Journal of Molecular Catalysis A: Chemical 305 (2009) 170–177

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

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

Metal oxide nanowires: Preparation and application in gas sensing

Elisabetta Comini*, Guido Faglia, Matteo Ferroni, Andrea Ponzoni, Alberto Vomiero, Giorgio Sberveglieri

SENSOR Lab, CNR-INFM, Brescia University, via Valotti 9, 25133 Brescia, Italy

ARTICLE INFO

Article history:
Available online 19 January 2009

Keywords:
Nanowires
Metal oxides
Gas sensors
Heterostructures
Acetonitrile

ABSTRACT

Quasi one-dimensional nanowires of metal oxides are promising for the development of nano-devices. Sn, In, and Zn oxides were produced in form of single-crystalline nanowires through condensation from vapor phase. Furthermore longitudinal and radial heterostructures have been prepared. Nanowires growth occurs in controlled condition and allows the exploitation of size reduction effects on the electrical response to gases. Preparation, microstructural, morphological and electrical characterizations of nanowires are presented and the peculiarities of these innovative structures are highlighted.

1. Introduction

One-dimensional metal oxide semiconductor (MOX) nanowires, are interesting components for bottom-up fabrication of nanoscaled devices.

One-dimensional semiconducting nanostructures have extensive applications in sensors [1–4] optoelectronics [5], electronics, and photonics [6–11].

Nanowires bundles of metal oxides have been recently investigated for application in dye sensitized solar cells (DSC), due to their low electrical resistivity with respect to polycrystalline networks like TiO_2 nanograins presently applied in Graetzel cells [12,13].

Thanks to their intrinsic dimensions (diameters of 20–100 nm and lengths of a few micrometers) the devices produced can be very small, may have improved performance, extremely reduced power consumption that makes them appealing for applications in biological devices, nanorobotics, security monitoring, and defense technology.

The gas-sensing field for example has been extremely reassessed by the advent of quasi one-dimensional nanostructures. Quasi-1D semiconducting metal oxides, carbon nanotubes, and nano porous materials have been used as sensing elements for the preparation of conductometric sensors. They have several properties attractive for chemical sensing application: their high surface to bulk ratio; most of the atoms are available for surface reactions with surrounding molecules. The Debye length (a measure of the electronic 'cross-talk' between the surface processes and bulk electronic structure) is comparable to their lateral dimension therefore electronic properties are strongly influenced by surface processes. Moreover, nowadays fine control over the faceting, morphology, composition, doping level, defined stoichiometry and high crystallinity can be achieved. On the contrary in traditional polycrystalline gas sensors, the high temperature required for the surface reactions to take place induces a grain growth by coalescence and prevents the achievement of very stable materials. The required anisotropic growth can be obtained in different conditions, due to the crystallographic structure of the substrate, to the confinement obtained by a template, controlling other growth parameters. We have focused our research to the technique used for the preparation of most of single-crystalline gas sensor, i.e. bottom up processes.

This work presents the preparation of Sn and In oxide nanostructures focusing on their exploitation for nanoelectronic applications. A methodology to prepare hetero structures and conductometric gas sensors is presented. The functional tests have been focused on the conductometric devices for acetonitrile (C_2H_3N) sensing. The importance of detecting acetonitrile (in the following shorted as ACN) is strongly due to warfare applications, where it is used as simulant for cyanide compounds during the development of cyanide detectors [14,15]. Few works have been published yet concerning the use of metal oxide based gas sensors to detect similar gases, most of them focused on tin oxide layers prepared by thin or thick film technologies. These works showed the suitability of such materials to detect ACN at ppm concentrations, but further work is necessary to exploit the contribution hat these materials could give to the field, especially using nanowires based devices, which open the prospective of achieving improved sensitivity and stability.

2. Experimental

2.1. Preparation procedure

Metal oxide nano-crystals have been prepared according to the recently proposed evaporation–condensation process, with

* Corresponding author.
E-mail address: comini@sensor.ing.unibs.it (E. Comini).

1381-1169/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2009.01.009

Vapour–Solid (VS) and Vapour–Liquid–Solid (VLS) growth mechanism. Such a deposition technique consists of thermally driven evaporation of bulk metal oxides followed by condensation.

The materials studied were In oxide and Sn oxide. The experimental set-up for the oxide deposition consists of a high temperature alumina furnace capable to activate decomposition of the oxide precursors and to promote evaporation. The evaporation temperature was 1500 °C and 1370 °C for In oxide and Sn oxide, respectively. The controlled pressure of the inert atmosphere and the gradient of temperature within the furnace allow condensation and nucleation of the nanostructures downstream the inert Ar gas flow. The pressure was in the range 50–200 mbar and the flux in the range 50–200 standard cubic centimetres per minute (sccm). These peculiar non-equilibrium conditions promote formation of nanosized 1D structures. The pressure, the temperature gradient and the carrier flux have to be strictly controlled in order to guarantee the reproducibility of the deposition process. Catalyzed and catalyst-free growth was exploited, in order to investigate the influence of the catalysts on the shape and dimensions of the nanowires and on the consequent modification of their functional properties. To prevent the nanowires from contamination, two deposition systems were separately used.

The noble metal catalysts such as In, Pd, Pt and Au were deposited by sputtering on the substrate. In order to have cluster formation and not a continuous film we have reduced the deposition time and the applied power to the target, 20 W and 1 s, 50 W and 2 s, 50 W and 10 s, 50 W and 5 s, respectively. The ability to control the size and dispersion of the catalyser is fundamental since it allows in turn the control of the size and dispersion of nanowires.

Au nanoparticles with a well-defined cluster dimension dispersed in a colloidal solution (BBInternational) were also used as catalysts.

Indium and tin oxide nanowires have been produced using different catalysts over different substrates. In, Au and Pt were applied for substrate seeding before condensation for indium oxide nanowires preparation. While Pt, Au, Sn and Pd were used for tin oxide nanowires preparation. Polycrystalline Al_2O_3, a-plane sapphire, silicon and silicon carbide substrates were used. Different growth mechanisms were involved depending on the catalyst and the substrate.

2.2. Electron microscope

Scanning and transmission electron microscopy (SEM and TEM) have been carried out in order to determine the degree of homogeneity and crystalline arrangement.

The as-prepared structures were observed at low accelerating voltage, in order to avoid the electrostatic charging of the insulating substrate. The optimal voltage for observation of un-prepared specimens was found to be in the 2–3 keV range.

The nanostructures have been removed from the substrate used for deposition through dry scratching with a razor blade and dropped over a standard holey carbon film grid. Standard removal trough sonication in alcohol has been avoided to prevent the thin structures from breaking. The thin substrate was used for both conventional TEM observation and Energy Dispersive X-ray Spectroscopy (EDX) analysis at the SEM with improved spatial resolution. In addition, the conductive carbon film allowed one to increase the beam voltage up to 20 keV for effective generation of the characteristics X-rays from the specimen.

High-resolution TEM imaging is useful for investigation of the termination of the nanowire lateral sides and apex. Electron diffraction (ED) and analysis of zero-order and higher order Laue-zones allows precise determination of unit cell and space group.

The nano-manipulation set-up for in-situ electrical measurement was implemented in a LEO 1525 FEG SEM operated at the 3–5 keV accelerating voltage range. The manipulation system was based on two Kleindiek piezo-actuated probes, capable of sub nanometric positioning resolution, and a Keithley mod 6487 picoammeter/voltage source.

2.3. Atomic force microscope

The morphology has been investigated by means of Atomic Force Microscopy (AFM). Measurements have been carried out in air with a Thermomicroscope-Veeco CP-Research working in tapping mode with high-resolution silicon tip (Nanosensors, SSS-NCHR model). The sharp tip termination (nominal radius value is 2 nm) together with its high aspect ratio [16] reduce the tip-sample convolution effects that can alter the proper imaging of structures characterized by sharp height-steps such as nanowires and nanobelts.

Since these nanostructures grow perpendicularly to the substrate and cannot be easily measured as grown by AFM, they have been transferred over a flat Si/SiO_2 substrate by slightly frictioning the two substrates (Si/SiO_2 and alumina) together, obtaining dispersed nanostructures horizontally laying over the flat Si/SiO_2 substrate.

2.4. Functional measurements

Gas sensing tests have been carried out by flow through method in a thermostatic sealed chamber with controlled temperature and humidity. Dry air certified bottles and permeation tubes have been used as gas source [17] and certified mass flow controllers to reproduce desired gaseous composition inside the test chamber. A detailed description of the setup is reported in [18].

All measurements have been carried out at a constant flow of 0.3 Standard Litre per Minute (slm), constant humidity and chamber temperature (RH = 30% @ 20 °C).

3. Results and discussion

3.1. Indium oxide

Application of In thin layer over polycrystalline alumina (Fig. 1, top) resulted in formation of In_2O_3 nanograins during the preliminary heating of the furnace, and consequent nanowires nucleation and growth according to the direct vapor solid (VS) mechanism [19]. Each nanowire nucleates from an In_2O_3 nanograin, as clearly visible in the inset of Fig. 1, top, which illustrates the early condensation stage of the process. Prolonged condensation results in formation of a nanowires bundle. Au and Pt, instead, do not interact with oxygen during the transient heating, and act as liquid catalyst during the condensation step. They are able to capture the volatiles transported by the Ar flux, forming a eutectic alloy. Precipitation of In occurs when the supersaturation is reached, and the nanowire originates from the liquid catalytic tip, which indefinitely remains at the apex of the nanowire (vapor–liquid–solid (VLS) growth mechanism) [20]. Depending on the substrate, the nanowire can grow either randomly oriented, in case of polycrystalline substrate (Fig. 1, center), or along preferential direction. In case of a-sapphire substrate, good matching exists between the lattice of the substrate (lattice constant $a = 0.476$ nm) and of the In_2O_3 nanowires ($a = 1.01$ nm), inducing perfect alignment of most nanowires to the direction normal to the substrate surface (Fig. 1, bottom).

3.2. Tin oxide

Concerning tin oxide nanostructures Fig. 2 reports the summary of the morphologies obtained for each catalyst at different deposition temperatures using alumina substrates. The use of Pt catalyst