Angewandte
International Edition Chemie

DOI: 10.1002/anie.201207258

Gas Sensors

Monitoring Gas Sensors at Work: Operando Raman–FTIR Study of Ethanol Detection by Indium Oxide**

*Sandra Sänze, Aleksander Gurlo, and Christian Hess**

Metal-oxide semiconductors such as In_2O_3 have been used widely as gas sensing materials because of their high sensitivity to target gases and their simple fabrication.[1–3] Their operation is based on changes in the electrical conductivity of the material through adsorption of gas molecules on the surface of the semiconductor. Despite progress in the field, a detailed mechanistic understanding of the gas sensing process is still lacking. The knowledge-based development of better gas sensors with increased selectivity and sensitivity will crucially depend on the development of experimental approaches which allow for simultaneous measurement of the sensor response, adsorbed species, changes in the metal-oxide material, and gas-phase composition (operando approach).[4] Ultimately, by correlating these results, the mode of operation of gas sensors can be elucidated.

To demonstrate the potential of this approach, we present an operando Raman–FTIR study of the sensing of ethanol gas by bixbyite-type indium oxide (c-In_2O_3). Adsorbed species and changes to the indium oxide during the gas sensing process can be observed using visible Raman spectroscopy Raman spectroscopy was chosen because it has the potential to detect both adsorbed species, including anionic oxygen species, and changes in the metal-oxide structure. Simultaneous recording of gas-phase FTIR spectra allows quantification of the gas-phase composition. Such operando Raman studies on gas sensors have not been reported before. The developed experimental setup is shown schematically in Figure 1. Simultaneous resistance and Raman spectroscopic measurements on the In_2O_3 gas sensor were performed in a teflon cell equipped with a flat optical quartz window. The gas outlet was analyzed by FTIR spectroscopy.

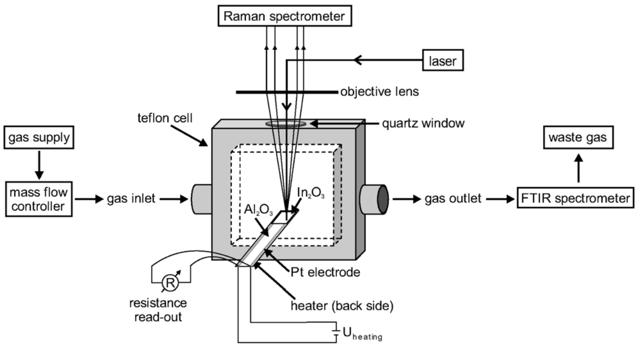


Figure 1. The operando Raman-FTIR setup, which allows for simultaneous measurement of the sensor response (dc electrical conductivity), Raman spectra of the sensor material, and FTIR spectra of the gas-phase composition.

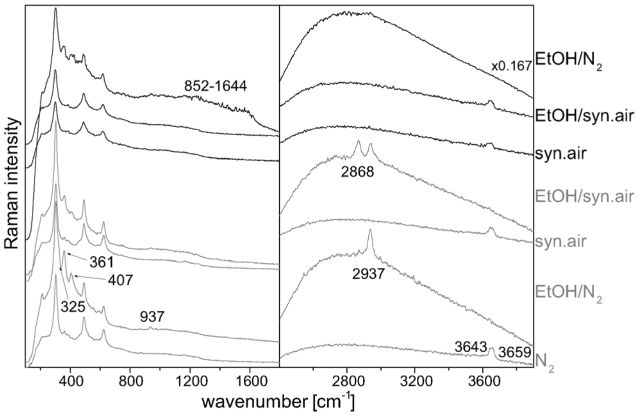


Figure 2. Operando Raman spectra of the sensing of ethanol gas by indium oxide at 190 °C (gray) and 325 °C (black). Spectra are offset for clarity.

Figure 2 depicts representative Raman spectra of the operando experiments at 190 °C and 325 °C, with the spectra shown bottom-up in the measured sequences. The indium oxide bands at 304, 361, 493, and 624 cm^{-1} in the spectrum recorded at 190 °C in nitrogen confirm the bixbyite-type c-In_2O_3.[5] The Raman bands at 304 and 361 cm^{-1} are attributed to the bending vibration ($\delta(InO_6)$) of the octahedron and the In-O-In stretch vibration (υ(In-O-In)), respectively. The bands at 493 and 624 cm^{-1} are due to stretching vibrations of the octahedron ($\upsilon(InO_6)$).[6,7] The high-frequency region of the Raman spectrum is characterized by two bands at 3643 and 3659 cm^{-1}, which are attributed to bridged surface hydroxy species.[8] No anionic oxygen species such as $O_2{}^{-}{}_{ads}$ were detected on the surface.

Upon exposure of the sample to 250 ppm ethanol in nitrogen (EtOH/N_2) at 190 °C (flow rate: 40 mL min^{-1}), the intensity of the band at 361 cm^{-1} increases and a new band and a shoulder appear at 407 and 325 cm^{-1}, respectively.[9,10] According to the literature,[12] the latter two features result from reduced indium oxide species near the surface, as these bands disappear again when the sample is exposed to oxygen

---

[*] S. Sänze, Prof. Dr. C. Hess
Eduard-Zintl-Institut für Anorganische und Physikalische Chemie
Technische Universität Darmstadt
Petersenstrasse 20, 64287 Darmstadt (Germany)
E-mail: hess@pc.chemie.tu-darmstadt.de
Homepage: http://www.chemie.tu-darmstadt.de/hess
Dr. A. Gurlo
Fachbereich Material- und Geowissenschaften
Technische Universität Darmstadt
Petersenstrasse 23, 64287 Darmstadt (Germany)

[**] We thank Karl Kopp for technical support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201207258.

(Figure 2). This behavior indicates that near-surface regions can be reversibly switched between an oxidized and a reduced state. In contrast, reduced In_2O_3 species inside the deeper bulk regions of the indium oxide crystallites cannot be reoxidized at this temperature.[12] Moreover, as shown in Figure 2, in the presence of ethanol, the hydroxy band at 3659 cm^{-1} disappears and the band at 3643 cm^{-1} becomes weaker because reaction with ethanol results in the formation of acetate groups. The latter adsorbate species is characterized by new Raman bands at 937 (υ(C-C), C-C symmetric stretch) and 2937 cm^{-1} (υ(CH), CH_3 symmetric stretch).[13] However, a contribution to the 2937 cm^{-1} band from adsorbed ethanol can not be ruled out.[14] Both bands were also observed during the reaction of acetaldehyde with indium oxide under the same conditions. When the ethanol source is switched off, the intensities of the bands at 937 and 2937 cm^{-1} decrease and those of the hydroxy bands increase again. As will be shown in Figure 3, these changes in intensity are slow at 190 °C because of the stability of the adsorbed acetate species.

Exposing the gas sensor at 190 °C to 250 ppm ethanol in synthetic air (EtOH/syn. air) results in a smaller degree of reduction of the indium oxide compared to EtOH/N_2 (indicated by the lower intensity of the 407 and 325 cm^{-1} features). In addition, in the presence of oxygen, a new strong Raman band at 2868 cm^{-1} (υ(CH)) is observed in addition to the bands at 937 and 2937 cm^{-1}. This strong band is assigned, in accordance with the literature, to the C–H symmetric stretch of a formate-like species.[15] In contrast to the behavior observed in pure nitrogen, the spectroscopic changes caused by the presence of ethanol were completely reversible in synthetic air, including the restoration of the initial background intensity of the spectrum.

The operando Raman spectra shown at the top of Figure 2 were recorded at 325 °C. The spectrum in synthetic air resembles the previously described spectrum recorded at 190 °C. The addition of 250 ppm ethanol to the feed does not induce any significant changes in the spectra. In contrast, the absence of oxygen has a dramatic effect on the Raman spectra recorded in the presence of ethanol. The intensity of the features at 325 and 407 cm^{-1} increases, thus indicating reduction of the indium oxide.[9] Furthermore, broad bands at 852–1644 cm^{-1} arising from carbon species, as well as CH_x-related bands between 2670 and 2958 cm^{-1}, are observed that originate from adsorbate decomposition. This conclusion is supported by temperature-dependent spectra.[16] As a consequence of the presence of a carbon overlayer, the hydroxy Raman bands are no longer observable. In contrast to the reaction at 190 °C, the changes in the spectra caused by the presence of ethanol were reversible in pure nitrogen.

Simultaneously to the Raman measurements, the FTIR spectra of the gas products as well as the sensor resistance were recorded. As discussed in detail in the following, there is a temporal correlation between the sensor resistance and the intensity of the spectroscopic bands (Figure 3). The assignments of the relevant Raman and IR bands are listed in Tables 1 and 2, respectively. Details on the ethanol conversion and the concentrations of gas-phase products are given in Table S1 in the Supporting Information. As shown in Figure 3, switching the gas atmosphere from nitrogen to 250 ppm EtOH/N_2 at 190 °C results in the indium oxide being reduced, bridged surface hydroxy groups vanishing, and adsorbed acetate species appearing. The low conversion rate at 190 °C results in the concentrations of the reaction products being near the FTIR detection limit.

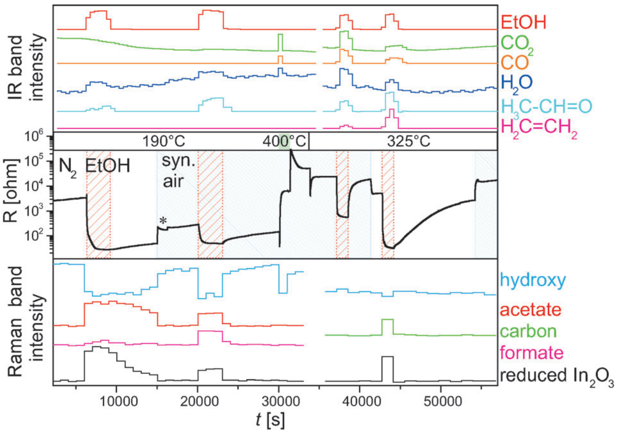


Figure 3. Temporal correlation of spectroscopic data and sensor resistance for the operando Raman-FTIR experiment of ethanol gas sensing by indium oxide. *: 10% O_2 + 90% N_2.

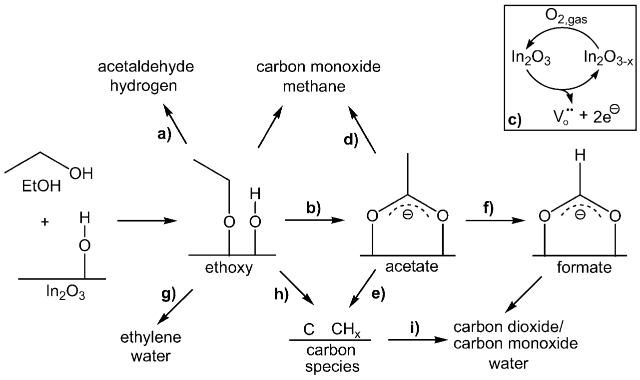
Table 1: Assignment of the Raman bands from Figure 2 used for the correlation in Figure 3.

Wavenumber [cm^{-1}]	Vibration	Assignment
407		reduced In_2O_3[12]
937	υ(C-C)	acetate
852–1644		carbon
2868	υ(CH)	formate,[15] adsorbed ethanol[14]
2937	υ(CH)	acetate,[13] adsorbed ethanol[14]
3659	υ(OH)	bridging hydroxy groups[8]

Table 2: Assignment of the IR gas-phase bands used for the correlation in Figure 3.

Wavenumber [cm^{-1}]	Gas
2903	EtOH
2361	CO_2
2178	CO
3902	H_2O
2733	H_3C-CH=O
3140	$H_2C=CH_2$

Thus, the only measured gas-phase products under these conditions were acetaldehyde and water.[17] On the basis of these observations, we propose the following reaction mechanism (Scheme 1):[18] After adsorption of the ethanol on the indium oxide surface, it dissociates to an ethoxy species, which can either desorb as acetaldehyde from the surface through dehydrogenation (Scheme 1 a) or react with surface hydroxy groups to form acetate (Scheme 1 b). Hydrogen released during the reaction can combine with hydrogen atoms, oxygen atoms, or hydroxy groups to form gaseous hydrogen, surface hydroxy groups, or water.



Scheme 1. Proposed mechanism of the sensing of ethanol gas by indium oxide. For details see the text.

The indium oxide is reduced during the course of the redox reaction (Scheme 1 c). These changes are accompanied by a strong decrease in the sensor resistance. According to the literature,[4] the sensor response is explained by changes in the electric surface potential resulting from "ionosorption" of gaseous molecules (ionosorption model) or by changes in the oxygen stoichiometry, that is, by variation of the amount of (sub-)surface oxygen vacancies and their ionization (reduction–reoxidation mechanism).

Our results show that ethanol is oxidized to adsorbed acetate by the indium oxide releasing electrons to the conduction band, and consequently the resistance decreases. The reduced In_2O_3 near the surface indicates the formation of oxygen vacancies and ionization (Scheme 1 c), which increases the conductivity. A further reason for the strong sensor response and the low ethanol conversion is the stability of the acetate preventing the sensor material from reaching its initial surface state. This is apparent from the slow reoxidation of indium oxide as well as only small changes being observed in the adsorbate and surface hydroxy band intensities when the ethanol source is turned off (Figure 3). Changes in the gas-phase composition are too small to measure in the absence of ethanol. The resistance increases very slowly because of traces of oxygen from air in the nitrogen gas and/or tubing leading to oxidation of the indium oxide, and accordingly removal of the oxygen vacancies (Scheme 1 c). Thermal decomposition of acetate (Scheme 1 d,e) enables the sensor to start returning to the initial surface state.

When oxygen is added, the intensity of the reduced In_2O_3 drops and the intensities of the surface hydroxy groups strongly increase, eventually reaching their initial state prior to the reaction with ethanol (Figure 3). The adsorbate-related bands also disappear immediately, which is attributed to decomposition and further oxidation of acetate. Based on the spectroscopic observation of formate-like species in EtOH/syn. air at 190 °C, we propose, in accordance with the literature,[19] that the acetate decomposes to formate-like species by reaction with coadsorbed oxygen, thereby releasing CO_2 (Scheme 1 f). Further decomposition of the formate-like species to CO_2 by attack of coadsorbing oxygen decreases the amount of adsorbates below the spectroscopic detection limit. The prompt increase in the sensor resistance upon exposure to oxygen is readily explained by the fast reoxidation of the indium oxide removing electrons from the conduction band. As at 190 °C, some adsorbate species remain on the surface, and the resistance does not return to its original value.

The reduction of indium oxide is less pronounced upon exposure to 250 ppm ethanol in synthetic air than in EtOH/N_2 because of the immediate reoxidation by oxygen. The band corresponding to the surface hydroxy groups largely disappears, similar as in EtOH/N_2, but the the adsorbate-related Raman bands change: In EtOH/syn. air, less acetate is observed because of its partial decomposition to formate-like species. Acetaldehyde, carbon dioxide, and water were observed as reaction products. Compared to the reaction in EtOH/N_2, acetaldehyde can be formed at a higher rate because there are a larger number of free sites resulting from the lower stability of acetate groups in the presence of oxygen.[19] As discussed above, the proposed mechanism is the decomposition to CO_2 via formate-like species (Scheme 1 f). The fact that the resistance does not decrease as much as in EtOH/N_2 can be explained by the permanent reoxidation of indium oxide resulting in an overall smaller degree of reduction. Furthermore, the presence of different stable adsorbate species may also play a role.

In synthetic air, the changes in the Raman spectra caused by the ethanol reaction were largely reversible, that is, indium oxide was oxidized, the hydroxy groups were restored, and the adsorbate-related bands disappeared. Compared to switching from nitrogen to synthetic air at 190 °C, the resistance shows only a slow increase after reaction with ethanol in synthetic air, which is correlated with the slowly decreasing formation of carbon dioxide, according to Scheme 1 f. Although no adsorbed species are visible in the Raman spectra under these conditions, CO_2 still desorps from the sensor surface. This observation underlines the importance of simultaneous gas-phase analysis to allow for interpretation of sensor activity in the case of adsorbate concentrations below the Raman detection limit. Figure 3 shows that these remaining adsorbate species have a profound effect on the resistance, which is significantly below its initial level.

To remove all adsorbates from the surface, the sensor was heated to 400 °C. Desorption of the remaining adsorbates through thermal decomposition results in the formation of CO, CO_2, and H_2O as identified by FTIR spectroscopy (Scheme 1 d–f). In contrast to normal semiconductor behavior, that is, a decrease in resistance on heating, an increase in resistance was observed because of adsorbate desorption. When the temperature was reduced to 190 °C again, the resistance had a significantly higher value than that prior to heating and adsorbate removal; finally, a further heating to 325 °C resulted in normal semiconductor behavior, that is, a decrease in resistance.

Significantly higher gas product concentrations were observed in EtOH/syn. air at 325 °C than at 190 °C. CO_2, H_2O, acetaldehyde, ethylene, and CO were detected as reaction products. The formation of acetaldehyde is proposed to proceed according to Scheme 1 a, and with the ethylene and water resulting from dehydration of ethoxy species (Scheme 1 g). CO_2 and CO are produced from decomposition of acetate/ethoxy species via formate and/or carbon (Scheme 1 e,f,h).[19] As indicated by the increased formation of product, surface processes are much faster at 325 °C. Consequently, the presence of adsorbate species on the sensor surface is not observed. Furthermore, the Raman spectra do not show any reduced indium oxide. However, this behavior does not exclude a permanent reduction and reoxidation of the indium oxide.

When the feed was switched to synthetic air at 325 °C, the resistance approached its initial value. The Raman spectra showed no changes and the concentrations of gas products subsided to zero. Switching from synthetic air to nitrogen resulted in a decrease in the resistance, which may be explained by an increase in the concentration of oxygen vacancies.

The decrease in resistance in EtOH/N_2 at 325 °C was greater than in EtOH/syn. air because of the absence of reoxidation by oxygen (Figure 3). As shown by the Raman spectra, the indium oxide is similarly reduced as at 190 °C in EtOH/N_2 (Scheme 1 c). However, at 325 °C no hydroxy bands are observed as a result of carbon deposition onto the oxide surface through ethanol decomposition (Scheme 1 e,h). A higher ethanol conversion was observed than at 190 °C. CO_2, H_2O, acetaldehyde, ethylene, and CO were detected as gas products, which were formed as discussed above (Scheme 1 a,g,i).[20]

Switching back to pure nitrogen leads to an increase in resistance which is not as fast as in the presence of oxygen at 325 °C but faster than at 190 °C. The resistance nearly returns to its initial value. The changes caused by exposure to ethanol were also reversible in the Raman spectra. The bands related to reduced indium oxide and deposited surface carbon disappear, while those related to hydroxy groups reappear (Scheme 1 c,i). This observation indicates that at 325 °C, in contrast to the behavior at 190 °C, diffusion processes in indium oxide from the bulk to the surface are fast enough to provide oxygen for reoxidation of the indium oxide and oxidation of residual carbon. In pure nitrogen, the gas products vanish except for CO_2, which decreases more slowly than in synthetic air because the oxidation of surface carbon to carbon dioxide is limited by traces of oxygen or by the indium oxide as a further oxygen source. Finally, when oxygen was introduced, the resistance increased at once to the initial state in synthetic air because of a refilling of the oxygen vacancies.

We have demonstrated the potential of operando Raman-FTIR spectroscopy to gain new insight into the mode of operation of metal-oxide gas sensors. In particular, Raman spectroscopy allows for the observation of changes in the sensor's properties (oxidation state), surface hydroxy groups, and the presence of adsorbates. In the case of ethanol gas sensing, the mechanism strongly depends on the gas environment and temperature, with both influencing the surface species that are observed. The sensor signal is correlated with the nature of the adsorbates, the presence of surface hydroxy groups, and the indium oxide oxidation state. To this end, surface hydroxy groups may influence the sensor response either directly and/or as a reactant to form adsorbates. A gas sensing mechanism solely based on the formation/ionization and refilling of oxygen vacancies can be excluded. Our study underlines that detailed spectroscopic analysis under the working conditions of the gas sensor is essential to unravel its mode of operation.

Received: September 7, 2012
Revised: November 6, 2012

Keywords: gas sensors · indium oxide · operando study · Raman spectroscopy · surface chemistry

---

[1] D. E. Williams, *Sens. Actuators B* **1999**, *57*, 1–16.
[2] N. Barsan, D. Koziej, U. Weimar, *Sens. Actuators B* **2007**, *121*, 18–35.
[3] G. Korotcenkov, *Mater. Sci. Eng. B* **2007**, *139*, 1–23.
[4] A. Gurlo, R. Riedel, *Angew. Chem.* **2007**, *119*, 3900–3923; *Angew. Chem. Int. Ed.* **2007**, *46*, 3826–3848.
[5] C. Y. Wang, Y. Dai, J. Pezoldt, B. Lu, Th. Kups, V. Cimalla, O. Ambacher, *Cryst. Growth Des.* **2008**, *8*, 1257–1260.
[6] W. Yin, J. Su, M. Cao, C. Ni, S. G. Cloutier, Z. Huang, X. Ma, L. Ren, C. Hu, B. Wei, *J. Phys. Chem. C* **2009**, *113*, 19493–19499.
[7] Additional features were observed at 213 and 388 cm^{-1}.
[8] A. N. Kharlanov, O. A. Turakulova, V. V. Lunin, *Kinet. Catal.* **2004**, *45*, 260–265.
[9] The increase in background intensity in the high-frequency region is attributed to surface- and/or adsorbate-induced fluorescence.
[10] The formation of $In(OH)_3$ (142, 186, 208, 227, 309, 376, 660, 670 cm^{-1})[11] or InO(OH) (1333, 1569 cm^{-1})[11] can be ruled out.
[11] J. Yang, R. L. Frost, W. N. Martens, *J. Therm. Anal. Calorim.* **2010**, *100*, 109–116.
[12] T. Bielz, H. Lorenz, W. Jochum, R. Kaindl, F. Klauser, B. Klötzer, S. Penner, *J. Phys. Chem. C* **2010**, *114*, 9022–9029.
[13] R. D. Yang, S. Tripathy, Y. Li, H. Sue, *Chem. Phys. Lett.* **2005**, *411*, 150–154.
[14] W. Zhang, S. T. Oyama, *J. Phys. Chem.* **1996**, *100*, 10759–10767.
[15] S. Schrödle, F. G. Moore, G. L. Richmond, *J. Phys. Chem. C* **2007**, *111*, 8050–8059.
[16] These experiments show a correlation between the disappearance of the adsorbate-related bands and the appearance of the carbon- and CH_x-related bands starting at about 300 °C.
[17] Products other than acetaldehyde, for example, ethylene, are not excluded, but are more difficult to detect because of their lower IR activity.
[18] D. Kohl, *Sens. Actuators* **1989**, *18*, 71–113.
[19] A. G. Sault, R. J. Madix, *J. Phys. Chem.* **1986**, *90*, 4723–4725.
[20] Acetone was identified by mass spectroscopy in separate experiments.