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Thermally-induced microstructural evolution in nanoparticle-based CuO, WO_3 and CuO–WO_3 thin films for hydrogen gas sensing

Kalyani Shaji [a,1], Stanislav Haviar [a,1], Petr Zeman [a,1], Michal Procházka [b,1], Radomír Čerstvý [a,1], Nirmal Kumar [a], Jiří Čapek [a,*,1]

[a] Department of Physics and NTIS - European Centre of Excellence, University of West Bohemia in Pilsen, Univerzitní 8, Plzeň, 301 00, Czech Republic
[b] New Technologies–Research Centre, University of West Bohemia in Pilsen, Univerzitní 8, Plzeň, 301 00, Czech Republic

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ABSTRACT

This study systematically investigates the microstructural evolution of nanoparticle-based CuO, WO_3, and composite 'CuO–WO_3' thin films induced by their post-deposition annealing. The films were reactively deposited using a magnetron-based gas aggregation technique, with the composite films consisting of alternating monolayers of CuO and WO_3 nanoparticles. After deposition, the films were annealed in synthetic air at temperatures ranging from 200 to 400 °C and characterized using scanning electron microscopy, X-ray diffraction, Raman spectroscopy, and X-ray photoelectron spectroscopy. Annealing of the CuO films led to the most pronounced changes associated with a gradual enhancement of crystallinity accompanied by significant particle growth with increasing annealing temperature, while the WO_3 and CuO–WO_3 films were more thermally stable to crystallization and particle growth. Notably, at 400 °C, the CuO–WO_3 films crystallized into a novel γ-$CuWO_4$ phase. The annealed films were further evaluated for their gas-sensing performance upon H_2 exposure and the obtained results were analyzed in relation to film properties and the microstructural evolution induced by annealing.

1. Introduction

Hydrogen has gained significant interest as a clean and renewable energy carrier, which makes it a promising candidate for various applications, including power generation, large-scale energy storage, and chemical manufacturing [1,2]. However, its widespread applicability is hindered by safety concerns due to its low flammability limit (4% in air) and extremely low ignition energy (<0.02 mJ), which present substantial explosion risks [3]. Furthermore, delicate devices such as fuel cells require precise control of low hydrogen flow rates to ensure optimal performance. As a result, the development of reliable hydrogen sensing technologies is essential for monitoring and regulating hydrogen concentrations across various applications, ensuring both safe and efficient operations.

Among gas-sensing technologies, conductometric sensors have attracted considerable interest for their high sensitivity, fast response, and cost-effectiveness [4,5]. These sensors operate on the principle that the electrical conductivity of the sensing material changes in response to the target gases (analytes), which enables their detection and quantification. In particular, metal oxide semiconductors (MOS) are renowned for their superior performance as conductometric sensors [6,7]. In this case, gas species from the ambient atmosphere adsorb and desorb on the semiconductor surface, which alters the carrier concentration near the surface (known as the depletion layer (DL) for n-type MOS) and, in turn, the electrical properties of the material. Pure MOS sensors (not enhanced by noble-metal catalysts) are typically operated at elevated temperatures (200–400 °C) to facilitate the dissociation of H_2 molecules on the surface, which is a critical process for the sensing mechanism.

One of the key factors in the gas sensing performance is the microstructure of the sensing material, as it directly influences interactions between the sensing material and the analyte [8]. From this point of view, nanostructural materials are of particular interest. First, their high surface area significantly increases the number of active sites for gas adsorption and subsequent reactions. Second, optimizing the dimensions and spatial arrangement of the individual building blocks (e.g., nanoparticles (NPs), nanotubes) within the nanostructural materials significantly enhances the ability (known as transducer function) to convert chemical interactions with the analyte gases into a measurable electrical signal [9,10]. Third, so-called 'necks' can be formed at the

* Corresponding author.
E-mail address: jcapek@kfy.zcu.cz (J. Čapek).
[1] Researcher.

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