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

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## 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.

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

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## 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

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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.

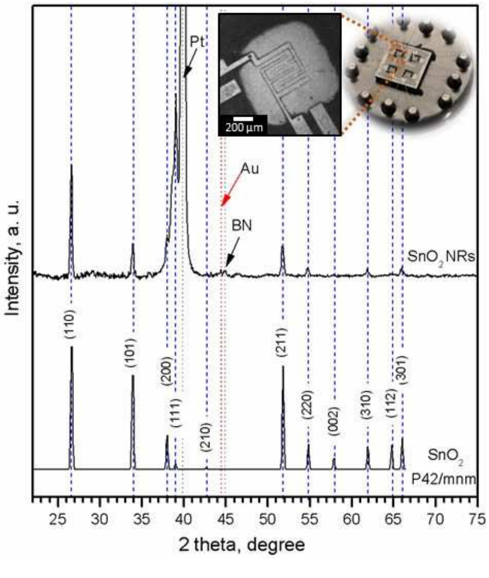

Fig. 1. XRD of a microsensor based on Au@$SnO_2$ NRs grown via AA-CVD. Diffraction peaks are indexed to a tetragonal phase (P42/mnm, ICCD card no. 41-1445) of tin oxide and face-centered cubic Au (Fm3m, ICCD card no. 4-0784). Platinum (Pt) and boron nitride (BN) diffraction peaks coming from the microsensor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

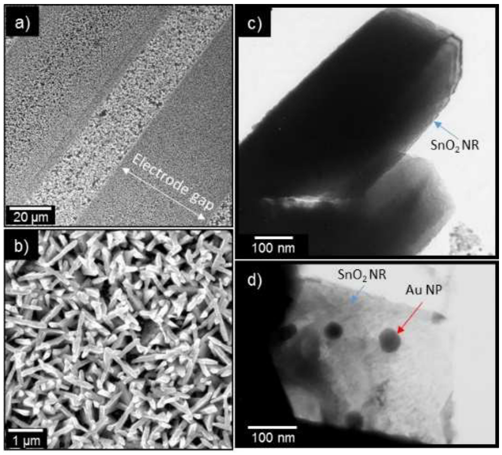

Fig. 2. Typical low (a) and high (b) magnifications SEM imaging of the $SnO_2$ and Au@$SnO_2$ NRs grown via AACVD on the µMP. TEM of a single $SnO_2$ (c) and Au@$SnO_2$ (d) NR.

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 |

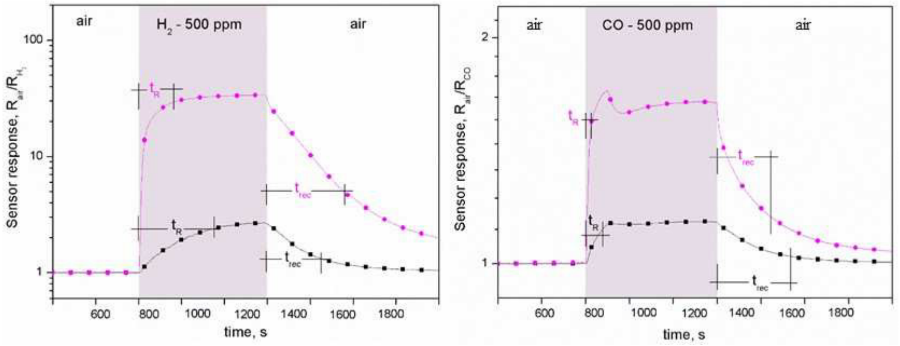

Fig. 3. Maximum sensor response recorded with the $SnO_2$ and Au@$SnO_2$ NRs towards 500 ppm of either $H_2$ or CO at 290 °C or 320 °C, respectively.

## 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.

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