Pd-Functionalized ZnO:Eu Columnar Films for Room-Temperature Hydrogen Gas Sensing: A Combined Experimental and Computational Approach

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Cristian Lupan,[1,*] Rasoul Khaledialidusti,[2] Abhishek Kumar Mishra,[3,*,‡] Vasile Postica,[1,‡] Maik-Ivo Terasa,[4] Nicolae Magariu,[1] Thierry Pauporté,[5,*] Bruno Viana,[5] Jonas Drewes,[6] Alexander Vahl,[6] Franz Faupel,[6] Rainer Adelung [4,*]

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[1] *Center for Nanotechnology and Nanosensors, Department of Microelectronics and Biomedical Engineering, Technical University of Moldova, 168, Stefan cel Mare Av., MD-2004, Chisinau, Republic of Moldova*

[2] *Department of Mechanical and Industrial Engineering, Norwegian University of Science and Technology (NTNU), 7491, Trondheim, Norway*

[3] *Department of Physics, School of Engineering, University of Petroleum & Energy Studies, Bidholi via Premnagar, Dehradun, 248007, India*

[4] *Functional Nanomaterials, Faculty of Engineering, Institute for Materials Science, Kiel University, Kaiserstr. 2, D-24143, Kiel, Germany*

[5] *PSL Université, Chimie ParisTech, CNRS, Institut de Recherche de Chimie Paris (IRCP), 11 rue P. et M. Curie, F, 75005 Paris, France*

[6] *Chair for Multicomponent Materials, Faculty of Engineering, Institute for Materials Science, Kiel University, Kaiserstr. 2, D-24143, Kiel, Germany*

*Corresponding authors:

Prof. Dr. Thierry Pauporté (thierry.pauporte@chimieparistech.psl.eu)
PSL University, CNRS, France

Prof. Dr. R. Adelung (ra@tf.uni-kiel.de)
Kiel University, Germany

Prof. Dr. Abhishek K. Mishra (akmishra@ddn.upes.ac.in)
University of Petroleum and Energy Studies, India

C. Lupan (cristian.lupan@mib.utm.md)
Technical University of Moldova, Republic of Moldova

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ABSTRACT

Reducing the operating temperature to room temperature is a serious obstacle on long-life sensitivity with long-term stability performances of gas sensors based on semiconducting oxides and this should be overcome by new nano-technological approaches. In this work, we report the structural, morphological, chemical, optical and gas detection characteristics of Eu-doped ZnO (ZnO:Eu) columnar films as a function of Eu content. The scanning electron microscopy (SEM) investigations showed that columnar films, grown via synthesis from chemical solutions (SCS) approach, are composed of densely packed columnar type grains. The sample sets with a content of ~0.05, 0.1, 0.15 and 0.2 at% of Eu in ZnO:Eu columnar films were studied. The surface functionalization was achieved using $PdCl_2$ aqueous solution with additional thermal annealing in air at 650 ºC. The temperature dependent gas-detection characteristics of Pd-functionalized ZnO:Eu columnar films were measured in detail, showing a good selectivity towards H_2 gas at operating OPT temperatures of 200 – 300 ºC among several test gases and volatile organic compounds (VOCs) vapors; such as methane, ammonia, acetone, ethanol, *n*-butanol and 2-propanol. At an operating temperature OPT of 250 ºC a high gas response I_{gas}/I_{air} ~ 115 for 100 ppm H_2 was obtained. Experimental results indicate that Eu-doping with an optimal content about 0.05 – 0.1 at% along with Pd-functionalization of ZnO columns leads to a reduction of the operating temperature of the H_2 gas sensor. DFT based computations provide mechanistic insights into the gas sensing mechanism by investigating interactions between the Pd-functionalized ZnO:Eu surface and H_2 gas molecules supporting the experimentally observed results. The proposed columnar materials and gas sensor structures would provide a special advantage in the fields of fundamental research, applied physics studies, ecological and industrial applications.

1. INTRODUCTION

One of the great challenges in stability and long-term detection of gas sensors based on semiconducting oxides is to reduce the operating temperature, specifically to the room temperature and this should be overcome by new nano-technological methods. Hybrid nano-materials, including new 2D materials [1–6], metal oxides [7–10] and other metallic systems [11] have shown exceptional promise for gas detecting and catalytic applications. Doping is an important procedure to control the sensor response with atomic surface arrangement as well as active adsorption sites for targeted gas, which are intentionally produced by doping foreign atoms in the oxides. In this context, doping of semiconducting/metal oxide nano- and microstructures with various rare earth (RE) elements, such as Tb, Er, Ce, La, Eu, etc. [1,12,13], becomes very important for improving the optical and electrical properties. This is fascinating for gas sensing applications as well due to their fast oxygen ion mobility, effective catalytic nature, and high surface basicity of the RE–based materials [1,14,15]. For instance, Xu and Yan fabricated a new fluorescent sensor based on Eu^{3+}-functionalized ZnO at metal–organic frameworks for volatile aldehyde gases (acetaldehyde, acraldehyde and formaldehyde) detection in ppb range at room temperature [16]. Somacescu *et al.* successfully synthesized binary ZnO–xEu_2O_3 (x = 5 wt%) oxide through a hydrothermal route demonstrating a high sensor signal down to 3 ppm of NO_2 gas, as well as a low sensitivity towards CO gas [2].

In this context, zinc oxide which corresponds to II and VI group semiconducting oxide material with a large bandgap (~3.37 eV, at room temperature (RT)) crystallizes in its hexagonal wurtzite phase as the most popular structure due to its stability at RT and this makes it an attractive material for doping with RE elements. However, the efficient adding of RE^{3+} ions into the ZnO lattice is challenging due to different technological approaches used, the large differences in ionic radii of