

Effects of the Pd Dopant on the Surface Reactions of SnO₂ Thick Film Sensors

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The aim of this study is to characterize different SnO₂ sensors (undoped and Pd doped) in operation conditions using simultaneously performed DRIFT (Diffuse Reflectance Infrared Fourier Transform) spectroscopy and DC measurements. The described experiments will help to understand the way in which the sensing mechanism takes place and the role played by the dopants.

The measurements were performed on both types of thick film sensors in dry and humidified synthetic air; CO was added in concentrations between 50 and 500ppm and the sensors were heated at temperatures between RT and 300°C.

DRIFT spectra recorded during a complete temperature cycle (RT→300°C→RT, with 50°C steps) for the undoped sensor are shown in Figure 1. The information is provided for the spectral ranges: 4000 to 3000cm⁻¹ corresponding to surface hydroxyl groups and water related species; 2000 to 1000 cm⁻¹ corresponding to surface carbonates and oxygen ions

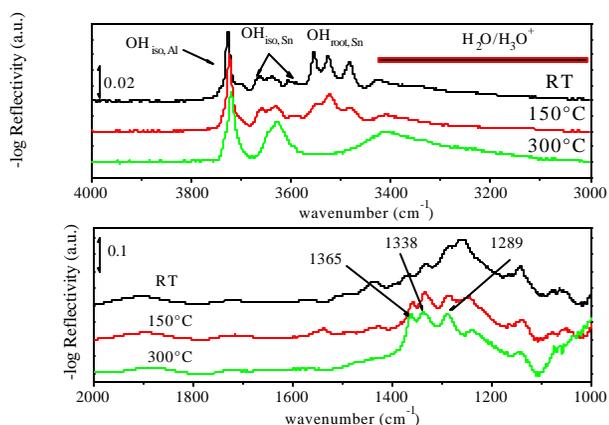


Fig 1: DRIFT spectra at different temperatures. Top: OH/H₂O range, bottom: carbonate range

One can see that at room temperature we detect bands belonging to: isolated/terminal OH groups on alumina at 3728 cm⁻¹ (Al-OH); bands assigned to isolated/terminal OH groups at 3662, 3629, 3611 cm⁻¹ on Sn; bands belonging to the rooted OH groups at 3555, 3525 and 3481 cm⁻¹ on tin; a broad band between 3420 and 3000 cm⁻¹ corresponding to the water related species. With the exception of the band assigned to the Al-OH vibration, all bands were found in the spectrum of SnO₂ powders investigated in previous experiments [1] with a different intensity distribution. For sensors, at all temperatures, in the reflectance spectra we observed a general increase of the background absorption caused by free electrical charges (electrons).

Increasing the temperature above 150°C decreases the intensity of the bands assigned as rooted OH groups; the form of the spectrum between 4000 and 3000cm⁻¹ change completely above 250°C.

For undoped sensors, in the range between 2000 and 1000cm⁻¹ we clearly observe three bands at 1363, 1335 and 1289 cm⁻¹ when the temperature is increased above 150°C. At the initial lower temperatures these bands are not well-defined. For the case of doped sensors, these

bands are not at all observable; they are, maybe, masked by the background absorption of free charges.

The spectra recorded during the cooling, indicate that, from the point of view of bands' intensity, the adsorption phenomena are only reversible for doped sensors. However, the bands' position are fully reversible for both sensors.

In addition to the temperature cycling experiments, the effect of exposure to different CO concentrations were studied. The CO measurements were performed at 300°C in dry and humid air (50% r.h.). The sensors show different spectroscopic and electrical behavior upon CO exposure; this fact can be observed especially for influence of humidity. There is a clear correlation between the sensor signal and the generation of H₃O⁺ species and one can observe that the influence of humidity on both is different for undoped and doped sensors: they increase with increasing humidity for the doped sensors and decrease with increasing humidity for the undoped sensors (see Fig. 2). Also, the influence of the humidity change is much more important for the case of doped sensors. The generation of H₃O⁺ species appears to be, together with the reaction with oxygen ions the source for the resistance decrease upon CO exposure. It also appears that for the doped sensors, the reaction with hydroxyl groups, which is the origin of the generation of H₃O⁺ species, can not take place in the absence of humidity.

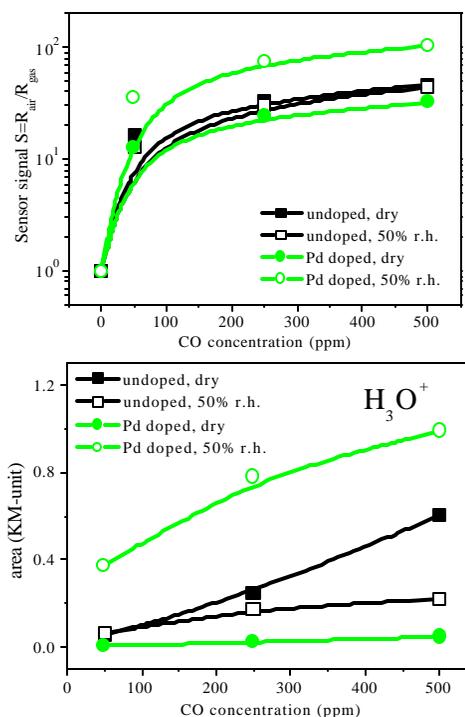


Fig 2. top: Sensor signal of Pd and undoped sensor in dry and humid air. Bottom: Band analysis for hydrated proton species in dry and humid air.

Obviously the reaction takes place differently when the dopant is present; in order to clarify the reaction mechanism experiments are currently performed.

References:

- [1] S.Emiroglu, N.Barsan, U.Weimar, V.Hoffmann, Thin Solid Films 391, 2001, 176-185