

WO₃ Based Gas Sensors †

Anna Staerz ¹, Simona Somacescu ², Mauro Epifani ³, Tamara Russ ¹, Udo Weimar ¹ and Nicolae Barsan ^{1,*}

¹ Institute for Physical and Theoretical Chemistry, Eberhard Karls University of Tuebingen, 72076 Tuebingen, Germany; anna.staerz@ipc.uni-tuebingen.de (A.S.); tamara.russ@ipc.uni-tuebingen.de (T.R.); upw@ipc.uni-tuebingen.de (U.W.)

² Ilie Murgulescu Institute of Physical Chemistry, Romanian Academy, Spl. Independentei 202, 060021 Bucharest, Romania; somacescu.simona@gmail.com

³ Consiglio Nazionale delle Ricerche, Istituto per la Microelettronica ed i Microsistemi (C.N.R.–I.M.M.), Via Monteroni, 73100 Lecce, Italy; mauro.epifani@le.imm.cnr.it

* Correspondence: nb@ipc.uni-tuebingen.de; Tel.: +49 7071 29 78761

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Abstract: WO₃ is a commonly used material for gas sensing. Although a great deal of research has been done on how to tune sensors based on WO₃, no clear consensus exists on what characteristics are inherent to the metal oxide: This work looks at six different WO₃ samples and aims to identify which characteristics are common to all materials. Specifically, the interaction of the samples with humidity is examined.

Keywords: WO₃; gas sensor; humidity; acetone

1. Introduction

WO₃ is one of the most commonly used materials for gas sensing. Numerous publications exist which describe how the sensing characteristics of WO₃ can be tuned using changes in morphology [1], loading [2–4] or doping. There is however no study to date that determines what the inherent sensing characteristics of WO₃ are. By comparing sensors based on WO₃, In₂O₃ and SnO₂ commercially available powder from Sigma Aldrich certain intriguing characteristics can be identified. In addition, at 300 °C humidity oxidizes all the samples. The mechanism is examined further using DRIFT spectroscopy.

2. Experimental

The RO sample was prepared via a hydrothermal method using a nonionic surfactant as a structural agent. The hollow sphere samples were prepared as previously described [5–7]. The WO₃ platelets were synthesized as previously reported using P123 [8]. The ME samples were prepared following the previously reported method [9]. The SA sample is commercially available nanopowder from Sigma Aldrich. Commercially available In₂O₃ and SnO₂ from Sigma Aldrich were used as a comparison.

3. Results and Discussion

The samples were characterized using XRD, SEM, DC resistance measurements, and diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. In addition to the six different WO₃ samples, commercially available In₂O₃ and SnO₂ were tested as a comparison. Morphologically, the samples vary from random particles to particles arranged in spheres and even single crystalline platelets. This can be seen in Figure 1.

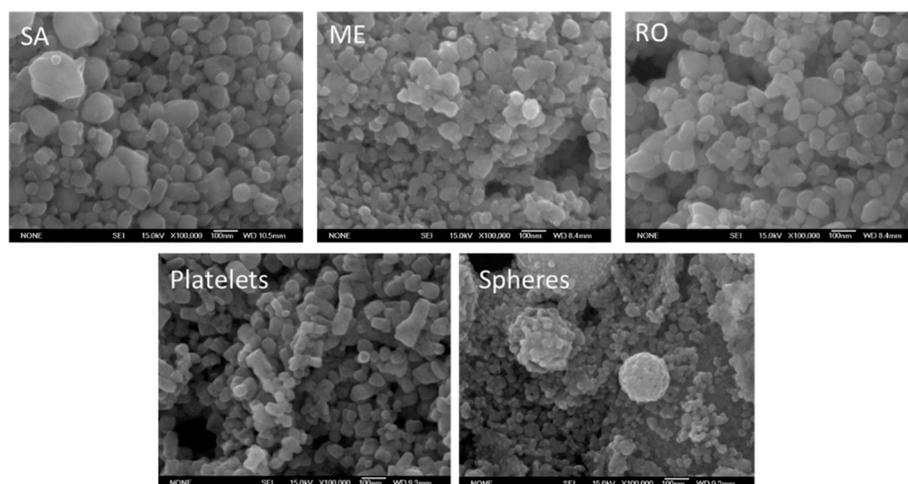


Figure 1. SEM pictures of the sensitive WO_3 layer.

At room temperature, the RO, ME and SA samples appear, as expected, to be in the gamma phase with good crystalline quality. Tungsten trioxide is known to have different temperature dependent crystal structures. As the sensors are operated at 300 °C, operando XRD is necessary to determine the crystal phase which is present during sensor operation. For the SA, ME and Spherical sample a mixed gamma/beta phase is present at 300 °C. From the measurements done at room temperature after the heating, it can be seen that the phase transition is reversible. It has been previously reported that this mixed phase is stable [10]. The XRD results are shown in Figure 2.

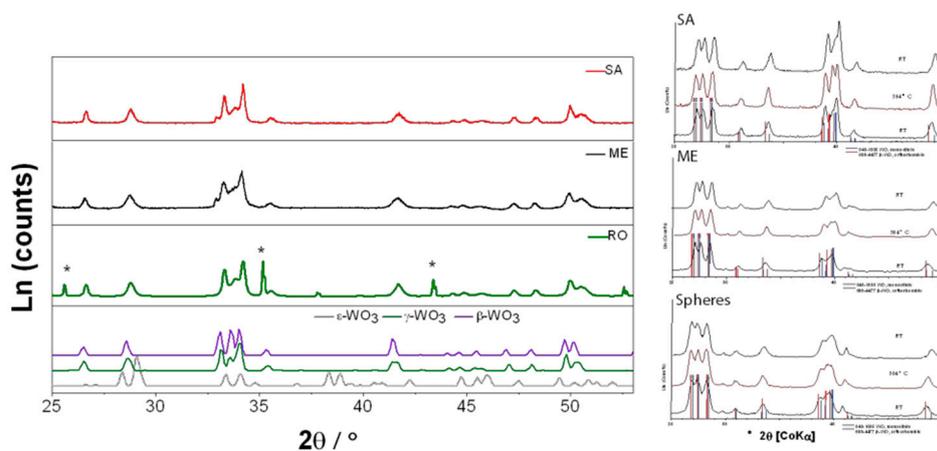


Figure 2. Left The XRD patterns of the sensitive layer at room temperature (the peaks labeled with a * are attributed to Al_2O_3).

The comparison of sensors based on commercially available In_2O_3 , and SnO_2 with the WO_3 samples reveals the inherent characteristics of WO_3 . Like SnO_2 , the response of WO_3 to NO_2 decreases as a result of humidity and the responses to ethanol are high and practically humidity independent. WO_3 is a commonly used base material for the detection of biomarkers such as acetone and toluene. Although most published research considers loaded or doped WO_3 , here it can be seen that in comparison to SnO_2 and In_2O_3 it is inherently well suited for the detection of acetone in particular in the presence of humidity. This result is true for all the examined WO_3 sensors (see Figure 3). Although the different WO_3 samples show varying strengths in their response to toluene in all cases the response increase with humidity (the opposite behavior is true for SnO_2 and In_2O_3).

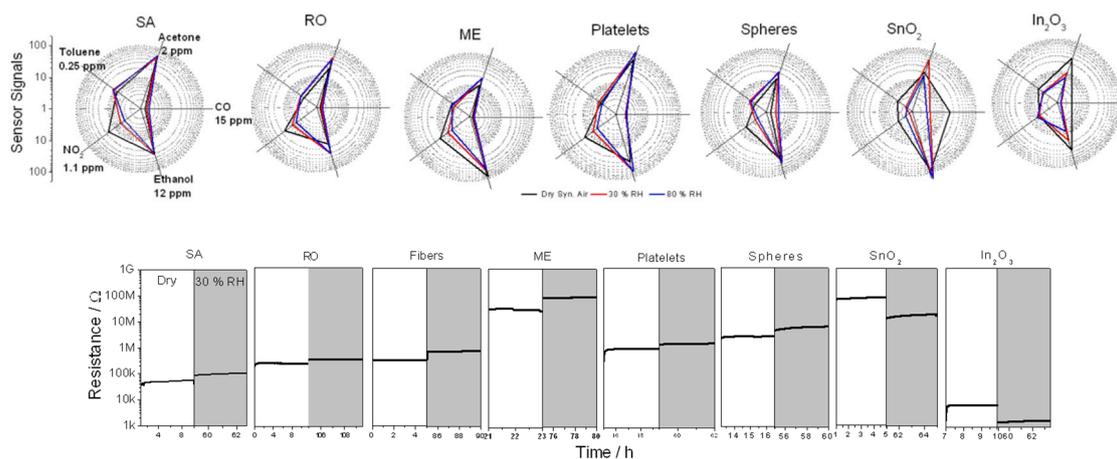


Figure 3. (Top) The sensor signal calculated based on the DC resistance measurements (in the case of reducing gases the resistance in air was divided by that during gas exposure, while for oxidizing gases the inverse relationship was used). (Bottom) The baseline resistance is shown of the sensors in dry air and in 30 %RH.

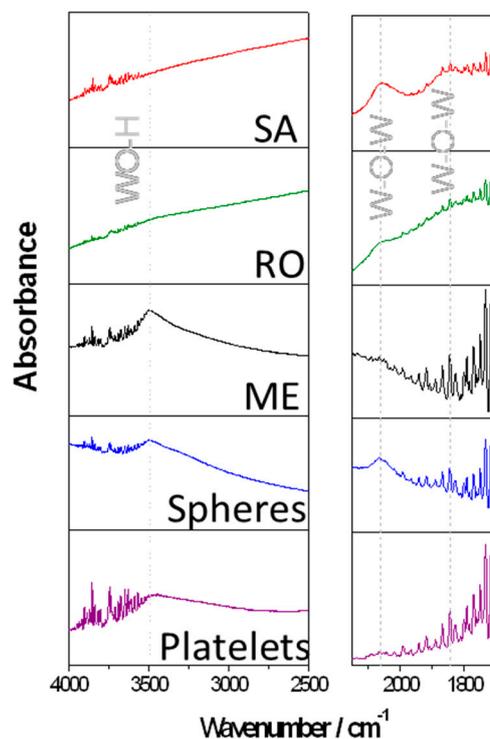


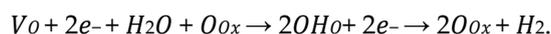
Figure 4. The operando DRIFT spectra of the WO₃ sensors during exposure to 10% RH. The spectra taken in humidity were referenced to those taken in dry air.

In addition all WO₃ sensors show low sensors responses to CO (especially in comparison to SnO₂) but in comparison to SnO₂ the response of the WO₃ sensors increases with humidity. For certain materials in the past, this has been attributed to the oxidizing effect of humidity on WO₃. While humidity normally decreases the resistance of SnO₂ and In₂O₃, it has been reported that humidity can increase the resistance of WO₃ at 300 °C. This result was confirmed for all the examined samples. Using DRIFT spectroscopy, the interaction mechanism of the samples with humidity was examined, seen in Figure 4.

In all cases exposure to humidity lead to an increase in the bands attributed to tungsten-oxygen lattice bonds. In the case of the SA sample and the RO sample, no significant formation of hydroxyl groups is visible. The following mechanism has been suggested [10]:



In the case of the other samples, the oxidation bands are less visible and the formation of hydroxyl groups can be seen. One possible explanation would be that the formation of hydroxyl groups is an intermediary step from which H₂ is released and the surface is oxidized. This step would be charge neutral:



From the work here it is possible to understand which characteristics are inherent to WO₃. This information is vital when making a decision whether WO₃ based sensors are suited for a certain application, and for understanding how the characteristics change as a result of loading or synthesis method. The reaction with humidity was examined more carefully, as atmospheric water is omnipresent in real world applications.

Author Contributions: All authors contributed equally to the preparation and research work involved in preparing this manuscript.

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