DOI 10.5162/IMCS2012/7.3.1

Operando spectroscopic study of the EtOH gas sensing mechanism of In_2O_3

S. Sänze, C. Hess
Eduard-Zintl-Institut für Anorganische und Physikalische Chemie, Technische Universität Darmstadt, Petersenstraße 20, 64287 Darmstadt, Germany,
saenze@chemie.tu-darmstadt.de, hess@pc.chemie.tu-darmstadt.de

Abstract:

By using operando Raman spectroscopy, we studied the ethanol gas sensing mechanism of indium oxide. New Raman bands due to adsorbates at 937, 2868, 2939 cm^{-1} as well as changes of the Raman spectrum of the indium oxide sensor at 407, 3644 and 3658 cm^{-1} were detected. The adsorbates are identified as acetate and formate species and the changes of the indium oxide bands originate from reduced indium oxide. With FTIR gas-phase spectroscopy, the gas products of the EtOH sensing process were quantified and by measuring simultaneously the sensor resistance, we could correlate the sensing process to the spectroscopic changes.

Key words: operando, Raman-FTIR spectroscopy, EtOH gas sensing, mechanism study

Motivation

To develop better sensors with increased selectivity and sensitivity, it is important to understand the sensing process. To gain mechanistic insight, we use operando spectroscopy. In the case of gas sensing, this means to combine an in situ spectroscopic study of an active sensing element with the simultaneous monitoring of the gas composition and simultaneous read-out of the sensor resistance in the same experiment and on the same sample. Thus, the relation between sensor response, gas composition, adsorbed species and changes of the metal-oxide can be elucidated.[1]

Experimental setup

Simultaneous electrical measurements and Raman spectroscopy at an indium oxide gas sensor were performed in a Teflon cell equipped with a quartz window. The incoming gas was supplied by mass flow controllers. After the sensor reaction, the gas composition was quantified with FTIR spectroscopy. As gas sensor an In_2O_3 layer on an Al_2O_3 transducer substrate with interdigitated Pt-electrodes was used. On the back of the substrate was a Pt-heater.

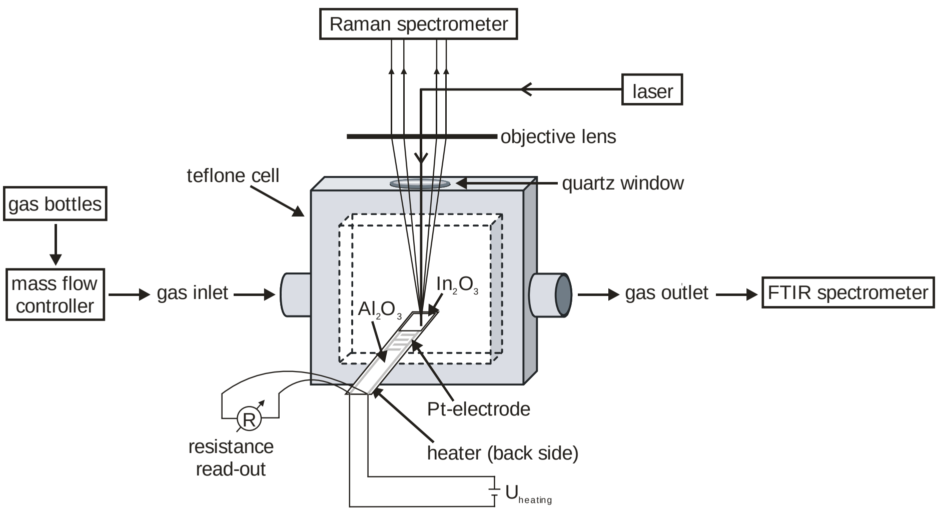

Fig. 1. Setup for an operando experiment at metal-oxide gas sensors.

Results

A major goal of the present operando Raman-FTIR study was the detection of adsorbates on the indium oxide gas sensor during the ethanol sensing process. For that purpose the gas atmosphere was varied in the sequence nitrogen, 250 ppm ethanol in nitrogen, nitrogen (or synthetic air, 250 ppm ethanol in synthetic air, synthetic air) at 190°C while Raman spectra, FTIR gas-phase spectra and the resistance were recorded. Representative Raman spectra are shown in Fig. 2. The temperature of the sensor was set to 190°C as to resemble operating conditions close to maximum sensitivity of the sensor.

When the sensor was exposed to EtOH, a new Raman band appeared at 407 cm^{-1}, which we assign to reduced indium oxide.[2] Moreover, the bridged hydroxyl groups (3644, 3658 cm^{-1}) on the surface [3] disappeared in the presence of ethanol gas, which is readily explained by the reaction of hydroxyl groups with adsorbed ethanol forming acetate groups. The latter species are characterized by Raman bands at 937 and 2939 cm^{-1}.[4]

In the presence of oxygen the Raman band due to reduced indium oxide was less intensive and additional strong Raman band at 2868 cm^{-1} as well as weaker bands appeared, which are attributed to formate species.[5] All changes caused by the presence of EtOH were completely reversible. Simultaneously to the Raman measurement, the sensor resistance and the gas-phase composition was measured. Consistent with the presence of surface acetate and formate species acetaldehyde and carbon dioxide were detected as gas-phase products.

Our results on EtOH gas sensing using In_2O_3 demonstrate the potential of operando Raman spectroscopy to gain new insight into the mode of operation of metal-oxide gas sensors.

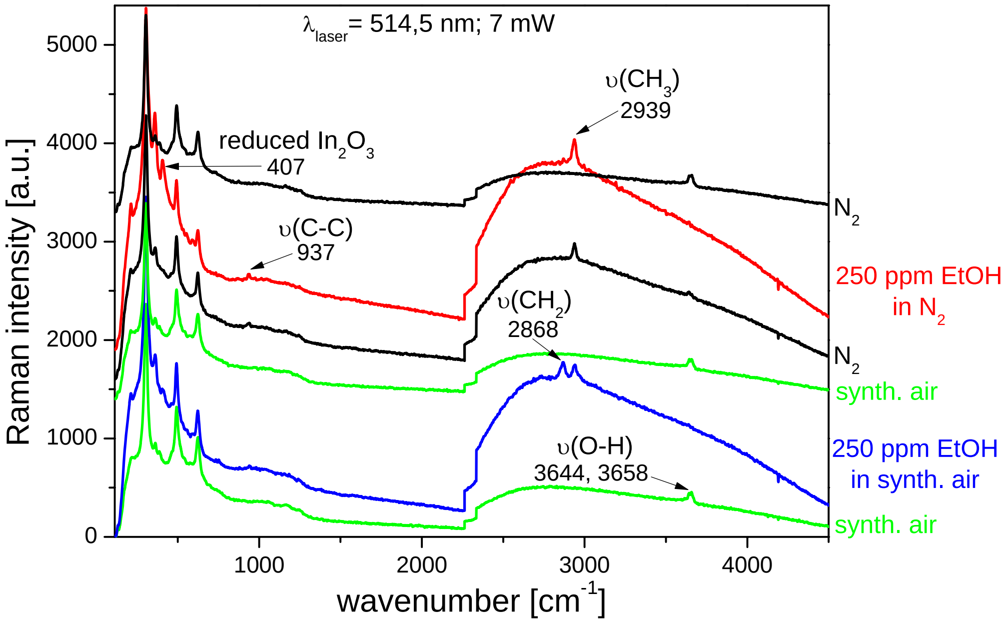

Fig. 2. Exemplary Raman spectra during EtOH sensing by In_2O_3 at 190°C in nitrogen or synthetic air (20% O_2/80% N_2). Measuring conditions: c(EtOH) = 250 ppm; gas flow = 20 ml/min; laser wavelength = 514,5 nm; laser power = 7 mW, measuring time = 1000 sec, measuring sequence: top down.

Acknowledgements

The authors thank Karl Kopp for technical support and Aleksander Gurlo for cooperation in sensor cell design.

References

[1] A. Gurlo, R. Riedel, In Situ and Operando Spectroscopy for Assessing Mechanisms of Gas Sensing, *Angew. Chem. Int. Ed.* 46, 3826-3848 (2007); doi: 10.1002/anie.200602597

[2] T. Bielz, H. Lorenz, W. Jochum, R. Kaindl, F. Klauser, B. Klötzer, S. Penner, Hydrogen on In_2O_3: Reducibility, Bonding, Defect Formation, and Reactivity, *J. Phys. Chem. C* 114, 9022-9029 (2010); doi: 10.1021/jp1017423

[3] A. N. Kharlanov, O. A. Turakulova, V. V. Lunin, Effect of Indium Oxide Modification on the Phase Composition, the Structure of a Hydroxyl Cover, and the Electron-Acceptor Properties of Zirconium Dioxide, *Kinetics and Catalysis* 45(2), 260-264 (2004); doi: 10.1023/B:KICA.0000023801.86194.d8

[4] R. D. Yang, S. Tripathy, Y. Li, H. Sue, Photoluminescence and micro-Raman

scattering in ZnO nanoparticles: The influence of acetate adsorption, *Chemical Physics Letters* 411, 150–154 (2005); doi:10.1016/j.cplett.2005.05.125

[5] S. Schrödle, F. G. Moore, G. L. Richmond, In situ Investigation of Carboxylate Adsorption at the Fluorite/Water Interface by Sum Frequency Spectroscopy, *J. Phys. Chem. C* 111, 8050-8059 (2007); doi: 10.1021/jp071248e