Batch Fabrication of Nanostructured Heterogeneous Microarrays for Chemical Sensing

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ABSTRACT

Deposition of nanoparticles from the gas phase is becoming an enabling technology for batch production of nanostructured devices. Supersonic clusters beam deposition (SCBD) has been shown as a viable route for the production of nanostructured thin films. Due to high deposition rates, high lateral resolution, low temperature processing, SCBD can be used for the direct integration of nanostructured films on micro-fabricated platforms with limited or no post-growth processing. Here we present the industrial opportunities for batch fabrication of chemical sensor microarrays having nanostructured films of transition metal oxides as active elements, deposited on micro-fabricated substrates. Results on the detection of several gas species will be reported.

Keywords: gas sensors, thin film, nanostructure, batch deposition, clusters

1 INTRODUCTION

The chemical composition of the surface of semiconductor metal oxides at high temperature is in equilibrium with the atmosphere to which it is exposed. If the atmosphere changes, alteration of the surface chemistry also occurs, as a consequence. The electrical conductivity of the oxide surface follows these modifications. This phenomenon is exploited in conductimetric gas sensors [1]. The most important materials for conductimetric gas sensors are semiconductor metal oxides, such as SnO_2, TiO_2, WO_3, In_2O_3, ZnO, Fe_2O_3.

The use of nanostructured oxide films as sensing layer has recently attracted conspicuous interest due to their huge specific surface increasing the interaction with gas-phase species. Several methods can be used to produce nanostructured oxide films, from sol-gel and wet chemistry processes in general, to physical methods such as sputtering or evaporation.

Among various deposition techniques, Supersonic Cluster Beam Deposition (SCBD) appeared to be very promising as nanoparticles can be directly deposited on micro-machined platforms with limited or no post-growth processing [2, 3].

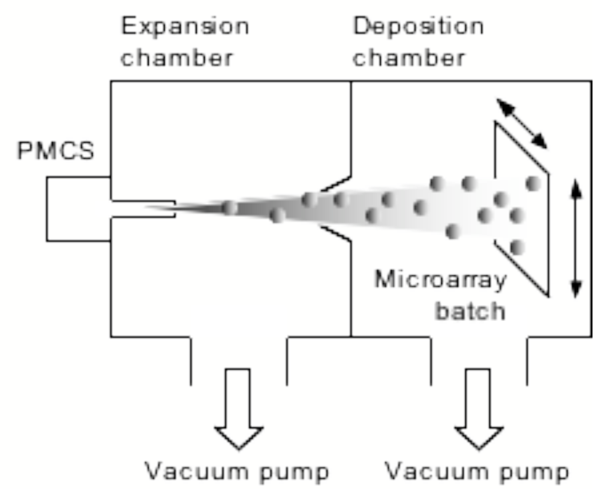

Figure 1. Schematic structure of the SCBD apparatus with nanoparticle source (PMCS), beam formation region (expansion chamber), and deposition chamber. Here a motorized sample holder equipped with hard mask system is located for batch deposition of microarrays.

The low energy characterizing the cluster-surface impact and the limited diffusion of the clusters are fundamental characteristics of SCBD process, causing the film to grow accordingly to a highly porous structure at the nanoscales. In addition, SCBD offers the possibility to deposit nanostructured films on every kind of substrates, at room temperature, in ultra-clean conditions. Due to the high collimation of the cluster beam, patterned depositions with sub-micrometric resolution can be obtained by hard mask method [4]. This permits high-throughput parallel deposition of identical devices (batch) avoiding the use of photoresist and chemical etching, typical of photolithographic process, that could contaminate the platform/substrate surface. For example, direct integration of nanostructured materials is possible on micro-machined silicon wafers hosting large number (hundreds) of suspended membranes.

Here, we report on batch deposition of chemical sensors, based on heterogeneous microarrays of nanostructured oxides films, by SCBD. We also report on their sensing properties respect to several chemical species: from those related to environmental pollution, to volatile organic compounds (VOC), such as ethanol, to explosive-combustible gases, such as hydrogen.

2 EXPERIMENTAL

Films of nanostructured TiO_2, WO_3, SnO_2, MoO_3, PdO_x, and Fe_2O_3 having thickness around some hundreds of nanometers, were easily produced by SCBD. The cluster beam was generated by a Pulsed Microplasma Cluster Source (PMCS) [5]. The operation principle of the PMCS is based on the ablation of a cylindrical metallic target by a plasma jet of argon, ignited by a pulsed electric discharge. After ablation, metallic atoms thermalize into the inert gas and re-condense to form clusters that are entrained by the gas flux towards PMCS exit nozzle and extracted by nozzle expansion. A set of aerodynamic lenses [6] collects the gas-nanoparticles stream from PMCS nozzle and forces the nanoparticles to concentrate close to beam axis, increasing the beam collimation (divergence < 20 mrad), and the in-axis intensity. The beam collimation allows the separation of the deposition chamber from the nozzle expansion chamber, with differential vacuum, in order to reach ultra-clean conditions in deposition chamber. Various PMCS beamlines can face the same deposition chamber for co-deposition or multi-layer deposition. The deposition chamber is equipped with a motorized manipulator to allow the coverage of a relatively large area (50×220 mm^2), by sample holder rastering. Fig. 1 schematically shows the structure of the deposition apparatus.

By exploiting hard mask patterning, we developed micro-machined alumina platforms having an array structure in order to deposit different oxides on each single element of the array. Such a device is named heterogeneous microarray. A meander heater on back side and a Pt thin-wire thermometer were integrated on the platform to control the operation temperature of the microarray. Fig. 2 shows the layout of the micro-machined alumina platform. The sample holder into the deposition chamber was developed in order to host up to 25 platforms for batch deposition.

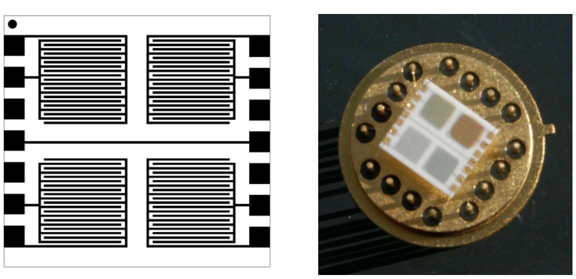

Figure 2. Left: layout of the micro-machined platform of the microarray. On front side, beside the four pairs of interdigitized metallizations, a Pt thin-wire thermometer was integrated, while on back side a thin film heater is present. The dimensions are 6 × 6.5 mm^2. Right: the microarray assembled into a standard 16 pin TO package.

The sensing materials composing the four elements of the microarray can be chosen among TiO_2, WO_3, SnO_2, MoO_3, PdO_x, and Fe_2O_3, tailoring the device to its final application.

The proper oxide stoichiometry is reached during post-deposition high temperature annealing in air (450°C, 24h). Beside stoichiometry adjustment, annealing is also needed to fix the nanostructure of the sensing materials in order to avoid any further modification during microarray operation.

3 RESULTS AND DISCUSSION

The as-deposited films have an amorphous and porous structure at the nanoscales, attributed to particle impact with low kinetic energy and limited diffusion. These are common features for almost all the nanostructured materials produced by PMCS. As an example, Fig. 3 shows a Transmission Electron Microscopy (TEM) image of as-deposited tin oxide film.

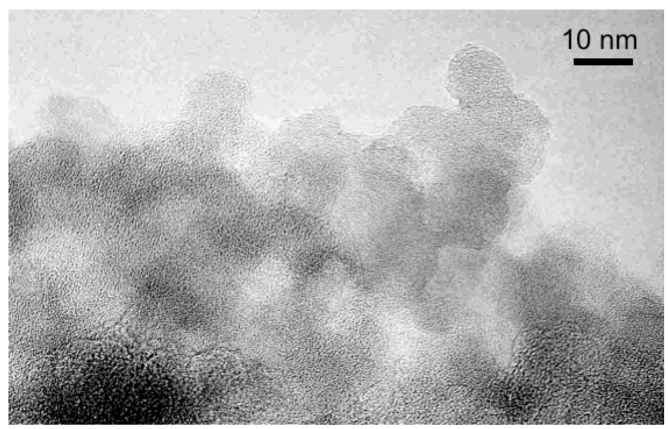

Figure 3. TEM image of as-deposited tin oxide sample. The film is composed by amorphous nanoparticles having an average size of 10 nm, assembled in a porous structure.

The as-deposited material is composed by nanoparticles having an average size of 10 nm, assembled in a porous structure. No evidence of lattice fringes is visible inside nanoparticles indicating amorphous structure. Typically, lattice fringes are discernible after the annealing process, indicating that nanoparticles reached a polycrystalline structure. It has to be emphasized that annealing at temperatures up to 500 °C causes small grain growth and coalescence, thus the porous structure is preserved. This is crucial for all the applications where devices operate at high temperature, such as conductimetric gas sensors.

The sensing properties of the nanostructured oxide films were evaluated with respect to various species related to environmental pollution, such as CO, NO, NO_2, and SO_2, as well as VOC, such as ethanol, methanol, ethylene, and explosive-combustible gases, such as hydrogen, methane and propane. By means of an automatic mixing system based on mass flow controllers, these compounds were added at trace level to pure dry air flowing into a test chamber.

A simple, low-cost, front-end electronic was specifically developed to acquire the signals from the microarray sensor during the test sequence. Fig. 4 shows, as examples, the response of nanostructured SnO_2 and WO_3 films to ethanol, acquired at the same time from the microarray. Few tens of minutes are needed for WO_3 baseline stabilization, while two hours for SnO_2 one. During the baseline stabilization time the sensing elements are already able to detect reactive species. Response and recovery times are generally in the range of few tens of seconds. Sensitivity levels in the ppm range and below were achieved for most of the tested gas species.

Baseline stability, fast response and recovery, high sensitivity, role of the operation temperature, effect of humidity, are the general issues to be addressed.

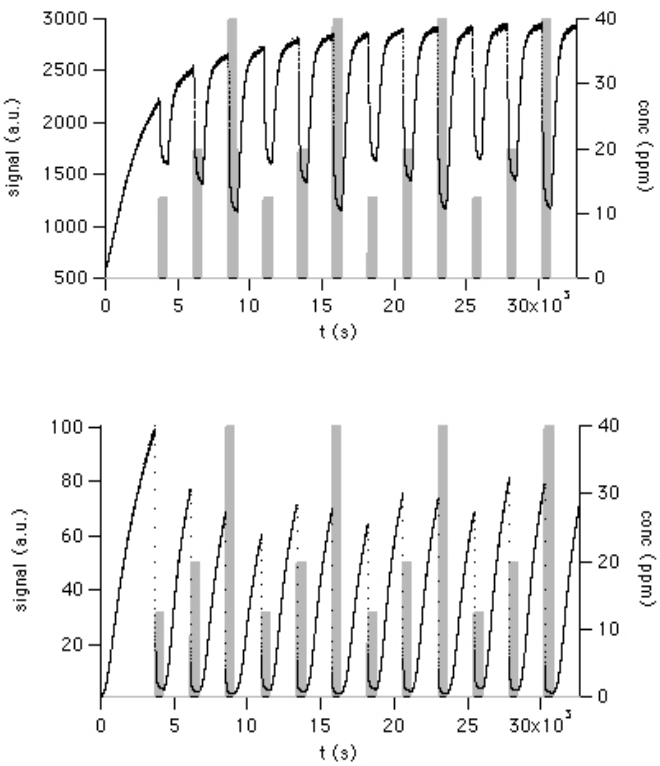

Figure 4. Response of nanostructured SnO_2 (top) and WO_3 (bottom) to ethanol. The measure was carried out at 350 °C. The grey bars indicate the real concentration of the compound under analysis, referred to right axis.

4 CONCLUSIONS

Highly porous nanostructured metal oxide films for gas sensing applications can be prepared by SCBD using PMCS. Sensing materials can be chosen from a list including, up to now, TiO_2, WO_3, SnO_2, MoO_3, PdO_x, and Fe_2O_3. By hard mask patterning, it is possible to prepare in batch devices having a microarray structure with different oxides as sensing elements (heterogeneous array). Batch deposition of up to 25 identical devices was performed with the present experimental set-up. The characterization of the gas sensing properties of each single nanostructured metal oxide composing the microarray shows good results, in terms of sensitivity, response amplitude, response and recovery times, respect to species related to environmental pollution, VOC, and explosive-combustible gases.

The use of a combinatorial approach in microarray fabrication integrated with neural network analysis for data handling can be of great help for the understanding of the mechanisms underlying gas selectivity and for the efficient and inexpensive realization of devices, for large-area atmosphere monitoring.

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