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Short communication

Extending the toolbox for gas sensor research: Operando UV/vis diffuse reflectance spectroscopy on SnO_2-based gas sensors

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ABSTRACT

This work demonstrates the feasibility and benefit of operando UV/vis spectroscopy on SnO_2-based gas sensors. The results on the different SnO_2 sensing materials studied show an effect of the material's calcination temperature on the optical band gap and further indicate a dependence of the amount of reducible SnO_2 on the grain size. To our knowledge this is the first report of a successful measurement of UV/vis spectra recorded from an operating gas sensor.

1. Introduction

Since in the 1950s the first reports of the gas sensing properties of semiconducting metal oxides (SMOX) appeared, models were developed to describe the working principle of the gas-solid interaction [1,2]. However, many models were based on information obtained by a surface science approach, i.e. the study of single crystals using UHV technologies [3,4], causing a gap between the conditions of the experimental work and real life applications. State of the art gas sensors research aims to study gas sensors in realistic conditions, i.e. measurements done on real gas sensing devices at operation temperatures, in realistic atmosphere compositions and pressure; an approach which is referred as operando research [5]. Current spectroscopic techniques range from molecular spectroscopy (infrared and Raman spectroscopy) to hard X-ray absorption spectroscopy [5–8], determining chemical and structural properties. Thus it is surprising that UV/vis spectroscopy is used mainly for ex situ characterization [9] and not as an operando technique, since it provides valuable information on the electronic structure of the material as well as the oxidation state, size and shape of noble metal loadings if present as metal or oxide clusters [10]. To our knowledge we report the first time a successful measurement of UV/vis spectra on SMOX gas sensors under operation conditions.

2. Experimental

Similar to operando infrared spectroscopy on gas sensors operando UV/vis spectroscopy was performed using a commercial diffuse reflectance mirror optic (Harrick, Praying Mantis) [11]. The light source (Mikropack DH-2000-BAL, halogen and deuterium lamp) and the FFT-CCD UV/vis spectrometer (Ocean Optics, Maya 2000) were connected to the mirror optic using optical fibres. By using a beam shutter the sensors were only exposed to UV/vis radiation when recording a spectrum. To reduce the influence of external stray light the whole setup was placed in a dark compartment. Spectra were recorded with 60 ms integration time averaging 256 scans and referenced to $BaSO_4$ which was deposited on a gas sensor substrate like the sensing materials. The sensors were placed in a home-made operando cell equipped with a quartz glass window, which allowed recording UV/vis spectra in reflectance geometry while controlling the sensor's temperature (300 °C), the atmospheric composition (flow rate 150 sccm) and measuring its resistance (Keithley 199 DMM). The gases were purchased by Westfalen AG with purities described elsewhere and dosed using a home-made gas mixing station [12]. During the experiments in nitrogen the oxygen background was monitored (Zirox, SMG 4) and found to be 5.7 ± 0.4 ppm. For the operando UV/vis-DRS measurements two different samples were measured – undoped

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SnO_2 calcined at 450 °C/8 h and 1000 °C/8 h, denoted as UD450 and UD1000, respectively. The synthesis of the SnO_2 materials and the sensor fabrication is described elsewhere [12].

3. Results and discussion

When exposing a semiconductor to electromagnetic radiation, which photon energy is larger than the semiconductor's band gap, valence band electrons are excited to the conduction band. This excitation of electrons or a UV-induced surface reaction may alter the results of the sensing experiment. Therefore the effect of the UV/vis radiation on the sensors was studied under operation conditions to exclude an impact of the radiation on the experiment. The effect of UV/vis exposure (Supporting Information S1a and b) demonstrates, that the radiation changes the sensor resistance by 2.6% (UD1000) and 12.0% (UD450), which recovers within minutes after stopping the irradiation. In order to analyze the effect of light on the gas sensing properties more in detail, gas sensing experiments were carried out, without UV/vis exposure, with permanent UV/vis exposure and using a shutter only opened for measuring spectra (see Supporting Information S2). The sensor signals ($S = R_{baseline}/R_{gas}$) for 50 ppm CO in dry air were found to be 5.0, 4.7 and 4.9, respectively, i.e. the UV/vis radiation does not significantly increase or decrease the sensor signal. Based on these findings an appreciable beam effect or beam damaging of the sensors can be excluded under operation conditions. However, these findings cannot be generalized for all sensing materials and experimental conditions.

Since there is no effect of the radiation the evaluation of the data does not subject any special restrictions. For both sensors the optical band gaps were estimated in dry air at room temperature and 300 °C by plotting $\alpha h\nu$ as a function of $h\nu$, where E_{Gap} corresponds to the intercept with the x-axis [10,13,14]. The reflectance was transformed in the absorbance using the Kubelka-Munk relation. At room temperature the obtained value 3.65 eV for UD1000 is in line with the literature value of 3.6 eV [14]. The lower value of 3.24 eV for UD450 is most likely caused by a higher oxygen deficiency due to the lower calcination temperature; similar trends are reported in literature [15]. When heating the sensor to 300 °C the optical band gap shifts to 3.48 eV and 2.91 eV for UD1000 and UD450, respectively; these shifts are in line with the ones reported in the literature [14].

Fig. 1 shows the UV/vis reflectance spectra of UD1000 (a) and UD450 (b) recorded in various atmospheric conditions; the corresponding resistance measurements are shown in Fig. 2. The observed resistance changes for CO exposure in dry air and dry nitrogen are in line with previous reports [12,16], i.e. the resistance change is higher in nitrogen. Also as expected, the resistance increases when dosing oxygen in dry nitrogen [17]. For both materials one observes a significant change of the reflectance, depending on the composition of the atmosphere. The decreased reflectance is caused by an increased absorption of the sample, originating from two possible factors: (i) the absorption of the free charge carriers and (ii) the reduction of SnO_2. The free charge carrier absorption is proportional to λ^2 and was found to be dominant above 800 nm [18]. Strong changes of the colour and UV/vis spectrum of reduced SnO_2 phase (SnO_x) are described in literature, e.g. obtained by reducing SnO_2 at 500 °C in vacuum [19]. It should be noted, that the reduction product was not found to be SnO and the changes are ascribed to the formation of oxygen vacancies [19]. In Fig. 1, the largest decrease is observed when dosing CO in the absence of oxygen, i.e. an atmosphere where the reduction of SnO_2 is most effective due to the lack of an appreciable re-oxidation. The spectra of the other atmospheric compositions are found in between the reduced states (300 ppm CO in dry nitrogen) and

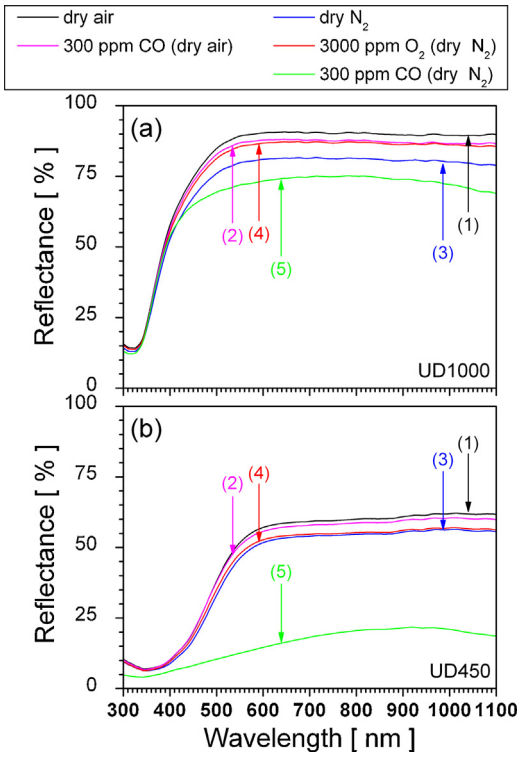

Fig. 1. UV/vis spectra recorded from UD1000 (a) and UD450 (b) in different gas atmospheres: dry air (1), 300 ppm CO in dry air (2), dry N_2 (3), 3000 ppm O_2 in dry N_2 (4) and 300 ppm CO in dry N_2 (5). The sensors were heated to 300 °C during all experiments.

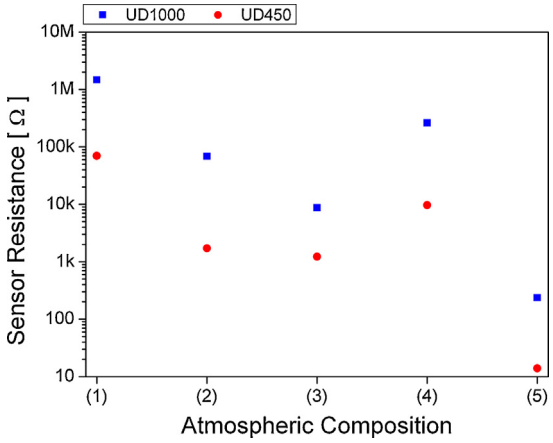

Fig. 2. Sensor resistance of UD1000 (blue squares) and UD450 (red circles) measured simultaneously to the spectra (Fig. 1) in different gas atmospheres: dry air (1), 300 ppm CO in dry air (2), dry N_2 (3), 3000 ppm O_2 in dry N_2 (4) and 300 ppm CO in dry N_2 (5). The sensors were heated to 300 °C during all experiments. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the spectra recorded in dry air. The less effective reduction of SnO_2 in oxygen containing atmospheres can be ascribed to the interplay of reduction and re-oxidation of SnO_2 as recently propose from current IR-spectroscopic measurements [12]. However, even under CO exposure in the absence of oxygen UD1000 and UD450 still present band gaps at 3.50 eV and 2.88 eV, respectively, which are attributed to SnO_2. Similar band gaps were found for the dry nitrogen atmosphere: 3.48 eV and 2.88 eV, respectively. Consequently, both materials may still have unaffected regions of the grains, i.e. a bulk volume, excluding a full reduction of the SnO_2 grains. As visible form Fig. 1, the reflectance of UD1000 and