Batch fabrication of microsensor arrays by TiO_2 nanoparticle beam deposition

P. Milani[1*], E. Barborini[1], P. Piseri[1], S. Iannotta[2], P. Siciliano[3]

[1]CIMAINA-Dipartimento di Fisica, Università di Milano, Via Celoria 16, 20133 Milano, Italy
[2]CNR – Institute of Photonics and Nanotechnology – Trento Division – 38050 Povo di Trento, Italy
[3]CNR – Institute of Microelectronics and Microsystems – Lecce Division – Via Arnesano, Lecce, Italy

ABSTRACT

Here we present the production and characterization of chemical microsensors based on nanostructured TiO_2 deposited on microfabricated platforms. Aerodinamically filtered SCBD allows to control the nanoparticle size and to deposit in batch on microplatform arrays by using stencil masks. Since the material retains the memory of the precursor clusters, it is possible, by thermal annealing, to prepare arrays with elements characterized by different crystalline phase, grain size and porosity. This allows a novel combinatorial approach to the large-scale fabrication of multi-element micro- and nanosensing devices.

keywords: nanostructure, oxides, film, patterning, sensors

Among nanostructured transition metal oxides, TiO_2 is attracting a growing interest due to its widespread technological applications, ranging from photocatalysis to solar energy conversion, to gas sensing. The key point is the coexistence of suitable functional properties of TiO_2 with the huge surface available in nanostructured systems.

For the fabrication of gas- and bio-sensors the TiO_2 surface area, the micro- and nanostructure play a key role since the performances of these devices depend on reactions occurring at the surface and at the grain boundaries [1,2,3]. Engineering the surface structure and morphology, therefore, is of paramount importance for the integration of the nanostructured material into an effective device.

Up to now a deep comprehension of the role of film characteristics (stoichiometry, crystallographic phase, grain size distribution, porosity, roughness) in determining gas sensing properties is still lacking. The reason lays on the absence of independent control on each variable, due to their reciprocal influence. Many efforts have been directed to the control of TiO_2 surface nanostructure, however several problems still remain to be solved. For example, annealing significantly changes at the same time the microstructure, the crystalline phase and the nanoparticle dimensions of nanostructured titania [4,5]. This means that these parameters cannot be controlled independently. Another major issue is that conventional production and processing methods based on solid state or wet chemistry are not suitable for integration with batch microfabrication technology typical of microelectromechanical systems (MEMS) [6]. In particular the fabrication of arrays of microsensors for environmental monitoring, hazardous substances detection and food monitoring require a very precise control of the sensor material structure coupled to a combinatorial approach to explore and produce a larger number of different structures [6].

Alternatively to conventional synthesis methods, deposition of clusters from the gas phase is becoming an enabling technology for the production of nanostructured materials. Among different experimental approaches, supersonic clusters beam deposition (SCBD) has been shown as a viable route for the production of nanostructured systems ranging from organized nanoislands to nanostructured thin films [7,8]. Moreover, SCBD offers the possibility to synthesise films controlling the grain size distribution, the phase, the micro and nano porosity, and the width of the optical gap. Films with engineered properties can thus be synthesized.

Here we present the production and characterization of chemical microsensors based on nanostructured TiO_2 deposited on microfabricated platforms. Aerodynamically filtered SCBD allows to control the nanoparticle size and to deposit in batch on microplatform arrays by using stencil masks [9,10]. Since the material retains the memory of the precursor clusters, it is possible, by thermal annealing, to prepare arrays with elements characterized by different crystalline phase, grain size and porosity [10,11]. This allows a novel combinatorial approach to the large-scale fabrication of multi-element micro- and nanosensing devices [11]

Clusters are generated by a pulsed microplasma cluster source (PMCS). The principle of operation of a PMCS consists in the sputtering of a titanium rod by inert gas plasma ignited with a pulsed electric discharge [12]. After each pulse the ablated material inside the source condenses to form clusters. The clusters-inert gas mixture exits the source through a nozzle producing a seeded supersonic beam that can be intercepted by a substrate kept at room temperature. Deposition occurs under high vacuum conditions. The as-deposited films, after exposition to air, are stoichiometric [10,13].

During the expansion of the cluster beam an aerodynamic mass separation takes place causing the divergence of smaller clusters away from the beam axis, while larger clusters concentrate in the central part of the beam [14,15]. The exploitation of aerodynamic mass separation enabled us to produce cluster-assembled TiO_2 films characterized by a gradual change in size of deposited clusters [10].

Surface morphology can be also controlled acting on size distribution of cluster precursors by means of inertia-based filtering devices (aerodynamic lenses) fitted to cluster beam source. Strong removal of large mass clusters leads to flat films with grain size of ~15 nm and surface roughness of ~20 nm. At the opposite, the unfiltered beam leads to the synthesis of films with very high roughness extending up to micrometric scale, due to the presence in the beam of re-suspended large size agglomerates. Atomic force microscopy and scanning electron microscopy have been used to characterize the film morphology.

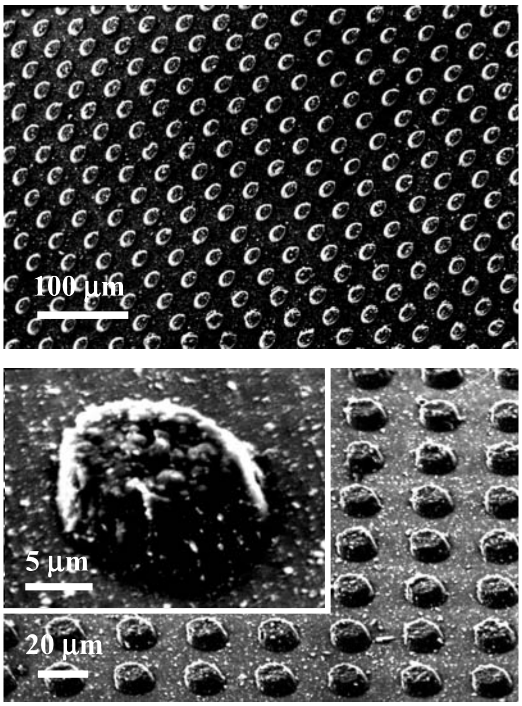

Figure 1: Microarrays produced by SCBD

Aerodynamic mass separation also affects the phase composition of the films. Films grown with the particulate close to the beam axis are composed of nanometric rutile crystals embedded into an amorphous matrix, while collecting the extreme periphery of the beam the films simply have an amorphous structure. Phase composition can be completely controlled by annealing processes: films containing rutile nanocrystals undergo grain growth by adding material from amorphous fraction; amorphous films follow the known phase transition route, switching to anatase at 400 °C and subsequently to rutile at 600 °C. We demonstrated that annealing processes up to 1000 °C do not destroy the nanostructure. Raman spectroscopy and X-rays diffraction have been used to characterize the phase composition and the size of nanocrystals.

One of the key feature of supersonic expansions is the high collimation of the particles beam. Exploiting this feature we were able to deposit regular patterns with a submicrometric lateral resolution by the use of stencil masks [9,10] (Fig. 1).

Aerodynamic separation effects can also be exploited to deposit in different regions different cluster mass distributions. It will be thus possible to batch fabricate arrays of sensors on micromachined platforms by depositing the clusters in selected areas. The arrays can then undergo to a single annealing step to create a large number of devices based on the same architecture but with the sensing material with different nanostructure and hence different performances.

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*email: pmilani@mi.infn.it
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