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Extended Abstract

Shining Light on Indium Oxide Gas Sensors at Work: A Combined *Operando* Raman/UV-Vis/FT-IR Spectroscopic Study †

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1. Introduction

Understanding the mode of operation of metal-oxide gas sensors (e.g., SnO_2, In_2O_3) is of great scientific and economic interest. Such a knowledge based approach requires the development and application of spectroscopic tools to monitor the relevant surface and bulk processes under working conditions (*operando* approach) [1,2] In previous studies on In_2O_3 sensors, we applied combined *operando* Raman/gas-phase FT-IR spectroscopy to ethanol gas sensing [2,3] In this contribution, we will present recent results on ethanol and CO detection using undoped and Ag doped In_2O_3 gas sensors, demonstrating the advantages of (i) *operando* Surface Enhanced Raman Spectroscopy (SERS) to monitor the metal oxidation state, and (ii) extending the *operando* Raman/FT-IR setup by UV-Vis spectroscopy to reveal the degree of In_2O_3 reduction.

2. Experimental

In_2O_3 was prepared by precipitation of indium (III) nitrate hydrate. $AgNO_3$ was added to yield a 1 wt% Ag/In_2O_3 sample by calcination. XPS analysis revealed a mixture of metallic (52%) and oxidized (48%) Ag on the surface. For gas sensing experiments an Al_2O_3-transducer substrate with interdigitated Pt-electrodes on one side and a meander Pt-heater on the other side was employed. *Operando* experiments were performed in a Teflon cell equipped with an optical window based on the design shown in Ref. [2]. The exhaust was analyzed by FT-IR spectroscopy. Raman spectra were recorded at 514.5 and 632.8 nm excitation. For details see Refs. [2,3].

3. Results

Previous *operando* Raman studies on undoped In_2O_3 gas sensors have shown that during ethanol (EtOH) gas sensing the sensor signal can be directly correlated with the nature of the adsorbates, the presence of surface hydroxyl groups and the indium oxide oxidation state [2,3] Turning now to recent results on Ag doped In_2O_3, Figure 1 shows *operando* Raman spectra recorded after switching from air to 250 ppm EtOH/air at 190 °C. At higher wavenumbers, the disappearance of hydroxyl groups at 3639 and 3656 cm^{-1} (O–H stretch) is accompanied by the formation of acetate based on the bands at 871 cm^{-1} (C–C stretch) and 2935 cm^{-1} (C–H stretch) [3]. Interestingly, upon exposure to 250 ppm EtOH/air, the low wavenumber region shows dramatic changes, which are reversible and which can be related to the change in the Ag state during EtOH sensing. In fact, the strong intensity increase in the In_2O_3 phonons (see Figure 1) is attributed to the EtOH surface reduction of oxidized to metallic Ag giving rise to a Raman enhancement based on Surface Enhanced Raman Spectroscopy (SERS), thus enabling the metal oxidation state to be elucidated under working conditions of the gas sensor.

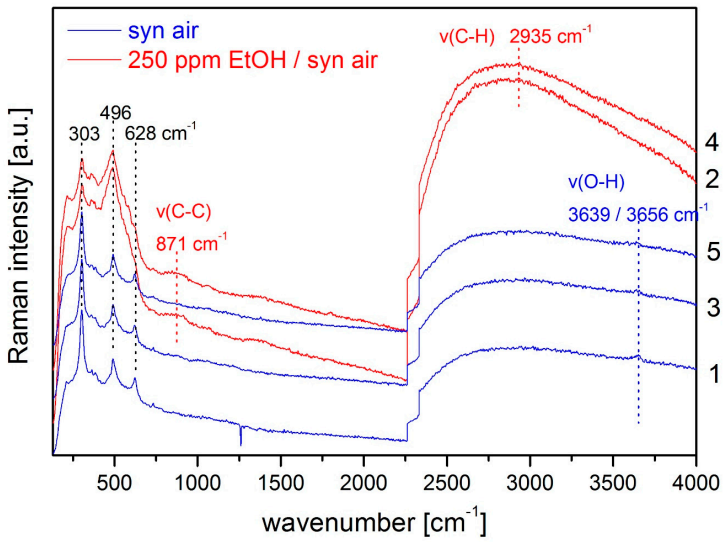

Figure 1. *Operando* Raman spectra during EtOH sensing at 190°C using 1 wt% Ag/In_2O_3.

To extend the information from *operando* experiments by UV-Vis spectroscopy a new *operando* cell was built on the basis of previous cell designs [2]. We illustrate its potential in combined *operando* Raman/UV-Vis/FT-IR spectroscopic experiments on In_2O_3 gas sensors during EtOH and CO gas sensing. For example, in experiments during CO sensing (500 ppm), resistance measurements can be correlated with (i) simultaneous FT-IR gas phase spectra showing changes in the gas-phase composition (CO, CO_2, H_2O); (ii) Raman spectra revealing information on adsorbates (carbonate, formate) and hydroxy species, while in contrast to ceria no super-/peroxide species are observed [4], and (iii) UV-Vis spectra indicating In_2O_3 reduction by increased Vis absorption. Very recent experiments on SnO_2 and CeO_2 gas sensors demonstrate the general applicability of the combined *operando* approach.

4. Conclusions

Our studies highlight the potential of combined *operando* spectroscopic characterization of metal-oxide gas sensors for elucidating their mode of operation on a molecular level.

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