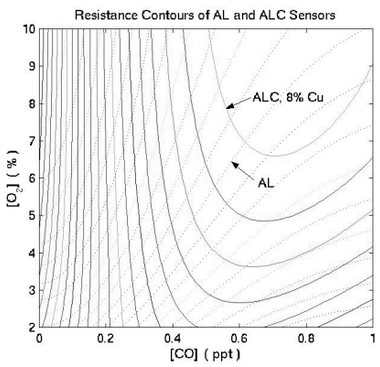

Figure 3. Contour plot generated from resistance data of 10% La_2O_3-TiO_2 and 8% CuO-10% La_2O_3-TiO_2 sensors with 0-1000 ppm CO and 2-10% O_2.