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Sensing with Noble Metal Oxide Loaded WO_3

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Abstract:
WO_3 is one of the most commonly used materials for commercially available semiconducting metal oxide based gas sensors. In most cases, noble metals are added to WO_3 to increase stability and tune its sensing characteristics. In order to deliberately tune SMOX based sensors, understanding how the presence of the noble additives affects sensing would be helpful. Here using, DC resistance measurements and operando diffuse reflectance infrared Fourier spectroscopy (DRIFTS) the previously suggested sensing mechanism for Rh_2O_3 loading has been verified and expanded to platinum oxide-loaded WO_3. It is proven that the reactions between the noble metal oxide and the analyte gases are responsible for the reception. In turn the resulting changes in the heterojunction characteristics control the transduction

Key words: SMOX Sensors, WO_3, Fermi Level Sensitization, Noble Metal Oxide

Introduction

In an attempt to increase stability and to tune the sensing characteristics of semiconducting metal oxides (SMOX), noble metal oxides additives are used. Understanding how these additives change sensing with SMOX based sensors is essential to enable the intentional tuning of their characteristics. One of the most used SMOX for fabricating gas sensors is WO_3. Previous results, found on Rh_2O_3 loaded WO_3 hollow spheres, indicated a Fermi-level-control type of sensitization. Verifying the generality of that mechanism for Rh_2O_3 loaded WO_3 is the first objective of this contribution. The second objective is to check if such a sensitization mechanism is also valid for different noble metal additives. To achieve the first objective: we changed the WO_3 base material and loaded it with Rh_2O_3 by using impregnation with $RhCl_3$. Using noble metal chlorides is a versatile and frequently used method to load SMOX materials. As a first step for meeting the second objective the WO_3 sample was loaded with PtOx. To study the impact of loading on sensing, the as obtained samples were investigated using DC resistance and DRIFTS measurements.

Experimental

The surface loading of the samples was done analogously to Choi et al. [1]: an aqueous slurry of 0.023 g of $RhCl_3xH_2O$ (Sigma Aldrich, 99.98% trace metals) and 0.5g of WO_3 (Sigma Aldrich, nanopowder, >100 nm particle size) in 5 ml of water was stirred at 80 °C for two hours, dried at 70 °C overnight. To ensure homogeneity, the received powder was ground using a mortar and pestle and re-suspended in 5 ml water, stirred for 2 hours at 80 °C and then dried again overnight at 70 °C. The powder was then calcined for 1 hour at 500 °C in a tubular furnace. The procedure was repeated with 0.018 g $PtCl_2$ (Premion, 99.98% trace metals 0.5g of WO_3 (Sigma Aldrich, nanopowder, >100 nm particle size) for the 5at% Pt loaded sample. To fabricate the sensors, the procedure described in [2] was used. The responses of the loaded sensors were measured at 300 °C to CO, acetone, toluene, NO_2 and ethanol in varying humidity concentrations using a fully automated gas mixing station. The surface reactions of the materials was examined using in operando DRIFTS as described in [3].

Results and Discussion

The sensor response was calculated using the ratio between the resistances in the reference condition divided by that in the reducing gas (the opposite is true for oxidizing gases). For both loadings, it was found that the sensor response of the samples is drastically different from that of the unloaded WO_3 sample.

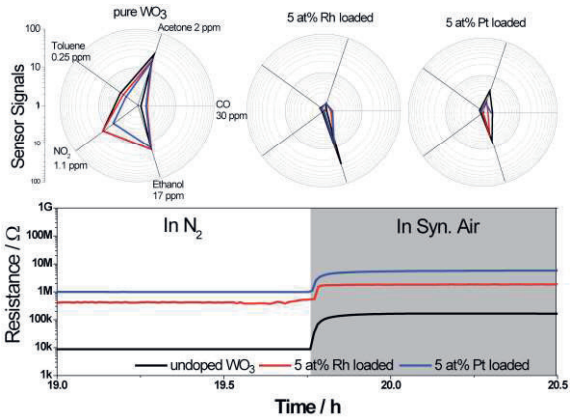

Fig. 1. Polar Plots of the sensor signals, and resistance measurements done in N_2 used to calculate the band bending which results from the surface loading are shown.

The band bending (see [4] for the calculation method) detected in the loaded samples indicates a significant electronic coupling between the noble metal oxide and WO_3 in both cases. For the Rh-loaded sample a bending of 191 meV was calculated while for the Pt loaded sample 233 meV was determined. In the DRIFT measurements done while exposing the sensor to CO in low oxygen background, very interesting results were obtained. The rhodium loaded sensor shows an increase in bands attributed to tungsten oxygen bonds for lower concentrations of CO. At higher concentration (over the stoichiometric value of O_2 needed for the complete conversion of CO to CO_2), the reduction of the WO_3 lattice and the formation of metallic rhodium carbonyls are observed. These results support the previously reported mechanism, which states that the reaction between Rh_2O_3 and the analyte gas is responsible for the reception and that the transduction is controlled by the surface heterojunctions formed between the base material and the additive clusters [2]. The situation for the Pt-loaded WO_3 is similar. At lower CO concentrations, there is no reduction of WO_3 visible. At 50 ppm two different carbonyl species are visible at 2151 cm^{-1} and 2084 cm^{-1}. At higher CO concentrations, the band attributed to oxidized Pt^{nt}-CO disappears while that at 2084 cm^{-1} attributed to metallic Pt-CO increases[4]. This indicates, similar to the results for WO_3 and Rh_2O_3 clusters and the reports for SnO_2[4], that the surface reaction responsible for the sensor response is between the analyte gas and the surface PtO_x-clusters.

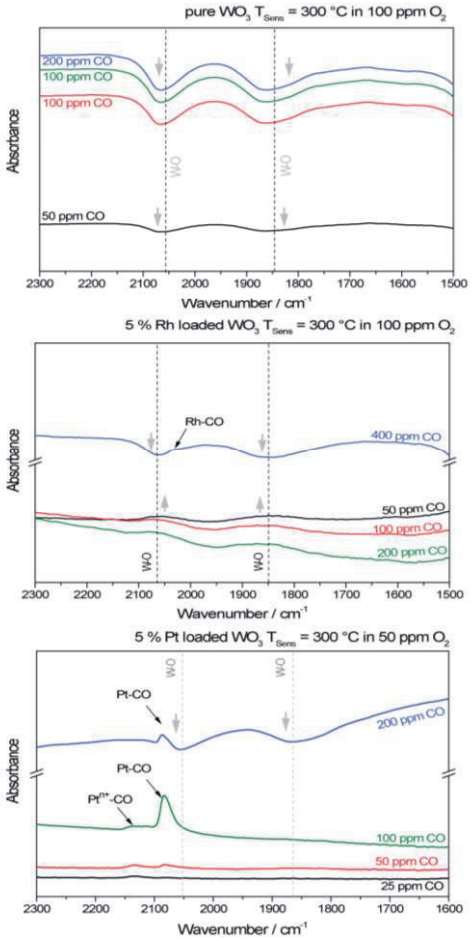

Fig. 2. Operando DRIFT absorbance spectra done on sensors in low oxygen background during exposure to CO are shown.

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