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WO_3 Nanowires Decorated with Nickel Oxide Nanoparticles for H_2S Detection

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Abstract:
Single-step or two-step aerosol assisted chemical vapor deposition methods have been used to grow single crystalline tungsten oxide nanowires loaded with different concentrations of nickel oxide nanoparticles. Working temperatures and nickel loadings were studied and optimized to achieve the optimal working conditions for detecting hydrogen sulfide. Morphology, crystalline structure, composition, sensing properties and mechanisms will be presented and discussed in detail. The two-step method allows for controlling Ni loading in a wide range while keeping constant particle size.

Key words: tungsten oxide nanowires, nickel oxide nanoparticles, metal loading, gas sensing.

Introduction

Global emissions of gas pollutants have exponentially risen in the past decades. Developing stable, highly sensitive and selective inexpensive sensors has been a major driver in the development of nanosized metal oxides gas sensors. Here we focus on the growth, through aerosol assisted chemical vapor deposition, of n-type WO_3 nanowires loaded with p-type nickel oxide nanoparticles. The objective is to achieve both chemical and electronic sensitization effects to achieve sensitive and potentially selective H_2S metal oxide sensors [1]. The effect of nickel oxide nanoparticles can enhance the sensor response through a reversible sulfurization mechanism. Different routes are explored to effectively achieve a wide range of Ni loading, so optimization can be envisaged.

Experimental

Two approaches were used to grow the nickel loaded tungsten oxide wires. The one step methodology consisted on mixing 50 mg of $W(CO)_6$ as WO_3 organic precursor with 2.5 mg or 5 mg of $Ni(acac)_2$ as organic precursor for nickel nanoparticles in a solution of acetone: methanol (ratio 3:1). Once the deposition is finished the sensors were annealed inside a muffle heated at 5 ºC/min up to 500 ºC and hold for 120 minutes, to remove the carbon impurities found due to the solvents and the precursors used. The two steps methodology consists of growing in first place the nanowires forest, perform the annealing step described above and subsequently a second AACVD process is performed to load the nickel mixing 2.5 mg or 5 mg $Ni(acac)_2$ in 10 ml of methanol. Finally, the sensors are placed inside the muffle to perform a second annealing. Through this methodology a set of 5 different types of sensors were obtained: pure WO_3, a single step low Ni-loaded or high Ni-loaded WO_3, and a double step low or high Ni-loaded WO_3. These are labelled as WO_3, 1LC,1HC, 2LC and 2HC, respectively. The structure, morphology and composition of sensors were characterized via XRD, E-SEM, HRTEM and XPS.

Sensors were exposed to a continuous flow of different concentrations of H_2S, NO_2, CH_4 and ethanol under dry conditions and humidified conditions for H_2S were also measured. The effect of sensor operating temperature was studied too.

Results

Material characterization

Fig 1 shows a well-defined nanowire forest with nickel nanoparticles covering their tips. Also, HRTEM shows their high crystallinity. XRD revealed a quasi-stoichiometric WO_3 with a P-1 space group belonging to a triclinic structure fitting well with the JPCDS 73-0305. The chemical composition (derived from XPS) of a few samples is summarized in Table 1.

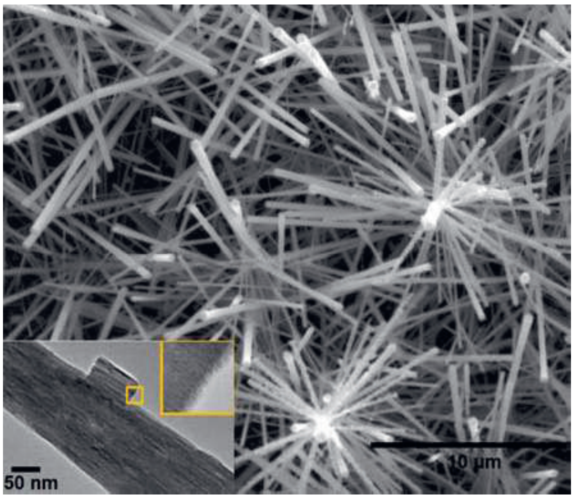

Fig.1. ESEM an HR-TEM image from WO_3 2Ni/HC.

Tab. 1: XPS quantitative analysis for Ni/HC sensors.

	W wt%	O wt%	Ni wt%
WO_3	25.0	75.0	-
1HC	22.0	76.0	**2.0**
2HC	20.0	65.0	**15.0**

Despite using the same quantity of nickel organic precursor, the 1 step methodology revealed a poor loading in contrast with the two steps methodology which is more efficient and results in a higher nickel-loading in the nanowires forest surface.

Gas sensing results

The optimal operating temperature was determined for the different sensors and gases tested. Highly Ni-loaded tungsten oxide nanowires are very sensitive to hydrogen sulfide. Employing the 2-step synthesis process, highly Ni-loaded nanowires are 5-fold more sensitive to H_2S than pure WO_3 nanowires. In addition, the optimal working temperature is decreased from 250 °C to 150 °C. This sensor is far more responsive to hydrogen sulfide than to any of the other species tested. Fig. 2 shows these results. Furthermore, the 2HC sensor was tested under humid conditions. At 35 %R.H. the response increases towards low H_2S concentrations, lowering the detection limit down to ppb level. Responsiveness, however, decreases at high hydrogen sulfide concentrations. This behavior can be due to hydroxyl groups present at the surface, which compete with oxygen for surface sites, decreasing the available reactive oxygen for H_2S at higher concentrations.

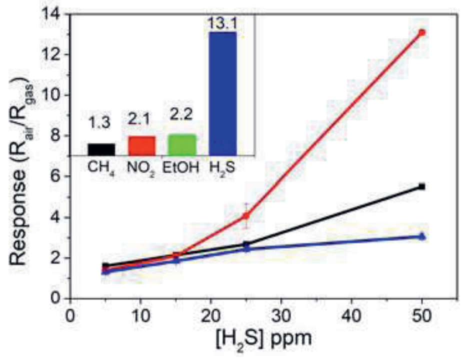

Fig. 2: Response towards H_2S of 2HC (red) 1HC (black) and WO_3 (blue) sensors at their optimal working temperature. Inset: Response of the 2HC sensor for the different species tested.

Gas sensing mechanism

The reaction mechanism involved in H_2S sensing relies on oxygen surface species [2].

$$O_2^-{}_{(ads)} + e^- \; 2O^-{}_{(ads)} \; (150–400\ °C) \quad (1)$$

$$H_2S + 3O^- \rightarrow SO_2 + H_2O + 3e^- \quad (2)$$

The nickel nanoparticles suffer a sulfurization which can be partially reversible through the following mechanism [3]:

$$NiO_{(s)} + H_2S_{(g)} \rightarrow NiS_{(s)} + H_2O_{(g)} \quad (3)$$

$$3NiS_{(g)} + 2H^+{}_{(aq)} \rightarrow Ni_3S_{2(s)} + H_2S_{(g)} \quad (4)$$

$$Ni_3S_{2(s)} + 7/2O_{2(g)} \rightarrow 3NiO_{(s)} + 2SO_{2(g)} \quad (5)$$

$$Ni_3S_{2(s)} + 9/2O_{2(g)} \rightarrow 2\ NiSO_{4(s)} + NiO_{(s)} \quad (6)$$

Conclusions

The AACVD method has been employed successfully to grow WO_3 nanowires loaded efficiently with nickel oxide nanoparticles increasing significantly sensor response towards H_2S. A study to determine the optimal working temperature and nickel loading has been carried out. Full details will be shown at the conference.

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