Gas Sensor Arrays by Supersonic Cluster Beam Deposition

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ABSTRACT

Supersonic cluster beam deposition was employed to produce nanostructured thin films of transition metal oxides to be used as gas sensors. Due to high nanoparticle beam collimation, patterned deposition was easily obtained by using hard masks, achieving sub-micrometric resolution. To exploit hard mask patterning micro-machined substrates having an array structure were developed in order to deposit materials with different properties on each single element of the array. Results on the deposition of nanostructured TiO_2, WO_3, SnO_2 and on the detection of volatile organic compounds (VOC) and gases related to environmental pollution (such as NO_x) are reported.

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

1 INTRODUCTION

Films of metal oxides kept at high temperature change their electrical conductivity in presence of reactive gases [1]. This process is generally reversible and the original conductivity is restored after desorption of the reactive species. In fact, at a certain temperature the chemical composition of the metal oxide surface reaches an equilibrium state with the chemical composition of the atmosphere to which it is exposed. Modifications in chemical composition of the atmosphere change the equilibrium conditions and the surface chemistry, as a consequence. The electrical properties of the film, such as conductivity, follow these changes. Gas sensors based on these phenomena have been developed, reaching market requests in 1968. The most important materials for gas sensing applications are simple metal oxides, such as SnO_2, TiO_2, WO_3, In_2O_3, ZnO.

Recently, the use of nanostructured thin films as sensing materials attracted interest due to the possibility to enormously increase the specific surface area of the films, that is the fundamental parameter for most applications relying on gas-solid interactions. Deposition of nanoparticles on sensor substrates by wet chemistry methods such as screen printing or doctor blading typically results in rather thick films and is prone to crack development upon evaporation of the solvent. These drawbacks can be circumvented by direct gas phase nanoparticle synthesis and deposition. Among various deposition techniques, supersonic cluster beam deposition (SCBD) turned out to be very promising as nanoparticles of controlled and selected size are directly deposited on substrates without the need of additional treatment and coating steps [2, 3]. Another advantage is the possibility to obtain porous nanostructured films on every kind of micro-machined platform at room temperature and in ultra-clean conditions. A broad variety of substrates is available, including suspended silicon membranes. Soft landing and limited diffusion are characteristics of the deposition process, causing the film to grow accordingly to a highly porous structure at the nanoscale. By using hard masks with micrometric resolution, patterned films can be obtained [4].

Here, we report on the gas sensing properties of nanostructured thin films of transition metal oxides made with the SCBD technique.

2 EXPERIMENTAL

Supersonic cluster beam deposition was employed to produce nanostructured thin films of TiO_2, WO_3, SnO_2. The cluster beam was generated by a pulsed microplasma cluster source (PMCS) [2, 5]. The operation principle of the PMCS is based on the ablation of a metallic rod by a plasma jet (He or Ar), ignited by a pulsed electric discharge in high vacuum conditions. After ablation, metallic atoms thermalize into inert gas and condense to form clusters that are entrained by the gas flux towards the PMCS exit nozzle. The nanoparticles are extracted from the PMCS by supersonic expansion and deposited on a substrate intersecting the beam [2, 3]. Following nozzle expansion, the cluster beam is directed through a set of aerodynamic lenses [6] in order to achieve beam stability, high collimation, high in-axis intensity, and high deposition rates.

The growth of nanostructured films takes place at room temperature on substrates exposed to the cluster beam. Due to the high collimation of the beam, patterned depositions were easily obtained by hard mask method. Figure 1 schematically shows the deposition technique. Soft landing and limited diffusion cause the film to grow to a highly

porous structure. Exposition to air causes the oxidation of the films. The proper oxide stoichiometry is reached during post-deposition high temperature annealing in air. Besides stoichiometry adjustment, annealing is needed to fix the nanostructure of the sensing materials in order to avoid any further modification during sensor operation.

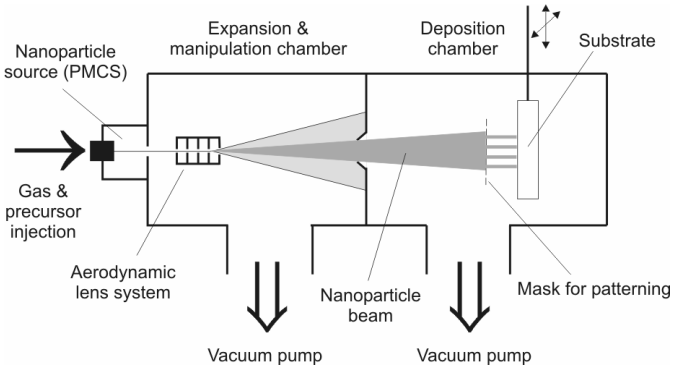

Figure 1: Schematic of the supersonic cluster beam deposition (SCBD) unit with nanoparticle source, particle size selection / beam formation zone and mask for patterned deposition.

3 RESULTS AND DISCUSSION

Figure 2 shows the nanostructure of an as-deposited tungsten oxide film in transmission electron microscopy (TEM).

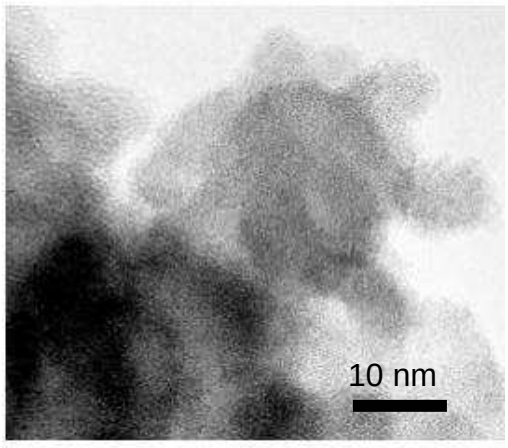

Figure 2: TEM image of deposited amorphous tungsten oxide nanoparticles of 5 to 10 nm diameter.

The film has an open and porous structure at the nanoscale attributed to particle impact with low kinetic energy. Due to their small size and low mass, nanoparticles acquire very little kinetic energy, even when accelerated to supersonic velocity. No lattice fringes are discernible in the as-deposited nanoparticles shown in Figure 2, indicating an amorphous state. By annealing of the film, the amorphous grains rearrange into a polycrystalline nanostructure.

The gas sensing properties of the films were evaluated with respect to various gaseous species interesting for environmental monitoring, such as CO, NO_x and SO_2, as well as volatile organic compounds (VOC), such as ethanol. Measurements were carried out in a temperature-controlled test cell under well defined atmosphere. The composition of the gaseous atmosphere could be controlled by precision mass-flow meters in a 5-line mixing system. Thereby, individual gaseous compounds could be added at trace impurity level to an inert carrier gas or oxygen/nitrogen mixtures. An electrometer was used to measure the current across the films at a fixed voltage of 5 V during the test sequence, consisting in the injections of suitable amounts of gas into test cell. The injection protocol and the signal acquisition were automatically processed by a PC. Figure 3 shows the response of nanostructured WO_3 film to NO_2 at concentrations less than 10 ppm. The temperature of the sensor was kept constant at 200 °C.

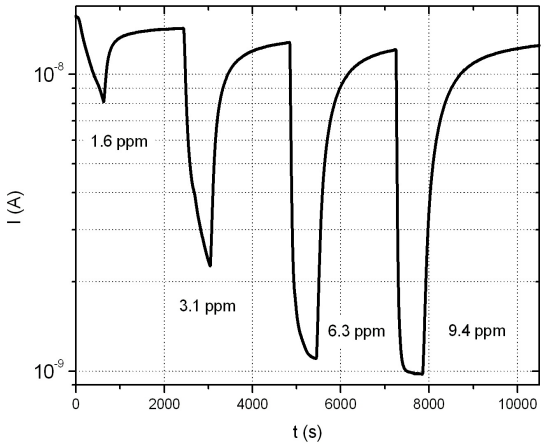

Figure 3: Response of a sensor with nanostructured WO_3 layer to different concentrations of NO_2.

The four peaks of current decreasing correspond to the injection in the test cell of 1.6, 3.1, 6.3, and 9.4 ppm of NO_2. Time sequence was 10' on-time, 30' off-time.

By exploiting hard mask patterning, we developed micro-machined substrates having a 4x4 array structure in order to deposit different oxides on each single element of the array. A thin film heater and a Pt thin wire thermometer were integrated on the back and on the front side of the substrate to control the operation temperature of the sensor. Batch deposition of micro-machined platforms was carried out in order to obtain multi-element sensors to interface neural network analysis algorithms.

4 CONCLUSIONS

Porous nanostructured metal oxide films for gas sensing applications can be prepared by supersonic cluster beam deposition and post-deposition thermal treatment. Using hard mask patterning, it is possible to simultaneaously prepare arrays with individual sensing elements. Alternatively, each array element can be coated with a different oxide resulting in gas sensors with different performance. The use of such a combinatorial approach can be of great help for the understanding of the mechanisms underlying gas selectivity and for the efficient and inexpensive realization of microsensor arrays, e.g. for environmental monitoring.

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