

1 Introduction and Motivation

Materials can be considered as ‘substances with properties that turn them into products, parts, devices or machines developed by mankind to fulfill physical, social, aesthetic and safety needs’ [Silva 1994]. Among the various classes of materials, metal oxides are the most common and most diverse material systems in terms of physical, chemical, and structural properties with applications as optical, magnetic, electronic, thermal, electrochemical, mechanical, and catalytic materials. Origin of this diversity is related to the variety of oxidation states, coordination number, symmetry, ligand-field stabilization of the metal ions, density, and stoichiometry of the oxide compounds [Vayssieres 2007]. Metal oxides exhibit insulating, semiconducting, conducting, or magnetic behavior.

Nanocrystalline oxide materials have significant technological advantages over traditional materials in terms of their properties due to size and interfacial effect. The control of a nanoparticle size, shape, composition and structure is necessary to ensure that the nanoparticles will meet the requirements specified by commercial applications. Consequently, existing synthesis and processing techniques are being continuously refined while at the same time novel methods are being developed. Many efforts are being made to synthesize nanocrystalline materials using a large number of methods based on solid, liquid or gas phase processes [Rodriguez and Fernandez-Garcia 2007]. Each technique has its own advantages and disadvantages. Gas phase processes allow the particle generation with unique combination of properties that in many cases cannot be obtained by other processes. In comparison to liquid phase methods, gas phase synthesis has the advantage that the particles are formed at high temperatures, which allows the formation of highly crystalline materials [Kodas and Hampden-Smith 1999] and particle contamination by byproducts is much lower. For the production of nanocrystalline materials from nanopowders produced by gas phase methods it is not only important to control the grain size but also, i.e. the particle morphology or agglomeration [Flagan and Lunden 1995]. The quality and application of nanostructured materials are strongly related to the particle and powder characteristics. Powders of small grain size, narrow size distribution, low degree of agglomeration and high purity are required for the fabrication of solid nanocrystalline materials and the exploitation of size effects in commercial applications.

The objective of this thesis is to optimize chemical vapor synthesis (CVS) for the production of high quality oxide particles (TiO_2 and ZnO) with controlled properties.

The first part of this thesis is focused on modeling of the CVS process to acquire insight into the particle formation and influence of time-temperature history

on particle characteristics, and to optimize the CVS process in order to obtain particles with low degree of agglomeration and high crystallinity. Additionally, it was studied how the particle number concentration has influence on the particle characteristics (size, degree of agglomeration and consequently width of particle size distribution). Titanium dioxide (TiO_2) was selected as a model material because it is widely experimentally and theoretically studied as an important material used in photocatalysis and dye-sensitized solar cells [O'Regan and Grätzel 1991] and detailed model description of the CVS process is feasible.

The second part of the thesis is focused on study of the nanoparticle structure (crystal and local) as one of the important factors that defines material property. Zinc oxide (ZnO) was used as a study system because it is very interesting non-magnetic semiconductor material which, according to the theoretical prediction, shows interesting magnetic properties upon zinc (Zn) substitution by cobalt (Co). The ability to precisely control the arrangements of dopant elements (here Co) and phase composition, is of great importance.

1.1 Review of Relevant Literature

1.1.1 Titanium Dioxide (TiO_2) and Control of Particle Characteristics

Titanium dioxide (TiO_2) is a semiconducting material used in a wide variety of technological applications as a photocatalyst, electrolyte in solar cells, gas sensor, white pigment, corrosion protective coating, optical coating, in memory devices, and in Li-based batteries [Chen and Mao 2007]. Because much experimental and theoretical information is available and the product of the CVS process is typically crystalline, consisting mostly of anatase, TiO_2 was chosen as a model material. This enables not only a detailed model description of the CVS process but also an extensive characterization of the as-synthesized particles.

Practical application of nanoparticles often involves the preparation of a colloidal suspension in order to deposit films. The microstructure of the resulting nanomaterial as well as its properties can be affected by the particle agglomeration [Maira et al. 2000]. Therefore, it is important to search for new ways or to improve already existing methods to obtain particles with a minimum degree of (hard) agglomeration.

The production of nanoparticles using flame synthesis is the gas phase method well theoretically and experimentally studied. In flame reactors the powder characteristics are mostly determined by the flame temperature and the particle residence time [Kammler et al. 2001]. The particle size, as well as the width of the particle size distribution, increases as the particles move up the flame. Coagulation becomes more pronounced at longer residence times [Tsantilis et al. 2002]. As a result, a distribution of time-temperature histories may be stored in the samples. Grass et al. [Grass et al. 2006] studied the evolution of hard- and soft-

agglomerates of TiO₂ particles made by gas phase and surface oxidation of titanium isopropoxide. They have found that particles with low degree of agglomeration or even non-agglomerated particles could be produced at low precursor feed, high maximum process temperature and at high cooling rates.

It has been shown that the width of particle size distribution has a strong influence on the sintering process of compacts. Studies by [Chappell et al. 1986, Ting and Lin 1995, e.g.] showed that the sintering ability (densification rate) of compacts decreases as the width of particle size distribution of the starting powder increases. For the liquid phase it has been shown that the droplet size distribution can be narrowed using an oscillating reactor [Pereira and Ni 2001] or segmented liquid flows [Jongen et al. 2003]. So far there are no reports on the influence of pulsed precursor flow in the gas phase on the particle size distribution.

1.1.2 Zinc Oxide (ZnO) and Control of Particle Composition

Zinc oxide (ZnO) is a semiconducting material with interesting optical, electrical (piezoelectric) and chemical (sensing) properties and is used in numerous applications [Schmidt-Mende and MacManus-Driscoll 2007] such as gas sensors, light emitting diodes, cantilevers, solar cells. Inspired by optimistic predictions, at first by Dietl [Dietl et al. 2000] later by Sato [Sato and Katayama-Yoshida 2001], extensive research effort have been performed by many groups on searching for room temperature ferromagnetism in transition metal (TM) doped ZnO. At first, the focus was only on films [Ueda et al. 2001], then the effort was directed toward the synthesis of nanocrystalline powders [Sharma et al. 2003, Lakshmi et al. 2009] with potential use in ferrofluids, opto-magneto-electronics, and biomedical applications. In many studies on ZnO doped with cobalt [Kim et al. 2007, Bouloude-nine et al. 2005, Chambers et al. 2006] or other TM elements [Jin et al. 2007, Kolesnik et al. 2004, Cong et al. 2006] contradictory results on magnetic properties have been reported. In the case of Co-doped ZnO paramagnetism [Martinez et al. 2005, Ney et al. 2008] or ferromagnetism at low [Yang et al. 2009], room [Lakshmi et al. 2009] or even high temperatures [Deka et al. 2004] was found. The ferromagnetism observed in several studies [Park et al. 2004, Norton et al. 2003, Blasco et al. 2006, Deka et al. 2006] had the origin in the second phases, but often the existence of second phases was not investigated [Behan et al. 2008]. The origin of the magnetic properties of TM-doped ZnO complex is still not well understood.

There are several concepts proposed to stabilize the ferromagnetism in ZnO. Table 1.1 gives an overview of these concepts. One proposal is based on bound magnetic polaron (BMP) [Coey et al. 2005] according to which ferromagnetism can be established only when the concentration of magnetic cations is lower than the percolation threshold in wurtzite structure ($x_p = 0.18$) and the concentration of polarons is higher than percolation threshold ($\delta_p = 0.0015$). Opposite to the BMP approach, several authors [Lee and Chang 2004, Sandratskii and Bruno 2006,

Nayak et al. 2008] reported that due to the short range nature of the ferromagnetic coupling, a heavy incorporation of dopant atoms is required to stabilize the ferromagnetic states. Codoping (simultaneous presence of two dopant elements) with acceptor and/or donor elements has also been proposed as a potential means to establish the ferromagnetic coupling of TM ions (“carrier mediated ferromagnetism”) [Sluiter et al. 2005, Gopal and Spaldin 2006]. Most recently, study on Mn-doped ZnO system, suggest that ferromagnetic ordering can be stabilized by presence of grain-boundaries and vacancies (“grain-boundary foam”) [Straumal et al. 2009A]. Experimentally, the most challenging approach is the substitutional incorporation of higher quantities of dopant atoms into the ZnO wurtzite lattice due to their thermodynamic solubility limit [Straumal et al. 2008]. Not only is a high quantity of dopant atoms required, but also their homogeneous distribution on Zn (substitutional) sites inside of the lattice.

Table. 1.1. Reported concepts for the stabilization of ferromagnetic ordering in ZnO

Mechanism	Reference
Bound magnetic polaron ($x_p < 0.18$)	Coey et al. 2005
Heavy incorporation of dopant atoms ($x_p > 0.18$)	Lee et al. 2004, Sandratskii et al. 2006, Nayak et al. 2008
Additional free carriers (codoping e.g. Co,Li)	Sluiter et al. 2005, Gopal and Spaldin 2006
Grain-boundary foam (defects)	Straumal et al. 2009A