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Hybrid titania–zincphthalocyanine nanostructured multilayers with novel gas sensing properties

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Abstract

Gas sensors based on hybrid ZnPc–TiO_2 nanostructures, produced by molecules and clusters both deposited by supersonic beams, demonstrate enhanced properties in terms of sensitivity, stability and recovery times with respect to pure ZnPc. The hybrid sensors produced by successive deposition of the molecules and the TiO_2 clusters show the ability to detect reducing gases, such as methanol, to which the response of metal-phthalocyanines is quite poor. A mechanism based on the formation of chemical bonding, activated by the kinetic energy of the molecules and the strong reactivity of the inorganic clusters, is proposed as being at the basis of electron transfer occurring between the inorganic nanostructure and the molecule. This mechanism would explain the rise of new gas sensing properties of this novel class of nano-hybrid materials.

Keywords: Gas sensors; Hybrid nanostructures; ZnPc; TiO_2; Supersonic molecular and cluster beams

1. Introduction

Organic–inorganic hybrid nanostructures are receiving considerable attention aiming at developing “smart” materials with new tailored properties [1]. This has given rise to new research approaches in different fields among which gas sensing is one of the most interesting. Indeed the idea of combining the stability of metal oxides with the properties of organic molecules, such as sensitivity and enhanced selectivity tailorable by chemical engineering, is a very intriguing and promising approach to the fabrication of novel classes of devices overcoming present limits.

Metal-phthalocyanines (MPc) are among the most studied class of molecules for gas sensing applications, since their electric properties strongly depend on the chemical composition of the surrounding atmosphere [2,3]. By virtue of their delocalized π-electron system they are good electron donors and show high sensitivity to oxidizing gases, while a very low interaction with reducing species has been observed so far [4]. In the form of thin films, usually prepared by vacuum evaporation, MPc behave as p-type semiconductors. In this work we show and discuss the enhanced gas sensing properties of hybrid sensors consisting of alternating layers of zinc-phthalocyanine (ZnPc) and nanostructured titania (n-TiO_2) deposited by means of supersonic molecular and cluster beams [5,6]. Distinctive of this technique is the ability to control critical parameters as the precursor’s kinetic energy and the cluster size and crystalline phase. Unprecedented results have been already obtained in the growth of highly oriented organic films for electronic device applications [7] and n-TiO_2 gas sensors [8]. Here the main goal is the synthesis of tailored hybrid materials with different structure and interfaces, in which the interaction between the species gives rise to new sensing properties. This approach has been already explored in the case of n-TiO_2–CuPc hybrids obtaining a substantial improvement in stability and sensitivity to reducing gases with respect to pure CuPc films [9]. In this paper we report on the use of zinc as central metallic atom and the introduction of a new three-layer device architecture.

2. Experimental

The deposition of thin films of ZnPc molecules and the TiO_2 clusters was performed in an UHV apparatus specifically designed to develop the synthesis of hybrid materials in a co-

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deposition scheme together with in situ characterization of the related processes by means of several optical and electron spectroscopy techniques (ellipsometry, UPS, XPS, Auger, LEED). The supersonic beam source used for the deposition of organic molecules consists of a quartz tube at the end of which is located a nozzle typically 50–100 μm in diameter. The raw MPc powder is sublimed within the quartz tube by joule heating so that the molecules can seed the much higher pressure of an inert carrier gas, usually He, introduced in the source. Through the nozzle a supersonic beam, seeded with the molecular species, is then formed. The kinetic energy E_k of the molecules can be controlled by the choice of the carrier gas, the percentage of seeding, the gas pressure and the source temperature so that it can be finely tuned up to several tens of eV (about 15 eV in these experiments) [5]. A pulsed microplasma cluster source (PMCS) has been used to deposit the titania clusters [10]. Briefly, its working principle is based on cluster condensation in a buffer gas after an intense discharge between two electrodes, in this case made of two titanium rods. The aggregates are seeded in the supersonic jet formed by the expansion of the gas: in these experiments helium plus a small oxygen percentage was used in order to obtain the direct formation of titania clusters. The mass distribution ranges from a few to some thousands of atoms and can be tuned by changing the operation parameters of the source or by exploiting aerodynamic mass separation effects. Cluster assembled titania films display a nanocrystalline structure at room temperature, as proved by XRD characterization [8].

The sensors were synthesized onto alumina substrates with seven pairs of gold interdigited electrodes (200 μm spacing, thickness 400 nm) and platinum heaters. Three different types of sensors were prepared varying their architecture but keeping a constant total thickness of about 100 nm: (i) pure ZnPc devices; (ii) two-layer hybrids (the 2L sensors in the following) with ZnPc deposited onto n-TiO_2, the thickness of both layers being 50 nm; (iii) three-layer hybrids (3L sensor) with a titania film between two organic layers, about 30 nm thick each. The deposition rates of ZnPc and n-TiO_2 were kept at about the same values and precisely 0.4 nm/min and 0.3 nm/min, respectively, as monitored by means of a quartz microbalance. Only minor deviations in the conductivity of different sensors of the same type were observed, proving that experimental data were not affected by non-reliable contacts between the gold electrodes and the active materials.

The devices were tested in a system equipped with MKS mass flow controllers and meters and a Keithley 6517A electrometer. Up to eight sensors can be hosted in the chamber and simultaneously tested in the same conditions. The sensors were exposed to a pure dry air flux of 100 sccm, then methanol was introduced in several cycles of about 20 min at increasing concentrations of 10, 20, 50 and 100 ppm, each one followed by an equivalent time for recovery.

3. Results and discussion

Depending on the device architecture the three types of sensors investigated display different morphologies and physical properties. First of all, we have observed large changes in the conductivity of the sensors, as shown in Fig. 1 where the typical dynamic response to methanol is plotted at 150 °C, the temperature where the best sensing performances were achieved in term of stability, sensitivity and recovering ability. It clearly appears that the ZnPc film has a much higher conductivity than the 2L sensor, in which n-TiO_2 is deposited first. This difference is due not only to the high resistivity of nanostructured titania, but also to the morphology of the ZnPc layer deposited onto the oxide, which is very different from the case of deposition onto alumina. In order to elucidate the morphologic structure of the sensors, Fig. 2 reports SEM images of the organic film deposited both onto the bare Al_2O_3 substrate and on cluster-assembled titania. The image of a 100 nm thick n-TiO_2 film grown onto SiO_2 is also shown for reference. The morphology of the oxide surface is very irregular and composed by grains of sizes ranging from 5 to less than 15 nm, confirming precedent AFM studies on very similar samples [8]. The films are strongly porous with the presence of large voids on the surface and ellipsometric measurements indicating an average porosity of the material of about 50%. In Fig. 2b, among ZnPc tile-like structures one can easily recognize the same oxide morphology. Such a high roughness on a nanometric scale makes the organic layer grow with a lower effective thickness, a smaller average crystalline size and a less connected structure with respect to the case of alumina (Fig. 2a), resulting in a poorly conductive film. The contribution of the ZnPc layer to the conductivity of the 2L sensor cannot be excluded *a priori*, since the titania layer is not supposed to completely cover the electrodes due to their large thickness (greater than the one of the sensing film) and the high directionality of the cluster beam.

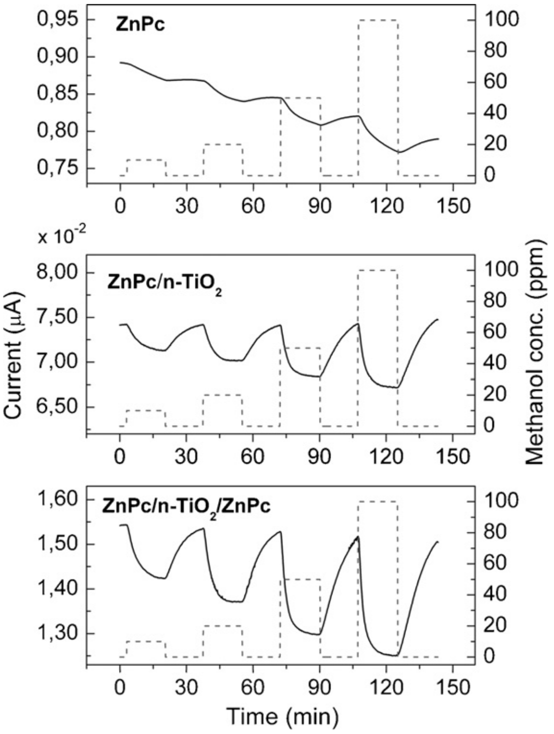

Fig. 1. Dynamic response of hybrid and pure ZnPc sensors at $T = 150\,^{\circ}C$ to methanol in cycles of exposures of 10, 20, 50 and 100 ppm.