Cite this paper as : O. Lupan, D. Santos-Carballal, N. Ababii, N. Magariu, S. Hansen, A. Vahl, L. Zimoch, M. Hoppe, T. Pauporté, V. Galstyan, V. Sontea, L. Chow, N. H de Leeuw, F. Faupel, R. Adelung, E. Comini, $TiO_2/Cu_2O/CuO$ Multi-nanolayers as Sensors for H_2 and VOCs: An Experimental and Theoretical Investigation.
ACS Appl. Mater. Interfaces 13 (2021) 32363–32380.

$TiO_2/Cu_2O/CuO$ Multi-Nanolayers as Sensors for H_2 and VOCs: An Experimental and Theoretical Investigation

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ABSTRACT

Highly sensitive $TiO_2/Cu_2O/CuO$ multi-nanolayers have been grown in various thicknesses by a cost-effective and reproducible combined spray-sputtering-annealing approach. The ultra-thin TiO_2 films were deposited by spray pyrolysis on top of sputtered-annealed Cu_2O/CuO nanolayers to enhance their gas sensing performance and to improve their protection against corrosion at high operating temperatures. The prepared heterostructures have been investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD), ultraviolet visible (UV-Vis) and microRaman spectroscopy. The gas sensing properties were measured at several operating temperatures, where the nanolayered sensors with oxide thicknesses of between 20 and 30 nm (Cu_2O/CuO nanolayers) exhibited a high response and excellent selectivity to ethanol vapour only after thermal annealing at 420°C. The results obtained at an operating temperature of 350 °C demonstrate that the CuO/Cu_2O nanolayers with a thickness between 20 and 30 nm are sensitive mainly to ethanol vapour, with a response of ~150. The response changes from ethanol vapors to hydrogen gas as CuO/Cu_2O nanolayers thickness changes from 50 nm to 20 nm.

Density functional theory-based calculations were carried out of the geometries of the $CuO(\bar{1}11)/Cu_2O(111)$ and $TiO_2(111)/CuO(\bar{1}11)/Cu_2O(111)$ heterostructures and their sensing mechanism towards alcohols of different chain lengths and molecular hydrogen. The reconstructed hexagonal $Cu_2O(111)$ surface and the reconstructed monoclinic $CuO(\bar{1}11)$ and $TiO_2(111)$ facets, all terminated in an O layer, lead to the lowest surface energies for each isolated material. We studied the formation of the binary and ternary heteroepitaxial interfaces for the surface planes with the best matching lattices. Despite the impact of the $Cu_2O(111)$ substrate in lowering the atomic charges of the $CuO(\bar{1}11)$ adlayer in the binary sensor, we found that it is the different surface structures of the $CuO(\bar{1}11)/Cu_2O(111)$ and $TiO_2(111)/CuO(\bar{1}11)/Cu_2O(111)$ devices that are fundamental in driving the change in the sensitivity response observed experimentally.

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The experimental data presented here, supported by the computational results, promote the use of the multi-nanolayered films tested in this work as reliable, accurate and selective sensor structures for the tracking of gases at low concentrations.

KEYWORDS: Nanolayers, Nanomaterials, Multilayered Films, CuO, *p*-type, Cu_2O, TiO_2, sensor

1. Introduction

Functional nanomaterials, including semiconducting oxide heterostructures with tunable performances, are an essential part of semiconductor-powered devices. However, synthesizing such nanocomposites has to be highly specific with respect to phase control at the nanoscopic level. Heterojunctions between different semiconductor oxide nanocrystals, especially based on ultrathin films with mixed phases, may improve the characteristics of gas sensors due to their unique detecting mechanism [1–4]. The specific features of the heterojunction in nanocrystalline multi-layered composites is crucial to control the gas sensing characteristics, i.e. selectivity and gas response of the sensor, as a result of the top surface and interface phenomena [1,5,6]. A seminal work by Brattain and Bardeen [7] reported that gas adsorption on semiconducting surfaces produces a change of its electrical conductance [7], which has contributed to the further development of the sensor industry based on solid state materials.

From the nanotechnology point of view, metallic copper (Cu) and its oxides have received much attention due to their variety of real applications, particularly in the field of new nanotechnology components for microelectronics [4,8,9]. Copper oxides are *p*-type semiconducting oxides and can be obtained in forms such as cuprite (Cu_2O) and cupric oxide (CuO), which depends