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Metal Oxides and Noble Metal Additives in the Nanocrystalline Regime. Enhancement of the Performances of Chemoresistive Gas-Sensors and Novel Interpretation Issues

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The modification of metal oxides by additives or dopants is well known for improving the performances of resulting chemoresistive gas-sensors. Common additives are transition metals, dispersed as ions in the oxide structure, or noble metals, usually present as nanoparticles dispersed among the oxide grains. Noble metals may induce electronic sensitization, based on the modification of the electronic properties of the host oxide, or spillover. As recently summarized: "In the case of the spillover mechanism, the target/analyte molecule is adsorbed onto the noble-metal-oxide cluster which leads to a weakening of its molecular bond. The adsorbate is transferred onto the support material where the reaction takes place. In the Fermi-level pinning mechanism, the gas detection reaction takes place on the surface of the noble metal cluster. The cluster electronically interacts with the base material and the contact pins the Fermi levels of both materials. If the work function of the noble-metal-oxide cluster is changed upon interacting with an analyte gas, the depletion layer in the base material caused by the contact is also affected."[1] The same authors also note that clear evidence of these mechanisms is seldom presented, as expected from the complexity of the underlying phenomena and the difficulty of suitable experimental observations. The use of nanocrystalline metal oxides is another feature widely accepted in gas-sensing field as deeply beneficial for the performances of chemoresistive gas-sensors, after the early report by Yamazoe [2]. Advanced synthesis techniques give the opportunity of combining the two approaches, by adding noble metal nanocrystals to nanocrystalline metal oxides, while at the same time retaining the nanocrystalline feature of the host oxide even at high operating temperatures. Nevertheless, if we refer to the above description of the possible interaction mechanisms between the noble metal and the host, we realize that the current description comprises an oxide host whose grain are implicitly assumed to be much larger than the noble metal guest structures. In the present work, on one hand the synthetic approaches will be described resulting in co-existence of nanocrystalline guest oxide and noble metal additive. The Pd-SnO2, Pt-TiO2 and Rh-TiO2 systems will be in particular reviewed. It will be confirmed that noble metal addition can effectively boost the sensor response with respect to the pure oxide. On the other hand, hints will be provided about additional issues with respect to "traditional"systems, for instance: i) possible doping of the metal host by noble metal cations, modifying the electronic properties of the oxide to a more relevant extent with respect to bulk materials; ii) necessity of considering structural modifications induced by noble metals additives on the oxide host. Above all, the necessity will be suggested of overcoming the traditional view of spillover and electronic sensitization, by finding a model capable of introducing a microscopic description of the interaction between the two components.

[1] A. Staerz, I. Boehme, D. Degler, M. Bahri, D. Doronkin, A. Zimina, H. Brinkmann, S. Herrmann, B. Junker, O. Ersen, J.-D. Grunwaldt, U. Weimar, N. Barsan, Rhodium Oxide Surface-Loaded Gas Sensors, Nanomaterials, 8 (2018) 892.
[2] N. Yamazoe, Sens. Actuators, B 5 (1991) 7-19.

Summary

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