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Enhanced performances of sensors based on ALD-synthesized MO_x/CNTs composites

Authors (R. Di Chio[1], K. Moulaee[1], G. Neri[1])

[1] Department of Engineering, University of Messina, C.da Di Dio, 98166 Messina

Heterostructures made from semiconducting metal oxides (SMOX) are fundamental for the development of high-performance gas sensors. Yet, despite the recognition of their importance in real applications, the understanding of the transduction mechanism either related to the heterojunction or simply to the core and shell materials is still lacking. A better understanding of the sensing response of heterostructured nanomaterials requires the engineering of heterojunctions with well-defined core and shell layers. This was possible by using the Atomic Layer Deposition technique which allows precise control over the film thickness, as fine as one monolayer. Carbon Nanotubes have been employed as conductive support for dispersing and stabilizing metal and/or metal oxide nanoparticles. These highly conductive substrates allowed us to operate the devices at relatively low temperatures while not being involved in the sensing response.

The electrical properties of the synthesized samples have been investigated to correlate the MO_x layer thickness to the baseline resistance. After that, the response toward low concentrations of target gases (acetone, ethanol, H_2, NO_2) has been assessed. All the materials showed good sensing properties in terms of high response and good signal stability. The response of MO_x/CNTs sensor to gases follows a volcano curve, reaching a maximum at an optimal layer thickness of about 4-6 nm.

The sensing mechanism of MO_x-CNTs composites can then be explained by assuming the formation of a p-n heterojunction between the MO_x film and the carbon nanotube support. The formation and height of the energy barrier are determined by the metal oxide morphology (layer compactness, thickness) and CNTs characteristics.

To confirm the main role of the heterojunctions in the sensing process, bilayers MO_x-Al_2O_3-CNTs materials have been prepared and tested towards target gases. Due to the insulating character of the intermediate Al_2O_3 layer, however, no electronic coupling may occur, and the electronic conduction is due only to the MOx shell.

In conclusion, the remarkable sensing performances of the MO_x-CNTs heterostructures can be attributed to the homogeneous and conformal MO_x layer provided by the ALD technique which also allowed to synthesize samples with optimized MO_x shell thickness. The CNTs employed as support materials provided a high surface area and an optimal electronic coupling between the core and the shell of the materials.

Corresponding author:

R. Di Chio

Contact information

r.dichio@unime.it