

Integrated Gas-Phase Manufacturing of Nanostructured Particulate Films

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ABSTRACT

An integrated process for controlled one-step production of nanostructured particulate thin films was realized by combining gas-phase (dry) nanoparticle synthesis, aerodynamic particle manipulation, size selection and deposition. Such films find industrial application for instance in fuel cells, supercapacitors, gas sensors or catalytic surfaces. The manufacturing process merges high-temperature flame or plasma synthesis of nanoparticles and supersonic nozzle expansion, thus benefiting from combined technological advantages. The integrated production technology for nanostructured thin films is presented by the example of titania for gas sensors.

Keywords: thin film, nanostructure, gas-phase synthesis, aerosol deposition, clusters, gas sensors

1 INTRODUCTION

Gas phase synthesis, specifically gas-to-particle conversion, is one of the industrially most relevant routes to nanoparticles. Typically, these processes operate in continuous mode and only a few steps, namely precursor delivery, particle formation and collection are necessary to obtain the product nanoparticles. Compared to wet chemistry processes, gas phase nanoparticle manufacture does not involve the tedious and expensive steps of solid-liquid separation, washing and drying and avoids the use of high liquid volumes and surfactants [1].

A range of synthesis methods has been established from which the appropriate process can be selected depending on the material, composition and property requirements of the product particles. Flame [2], plasma [3] and hot wall reactors are the most prominent examples producing nanoparticles at a commercial scale. Flame reactors offer high level control over nanoparticle size, morphology, composition and crystallinity [4, 5]. They are commonly used for industrial production of metal-oxide and carbon nanoparticles. Plasma reactors have the advantage that they can also be operated in oxygen-free atmosphere, thus allowing the production of non-oxide ceramic and metal nanoparticles. Hot wall reactors can be operated in inert and reactive atmospheres and typically offer excellent control over nanoparticle properties due to their well defined

flow field. Disadvantages are limitations in the processing temperature, wall deposition and efficiency.

In most gas-phase processes, the produced nanoparticles are collected on filters or cold surfaces directly after synthesis and are then recovered in the form of powders. Depending on the process parameters, these can have a rather broad particle size distribution, as particles with different temperature-time history are experience different growth conditions. For many applications requiring a narrow particle size distribution, a refinement of the particle population is necessary. A promising strategy for gas-phase manipulation of the particle population is the exploitation of nanoparticle inertial properties which is gaining an increased interest for the fabrication of nanostructured systems [6, 7]. An example is the expansion of the aerosol through a system of nozzles and aerodynamic lenses [8] that allows the gas-phase selection of a nanoparticle size fraction and focusing of particles to a beam. Particle as well as beam size can be controlled by the system pressure and the geometric arrangement of the nozzles.

Effective post-synthesis treatment of nanoparticles made in the gas phase such as high temperature annealing [9, 10] have been demonstrated, as well as the compatibility of aerosol methods with the high purity standards of the semiconductor industry [11]. Positioning of gas phase particles on a surface with a resolution in the 100 nm range and smaller has been shown [12] as well as the possibility to micropattern particle assembled thin films [13].

Here we report on the integration of a high temperature aerosol reactor for nanoparticle synthesis with a gas-phase particle manipulation stage and a deposition unit into a one-step process for production of nanostructured thin films. The manipulation stage includes supersonic expansion of the aerosol through a system of nozzles and focussing by aerodynamic lenses. The integration of the technologies yields high intensity nanoparticle beams. Coating of a 1000 cm² surface with a 100 nm thin carbon film was demonstrated in less than 1 hour, even with a laboratory-scale apparatus.

2 EXPERIMENTAL

Nanoparticles were produced in a pulsed microplasma cluster source (PMCS) [14, 15]. 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. Small amounts of oxygen in the atmosphere can lead to oxidation of clusters. Figure 1 shows how nanoparticles are extracted from the PMCS by supersonic expansion and deposited on a substrate intersecting the beam [15, 16].

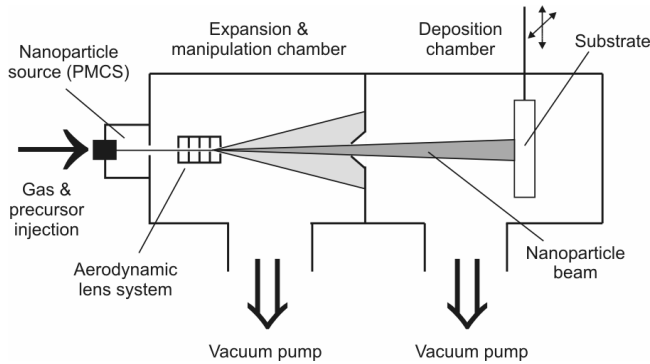


Figure 1: Schematic of the production apparatus with nanoparticle source, particle size selection / beam formation zone and deposition chamber.

Following nozzle expansion, the cluster beam was directed through a set of aerodynamic lenses [8] 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.

3 RESULTS AND DISCUSSION

Figure 2 is a transmission electron microscopy image (performed with a JEOL JEM-4000EX II, 400 KeV) showing the nanostructure of a titania film.

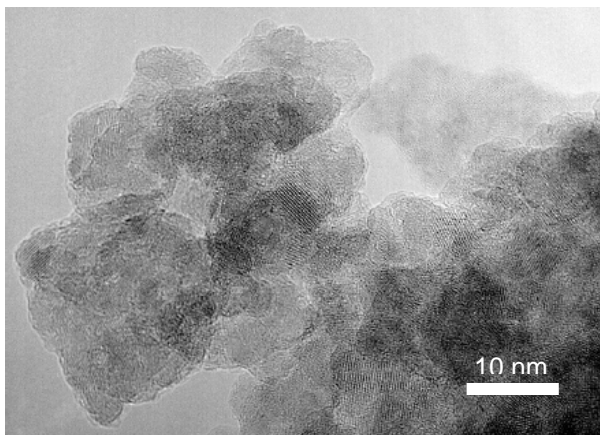


Figure 2: TEM image of deposited crystalline titania nanoparticles of 5 to 10 nm grain size surrounded by an amorphous titania matrix.

Grains with size of about 5 nm are aggregated to larger particles of 50 to 100 nm diameter. Particles are randomly assembled to constitute a porous structure, typical for the ballistic aggregation regime. Lattice fringes are discernible in some of the deposited clusters indicating their crystalline nature. Crystalline phases have been identified by lattice spacing analysis, indicating the coexistence of rutile and anatase nanocrystals. The major fraction of the film, however, appears to be amorphous titania. After annealing of the film at 450°C in air for 4 h, the film is still characterized by anatase and rutile nanocrystals with dimensions close to the ones of the as-deposited film. The absence of a substantial macroscopic grain growth during annealing is of fundamental importance for gas sensing applications since nanostructured sensors are typically operated at relatively high temperature (up to 500 °C) [17].

Due to the high collimation of the beam, patterned depositions can be obtained easily by using micromachined hard masks. Figure 3 shows such a patterned film of deposited carbon clusters that can be used as humidity sensors [18, 19].

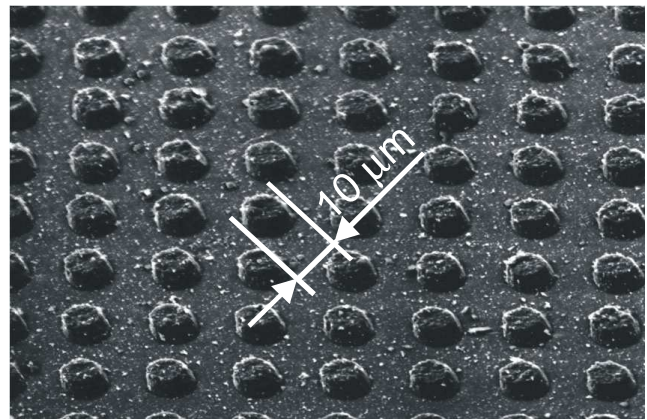


Figure 3: Nanostructured patterned film with submicron resolution by the use of masks.

The pattern has been obtained by using a nickel round hole grid of 3 mm diameter. Atomic force microscopy revealed granularity at the nanometer scale based on the assembling of grains with a mean diameter of 20 nm. The thickness of the deposited layers can be controlled by the deposition time and the location of the individual array element.

This capability of the supersonic cluster beam deposition technique to fabricate micropatterns can be employed for the parallel fabrication of arrays of active elements, e.g. for VOC sensing. Therefore, 210 sensors with different thickness were fabricated by controlled one-step cluster beam deposition on an alumina wafer where a 14x15 array of interdigitated gold electrodes has been previously microfabricated [20]. After thermal annealing (450°C, 4h), three elements were selected from different

array locations and characterized by their sensing performance. Therefore, the current at a constant potential of 10 V was monitored during the exposure to a controlled atmosphere of air and up to 200 ppm of methanol. The three sensors exhibited a different dynamic response with current peak values of about 2×10^{-7} , 3×10^{-7} and 4.5×10^{-7} A. After switching the atmosphere back to pure air, the current decreased to the initial value, showing the regeneration capacity of the sensor.

4 CONCLUSIONS

Nanostructured films were deposited on different substrates including micromachined alumina wafers using an integrated nanoparticle synthesis, gas phase manipulation and deposition apparatus. Here the unit was operated with a pulsed microplasma cluster source but other aerosol reactors such as flame or hot wall can also be interfaced. Due to the high collimation of the particle beam created in the gas phase manipulation stage of the apparatus, patterned depositions can be obtained by using micromachined hard masks. Such patterned coatings can be used for instance in the fabrication of efficient and inexpensive chemical gas sensor arrays.

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