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Semiconducting tin oxide nanowires and thin films for Chemical Warfare Agents detection

G. Sberveglieri *, C. Baratto, E. Comini, G. Faglia, M. Ferroni, M. Pardo, A. Ponzoni, A. Vomiero

CNR-INFM SENSOR Lab and Università di Brescia, Dipartimento di Chimica e Fisica, Via Valotti 9, I-25133 Brescia, Italy

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ABSTRACT

In this work we report the preparation and structural characterization of tin oxide nanowires as functional materials for the development of chemical sensors. Aspects of material preparation relevant for gas sensing applications, such as the control of the wire diameter, are emphasized. The functional characterization is focused on the detection of Chemical Warfare Agents (CWAs) simulants, with particular regard to poisoning effects induced by dimethyl methyl phosphonate (DMMP), a simulant for Sarin nerve agent. Tin oxide thin films, prepared by means of rheotaxial growth and thermal oxidation (RGTO) technique, are used as reference to better compare the performance of nanowires with thin films traditionally used in gas sensing field.

1. Introduction

Recently, a new class of metal oxide nanostructures has been produced attracting large interest due to their peculiar physical–chemical properties, which arise from the possibility to reduce the crystal size down to the scale of the electronic wave-function [1].

These nanostructures, namely nanowires, nanobelts, nanoribbons, are single crystals growing according to crystalline directions and featuring lateral surfaces corresponding to well defined crystalline planes. Properly setting the synthesis parameters, such structures can be grown according to different crystallographic axes [2] and their size can be controlled within a wide range of scales, so that single crystalline wires can be obtained with lateral dimensions ranging from few nm to few microns [3] and length up to few mm.

Their electrical properties have been widely investigated, showing high electrical mobility [4], typical of single crystals, compared to the lower values exhibited by ceramic materials, whose electrical properties are largely dependent on grain boundaries.

Nowadays, several works are addressed to develop synthesis methods and assembly or manipulation procedures that use such nanomaterials as building blocks for complex architectures and devices [2,5].

Focusing on solid-state gas sensors, the peculiar structure and morphology of nanowires are promising features for the development of highly sensitive and stable gas sensors [6]. In particular, the high sensitivity is related to the nanosized lateral dimensions of nanowires, which can be scaled down to values comparable with the space charge region depth (few tens of nm, [7]) arising from reactions underlying the metal oxide sensing mechanism [7]. The possibility to prepare devices based on single nanowires or aligned nanowires opens the prospective to develop sensors free from grain boundaries, which have been recognized as one of the sources of long time drift in metal oxide ceramic layers. Due to the high temperature (usually 200–450 °C) required to optimize the oxide–gas interaction/transduction mechanisms, ceramic oxides usually undergo grain-coarsening phenomena with time [8]. According to XRD and electron microscopy analysis, these phenomena often start from grain boundaries [9]. Furthermore, it has been shown that nanowires open the prospective to develop gas sensors working at room temperature, based on the principle of electron mobility decreased by adsorbed molecules that act as scattering centres [10].

In this work we report our results on the development of gas sensors based on tin oxide nanowires. The growth method and the underlying mechanisms are described emphasizing those aspects that are fundamental for the preparation of the gas sensor device. The functional characterization is addressed to the detection of Chemical Warfare Agents (CWAs) simulants. In particular, the work is focused on the detection of dimethyl methyl phosphonate (DMMP), a simulant for Sarin nerve agent, with particular regard to its poisoning effects. Results are compared with performance obtained by gas sensors prepared by means of thin-film technology.

2. Materials synthesis and sensor device preparation

2.1. Tin oxide nanowires

Tin oxide nanowires have been synthesized via evaporation–condensation method. This method consists in the evaporation of the metal oxide precursor and the transport of the vapour from the source to the substrates by a gas carrier. The deposition is performed in a tubular furnace, where a temperature profile is obtained by means of three heaters distributed along the tube. The deposition process is carried out at constant pressure (100 mbar), evaporating the tin

* Corresponding author. Tel.: +39 030 3715771; fax: +39 030 2091271.
E-mail address: Giorgio.sberveglieri@ing.unibs.it (G. Sberveglieri).

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dioxide powders at the temperature of 1370 °C. Vapours are transported downstream to colder regions by an Ar flow of 75 sccm. Tin oxide nanowires grow at temperatures ranging from 430 to 470 °C over substrates provided by a catalyst layer (Pt nanoparticles) deposited by DC Magnetron Sputtering [11].

The use of catalyst to control nanowires growth is fundamental for the development of the sensor devices. The metallic seeds act as nucleation sites that promote the growth of nanowire structures according to the Vapour–Liquid–Solid (VLS) or Vapor–Solid–Solid (VSS) mechanism [12,13]. By this method, it is possible to control the nanowire size and density by controlling the seeds size and density.

Differently, the use of non-seeded substrates causes the growth of larger wires. Without seeds, oxide particles (also few μm large) deposit during the initial stage of the condensation process and large wired-structures grow from such oxidic seeds by means of Vapour–Solid (VS) mechanism. A detailed analysis of the different control degree obtained by the use of seeded and non-seeded substrates is reported in [3]. In the same work, the early stage of nanowire growth has been investigated by means of short-time (few minutes) depositions. In such conditions a small amount of oxide condense and it is possible to observe the substrate underlying the deposited oxide. SEM analysis revealed that, once synthesis parameters have been optimized, vapours condensation is promoted only at the catalyst–substrate interface (first) and then, during the nanowire growth, at the catalyst–nanowire interface [3]. This work was fundamental to verify that during the growth of nanowires there is no fraction of vapours condensing to grow a continuous film.

2.2. Tin oxide thin films

Thin films have been deposited by rheotaxial growth and thermal oxidation (RGTO) technique [14,15], chosen in this work as a reference to compare the performance of nanowires with materials traditionally adopted in gas sensing field. Briefly, the RGTO technique consists of two deposition steps: first the preparation of a metallic thin film by DC magnetron sputtering from a tin target on a substrate kept at a temperature higher than the melting point of the metal that causes the formation of separated spherical clusters instead of flat film. Then, the metallic layer undergoes a thermal oxidation cycle in order to get a stable stoichiometric composition. At the same time, the oxidation process increases the volume of such particles that became interconnected forming a conductive path for electrical characterization. Further details can be found in [14].

3. Morphological and structural characterization

3.1. Tin oxide nanowires

As shown in the secondary-electrons (SE) SEM image reported in Fig. 1, nanowires are long structures with uniform lateral dimension (about 100 nm) and very high aspect-ratio. The connected network of nanowires features a large degree of porosity. Extensive TEM analysis [11,12] showed that these nanostructures are single crystals featuring the SnO_2 cassiterite structure and growing along the [101] direction, with atomically sharp termination of lateral sides.

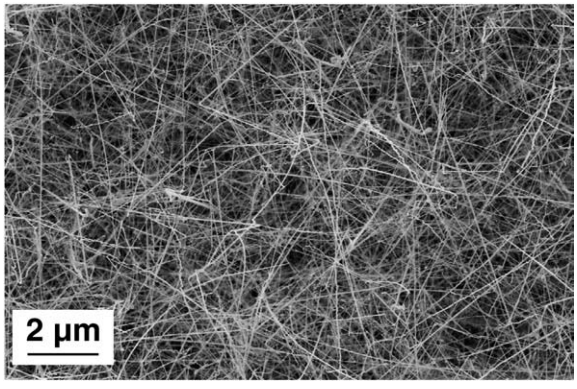

Fig. 1. SE SEM image of tin oxide nanowires.

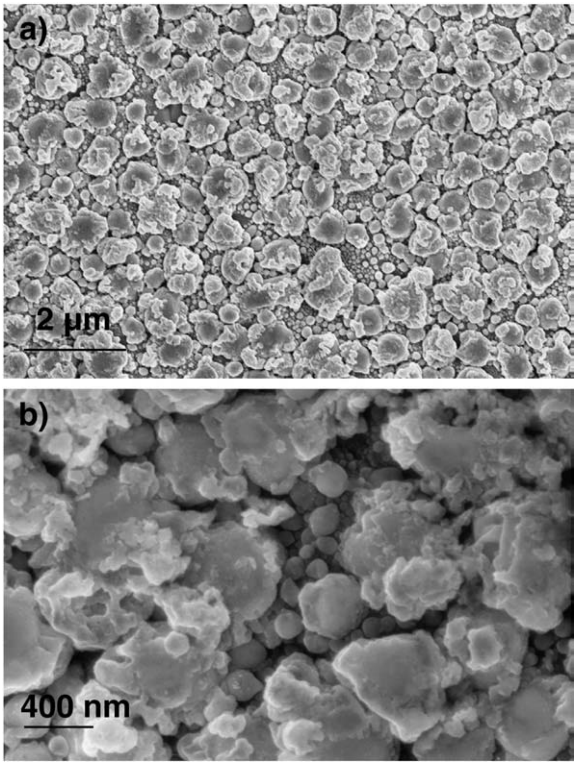

Fig. 2. SE SEM images of tin oxide RGTO film: (a) panoramic view of the layer; (b) highly-magnified image of the polycrystalline RGTO aggregates.

The adsorption mechanism is reasonably supposed to be different respect to traditional layers composed by grains with rounded morphology, i.e. exposing to the environment different crystalline planes. In the nanowire case, the surfaces exposed to the environment correspond to well-defined crystalline planes and surface termination is known to deeply affect surface reactivity [16].

3.2. Tin oxide thin films

RGTO is a deposition technique suited to prepare polycrystalline thin-films composed by interconnected particles (Fig. 2a) with granular morphology and large surface area (at least compared with other thin-film technologies). The highly-magnified SEM image shown in Fig. 2b) reveals the rough surface of the layer and the small crystallites in the agglomerates. According to TEM analysis reported in [14], the aggregates shown in the SEM images are formed by nanometric grains. Crystallites correspond to the cassiterite SnO_2 and feature rounded morphology, thus exposing different crystalline planes to the environment.

4. Gas sensing characterization

For gas sensing characterization, 200 μm spaced Pt electrodes and a Pt meander (that acts both as heater and temperature probe) were deposited on 2 mm × 2 mm × 0.25 mm alumina substrates, where the oxide layer (both for thin films and nanowires) was previously grown.

Gas sensing measurements have been carried out in a temperature-stabilized sealed chamber at 20 °C in constant humidity conditions (relative humidity RH = 30% at 20 °C). According to literature [17–20], dimethyl methyl phosphonate (DMMP) and acetonitrile were used as simulants for Sarin nerve agent and cyanide compounds respectively.