

3. Synthesis methods of nanoparticles in the gas phase

The synthesis methods for nanoparticles can be divided into three main groups. The first group comprises the liquid-phase methods, which apply chemical reactions in solvents. This leads to colloids, in which the nanoparticles formed can be stabilized against aggregation by surfactants or ligands. The second group consists of methods basing on surface growth under vacuum conditions. Diffusion of atoms or small clusters on suitable substrates can lead to island formation, which can be seen as nanoparticles. An important example is Stranski-Krastanow growth, which is used for growing III-V quantum dots. The last group, gas-phase synthesis, is the subject of this Chapter.

Most synthesis methods of nanoparticles in the gas phase are based on homogeneous nucleation in the gas phase and subsequent condensation and coagulation. The ablation of a solid source with a pulsed laser can also yield nanoparticles, but the formation mechanism is at present not very clear. A micron-sized aerosol droplet may also yield nanoparticles by evaporating a solute-containing droplet. Electrospray systems are often applied as droplet generators, as they produce very small droplets being quite monodisperse in comparison to other spray processes. Additionally, droplet explosion due to an electrical charge which exceeds the Rayleigh limit during evaporation may yield even smaller droplets. Finally, initiating homogeneous nucleation inside aerosol droplets can result in many nanosized nuclei in the droplet, which upon drying will yield nanoparticles. This is, in fact, not a formation mechanism in the gas phase but for sake of completeness it will be shortly discussed in this Chapter, as this so-called spray pyrolysis is a well-known aerosol synthesis route. In the following sections these methods will be described in detail. Part of this material has been published (Kruis *et al.*, 1998d). A preview of the gas-phase synthesis methods is shown in Fig. 3.1.

3.1 Processes based on homogeneous nucleation in the gas phase

Several methods with which condensable monomers are produced will be dealt with hereby. The generation of nanoparticles from the vapor phase requires the establishment of supersaturation. This is made possible by physical or chemical methods. The physical methods involve some form of cooling of the monomers, by expansion, by mixing with a cooler gas or by heat transfer to the surroundings.

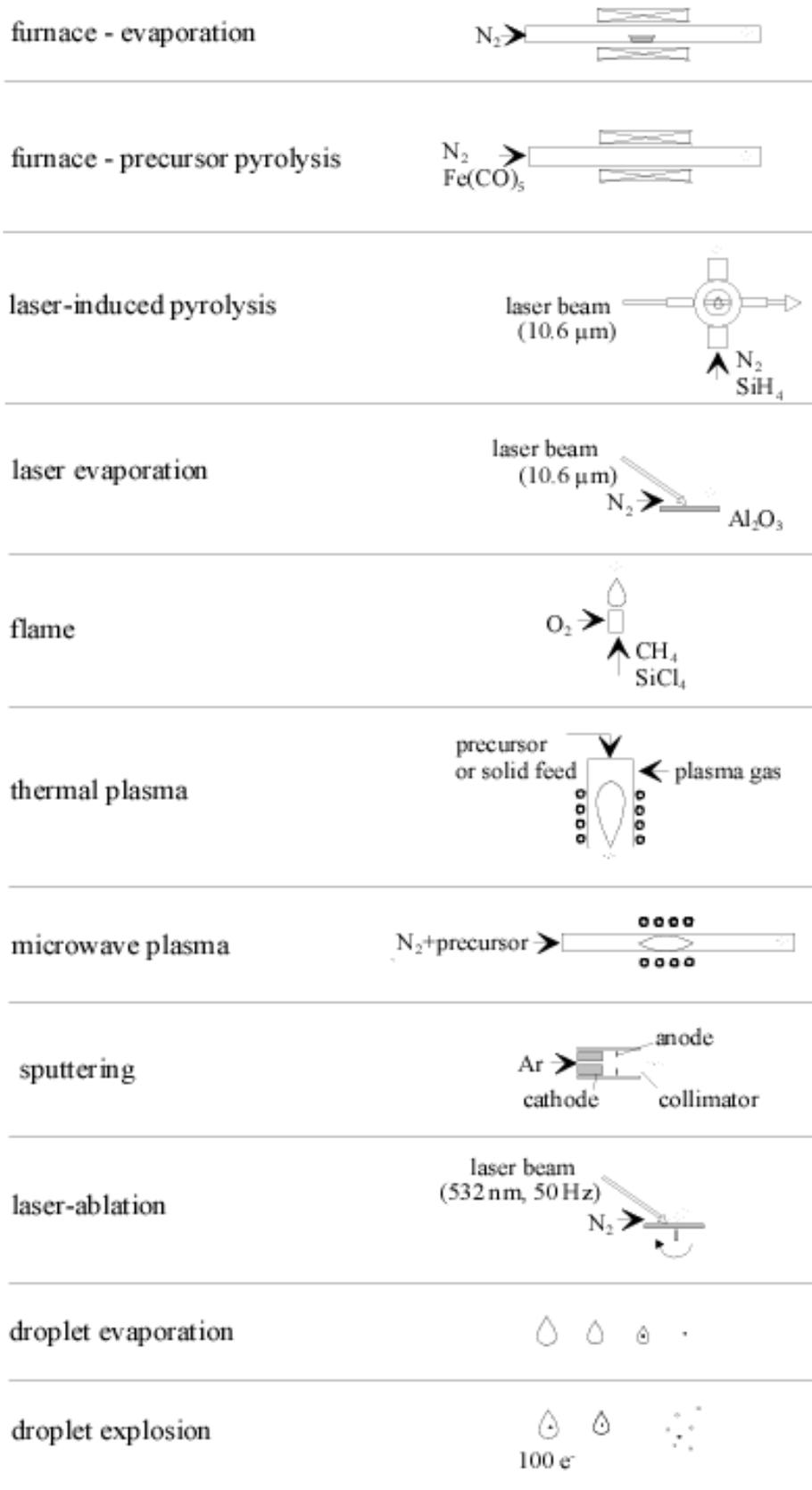


Fig. 3.1. Schematic view of different synthesis methods.

Supersaturation can be achieved also by chemical reactions which produce a nonvolatile condensable product. These reactions are usually decomposition reactions initiated by a rise in temperature and used extensively in laser and flame reactors.

Various heating and evaporation methods of interest will be dealt with in the next section. Furthermore, methods for rapidly cooling the vapor will be described because fast cooling processes are especially important when very small particles have to be synthesized and when the formation of hard agglomerates has to be avoided.

3.1.1 Furnace flow reactors

Oven sources are the simplest systems to produce a saturated vapor for substances having a large vapor pressure at intermediate temperatures up to about 1700°C. A crucible containing the source material is placed in a heated flow of inert carrier gas. This has the disadvantage that the operating temperature is limited by the choice of crucible material and that impurities from the crucible might be incorporated in the nanoparticles. Nanoparticles are formed by subsequent cooling, such as natural cooling or dilution cooling. For very small particles a rapid temperature decrease is needed which can be achieved by the free jet expansion method described later. Another method is cooling in a turbulent jet (Bartz *et al.*, 1987). Materials with too low vapor pressure for obtaining appreciable particle density have to be fed in the form of suitable precursors, such as organometallics or metal carbonyls, in the furnace. These decompose in the oven to yield a condensable material. Using furnace flow reactors, elemental nanoparticles such as Ag (Scheibel and Porstendorfer, 1983) and Ga (Deppert *et al.*, 1996) and also compounds such as PbS (Kruis *et al.*, 1996) can be obtained.

3.1.2 Laser reactors

In the laser pyrolysis technique, being a special class of laser processing techniques (Peled *et al.*, 1996), a flowing reactant gas is heated rapidly with an IR laser such as a cw CO₂ laser. The source molecules are heated selectively by absorption of the laser beam energy, whereas the carrier gas is only indirectly heated by collisions with the reactant molecules. A gas phase decomposition of the reactants takes place due to the temperature increase and supersaturation is created. As an example, SiH₄ pyrolysis results in Si nanoparticle formation (Kruis *et al.*, 1998b) and Fe(CO)₅ decomposition leads to Fe nanoparticles (Majima *et al.*, 1994). The main advantage of laser-heating in gas-flow systems is the absence of heated walls which reduces the danger of product contamination.

UV lasers can be used to obtain photochemical dissociation. Tamir and Berger (1995) showed that SiH_4 can be dissociated by a two-photon absorption of an ArF excimer laser beam with a wavelength of 193 nm, forming nanoparticles.

3.1.3 Laser vaporization of solids

This technique uses a laser which evaporates a sample target in an inert gas flow reactor (Powers *et al.*, 1982). The source material is locally heated to a high temperature enabling thus vaporization. The vapor is cooled by collisions with the inert gas molecules and the resulting supersaturation induces nanoparticle formation. Kato (1976) used a continuous-wave CO_2 laser with a power of 100 W. Nanoparticles between 6 and 100 nm of many complex refractory oxides such as Fe_3O_4 , CaTiO_3 and Mg_2SiO_4 were synthesized under an inert gas pressure of 1 mbar to 5 bar from powders, single crystals or sintered blocks. Nanocomposites can also be produced, as shown e.g. by Chow *et al.* (1989). They evaporated simultaneously a metallic and a ceramic target by a cw CO_2 laser creating a composite film close to the target. The matrix consisted of Al and the dispersed phase consisted of amorphous SiO_2 fibers with diameters between 25 and 120 nm.

3.1.4 Flame reactors

Nanoparticles are produced by employing the flame heat to initiate chemical reactions producing condensable monomers. The flame route has the advantage of being an inexpensive method, however usually it yields agglomerated particles. An example is the oxidation of TiCl_4 , SiCl_4 or SnCl_4 in a CH_4/O_2 flame leading to TiO_2 , SiO_2 or SnO_2 particles with primary particle sizes between 10 and 100 nm (Vemury *et al.*, 1997). More complex products can be also obtained. Zachariah *et al.* (1995) added small amounts of $\text{Fe}(\text{CO})_5$ and $\text{SiO}_2(\text{CH}_3)_6$ to a premixed CH_4/O_2 flame with temperatures at about 2000°C, forming Fe_3O_4 particles of 5-10 nm embedded in larger SiO_2 host particles. The synthesis was conducted at relatively high temperatures under oxygen-rich conditions to minimize carbon contamination.

A method to reduce the agglomeration of nanoparticles, avoiding oxidation, is to encapsulate them within a material which can be later removed. Dufoux and Axelbaum (1995) applied a Na coflow flame with a burner consisting of several concentric tubes. A TiCl_4 vapor was fed to the central tube while the Na vapor was fed to the concentric surrounding tube. An inert gas acts as a sheath gas between these two flows and shields the flame from ambient air. Ti particles with sizes of 10-30 nm were produced and were confined within larger NaCl particles. The NaCl can be removed by washing with water, glycerin or by sublimation.

3.1.5 Plasma reactors

A plasma can also deliver the energy necessary to cause evaporation or initiate chemical reactions. The plasma temperatures are in the order of 10^4 °C, decomposing the reactants into ions and dissociating atoms and radicals. Solid powder feeds can also be decomposed by the plasma. Nanoparticles are formed upon cooling while exiting the plasma region. Main types of the thermal plasmas are dc plasma jet, dc arc plasma and rf induction plasma (Young and Pfender, 1985). A small laboratory plasma system, the inductively coupled plasma (ICP), is often used at atmospheric pressures in combination with an aerosol spray system employing an ultrasonic atomizer. This technique is called spray-ICP (Kagawa *et al.*, 1993). As the residence time of the droplets in the plasma is very short it is important that the droplet sizes are small in order to obtain complete evaporation. Complex materials such as multicomponent oxides can be obtained by using appropriate mixtures. By using a solution of $\text{Ba}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$ in water, Mizoguchi *et al.* (1994) obtained by spray-ICP $\text{BaFe}_{12}\text{O}_{19}$ nanoparticles with sizes between 10 and 50 nm. In most cases, the plasma-generated vapors are quenched by mixing with a cold gas. This leads to high cooling rates, but also to nonuniform cooling which deteriorates the uniformity of the produced particles. Rao *et al.* (1995a,b) used a subsonic nozzle expansion after a dc arc plasma in order to obtain more uniform cooling rates.

Another method uses a microwave-generated plasma, in which temperatures between 300°C and 900 °C can be obtained. The plasma enhances the kinetics of the chemical reactions leading to nanoparticle formation due to ionization and dissociation of the reactive molecules. Since the lower temperature decreases the sinter rate, the formation of hard agglomerates is reduced (Vollath and Sickafus, 1992).

3.1.6 Spark source and exploding wire

A high-current spark between two solid electrodes can be used to evaporate the electrode material for creating nanoparticles. At the electrodes a plasma is formed. This technique is used for materials with a high melting point such as Si or C, which cannot be evaporated in a furnace. Saunders *et al.* (1993a) used an electric spark with an energy between 50 mJ and 150 mJ to evaporate material from crystalline Si electrodes. A continuous flow of Ar transports Si crystallites formed, of sizes 2 - 4 nm, to the collection substrate. Reactive evaporation is also possible by adding a suitable reactant gas. As an example, SiC nanoparticles were formed when an arc source generated a discharge between two Si electrodes in 500 mbar of CH_4 , and Al_2O_3 was obtained from Al electrodes in a mixture of 130 mbar O_2 and 420 mbar Ar (Hayashi, 1987).

A closely related technique is the exploding wire, in which the wire material is vaporized instantaneously by a capacitor in a chamber filled with an inert gas. This method has the disadvantage of being non-repetitive. As an example, GaAs nanoparticles were synthesized by using a GaAs wire (Saunders *et al.*, 1992).

3.1.7 Sputtering

Sputtering is a method of vaporizing materials from a solid surface by bombardment with high-velocity ions of an inert gas, causing an ejection of atoms and clusters. Sputter sources such as an ion gun or an hollow-cathode plasma sputter source are normally used in vacuum systems, below 10^{-3} mbar, as a higher pressure hinders the transportation of the sputtered material. Instead of ions, electrons from an electron gun can be also used. Iwama *et al.* (1982) operated an electron gun at 10^{-5} mbar separated by a differential pumping system from a 1 mbar evaporation chamber in order to evaporate Ti and Al targets in a N_2 or NH_3 atmosphere, producing TiN and AlN nanoparticles smaller than 10 nm. Günther and Kumpmann (1992) applied an electron beam in an inert gas atmosphere with pressures up to 5 mbar in order to produce 5 nm Al_2O_3 and SiO_2 particles. Hahn and Averback (1990) showed that a DC/RF magnetron sputter source can be operated in the mbar range, ejecting nanoparticles of sizes between 5 and 20 nm. Sputtering has the advantage that it is mainly the target material which is heated and that the composition of the sputtered material is the same as that of the target.

3.1.8 Inert gas condensation

One of the earliest methods used to synthesize nanoparticles, is the evaporation of a material in a cool inert gas, usually He or Ar, at low pressures conditions, of the order of 1 mbar. It is usually called 'inert gas evaporation'. Common vaporization methods are resistive evaporation (Tasaki *et al.*, 1965), laser evaporation (Chow *et al.*, 1989) and sputtering (Hahn and Averback, 1990). A convective flow of inert gas passes over the evaporation source and transports the nanoparticles formed above the evaporative source via thermophoresis towards a substrate with a liquid N_2 cooled surface (Granqvist and Buhrman, 1976). A modification which consists of a scraper and a collection funnel allows the production of relatively large quantities of nanoparticles, which are agglomerated but do not form hard agglomerates and which can be compacted in the apparatus itself without exposing them to air. This method was pioneered by the group of Birringer and Gleiter (Biringger *et al.*, 1984). Increased pressure or increased molecular weight of the inert gas leads to an increase in the mean particle size. This so-called Inert Gas Condensation method is already used on a

commercial scale for a wide range of materials. Also reactive condensation is possible, usually by adding O₂ to the inert gas in order to produce nanosized ceramic particles (Siegel, 1994). Another method replaces the evaporation boat by a hot-wall tubular reactor into which an organometallic precursor in a carrier gas is introduced. This process is known as Chemical Vapor Condensation referring to the chemical reactions taking place as opposed to the inert gas condensation method (Kear and Strutt, 1995). Finally, the Gas Deposition Method is also used in industry. In this method, nanoparticles are formed by evaporation in an inert gas at atmospheric pressure and transported by a special designed transfer pipe to the spray chamber at a pressure of about 0.3 mbar. By moving the nozzle at the end of the transfer pipe, the particles which have a mean velocity of 300 m/s can be deposited in required places on the substrate in the spray chamber. Using this technique writing micron-sized patterns was demonstrated. (Oda *et al.*, 1992).

3.1.9 Expansion-cooling

Expansion of a condensable gas through a nozzle leads to cooling of the gas and a subsequent homogeneous nucleation and condensation. Turner *et al.* (1988) showed by numerical simulations that by expanding an organometallic precursor in N₂ in a subsonic nozzle results in the formation of particles of about 100 nm with a relative narrow size distribution. The expansion caused the pressure to decrease from 2 bar to 0.75 bar. In order to produce nanoparticles smaller than 5 nm, supersonic free jets expanding in a vacuum chamber with pressures smaller than 10⁻⁴ mbar have been used. (Yamada *et al.*, 1987). In the work of Bowles *et al.* (1981) an inert gas containing a metal vapor was subjected to multiple expansions. Nuclei are formed as a result of two sonic expansions. Then a nuclei growth region in a subsonic, low-pressure reactor produced nanoparticles with mean sizes below 2.5 nm. The separation of nucleation and condensation processes results in a narrower size distribution than usually achieved by supersonic expansion. Further growth is stopped by expansion in a vacuum. Converging nozzles which create an adiabatic expansion in a low-pressure flow have also been used to produce nanoparticles (Bayazitoglu *et al.*, 1996). Although the particles sizes are larger than in a vacuum expansion, particles of the order of 100 nm were obtained with a relatively high production rate. Rao *et al.* (1995a,b) produced 4-10 nm sized nanoparticles by expanding a thermal plasma carrying vapor-phase precursors through a ceramic-lined subsonic nozzle. A special nozzle design minimizes boundary layer effects and approaches a one-dimensional temperature gradient in the flow direction. This leads to a highly uniform quench rate and thus to nanoparticles with a narrow size distribution.

3.2 Laser ablation of solids

Laser ablation is a technique in which a pulsed laser rapidly heats a very thin (< 100 nm) layer of substrate material, resulting in the formation of an energetic plasma above the substrate. This technique should be distinguished from laser vaporization, as apart from atoms and ions also fragments of solid or liquid material are ablated from the substrate surface which vary in size from sub-nanometric to micrometric. Therefore it cannot be considered as a pure homogeneous nucleation process. The pulse duration and energy determines the relative amounts of ablated atoms and particles. The nonequilibrium nature of the short-pulse (10-50 ns) laser heating enables the synthesis of nanoparticles of materials which normally would decompose when vaporized directly, such as most semiconductors and superconductive materials. Typically used lasers are the Nd:YAG (532 nm) and excimer (191, 248 and 308 nm) lasers. The material removal rate by laser ablation decreases with longer target exposure times, therefore the target is usually rotated. When used for producing films, this technique is called pulsed laser deposition (PLD). Here, the fine particles are not desired as they deteriorate the film quality and the operating conditions are chosen so as to minimize particle formation (Venkatesan and Green, 1996). Yamamoto and Mazumder (1996) showed that laser ablation of NbAl₃ at He pressures of 0.1 mbar did not produce any nanoparticles while an operating pressure of 1 mbar resulted in the formation of 6 nm nanoparticles with the same stoichiometry as the substrate. Typical production rates are in the order of micrograms per pulse with pulse frequencies of about 50 Hz, yielding 10-100 mg powder per hour. Reactive laser ablation in which a reaction of the ablated material with the reactor gas occurs is also used. Johnston *et al.* (1992) ablated an Al target in an O₂ atmosphere, producing Al₂O₃ nanoparticles.

3.3 Electrospray systems

A simple way to produce nanoparticles is to evaporate micron-sized droplets of a dilute solution. By choosing the appropriate solute concentration, nanosized particles consisting of the solid residue can be obtained. For instance, drying a 1 μm droplet containing a 1 ppm solution of NaCl will yield a 10 nm NaCl particle. A serious problem here is that all the impurities present in the liquid will concentrate in the solid residue (Rulison and Flagan, 1994). Furthermore, it is necessary to start from small droplet sizes which are difficult to obtain in normal spray systems.

Chen and Pui *et al.* (1995) showed that an electrospray system operated in the cone-jet mode could yield small droplets with a narrow size distribution. To avoid droplet explosion during evaporation, the highly charged aerosol is first passed through a radioactive neutralizer before the evaporation takes place. It is important

here to avoid droplet explosion since that would deteriorate the narrowness of the size distribution. Using a sucrose solution, particles as small as 4 nm were obtained. In another work (Hull *et al.*, 1997) Ag particles with a mean size of 10 nm were produced by electrospraying a dilute AgNO₃ solution in methanol onto a grounded substrate. A 1 mW He-Ne laser focused just below the capillary tip of the electrospray catalyzed the reduction of the Ag⁺ ion. The droplets were not discharged before evaporation in this case, so Rayleigh explosion is probable.

Kim and Rye (1994) developed a special charge injection technique in order to obtain very high charge densities. It is stated that the higher the surface charge density of the electrospray jet is, the smaller is the size of the ejected droplets. The system consists of a spray capillary containing a sharp needle connected to a high voltage supply. This charge injection system stabilizes the multijet-mode, in which a large number of small droplet-emitting jets form on the wetted capillary surface. Spraying a 10 vol.-% TEOS solution in ethanol in a chamber filled with O₂ resulted in 30-100 nm sized SiO₂ particles.

3.4 Spray pyrolysis

In spray pyrolysis, a droplet containing a solute is evaporated or dissociated by a chemical reaction. During the shrinkage of the droplet, a supersaturated solution is created, as the amount of solute remains constant, and small particles may form inside the droplet. Spray pyrolysis normally results in micron-sized particles which often have a hollow shape. This method is intermediate between gas-phase and liquid-phase, as the droplets are gas-carried, but the particle formation inside the droplets is in the liquid phase.

In some cases, nanoparticles were obtained. Lyons *et al.* (1992) obtained nanocrystalline PdO and V₂O₅ particles by spray pyrolysis. The droplets containing a precursor solution were decomposed at relatively low temperatures. This method avoids grain growth and densification, while the temperature is still high enough to fully decompose the precursors. The product consisted of 5 to 10 nm crystallites packed together in spheres, showing the form of the originating droplet and demonstrating that the droplets were not fragmented. This possibility was suggested theoretically by Leong (1987) who pointed out that formation of multiple crystals in a droplet is possible when the solubility is low, the solute mass is high or the rate of solvent evaporation is high. Kang *et al.* (1995) showed that in spray pyrolysis of ultrasonically nebulized nitrate or acetate solutions the particle size can be reduced to about 10 nm by using a low pressure system (80 mbar). The same phenomenon was observed when zinc acetate droplets of 2 μm were generated by expanding a liquid through a glass filter into a low pressure chamber and subsequently pyrolyzed,

yielding ZnO nanoparticles (<20 nm). A mechanism was proposed in which gas evolution, due to solute decomposition with increasing temperature, resulted in the fragmentation of droplet containing the nanocrystals (Kang and Park, 1996a). However, by varying the solution concentration it only changed the particle size marginally, indicating a more complex mechanism (Kang and Park, 1996b).

3.5 Conclusions: processes suitable for functional applications

In many cases the choice of the process or precursors is based on economic considerations (Kruis *et al.*, 1992). For structural applications such as production of ceramics, a process capable of producing larger quantities of nanoparticle powder is necessary, such as flame or plasma reactors. For functional applications, however, the quality more than the quantity of the nanoparticles is decisive, as most of the functional applications need only thin films. The purity of the nanoparticles is also very important, so that most processes basing on chemical reactions are not suitable due to incorporation of byproducts in or on the nanoparticles. Processes based on pure physical processes are, therefore, used more often.

One of the most simple methods is evaporation of a source material in a flowing gas, followed by condensation into nanoparticles in the cooler parts of the system. A good purity can be obtained by using a purified inert gas and high-quality source material. It is difficult, however, to avoid some contamination of the particle surface with residual gas impurities. These contaminations can be reduced by reducing the process pressure, thereby reducing the number of collisions of gas collisions with the particle surface.

The evaporation method is not always suitable for synthesizing compounds, such as compound semiconductors. We found that direct evaporation of GaAs and InP is not possible due to decomposition (Deppert *et al.*, 1998). The use of chemical reactions with synthesized metal nanoparticles is one possibility to obtain the desired stoichiometry. Another possibility is the use of laser ablation, in which the stoichiometry of the ablated material is more or less retained.

Another problem of the usual evaporation-condensation process is that the particle size distributions are relatively wide. The geometrical standard deviation is at least 1.35 due to Brownian coagulation. But the Brownian coagulation can also be made useful for obtaining composite materials. As the evaporation-condensation process is the process of choice in this work, important phenomena occurring in this process will be investigated in the next Chapter.