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Assessment and modeling of NH_3-SnO_2 interactions using individual nanowires

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Abstract

To date, studies on the interactions between ammonia and monocrystalline SnO_2 surface have been scarcely explored in real conditions. On the contrary, thin and thick films are used to that end, despite their electrical signal is affected by intrinsic limitations that distort the response. Here, individual and well-faceted SnO_2 nanowires were used as sensors in which the ammonia detection characteristics of this metal oxide were evaluated. After confronting experimental data with simulations, it was concluded that both lattice and pre-adsorbed oxygen species play a key role to complete the reaction pathway of ammonia onto SnO_2, with N_2 and H_2O as resulting products. This explained the response and dynamics of such devices as function of ammonia concentration and temperature. Moreover, the blocking influence of humidity on the ammonia response was explored. These results provide new insights into the fundamentals of the NH_3-SnO_2 interactions.

Keywords: SnO_2; NH_3; H_2O; sensing; modelling; DFT; nanowire; FIB

1. Introduction

NH_3 is a dangerous pollutant with a characteristic pungent odour, highly toxic for fishes and amphibians even at diluted concentrations [1]. The exposure to high concentrations of this gas can result in lung damage and, in the worst cases, in death for humans [2]. Ammonia is thus classified as dangerous by international regulations [3-4]. For this reason, real-time detection of NH_3 in practical applications, such as air quality monitoring in commercial airplanes and control of power production plants and

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chemical industry, is a must. Moreover, new technologies employing this compound as energy carrier also require sophisticated safety controls [5].

From more than five decades ago, metal oxides in form of thick or thin films have been used to monitor the presence of air pollutants, being NH_3 detection a field of research in which significant progress has been made both in terms of fundamental understanding of the chemical reactions involved in the sensing mechanisms as well as on the technological development of devices [6]. Traditionally, WO_3, MoO_3 and In_2O_3 have been the preferable metal oxides for this purpose [7].

To date, quasi-one-dimensional (1D) metal oxides nanostructures, such as nanowires and nanotubes, have shown promising features for gas sensing, optoelectronics and energy applications [8-11], and offer unique properties to develop innovative technologies [12-14]. Working into the direction of nanowire-based systems, the integration of active characteristics in a single device remains a challenge and concentrates intensive research efforts [12-13]. In this context, SnO_2 nanowires have been used to detect NH_3 in the same manner as SnO_2 nanoparticles and films [15-17]. Recently, it was demonstrated that SnO_2 nanowires showed even better NH_3 gas-sensing performances than that of ZnO and WO_3 nanowires sensors [18]. Moreover, the integration of individual SnO_2 nanowires in microhotplates was successfully demonstrated[19].

In this work, we report on the prototyping of individual SnO_2 nanowire devices and the study of their NH_3 sensing characteristics in terms of sensitivity and device stability, paying special attention to the interfering effects by humidity. Actually, the electrical properties of SnO_2 nanowires are strongly influenced by environmental moisture [20-21], and interfering cross sensitivity with target analytes such as NH_3 may play a key role that will determine the use of metal oxide nanowires in real applications. Here, we evaluate the degree of interaction and model the competing effect between the two gases. On the whole, our experimental data on NH_3 sensing were confronted to Density Functional Theory (DFT) calculations, demonstrating that SnO_2 nanowires show excellent responses to this pollutant. These results may significantly advance our present knowledge of the state of the art of SnO_2 nanotechnologies.

2. Experimental details

As-grown SnO_2 nanowires grown by CVD were dispersed in ethanol by sonication [22]. Later, a drop of this suspension was put onto a chip with pre-patterned gold microelectrodes. Individual nanowires were electrically contacted by direct Focused-Ion-Beam (FIB) platinum deposition, using a FEI Dual-Beam Strata 235 instrument combined with a trimethyl(methylcyclopentadienyl)platinum [$(CH_3)_3CH_3C_5H_4Pt$] injector to deposit platinum, following a process described elsewhere (Fig.1) [23]. Electrical measurements were performed using a Keithley 2400 Source Meter Unit (SMU). For gas sensing experiments, the devices were placed in a Linkam chamber with an integrated heater; the gas flow ($\geq$ 99.999% purity) was regulated by mass flow controllers and the working temperature was never higher than 380 ºC to avoid damaging FIB contacts [24-25]. DFT calculations were performed with the Vienna ab-initio simulation Package (VASP). Core electrons were represented by the projector-augmented wave (PAW) potentials while plane waves were used to represent valence electrons. A cut off energy of 400 eV for the kinetic energy of these plane waves was applied and the Revised-Perdew-Burke-Ernzerhof (RPBE) functional was chosen to treat the exchange correlation potentials. The surface slab used to perform the calculations contained five SnO_2 (110) layers with a (2×1) supercell configuration.

3. Results

The typical performance of an individual nanowire when exposed to NH_3 is depicted in Fig.1. As expected, the sensing mechanism in SnO_2 is a thermally activated process with a maximum response in

the range from 215 to 250 ºC. At this temperature, gas concentrations from ppb to hundreds of ppm were detected without evidence of saturation at the highest values. This result is in good agreement with previous reports [19], and it shows that surface coverage of chemisorbed NH_3 was much lower than that of oxygen $\theta(NH_3) < \theta(O^-)$ in the tested analyte concentration range, according to a model developed previously [26]. Actually, the sensing mechanism of NH_3 in SnO_2 is usually explained in terms of the interaction between ammonia molecules and both adsorbed and lattice oxygen species at the surface. The reaction energy of the sensing path that potentially describe this interaction, with the main resulting products N_2 and H_2O, was evaluated by theoretical calculations ($\Delta E = 0.54$ eV) demonstrating that NH_3 undergoes a complex dehydrogenation process before completing the sensing response;

$$SnO_2 + NH_3 \rightarrow \tfrac{1}{2}\, N_2 + SnO_{2-x} + 3/2\, H_2O \qquad (1)$$

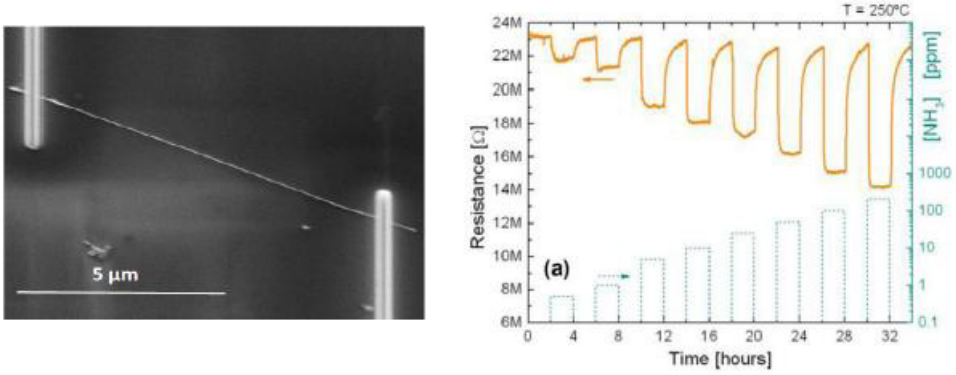

Fig. 1 (left) General view of a SnO_2 nanowire device after the FIB-fabrication process. (right) SnO_2 nanowire response towards sequential pulses of ammonia (500 ppb to 200 ppm) in dry air at a temperature of 250 ºC.

The coupled effects between H_2O and NH_3 for a single nanowire sensor revealed a competing mechanism between the two gases, since the sum of the responses did not correspond to the simple addition of individual ones (Fig.2). In fact, the response to ammonia was always lower in humid synthetic air, up to 80 %, than the value monitored in dry synthetic air. This is a serious drawback for real applications in which fluctuating humidity level in the environment may lead to false NH_3 concentration read-outs. For this reason, the design of future devices should take into account this effect. To minimize it, the use of external filters might be considered an effective solution.

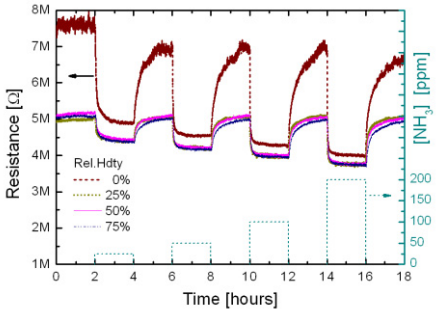

Fig. 2 SnO_2 nanowire response towards sequential pulses of ammonia (25 to 200 ppm) in dry air and different humidity levels at a temperature of 250 ºC.

4. Conclusions

In summary, the sensing performances of individual SnO_2 nanowires grown by CVD were evaluated. By investigation of the sensitivity, recovery time and device stability, it was found that SnO_2 nanowires exhibit excellent characteristics to be used with this purpose. NH_3 concentrations ranging from ppb to hundreds of ppm were successfully detected without any signal of response saturation. The optimal working temperature was found around 235 ºC, low enough to guarantee any damage of the FIB-electrical platinum used to contact the nanowires. Under these conditions, some of these devices were operated for long periods (months) without any evidence of degradation. NH_3 response was strongly hindered with increasing moisture, revealing the competition for the adsorption sites on the surface responsible for sensing. This should be taken into account as a critical point when transferring SnO_2 nanowires to real NH_3 applications in which moisture is commonly present in air. Finally, DFT calculations showed the key role of oxygen species at the metal oxide surface to complete the reaction pathway of ammonia onto SnO_2, with N_2 and H_2O as resulting products.

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