Operando DRIFT Measurements on a Tin Dioxide Based Gas Sensor
Katharina Großmann*, Nicolae Barsan², Udo Weimar³

*Institute of Physical Chemistry, University of Tübingen, Auf der Morgenstelle 15, 72076 Tübingen

Abstract

Tin dioxide based gas sensors with 1 % Pd doping were investigated by using DRIFT spectroscopy and DC resistance measurements in Operando conditions. The surface was characterized at 250°C in synthetic air and the change of the surface species was monitored during the exposure to hydrogen and deuterium test gases. In this manner it was possible to follow which kind of hydrogen associated compounds are produced/consumed during the reaction with the test gas.

© 2010 Published by Elsevier Ltd.

Keywords: DRIFT; reaction mechanism; Hydrogen sensor

1. Introduction

Tin dioxide is a widely used sensitive material in gas sensor applications for many reasons. The main cause of the change of the sensor resistance can be traced back to a ionosorption process and explained in terms of a electron transfer from the semiconductor to adsorbed surface species or the other way around [1]. The target gas reaction and associated charge transfer is strongly influenced by the already present surface species (like e.g. hydroxyls) following the reaction with the background atmosphere. Spectroscopic acquisition techniques are extremely powerful for the characterization of metal oxides since they can provide details about the active surface sites and reveal insight into the reaction process [2], which was of main interest in this study. Here, with the intention to understand the surface reactions of tin dioxide based sensors, complementary measurements (DRIFT and DC resistance measurements) were simultaneously performed. The chosen target gas was hydrogen because of the following reasons:

• Hydrogen and hydrogen containing gases are relevant targets for many gas sensors applications;
• Many species associated with hydrogen were found, by DRIFTS on sensors, to be present at the surface on SnO₂ and most of them changed during the reaction with reducing gases [3, 4];
• There is not enough information allowing to safely identified the surface species when performing DRIFTS on sensors because in most cases the work is performed on powders;
• In the case of hydrogen we are lucky to have one of its isotopes, deuterium at hand; it is reacting chemically in the same way like hydrogen, but the reaction products are appearing in a different area of spectrum because of the different mass.

* Corresponding author. Tel.: 07071-2978682; E-mail address: Katharina.Grossmann@ipc.uni-tuebingen.de.

1877-7058 © 2010 Published by Elsevier Ltd. Open access under CC BY-NC license. doi:10.1016/j.proeng.2010.09.062
The use of both hydrogen and deuterium helped us to make sure that the assignment of the hydrogen related surface species are correct and to distinguish between reaction products which are only built out of the reaction with \( \text{H}_2/\text{D}_2 \) and those that have other origins.

Table 1

| Nomenclature |
|---------------|
| DRIFTS        | Diffuse reflectance Fourier transform infrared spectroscopy |

2. Experiments

2.1 Measurements with 30 ppm hydrogen

The \( \text{H}_2 \) sensing mechanism was explored by applying the Operando investigation approach. Resistance and DRIFT measurements were simultaneously performed during hydrogen exposure at 250 °C in a background of dry air (with possible small amounts (ppm range) of impurities like e.g. water vapors). This combination of techniques helps the correlation between changes of surface species and electrical effects and by that identifying the species that are responsible for the change of the sensor resistance. The left upper part in fig. 1 shows 2 single channel spectra: the black line indicates the spectrum recorded in dry air, the red line during exposure to 30 ppm hydrogen. In the left lower part the absorbance spectrum is shown; calculated out of those single channel spectra (\(- \log(\text{SC}_\text{H}_2/\text{SC}_\text{air})\)). Six bands related to different kinds of OH groups can be found (Table 2).

The minima in the absorbance spectrum indicate the consumption of present OH groups, whereas the maxima denote the creation of new OH groups. Possible reactions concerning OH groups and water related species are [5, 6]:

1. **Consumption of OH groups:**
   \[
   \text{H}_2 + \text{H}_2 \text{ad} \rightarrow 2\text{H}_\text{ad}
   \]  

2. **Creation of OH groups:**
   \[
   \text{H}_\text{ad} + \text{O}_\text{ad} + \text{Sn}^+ \rightarrow \text{H}_2\text{O} + \text{Sn} \quad \text{(2)}
   \]  

   \[
   \text{H}_\text{ad} + \text{O}_\text{ad} \rightarrow \text{OH}_\text{ad} + \text{e}^-
   \]  

Figure 1 a) upper spectra: single channel spectra at 250°C in dry air and under exposure of hydrogen, lower spectrum: resulting absorbance spectrum; b) simultaneously recorded resistance measurement; the hatched areas indicate the period in which the DRIFT spectra are recorded.
\[
\begin{align*}
H_{\text{ad}} + O_{\text{ad}} + \text{Sn} & \rightarrow \text{Sn}^{+} \rightarrow O + S + e^- \\
H_2O + \text{Sn} + O_{\text{ad}} & \rightarrow \left(\text{Sn}^{+} - \text{OH}^-\right) + S + e^- \\
\end{align*}
\]

(4)

(5)

2.2 Measurements with 30 ppm deuterium

The experiments with D₂ were performed in the same way like the hydrogen experiments. The exchange of the OH groups with OD groups yields to a shift in the spectra by a factor of 0.737. This fact enables the assignment of corresponding OH / OD groups and hence the identification of OH groups which are exclusively build by the reaction with hydrogen. Table 2 denotes the wavenumber of the OH groups (left), the, out of those values, calculated (expected) wavenumbers for OD (middle) and the actually found wavenumber of OD (right).

| Wavenumber OH [cm⁻¹] | Calculated wavenumber OD [cm⁻¹] | Found wavenumber OD [cm⁻¹] |
|----------------------|---------------------------------|---------------------------|
| 1 3723               | 1' 2744                         | 1' 2745                   |
| 2 3660               | 2' 2697                         | 2' 2699                   |
| 3 3629               | 3' 2679                         | 3' 2676                   |
| 4 3585               | 4' 2645                         | 4' 2643                   |
| 5 3531               | 5' 2614                         | 5' -                      |
| 6 3482               | 6' 2586                         | 6' -                      |

Table 2 - Wavenumbers

![Figure 2 left: SC spectra recorded in synthetic air and under exposure of D₂; right: simultaneously recorded resistance measurement, the hatched areas indicate the period in which the DRIFT spectra are recorded](image)

Comparing the two areas in the spectrum, it is possible – via the shift factor – to indentify 4 out of 6 signals. The absorbance spectrum in fig. 2, which is calculated out of the shown single channel spectra, provides even more information about the reactions which were taking place.

Signal 1 / 3 and 1' / 3':

The measurements with hydrogen revealed a consumption of OH groups. This is also valid for the measurements with deuterium (see signal 1 and 3 in the OH area: still minimum); if one calculates the shift of this wavenumber for the exchange of hydrogen by deuterium, a small maximum peak in the OD region can be found. This leads to the conclusion that not only consumption is taking place, but, at the same time, also a rebuilding of the same OH i.e. OD groups.
Signal 2 / 4 and 2’ / 4’:
Those bands are in line with our expectations: we found a creation of OH groups under exposure to hydrogen. The maxima in the absorbance spectrum, which were indicating this fact, are – as a matter of fact - not visible during the reaction with deuterium, but the equivalent OD groups are built and appear in the OD region at the expected, calculated wavenumber (Nr 2’ and 4’).
The bands 5 and 6 (probably rooted OH groups), which are present in the hydrogen spectrum, have no equivalent in the OD area. Those reaction products can be the result of an interaction between water and hydrogen. Since the system is not completely tight, a small amount of water impurities (in the ppm range) is present and can influence the reaction.

3. Conclusion and Outlook

The reaction mechanism of hydrogen on the sensor surface was investigated by using DRIFTS spectroscopy. In order to prove the former results, hydrogen was exchanged by deuterium. These new experiments proved the assignment of OH and pointed out at two new aspects:
- The consumption of defined OH groups is in equilibrium with the creation of the same
- Some features in the OH area were not generated with D₂. This suggests the assumption that those OH species can only be generated by interactions with water.
The next steps are the elimination of the water impurities and measurements with small, defined amounts of water and deuterated water in order to replicate the results in the OD region and to reveal the role of water i.e. the interplay between the same and other gases / surfaces.

Acknowledgements

K. G., N. B. and U. W. are thankful to DFG support through WE 3662/1-2 and R. Pavelko for the preparation of the samples.

References
[1] S. Morrison, The Chemical Physics of Surfaces, 1977, Plenum Press, New York
[2] Barsan, N.; Koziej, D.; Weimar, U. Sens. Actuators, B 2007, 121, 18–35.
[3] “DRIFT studies of thick film undoped and Pd-doped SnO₂ sensors: temperature changes effect and CO detection in the presence of water vapour”, S. Harbeck, A. Szatvanyi, N. Barsan, U. Weimar, V. Hoffmann, Thin Solid Films 436 (2003) 76-83.
[4] “Complementary phenomenological and spectroscopic studies of propane sensing with tin dioxide based sensors”, D. Koziej, N. Bärsan, V. Hoffmann, J. Szuber, U. Weimar, Sensors and Actuators B 108 (1-2) (2005) 75-83
[5] G. Heiland and D. Kohl in T. Seiyama (ed.), Chemical Sensor Technology, Vol. 1, Kodansha, Tokyo, Ch. 2 15-38.
[6] N. Barsan, M. Schweizer-Berberich, and W. Göpel, Fundamentals and Practical Applications to Design Nanoscaled SnO₂ Gas Sensors: A Status Report, Fresenius Journal of Analytical Chemistry (1999) 365, 287–304