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Pt-nanoparticles decorated Amorphous/Crystalline *a*-V_2O_5/VO_2 Thin Films for NO_2 and H_2 sensing

Maria Basso[1], Valentina Paolucci[2], Vittorio Ricci[2], Natarajan Thirugnanam[1], Alessandro Martucci[1], Carlo Cantalini[2]

[1]Department of Industrial Engineering (DIIIE), University of L'Aquila, Roio 67100 L'Aquila, Italy.

[2]Department of Industrial Engineering (DII), University of Padova, Via Marzolo 9, Padova 35131, Italy.

Corresponding email: vittorio.ricci@graduate.univaq.it

Summary:

We report that nanosecond pulsed laser annealing (PLA) of solution based VO_2 thin films yields high surface area amorphous/crystalline *a*-V_2O_5/VO_2 nanostructures with promising chemoresistive gas sensing response to NO_2 (400 ppb –1 ppm) at 100 °C temperature. In addition, Pt-nanoparticles (Pt-NPs) decorated *a*-V_2O_5/VO_2 show excellent response to H_2 (5 – 100 ppm) with limit of detection (LOD) as low as 5 ppm. Remarkably Pt-NPs loading resulted to neutralize the humidity cross response (10 - 80% RH) to H_2 sensing, opening new perspectives for selective H_2 detection in humid environments.

Keywords: VO_2, V_2O_5, Pt-Decorated, chemoresistive, NO_2, H_2, gas sensor

Background, Motivation an Objective

Vanadium V_xO_y metal-oxides (V-MO), enclosing a large variety of the vanadium element in several oxidation states, (i.e. V^{3+}, V^{4+}, and V^{5+}), have been acknowledged as promising *n*-type material interfaces in gas sensing applications [1]. V-MO films have been deposited over dedicated substrates, using various physical and chemical techniques, such as thermal evaporation, electron beam evaporation, magnetron sputtering, sol−gel, electrochemical deposition, and hydrothermal methods. Moreover, recent investigations highlighted that V-MO nanostructures can be conveniently decorated with catalytic nanoparticles [2], or eventually engineered in complex heterostructures [3], to exploit superior room temperature gas sensing properties. All the above-mentioned synthesis techniques require however, high annealing temperatures (~ 550 °C) to properly fix crystallinity and stoichiometry, which severely endanger the mechanical adhesion of the metal electrodes (Ta/Pt) with the SiO_2 and Si_3N_4 substrates. To solve this problem, we applied nanosecond pulsed laser annealing (ns-PLA), which allows for local temperature increases within the film without involving the substrate, to synthesize amorphous/crystalline *a*-V_2O_5/VO_2 heterostructures chemoresistive gas sensors for NO_2 detection (400 ppb –1 ppm) at 100 °C operating temperature. We also demonstrated that Pt-nanoparticles (Pt-NPs) decoration greatly improves both the H_2 gas response (5 – 100 ppm) and the humidity cross sensitivity.

Description of the New Method or System

The versatility of sol-gel reactions was combined with ultrafast ns-PLA for the simultaneous crystallization and nanostructuring of V-MO thin films. Specifically, V-MO thin films were synthetized from a non-carcinogenic precursor and irradiated with a KrF excimer laser at room temperature in air. As shown in Fig. 1, the irradiation with 10 laser pulses induces the crystallization of a VO_2 phase inside an amorphous matrix. XPS analysis revealed that the composition of the amorphous phase is V_2O_5, which resulted to be dominant (~ 80%) as respect to crystalline VO_2 (~ 20%). In conclusion we synthesized an amorphous/crystalline *a*-V_2O_5/VO_2 heterostructure as a novel interface for gas sensing applications.

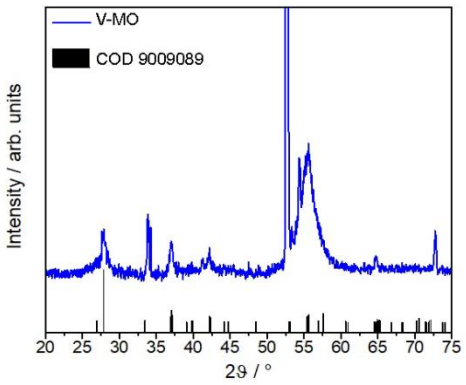

Fig. 1. Grazing Incidence GI-XRD of 10 ns-PLA annealed sol-gel deposited V-MO thin film. Peaks attributed to crystalline VO_2.

Results and Discussion

We firstly investigated the electrical response to NO_2 (10 – 80% @25 °C) of the *a*-V_2O_5/VO_2 heterostructure, in dry air at 100 °C operating temperature (OT), as shown in Fig. 2.

Upon exposure to NO_2 resistance increases, yielding a sensor's signal response (RR = R_g/R_a) of 1.6 ± 0.2 corresponding to 1 ppm NO_2 and a limit of detection (LOD) of 400 ppb.

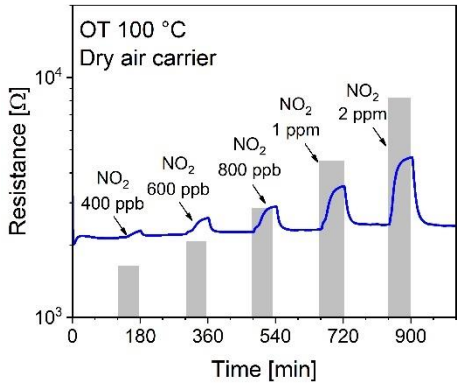

Fig. 2. Gas sensing response of the a-V_2O_5/VO_2 to NO_2 (400 ppb - 2 ppm) in dry air at 100 °C operating temperature (OT).

Considering that *a*-V_2O_5/VO_2 heterostructure scarcely responds to H_2 gas (here not shown), *a*-V_2O_5/VO_2 heterostructure was decorated with Pt-NPs and the H_2 response recorded as shown in Fig. 3.

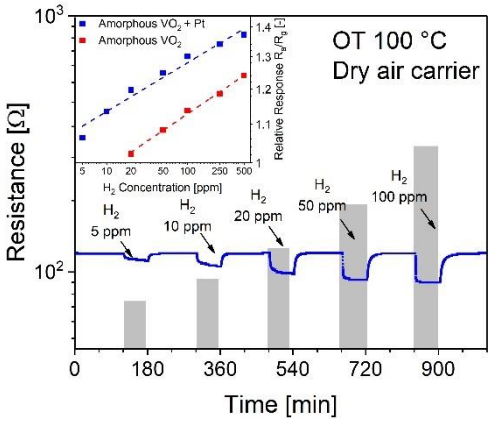

Fig. 3. Gas sensing response of the Pt-NPs decorated a-V_2O_5/VO_2 to H_2 (5 ppm - 100 ppm) in dry air at 100 °C. Inset: comparison of the calibration lines of the a-V_2O_5/VO_2 (red line) and Pt-NPs decorated a-V_2O_5/VO_2 (blue line).

Pt-NPs decoration highly improves the H_2 gas response. LOD as low as 5 ppm H_2 and a linear response of the calibration line (inset of Fig. 3) at 100 °C OT, confirm the positive effect of Pt-NPs decoration over *a*-V_2O_5/VO_2. As an interesting remark, we noticed (here not shown) that Pt-NPs decoration of *a*-V_2O_5/VO_2 almost annihilates NO_2 gas response.

Humidity cross sensitivity test in the 10 - 80% RH range (RH @25 °C) revealed a substantial lack of selectivity of the *a*-V_2O_5/VO_2 interface to detect NO_2 gas in humid environment. Opposedly, Pt-NPs *a*-V_2O_5/VO_2 interface exhibits an excellent selectivity to detect H_2 gas in the presence of humidity.

As a concluding remark, we envisaged two gas sensing mechanisms. The first considers the "not decorated", the second the "decorated" *a*-V_2O_5/VO_2 heterostructures, when exposed to NO_2 and H_2 gases.

Not decorated *a*-V_2O_5/VO_2 heterostructure responds according to reactions (1) and (2) to NO_2 and H_2 gases. The stronger electronegativity of NO_2 molecules, as respect to H_2, accounts for the prevalence of reaction (1) as respect to reaction (2). This situation is experimentally demonstrated by the higher response to NO_2 as respect to H_2 of the *a*-V_2O_5/VO_2 interface.

$$2H_2 + (O_2' - V_O^{\bullet\bullet})_{ADS} \rightleftharpoons 2H_2O_{(g)} + V_O^{\bullet\bullet} + e' \quad (1)$$

$$NO_{2(g)} + (O_2' - V_O^{\bullet\bullet})_{ADS} \rightleftharpoons (NO_2' - V_O^{\bullet\bullet})_{ADS} + O_{2(g)} \quad (2)$$

Platinum in Pt-NPs decorated *a*-V_2O_5/VO_2 heterostructure acts as a catalyst which activates the dissociation of hydrogen molecule to atomic H, which diffuses into the *a*-V_2O_5/VO_2 layer resulting in the hydrogenation (reaction (3)) of V_2O_5 into $H_xV_2O_5$ [4].

$$V_2O_5 + \mathrm{H} \rightleftharpoons H_xV_2O_5 \quad (3)$$

$$4H_xV_2O_5 + O_2' \rightleftharpoons 4V_2O_5 + 2H_2\mathrm{O} + \mathrm{e}' \quad (4)$$

Beside reaction (2), which always contributes to the decrease of the resistance, regardless the Pt-NPs decorating effect, in Pt-NPs decorated *a*-V_2O_5/VO_2, reaction (4) further contributes to the production of electrons. In conclusion, for Pt-NPs decorated film reaction (4) accounts for the enhanced response of the decorated platforms as respect to the not decorated ones to H_2 gas, as attested by the calibration lines in the inset of Fig. 3.

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