2. Electronic, optical and magnetic application of nanoparticles

In this chapter, the use of nanoparticles for electronic, optical and magnetic applications is discussed. A broad spectrum of materials including insulators, semiconductors, superconductors, metals and alloys, optical, and artificially structured materials can be used for these purposes. Most applications use films composed of nanoparticles, supported by a substrate material. Part of the material presented here has been published (Kruis *et al.*, 1998d). In this chapter the main phenomena making specific applications possible are reviewed, while in Chapter 5 examples of gas-phase synthesis methods aiming at these applications are given.

2.1 Microelectronic and optoelectronic applications of zero-dimensional structures (quantum dots)

Nanoparticles have been suggested recently for various potential applications in electronics where quantum confinement effects may be of advantage. When electrons are confined to a small domain such as a nanoparticle the system is called a 'quantum dot' or zero-dimensional (0-D) structure. Then the electrons are behaving like 'particles-in-a-box' and their resulting new energy levels are determined by quantum 'confinement' effects. These new energy levels give rise to a modification of the optoelectronic properties as compared to the corresponding properties determined by the bulk material electronic structure (Brus, 1983; Yoffe, 1993). As a result, discrete energy levels are needed to describe the electron excitation and transport in quantum dots. Quantum confinement effects lead for example to higher energy level transitions as compared to the bulk material observed as a shorter wavelength optical absorption edge, indicated by a spectral 'blue shift'. An example is given in Fig. 2.1.

Quantum dots can be used also to produce light emitters of various colors by 'band gap tuning' using particle size effects rather than the current complex techniques of synthesizing compound semiconductors (Service, 1996). Another advantage of 0-D semiconductor structures stems from the very long life time of electrons in the excited states, which is an important requirement in laser optical applications (Weisbuch and Vinter, 1991).
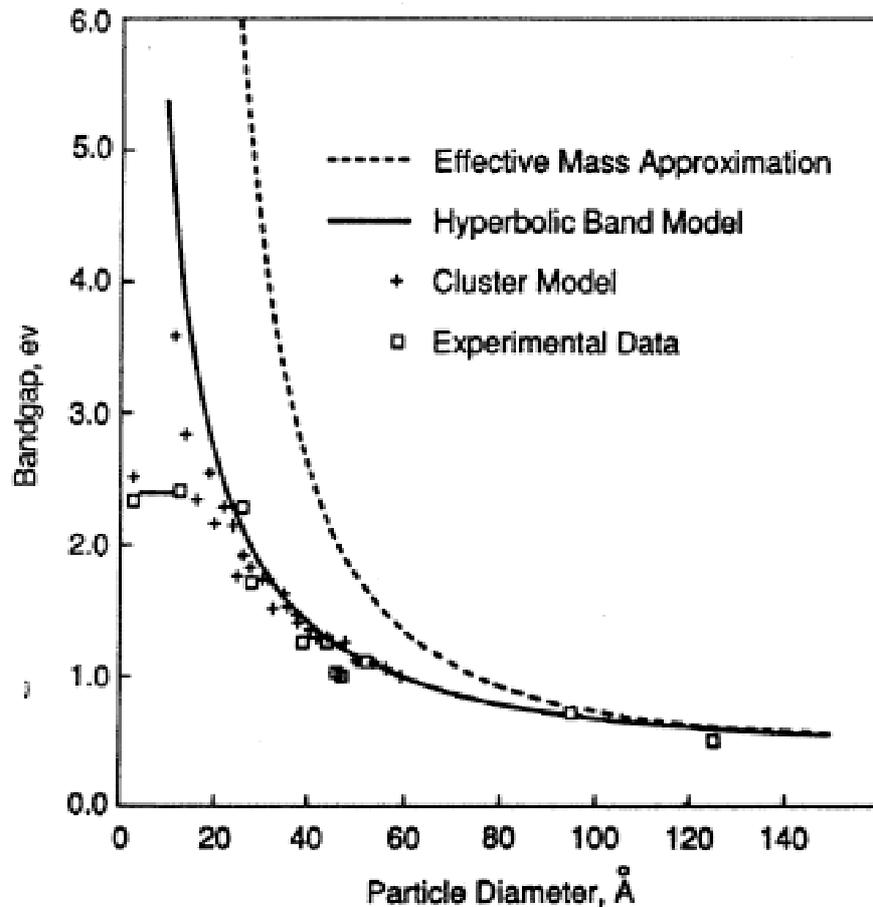
Fig. 2.1. Band gap of PbS as function of particle diameter (Wang et al., 1987)

Alivisatos (1996) produced light-emitting diodes (LED) with high conversion efficiencies (10 %) by using quantum dots embedded in polymer matrices. Moreover, quantum dots were employed in LEDs with a voltage-controlled, tunable output color by Colvin *et al.* (1994), as shown in Fig. 2.2, who assembled CdSe nanoparticles on the surface of an electroluminescent polymer (PPV). The LEDs emitted green light from the polymer and red light from the nanoparticle layer, being also color tunable as a function of the applied voltage. Finally, lasers based upon such structures are expected to have a higher gain and to lase at much lower electrical threshold as compared to current available laser technologies (Weisbuch and Vinter, 1991).

Although these applications seem very attractive, the processes for producing quantum dots devices are very demanding technologically. The preparation of the semiconducting nanoparticles need highly accurate steps during the production stages such as (Salata *et al.*, 1994): 1) good controllability of the particle size, 2) monodispersivity, 3) passivation of the surface, 4) good control of the particle shape. A good stability against degradation is needed, as observed in many cases where

8

properties of the nanoparticles vary with time. A current technological approach to circumvent the inherent reactivity and instability of nanoparticles is by imbedding them in a glass (Ohtsuka *et al.*, 1992) or in a semiconductor having a wider band gap (Danek *et al.*, 1994). These nanocomposite structures can then be used in real life optical and electrooptical applications.
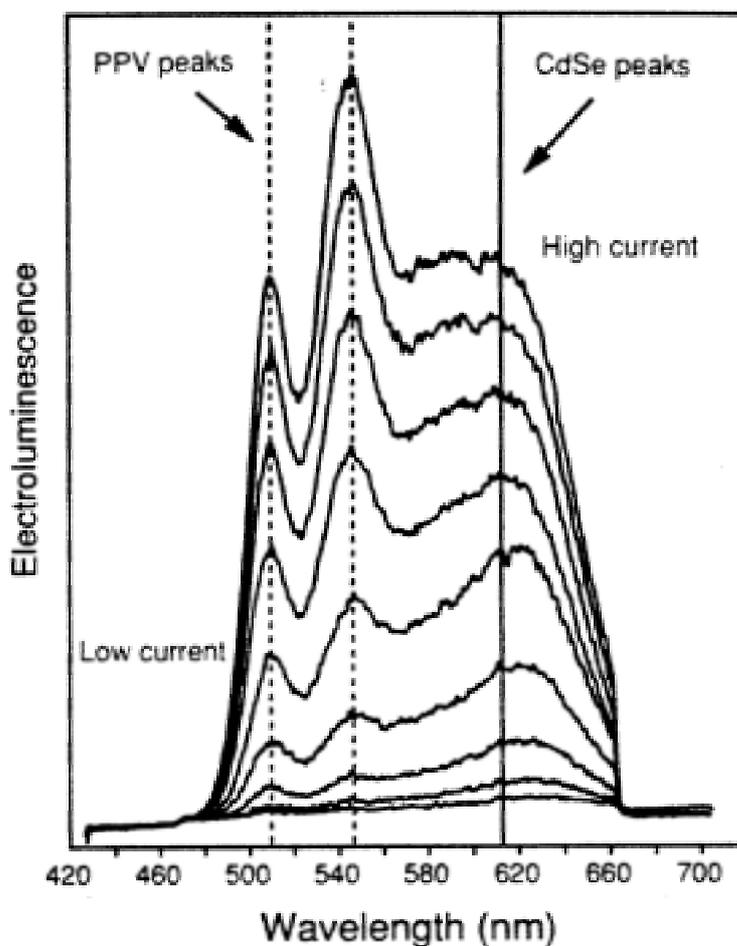

Fig. 2.2. Electroluminescence as function of current for use in LEDs with a voltage-controlled, tunable output color (Colvin et al., 1994).

Enhancement of the nonlinear optical properties by quantum size effects are also of great interest today. This effect has been applied already commercially for producing optical cut-off color filters based on CdS_xSe_{1-x} nanoparticles embedded in silicate glasses. It is expected also that nanoparticles such as CdS, CdSe, GaAs and Si dispersed in glasses will have applications in fast optical switches and optical fibers based on the nonlinear optical behavior (Yoffe, 1993). In nonlinear optical materials, the refractive index can be changed either by carrier injection or by applying electrical fields (Brus, 1991). This change in the refractive index allows electronic modulation of light, enabling for instance faster electro-optical switching as compared to electronical

9

switching.

Another potential application of quantum dots is the fabrication of optical memories. A 3-D array of quantum dots which are addressed optically can pack in the same volume much larger amounts of information than current planar-based microelectronic memory devices. This can be done for instance by spectral hole burning (Peyghambarian *et al.*, 1996), in which those quantum dots in resonance with a specific laser wavelength will be excited and thus 'bleach'. This enables thus 'writing' a '0' or a '1' memory 'state' with a resolution smaller than the size of the laser spot.

For semiconductor applications other than optical, the nanoparticles should be contacted electrically efficiently. This forms one main difficulty for producing electronic devices based on quantum dots. Since attaching electrical leads to an array of quantum dots is a formidable technological task, one way of making an efficient contact is by using a semiconductor structure consisting of an ensemble of quantum dots. The voltage-tunable LED described earlier is a successfully implemented example which uses a matrix of quantum dots. Another example of efficient contacts can be found in photovoltaics. Hodes *et al.* (1987) measured photocurrents arising from a film consisting of CdSe nanoparticles on glass and reported quantum effects. To allow conversion of significant quantities of light into an electrical current for obtaining an efficient solar cell, a rather 'thick' film up to twenty monolayers of particles had to be deposited. Increasing the contact area between nanoparticles and electrode to increase the signals is possible by depositing the nanoparticles on a very porous TiO_2 electrode. (Weller, 1993).

In microelectronics, the need for faster switching times calls for a reduction in the size of the electronic components. At present, one switching cycle in a transistor gives rise to the movement of many thousands of electrons, requiring a considerable amount of switching energy and producing excessive heat which can hardly be dissipated in high-frequency applications. This calls for developing single-electron devices, in which the switching occurs with the motion of only a single electron. Such a device may be realized by a quantum dot in which the charge of an added electron effectively blocks the flow of other electrons by the so-called 'Coulomb blockade'. Both switching, which performs logic operations, and storage of information are possible with these devices. Here again, one finds that electrical contacts are very hard to produce (Lüth, 1995). Such contacts were nevertheless obtained by Bezryadin *et al.* (1997), using an liquid-phase electrostatic trapping method of Pd nanoparticles between nanoelectrodes with a 4 nm gap.

2.2 Luminescent nanocrystalline silicon and other materials

Porous structures and other nanometer sized particles have found in the last decade a very important potential application for electrolumiscent silicon based devices. The interest in luminescent Si is due to the desire for integration of optoelectronic devices, based now mainly on III-V semiconductors which are not yet integrable monolithically with the dominant Si microelectronics (Kanemitsu, 1995). Light-emitting Si hence would open the way to optical and electrical functionality on one integrated monolithic Si chip. Silicon electroluminescence, in which the luminescence is controlled electrically, would enable also to implement new devices such as light-emitting diodes, with voltage tuned color, and also many other optoelectronic integrated circuits concepts. Being an indirect-gap semiconductor in which interband transitions need phonons (a quantum of energy associated with atomic vibrations), Si in its bulk form is not luminescent, as radiative transitions are of very low probability. Takagi *et al.* (1990) observed visible luminescence from Si nanocrystals at room temperature although the phenomenon was first observed in porous silicon. Until now, there is no generally accepted mechanism for visible luminescence although there are indications that the light absorption by the nanoparticle is influenced by quantum effects and the photoluminescence is dominated by the electronic states of the surface (Kanemitsu, 1995, Prokes, 1996).

Seraphin *et al.* (1996) reported that unpassivated Si nanoparticles exhibit no visible photoluminescence. As the particles age in air, the surface becomes passivated gradually with SiO_2 and exhibits a strong orange emission behavior. Koch and Petrova-Koch (1996) even reported luminescence from SiO_2 nanoparticles. Other nanoparticles of indirect-gap semiconductors such as Ge (Kanemitsu *et al.*, 1992) and SiC (Mimura *et al.*, 1994) showed also luminescence in the visible.

2.3 Gas sensors

Gas sensors have nowadays many established production technologies. It seems however that this field can take advantage from the nanoparticles recent developments as well. A gas sensor consist quite generally of a material with measurable physical properties such as electrical or optical, which change when a gas is present. A solid state chemical sensor selectively converts microscopic chemical interactions into a measurable electrical signal. Sensors should possess selective and reversible sensing properties and be compatible with the transducer device (Holtz *et al.*, 1996). The simplest 'nanomaterials' based sensor concept involves measuring the changes in the electrical resistance of a nanocrystalline metal when exposed to hydrogen. Volkening *et al.* (1995) used palladium nanoparticles (10-15 nm) for hydrogen sensing, since the Pd-H system is well understood in terms of the dissociative reactions of H_2 at the Pd

surface and the diffusive properties of H_2 into Pd. They found the response in the nanocrystalline material to be faster as compared to palladium with conventional micron-size particles, due to the smaller diffusion distances.

Traditionally, semiconducting oxides such as SnO_2, ZnO and Fe_2O_3 are used extensively in gas sensor technology (Göpel, 1996). Usually, the sensor is constructed as a porous sintered ceramic body, heated between 300 °C and 700 °C. The sensing behavior appears to be governed by the adsorption of oxygen in the neck regions between the grains. A positive space charge, also called depletion layer, develops in the oxide layer as electrons transfer to the adsorbed oxygen, and a negative charge accumulates on the surface. Reducing gases can remove some of the O^{2-} ions from the surface, thereby increasing the electrical conductivity (Moulson and Herbert, 1990).

The sensitivity of gas sensors can be increased by doping, usually with noble metal catalysts such as platinum, rhodium or palladium. Labeau *et al.* (1993, 1994) investigated the sensitivity of a nanocrystalline SnO_2 gas sensor doped with Pt and Pd nanoparticles. These particles probably act as a catalyst for the adsorption of CO and ethanol molecules, leading to a lower activation energy of the surface reactions. In the work of Gautheron *et al.* (1993), the CO sensitivity was increased by a factor of 30 by adding Pd nanoparticles.

2.4 Resistors and varistors

Nanometer particles have found new applications also in the production of resistors and varistors. Granular films consisting of small conducting particles embedded in an insulating matrix of ceramic or glass exhibit a great variability of the electrical conductivity. It was also shown that by a proper control of the volume fraction of W in Al_2O_3 stable, high-resistance films with a low temperature coefficient of resistivity(TCR) can be produced (Abeles *et al.,* 1975). When the particle size can also be controlled, a wider range of the electrical transport properties is attainable, making these materials suitable for thick film resistors production. The electrical resistance is modeled here by percolation and quantum effects such as electron tunneling (Kundu and Chakravorty, 1996). An example of thick film resistors whose resistivities can be controlled by changing the nanoparticle size is the LaB_6 nanoparticle-glass nanocomposite system, which is compatible with copper hybrid integrated circuits (Ito *et al.*, 1991).

Since varistors are voltage-dependent resistors, characterized by a very low resistance at high voltage, they are used for protection of low-power circuits from high-voltage transients. They are prepared from sintered ceramic materials such as ZnO or SiC with some added minor constituents. The resistance is assumed to be controlled by either direct grain-boundary contacts or by intergranular insulating layers

between the conducting grains. The use of nanoparticles with their large volume of grain boundaries in varistors is expected to improve their properties. Brankovic *et al.* (1994) investigated ZnO based varistors. Using particles with sizes below 100 nm, a varistor with more homogeneous phase distribution and microstructure was obtained, resulting in good nonlinear electrical characteristics. Viswanath *et al.* (1995) applied ZnO nanoparticles of 3 - 10 nm. Apart from good nonlinear characteristics, the normalized breakdown voltage was increased by a factor of 20 in comparison to coarse-grained ZnO varistors.

2.5 Conducting films

Nanometer structured, polycrystalline conducting thin films, have found potential also in the production of transparent conductive electrodes for photoconductor and solar cells applications. Polycrystalline thick films made of closely packed crystalline grains are often used for optoelectronic films. They are used for instance to conduct electrical charges in devices such as solar cells, displays and other applications where a large surface area is needed and epitaxial films are not feasible. These polycrystalline films are nowadays routinely made by spray technologies which have substantial advantages being inexpensive, using only small amounts of material and with high deposition rates (Service, 1996). However, conventional spraying techniques produce a relatively rough film surface with many gaps due to the micrometric size of the droplets. These gaps might reach from the surface of the film down to the substrate decreasing thereby the electrical conductivity of the films. By spraying a colloid of 3 nm nanoparticles on a heated substrate, Pehnt *et al.* (1995) produced very smooth conducting thin CdTe films without gaps and with a roughness smaller than 5 nm, for use in solar cells.

Thin films of wide optical band gap oxides such as SnO_2 and In_2O_3 which are transparent in the visible spectral region are applied in many areas, e.g. as electrodes and anti-reflection coatings in solar cells, photodetectors and charge-coupled imaging devices. Transparent conducting films require high transmission in the visible region and a high or even metallic-like electrical conductivity (Chopra *et al.*, 1983). For this end, inhomogeneities in the film created by the presence of large particles, causing detrimental light absorption and scattering in the visible region, can be minimized by preparing films from nanoparticles. Another advantage obtained with nanomaterials is control on the absorption characteristics by particle size variation leading to quantum confinement effects as described previously. Zhao and Pan (1994) showed that the IR absorption peaks of a film composed of ZnO nanoparticles can be changed by varying the particle size.

Another potentially applicable phenomenon is the electrical bistability of a thin

layer of Ag nanoparticles sandwiched between two layers of a conducting polymer. Up to a certain threshold voltage, no current flows while above it the conductance increases by a factor of 10^7 rendering the film conductive. These films can thus have switching applications in electronics. (Gao *et al.*, 1995)

2.6 Capacitive materials

Dielectric elements based on nanometer structures are of recent interest due to the reduction in capacitance caused by the continuing scaling down of dynamic random access memories (DRAMs). Since materials with a high dielectric constant can store more electrical charges in capacitors, materials with ever larger dielectric permittivities are sought for the shrinking DRAMs. One method for increasing the dielectric permittivity is by dispersing conductive particles in a dielectric matrix.The dissipation factor becomes, in this case however, too large. Kundu and Chakravorty (1995) showed that 2-8 nm Ag nanoparticles in a lead zirconate titanate (PZT) matrix has a high dielectric permittivity with low dissipation factor. The smaller particles led to lower dielectric permittivities but on the other hand improved the dissipation factor. Vezzoli *et al.* (1994) showed from the percolation theory of dielectrics that an optimal topology for high dielectric nanocomposites consists of ellipsoidal metal particles with a small interparticle spacing in the insulating matrix. A high dielectric constant of 5000 was obtained by embedding elongated Au nanoparticles with a length of 80 nm and a width of 30 nm in a matrix of SiO_2.

2.7 High-temperature superconductors (HTS)

Nanoparticles are currently suggested as a solution to 'flux pinning' improvement in HTS devices. The problem occurs if the magnetic flux entering the HTS material is not distorted or 'pinned' by suitable defects. Then, the material looses its superconducting properties. In general, non-superconducting particles can act as flux pinning centers in a superconductive material. Nanoparticles can be used as defects when added to the superconducting material enhancing flux pinning, and increasing thereby the critical current density. Chadda *et al.* (1991) reported that small-grained , 25-50 nm precursor particles of $YBa_2Cu_3O_{7-x}$ and CuO were necessary to obtain $YBa_2Cu_4O_8$, which upon heat treatment developed $YBa_2Cu_3O_{7-x}$ with CuO flux pinning centers. Takao *et al.* (1996) added $BaZrO_3$ nanoparticles to an HTS material, $YBa_2Cu_3O_7$, and obtained an increase of more than one order of magnitude in the critical current density.

2.8 Thermoelectric materials

14

Nanoparticles can be used also for producing thermoelectric materials. The thermoelectric effect creates a voltage difference between two conductor junctions kept at different temperatures. This effect is used mainly for thermocouple-type sensors. Kizaki *et al.* (1993) produced thermoelectric thin films of an nanometric-structured Fe-Si alloy. Using $FeSi_{2+x}$ (0<x<1) nanoparticles allowed film deposition at low temperatures. A homogeneous film of mixed Fe and SiO nanoparticles of some 10 nm showed after thermal treatment a high Seebeck coefficient of $-1400 \, \mu V \, K^{-1}$.

2.9 Optical materials

Inorganic pigments such as TiO_2 are used to absorb and scatter UV radiation (Parker, 1996). The particles normally used for pigments, however, impart an unfavorable whiteness to the protected surface. Since the scattered light intensity is a function of the wavelength of the incident light and the particle diameter, an optimal particle size can be found which attenuates UV but only slightly attenuates the visible light. This particle size happens to be located in the nanometer size range. Nanoparticles in a suitable dispersion are already commercially used for solar protection creames and in films which protect plastics against color degradation. Another successful development is the use of pigments as an active scattering medium in a semiconducting polymer. Hide *et al.*(1996) was able thus to obtain laser emission from a semiconducting polymer, MEH-PPV, by incorporating TiO_2 nanoparticles in the polymeric medium. The random scattering by the nanoparticles significantly increases the path length traversed by the emitted light, and lasing occurs if gain by multiple scattering exceeds loss by absorption.

Another optical phenomenon uses electrochromism in nanomaterials. In electrochromic materials the optical properties can be altered reversibly by applying an electric field. Windows made from these materials allow the control of solar energy inflow into buildings and are used also to produce mirrors with a variable reflectance and nonemissive displays with a high-contrast. Estrada *et al.* (1988) showed that the solar transmittance of a NiO_xH_y film with a grain size of about 10 nm could be changed between 29 and 74 %. Chen *et al.* (1995) showed that NiO films consisting of 5-10 nm sized grains have good electrochromic characteristics and that their performance becomes poorer with increasing grain size. The large number of grain boundaries is thought to play an important role in the transport of the alkali metal ions, which are responsible for the coloring, into the grains.

2.10 Magnetic materials

15

Magnetic nanoparticles approach the size of a single magnetic domain, in which the magnetic spins are aligned all to produce a magnetic moment in one direction. The particle size for single-domain formation in the ferromagnetic elements Fe, Co and Ni is typically several tens of nanometers. For applications using high density magnetic recording materials a high coercivity (representing the resistance to demagnetization) and a high magnetization are essential. It was shown that a maximum value for the coercivity is obtained for nanocrystalline magnetic materials with crystallite in size close to the single magnetic domain. Crystallite sizes smaller and larger than the magnetic domain lead to a sharp decrease in the coercivity. Fe powder with a crystallite size of 13 nm showed a coercivity of 900 Oe in comparison with 10 Oe in bulk Fe (Gangopadhyay *et al.*, 1992). Greatly enhanced values of the coercivity occur in ferromagnetic nanometer-sized metal particles embedded in an insulating oxide film. Xiao and Chien (1987) reported for a Fe-SiO_2 nanocomposite magnetic coercivities as high as 2500 Oe.

In contrast to hard magnetic materials, soft magnetic materials need the other extreme, i.e., very low coercivities. Typical examples are FeSi and FeNi alloys, ferrites and garnets. They are used in power transformers, magnetic recording heads and microwave applications. Until ten years ago, relatively coarse-grained alloys were used since smaller grain sizes caused an increase in the coercivity. It was found however that a maximum in the coercivity vs. grain size curve occurs at about 100 nm (Fig. 2.3). For smaller particles then the coercivity decreases steeply. An alloy with 10 - 20 nm nanocrystals embedded in an amorphous phase shows very low values for the coercivity. Additional useful properties of these materials are very low eddy-current losses and good high-frequency properties. (Yoshizawa *et al.*, 1988, Yamauchi and Yoshizawa, 1995).

Nanocomposites have also good potential in magnetic refrigeration technology (Zachariah *et al.*, 1995) based on the magnetocaloric effect. Bulk magnetic materials show usually a decrease in magnetization upon temperature increase and limits the temperature range in one refrigeration cycle. Superparamagnetic nanoparticles in a non-magnetic host can overcome this limitation by combining the higher magnetization of ferromagnets with the higher magnetocaloric effect of paramagnets. Zachariah *et al.* (1995) found a superparamagnetic behavior for 5-10 nm Fe_2O_3 particles embedded in much bigger SiO_2 particles.
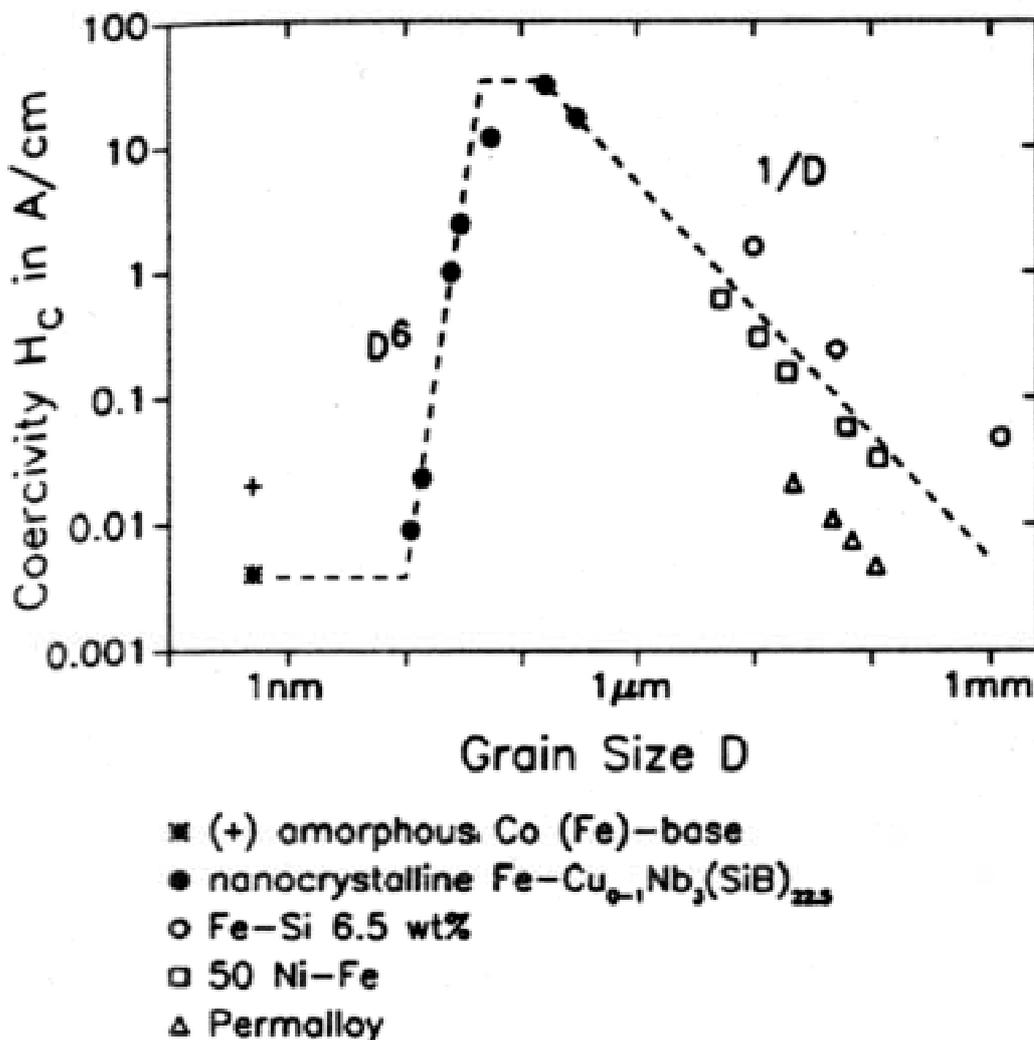
Fig. 2.3. Dependence of coercivity on crystallite size for various soft magnetic alloys (Herzer, 1990).

A novel important property found in recent years for nanocomposites is the giant magnetoresistance (GMR) effect. This is the phenomenon of a large decrease in the electrical resistivity of certain materials when exposed to a magnetic field. The resistivity-temperature change can be up to 80 % as compared to only a few percent in regular metals. Its applications are for magnetic sensors and for new storage devices with very high density. First discovered in magnetic multilayers, it was also found in the granular Co-Cu system, in which ferromagnetic Co nanocrystals are dispersed in a nonmagnetic Cu matrix (Xiao *et al*., 1992). The magnetic field aligns the ferromagnetic domains, and reduces the scattering of electrons, thereby decreasing the electric resistivity. GMR is observed in immiscible metals, such as Co-Cu, Fe-Ag, Fe-Cu, Fe-Au and Co-Ag. The smaller the particle size, the bigger the GMR effect is. The

17

effect is highest near the percolation threshold (Wang and Xiao, 1994).

2.11 Conclusions: control parameters for properties of functional applications

As shown at length in this chapter, there are many parameters influencing the properties of functional applications based on nanoparticles. These are:

- Mean particle size
- Width of the particle size distribution
- Crystalline properties, such as the crystal phase and the size of the crystallites
- Chemical composition, e.g. deviation from stoichiometry
- Amount of impurities present in the nanoparticles or on the surface
- 'Packing' of the nanoparticles, e.g. intimately contacting (nanophase materials), forming a porous film or with sintered connections between them ('necks')
- Mixing with other material, e.g. imbedded in a matrix (glass, ceramic material or polymer) or in close contact with other nanoparticles (e.g. SnO_2 gas sensors doped with noble metal nanoparticles)

Depending on the application, one or more of these parameters should be controllable. It is the process which yields these properties. Gas-phase processes, although having some drawbacks, have a high level of control. The different gas-phase synthesis methods will be described in the next chapter.

A review of synthesis of nanoparticles in the gas phase for electronic, optical and magnetic applications