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## **TiO<sub>2</sub>/Cu<sub>2</sub>O/CuO Multi-Nanolayers as Sensors for H<sub>2</sub> and VOCs: An Experimental and Theoretical Investigation**

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### ABSTRACT

Highly sensitive TiO<sub>2</sub>/Cu<sub>2</sub>O/CuO multi-nanolayers have been grown in various thicknesses by a cost-effective and reproducible combined spray-sputtering-annealing approach. The ultra-thin TiO<sub>2</sub> films were deposited by spray pyrolysis on top of sputtered-annealed Cu<sub>2</sub>O/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<sub>2</sub>O/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<sub>2</sub>O 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<sub>2</sub>O 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<sub>2</sub>O(111) and TiO<sub>2</sub>(111)/CuO( $\bar{1}11$ )/Cu<sub>2</sub>O(111) heterostructures and their sensing mechanism towards alcohols of different chain lengths and molecular hydrogen. The reconstructed hexagonal Cu<sub>2</sub>O(111) surface and the reconstructed monoclinic CuO( $\bar{1}11$ ) and TiO<sub>2</sub>(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<sub>2</sub>O(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<sub>2</sub>O(111) and TiO<sub>2</sub>(111)/CuO( $\bar{1}11$ )/Cu<sub>2</sub>O(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<sub>2</sub>O, TiO<sub>2</sub>, 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<sup>1-4</sup>. The specific features of the heterojunction in nanocrystalline multilayered 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<sup>1,5,6</sup>. A seminal work by Brattain and Bardeen<sup>7</sup> reported that gas adsorption on semiconducting surfaces produces a change of its electrical conductance<sup>7</sup>, 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<sup>4,8,9</sup>. Copper oxides are *p*-type semiconducting oxides and can be obtained in forms such as cuprite (Cu<sub>2</sub>O) and cupric oxide (CuO), which depends

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on the valence state of copper. The cuprous oxide cuprite (Cu<sub>2</sub>O) is amongst the earliest semiconducting oxides used in solid state electronics<sup>6,10,11</sup>. Although cuprite has been the focus of numerous experimental and theoretical studies<sup>1,7,12–14</sup>, including its vibrational and optical properties, the electronic properties of Cu<sub>2</sub>O continue to puzzle the scientific community. As applications of Cu<sub>2</sub>O in nanoelectronics, photovoltaics, solid-state electronics, biosensing and spintronics emerge,<sup>4,9,15</sup> as well as light-driven purification of wastewater,<sup>8</sup> understanding at the atomic level of the electronic structure of Cu<sub>2</sub>O is important for the control its properties and of identification of future applications in devices or nanodevices.

CuO has a band gap in the range 1.2 – 2.1 eV, with *p*-type semiconducting properties<sup>12</sup> with significant potential for sensing applications, especially in mixed CuO/Cu<sub>2</sub>O phases<sup>6,11</sup>. A summary of gas sensor structures based on copper oxide nanomaterials can be found in several reviews<sup>16–20</sup>.

The (111) surface has been found, both in simulations<sup>13,21</sup> and experimentally<sup>22</sup>, to be the most stable cuprite (Cu<sub>2</sub>O) plane under a range of different conditions. Furthermore, the almost complementary ( $\bar{1}11$ ) facet was observed to be highly prominent in the crystals of the more oxidised tenorite (CuO) phase<sup>23</sup>. Although less stable than other planes, the anatase TiO<sub>2</sub>(111) surface has been reported as one of the most reactive for photocatalytic applications<sup>24</sup> and in H<sub>2</sub> evolution<sup>25</sup>.

Inorganic UV absorbers such as TiO<sub>2</sub>, ZnO and CeO<sub>2</sub> are generally employed in shielding applications for the ultraviolet (UV) protection of different surfaces<sup>26,27</sup>, where effective physical nano-coating barriers are needed for high temperature applications<sup>28</sup>. Titania (TiO<sub>2</sub>) nano-coatings are used extensively to increase surface hardness and adhesive strength; to provide long term and high temperature protection against corrosion; to enhance tribological properties; and to improve the design of the transparent coatings of self-cleaning surfaces<sup>27–30</sup>.