Sensors and Actuators B 238 (2017) 447–454

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Gas sensors based on individual indium oxide nanowire

Guillem Domènech-Gil[a,*], Sven Barth[b], Jordi Samà[a], Paolo Pellegrino[a], Isabel Gràcia[c], Carles Cané[c], Albert Romano-Rodriguez[a]

[a] Universitat de Barcelona (UB), MIND-Departament of Engineering and Institute of Nanoscience and Nanotechnology (IN2UB), c/Martí i Franquès 1, E-08028 Barcelona, Spain
[b] ViennaUniversity of Technology (TUW), Institute of Materials Chemistry, Am Getreidemarkt 9/BC/02, A-1060 Vienna, Austria
[c] Consejo Superior de Investigaciones Científicas (CSIC), Institut de Microelectrònica de Barcelona (IMB-CNM), Campus UAB, E-08193, Bellaterra, Spain

ARTICLE INFO

Article history:
Received 8 January 2016
Received in revised form 1 July 2016
Accepted 17 July 2016
Available online 18 July 2016

Keywords:
Indium oxide
Nanowires
Gas nanosensor
Chemoresistor

ABSTRACT

Indium oxide nanostructures have been prepared by carbothermal reduction method. From them, nanowires have been structurally and optically characterized using X-ray diffraction, scanning and transmission electron microscopy and photoluminescence. The indium oxide nanowires have been removed from the substrate and contacted by Focused Electron- and Focused Ion-Beam Induced Deposition techniques to interdigitates on suspended microhotplates, which allow heating up to 300 °C with a low power consumption of only 8 mW. The gas response of the tested devices towards ethanol, carbon monoxide and nitrogen dioxide diluted in dry synthetic air at different concentrations and temperatures has been carried out showing a selectivity towards ethanol with responses up to 50% at temperatures between 200 and 300 °C, while only small response to high concentrations of carbon monoxide and nitrogen dioxide is observed.

1. Introduction

Indium oxide (In_2O_3) is a transparent n-type semiconductor with a direct band-gap of about 3.6 eV [1]. Among several different applications, In_2O_3 thin films have been widely used as gas sensor for detecting toxic gases in air [2–4]. The use of nanostructured In_2O_3 for sensing gases like NO_2, O_3 or CO, has been reported in literature proving the potential for sensing applications [5–7]. Using nanowires (NWs) as main active components of a sensing system, due to the increased surface to volume ratio of the material combined with their high crystallinity, is expected to give rise to a corresponding enhancement of the sensing properties. A further benefit of such morphology is its considerably lower power consumption as compared to their bulk counterpart, attainable by an adequate device layout, allowing to match the limits required in mobile gas sensing applications [5,6]. Chemical Vapour Deposition (CVD) is extensively employed in the synthesis of In_2O_3 NWs due to the feasibility of growing monocrystalline structures. The NW morphology of the metal oxide semiconducting materials has been demonstrated to present high sensitivities, up to parts per billions (ppb), towards gases like CO or H_2 [5,7–13] as a function of their surface features. However, the selectivity still is an issue, as for most semiconducting metal oxides. Other In_2O_3 morphologies can also be synthesized, such as nanorods or nanooctahedra [14–19] but, due to the difficulty of assembling them individually onto substrates with electrodes for fabricating sensing devices, they remain almost unexplored, while they might present equally interesting properties for gas sensing applications.

Several methods for the synthesis of In_2O_3 nanostructures have been proposed in literature, which can be divided in two broad categories, namely the solution-based techniques and the vapour-phase processes. Liquid- or solution-based techniques include approaches such as electrodeposition [20], which provides a rapid synthesis method for polycrystalline NW growth. Vapour-phase techniques comprehends methods such as molecular beam epitaxy [21], laser ablation [22] as well as CVD [23], among others, which allow the growth of monocrystalline NWs. A drawback related to this latter is the long time needed for the deposition when compared to the electrodeposition technique, due to the high temperatures required for heating up and cooling of the whole quartz tube. A CVD-like process which is less time-consuming and more energy-efficient is based on the growth of monocrystalline NWs on top of microhotplates, using a small heater incorporated in the microstructure, which allows to achieve the temperature required for the precursor decomposition with only few mW [24,25]. However, this approach allows the growth of a NWs network, and does

* Corresponding author.
E-mail address: guillemdom@gmail.com (G. Domènech-Gil).

http://dx.doi.org/10.1016/j.snb.2016.07.084
0925-4005/

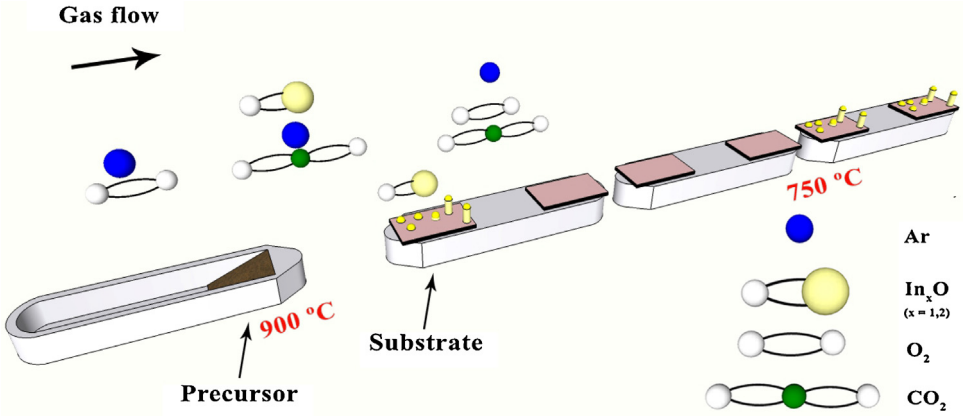

Fig. 1. Scheme of the experimental layout inside the quartz tube furnace used for the growth of indium oxide.

not allow to extract the information of the sensing mechanisms of the individual NWs.

Ethanol limit values for drivers in European countries range between 0.1 and 0.5 mg/l in blood. The conversion of these values into concentration of ethanol in human breath gives values between 30 and 130 ppm. For this reason, ethanol gas sensors would be highly desirable in this established range.

This work focuses on the vapour-liquid-solid (VLS) growth of In_2O_3 nanostructures by CVD in a quartz tube furnace using gold as growth catalyst [21,22]. A comprehensive study will be presented, which includes the growth of different In_2O_3 nanostructures in the deposition chamber, their characterization and the testing of gas sensing properties of devices fabricated on individual In_2O_3 NWs towards different gases, with a special focus in ethanol.

2. Experimental

The synthesis of In_2O_3 nanostructures has been carried out by CVD of In_2O_3 powder reduced by the carbothermal process according to a VLS mechanism, first reported by Wagner et al. [26]. The preparation process started with the precursor material: pure In_2O_3 (99.99%) nanopowder was mixed for 20 min in an agate mortar with graphite powder in a 4:1 wt proportion. For each experiment 0.25 g of precursor material was used. The substrates were $0.5 \times 0.5\ cm^2$ pieces cut from a 4-inch thermally oxidized Si wafer, with a 0.5 μm-thick SiO_2 layer. These substrates were Au sputter-covered for 20 s, which should give rise to a thin and discontinuous Au layer.

The growth was carried out in a 2″ diameter quartz tube inserted into a Lindbergh three-zone furnace, allowing the independent control of the different zone temperatures. The configuration of the furnace limits the temperature difference among the adjoining zones to about 150 °C, constraining the experimental conditions. The solid source of In_2O_3 requires high evaporation temperatures, around 1300 °C, a value that can be lowered by promoting a carbothermal reduction, where the graphite precursor is oxidized to CO_2 by reducing the In_2O_3 to metallic indium, which evaporates at much lower temperatures. A rotatory pump and a gas flow injection system were connected at the end and beginning of the furnace tube, respectively, allowing the mixture of different gases and the control of the internal tube pressure from atmospheric down to 7 mTorr. The CVD gas injection system is formed by 4 MKS Mass-Flow controllers. The indium vapour arising from the reduction of the oxide source material is transported to the collection area by a carrier gas, consisting of pure argon (5 N quality) and very low levels of pure oxygen, with concentrations ranging from 0.003 to 0.1% in volume. The growth experiments have covered a pressure range from 2 to 100 Torr. A sketch of the experimental layout is depicted in Fig. 1, where the location of the precursor and the set of substrates can be identified.

In our experiments, the NW growth occurs when, locating the precursor in the first furnace zone adjacent to the gas injection system, the temperature was fixed at 900 °C. The substrate temperature has been fixed at 750 °C in the central portion of the second furnace zone, with a decreasing temperature slope from this point towards the back-end of the quartz tube where the temperature reaches values around 600 °C. A gas mixture of oxygen diluted in Ar with at a total gas flow rate of 500 ml/min at 100 Torr was used.

The In_2O_3 nanostructures were investigated using a Jeol J7100F Field Emission Scanning Electron Microscope (SEM), a Jeol J2100 Transmission Electron Microscope (TEM) and a Siemens D-500 X-Ray Diffractometer (XRD). Photoluminescence (PL) characterization has been carried out in a home-made setup by exciting the sample with the 325 nm line of a He-Cd laser, with an estimated power density of $10\ W/cm^2$.

The grown In_2O_3 NWs were transferred to microhotplates with pre-patterned electrodes by immersing the substrate in a vial with few millilitres of pure (96%) ethanol, sonicating the vial to promote the detachment of the nanostructures from the growth substrate's surface and depositing solution droplets onto the microhotplates. Each microhotplate, fabricated by surface micromachining, contains a buried Pt heater and pre-patterned Ti/Pt microelectrodes, with a thickness of 5/80 nm, respectively. The heating area is located only in the microhotplate, allowing to reach temperatures up to 300 °C with a power consumption of 8 mW. In_2O_3 NWs were electrically contacted using a using a FEI Dual-Beam Strata 235 or a FEI Helios Nanolab 650 (FIB) instruments, equipped with a trimethylcyclopentadienyl–platinum ($(CH3)_3CH_3C_5H_4Pt$) injector for Pt deposition. The electron and the Ga^+ ion beams were accelerated to 5 and 30 kV, respectively. The complete procedure for this contact fabrication method is explained in detail elsewhere [27] and is used to prevent any exposure of the NW to Ga ions that would modify the structural and electrical properties of the NW. Finally, the chips containing the microhotplates were glued to a TO-8 support and electrically contacted using a ball bonding machine. The gas sensing measurements are performed inside a self-constructed stainless steel gas chamber, of 8.6 ml volume, connected to a Gometrics MGP2 gas mixer with 4 Bronkhorst Mass-Flow Controllers. Constant flow of 200 ml/min was kept for the gas measurements. A Keithley 2602A dual Source Measure Unit allowed to control simultaneously the sensor's resistance and the voltage for heating the microhotplate. Electrical measurements and flowing gases were controlled by a home-developed Labview software.

Several gas sensors containing, each of them, one single contacted In_2O_3 NW was characterized towards different gases