Available online at www.sciencedirect.com

ScienceDirect

Procedia Engineering 168 (2016) 1078 – 1081

Procedia Engineering

www.elsevier.com/locate/procedia

30th Eurosensors Conference, EUROSENSORS 2016

Micromachined gas sensors based on Au-functionalized SnO_2 nanorods directly integrated without catalyst seeds *via* AA-CVD

S. Vallejos,[a]* S. Selina,[b] F. E. Annanouch,[c, e] I. Gràcia,[d] E. Llobet,[c] C. Blackman[b]

[a]*SIX Research Centre, Brno University of Technology, Brno, Czech Republic*
[b]*Department of Chemistry, University College London, London, UK*
[c]*MINOS-EMaS, Departament d'Enginyeria Electrònica, Universitat Rovira i Virgili, Tarragona, Spain*
[d]*Instituto de Microelectrónica de Barcelona (IMB-CNM, CSIC), Barcelona, Spain*
[e]*Aix Marseille Université, Université de Toulon, IM2NP UMR 7334, Marseille, France*

Abstract

Tin oxide nanorods functionalized with Au nanoparticles are vapour synthesised at relatively lower temperatures than previously reported and without the need of catalyst seeds using co-deposition method *via* aerosol-assisted chemical vapour deposition. These functionalized structures formed directly, in a single-step process, on silicon micromachined platforms are tested toward H_2, showing 12-fold greater response, 6-fold faster response time and better selectivity to CO compared to a similar non-functionalized system. Results show the significance of these method to form highly gas sensitive nanostructures compatible with the complementary electronic for the fabrication of gas microsensor devices.

Peer-review under responsibility of the organizing committee of the 30th Eurosensors Conference

Keywords: Nanostructures; tin oxide; functionalization; AACVD; gas sensors

1. Introduction

Tin oxide is an intrinsic n-type wide-bandgap semiconducting metal oxide with applications in transparent conducting electrodes, solar cells and gas sensors.[1, 2] In particular, tin oxide is used in most current commercial resistive gas sensors and is the most studied material in the gas sensing literature, with demonstrated sensitivity to

* Corresponding author. Tel.: +420 541 146 153; fax: +420 541 146 2198.
E-mail address: vargas@feec.vutbr.cz

Peer-review under responsibility of the organizing committee of the 30th Eurosensors Conference
doi:10.1016/j.proeng.2016.11.344

carbon monoxide, hydrogen, ethanol, and nitrogen dioxide, amongst others.[2-4] Whilst tin oxide nanorods (NRs) have been synthetized (often with catalyst seeds) using various routes, including chemical vapour deposition (CVD), the formation of these structures via aerosol-assisted (AA) CVD without catalyst seeds, i.e., via vapor-solid (VS) mechanism, and their in-situ functionalization with Au nanoparticles (NPs) have not been developed before. AA-CVD works at atmospheric pressure and relies on a solution-based delivery approach, providing advantages over traditional CVD as it allows for a wider range of precursors to be utilised. It also allows for the functionalization of SMOx nanostructures with metal NPs in a single processing step *via* co-deposition, as demonstrated previously for incorporation of gold or platinum NPs segregated at the surface of tungsten oxide nanostructures.[5]

Here we report the AA-CVD of Au-functionalised and non-functionalized tin oxide NRs (Au@SnO_2 and SnO_2, respectively) directly on silicon micromachined platforms (μMP) for the fabrication of chemoresistive gas sensors.

2. Materials and Methods

Au@SnO_2 and SnO_2 NRs were deposited directly on μMP at 620 °C *via* AA-CVD of a mixture of tin (IV) chloride pentahydrate (30 mg, $SnCl_4.5H_2O$, Sigma-Aldrich, ≥98%) and tetrachloroauric acid trihydrate (4.2 mg, $HAuCl_4 \cdot 3H_2O$, Sigma-Aldrich, 99.9%) dissolved in acetone (15 ml, Sigma-Aldrich, ≥99.6%) or only tin (IV) chloride pentahydrate (30 mg, $SnCl_4.5H_2O$, Sigma-Aldrich, ≥98%) dissolved in acetone (15 ml, Sigma-Aldrich, ≥99.6%), respectively, using the method and system reported previously.[5] The μMP consisted of an array of four $SiO_2/Si_3N_4/SiO_2$ membrane, each of them with isolated polysilicon heaters and platinum electrodes (gap: 50 μm, thick: 0.2 μm).[6] The sensing films were deposited on the μMP using a shadow mask in order to protect the contacts and subsequently bonded in a TO-8 package (inset in **Fig. 1**).

The morphology of the samples was examined using SEM (Tescan FE Mira II LMU) and TEM (JEOL JEM-100CX II, 100 kV). The structure using XRD (Rigaku Smartlab 9kW) and the chemical composition using WDX (Philips, XL30ESEM). Gas sensors were tested in a continuous flow (200 sccm) test chamber (280 cm^3) comprised of a mass flow system (Bronkhorst hi-tech 7.03.241) and calibrated cylinders of hydrogen (H_2, Praxair, 1000 ppm), carbon monoxide (CO, Praxair, 1000 ppm) and synthetic air (Carburos Metálicos, 99.99%) as described previously.[6] The sensor response was defined as $R = R_a/R_{gas}$, where R_a is the sensor resistance in air and R_{gas} the sensor resistance after 10 min of the analyte exposure. The response time (t_R) was defined as the time required for the sensor to reach 90% of the sensor response, and the recovery time (t_{rec}) as the time required to reach 10% of the initial baseline resistance after the analyte was purged.

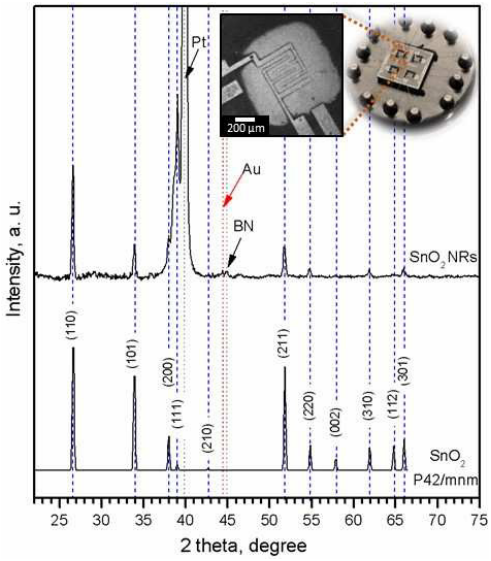

Fig. 1. XRD of a microsensor based on Au@SnO_2 NRs grown via AA-CVD. Diffraction peaks are indexed to a tetragonal phase (P42/mnm, ICCD card no. 41-1445) of tin oxide and face-centered cubic Au (Fm3m, ICCD card no. 4-0784). Platinum (Pt) and boron nitride (BN) diffraction peaks coming from the microsensor platform are also identified.

3. Results and discussion

XRD of the films composed of Au@SnO_2 and SnO_2 NRs indicated the presence of tetragonal SnO_2 (P42mnm space group, *a*=4.7382 Å, *c*=3.1871 Å; ICCD card no. 411-1445) with a week diffraction at 44.3 degrees in the Au@SnO_2 films corresponding to the (200) reflections of face-centered cubic Au (Fm3m space group, *a*=4.07860 Å; ICCD card no. 04-0784) (**Fig. 1**). XPS of the films indicated a (0.9 at.%) 3.7 wt.% Au in the films with the characteristics of Au 4f core level spectra being in agreement with that reported for gold metal,[5] which suggests the gold NPs incorporated at the surface of the tin oxide NRs are in the metallic state.

SEM of the µMP showed films composed of non-aligned NRs, grown uniformly on the electrodes (**Fig. 2a** and **2b**). Similarly, TEM confirmed the formation of prism-like NRs terminated in a pyramidal cap and the incorporation of Au NPs (~35 nm) with spherical morphologies at the NR surface (**Fig. 2c** and **2d**), proving consistency with our previous observations for the co-deposition of tungsten oxide and gold *via* AA-CVD.[5] The non-functionalized NRs grown on the µMP *via* AA-CVD showed similar morphological, chemical and crystal structure for SnO_2.

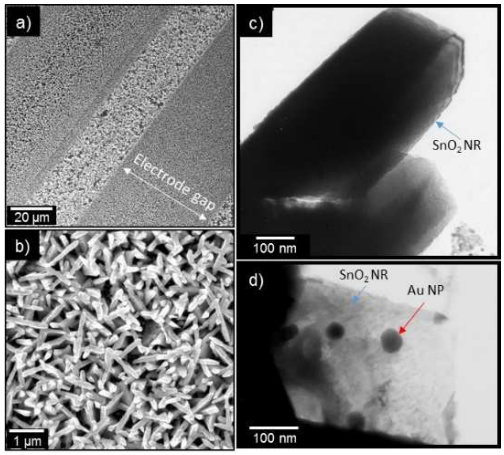

Fig. 2. Typical low (a) and high (b) magnifications SEM imaging of the SnO_2 and Au@SnO_2 NRs grown via AACVD on the µMP. TEM of a single SnO_2 (c) and Au@SnO_2 (d) NR.

Test of the samples towards H_2 and CO registered stable signal and very low drift of electrical resistance over the testing period, with the Au@SnO_2 sensors showing enhanced sensing characteristics compared to SnO_2 sensors, which included higher and faster response and lower-cross response (**Table 1** and **Fig. 3**). A comparison of these results with those recorded for similar systems synthesised *via* sol-gel in the literature[7] revealed nearly 7 times higher values for our Au@SnO_2 NRs, suggesting the AA-CVD method presented here allows for not only a direct integration with µMP, but also for an effective functionalization of SnO_2.

Table 1. Sensor response and cross-response (ΔR) towards H_2 and CO for the SnO_2 and Au@SnO_2 sensors operating at 290 °C.

Analytes & cross-response	Response, R_a/R_{gas}	
	SnO_2	Au@SnO_2
250 ppm H_2	3.3	35.4
500 ppm H_2	3.8	41.1
250 ppm CO	1.1	1.6
500 ppm CO	1.2	1.9
ΔR500 ppm= (R_{H2}-R_{CO})	2.6	39.2

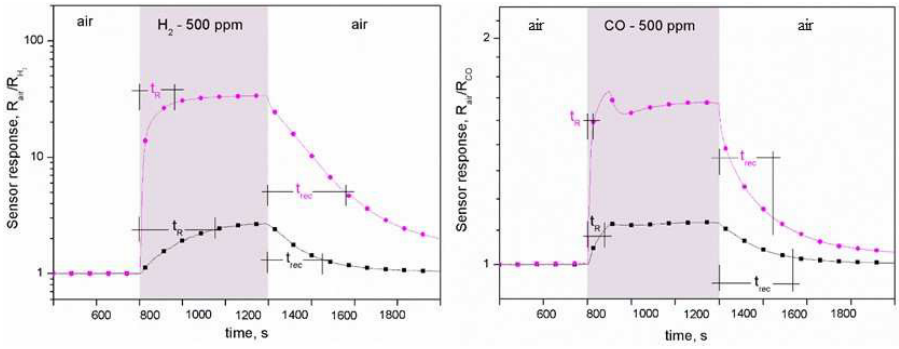

Fig. 3. Maximum sensor response recorded with the SnO_2 and Au@SnO_2 NRs towards 500 ppm of either H_2 or CO at 290 °C or 320 °C, respectively.

4. Conclusion

Micromachined chemoresistive gas sensors based on SnO_2 and Au@SnO_2 NRs were developed using AA-CVD of $SnCl_4 \cdot 5H_2O$ at 620 °C, a much lower onset temperature compared to other CVD methods based on a VS mechanism, which typically requires temperatures exceeding 850 °C. The gas microsensors were validated towards H_2 and CO and show sensing properties that are in agreement with the literature, with notable enhancement of sensing properties for Au@SnO_2 NRs which showed 12-fold higher response with 6-fold faster response and improved selectivity to H_2 compared to the gas sensors based on intrinsic SnO_2 NRs.

Acknowledgements

S.V. is supported by the SoMoPro II Programme, cofinanced by the European Union and the South-Moravian Region, via Grant 4SGA8678. E.L. is supported by the Catalan Institution for Research and Advanced Studies via the ICREA Academia Award. This work was funded in part by MINECO under grant no TEC2013-48147 and TEC2015-71663-R, and was carried out using the infrastructures of the SIX Research Centre and the core facilities of CEITEC - Central European Institute of Technology under CEITEC - open access project, ID number LM2011020, by the Ministry of Education, Youth and Sports of the Czech Republic.

References

[1] M. Batzill, U. Diebold, The surface and materials science of tin oxide, Prog. Surf. Sci. 79 (2005) 47-154.
[2] J. Pan, H. Shen, S. Mathur, One-Dimensional SnO_2 Nanostructures: Synthesis and Applications, J. Nanothecnology 2012 (2012) 12.
[3] J. F. McAleer, P. T. Moseley, J. O. W. Norris, D. E. Williams, B. C. Tofield, Tin Dioxide Gas Sensors. Part 2.-The Role of Surface Additives, J. Chem. Soc., Faraday Trans. 1 84 (1988) 441-457.
[4] S. Vallejos, F. Di Maggio, T. Shujah, C. Blackman, Chemical vapour deposition of gas sensitive metal oxides, Chemosensors 4 (2016) 4.
[5] S. Vallejos, P. Umek, T. Stoycheva, F. Annanouch, E. Llobet, X. Correig, P. De Marco, C. Bittencourt, C. Blackman, Single-step deposition of Au- and Pt-nanoparticle-functionalized tungsten oxide nanoneedles synthesized via aerosol-assisted CVD, and used for fabrication of selective gas microsensor arrays, Adv. Funct. Mater. 23 (2013) 1313-1322.
[6] S. Vallejos, V. Khatko, J. Calderer, I. Gracia, C. Canè, E. Llobet, X. Correig, Micro-machined WO_3-based sensors selective to oxidizing gases, Sens. Actuators B 132 (2008) 209-215.
[7] X.-T. Yin, X.-M. Guo, Sensitivity and selectivity of (Au, Pt, Pd)-loaded and (In, Fe)-doped SnO_2 sensors for H_2 and CO detection, J Mater Sci: Mater Electron 25 (2014) 4960-4966.