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Nanostructured Materials Based on Thin Films and Nanoclusters for Hydrogen Gas Sensing †

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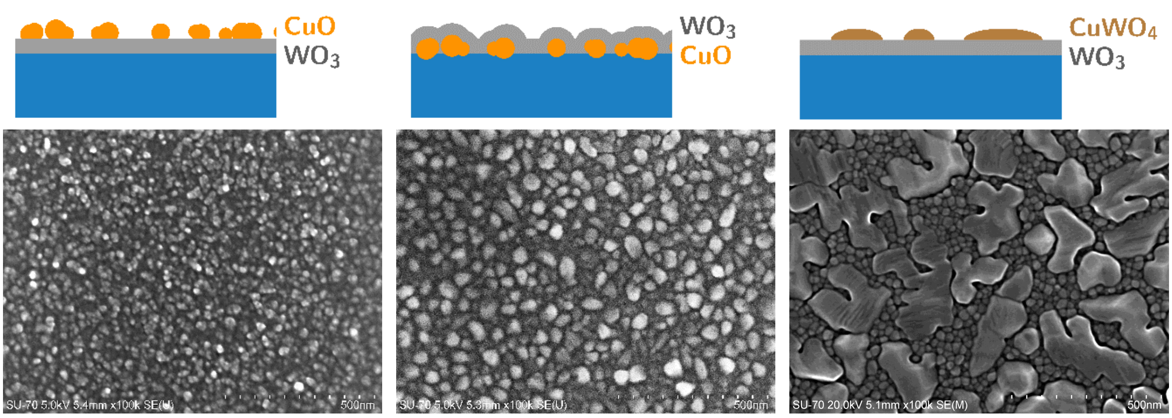
Abstract: In this paper, we present two approaches to synthesize nanostructured metal oxide semiconductors in a form of multi-layer thin films later assembled as a conductometric gas-sensors. The first approach produces a combination of thin solid film of tungsten trioxide (WO_3) with nanoclusters of cupric oxide (CuO) prepared by a magnetron-based gas aggregation cluster source (GAS). The second method is a two-step reactive magnetron sputtering forming a nanostructured copper tungstate ($CuWO_4$) on-top of a WO_3 film. Both methods lead to synthesis of nanosized hetero-junctions. These greatly improve the sensorial response to hydrogen in comparison with a WO_3 thin film alone.

Keywords: WO_3; CuO; nanoclusters; GAS; conductometric sensor; hydrogen sensing; nanosized hetero junction

1. Introduction

Nanostructured metal-oxide semiconductors (MOS) have been investigated for their sensorial activity for more than fifty years. A tremendously large variety of synthesis methods was developed [1]. Usually, these methods are wet-techniques or CVD ones, all providing a cheap and easy way to prepare a sufficiency of MOS. However, sometimes the tuning of the nanostructural properties or using the recipes for a wider spectrum of materials is complicated or even not possible [2].

In this work we present two magnetron-based techniques which enabled us to synthesize nanostructured composite materials later utilized as a conductometric hydrogen gas sensor. Materials exhibit enhanced sensitivity towards H_2 thanks to the nano-structure.



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

Figure 1. SEM micrographs of investigated structures. (**a**) CuO clusters on the WO_3 film; (**b**) CuO cluster covered with WO_3 film; (**c**) $CuWO_4$ nanostructures on WO_3 thin film.

2. Materials and Methods

Thin films of WO_3 were deposited on SiO_2 substrates using a reactive dc magnetron sputtering (60 W) from a metallic target. A mixture of argon and oxygen at a partial pressure ratio of 1:3 was used as a working gas. The substrate was heated to 400 °C.

Clusters of CuO were deposited from the copper target in the gas aggregation gas cluster source using a clean Ar as a working gas. The detailed description of the vacuum chamber and further parameters can be found in Ref [3].

$CuWO_4$ nanostructures were formed by reactive deposition from a copper metallic target using a reactive rf sputtering (230 W) in a mixture of argon and oxygen at a partial pressure ratio of 1:4. The substrate was heated to 400 °C. For more details see Ref. [4].

3. Results and Discussion

The SEM topographies of referred materials can be found in Figure 1. The relative response towards hydrogen of composite was increased in comparison with WO_3 thin film alone as can be seen in Figure 2. Only the proper amount of CuO or $CuWO_4$ leads to enhancement. The response of WO_3 decreases to low concentration or to high amount of added material (not shown).

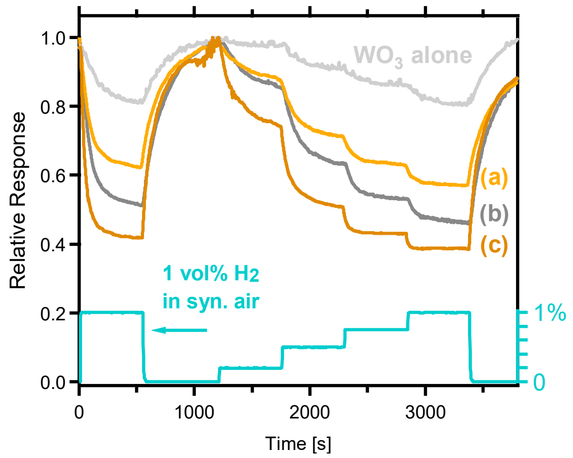


Figure 2. Relative response (i.e., relative resistance change) towards time-varied hydrogen concentration in synthetic air. The optimum temperature was picked for individual structures. See caption of Figure 1 for traces description.

The explanation is based on the formation of nanosized heterojunctions which reduces the conductive channel in thin film. For CuO clusters and WO_3 they are *p*-*n* type, and in case of $CuWO_4$ they are hetero *n*-*n*. Further details can be found in papers [3,4].

4. Conclusions

We were able to enhance the sensorial response of WO_3 thin film towards hydrogen by synthetizing CuO nanoclusters or $CuWO_4$ nanostructures. The deposition techniques are advantageous for their integration with microcircuit devices since they do not require any wet steps and the materials were used "as-deposited" without any need of annealing or sintering.

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Conflicts of Interest: Authors declare no conflict of interest.

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