Gas-Phase Synthesis of Nanostructured Particulate Films

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Abstract

Nanostructured films find increasing industrial application for instance in membranes, gas sensors, fuel cells, catalytic layers, biocompatible surfaces, batteries, and electronic components. The performance of these functional layers can be improved by using nanoparticles as building blocks and thereby incorporating their extraordinary physical and chemical properties into the three-dimensional film structure.

This article presents an overview of recent research on gas-phase methods for the production of such nanostructured films. Nanoparticle synthesis, methods for gas-phase particle manipulation as well as particle deposition are addressed. Emphasis is placed on flame and hot wall reactors for nanoparticle production along with cluster-beam deposition techniques. Means for gas-phase particle size selection and nanoparticle beam formation by expansion nozzles, aerodynamic lenses or electric charging are introduced. It is highlighted how the deposition process can be controlled to yield either highly porous nanostructured films or precisely ordered arrays of 1D, 2D and 3D nanostructures to fabricate microsensors, catalytic microreactors or of semiconductor nanowires.

Keywords: Thin films, Nanoparticles, Aerosol synthesis, Cluster-beam deposition, Nanostructured coatings

1. Introduction

A wide variety of gas-phase techniques has been developed for the fabrication of films. Apart from physical vapor deposition (PVD), the most extensively studied processes are chemical vapor deposition (CVD), spray pyrolysis (droplet deposition) and thermophoretic deposition of particles for optical fiber production†. The broad range of gas-phase technologies for film generation requires a categorization and restriction of the topic which is done here by the morphology of the deposited layers. Vapor and droplet deposition techniques usually result in films that are dense at the atomic level, while particle deposition processes usually give porous nanostructures consisting of individual nanoparticles (Fig. 1). The latter are the focus of this article.

The generation of nanostructured particulate films involves at least two steps, the formation of solid particles and the subsequent deposition on a substrate. In many processes, gas-phase modification or manip-
The general term "manipulation" is used here with special reference to the following meanings: i) the ability to sort the objects in terms of a size or geometry classification; ii) the ability to control the position and sometimes the velocity of the nanoscale objects and iii) the ability to modify them physically or chemically. The need for the first ability is due to the fact that most of the available synthetic routes for the production of nanoparticles are not able to produce a perfectly monodisperse population. Depending on the specific application, a refinement of the particle population is often necessary. The second and third requisites are naturally connected with the fabrication of a class of systems exploiting the extraordinary properties of the nanoscale objects, namely the "nanodevices". The possibility to integrate the particle production, manipulation and deposition stages into a continuous single process is one of the major advantages of the gas-phase route to nanostructured films that will be highlighted here.

Film formation by deposition of solid particles can be further categorized regarding the dominant deposition mechanism, namely inertial, thermophoretic and electrophoretic deposition. In inertial deposition, the inertia of typically accelerated particles is exploited. Thermophoretic deposition takes advantage of thermophoretic forces that act on particles when a temperature gradient is present, resulting in a momentum imbalance between the warmer and colder side of the particle and leading to particle deposition on cold surfaces. Electrophoresis is the deposition of charged particles in an electric field. Finally, a distinction can be made between vacuum and non-vacuum deposition processes.

2. Film Deposition Techniques

2.1 Non-vacuum approaches

This class of film formation routes involves gas-phase solid nanoparticle synthesis from liquid or gaseous precursors at or around atmospheric pressure and subsequent deposition on substrates. Due to deposition by thermophoresis, electrophoresis, diffusion or impaction with low kinetic energy, particles usually retain their shape so that the structural film properties depend on size and morphology control during particle synthesis.

The production of optical waveguide preforms is a prominent example for the industrial gas-phase manufacture of porous nanostructured films. Here, a flame torch is used to produce silica nanoparticles by introducing SiCl4 into a CH4/O2 or H2/O2 diffusion flame. SiO2 is synthesized by hydrolysis and/or direct oxidation, and rapidly condenses into solid primary particles which then grow by collision and coalescence to become hard agglomerates. The aerosol is then directed toward a deposition target where particles are primarily deposited by thermophoresis. The porous structures are later consolidated and drawn to form the optical fiber. An alternative manufacturing route for silica optical fiber preforms is the modified chemical vapor deposition process (MCVD). Here, the reactants flow inside a tube that is heated externally by a flame moving back and forth. Reaction and particle formation occurs inside the tube at temperatures between 1500 and 1800°C. The hot aerosol then flows down the tube where the particles deposit on the wall of lower temperature.

An approach similar to MCVD was applied by Kodas et al. for the production of thick superconducting ceramic wires and films. They sprayed a precursor solution into a hot wall reactor with oxygen carrier gas to form Ba2YCu3O7 particles. These were deposited directly from the gas phase onto the inside of the tube.
A gas-phase process relying on nanoparticle deposition by thermophoresis. Madler et al.\footnote{10} designed a two-stage hot wall aerosol reactor with deposition chamber in order to integrate Si/SiO$_2$ nanoparticles into memory devices. Nanoparticle deposition was based on thermophoretic forces. Their deposition chamber was designed to produce a controllable particle density profile along the silicon wafer substrate where particles were deposited uniformly. Thereby, Ostraat et al.\footnote{6} managed to overcome any concerns regarding particle contamination in microelectronic device fabrication, as particles typically create defects leading to device failure and introduce transition metal contamination that degrades performance. They successfully demonstrated that gas-phase nanoparticle and cluster production can be integrated with silicon-technology-based microelectronic device fabrication.

Also exploiting thermophoretic forces but using a flame process for particle synthesis, Skandan et al.\footnote{7} directly deposited SiO$_2$ and SnO$_2$ nanoparticles on substrates placed in a stagnation flow configuration in front of the flame reactor. Both burner and substrate were placed in a low-pressure (< 5 kPa) chamber to reduce the drag force on the particles relative to atmospheric conditions. Deposition was dominated by thermophoretic forces that were as much as two orders of magnitude larger than the drag force. By controlling the substrate temperature through cooling and variation of the distance to the burner, either porous particulate deposits or dense films were formed.

Thybo et al.\footnote{9} and Madler et al.\footnote{9} applied atmospheric pressure flame spray pyrolysis for the production of multi-component nanoparticles that were deposited by thermophoresis on cooled substrates mounted above the flame. The highly porous layers were used as catalysts\footnote{10} and gas sensors\footnote{10}, respectively. Madler et al.\footnote{9} described film growth by a simple model accounting for particle deposition by diffusion and thermophoresis.

A gas-phase process relying on nanoparticle deposition by impaction was proposed by Kashu et al.\footnote{10} Therefore, the aerosol produced by evaporation/condensation methods was expanded through a flow nozzle into a deposition chamber. Impaction occurred onto a temperature-controlled substrate that could be positioned in the chamber. Kashu et al.\footnote{10} point out that the deposited films do not require any post-deposition heat treatment, as the particles made in a high-temperature gas-phase process are typically already crystalline. This has advantages especially for the production of homogeneous films consisting of several materials. Here, vacuum film deposition methods such as co-evaporation or co-sputtering would require a post-deposition heat treatment to achieve a crystalline film structure which could lead to phase segregation or rearrangement of the deposited layer.

Inertial deposition of nanoparticles was also applied by Adachi et al.\footnote{12}, preparing SnO nanoparticles in an aerosol flow reactor and forming gas-sensing layers on substrates equipped with electrodes. Therefore, the aerosol was expanded through a critical flow nozzle into a 30-Torr deposition chamber. The 2 × 3-mm$^2$ film had a thickness of about 40 μm and high porosity. Also, particulate zirconia-silver coatings were made using this approach.\footnote{12}

In electrophoretic deposition, nanoparticles are charged during or after gas-phase synthesis and brought into a region with an electric field that drives them to a surface where they deposit. The main motivation for using electrophoretic deposition is the high deposition efficiency that can be obtained\footnote{13}. Investigating the effect of an applied electric field on the deposition rate of flame-made silica nanoparticles, Hwang and Daily\footnote{13} observed an increase of up to 35% over pure thermophoresis.

Often, electrophoretic deposition is combined with the use of a differential mobility analyzer that exploits the differences in the electrical mobility of charged particles to size-select a monodisperse fraction of a polydisperse aerosol. Wiedensohler et al.\footnote{14} for instance, deposited size-selected charged Ag particles made by evaporation-condensation of silver onto InP structures for application in lasers. Kruis et al.\footnote{15}, Kennedy et al.\footnote{16,17} and Krinke et al.\footnote{18,19} also applied this combined size classification-electrophoretic deposition process, as is discussed in more detail in Chapter 3.1 of this article.

### 2.2 Vacuum techniques

Vacuum processes for solid-particle deposition usually rely on expansion techniques that pass particles in a gas through an orifice or nozzle, after which expansion takes place to give a beam of particles that can be deposited onto surfaces.\footnote{13} Fig. 2 is a schematic of such a cluster-beam deposition (CBD) process. Generally, one can distinguish between neutral and ionized cluster-beam deposition. In ionized
CBD, particles are formed by an expansion of a vapor into vacuum, which is followed by particle formation and subsequent charging. The charged particles are then accelerated in an electric field toward the substrate where they deposit.[1] Due to the acceleration, particles gain high kinetic energy which leads to extensive atomic migration and even breakage during impaction. The kinetic energy of the clusters can be controlled by the acceleration voltage. In neutral cluster-beam deposition, the particles are not ionized or accelerated in an electric field before deposition[1, 20]. As a result, the particles acquire less kinetic energy and generally keep their shape upon impaction[20].

The starting vapor can be generated by a variety of means such as Joule heating of a material in a crucible, laser ablation, sputtering, or arc discharge[20, 21]. A broad range of materials including metals, metal oxides, and organics can be processed. Cluster sources can be catalogued by considering the regimes governing gas introduction and extraction: continuous or pulsed, effusive or supersonic. For cluster-beam deposition under vacuum conditions, a continuous gas flow must be compatible with stringent vacuum requirements and hence only effusive regimes are of practical interest. The realization and operation of pulsed cluster sources appears to be more complicated compared with continuous ones, but the reduced gas load has the advantage of allowing the use of a supersonic expansion regime and the compatibility with HV and UHV standards. An advantage of all CBD techniques is the separation between the particle formation region and the substrate, allowing deposition on temperature-sensitive materials such as polymers. These aspects are of fundamental importance for applications and in particular for the compatibility of CBD processes with microfabrication and planar technologies[22].

In order to improve the performance of cluster sources and to develop them toward a continuous process for fabrication of nanostructured coatings, the ablation plasma has to be confined to a well-defined target region, thus achieving high efficiency in material vaporization. Furthermore, the carrier gas load has to be kept low to avoid large pumping systems. Source geometry and dimensions should also be optimized to produce intense and stable cluster beams.

Pulsed microplasma cluster sources (PMCS) are an approach to fulfill these demands[23]. The working principle of PMCS is based on the spatially confined pulsed plasma discharge ablation of a target placed in a condensation chamber. The vaporized species is quenched by a pulse of inert gas and condenses to form clusters[24].

Schematically, the source consists of a ceramic body with a channel drilled through to perpendicularly intersect a larger cylindrical cavity (Fig. 3). The channel holds the target to be vaporized which typically is connected to the negative pole of a power source, thus acting as a cathode. The anode can be placed at any location inside the cavity or can also be introduced through the channel, opposite the cathode. A pulsed valve for introduction of inert carrier gas closes one side of the cavity while a nozzle is

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**Fig. 2** Schematic of a cluster-beam deposition apparatus according to Barborini et al.[61]. Nanoparticles produced with a pulsed microplasma cluster source (PMCS, see Fig. 3) are first expanded through a nozzle into an expansion and manipulation chamber with aerodynamic focuser (see Chapter 3.2) and are then drawn through a skimmer into the differentially pumped deposition chamber where they are deposited onto the substrate. The substrate can be positioned in the xy-plane allowing the coating of large areas as well as position-selective deposition.
located in the opposite cavity wall. The valve, backed with a high gas pressure, delivers inert gas pulses to the source cavity with an opening time of a few hundred microseconds. If the pulsed valve is closed, the source cavity is at the same pressure as the first vacuum chamber. Once the valve opens, the large pressure difference causes the formation of a supersonic gas jet directed against the cathode. A pulsed voltage (typical duration: 50 ms) applied between the electrodes ionizes the gas and generates a plasma. This is accelerated against the cathode and ablates the material that thermalizes and condenses to form clusters. Due to the aerodynamic confinement of the plasma in the cavity, the sputtering process is restricted to a cathode area of less than 1 mm². A continuous process can be achieved by rotational and translational movement of the cathode (Fig. 3b). The pressure difference to the adjacent expansion chamber drives the aerosol expansion through the nozzle in the form of a supersonic beam.

For a graphite cathode, a log-normal cluster mass distribution in a range from a few tenths to several thousands of atoms per cluster with an average size of about 1000 atoms/cluster is obtained with the PMCS. By operating the PMCS with a pulse frequency of 5 Hz, deposition rates of 100 µm/hour over a surface of 1 cm² placed at 500 mm from the exit of the nozzle can be achieved. The introduction of precursors into a PMCS, the use of alloy electrodes and the combination of several PMCS in one deposition apparatus easily allow formation of doped or multicomponent films of controlled composition. By changing the particle synthesis conditions, the nanoparticle size, morphology, crystallinity and chemistry can be tuned to meet the desired film properties. Random stacking of clusters leads to a high porosity texture with mesoscale granularity characterized by pores in the range of 2-50 nm and high specific surface area.

PMCSs have been used for the production of devices such as supercapacitors, gas sensors or high-throughput screening arrays for biological applications. PMCSs can be equipped with focalization devices as will be described in Section 3.2 in order to further improve cluster-beam intensity and patterning capabilities.

3. Gas-phase Manipulation and Patterning

A crucial point to be solved for a real technological breakthrough of the bottom-up approach to nanotechnology is the possibility to modify and manipulate nanoparticle building blocks prior to their assembly into nanodevices. Particle composition, crystallinity, size and morphology can be controlled to a certain extent in the synthesis step. Depending on the application, a post-synthesis functionalization or passivation of the particle surface might be necessary as well as a refinement of the particle size distribution, as gas-phase synthesis does not usually give monodisperse particles. Particle size and morphology also affect the porosity and roughness of the deposited layers, underlining the importance of size and morphology control. For the assembly of films by nanoparticle deposition, positioning of the nanoparticles on the substrate surface is of importance as it directly affects film homogeneity or the ability of patterned deposition with high lateral resolution.
3.1 Particle size separation
A narrow size fraction can be extracted from a polydisperse aerosol by a differential mobility analyzer (DMA)\(^30,32\). The DMA operates as an electrostatic classifier that selects charged particles of a certain size based on the balance between drag and opposing electric forces in an electric field. The size of the extracted particles can be controlled by varying the electric field strength\(^33,34\).

Kennedy et al.\(^16,17\) integrated a DMA along with an in-flight annealing zone into their process for production of nanostructured tin oxide films for gas sensing applications. Nanoparticles were produced from sublimated SnO in an aerosol flow condenser, followed by aerosol charging and DMA size fractionation. The size-classified aerosol was introduced into a second furnace for sintering, crystallization and partial oxidation to SnO\(_x\) nanoparticles that were deposited on a gas sensor substrate with interdigitized electrodes using an electrostatic precipitator or a low-pressure impactor. Nanostructured porous films of quasi monosized nanoparticles were grown and heat-treated to form conducting necks between the particles for better charge transfer in the gas-sensor application. The process of Kennedy et al.\(^16,17\) illustrates the possibility of integrated gas-phase production of nanostructured particulate films with a series of individually controllable particle manipulation steps. Such an integrated process was also used, e.g. by Kruijts et al.\(^33\) for the gas-phase preparation of size-classified PbS nanoparticles and by Krinke et al.\(^18,19\) for patterned nanoparticle deposition.

An alternative means for particle size separation in the gas phase is by exploiting aerodynamic effects. As an aerosol jet is forced by an obstacle to make a sharp (e.g. 90°) turn, particles will follow the gas flow depending on their inertia (Fig. 4). If the inertia exceeds the drag action of the gas flow, particles are unable to follow the stream lines and impact on the surface of the obstacle. The parameter governing particle impaction is the Stokes number which is defined as the ratio of the particle stopping distance \(\tau\) at the average velocity of the initial jet \(U\) to the jet radius \(D_j/2\):

\[
St = \frac{\tau \cdot U}{D_j/2} = \frac{\rho_p d_p^2 U C_c}{9 \eta D_j},
\]

where \(\rho_p\) and \(d_p\) are the particle density and diameter, respectively, \(C_c\) is the Cunningham correction factor and \(\eta\) is the dynamic viscosity of the gas\(^33\). In aerosol science, this effect has long been used in cascade impactors for size-selective particle sampling on collection plates\(^33,34\).

3.2 Particle focusing
Aerodynamic effects can also be used to concentrate particles at given positions in the flow field. Fig. 5 shows that the trajectory of particles with \(St \approx 1\) only slightly decouples from the gas stream lines. This effect can be used to focus particles to a beam. Using only aerodynamics effects induced by nozzles, Liu et al.\(^35,36\) produced such an enriched stream of particles. This was achieved with a system of so-called aerodynamic lenses consisting of successive axis-symmetric contractions-enlargements of the aerosol flow passage (Fig. 5). The work of Liu et al.\(^35,36\) was inspired by the research carried out by Fernandez de la Mora and co-workers\(^37,38\), who revealed the possibility of particle focusing and the existence of a common focal point for the near-axis particles when expanding an aerosol through a thin-plate orifice. The novelty of the work of Liu et al.\(^35,36\) is that they employed thin-plate orifices in a confined passage to manipulate the spatial distribution of particles prior to the nozzle and the subsequent free jet expansion (Fig. 5).

The integration of an aerodynamic focusing device into CBD leads to particle beams of high directional-ity, collimation and intensity. Depending on the mag-
The magnitude of focusing and the focuser-substrate distance, the beam diameter at the substrate can be reduced from several centimeters to a few millimeters. By substrate movement with a translational stage, nanostructured particulate films can be deposited over relatively large areas.

### 3.3 Patterned deposition

The fabrication of functional devices based on nanostructured materials often requires the ability to assemble nanoparticles in micrometer and submicrometer patterns with high precision and compatibility with planar technology. Physical and chemical vapor deposition techniques have long been used for the patterning of semiconductor, metallic and polymeric films and for the production of dot arrays. These techniques require putting resists or stamps in contact with a substrate that undergoes different pre- or post-deposition etching or thermal treatments.

The effect of such treatments on particle-assembled films has not been investigated systematically, however, several problems due to the porosity and granularity of nanostructured layers can be expected. For nanostructured films, a non-contact patterning would thus be highly desirable, and, in principle, it would be viable, e.g. by depositing particle beams on a substrate through a stencil mask.

Due to their high directionality, collimation and intensity, supersonic cluster beams are well-suited for the patterned deposition of films through masks that are placed into the beam in front of the substrate. The particles are concentrated at the center axis of the lens system, forming a beam.

### Fig. 5

Simulation of the gas flow (a) and trajectories of 15-nm particles (b) in an aerodynamic lens system according to Di Fonzo et al. The particles are concentrated at the center axis of the lens system, forming a beam.
panding the plasma supersonically through a nozzle. The aerodynamic lens system was placed about 75 cm from the expansion nozzle. The highly collimated particle beam exiting the lens system was deposited on a substrate downstream of the exit nozzle without any masks.

For gas-phase deposition of nanoparticles that travel at moderate velocity rather than at supersonic conditions, other patterning mechanisms have been developed based on low-range attractive forces, i.e., thermophoretic and electrostatic forces. Patterning with hard masks has been applied for the deposition of nanoparticles from the aerosol plume of flame reactors by thermophoresis and diffusion

Thybo et al. used a lift-off process with a standard photolithographic mask to fabricate porous nanoparticulate catalytic layers for microreactors. Fig. 7 shows how the substrate was first spin-coated with a 1.5-μm-thick layer of photosensitive polymer where the regions for deposition were afterwards dissolved in a NaOH solution. Then, the water-cooled substrate was positioned above the flame of an aerosol reactor to deposit a porous 50-150 μm layer of nanoparticles by thermophoresis and diffusion. Finally, the photoresist was dissolved in acetone, whereby the catalyst particles on the photoresist were removed from the sample. Although the roughness of the pattern edges was below 100 μm, the submicrometer resolution of the cluster-beam deposition approach could not be reached.

An approach for the patterned deposition by electrophoresis is the creation of a charge pattern on the substrate in a first stage and the subsequent deposition of charged particles. Krinke et al. created charge patterns using polydimethylsiloxane (PDMS) stamps to deposit monodisperse singly charged nanoparticles on oxidized silicon surfaces. With this technique, they were able to form particle-based nanowires with a thickness down to 100 nm and spaced 2000 nm apart.

3.4 Physical and chemical modification

Basically, all gas-phase processes involving particle formation and in-situ surface coating or functionalization can be coupled with one of the deposition methods described above. Most research in the field has focused on obtaining a powder rather than a film, though. The studies of Kodas and co-workers give examples showing how the particle composition and morphology can be changed by in-situ gas-phase coating processes in hot-wall reactors. The formation of functional coatings on oxide nanoparticles can
also be achieved by introduction of multiple precur-
sors into spray flames. Such multicomponent par-
ticles were deposited on substrates directly from the
gas-phase to give nanoparticulate films for gas sens-
ing or catalysis.

Effective post-synthesis treatment of nanoparticles
has been demonstrated, for instance, for the morphol-
ogy control of initially produced gold agglomerates
by in-flight high temperature annealing and sinter-
ing. Nanda et al. used this method for band-gap
tuning of PbS nanoparticles in tubular flow reactors.
Kennedy et al. and Ostraat et al. integrated a
post-synthesis oxidation stage to convert SnO into
SnOx nanoparticles and to passivate Si nanoparticles
with an oxide layer, respectively.

In-flight nanoparticle coating prior to deposition
in an electrostatic precipitator was demonstrated by
Karlsson et al. Here, Au nanoparticles were pro-
duced first by evaporation-condensation with subse-
quent annealing similar to Magnusson et al., and
then coated with Ga. For this purpose, a ceramic boat
containing Ga metal was placed inside a third furnace
downstream of the sintering furnace (Fig. 8). The
Ga vapor was transported out of the evaporation fur-
nace together with the flow of the Au aerosol. As the
vapor left the hot zone it became supersaturated and
condensed upon the Au particles. Au–Ga compound
particles were thus formed through heterogeneous
nucleation with the Au cores acting as condensation
corei.

4. Applications of Nanoparticulate Films

Clusters and nanoparticles of metals, carbon and
semiconductors have been extensively studied in the
gas phase with particular attention to their electronic,
optoelectronic, optical, and magnetic properties,
as is apparent from recent comprehensive reports
that also address nanostructured films. Here,
applications in catalysis and biotechnology are intro-
duced briefly while the fabrication of gas sensors is
discussed in more detail.

4.1 Gas sensors

Gas sensors are a prominent, example of functional
materials where the use of nanoparticles was shown
to significantly improve the performance. Compar-
ing the sensitivity of dense nanoparticulate films
with that of porous films, Ogawa et al. observed a
greatly increased sensitivity for ethanol of the latter
structure. This was explained on the basis of Hall
measurements, which showed that the carrier mobili-
ty is strongly dependent on the ethanol concentration
for the porous nanocrystalline films while no depen-
dence was found for the dense film. The high specific
surface area of nanostructured particulate films is
usually easily accessible for gases due to the high po-
rosity (up to 98%), allowing fast transport of the ads-
sorbing and desorbing species. The use of masks has
been demonstrated successfully, confining particle
deposition to the sensing area of a single element
or even for the production of entire libraries with
210 gas sensors in one step (Fig. 9). Furthermore,
the possibility to obtain homogeneous and crack-free
sensing layers makes gas-phase nanoparticle syn-
thesis with direct deposition a promising manufactur-
ing route for solid state gas sensors.

Here, the fabrication of gas sensors with nano-
structured TiO$_2$, WO$_3$ and SnO$_2$ sensing layers by supersonic cluster-beam deposition and their performance in the detection of volatile organic compounds (VOC) and gases related to environmental pollution (such as NOx) are reported.

A supersonic cluster-beam deposition apparatus (SCBD, Fig. 2) was used to generate and deposit nanoparticles on gas sensor substrates. Clusters of titanium, tungsten and tin were generated by a pulsed microplasma cluster source (PMCS) as described in Section 2.2 and Fig. 3a. Therefore, a high-purity metal rod (6 mm diameter, approx. 10 cm length) of the material to be deposited was inserted into the PMCS cavity (diameter ~ 1.2 cm), attached to a rotational stage and connected to the negative pole of a high-voltage power supply. Pulses of argon were introduced into the cavity by means of a solenoid valve, operated at a frequency of 10 Hz. With a few hundred microseconds delay, an electric discharge triggered by the valve was used to ignite a plasma jet impinging on the metallic rod and ablating material that vaporized and condensed into metallic nanoparticles. These were entrained by the gas flux toward the PMCS exit nozzle and expended into the adjacent expansion chamber kept at differential vacuum (10$^{-3}$ mbar).

A set of 5 aerodynamic lenses as shown in Fig. 5 installed on the same axis as the expansion nozzle near the inlet of the expansion chamber was used to concentrate the nanoparticles onto the center axis, forming a collimated particle beam with less than 20 mrad divergence. The particle beam entered the differentially pumped deposition chamber through a skimmer with a 2-mm opening, impinging on the substrate through a hard mask (Fig. 6a). The substrate was kept at room temperature and could be positioned by a 4-axis motorized manipulator that even allowed large-area ($50 \times 220$ mm$^2$) depositions by substrate rastering.

The sensor substrates were made of micro-machined alumina with integrated thin film heater and Pt thin-wire thermometer for temperature control during sensor operation. Micro-machined platforms having an array structure (Fig. 10a) were used to deposit different oxides on each single element of the array by exploiting hard mask patterning. After cluster deposition, the substrates were annealed in air at 400°C in order to obtain the proper oxide stoichiometry as well as a nanostructure and crystallinity that is stable during sensor operation up to 300°C. Fig. 10b shows an array of four sensing elements (TiO$_2$, WO$_3$, SnO$_2$ and one blank element for reference) after annealing and connected to signal read-out and analysis electronics.

The as-deposited films had an amorphous and porous structure at the nanoscale, attributed to particle impact with low kinetic energy and limited diffusion. After annealing, the amorphous grains rearranged into a crystalline structure. For example, Fig. 11 shows transmission electron microscopy (TEM) images of as-deposited (Fig. 11a) and 200°C-annealed (Fig. 11b) tungsten oxide films. The as-deposited material was composed of nanoparticles with an average size of about 10 nm. No lattice fringes were discernible, indicating an amorphous structure. After annealing, a number of nanoparticles showed crystal lattices, indicating the transformation into a polycrystalline film, while average particle size and film morphology appeared to be largely unaffected.

The sensing properties of the films were evaluated for CO, NO, NO$_x$, and SO$_x$, as well as for ethanol. By means of an automatic mass-flow-controller-based gas mixing system, these compounds were added at trace level to pure dry air flowing into a test chamber. An electrometer was used to measure the current across the film during the test sequence. Fig. 12 shows
examples of the gas sensor performance, namely the
response of the SnO₂, WO₃ and TiO₂ sensors to SO₂,
NO₂, and ethanol, respectively. The titania film was
doped with Pd in a two-step multi-layer deposition
process involving two cluster sources. All sensors
showed a fast response to trace gas injection. NO₂
was detected by WO₃ at the ppm level (Fig. 12b),
while SO₂ and ethanol were registered with an accu-
rate of about 5 ppm by SnO₂ and Pd/TiO₂ sensors, as
is shown in Figs. 12a and 12c respectively.

The realization of complex sensor arrays with a
large range of materials and material compositions by
cluster-beam deposition and hard mask patterning in
combination with neural network analysis for signal
read-out might be a promising route to the efficient
and inexpensive realization of gas microsensors, e.g.
for environmental monitoring.

4.2 Catalysis

Applications in heterogeneous catalysis benefit
from the high specific surface area and porosity of
nanostructured particulate films⁸. Even though the
coating of large-area supports has not been reported
yet, methods such as flame spray deposition are
promising techniques for depositing porous catalyst
layers directly into microsystems by using masks⁸.
Cluster-beam deposition has been used to coat 10 ×
10 mm² glass substrates with Ti-Si binary oxide films
for photocatalytic decomposition of NO under UV light radiation\textsuperscript{56}. Zhou et al.\textsuperscript{57} used combined cluster-beam deposition and metal ion implantation to produce nanostructured vanadium-doped TiO\textsubscript{2} films that showed photocatalytic decomposition of formic acid even under visible light radiation. Furthermore, cluster-beam deposition techniques can be employed to manufacture model catalysts by deposition of single monosize clusters for fundamental studies on heterogeneously catalyzed chemical reactions\textsuperscript{58-60}.

### 4.3 Biotechnology

In biotechnological applications, the surface roughness of nanostructured particulate films can be exploited. Carbone et al.\textsuperscript{28} characterized the biocompatibility of nanostructured TiO\textsubscript{2} films produced by the deposition of a supersonic beam of TiO\textsubscript{2} clusters. The cluster-assembled film supported normal growth and adhesion of primary and cancer cells with no need for coating with extracellular matrix proteins. Physical analysis showed that the films possess a nanoscale granularity and porosity mimicking that of typical extracellular matrix structures and adsorption properties that could allow surface functionalization with different macromolecules such as DNA, proteins, and peptides. Films of nanostructured titania are proposed as an optimal substrate for different applications in cell-based assays, biosensors, bioactive orthopedic, dental and vascular implants or microfabricated medical devices. Patterned deposition could be applied for the fabrication of microarrays for proteomics, genomics and post-genomic applications.

### 5. Conclusions

Gas-phase technology has been shown to offer versatile techniques for one-step synthesis of nanostructured particulate films. A range of gas-phase routes are available for nanoparticle synthesis such as flame, plasma or evaporation/condensation that are already employed for commercial manufacture of nanoparticles. Post-synthesis in-flight annealing, coating and functionalization has been demonstrated as well as particle size selection and focusing. Hard mask techniques adopted from microfabrication technology have been successfully applied for the generation of 1-, 2-, and 3-D nanoparticulate patterns. Deposition rates of several mm/min for non-vacuum "aerosol" approaches allow the growth of thin particulate films ( < 1 \textmu m) within seconds and also make deposition of thick films ( > 10 \textmu m) commercially feasible. Compared to standard thick film technology such as screen printing or tape casting, gas-phase techniques do not involve the intermediate steps of paste or slurry generation and are not prone to crack formation\textsuperscript{7}.

Vacuum techniques such as cluster-beam deposition offer nanoparticle deposition with high lateral
resolution as well as compatibility with silicon-based microfabrication technologies. A drawback of many vacuum techniques is the low nanoparticle production rate or the requirement of huge pumping capacities. A combination of aerosol and vacuum approaches might thus lead to the integration of nanofabrication and microfabrication at an industrial level, as was indicated by the example of solid state gas sensors.

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Karsten Wegner studied process engineering at the universities of Karlsruhe (Germany) and Cincinnati (U.S.A.). After his graduation in 1998, he joined the group of Prof. Sotiris E. Pratsinis at the Swiss Federal Institute of Technology (ETH) in Zurich to carry out his doctoral studies on gas-phase production of nanoparticles. From 2002 to 2004, he was leader of a research consortium on ceramic nanoparticles, sponsored by the Swiss Commission for Technology and Innovation (CTI). Dr. Wegner was co-founder of the start-up company “FlamePowders” that focused on industrial flame synthesis of nanopowders and was CEO and vice president of FlamePowders before working as a technology and business development consultant with Tethis (Milan). He also holds a position at ETH Zurich, where he has been lecturing mass transfer and nanotechnology courses since 2003. Dr. Wegner has co-authored over 20 scientific publications, book chapters and patents in the field of nanomaterials.

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Paolo Milani is professor at the Department of Physics, University of Milan and head of the Laboratory of Molecular Beams and Nanocrystalline Materials (LGM). After his graduation in Physics at the University of Pavia (Italy) in 1984, Paolo Milani obtained his Ph.D. from the Swiss Federal Institute of Technology in Lausanne. From 1987 to 1991 he was research associate at the Laboratory of Molecular and Laser Physics at the University of Nijmegen (the Netherlands) and the Centro di Fisica degli Stati Aggregati (CeFSA) of the Italian National Research Center (CNR) in Trento, Italy.

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He holds four international patents in the nanotechnology field that are currently exploited industrially and is co-author of more than 120 scientific publications, international reviews, a monography on nanostructured materials and has co-edited a volume on nanostructured carbon. Prof. Milani is member of the editorial boards of the Encyclopedia of Nanotechnology, of the American Scientific Publishers Association and of the Journal of Nanoscience and Nanotechnology. He has received the “U. Campisano” award from the Italian Institute for the Physics of Matter (INFM) in 2000 for his outstanding research contributions and the “Luigi Tartufari” Prize of the National Academy dei Lincei in 2006 as the leader of his research team.

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