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Micromachined gas sensors based on tungsten oxide nanoneedles directly integrated via aerosol assisted CVD

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ABSTRACT

Micromachined gas sensors based on tungsten oxide nanostructures (NSs) in the form of polycrystalline films, non-aligned and quasi-aligned nanoneedles (NNs) films are fabricated by integrating various microsystems technology steps with aerosol assisted chemical vapour deposition (AACVD). Measurement of the performance of these structures to various analytes, including NO_2, H_2, EtOH, H_2S, CO, C_6H_6, demonstrate enhanced sensing properties for gas sensors based on films comprised of NNs as opposed to polycrystalline, with non-aligned NNs films showing the greatest sensor responses. A marked contribution of the NNs diameter to the sensor response is noticed, particularly for sensors composed of NNs with diameters between 25 and 50 nm. In addition, fabrication variables such as the NNs arrangement and the electrode geometry suggest their contribution to the sensor response is connected with the effects of the gaseous analytes at the surface, i.e. whether these analytes act as reducing or oxidizing agents.

1. Introduction

Metal oxide (MOX) gas sensors are relevant to numerous industries, including automotive, environmental control, security and medical diagnostics, due to their sensitivity to a number of gaseous species, relatively low detection limits (at the levels of ppm or even ppb), compact size, simple architecture, and low cost production. Among MOX used for gas sensing applications (e.g. SnO_2, WO_3, In_2O_3, ZnO, TiO_2, V_2O_5) [1], tungsten oxide has attracted much attention due to its sensitivity to gases such as NO_x [2,3], O_3 [4,5] H_2 [6,7], H_2S [8,9], SO_2 [9] and EtOH [7,10], and its particular electronic and optical properties which induce the output sensor response either via electrical conductivity changes or alteration of optical properties [11]. Quasi-one-dimensional NSs (e.g. nanowires, nanotubes, nanorods, nanobelts) have emerged as promising materials for gas sensing applications basically due to their increased surface-to-volume ratio. However, the advantage of these structures, over bulk materials, also goes beyond that of simply increasing the active surface area, providing the possibility of tuning the concentration of adsorption sites, the energy levels within the material and the adsorption/desorption energies of interacting gas molecules, due to their particular well-orientated crystallographic structure [12].

To date, several reports in the literature have demonstrated the advantages of these novel materials in gas sensing applications [13,14], with some of the methods [14] employed to integrate nanostructured MOX on gas sensor platforms including the manipulation of single nanowires to form bridges between electrodes, or the utilization of vapour phase deposition, either via bottom-up or with the aid of templates fabricated via top-down technology [13]. However, many studies are not conducted on 'real devices' (i.e. packaged sensing platforms consisting of integrated electrodes and heater), which provides only a view of the sensing material properties rather than the properties of the overall sensor device, precisely because the synthesis of quasi-one-dimensional NSs and their integration in the fabrication process of a device remains a particular research challenge. This arises because of the stringent conditions placed on the production methods by NS materials, requiring elevated temperatures (e.g. chemical vapour deposition methods) and/or extra fabrication steps (e.g. catalyst seeding or wet/dry transfer steps), increase the production costs and prevent their scalable production.

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We have previously developed a method for synthesis of MOX-NSs via AACVD [15] achieving deposition at relatively low temperatures (compared to other CVD methods of NS synthesis) with potential to be integrated in microelectronic fabrication due to its flexibility, high deposition rate, easy implementation and good prospects for low cost industrialization [16]. This method has been used to develop conventional ceramic gas sensors, based either on polycrystalline or NNs tungsten oxide, demonstrating its viability for direct deposition of quasi-one-dimensional NSs on traditional ceramic sensor platforms [17–19]. However, the gas sensing results of these devices revealed better sensing performance for polycrystalline-based sensors compared to NNs-based sensors, contrary to the stated in the literature for nanostructured sensing films. This suggested the need for engineering the platforms to enable utilization of the potentially enhanced properties of these structures [17]. Recently, similar observations have also been reported in the literature, and different strategies related to electrode design have been applied to improve the sensing performance of NSs grown via vapour–liquid–solid approach [20–22]. We have, demonstrated a novel single-step functionalization method for NSs via AACVD [23,24] and integrated this with micromachined substrates, although a study of the advantages and effectiveness of these platforms on the performance of NNs opposed to polycrystalline films, and an analysis of the influence of different fabrication variables to the overall sensor response has not previously been reported.

Here we report the direct integration of tungsten oxide NSs, either polycrystalline or NNs onto micromachined sensors. These new gas sensor devices, composed of membrane platforms with miniaturized heater and electrodes elements (consistent with NNs dimensions), have been evaluated for performance towards various gaseous species (NO_2, EtOH, H_2, H_2S, C_6H_6 and CO) and these optimized platforms are demonstrated to be more suitable for nanostructured sensing materials. Analysis of these and previous results obtained using ceramic sensors [17] elucidate some of the fabrication variables that contribute to the overall gas sensor response.

2. Material and methods

2.1. Gas sensor fabrication

Micromachined platforms were fabricated using various microsystems technology steps including, the deposition via sputtering of a meander-shape platinum heater (thick: 200 nm) and interdigitated platinum electrodes (gap: 50 μm and thick: 200 nm), both isolated by an interlevel oxide layer grown via CVD (thick: 700 nm) and suspended in a SiO_2/Si_3N_4 membrane (2 mm × 4.5 mm × 400 nm) formed by rear side KOH etching of the silicon wafer [25].

Tungsten oxide nanostructured films were grown onto the membranes at 350, 450, and 500 °C via AACVD of tungsten hexaphenoxide [$W(OPh)_6$, 100 mg], dissolved in a mixture (50:50) of acetone and toluene (20 cm^3), as reported previously [15]. A shadow mask was used during the deposition process, in order to protect the contacts and confine the film deposition to the membrane. After deposition, the structures were annealed in air at 500 °C for 2 h and subsequently bonded in a TO-8 package as shown in Fig. 1.

The morphology of the as-deposited and annealed films was examined using scanning electron microscopy (SEM—Carl Zeiss, Auriga Series, 3 keV) and transmission electron microscopy (TEM-JEOL 1011, 100 keV). TEM samples were prepared by removing the film from the substrate by sonication; this analysis was performed for NNs grown on control wafers, as TEM sample preparation for the structures grown on microsensors proved impossible due to the low quantity of material removed and the fragility of the micromachined membrane. The structure of the films was analyzed using X-ray diffraction (XRD—Bruker AXS D8-Discover, 40 kV, 40 mA, Cu$K\alpha$ radiation). Diffraction patterns were recorded from 15° to 40° 2θ. Identification of the crystal phases was achieved by comparison of the patterns with the ICDD database using Diffractplus Evaluation software and the mean crystallite size was analysed using TOPAS 3.1 program.

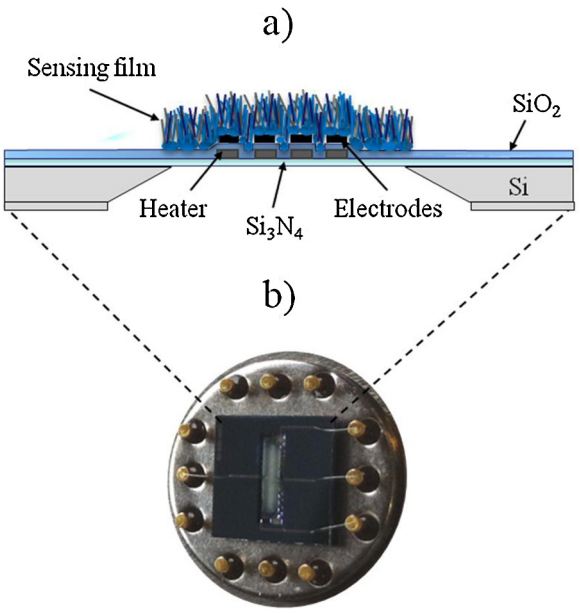

Fig. 1. Schematic view of the gas sensor section (a) and photo image of the micromachined sensor mounted on standard TO-8 package (b).

2.2. Gas sensing characterization

Gas sensing tests consisted in measuring the electrical resistance changes of the films towards various analytes at operating sensor temperatures between 150 and 300 °C. The sensors were exposed to each analyte for 10 min in a continuous flow (200 sccm) test chamber (280 cm^3), similarly to our previous work [17]. Subsequently the chamber was purged with air until the initial baseline resistance was recovered. The sensor response was defined as $R = R_{gas}/R_{air}$ for oxidizing gases and $R = R_{air}/R_{gas}$ for reducing gases; R_{air} represents the sensor resistance in air at stationary state and R_{gas} is the sensor resistance after 10 min of gas exposure. Calibrated cylinders of ethanol (EtOH, Carburos Metálicos, 20 ppm), hydrogen (H_2, Carburos Metálicos, 1000 ppm), carbon monoxide (CO, Carburos Metálicos, 1000 ppm), benzene (C_6H_6, Praxair, 10 ppm), hydrogen sulfide (H_2S, Praxair, 50 ppm) and nitrogen dioxide (NO_2, Praxair, 1 ppm), were mixed with pure synthetic air (Carburos Metálicos, 99.99%) in order to obtain the desired concentration (see Table 1). The whole testing period comprised of two months during

Table 1
Analytes and concentrations tested.

Analytes	Concentration (ppm)
Nitrogen dioxide	1
Ethanol	20
Hydrogen	1000
Carbon monoxide	100
Hydrogen sulfide	3
Benzene	10