ZnO based gas sensors and the response to NO_2: role of potassium contamination

C. Ewald[1], N. Saito[2], U. Weimar[1], N. Barsan[1]

[1]*Institute of Physical and Theoretical Chemistry (IPTC), University of Tuebingen, Auf der Morgenstelle 15, 72076 Tuebingen, Germany*

[2]*National Institute for Materials Science (NIMS), 1-1 Namiki, 3050044 Tsukuba, Japan*

carolin.ewald@ipc.uni-tuebingen.de

Zinc oxide is one of the earliest studied gas sensitive materials. [1] Nowadays it is well known that ZnO based gas sensors are sensitive towards NO_2, which is a harmful gas and for example present in exhaust fumes. The gas sensing mechanisms are typically influenced by the morphology of ZnO - a huge variety of different nanostructures is reported to date. [2] Unfortunately, common impurities such as Na or K may be unintentionally present at the sensitive layer, being able to influence the gas sensor response, as well. However, it is not yet known how exactly for example potassium as a contaminant is interacting with the ZnO surface and the atmosphere.

In former experiments, ZnO based gas sensors showed a peculiar response to NO_2. The resistance decreased instead of the expected increase for n-type semiconductors. Additionally, the sensor's response to oxygen in a background of nitrogen was relatively low compared to typical ZnO based gas sensors, with a high resistivity already in nitrogen. In EDX and XPS potassium was found and could be attributed to the experimental findings.

In terms of the response to oxygen, this behavior is not uncharacteristic. For instance, it is known that potassium doping can lead to an increase in resistivity of ZnO crystals. [3] The inverse response to NO_2 however could not be explained yet. In order to understand how potassium is involved in the obvious changes in the gas sensing mechanism, we intended to reproduce the found contamination by loading pure commercial ZnO with various concentrations of potassium. The sensors produced from the obtained powders were characterized via SEM, EDX, DC Resistance measurements and DRIFTS.

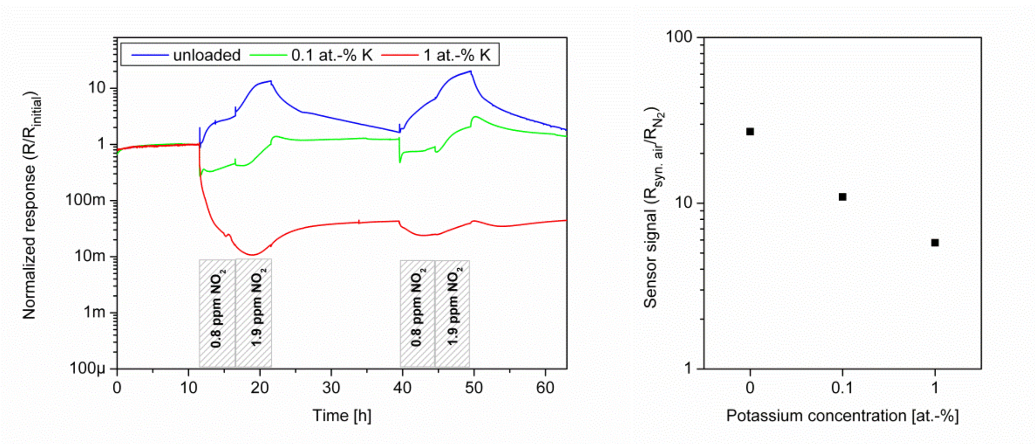
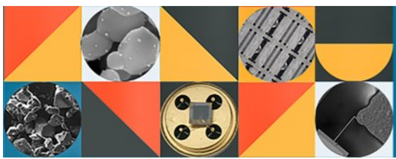


Fig. 1. Normalized responses of ZnO based gas sensors towards NO_2, loaded with different concentrations of potassium at 250 °C (left) and sensor signals towards 20.5 % oxygen at 250 °C (right)



Loading ZnO with potassium (0.1 at.-%) leads first to an inversion of the sensor response to NO_2. By increasing the concentration (1 at.-%), the resistance decreases strongly while the sensor recovers incompletely and exhibits a clearly smaller response at the second exposure. Operando DRIFTS measurements under exactly the same conditions enable to identify the functional groups involved in the sensing mechanism. Furthermore, the samples showed a decreasing response to oxygen with increasing potassium concentration. Beneath explanations according to the surface chemistry, electronic reasons might also play a role. One possible explanation could be that potassium acts as an acceptor at the surface, which causes already in nitrogen an initial band bending, leading to a higher resistivity.

[1] T. Seiyama, A. Kato, K. Fujiishi, M. Nagatani, Analytical Chemistry **34**, 1502-1503 (1962).
[2] R. Kumar, O. Al-Dossary, G. Kumar, A. Umar, Nano-Micro Lett. **7**, 97–120 (2015).
[3] N. S. Parmar, C. D. Corolewski, M. D. McCluskey, K. G. Lynn, AIP Adv. **5**, 057107 (2015).