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Abstract

ZnO/WS_2 Hybrid Material, for NO_2 Detection, via the Combination of AACVD and APCVD Techniques †

Shuja Bashir Malik , Eduard Llobet and Fatima Ezahra Annanouch *

Departament d'Enginyeria Electronica, Universitat Rovira i Virgili, Països Catalans 26, 43007 Tarragona, Spain; shujabashir.malik@urv.cat (S.B.M.); eduard.llobet@urv.cat (E.L.)

* Correspondence: fatimaezahra.annanouch@urv.cat

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Abstract: We report for the first time the successful synthesis of ZnO/WS_2 hybrid material using a combination of aerosol-assisted chemical vapor deposition (AA-CVD) and atmospheric pressure CVD techniques. The morphology and the composition of the grown films were investigated and the results confirm the co-existence of both materials. Moreover, gas-sensing results against 500 ppb of NO_2 revealed the influence of WS_2 material on the ZnO gas-sensing performance. The operating temperature shifted towards lower values, from 300 °C to 150 °C. Furthermore, at room temperature, the ZnO/WS_2 sensor was able to detect NO_2 at ppb level.

Keywords: gas sensors; metal oxides; TMDs; AACVD; APCVD; nanomaterials

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1. Introduction

Zinc oxide (ZnO) is an n-type semiconductor with a wide band gap of 3.3 eV and high chemical and thermal stability [1]. It has been extensively studied and employed in gas sensing applications due to its low cost, non-toxicity and excellent gas sensing response. However, ZnO-based gas sensors operate at high temperatures (300 °C to 500 °C) and suffer from lack of selectivity, which are issues that hinder their use in a range of real-time applications. In a quest to overcome these shortcomings, researchers have been drawn towards the synthesis of hybrid nanocomposites of metal oxides with two-dimensional (2D) nanomaterial, to create heterojunctions through the nanocomposite and achieve outstanding gas-sensing performance. In this context, tungsten disulfide (WS_2) is one of the most studied 2D transition metal-dichalcogenides materials (TMDs). It is characterized by its high sensitivity, stability and low operating temperature. The co-deposition of these new materials (TMDs) with metal oxides is very challenging, due to the problems that face their synthesis, for instance: low production yield and difficulties around their integration in standard transducing substrates. Here, we report, for the first time, the successful synthesis of ZnO/WS_2 nanocomposite for NO2 detection, using the combination of AACVD and APCVD.

2. Materials and Methods

WS_2 synthesis: WS2 synthesis was performed by using two deposition steps: the first is the AACVD of tungsten hexacarbonyl ($W(CO)_6$; 50 mg) dissolved in a mixture of acetone and methanol (20 mL) to form tungsten oxide nanoneedles. In the second step, the obtained nanoneedles were subjected to an ambient-pressure CVD sulfurization using a sulfur powder and argon as a carrier gas, which resulted in a homogenous film composed of WS_2 nanotriangles, directly grown on alumina sensor transducer (Pt interdigitated electrode from one side and a resistive Pt heater at the back side). More details can be found in our previous reports [2]. **ZnO/WS_2 synthesis**: herein, ZnO nanorods were directly grown on the top of WS_2-based alumina substrate using AACVD of $ZnCl_2$ dissolved in ethanol at 400 °C. Nitrogen was used as carrier gas and the deposition time was approximately 30 min.

3. Discussion

Figure 1a and b illustrates the morphology of bare ZnO nanorods and WS2 nanotriangles, respectively. Figure 1c and d shows the morphology of the obtained ZnO/WS_2 nanocomposite. As we can observe, ZnO nanorods were successfully grown on top of WS2 nanotriangles, using a simple combination of AACVD and APCVD techniques. To confirm the structure and the composition, we analyzed our samples (ZnO and ZnO/WS_2) with Raman (Figure 1e,f) and energy-dispersive spectroscopy (EDX) techniques (Figure 1g). The results confirm the simultaneous presence of multilayers of WS_2 and ZnO materials.

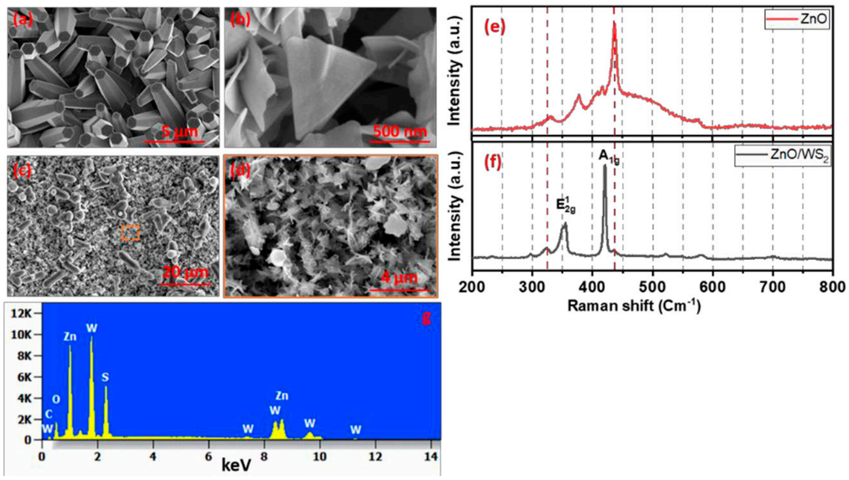

Figure 1. FESEM images of (**a**) ZnO, (**b**) WS_2, (**c**,**d**) ZnO/WS2, (**e**,**f**) Raman spectra and (**g**) EDX anaysis of ZnO/WS_2.

Furthermore, we have tested bare ZnO and ZnO/WS_2 gas sensors against 500 ppb of NO_2 at different working temperatures. According to the results (Figure 2a,b), bare ZnO showed no response below 200 °C and its optimal working temperature was considered at 300 °C. In contrast, the hybrid ZnO/WS_2 sensor was quite responsive at very low temperatures, especially at 150 °C where it shows stable and reproducible responses with good sensitivity (Figure 2c). This shift in the optimal working temperature demonstrates the effect of the addition of TMDs nanomaterials to the ZnO host matrix.

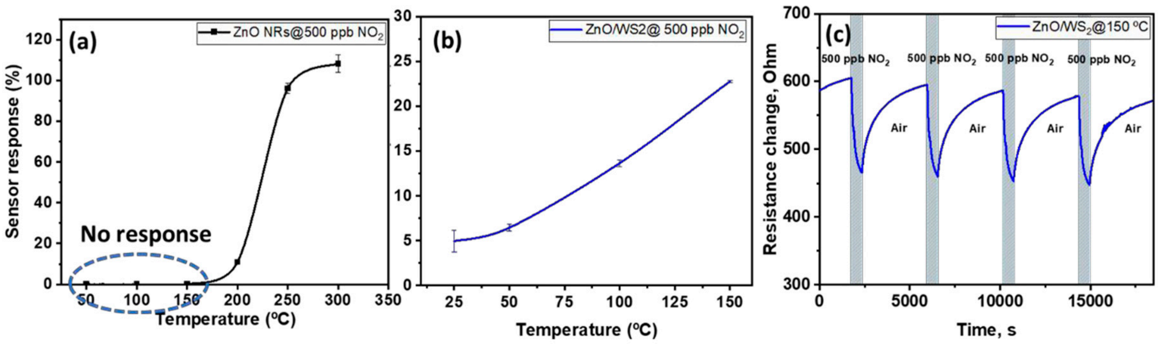

Figure 2. Sensor response as a function of temperature (**a**) ZnO, (**b**) ZnO/WS_2 and (**c**) example of ZnO/WS_2 resistance change in response to 500 ppb of NO_2.

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