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Atmospheric pressure fabrication of SnO_2-nanowires for highly sensitive CO and CH_4 detection

Anton Köck[a,*], Alexandra Tischner[a], Thomas Maier[a], Michael Kast[a], Christian Edtmaier[b], Christian Gspan[c], Gerald Kothleitner[c]

[a] Division Nano-System-Technologies, Austrian Research Centers GmbH – ARC, Donau-City-Strasse 1, 1220 Vienna, Austria
[b] Institute of Chemical Technologies and Analytics, Vienna University of Technology, 1040 Vienna, Austria
[c] Institute for Electron Microscopy and Fine Structure Research, Graz University of Technology, and Centre for Electron Microscopy Graz, 8010 Graz, Austria

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ABSTRACT

In this paper we report on a new approach for the fabrication of ultra-long single crystalline SnO_2-nanowires for gas sensing applications based on a combined spray pyrolysis and annealing process. The SnO_2-nanowires are grown on SiO_2-coated Si-substrates and exhibit diameters of 30–400 nm and lengths up to several 100 μm. The whole SnO_2-nanowire fabrication procedure is performed at atmospheric pressure and requires no vacuum. The experimental results suggest a competing evaporation and condensation process, which converts the nanocrystalline SnO_2-films into single crystalline SnO_2-nanowires directly on the chip. For the realization of gas sensors the SnO_2-nanowires are transferred to another SiO_2-coated Si-substrate. Evaporation of Ti/Au contact pads on both ends of single SnO_2-nanowires enables their direct use as sensing elements. The devices are very sensitive, are able to detect humidity, and concentrations of CO and CH_4 as low as a few ppm at operating temperatures of 200–250 °C. We believe that our fabrication procedure might be the technology of choice for the controlled fabrication of SnO_2-nanowires as highly sensitive gas sensing elements on a wafer scale.

1. Introduction

Numerous novel applications ranging from industrial process control and safety systems to environmental monitoring or disease diagnostics in medicine have a strongly increasing demand for highly sensitive gas detecting devices. Metal oxide-based gas sensors, which rely on changes of electrical conductance due to the interaction with the surrounding gas, have been developed over the years to established devices. Especially the employment of thin films has improved the sensor performance [1–4]. Among all metal oxides SnO_2 has become the most prominent sensing material and many SnO_2-based sensor devices have been realized so far [5–7]. The implementation of MEMS technology has further advanced the gas sensing device performance. Thermally insulated micro-hotplates, for example, have been integrated as platforms on CMOS-chips for the realization of sensor arrays comprising different polycrystalline materials and allow for adjustment of different temperatures to provide a certain level of selectivity [8–10].

A most powerful strategy to improve sensor performance is the implementation of nanostructured materials, such as nanocrystalline films or nanowires, which have a high surface to volume ratio and thus a strong interaction between the surrounding gas and the material. Several gas detecting devices utilizing metal oxide nanocrystals [11,12], nanorods [13–15], or nanosheets [16], for example, have been realized. Nanocrystalline sensing films, however, may have the problem of long-term sensor poisoning. Therefore, with respect to device stability single crystalline nanowires are favorable. Numerous fascinating devices based on nanowires as sensing probes for both chemical and biological analysis have been demonstrated so far [17,18]. Excellent reviews of nanowire sensor devices are given in Refs. [19,20]. The range of nanowire materials encompasses metals [21,22], semiconductors [17,23–25], metal oxides [26,27], carbon nanotubes [28,29], and polymers [30,31].

For gas sensing applications, which often require measurements in harsh environments, metal oxide nanowires are of particular importance because they have a high chemical resistance and thermal stability. Gas sensing has been successfully achieved with a variety of metal oxide nanowires, such as In_2O_3 nanowires [27,32] or WO_3 nanowire networks [33]. Also ZnO nanorods and nanowires have been employed for sensing applications [34,35], a field effect transistor configuration has been used for NO_2 and NH_3 sensing [36]. Arrays of individual nano- and mesowire sensors have been developed for hydrogen versus CO monoxide discrimination as a step towards the electronic nose [37].

* Corresponding author.
E-mail address: anton.koeck@arcs.ac.at (A. Köck).

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As SnO_2 has been the most prominent sensing material in conventional gas sensors, the major focus has been put on the fabrication and implementation of SnO_2 nanobelts and nanowires as sensing probes. Nanosensors based on SnO_2-belts with high sensitivity for CO, NO_2 and ethanol have been reported [26]. Detection of CO and O_2 has been achieved with template grown SnO_2 nanowires, while enhanced gas sensing has been demonstrated with Pd functionalized SnO_2 nanowires [38]. Tin oxide nanobelts have been integrated with microsystems for nerve agent detection [39]. Modified SnO_2 nanoribbons and nanowires have been developed for the detection of H_2S [40]; CO and humidity have been detected with single SnO_2 nanowires [41].

In this paper we report on atmospheric pressure synthesis of single crystalline SnO_2-nanowires directly on the Si-chip by spray pyrolysis and subsequent annealing. Our two-step SnO_2-nanowire fabrication procedure is very simple, requires no vacuum, and allows for straightforward upscaling the possible substrate to 6 in.-wafer size. We believe that our fabrication procedure might be the technology of choice for the controlled fabrication of SnO_2-nanowires as highly sensitive gas sensing elements on a wafer scale.

2. Experimental

The SnO_2-nanowires are fabricated in a two-step procedure: In a first step nanocrystalline SnO_2-films are fabricated by a spray pyrolysis process. These SnO_2 films have already been employed by us as gas sensing elements. Recently we have reported on SnO_2 thin-films gas sensors (thickness 50–100 nm) that show high sensitivity to humidity and are able to detect carbon monoxide down to a concentration of less than 5 ppm [42]. The experimental setup, shown in Fig. 1, consists of a 30 cm × 30 cm hotplate and a siphon-fed spray setup with an air atomizing spray nozzle (QuickMist QMJML, Spraying Systems Co.), which is positioned on the side of the hot plate allowing the atomized spray to flow parallel to the surface; distance to the samples is 20 cm. N_2 with a pressure of 0.8 bar is used as carrier gas; a siphon height of 10 cm results in a solution flow rate of 10 ml/min.

Si-wafers coated with a 750 nm thick SiO_2-layer were used as substrates for SnO_2-film deposition. Three different types of samples were prepared: The 2 cm × 2 cm large substrates were either directly used for SnO_2 deposition or sputter coated with a 40 nm thick Cu-layer, or 5 nm thick Au-layer, respectively, before SnO_2 deposition in order to study possible influence of catalytic metal films. The samples were directly placed on the hotplate heated up to a temperature of 500 °C. Spraying a 0.28 molar solution of tin chloride pentahydrate in ethyl acetate results in the formation of nanocrystalline SnO_2-layers on the substrates with a deposition rate of ~100 nm/min according to the (simplified) chemical reaction

$$SnCl_4 + 2H_2O = SnO_2 + 4HCl \quad (1)$$

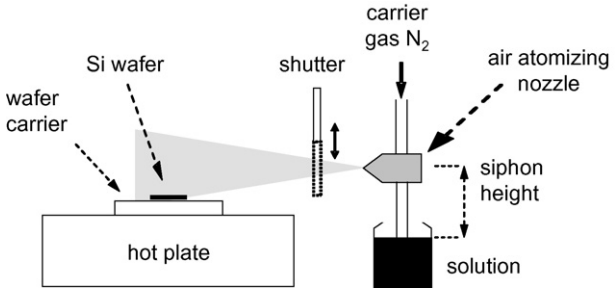

Fig. 1. Setup of spray pyrolysis process for parallel flow of atomized spray.

Spray duration was 2 min so that the resulting SnO_2 film thickness on all samples was around 200 nm. Subsequent to the deposition process, the samples were removed from the hotplate and immediately cooled to room temperature. The whole deposition procedure was performed in ambient air.

The second SnO_2-nanowire fabrication step is an annealing process: a tube furnace was heated up to temperatures of 800 °C, 900 °C and 1000 °C. The SnO_2-coated samples were placed into the heated furnace; due to the small thermal mass ramp-up time was negligible. The annealing process was performed in Ar-gas at atmospheric pressure, a slight Ar-gas flow was used during the process. Annealing time was 60 min for all samples, only the temperature was varied as critical parameter in order to find the best conditions for synthesizing ultra-long SnO_2 nanowires for sensor applications. All samples were annealed individually to exclude any mutual material growth or deposition of vaporized products. Immediately after the annealing process the samples were removed from the furnace and cooled in ambient air to room temperature.

3. Results and discussion

3.1. Tin oxide nanowire characterization

The following experimental results were found: For annealing temperature of 800 °C no nanowire growth was observed on all three types of samples. The samples with intermediate Cu- and Au-layers annealed at 900 °C showed white wool-like nanowires covering especially around the edges of the samples. A scanning electron microscopy image (SEM) shows SnO_2-nanowires with diameters of 30–400 nm and lengths up to several 100 μm directly on the samples (Fig. 2). The nanowire density was lower and nanowires tend to be shorter towards the middle of the samples. Growth of nanowires with lengths up to several 10 μm was also observed on samples without metallic intermediate layer. Areal density of nanowires, however, was orders of magnitude less than compared to samples with metallic intermediate layer. Annealing at a temperature of 1000 °C showed also wool-like nanowire growth on samples with intermediate Cu- and Au layers, but SEM analysis reveal that the nanowires significantly start branching and interconnecting to each other, which makes further processing of single nanowires as gas sensing elements difficult. A few nanowires are also found randomly distributed on samples without intermediate metal layers, but nanowires are only a few μm long.

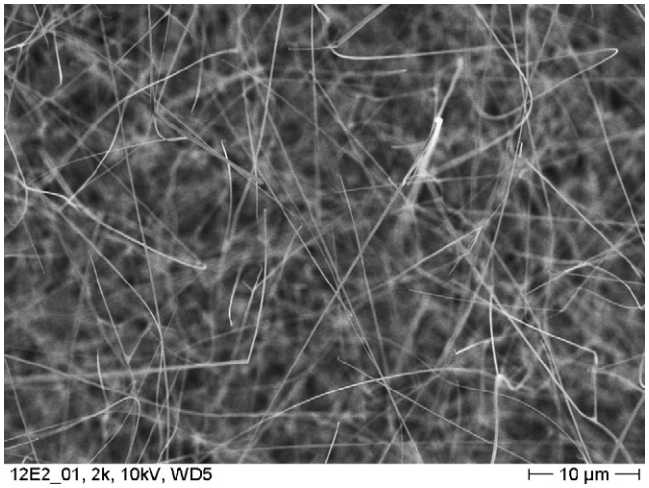

Fig. 2. SnO_2-nanowires fabricated on Si-samples. Nanowires have diameters of 30–400 nm and lengths up to several 100 μm.