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Mechanistic Model for UV light-enhanced NO_2 Sensing utilizing Ordered Mesoporous In_2O_3

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Abstract

Results on light-enhanced NO_2 sensing utilizing ordered mesoporous In_2O_3 are presented and interpreted by means of a new sensing model for ordered mesoporous indium oxide (In_2O_3) [1]. This model aims to explain the drop in electronic resistance of n-type semiconducting In_2O_3 under UV light exposure as well as the light-enhanced sensing properties to oxidizing gases. Compared to the conventional double Schottky model [2] the dominating factor for the resistance change is a change of oxygen vacancy donor states in the bulk phase due to photoreduction [3]. Comparison of conductivity measurements with varying oxygen partial pressure for ordered mesoporous and non-structured material shows an accumulative behavior in the case of the mesoporous material which can be related to faster photo reduction caused by the nanostructure. IR measurements reveal a donor level of 0.18 eV below the conduction band attributed to oxygen vacancies. The unique properties resulting from the structure allow low-temperature sensing of NO_2; especially the recovery times are significantly shorter for the mesoporous material.

Key words: mesoporous In_2O_3, photoreduction, oxygen donor level, low temperature, NO_2 sensor

Introduction

Cubic In_2O_3 is considered as an important material for the fabrication of sensitive layers for resistive gas sensors. Since it is particularly sensitive to oxidizing gases such as O_3 or NO_2 [4] but nearly insensitive to reducing gases (e.g. CO, NH_3, hydrocarbons) at low temperatures (100 – 150 °C) [5] it bears an inherent low cross-sensitivity to reducing gases. However, a low operating temperature for sensing O_3 or NO_2 results in long recovery times of the sensor signal. It is known, though, that illumination of the sensing layer with UV light (400 nm) [6] reduces recovery times by light-induced desorption of adsorbates. However, in non-structured ('bulk') In_2O_3 oxygen diffusion in the crystal lattice is slow [7] and therefore predominant over short-term effects caused by surface adsorbates.

To overcome this disadvantage ordered mesoporous In_2O_3 with high surface-to-volume ratio and nanometer–sized structure is used. Owing to the thin pore walls of the nanostructured material and their high accessibility for both gas molecules and UV light, oxygen diffusion in the crystal lattice does not play a major role any longer, and light-enhanced sensing even at room temperature is possible as will be shown for the example of NO_2.

Experimental

Mesoporous In_2O_3 was synthesized by structure replication (nanocasting) utilizing mesoporous KIT-6 silica as a rigid matrix [1] in two consecutive steps. In the first step ordered mesoporous silica is synthesized by utilization of supramolecular aggregates of amphiphiles as a structure director (soft template). In the second step the pores of the rigid silica matrix are filled with an indium oxide precursor ($In(NO_3)_3$) which is converted by thermal treatment to indium oxide. The silica matrix is

removed by chemical etching (NaOH). The mesoporous In_2O_3 has typical pore sizes and pore wall thicknesses of ca. 5 nm as confirmed by N_2 physisorption and an ordered periodic pore structure (verified by X-ray diffraction). For sensor fabrication the material was dispersed in water and deposited onto sensor substrates.

Sensing Model

We have recently discussed the impact of UV light on the electronic resistance of In_2O_3 in terms of a photoreduction effect [3]. Light-induced desorption of surface adsorbates leads to faster sensor signal recovery at room temperature. The pore wall thickness of the mesoporous In_2O_3 is below the UV light penetration depth (ca. 10 nm [8]), which explains a substantially faster signal recovery than for bulk In_2O_3 where slow lattice diffusion of oxygen becomes predominant (see figure 1).

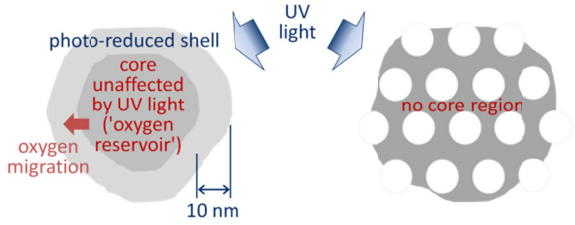

Figure 1. Model of the photoreduction effect in bulk-phase (granular) In_2O_3 with grain sizes significantly above the UV light penetration depth (left) and mesoporous In_2O_3 with a nanostructure which is nearly entirely affected by UV illumination (right) [3].

Results and Discussion

Figure 1 shows low-temperature (50 °C) NO_2 gas-sensing measurements using mesoporous In_2O_3. The photoreduction properties of the mesoporous In_2O_3 have strong influence on the sensing behavior. The gas response time is substantially shorter for the illuminated sensor; in the non-illuminated case the sensor does not reach a response level close to saturation within the measured time frame of 900 s. As in case of ozone sensing [9] this is attributed to photo-induced desorption. Also the response in the illuminated case is significantly higher at 50 °C operating temperature. In the framework of a new sensing model the sensing effect is described in terms of changes in oxygen defects and, hence, oxygen donor concentration, as opposed to the standard model based on a surface effect with adsorbate-caused depletion layers. Slow lattice diffusion of oxygen does not play a major role in the nanostructured material (contrary to bulk In_2O_3). The penetration depth of the light and the resulting photoreduction effect is above the thickness of the pore walls. Hence, in the mesoporous material nearly the entire volume is affected by the light treatment while in conventional, granular materials (diameter > 10 nm) slow diffusion of oxygen from the core regions (unaffected by light) to the outer regions occurs.

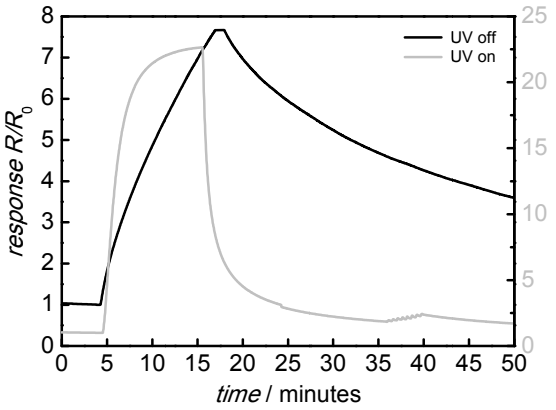

Figure 2: Gas response of mesoporous In_2O_3 to 5 ppm NO_2 at 50 °C operating temperature with and without illumination (400 nm). (The response is defined as R/R_0; R and R_0 are the electronic resistances in the presence and absence of NO_2.)

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