1. Introduction

Nanoparticles have attracted the attention of an increasing number of researchers from several disciplines in the last ten years. The term ‘nanoparticle’ came into frequent use in the early 1990s together with the related concepts, ‘nanoscaled’ or ‘nanosized’ particle. Until then, the more general terms submicron and ultrafine particles were used. The term nanoparticle is generally used now in materials science community to indicate particles with diameters smaller than 100 nm (El-Shall and Edelstein, 1996). The term nanoparticles is used here interchangeably to refer to particles in aerosols and particles in other situations respectively. A closely related but not identical concept, ‘cluster’, indicates smaller nanoparticles with less than 10^4 molecules or atoms, corresponding to a diameter of only a few nanometers.

Nanomaterials or nanostructured materials have a characteristic length scale of less than 100 nm, and therefore also include uni-axially stacked multilayers and coatings. A further subset can be distinguished in these nanomaterials, i.e. the nanophase materials which have a three-dimensional structure with a domain size smaller than 100 nm. Nanophase materials are usually produced by compaction of a powder of nanoparticles. They are characterized by a large number of grain boundary interfaces in which the local atomic arrangements are different from those of the crystal lattice (Weissmüller, 1996).

The small size of nanoparticles, which is responsible for the different properties (electronic, optical, electrical, magnetic, chemical and mechanical) of nanoparticles and nanostructured materials with respect to the bulk material, makes them suitable for new applications. Having a size between the molecular and bulk solid-state structures, nanoparticles have hybrid properties which are incompletely understood today, creating a challenge for theoreticians as well. Some examples of these properties are lower melting temperature (Goldstein *et al.*, 1992), increased solid-solid phase transition pressure (Tolbert and Alivisatos, 1995), lower effective Debye temperature (Fujita *et al.*, 1976), decreased ferroelectric phase transition temperature (Ishikawa *et al.*, 1988), higher self-diffusion coefficient (Horvath *et al.*, 1987), changed thermophysical properties (Qin *et al.*, 1996) and catalytic activity (Sarkas *et al.*, 1993).

‘Nanocomposites’ consist of nanoparticles dispersed in an continuous matrix, creating a compositional heterogeneity of the final structure. The nanocomposites usually involve a ceramic or polymeric matrix and are not restricted only to thin films. These materials show interesting properties such as alloying of normally immiscible materials (Linderoth and Moerup, 1990) and higher critical superconductor transition temperature (Goswami *et al.*, 1993).

The size-dependent properties of nanostructured materials make them interesting for potential technological applications. This has led before the 1990s to applications such as supported nanoscale catalysts and pigments, based mainly on the large surface area to volume ratio in these systems. After 1980, a renewed interest took place in nanomaterials research. Brus (1983) suggested quantum confinement effects to occur specifically in semiconductor nanoparticles. Birringer *et al.* (1984) developed a method for synthesizing amounts of weakly agglomerated nanoparticles for producing nanophase materials with a large volume fraction of grain boundaries. Improved mechanical properties of nanophase ceramics were observed in these materials, such as increased hardness by Koch and Cho (1992). Finally, one of many other important findings was the giant magnetoresistance in nanocomposites discovered by Carey *et al.* (1992).

This Habilitation Thesis concentrates on gas-phase processes for synthesizing nanoparticles. Methods for the synthesis of nanoparticles are also being developed in other than gas-phase processes such as colloidal systems where stabilization is used to prevent coagulation (Peled, 1997). However, gas-phase processing systems may prove better in some cases because of their following inherent advantages:

- Gas-phase processes are generally purer than liquid-based processes since even the most ultra-pure water contains traces of minerals, detrimental for electronic grade semiconductors. These impurities seem to be avoidable today only in vacuum and gas phase systems. Colloid chemistry has the advantage that nanoparticle aggregation can be avoided by the use of ligands. However, these molecules can lead to a change of the surface properties of the nanoparticles. This was shown clearly by Yu *et al.* (1997), who found that 'naked' SnO_2 nanoparticles formed by gas-phase synthesis showed the expected blue-shift in the absorption spectrum, whereas for ligand-stabilized SnO_2 nanoparticles an unexpected red-shift was detected which cannot be understood by quantum confinement theories.
- Aerosol processes have the potential to create complex chemical structures which are useful in producing multicomponent materials, such as high-temperature superconductors (Kodas, 1989).
- The process and product control are usually very good in aerosol processes. Particle size, crystallinity, degree of agglomeration, porosity, chemical homogeneity, stoichiometry, all these properties can be controlled with relative ease by either adjusting the process parameters or adding an extra processing step, e.g. sintering or size fractionation.
- Being a nonvacuum technique, aerosol synthesis provides a cheap alternative to expensive vacuum synthesis techniques in thin or thick film synthesis (Wang *et al.*,

1990). Furthermore, the much higher deposition rate as compared to vacuum techniques may enable mass production.

- An aerosol droplet resembles a very small reactor in which chemical segregation is minimized, as any phases formed cannot leave the particle (Kodas, 1989).
- Gas-phase processes for particle synthesis are usually continuous processes, while liquid-based synthesis processes or milling processes are often performed in a batch form. Batch processes can result in product characteristics which vary from one batch to another.

One important field of research deals with aerosol-assisted processes used for film synthesis in which liquid droplets dispersed in a gas are used as source and transport vehicles to the substrate. These processes are called aerosol-assisted chemical vapor deposition (AACVD) (Xu *et al*., 1994), aerosol metal-organic CVD (A-MOCVD) (Fröhlich *et al.*, 1995), the pyrosol process (Blandenet *et al.*, 1981) and aerosol CVD (Tourtin *et al.*, 1995). Common to these processes is the evaporation of micron-sized droplets in proximity to the substrate to produce epitaxial or polycrystalline films (Jergel *et al.*, 1992). Small nanocrystallites might be found in the films but are not formed in the gas phase, therefore these processes are not considered here.

In this Habilitation Thesis, various processes and techniques which can be applied for the synthesis of functional nanomaterials are described. By using the word 'functional', the classical distinction which is made in ceramics between structural and functional applications is applied. The structural applications are based on the mechanical properties of the nanostructured or nanophase materials, leading to, e.g., superplastic ceramics or extremely hard metals, using the nanoparticles rather as passive basic building units. Functional applications however rely on a transformation of external signals, such as the filtering of incident light, the change of electrical resistance in different gas concentrations and luminescent behaviour when electrically activated. The functional applications dealt with in this work are mainly electronic and optical.

In order to clarify the methodological approach followed here, the various disciplines involved are shown in Fig. 1.1. The functional applications all base on the special properties of nanoparticles, which are studied in physics, materials science and chemistry. Essential for practical application are the synthesis and handling techniques, here in the gas phase. The handling of nanoparticles, which is bringing the produced nanoparticles in the desired condition for the application, is an often underestimated but essential field. Examples of handling techniques are post-synthesis conditioning such as controlled oxidation, crystallisation and mixing but also the deposition onto suitable substrates. Here, the input of several other disciplines is essential, such as aerosol science for understanding particle behavior, materials science for understanding materials properties, aerosol instrumentation for process monitoring and process technology for process control and optimization.

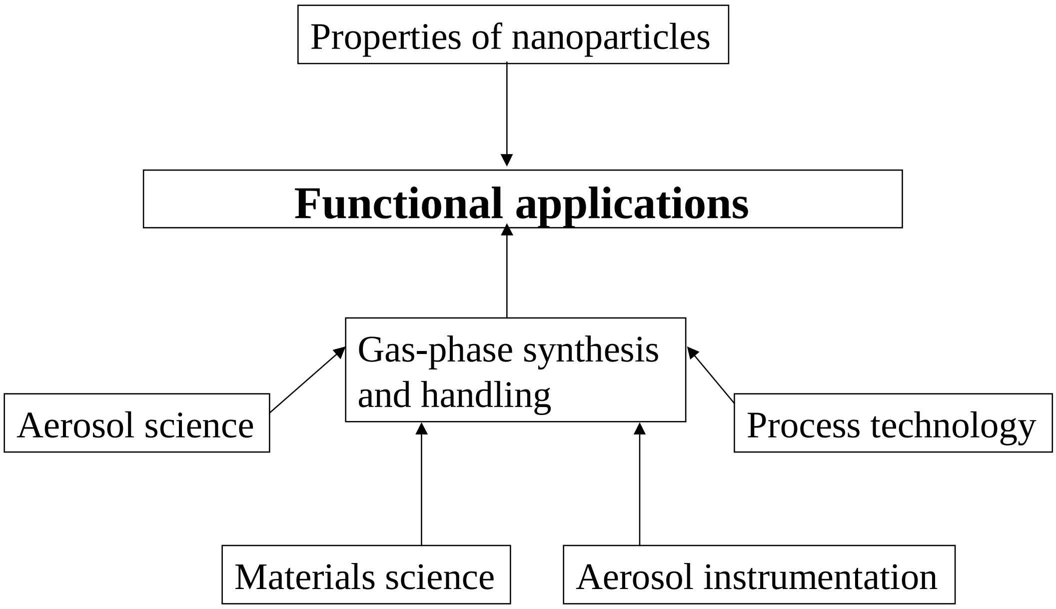

Fig. 1.1. The various disciplines contributing to functional applications based on gas-phase synthesized nanoparticles.

The organization of this Habilitation Thesis is as follows:

- *Chapter 2* gives an introduction into functional applications which are based on the special properties of nanoparticles. Electronic, optical and magnetic applications are discussed.
- *Chapter 3* gives an overview of the current synthesis methods of nanoparticles in the gas phase.
- *Chapter 4* concentrates on several physical phenomena occurring in the gas phase which are important for specific synthesis and handling methods of nanoparticles. The physical processes taking place during the evaporation-condensation synthesis technique applied in this work are modeled in order to understand the synthesis step and to facilitate synthesis of other materials. Aerosols are inherent instable, as the constituting particles tend to collect in flocs, so-called aggregates or agglomerates, when the temperature is below the melting point. This process is modeled by a Monte Carlo simulation technique in order to be able to describe complex systems, such as multi-component or multidimensional systems with several variables, e.g. particle size and charge. The method is useful for describing

the mixing of charged nanoparticles, which is an example of an handling technique and which is also studied experimentally in Chapter 7.

- *Chapter 5* reviews the various works done on the synthesis of nanoparticles in the gas phase for functional applications, arranged so as to emphasize the application rather than the method of preparation. The requirements for gas-phase processes suitable for functional applications are stated.
- *Chapter 6* describes experimental techniques which are important for the measurement and control of nanoparticle aerosols. These methods base on the transport of charged nanoparticle in an electric field. For obtaining charged nanoparticles, a new nanoparticle charger has been developed and characterized. Differential mobility analysis allows to fractionate charged nanoparticles according to their electrical mobility. This can be used for a direct particle size distribution analysis or for producing almost equal-sized nanoparticles (‘monodispersity’). Its potential for application at sub-atmospheric pressures will be investigated. An electrostatic precipitator suited for investigation of the electrical properties of thin nanoparticle films will be described.
- *Chapter 7* describes the synthesis of PbS and SnO_x nanoparticles which apply with the requirements for use in functional applications. Both materials are IV-VI semiconductors, where PbS is mainly interesting for its quantum confinement effects and SnO_x for its application in gas sensors. The quantum confinement effects in PbS are shown by means of a shift in the optical absorption spectrum. Furthermore, an experimental technique which allows the creation of nanoparticle pairs composed of two different chemical components is described. This can be used for the controlled doping of gas sensors.
- *Chapter 8* summarizes and concludes the work.