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Cobalt or Silver Doped WO_3 Nanowires Deposited by a Two-Step AACVD for Gas Sensing Applications †

E. Navarrete *, E. González, T. Vilic and E. Llobet

MINOS-EMaS, Universitat Rovira i Virgili, Tarragona, Spain; ernesto.gonzalez@estudiants.urv.cat (E.G.); Toni.vilic@urv.cat (T.V.); eduard.llobet@urv.cat (E.L.)

* Correspondence: eric.navarrete@urv.cat; Tel.: +34-682-511-711

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Abstract: A two-step procedure was implemented to obtain tungsten oxide nanowires (WO_3) doped with cobalt or silver oxide nanoparticles from metal-organic precursors, $W(CO)_6$, $Co(acac)_2$ and $Ag(acac)_2$. In the first step, nanowires were grown at 400 °C using an aerosol assisted chemical vapor deposition system (AA-CVD) and subsequently annealed at 500 °C for 2 h. In the second step, metal loading (at different doping levels) of the nanowires using the same system. These hybrid nanomaterials were grown on top of commercial alumina substrates that comprised interdigitated electrodes. The response of these nanomaterials toward H_2S and H_2 is investigated and discussed.

Keywords: nanowires; oxide nanoparticles; WO_3; Co; Ag; CVD; gas sensing

1. Introduction

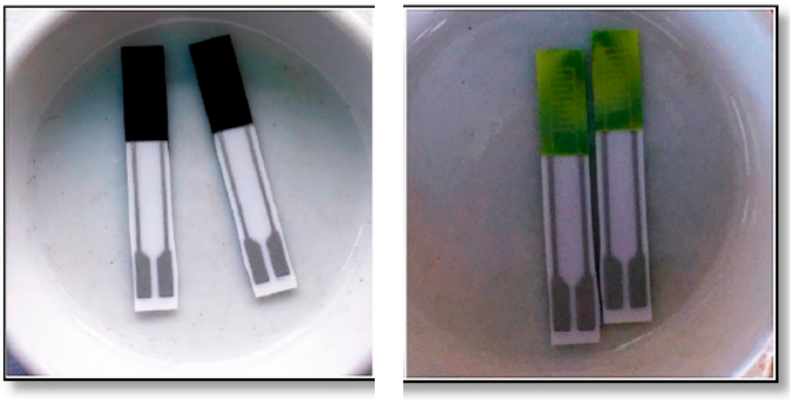
N-type metal-oxide such as SnO_2, In_2O_3 and WO_3 are known to be interesting materials for gas sensing applications. In order to obtain a gas sensor able to distinguish or being able to discriminate a particular gas from a mixture, a doping material can be introduced to the sensing layer structure to enhance or induce a change in the layer and subsequently obtain either a signal or a higher signal to a target gas. For this purpose, metal-oxide nanoparticles are used as dopant, as it has been demonstrated in our previous works, to perform such labor [1]. As AACVD is a flexible method to grow nanostructures we have successfully designed a 2 step procedure to grow and ensure the loading of dopants to the nanowires with noble metal nanoparticles such as Pt, Au and Pd [2]. Therefore, in order to further research the metal loading of nanomaterials, in this paper we report the functionalization of tungsten oxide nanowires using cobalt or silver oxides [3]. In addition, the use of sputtering has been envisaged too for loading, with a homogeneous distribution of silver nanoparticles, the surface of the nanowires.

2. Materials and Methods

2.1. Sensors Synthesis

The first step procedure consisted of the synthesis of the pure WO_3 nanowires using $W(CO)_6$ as an organic precursor, to interconnect the interdigitated electrodes of the commercial alumina sensors. In an analytic balance 50 mg $W(CO)_6$ were weighed and dissolved in a solution containing 15 mL of acetone and 5 mL of methanol. It has been studied experimentally that higher amounts of methanol leads to a nanoparticles formation instead of the desired nanowires, the main reason for this effect is the lower solubility of the organic precursor in the methanol in contrast with the acetone leading to a less homogenous solution that once is used in the CVD reactor displays a less effective precursor delivery. The solution is placed in a bath with a high frequency wave producer which through pulses converts the liquid solution into a spray containing microdroplets of the solvent with the precursor.

This spray is carried through a tube system using nitrogen (Aire premiere) towards a 400 °C preheated CVD reactor where the sensors are placed. Up to 4 sensors can be produced at the same time maintaining the reproducibility between them. Once the first deposition is done, the sensors have a dark-blue layer corresponding to the impurities belonging to different forms of carbon and other by-products, to remove them an annealing step is required. The annealing step is performed in a muffle at 500 °C during 2 h, with a temperature ramp of 5 °C/min, under a synthetic air flow to ensure a high concentration of oxygen in the chamber. The aim of the annealing is to remove carbon residues from the precursors and oxidize further the layer of WO_{3-X} formed during the AACVD to a stoichiometric WO_3 as shown in Figure 1.



(**a**) (**b**)

Figure 1. (**a**) Left, WO_{3-X} layer with impurities; (**b**) Right, WO_3 stoichiometric.

The second step of the procedure consists of loading the dopant agent into the surface layer of nanowires. To perform such work, two methods have been implemented; AACVD and sputtering. For the AACVD based doping procedure both cobalt and silver were used, respectively. In the first place 4 different solutions were prepared, all the solutions had 10 mL of methanol as a solvent and in each of them were dissolved 3 mg of $Ag(acac)_2$, 6 mg $Ag(acac)_2$, 5 mg $Co(acac)_2$ or 10 mg $Co(acac)_2$ all weighted in an analytical balance. Using the same procedure to grow the WO_3 nanowires, each solution was used to deliver the dopant agent to the sensor surface in order to obtain a $WO_{3\ (NW)}/CoO_{x\ (NP)}$ high concentration and low concentration sensor and $WO_{3\ (NW)}/AgO_{x\ (NP)}$ high concentration and low concentration sensor. Once the four sensors were prepared, due to the AACVD process, carbon impurities from the organic precursors used were deposited also in the surface. Therefore, a second annealing was performed to remove all the impurities and correspondingly boosted the oxidation of the nanoparticles.

The solubility of the silver organic precursor was too low to expect an efficient delivery and, therefore, a sputtering process was used as well to prepare new sensors. Setting the sputtering conditions during 10 s and 20 s in DC mode at 150 Watts two concentrations of nanoparticles were achieved.

2.2. Sensors Structural Characterization

To fully characterize the sensors a Transmission Electron Microscope, Jeol JEM-1011, (TEM) an Environmental Scanning Electron Microscope, (E-SEM) and XRD analysis were done to fully characterize the sensing layer, the main factors studied were: the nanowire morphology and orientation towards the substrate, the nanoparticle size and distribution, and the density and distribution of the layer.

2.3. Gas Sensing Methodology

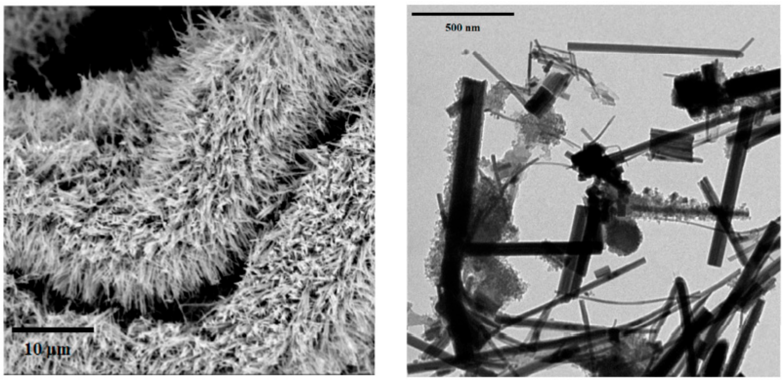
The sensors were placed inside a Teflon® chamber were the measurements would take place. The commercial alumina sensors have a platinum paste heater circuit in the back layer, which after the proper characterization, can be used to set the operating temperature of the sensors depending on the applied voltage. The gases chosen for being measured were H_2S, H_2. The conditions for the measurements were the following: three different temperatures were tested 150 °C, 200 °C and 250 °C. The concentrations analyzed were 5, 10, 15, 20 ppm for H_2 and 10, 15, 25, 50 ppm for H_2S.

The sensors were stabilized during 1 h under a 100 mL/min flow of synthetic dry air (Air Premier Purity: 99.995%) at the working temperature for each analysis. Each gas concentration was applied as a pulse during 30 min followed by a cleaning step using synthetic air during 30 min, the total flow volume was kept constant during the whole characterization at 100 mL/min using a mass flow to mix both the gas and synthetic air to obtain the desired concentration.

3. Results

3.1. Sensor Structural Results

The EDX results for CoO_x-doped nanowires confirm the presence of the nanoparticles recovering homogenously the nanowire, meanwhile the Ag-doped nanowires showed a clustered Ag_2O nanoparticles non-homogenously spread among the nanowires due to the low solubility of the precursor compound. These results are shown in Figure 2. As it can be seen also seen in Figure 2 (TEM analysis for Ag-loaded samples), some of the nanowires have been recovered by nanoparticles meanwhile others present a clean surface. This non-homogeneous loading for silver indicates that the low solubility of the silver precursor for AACVD is not suitable for homogeneously doping the nanomaterials.



(**a**) (**b**)

Figure 2. (**a**) Surface sensor's E-SEM image nanowires carpet doped with cobalt oxide nanoparticles; (**b**) TEM image of WO_3 nanowires and Ag_2O nanoparticles.

The XRD spectra shown here has been performed to the pure nanowires, as the nanoparticles size and concentration are too low and both are below the instrument limit detection. As it can be seen in Figure 3, the nanowires present a triclinic structure belonging to the spatial group P-1.

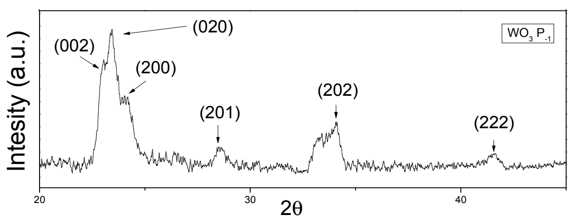
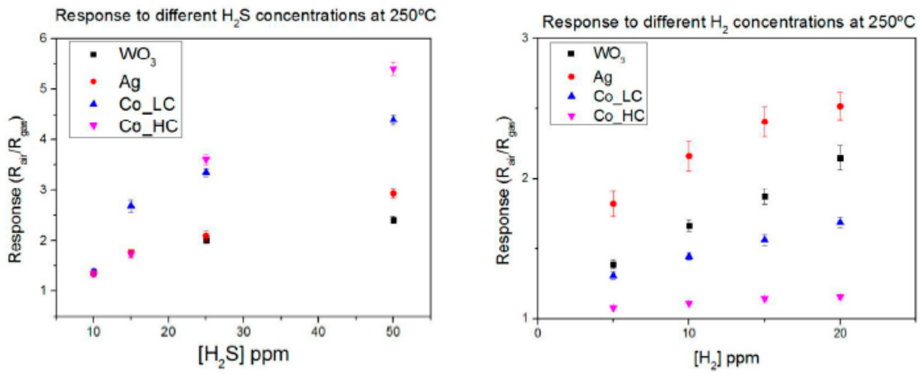


Figure 3. XRD spectra for WO_3 nanowires.

3.2. Gas Sensing Results

The best responses were obtained analyzing H_2S in comparison to H_2 results at 250 °C. The results have shown that both the cobalt based sensors and the silver based sensor have an opposite behavior towards this two gases analyzed. Cobalt based sensors are more selective towards H_2S even at the same concentration of 20 ppm as the silver based sensors working under H_2 exposure. The result for each gas tested are displayed in Figure 4.



(**a**) (**b**)

Figure 4. (**a**) Pure WO_3 and silver doped WO_3 sensors comparison; (**b**) Pure WO_3 and cobalt doped sensors comparison.

4. Conclusions

We have been able to develop a methodology to deliver different dopant agents in order to increase the sensitivity and selectivity of WO_3 nanowire gas sensors towards two specific gases. Furthermore, the nanostructure and gas sensing properties of these sensors have been characterized.

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Conflicts of Interest: The authors declare no conflict of interest.

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