Detectors based on Pd-doped and PdO-functionalized ZnO nanostructures

V. Postica, ¹ O. Lupan, ^{1,2,3}, N. Ababii, ¹ M. Hoppe, ³ R. Adelung, ³ L. Chow, ⁴ V. Sontea, ¹ P. Aschehoug, ² B. Viana, ² Th. Pauporté²

Department of Microelectronics and Biomedical Engineering, Technical University of Moldova, 168 Stefan cel Mare Blvd., MD-2004, Chisinau, Republic of Moldova
PSL Research University, Chimie ParisTech-CNRS, Institut de Recherche de Chimie Paris, UMR8247, 11 rue P. et M. Curie, 75005 Paris, France
Functional Nanomaterials, Institute for Materials Science, Kiel University, 24143 Kiel, Germany
Department of Physics, University of Central Florida, Orlando, FL 32816-2385, USA

ABSTRACT

In this work, zinc oxide (ZnO) nanostructured films were grown using a simple synthesis from chemical solutions (SCS) approach from aqueous baths at relatively low temperatures (< 95 °C). The samples were doped with Pd (0.17 at% Pd) and functionalized with PdO nanoparticles (NPs) using the PdCl₂ aqueous solution and subsequent thermal annealing at 650 °C for 30 min. The morphological, micro-Raman and optical properties of Pd modified samples were investigated in detail and were demonstrated to have high crystallinity. Gas sensing studies unveiled that compared to pure ZnO films, the Pd-doped ZnO (ZnO:Pd) nanostructured films showed a decrease in ethanol vapor response and slight increase in $\rm H_2$ response with low selectivity. However, the PdO-functionalized samples showed excellent $\rm H_2$ gas sensing properties with possibility to detect $\rm H_2$ gas even at room temperature (gas response of ~ 2). Up to 200 °C operating temperature the samples are highly selective to $\rm H_2$ gas, with highest response of ~ 12 at 150 °C. This study demonstrates that surface functionalization of n-ZnO nanostructured films with p-type oxides is very important for improvement of gas sensing properties.

Keywords: ZnO, nanostructured films, hydrogen gas, gas sensor.

1. INTRODUCTION

The common fossil fuels such as coal, natural gas, oil/petroleum are the main sources of energy nowadays. However, this type of energy is limited, non-renewable and has a big impact on air pollution. Therefore, in recent years a high demand for green and renewable energy sources is emerging. In this context, hydrogen gas is expected to become a new green and renewable energy source for different applications, such as aerospace, automobiles, households etc., in form of fuel cells 1 . The main advantage of hydrogen gas is the abundance on Earth (less than 1% is presented as molecular H_2 gas) 1 . However, due to problems with hydrogen-storage and because H_2 is an extremely dangerous gas, its use was limited and was not widely implemented in industry $^{1-2}$. Therefore, detection of H_2 is very important in many fields.

As an *n*-type metal oxide, ZnO is an excellent material for use in chemiresistive detection of different reducing and oxidizing gases ³. However, the ZnO has low selectivity to H₂ gas ⁴ which is why different methods to improve the H₂ gas sensing properties of ZnO micro- and nanostructures were proposed ⁵. Among them, the doping and surface functionalization with noble metals, especially Pd and PdO, were demonstrated to be highly efficient for the improvement of H₂ gas selectivity and for the reduction of the operating temperature down to room temperature ^{2,5-6}. For example, Lupan *et al.* integrated a single Pd modified ZnO nanowire for the fabrication of a highly selective and sensitive H₂ gas nanosensor ⁷. However, in the case of ZnO nanostructured films the high performances are harder to achieve due to low surface-to-volume ratio of films compared to different nanostructures such as nanowires, nanobelts, etc. ⁸. ZnO nanostructured films can be grown by different methods such as spray pyrolysis, chemical bath deposition,

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