Giant Chemo-Resistance of SnO disk-like structures

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A R T I C L E    I N F O

Article history:
Received 24 January 2013
Received in revised form 21 May 2013
Accepted 26 May 2013
Available online 3 June 2013

Keywords:
SnO
Giant chemo-resistance
Gas sensor

A B S T R A C T

Single crystalline SnO micro-disks, synthesized by a carbothermal reduction process, exhibited a nearly 1000-fold increase in resistance upon exposure to 100 ppm of NO₂ without addition of catalysts or dopants nor the existence of nano-sized dimensions. Moreover, the SnO displayed a greater than 100-fold selectivity to NO₂ over potential interferents including CO, H₂ and CH₄. The high sensor signal and exceptional selectivity for this novel sensor material are attributed to the existence of a high density of active lone pair electrons on the exposed (001) planes of the single crystalline SnO disks. This, thereby, identifies new means, not utilizing nano-dimensions, to achieve high gas sensitivity.

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1. Introduction

The increase in harmful gas emissions and the resultant threat to public health, particularly in urban environments, has stimulated research aimed at the development of highly sensitive and selective gas sensors suitable for air-quality monitoring [1]. NOₓ, CO, H₂S are considered particularly harmful to public health, even at low concentrations, given their negative impact on the human respiratory system [2,3]. Detection of these pollutant gases at ppm and ppb levels, with high sensitivity and selectivity, remains a major challenge [4]. While there are a number of means for detecting gases based on optical, gravimetric and electrical approaches, those based on monitoring changes in resistance of semiconducting oxides upon surface adsorption/desorption of gases (chemoresistance) offer key advantages including low cost processing, simple design and measurement, coupled with relatively high sensitivity [5–9]. SnO₂ has been the most highly investigated material in this class of sensors [10]. This has included investigation of different fabrication approaches to form thin films [11], nano [12–14], mesoporous [15], and macroporous structures [16,17], as well as the impact of various catalysts and dopants on sensor response [18–20]. To achieve higher sensitivity and selectivity, more complex multilayered and metal functionalized structures based on SnO₂ have been reported [21–23]. Despite these efforts, it has been difficult to obtain simple devices which combine high sensitivity and selectivity with long-term stability.

While SnO₂ is one of most studied materials for gas sensors applications, to the best of our knowledge, no sensor response has been reported for tin monoxide, SnO. This is not surprising given the difficulty in synthesizing this phase and its thermal decomposition at temperatures above 400 °C [24,25]. SnO is reportedly a p-type semiconductor with a tetragonal lattice (alpha lead monoxide) structure, layered in [001] direction and a band gap between 2.5 and 3.0 eV [26,27]. Recently, we have successfully synthesized SnO structures by a carbothermal reduction method, displaying both thermal and chemical stability for temperatures below 400 °C [25,28]. In this work, we report, for the first time, the gas sensor properties of SnO disk-like structures. As demonstrated below, these disk-like structures exhibit nearly three orders of magnitude change in resistance upon exposure to nitrogen dioxide gas at temperatures below that typical for oxide chemiresistors. The observation of “Giant Chemo-Resistance” (GCR) in SnO, not dependent on nanosize dimensions, we believe, opens up a new class of promising materials with exceptional gas sensor capabilities and unique surface chemistry.

2. Experimental

Disk-like structures were synthesized by a carbothermal reduction method using SnO₂ powder (Sigma–Aldrich, 99.9% purity) and carbon black (Union Carbide, >99% purity) in the molar ratio of 1.5:1(SnO₂:C). Optimized parameters used and details of this synthesis were previously reported [29]. Following synthesis, a dark wool-like material was removed from the inner walls of the alumina tube which had been maintained at a temperature between

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http://dx.doi.org/10.1016/j.snb.2013.05.087
350 and 450 °C. Both SnO nanobelts and disk-like structures were obtained in this synthesis, but it was possible to separate them by a sedimentation process in isopropyl alcohol. The main focus of this work is on the sedimented material (i.e., the micro-disks) which was separated and dried at 50 °C.

The morphological characteristics of the disk-like structures were examined by field emission scanning electron microscopy (FEG-SEM; JEOL, JSM-7500F). The phase and the crystallinity of the disk-like structures were studied by X-ray diffraction (XRD; Shimadzu, XRD 6000) using Cu Kα radiation and transmission electron microscopy (TEM; Philips, CM200) operated at 200 kV. Specific surface area was determined by the Brunauer–Emmett–Teller method (BET; Micromeritics instrument, ASAP 2000) under N2 adsorption/desorption experiments [30]. For the gas sensing measurements, the collected material from the sedimentation process was dispersed in isopropyl alcohol with the aid of an ultrasonic cleaner. This was followed by dripping the suspension directly onto alumina substrates coated with interdigitated platinum electrode arrays (100 μm Pt fingers spaced 200 μm apart). The substrates were then heated to 100 °C for 15 min to evaporate the solvent. Gas sensing tests were carried out by monitoring changes in resistance (using an HP34970A data acquisition switch unit) during cyclic exposure to different concentrations of NO2 (between 1 and 100 ppm) and H2, CH4, and CO (10 to 500 ppm) diluted in dry air (baseline gas). For this purpose, certified pre-mixed gas mixtures, containing a trace of the test gases diluted in dry air [NO2 (100 ppm) and H2, CH4, and CO (1000 ppm)] (Air Gas) were mixed with clean dry air, using mass flow controllers (MKS). The total gas flow rate (test plus balance gas) was maintained constant (200 sccm) during all tests. The sensor test devices were equilibrated in dry air for 12 h at each temperature before the beginning of each gas sensor measurement to insure a stable and reproducible baseline resistance. Gas sensor measurements were performed in the range from 100 to 300 °C with steps of 50 °C and the sensor signal was defined as \( R_{\text{gas}} / R_{\text{air}} \) for oxidizing gases and as \( R_{\text{air}} / R_{\text{gas}} \) for reducing gases, where \( R_{\text{air}} \) is the material resistance in air atmosphere and \( R_{\text{gas}} \) is the material resistance under the analyte gas presence.

In order to study the disks chemical stability during sensor test measurements, in situ X-ray Absorption Near Edge Spectroscopy (XANES) at the L-edge of Sn was performed during a simulated sensor test at the Brazilian Synchrotron Laboratory. To prepare the sample for XANES analysis, 2 mg of SnO disks were mixed with 50 mg of boron nitrite (BN) in an agate mortar. The powder was then pressed in a 12 mm diameter pellet at 8 kPa. The sample was mounted on a sample holder specially designed for in situ XANES measurements at high temperature, which was then introduced in a quartz tube furnace. XANES measurements were performed from 3900 to 4050 keV with sample maintained at 200 °C (best sensor response temperature). After reaching 200 °C under a N2 gas flux of 100 sccm, the sample was stabilized for 3 h following which the first spectrum was taken. The N2 was then substituted by dry air also at a flow rate of 100 sccm and another spectrum was taken after 30 min. Finally, the gas was switched back to pure N2 and a final spectrum was taken after 1 h. The spectrum of a SnO2 standard sample was also taken for comparison.

3. Results and discussion

Fig. 1 presents FEG-SEM images of the collected material, following separation by sedimentation, showing it to be predominantly composed of disk-like structures with flat and smooth surfaces. These disks have diameters ranging from about 100 nm up to dozens of micrometers. The smaller disks (in general, disks less than 1 μm diameter – Fig. 1b) exhibit an octagon-like faceted shape, while the larger disks are nearly perfectly circular in shape (Fig. 1c). Most disks have diameters greater than 1 μm and these structures are similar to those reported previously in the literature [24,28].

Fig. 2a shows a low-magnification TEM image of a disk with diameter of about 200 nm and faceted shape. The inset in Fig. 2b presents the SAD pattern of this disk and the isolated spots obtained are typical of single crystalline materials. All of the spots in the SAD pattern can be indexed by the latticestructure of SnO (tetragonal) (JCPDS card #6–395), agreeing with XRD results (not shown here). Fig. 2b also shows an HRTEM image of the disk, confirming that each disk is single crystalline. Occasionally, misoriented particles can be found at the disks’ extremities. The interplanar distance shown in Fig. 2b is 0.27 ± 0.01 nm, related to the (1 1 0) planes of the tetragonal structure of SnO, as observed by SAD. Combining SAD and HRTEM results, it was possible to affirm that the larger facets are (1 1 0) planes while the smaller ones are (1 0 0) planes, which is the same orientation observed by Dai et al. [24]. Moreover, the larger faces of the disks must be the (001) planes, which is perpendicular to the zone axis of the diffraction pattern.

Typical gas response measurements (\( R_{\text{NO}_2} / R_{\text{air}} \)) taken at 200 °C, as a function of time for periodic pulses of gases containing NO2 ranging from 1 to 100 ppm, each pulse lasting 20 min, are shown in Fig. 3. The sensor based on SnO disk-like structures exhibited a remarkably strong response when exposure to NO2 with an approximately 50-fold increase in resistance when exposed to 1 ppm NO2 and nearly a 3 orders of magnitude response to 100 ppm NO2. Given the exceptionally high sensitivities observed here, in combination with the fact that this is achieved without need for nano-structuring the material down to the 10 nm regime (see discussion below) and the chemosorption phenomenon nature related to it, we label this response “Giant Chemo-Resistance” (GCR).
For all levels of NO₂, the resistance \( R_{\text{res}} \) initially increases abruptly when exposed to the analyte gas, followed by an asymptotic change to the steady state with a similar behavior, but slower, observed for the recovery process. This is a typical n-type semiconductor sensor response, although SnO has been reported previously to be a p-type material [26,27]. Clearly, a wide band gap semiconductor such as SnO (\( \text{E}_\text{g} > 2.5 \text{eV} \)) can be either n or p type, depending on the doping or redox level. Given that the SnO investigated in this study was synthesized by a carbothermal reduction method, it is not surprising that these SnO specimens may be more oxygen deficient than those reported earlier and thus exhibiting n-type behavior. Thermopower and Hall effect studies are planned to determine the carrier density.

The sensor response to 100 ppm NO₂ versus temperature is shown plotted in Fig. 4, clearly demonstrating that the optimum operating temperature with respect to sensitivity is in the range of 200 °C. This is presumably a consequence of the competition between slow gas adsorption kinetics at lower temperatures and enhanced desorption at higher temperatures [31].

To study the oxidation state and the chemical stability of disks under different atmospheres at 200 °C, XANES measurements were performed under in situ conditions simulating the sensor test measurements. If any variation in the tin oxidation state should occur, a change in XANES spectrum would be observed. Fig. 5a shows the XANES spectrum obtained for the sample after 3 h stabilization in pure N₂ flux. It has four main absorption peaks, labeled as i, ii, iii and iv, characteristic of the SnO material spectrum [32], thereby confirming the +2 oxidation state of Sn in the micro disks. Comparing this result to the SnO₂ standard in Fig. 5d, it is clear that the SnO₂ signature (broad peak labeled 3,4,5) related to the \( 2p_{3/2} \rightarrow 6d \) transition, is not present in the XANES spectrum obtained for the SnO disks. Fig. 5b shows the XANES spectrum for the SnO disk sample following a 30 min exposure to dry air atmosphere while Fig. 5c displays the spectrum obtained after 1 h stabilization in pure N₂ following the dry air exposure. No change in the spectrum occurs for the SnO sample using either inert or oxidizing atmospheres, indicating good chemical stability for the SnO disk-like structures. The stability against oxidation of SnO to SnO₂ at 200°C was expected given that the observed degradation of SnO at about 400 °C is not an oxidation process, but a thermal activated decomposition process [25].

The sensor signal was found to follow a power law dependence on gas concentration of the form \( R \propto \rho \text{NO}_2^\beta \), with \( \beta \) in this case taking on the value of 0.64. Assuming that this dependence continues to
hold to lower NO₂ concentrations, a sensor response of ~13 is estimated for an exposure to 100 ppb of NO₂ [9]. This easily satisfies the National Ambient Air Quality Standards (NAAQS) requirement of being able to detect 100 ppb per hour, the standard for public health protection set by the U.S. Environmental Protection Agency [33]. It is important to reiterate that this outstanding response was obtained at 200 °C, well below the phase transition temperature observed for disk-like structures, therefore insuring stable operation [25]. Furthermore, given the micron rather than nanometer dimensions of these disks, their morphology should be less susceptible to coarsening with time and thereby less likely to exhibit short-term aging affects. Moreover, the level of sensitivity to NO₂ obtained here is one of the highest reported for catalyst-free tin-based chemiresistors. Few other GCR response reports have been published using catalyst-free SnO₂ systems [11,34].

Gas measurements were also performed to investigate the selectivity of SnO₂ disk-like structures to NO₂ versus other potential interferents. The sensor response for 100 ppm of NO₂, H₂, CO, and CH₄ in air at 200 °C is shown in the inset of Fig. 4. The sensor response was more than 200-fold larger for NO₂ than for H₂ and CO and nearly 1000-fold larger than to CH₄, demonstrating the remarkably high selectivity to NO₂ relative to these other common interference gases [21,35].

Gas sensor performance is highly influenced by surface area, with larger surface area leading to higher sensitivity [36,37]. In the present case, Brunauer–Emmett–Teller (BET) measurements shows a specific surface area of 8.0 m² g⁻¹, which cannot explain the giant gas response observed for the SnO₂ disk-like structures itself. Since the reports of Xu et al. in 1991 [38], showing markedly enhanced sensitivity of SnO₂ to CO and H₂ gases, as the dimensions of the SnO₂ particles decreased below 20–50 nm, many further reports of enhanced sensitivity of nanodimensioned metal oxide chemiresistive sensors have been reported [39,40]. These empirical observations were successfully modeled by Rothschild et al. [41] who took into account the unique characteristics of space charge regions in nanocrystalline semiconductors. This model accounts for the fact that when the radius of the grains, or the thickness of the film becomes smaller than the Debye length, typically on the order of 10 nm, the space charge regions generated at the crystallite or film surfaces overlap such that the entire volume of the crystallite or film becomes depleted of free charge carriers, leading to a much stronger modulation of resistance by adsorption of gases. While similar Debye lengths are calculated for SnO₂ (λ_D(SnO₂) ~ 7–20 nm at 200 °C, depending on carrier density), the much larger dimensions of the largely single crystalline SnO₂ disk structures studied here, typically between 70 and 250 nm thick, suggest that charge carrier depletion across the whole thickness of the disks cannot be responsible for the GCR sensor response observed here.

Recently, it was demonstrated that the sensitivity of SnO₂-based sensors can be improved by exposing specific facets at the surface [12], i.e., specific crystallographic planes can lead to higher sensitivity due to the chemical activity. As previously reported [24] and discussed further in this work, the SnO₂ disks studied here are bi-dimensional structures with large (001) exposed surface planes. For litharge structures, it is known that the (001) plane exhibits a high fraction of electronic lone pairs [42,43].

According to recent DFT calculations, the sterically active lone pair, normally ascribed to the filled Sn 5s² orbital, shows instead that the states responsible for the asymmetric Sn electron distribution are due to the coupling of unfilled Sn(5p) with the antibonding combination arising from interaction of Sn(5d) and O(2p) orbitals. These lone pairs, with relatively high energy states at the top of the valence band, can easily be excited by single photon absorption, making the SnO₂ film a potential candidate for chemical sensor applications.

In summary, this paper reports both the Giant Chemo-Resistance (GCR) response to NO₂ and the exceptionally high selectivity of SnO₂ disk-like structures, pointing to their potential use in environmental monitoring and safety applications, as well as serving as a new model system for oxide based semiconducting chemiresistor sensors. Possible sensor mechanisms are proposed with additional studies to be performed to obtain an improved understanding of the source(s) of SnO₂’s outstanding sensor response.

4. Conclusions

Using the carbothermal reduction process, it was possible to obtain temperature and chemically stable SnO₂ submicron and micron sized disk-like structures. The SnO₂ disk-like single crystalline structures exhibit an exceptionally high sensitivity to NO₂ with the highest sensor signal observed at 200 °C. At this temperature, sensor signal approaching ~1000 were observed for sensors exposed to 100 ppm NO₂. Furthermore, exceptional selectivity against potential interferent gases such as H₂, CO and CH₄ was also obtained. This Giant Chemo–Resistance (GCR) effect, suspected to be due to the large and highly active exposed SnO₂ (001) planes, points to this material as a particularly promising new sensor candidate material for detection of NO₂ and other gases of interest as well as identifying new means, not utilizing nano-dimensions, to achieve high gas sensitivity.

Acknowledgements

The authors acknowledge the São Paulo Research Foundation (FAPESP) (Proc. 2009/13491-7 and 2010/51959-8), and The National Council for Scientific and Technological Development (CNPq) (Proc. 200703/2011-3) for financial support to the seed project of international MIT/BRAZIL cooperation. TEM and FEG-SEM
facilities were provided by the IQ-UNESP. The authors also wish to acknowledge the Brazilian Synchrotron Laboratory for XANES facilities at XAFS2 beamline (proposal 14553) and Prof. Elson Longo for his helpful discussions. The authors have no competing financial interests related to this work.

References

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