Available online at www.sciencedirect.com

ScienceDirect

Procedia Engineering 87 (2014) 700 – 703

Procedia Engineering

www.elsevier.com/locate/procedia

EUROSENSORS 2014, the XXVIII edition of the conference series

Gas Sensing Properties of Metal-decorated Tungsten Oxide Nanowires Directly Grown onto Flexible Polymeric Hotplates

F.E. Annanouch[1], M. Camara[2], J.L. Ramírez[1,2], D. Briand[2], E. Llobet[1]
[1]*MINOS-EMaS, Universitat Rovira i Virgili, Tarragona, Spain*
[2] *EPFL-IMT SAMLAB, Neuchâtel, Switzerland*

Abstract

Aerosol assisted CVD (AACVD) is a self-catalyzed method that allows for growing single crystalline metal oxide nanowires at moderate temperatures (i.e. up to 380ºC). This is employed here to grow either Pt or Au-decorated tungsten oxide nanowires directly on flexible polymeric hotplates. E-SEM, EDX and XRD analysis have been used to investigate the morphology and the composition of the nanostructures grown. The functionality of the devices has been demonstrated by testing their gas sensing properties to ethanol, hydrogen and nitrogen dioxide. These flexible sensors show excellent and fast responses, good baseline recovery and repeatability. Tested over a few months, they show also excellent stability. These sensors are good candidates for being integrated in flexible tags for air quality control.

Peer-review under responsibility of the scientific committee of Eurosensors 2014

Keywords: AACVD; one dimentional nanostructures; gas sensors; flexible polymeric hotplates.

1. Introduction

Owing to their low cost, lightness, flexibility, easiness of processing and conformability, electrically and chemically inert polymeric or plastic sheets, represent an interesting opportunity for the fabrication of a new generation of gas sensors to be integrated in widespread, portable devices and smart objects. Aerosol assisted CVD, as shown by our prior results [1, 2], is a flexible, inexpensive and high-yield technique for growing metal oxides with remarkable gas sensing properties. Here we show the success of this technique in the growth of low-dimensional metal oxide nanostructures directly on flexible polymeric hotplates [3,4], e.g. suitable for integration in low cost tags. Furthermore, we show that the resulting devices exhibit a highly enhanced sensitivity towards small concentrations of hydrogen, ethanol and nitrogen dioxide, which represents a clear improvement in comparison to our previous works [1, 2].

Peer-review under responsibility of the scientific committee of Eurosensors 2014
doi:10.1016/j.proeng.2014.11.633

2. Experimental

Tungsten oxide nanowires functionalized with gold and platinum nanoparticles were directly co-deposited on a flexible polymeric microhotplate, via AACVD of tungsten hexacarbonyl (25 mg, W(CO)6, Sigma–Aldrich, ≥97%) dissolved in acetone (9 ml Acetone , Sigma-Aldrich, ≥99.6%) and either tetrachloroauric acid trihydrate (3,5 mg, $HAuCl_4 \cdot 3H_2O$, Sigma–Aldrich, 99.9%) or hexachloroplatinic acid hydrate (3,5 mg, $H_2PtCl_6 \cdot xH_2O$, Sigma–Aldrich, 99.9%) dissolved in methanol (3ml Methanol, Sigma-Aldrich, ≥99.6%). Substrates were cleaned with acetone and then with ethanol, dried in air and then placed inside the reactor. The solutions were kept in a glass flask and placed in an ultrasonic humidifier. The aerosol of solvents and precursors mixture was transported to the heated zone inside the reactor (380 °C), by using 500 ml/min of nitrogen as a carrier gas. The exhaust from the reactor was vented directly into the extraction system of a fume cupboard. The deposition time was between 15 to 20 min, until all the precursor had passed through the reactor. After deposition, annealing of the films was carried out at 350ºC for 3h with a constant flow (200 sccm) of synthetic air (Praxair, 99.99%).

Fig. 1 shows the flexible polymeric microhotplate mounted on a TO-8 package. Fifty micrometer thick Upilex-50S polyimide foil from UBE Industries, Ltd, was used as a gas sensor substrate. This material can withstand higher temperatures up to 450 °C. A double spiral shape-heater (Ti/Pt (20 nm/130 nm)) was deposited on the substrate by sputtering and patterned by a lift-off technique. A 700 nm thick photo-definable polyimide layer was spin-coated on the top of the heating area to electrically insulate the heater from the electrodes. And finally, interdigitated electrodes (Ti/Pt with a gap of 5µm and a square shape) were deposited on the top of the insulated film by sputtering and patterned by lift-off [3,4].

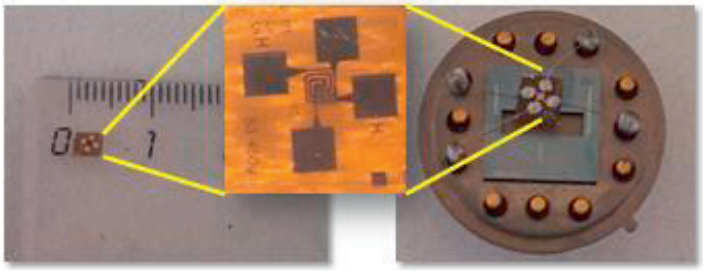

Fig. 1. Images of the nanowire flexible polymeric gas sensor before and after wire bonding to a TO-8 package for testing.

The morphology and the structural composition of the films were examined using Enviromental Scanning Electron Microscopy, X-ray Diffraction Analysis and Energy Dispersive X-ray Spectroscopy (E-SEM, XRD and EDX).

Gas sensing test of the sensors was carried out in a Teflon/Stainless steel test chamber (2×10^{-5} m^3), with continuous flow of 200 sccm. The desired concentrations of test gases were obtained employing calibrated gas bottles and PC-controlled mass flow controllers (Bronkhost Hitech 7.03.241). The sensors were exposed to the test gas during 10 min, and subsequently the chamber was purged with air during 30 minutes, which enabled recording the recovery of their baseline resistance. After this process, the sensors were ready for a new measurement. The sensor response (R) was defined as R= Ra/Rg for reducing gases and R= Rg/Ra for oxidizing gases, where Ra and Rg are the sensor resistance at stationary state in air and after 10 min of exposure to analytes, respectively.

3. Results and discussion

3.1. Surface morphology and structural characterization

A direct AACVD growth of functionalized WO_3 nanowires on a flexible polymeric microhotpale results in the formation of a thicker uniform bleu-black layer with homogenous distribution over the substrate. Fig. 2. a, shows an example of the synthetized WO_3 NWs, doped with Au nanoparticles grown at a temperature of 380°C. These Au or

Pt-decorated NWs are similar to the ones obtained in our previous works [1, 2]. The XRD pattern of the films (Fig.2.b) indicates the formation of monoclinic WO_3 NWs with preferred orientation in the [020] direction, and energy dispersive X-ray analysis confirms the presence of Pt or Au in the deposited layers, with an atomic ratio of 0.26 and 0.45 at.%.

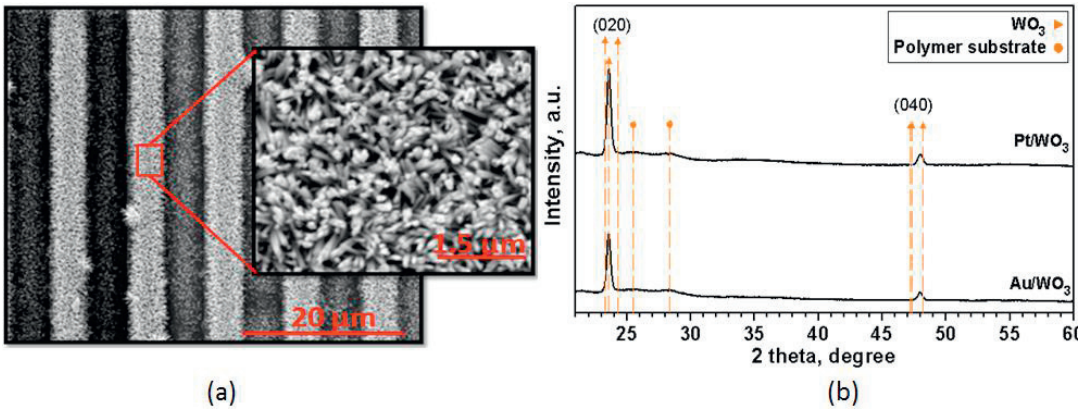

Fig. 2. (a) E-SEM image of the obtained WO_3 NWs doped with Au nanoparticles; (b) XRD pattern of functionalized WO_3 nanoneedles.

3.2. Gas sensing analysis

Ethanol, hydrogen and nitrogen dioxide were used as target gases to study the sensing characteristics of the fabricated sensors. The later exhibit an n-type semiconductor behavior (see Fig.3), i.e. decreasing electrical resistance when exposed to a reducing gas such as ethanol or H_2, and increasing electrical resistance when exposed to an oxidizing gas like NO_2. Moreover, the sensor responses were stable and reproducible with a fast response and recovery time.

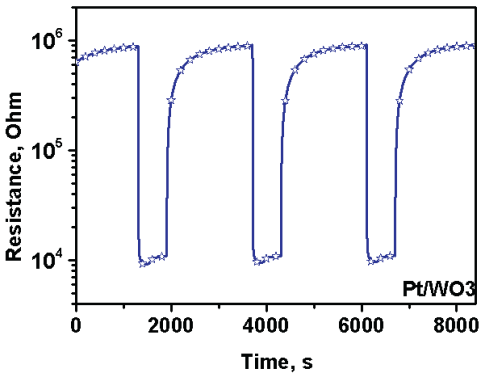

Fig. 3. Example of a Pt/WO_3 sensor response and recovery cycles toward 500 ppm of H_2 at a heater temperature of 200 ºC.

We have studied the effect of the temperature of the heating element on the sensor response. Pt-WO_3 NWs show very high hydrogen sensitivity and remarkable selectivity to this gas when the heater was operated at a power consumption of 50mW (see Fig. 4.a). On the other hand, Au-WO_3 NWs show good ethanol and NO_2 sensitivity and selectivity (see Fig. 4.b and c) when operated at higher temperature.

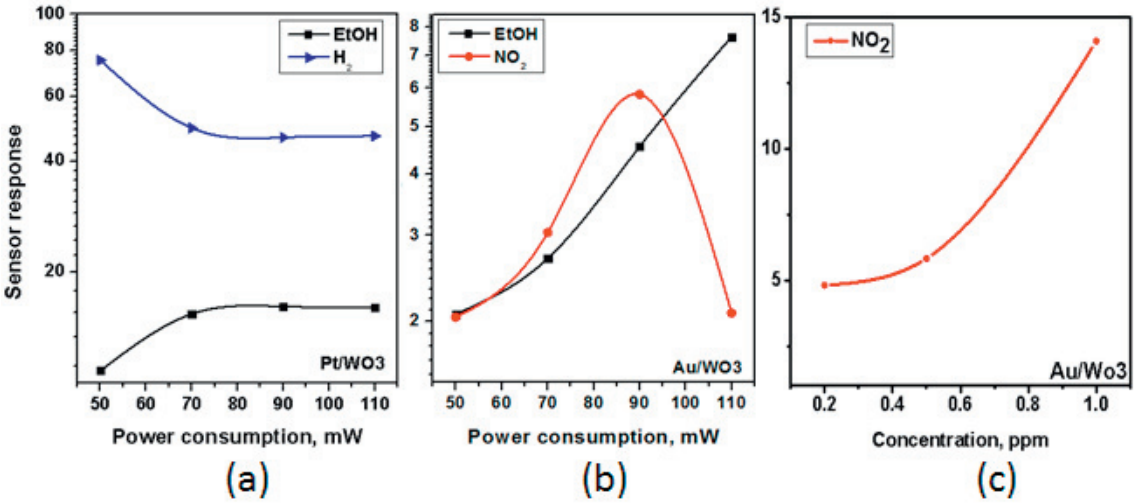

Fig. 4. (a) Sensor responses (R= Ra/Rg) to 80 ppm of EtOH and 500 ppm of H_2 as a function of the heater power consumption; (b) Sensor responses to 80 ppm of EtOH and 0.5 ppm of NO_2 as function of the heater power consumption; (c) Sensor responses (R= Rg/Ra) to 0.2, 0.5 and 1 ppm of NO_2 at a heater temperature of

4. Conclusion

Tungsten oxide nanowires functionalized with gold or platinum nanoparticles were directly deposited via AACVD on flexible polyimide transducers. These results demonstrated the capability of this technique to grow one dimensional nanostructure on this type of substrates. The microsensors fabricated showed appreciable responses to H_2, Ethanol and NO_2, with high sensitivity and good reproducibility. Furthermore, sensor based on Pt nanoparticles showed a remarkable selectivity toward H_2, while Au- functionalized WO_3 sensor showed good ethanol and NO_2 sensitivity and selectivity. As a future work, we will study the effect of humidity on the gas sensor responses, we will functionalize the WO_3 NWs with new metal additives such as Pd and Cu, and we will characterize the material morphology with other techniques like XPS, TEM, ect.

Acknowledgements

This work is supported in part by the Spanish Ministry of Science and Innovation under grant no. TEC2009-07107 by NATO under the Science for Peace Programme grant no. CBP.MD.CLG 983914, and the Autonomous Government of Catalonia under grant no. 2009 SGR 789.

References

[1] 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.

[2] F. E. Annanouch, S. Vallejos, T. Stoycheva, C. Blackman, and E. Llobet, "Aerosol Assisted Chemical Vapour deposition of Gas-SensitiveNanomaterials," Thin Solid Films, 548 (2013) 703-709.

[3] J. Courbat, M. Canonica, D. Teyssieux, D. Briand, N. F. de Rooij, "Design and Fabrication of Micro-Hotplates made on a Polyimide Foil: Electrothermal Simulation and Characterization to Achieve Power Consumption in the Low mW Range, " J. Micromech. Microeng, 21 (2011) 015014.

[4] J. Courbat, D. Briand, L. Yue, S. Raible, N.F. de Rooij, " Drop-Coated Metal-Oxide Gas Sensor on Polyimide Foil with Reduced Power Consumption for Wireless Applications, " Sensors and Actuators B, 161 (2012) 862–868.