

# 9 Materials in Nanotechnology

HELMUT SCHMIDT, Institut für Neue Materialien, Saarbrücken, Germany

## Contents

|       |   |     |
|-------|---|-----|
| 9.1   | Introduction . . . . .  | 276 |
| 9.2   | Sol-Gel Processing for Nanostructured Materials and Films . . . . . | 278 |
| 9.2.1 | Materials Synthesis . . . . .                                       | 278 |
| 9.3   | Formation of Films and Bulk Materials . . . . .                     | 283 |
| 9.4   | Potential for Sensors and Conclusion . . . . .                      | 291 |
| 9.5   | References . . . . .  | 292 |

## 9.1 Introduction

Nanostructured materials have gained increasing importance in research during the last decade. The reason for this interest is based on a variety of very special properties related to the small size of the phase dimension and, as a consequence, to a relatively high volume fraction of grain boundary phases. The basic phenomena, such as high diffusion coefficients, structure and other physical properties of these grain boundary phases, were described by Gleiter [1]. Interfaces of almost any kind of material possess structures different from those of the bulk. This is well known, for example, for polymer structures in adhesives, surface structures of metals, and others. If appropriate combinations of materials are chosen, interfacial structures can be used for specific alignments such as in Langmuir-Blodgett films or in micelle-type structures. Special properties can be expected in all cases where interfacial phases gain a significant volume fraction.

Another important factor is the large surface-to-volume ratio related to nanoscale particles. This leads to an enhancement of all types of reactions related to the surface of a system, such as catalysis. In the field of catalysis, high surface areas are required in order to obtain high overall reaction rates. However, in general, this type of material is based on porous carriers doped with active components such as noble metals. While these noble metal particles have diameters in the lower nanometer range, the processing of these materials can be considered as a true nanotechnology.

A basic process for synthesizing systems containing small disperse particles is doping a porous substrate with precursors which, through a chemical reaction (crystallization, nucleation, reduction, growth), form small particles on the support, in general, by surface diffusion processes on the carrier surface. However, these techniques do not lead to nanostructured materials in the sense that a porous or dense microstructure consisting of crystallites or amorphous particles with diameters in the lower nanometer range with a substantial volume fraction of an interfacial phase exists.

There is a series of problems related to nanotechnologies, starting from the fabrication of nanoscale particles, the control of agglomeration, processing them to green bodies, layers or coatings, and densifying them to bulk materials or dense films. Different techniques have been investigated in order to fabricate nanoscale materials. Chemical vapor condensation is widely used for metals in fundamental research [1], but has already gained significance for laboratory-scale preparation. Plasma-enhanced technologies have been developed by Trusov et al. [2], and powders are already being produced on a pilot scale. This is also valid for a chemical vapor reaction (CVR) process [3], where titanium nitride has been prepared very successfully. Other processes are high energetic milling and precipitation reactions. The latter, which involve wet chemistry, basically follow simple precipitation processes, which take place in supersaturated solutions and which follow the rules of nucleation and growth. In these systems, the critical nucleation radius has to be exceeded as a prerequisite for further growth. The growth reaction then continues following the thermodynamic drive since the precipitated system shows a lower free energy value than the dissolved system. This means, however, that, in general, the growth reaction only stops if the stock of precipitating ions is exhausted, which means if their concentration falls below the solubility product. In these cases the particle size of the precipitate can be tailored by adjusting concentration, solubility, and temperature if nucleation can be controlled. However, in cases of extremely low solubilities, as is the case with

the majority of interesting oxides (oxides for structural and functional ceramics) or metals, this route leads to very diluted systems in which it is difficult to separate powders from the solution and difficult to handle the process for industrial technologies, as shown by Matijevic [4]. In concentrated systems, however, agglomeration is unavoidable, leading to hard agglomerates.

The situation requires methods to control growth reaction, to stop it at a desired level, and to avoid agglomeration in order to keep the particles isolated for suitable further processing. In other words, one has to carry out precipitation reactions in such a way that stable colloids are produced in the first step in a sufficient concentration.

Stabilization of colloids can be achieved in various ways. The "simplest" way is to charge them electrically by the selective absorption of ions (for example, protons or hydroxyl ions), generating a surface potential and, as a consequence, repulsive forces between the equally charged particles. The theoretical background of electrically stabilized colloids has been treated extensively by Stern [5], who showed that actually an electric double layer is formed, preventing the colloids from agglomeration. Owing to the range of the electric forces (which can reach from several to 20 nm), the solid content of colloidal solution, in general, is low (from several up to 20% by volume for special cases). This type of low solid content colloidal solution (sols) can be transformed into gels by destabilization, for example by adjusting the pH to a range where the surface charges are neutralized (point of zero charge). In this case the van der Waals forces are strong enough to agglomerate the systems to fairly stable solids (gels), which, in general, show a disordered structure with respect to the particle arrangement which is responsible for the low solid content of these gels (<20% by volume). Processing of large parts is difficult owing to the large shrinkage concomitant with densification. If the sols are used for coatings, densification can be achieved fairly easily if the layer thickness does not exceed the critical size. This phenomenon has been investigated by Lange [6], who determined the critical thickness  $t_c$  obtained for crack-free coatings after firing according to Equation (9-1):

$$t \geq t_c = \frac{E \cdot G_c}{A \cdot \sigma^2} \quad (9-1)$$

where  $G_c$  = energy required to form cracks at the surface,  $t$  = thickness,  $A$  = constant,  $E$  = strain energy per unit volume and  $\sigma$  = triaxial tensile stress. This relation is valid for particulate systems with high particle-particle interaction, as it is the case in most oxidic systems.

Based on these considerations, two basic requirements for nanoprocessing of small particles have to be formulated. First, it is necessary to control the nucleation and growth process in such a way that the process can be stopped at a desired particle size and the particles can be stabilized at this level, and second, it is necessary to control the particle-particle interaction during "gelation" (or green part, layer or film formation) in such a way that high package densities can be obtained (for example, over 50% by volume for ceramic nanoparticle processing). A third option would be to treat the nanoscale particle for obtaining desired solid-state properties (for example, crystallinity, defect structure, or phases in multicomponent systems) in order to obtain desired properties in the solid material (for example, porous systems with the desired crystallinity after sintering while maintaining the nanoparticulate structure, eg, for sensor application).

In the following section, the advantages and disadvantages of the sol-gel process for obtaining nanocrystalline systems will be discussed.

## 9.2 Sol-Gel Processing for Nanostructured Materials and Films

### 9.2.1 Materials Synthesis

The synthesis of nanoparticulate systems is of great importance since it is the basis for processing these systems to solid materials such as films or bulks. In addition to the properties associated with the high surface-to-volume ratio, a variety of other properties of small particles and their processing to solid materials are of interest. These are quantum size effects such as quantum confinement and properties related to it such as high third-order non-linear susceptibilities if semiconductor or metal particles are considered, especially in combination with transparent matrices for embedding these particles. In these cases, so-called "nanocomposites" with high optical transparency become possible, unifying material properties related to the solid state of the particles and processing properties of, for example, a polymeric matrix. For this reason, the particle size has to be kept below the range at which Rayleigh scattering becomes disturbing, which is, in general, in the range of several nanometers.

Another interesting aspect is related to the surface defect structure of small particles, which, as already pointed out, is fairly high with respect to its volume fraction. These surface defect structures should lead to a considerable decrease in the sintering temperature if processed to ceramics. Independent of the type of mechanism to be assumed, as shown in Equations (9-2) and (9-3), the particle diameter affects the sintering rates considerably. Depending on a Nabarro-Herring or a Coble mechanism [7, 8], the particle diameter is efficient in a second- or third-order way to increase the sintering rate with decreasing size.

$$S_V = \frac{a \cdot \delta \cdot D_{GB} \cdot V_V \cdot \Delta\sigma}{d^3 \cdot k \cdot T} \quad (9-2)$$

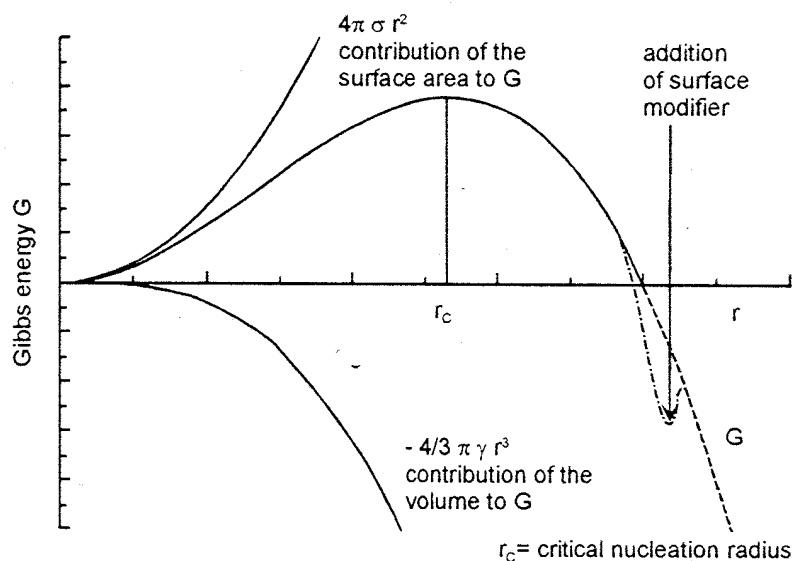
$$S_{GB} = \frac{b \cdot D_V \cdot V_V \cdot \Delta\sigma}{d^2 \cdot k \cdot T} \quad (9-3)$$

where  $S$  = sintering rate (subscripts V and GB = volume and grain boundary diffusion),  $a$  and  $b$  = constants,  $T$  = temperature,  $D_V$  = volume diffusion constant,  $D_{GB}$  = grain boundary diffusion constant,  $\delta$  = thickness of grain boundary,  $k$  = Boltzmann constant,  $\Delta\sigma$  = pressure difference,  $V_V$  = defect volume (voids) and  $d$  = grain diameter.

Another interesting point is the use of nanosized particles to coat sub-micrometer particles and to build up two-component systems with engineered grain boundaries, for example zinc oxide-based varistor ceramics. For this reason, it is necessary to precipitate colloids, for example, to establish a zeta potential on the colloids opposite to that of the particles to be coated and to precipitate them on the surface. This could be another interesting way of generating very special surface properties for catalysts or sensors.

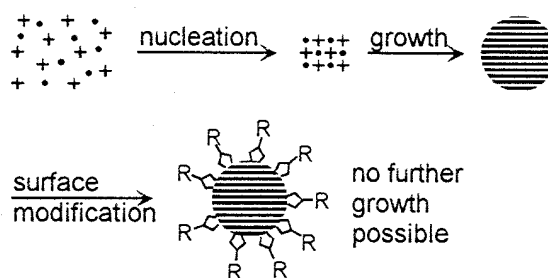
For the synthesis of nanoscale particulate systems by wet chemistry, it is essential to control growth and agglomeration, as mentioned above. In general, a precipitation reaction starts from homogeneous solution by a nucleation process. If the critical radius for nucleation is exceeded, the particle starts to grow, driven by thermodynamics. A simple thermodynamic consideration, as shown in Figure 9-1, shows that after nucleation particle growth is favored from thermodynamics. The growth reaction can be stopped by adding surface-active com-

ponents, leading to a metastable thermodynamic sink. In this case, the binding free energy for the surface-active components has to be lower than the free energy for further growth. This basis concept allows one to tailor particle size and particle distribution in a straightforward way, since chemistry provides several means of binding a variety of molecules to surfaces. For oxides, carboxylic acids, or  $\beta$ -diketones, amines or chelating molecules can be chosen, and for semiconductor or metals, electron-donating or -accepting groupings. Additionally, the concept allows one to control growth, to stabilize colloidal particles, and to "fit" them with special functions at the same time. If the size of the surface-modifying molecules is small, high packing densities can be expected in the case of compaction as long as these molecules do not interfere with each other too strongly. A schematic diagram of this concept is shown in Figure 9-2.



**Figure 9-1.**

Development of the free energy of the precipitating system after nucleation.

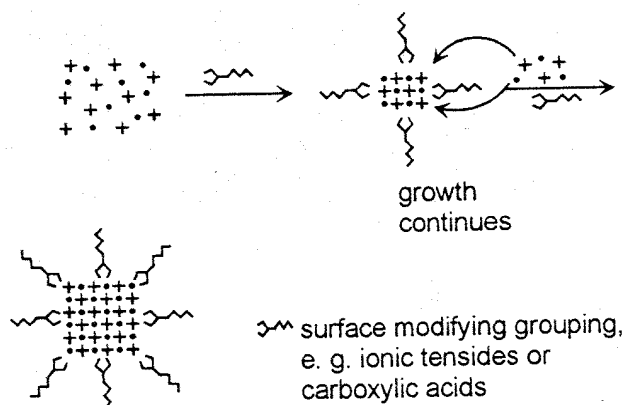


**Figure 9-2.**

Schematic diagram of the preparation of surface-stabilized colloids.

R: a: inert groupings like alkyl or aryl  
 b: functional groupings like acids or  
 c: reactive groupings like  $\text{OH}$   
 or "sol-gel" groupings, e.g.  $\sim\text{Si}(\text{OR})_3$

A prerequisite for a successful application of this concept is a controlled surface-to-particle bond. As shown elsewhere [9], carboxylic acids, for example, are bonded to boehmite particles very strongly in a mainly ionic form, as is typical for aluminium salts from organic acids ("colloidal salts"). If the binding strength of the surface-modifying compound is sufficient, the growth reaction can continue and the surface compound "moves" to the surface of the growing particle without leaving it. In this case, the surface-modifying component can be already present from the beginning of the reaction, as is shown schematically in Figure 9-3.

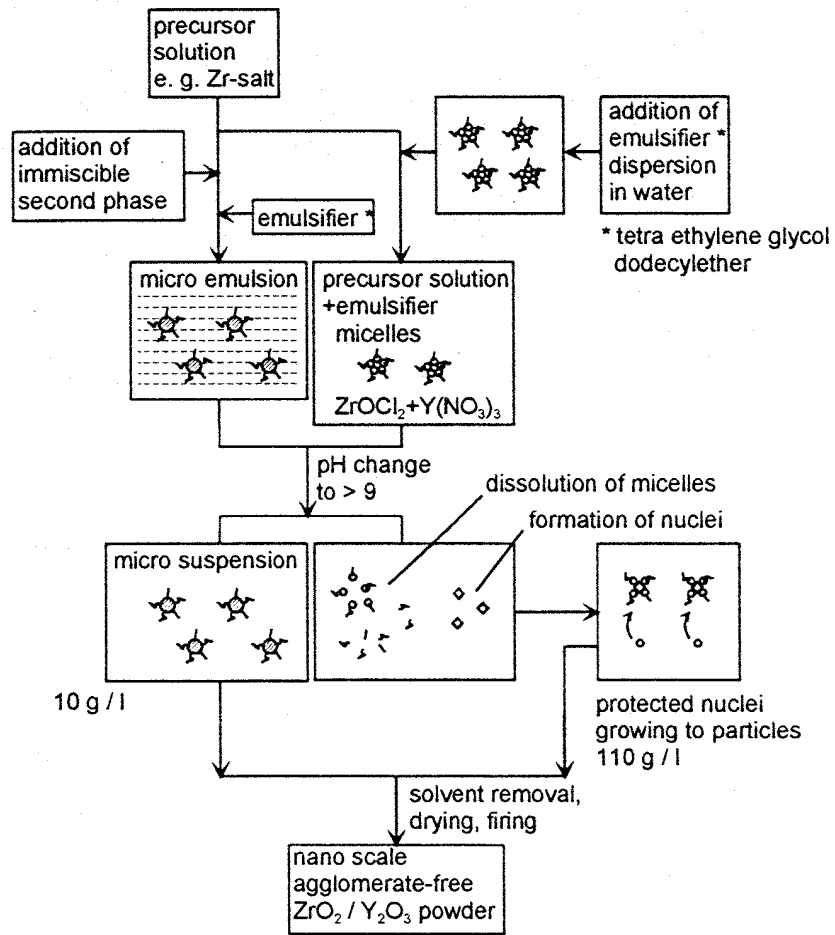
**Figure 9-3.**

Principles of a growth reaction in the presence of surface-modifying molecules.

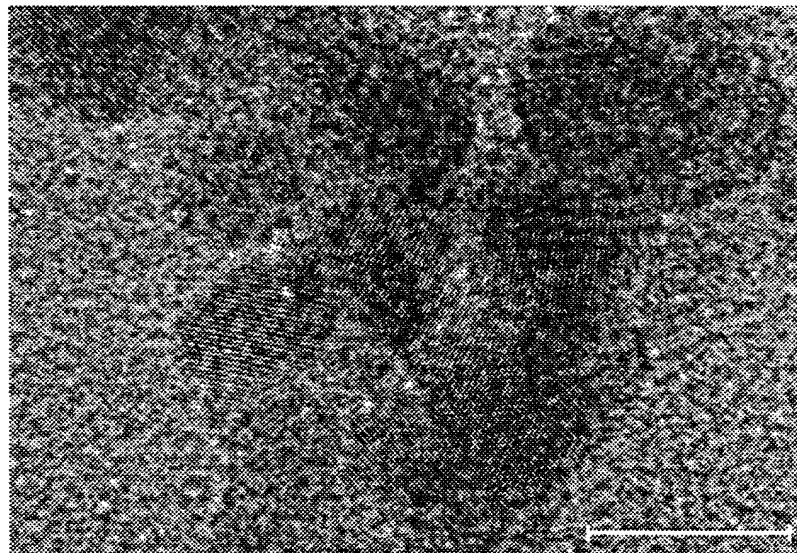
In this type of reaction, the surface modifier acts as a “coating”, only preventing agglomeration of nanoscale particles. It should be mentioned that stabilization of nanoscale particles can also be carried out by electric charges, of course, for example, by using appropriate pH values. However, this type of stabilization is very sensitive to the thermodynamic parameters of the system, especially concentration: as a rule, if the concentration exceeds a certain level, the electric shielding breaks down and leads to agglomeration. For example, as shown elsewhere [10], electrically stabilized boehmite sols cannot be concentrated to concentrations of more than 15–20% by volume without gelation. The gels are rigid and show no strength. If the electric stabilization is substituted by a carboxylic acid bonded to the surface (for example propionic acid), the solid content can be increased up to 45% by volume without gelation. These “sols”, of course, show increased viscosities, but are still plastically deformable, in contrast to the other gels.

Precipitations also can be carried out in so-called “mini-reactors”, ie, within small droplets with already nanosized diameters. For this purpose, thermodynamically stable microemulsions have to be prepared. For the stabilization of a second liquid phase within a liquid system both liquids have to be immiscible and the interfacial free energy has to be reduced in a way that the  $\Delta G$  value of the system is lower than it would be in the separated state. This can also be carried out with an emulsifier, as is well known [11–14]. These microemulsions can be prepared from aqueous solutions of sols, for example, and oxidic particles can be precipitated within the droplets leading to a microsuspension. By appropriate choice of the emulsifiers, the basic structure of the system can be maintained, and the particles are protected from agglomeration by the adsorbed emulsifiers. One of the major advantages of these systems is the easy way to prepare multicomponent systems even with very different concentrations of the single components. An alternative to this route is to add the emulsifier to the homogenous solution of sols and to precipitate by pH change [15, 16]. In this case, an aqueous dispersion of emulsifiers in which a micelle type of structure exists is added to the reacting system. In Figure 9-4, the basic principle of both these routes is given with yttria-doped zirconia as an example.

The suspensions obtained have to be heat treated up to 400 °C to obtain the crystalline phases. Owing to the coating of the particles, only a weak agglomeration is observed, which is responsible for full redispersability with, for example, amines as dispersants. In Figure 9-5 a high-resolution transmission electron micrograph of the  $ZrO_2$  nanoparticles treated at 400 °C and subsequently redispersed is shown. As can clearly be seen, the particle size ranges from 5 to 10 nm, and the particles are well crystallized.



**Figure 9-4.**  
Synthesis of  $\text{Y}_2\text{O}_3$ -doped  $\text{ZrO}_2$  by microemulsion and by controlled growth routes.



**Figure 9-5.**  
High-resolution transmission electron micrograph of nanocrystalline  $\text{ZrO}_2$  obtained by microemulsion or controlled growth techniques. The bar indicates 10 nm.

Another example is the synthesis of zirconia colloids from alkoxides in the presence of methacrylic acid. In such systems particle diameters between 5 and 30 nm can be obtained, depending on the surface-modifier concentration. Methacrylic acid also can be used for surface modification; this type has been used for the polymerization of particles into organic polymers, and in these systems crystalline (monoclinic) zirconia particles can be obtained at  $120^\circ\text{C}$  [17].





### 9.3 Formation of Films and Bulk Materials

In previous sections, the basic principles for the fabrication of nanoscale systems have been considered. To exploit these properties for various applications, it is necessary to process them into solidified materials such as films, coatings, or bulk materials. As is well known from sol-gel techniques, film formation can be achieved by dip coating of substrates into sols and drying and firing them to give materials of suitable density. However, as indicated by Equation (9-1), the film thickness that can be obtained is restricted to layers between several hundred nanometers and  $1\ \mu\text{m}$  owing to the limited relaxation of the heavily agglomerated systems. It is very difficult to control porosity and crystallinity at the same time because, based on the rules of thermodynamics, crystallization of sol particles at the same time reduces the porosity substantially. This process strongly depends on the type of system, so, for example, titania tends to crystallize very easily, whereas  $\alpha$ -alumina is much more difficult to obtain by this process. For this reason, an alternative route, solving at least some of the described problems, would be to synthesize the nanoscale particles independently of the sol formation and to “arrange them” in the form of films with a controlled package density. For this reason, it is necessary to control the particle-particle interaction and to use the principle of surface modification to obtain the appropriate surface properties.

This can be shown with colloidal silica as an example, used in form of aqueous or alcoholic suspensions. While coatings prepared from these sols can only be obtained with thicknesses of about  $0.5\text{--}10\ \mu\text{m}$  by a one-step dip-coating process, the surface modification of aqueous suspensions of colloidal silica with alkyl- or aryl-substituted silanes leads to the formation of films of thicknesses up to  $10\ \mu\text{m}$ . These films can be densified to silica by a heat treatment to almost 100% density without crack formation. Before densification, the films can be embossed on optical gratings, which is useful for optical technologies, eg, for incouplers. The systems can be doped and coated with functional groups for sensor applications. In Figure 9-7 an example of the embossing of these layers is shown.

Figure 9-7 clearly demonstrates that the shape of the structure is maintained during the firing process, which is very unusual for glass-like systems. The surprising fact is that the densification to almost fully dense  $\text{SiO}_2$  takes place at temperatures as low as  $500\ ^\circ\text{C}$ . This means that  $\text{SiO}_2$  layers can be prepared on a variety of substrates at four different medium temperature ranges. Since  $T$  never approaches  $T_g$ , the shape of the grating is maintained precisely.

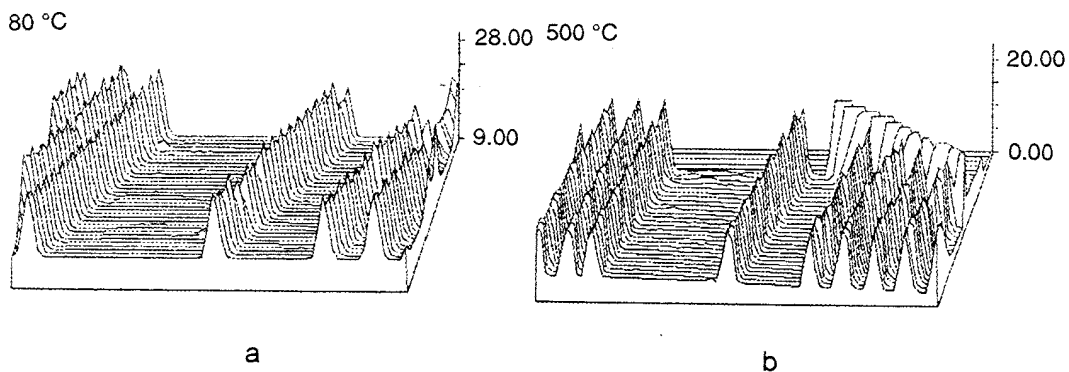
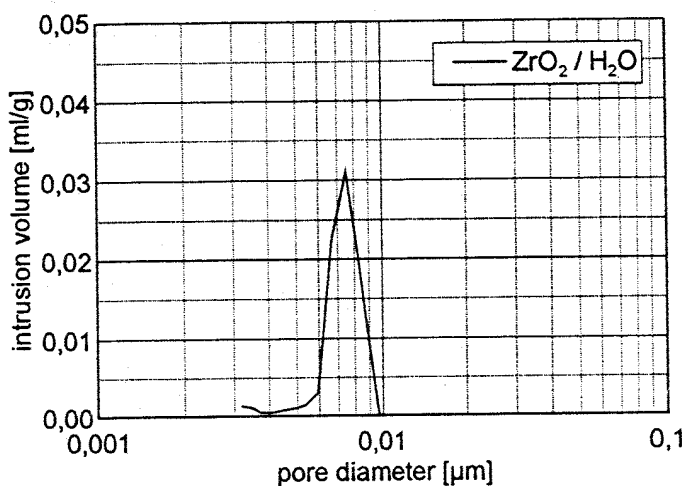


Figure 9-7. Comparison of an embossed  $\text{SiO}_2$  film (a) before heat treatment and (b) after  $500\ ^\circ\text{C}$  heat treatment (after [24]).

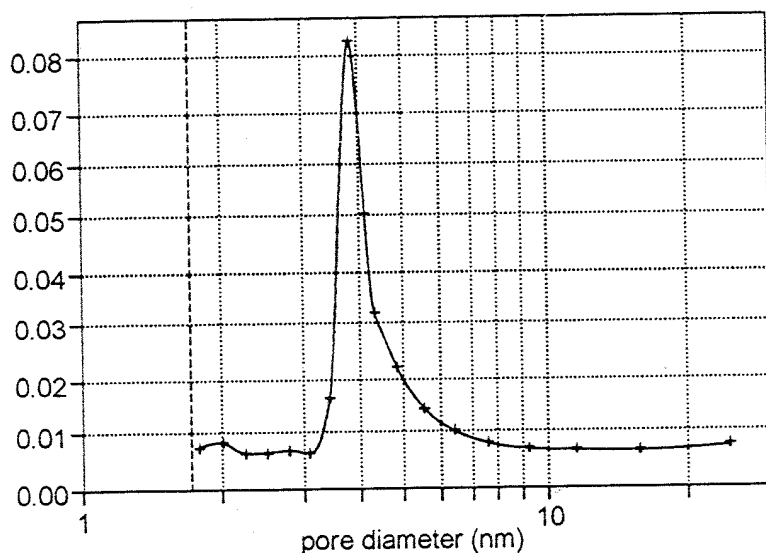
The porosity of films derived from particulate sols can be tailored by the particle size. In Figure 9-8 the pore size distribution of a zirconia green body with a particles size of about 50 nm is shown [25]. The zirconia is a commercially available product from Degussa with an average particle diameter of 50 nm, and the pore size is in the range 7–8 nm. The pore sizes that can be obtained depend strongly on the particle shape and the particle size distribution. If spherical monodispersed particles are present, the residual pore sizes are in the range of about one third of the particle diameter.



**Figure 9-8.**  
Pore size distribution of an extruded zirconia green body.

A very important finding with nanosized systems is that during sintering, the particle size does not increase, in general, except with densely packed nanostructured green bodies. That means that tailored pore sizes can be obtained as a function of particle diameter and temperature treatment, and further means that high specific surface areas are possible. Another example is ZnO films, derived from a controlled precipitation process from zinc acetate [26]. In Figure 9-9 the pore diameter of zinc oxide densified and crystallized at 200 °C in form of a transparent film is shown. In this case, the particle diameter is 20 nm and the pore sizes are also in the range of several nanometers.

X-ray patterns of the zinc oxide show that even with these small particle sizes, crystallization is well developed in the correct (modified wurzite) crystal structure.



**Figure 9-9.**  
Pore size distribution of ZnO film densified at 200 °C.

A prerequisite for all these types of nanotechnology is the surface modification as described above. In the case of zirconia, complex formers such as  $\beta$ -diketones have been used and for zinc oxide organic bases such as amines.

In another example,  $\alpha$ -alumina has been fabricated by a nanotechnology route [27, 28]. In this case, aluminium alkoxides were used and complexed with ethyl acetoacetate. The reaction is shown in Equation 9-4.



The particle size of these systems can be adjusted between 2 and 10 nm, depending on the type of  $\beta$ -diketone used. From these sols, films can be prepared by dip-coating, and these films are transformed into  $\alpha$ -alumina above 950 °C without forming any other alumina crystalline phases such as  $\gamma$ - or  $\theta$ - $\text{Al}_2\text{O}_3$ . If the sols are seeded by  $\alpha$ -nuclei, crystallization to  $\alpha$ -alumina starts at 800 °C. These films are completely transparent and show a high porosity at these temperatures. From high-resolution scanning electron micrographs, the particle size can be estimated and is between 10 and 20 nm.

In Figure 9-10 the crystallization behavior in unseeded gels as a function of temperature and in Figure 9-11 the pore size distribution are shown. Atomic force microscopy, however, shows additional pores in the range of about 50 nm, as shown in Figure 9-12 (the formation mechanism is not clear). It can be clearly seen that crystallization starts at 950 °C without any signs of phases other than  $\alpha$ -alumina. The pore size distribution is narrow and in the range of about 4 nm.

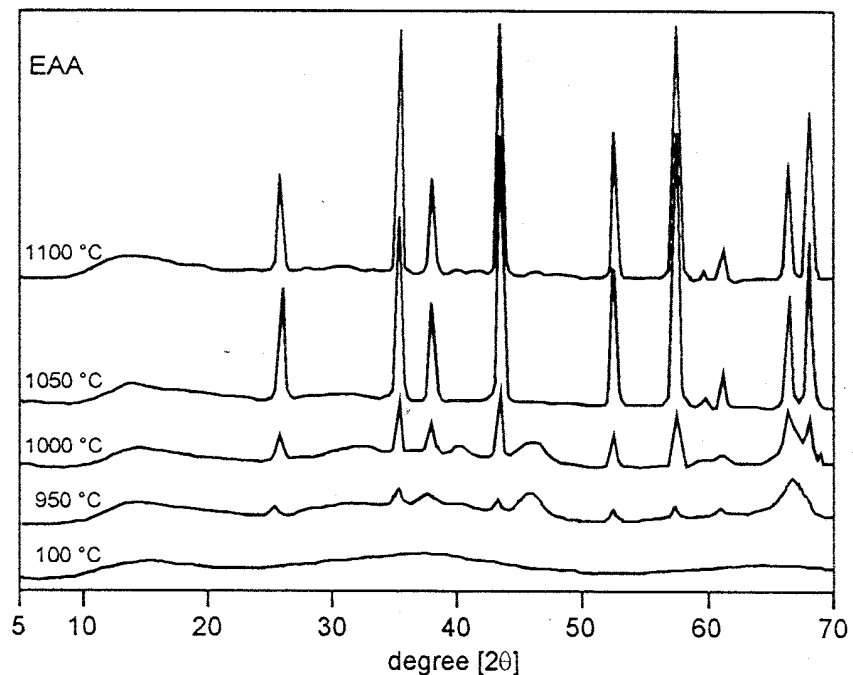
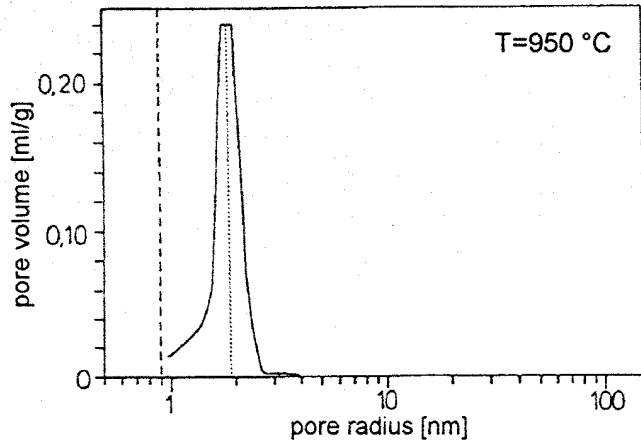
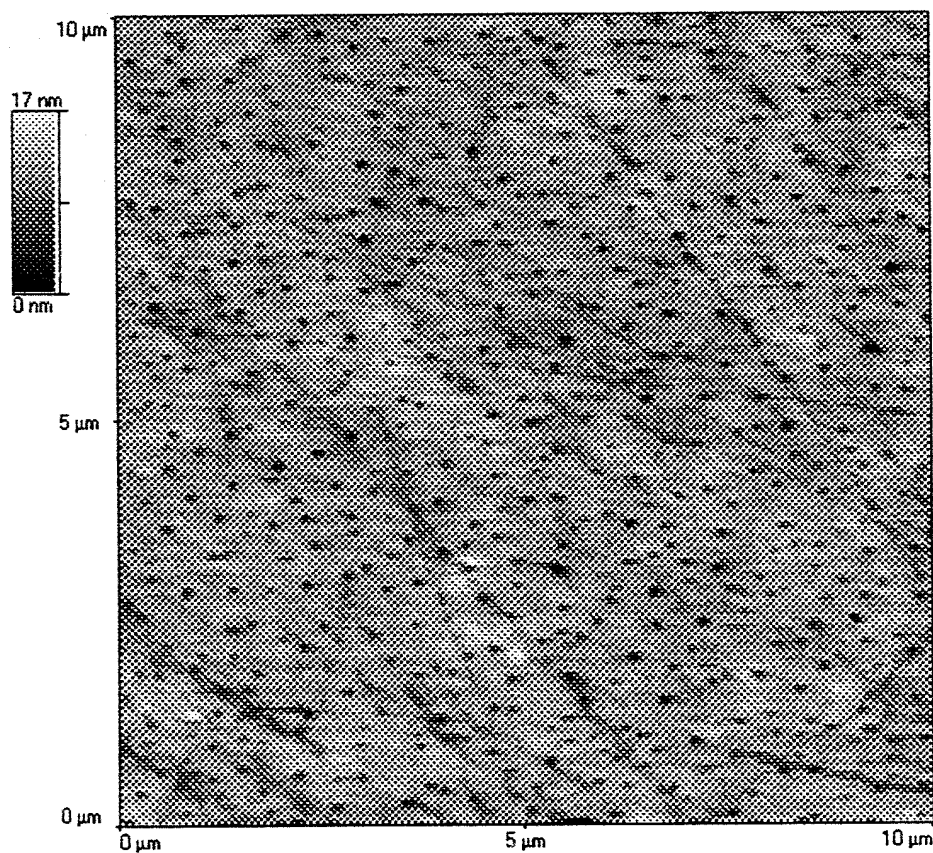


Figure 9-10. X-ray patterns of  $\alpha$ -alumina formation from ethyl acetoacetate-modified alumina sols.



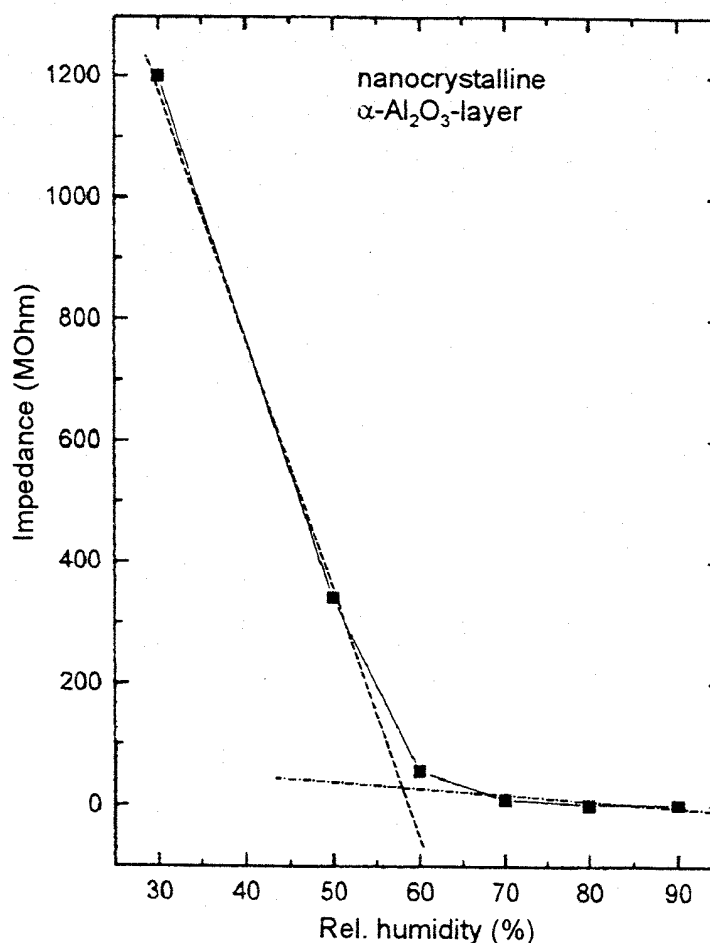
**Figure 9-11.** Pore size distribution of nanocrystalline  $\alpha$ - $\text{Al}_2\text{O}_3$ .



**Figure 9-12.** Atomic force micrograph of the  $\alpha$ - $\text{Al}_2\text{O}_3$  surface (transparent layer) of a layer treated at  $950^\circ\text{C}$ .

As in  $\gamma$ -alumina, in these  $\alpha$ -alumina films electrical conductivity has been measured as a function of the partial pressure of water vapor in the atmosphere. Films deposited on fused-silica substrates have been electrically contacted and tested for their sensor behavior for testing the dependence on water vapor pressure [29]. The results are shown in Figure 9-13.

As can be seen, there are two regimes with linear dependences of the water vapor pressure with respect to the impedance of the film. The phenomena to which this behavior can be attributed is not clear. One explanation could be that nanopores present in these films may be “filled” with increasing  $p_{\text{H}_2\text{O}}$  in the high-sensitivity regime. The experiments show that with nanoscale systems sensitivities with  $\alpha$ - $\text{Al}_2\text{O}_3$  are obtained otherwise only observed with



**Figure 9-13.**  
Impedance versus relative humidity plot for a nanocrystalline  $\alpha$ - $\text{Al}_2\text{O}_3$  layer (after [29]).

$\gamma$ - $\text{Al}_2\text{O}_3$ . It is expected that these  $\alpha$ -alumina films will show high long-term stability since  $\alpha$ -alumina is the stable phase. The system did not show any changes in properties after several years of storage. The significance of these results is that without using the nanotechnological approach,  $\alpha$ - $\text{Al}_2\text{O}_3$  is only obtained at temperatures above 1200 °C and, of even greater importance, with much larger particle sizes (sub- $\mu\text{m}$  or  $\mu\text{m}$  range). This type of system, however, does not show sufficient sensitivity owing to the small surface area.

Similar experiments have been carried out with tungsten oxide [29], and it could also be shown that a high sensitivity from surface conductivity as a function of water vapor pressure is possible with the nanostructured oxide. High sensitivity to water vapor pressure is only obtained when  $\text{WO}_3$  in nanoscale dimensions is present. The nanoscale phase is only present with heat treatment up to about 120 °C. In Figure 9-14 the surface of  $\text{WO}_3$  treated at 60 °C is shown.

The primary particle size was determined from the X-ray line width according to Scherrer's equation to be about 5 nm. With increasing crystallite size as a function of temperature, the sensitivity decreases, as shown in Figure 9-15 for an  $\text{Li}^+$ -doped system. At 500 °C the sensitivity is close to zero. By doping with  $\text{Li}^+$ , the sensitivity regime can be changed by three orders of magnitude. The layers have thicknesses of about 2–400 nm and are completely transparent. The dependence of impedance on water vapor pressure is shown in Figure 9-16.

The synthesis and processing of nanoscale systems using colloidal techniques including surface tailoring is a generalizable concept developed first of all for novel ceramic processing and for the preparation of optical nanocomposites. For this reason, it was necessary to prove that

nanoscale slurries can be processed to dense sintered bodies, which was not at all clear. The difficulties in conventional sol-gel processing are considerable. One of the most interesting results was recently obtained by Nass et al. [30] with nanoscale TiN. In these experiments several significant results were obtained. First, it was possible to disperse 30 nm diameter TiN prepared by chemical reaction (CVR) [3] to its genuine particle size by using a chelating surface modifier (guanidine propionate) and to prepare green bodies up to 60% by volume green density. It is assumed that the diamine grouping acts as strong chelating ligands for surface

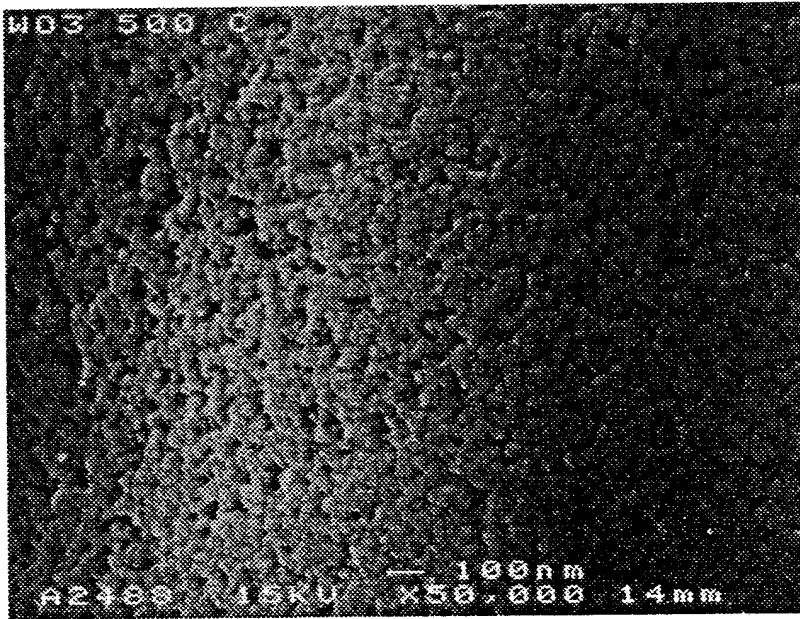


Figure 9-14. Surface of a transparent WO<sub>3</sub> layer treated at 60 °C.

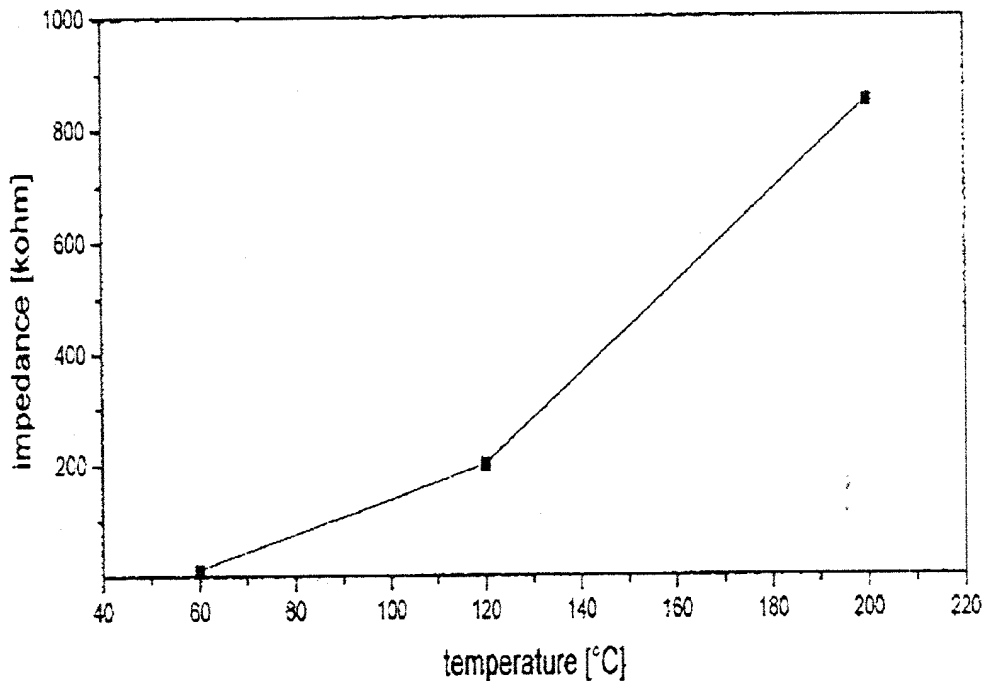


Figure 9-15. Decrease in sensitivity with temperature treatment (1 h at the indicated temperature) on a WO<sub>3</sub> layer on SiO<sub>2</sub> doped with 2.5 wt. % LiClO<sub>4</sub>.

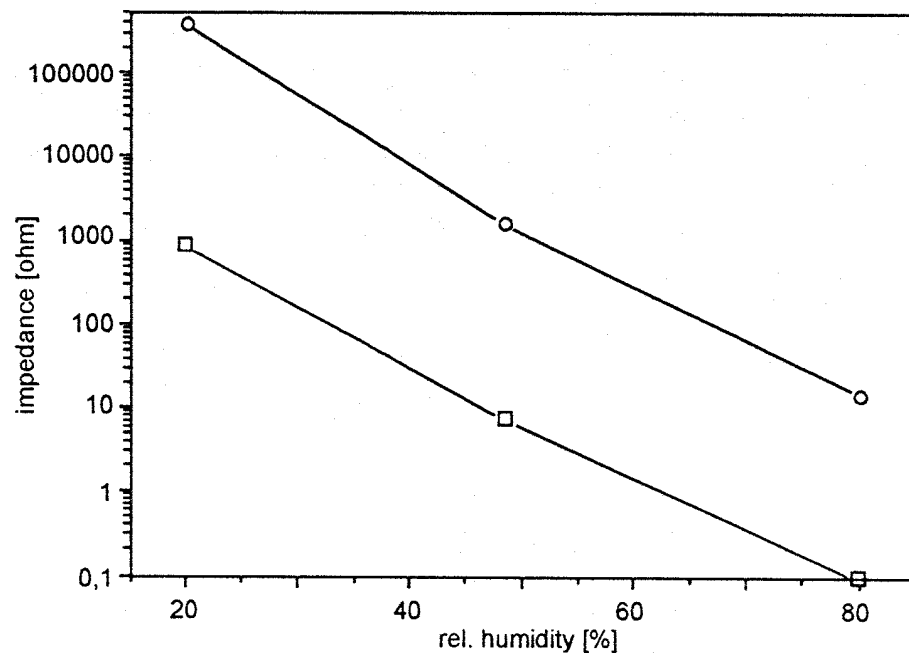


Figure 9-16.  $p_{\text{H}_2\text{O}}$  dependence of the sensitivity of (○) a doped and (□) an undoped  $\text{WO}_3$  layer on  $\text{SiO}_2$ .

$\text{Ti}^{4+}$  (oxidize layer). It is well known that conventional gels without surface modifiers do not show solid contents in this range (only up to 20% by volume) [31] with these high solid contents, and sintering temperatures of TiN films are as low as 1150 °C compared with >2000 °C with micrometer-scale technology. At this temperature no substantial grain growth is observed and the nanoscale structure is preserved. Further, it could be shown that TiN can be plastically deformed at 1150 °C by pressure. The fact that no grain growth takes place even at high temperatures shows that stable nanoscale phases can be obtained with an interesting potential for sensor application. Similar results with respect to lower sintering temperatures have been obtained with  $\text{ZrO}_2$  [32].

The concepts and the results obtained on the basis of these concepts show that by use of the chemical approach nano-scale systems can be prepared in a variety of systems, as already shown for ceramics, semiconductors [33], and metals. For processing them to solid materials, films, or coatings, very thorough control of the particle-particle interaction is necessary. Therefore, the surface of the colloids or nanoscale particles has to be modified with preferably small molecules attached to the surface by selected chemical bonds. This is a prerequisite for processing these systems to composites or ceramics whilst maintaining their nanostructured state.

As already mentioned above, the major advantage of nanotechnologies for film formation is the fact that tailored microstructures with well crystallized phases and a high specific surface area can be obtained, leading to both high stability and high sensitivity to all types of surface reactions.

Another type of nanosized structures with an interesting potential for sensors is related to the fact that with small particles dispersed in transparent matrices, optically transparent materials can be prepared if the particle size is below the Rayleigh scattering regime. Rayleigh scattering (also depending on the differences in the refractive indices between the particle and the matrix and the dielectric properties of the interface) depends on the particle diameter to the power of 3. This concept leads to a variety of interesting perspectives for optical sensors,

because solid-state properties of the inorganic phases in inorganic-organic composites can be used, and at the same time processing techniques typical for organic polymers can be employed. A variety of different solid-state properties of nanoscale particles are also of interest. These are passive properties such as refractive index and Abbé number to be used for property tailoring in coatings for optical sensors; chemical resistivity of organic polymers, eg, swelling in the presence of organic solvents, can be achieved by inorganic particle reinforcement. Quantum size effects are of interest in the quantum confinement regime of nanoscale semiconductor particles as well as plasmon resonance vibration in metals, and there are first results indicating that the optical properties can be changed by the type of ligands interfering with the particle surface.

Silver halide nanoscale particles dispersed in polymeric matrices show a photochromic behavior that can be established reversibly and irreversibly [34].

If these matrices are polymer-like, microengineering techniques can be employed, as shown by Schmidt [16]. In Figure 9-17, some optical properties obtained from nanocomposite materials are shown.

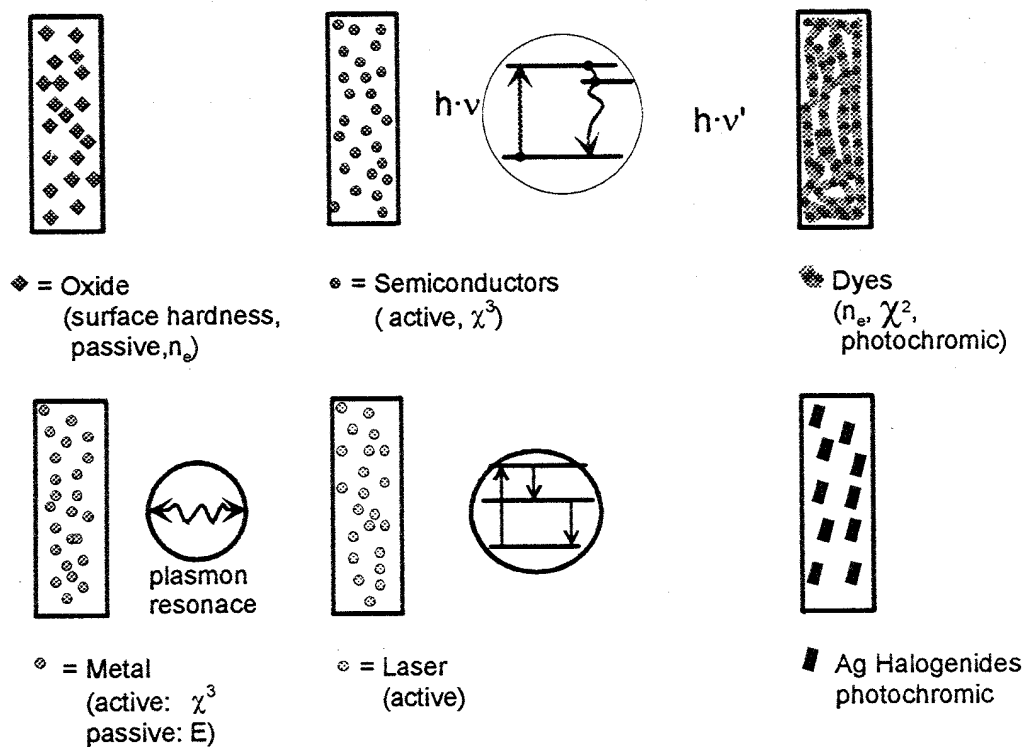


Figure 9-17. Some optical properties related to solid-state or electronic properties of small particles and/or molecules.

In combination with microengineering techniques such as embossing, photolithography, holographic techniques, or micropatterning by laser writing, components for optical sensors can be fabricated, and changes in structures of these particles should be applicable for sensors. Owing to their large interfaces, these systems should change optical properties by changing the interface in both the linear and nonlinear ranges. Figure 9-18 shows how these systems can be used for microengineering [35-37]. This is important for the fabrication of both optical components and sensing components.



Micropatterning techniques with inorganic-organic composite systems can also be used to fabricate pure inorganic systems after firing out the organic part.

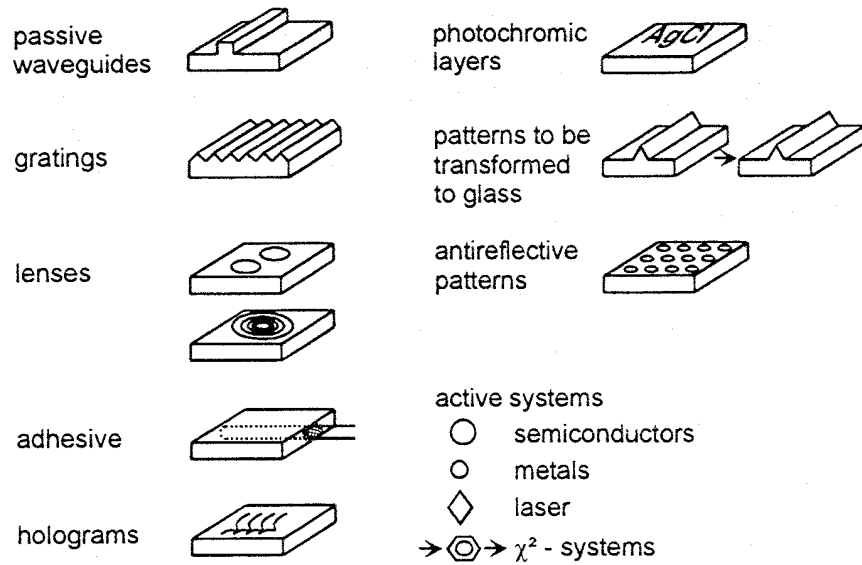


Figure 9-18. Possibilities for microengineering of different nanocomposite systems.

## 9.4 Potential for Sensors and Conclusion

The use of nanoscale systems has very interesting potential for sensor applications. First, as already shown with a few examples with nanostructured oxides, owing to the small particle size, thermodynamically stable systems can be used for sensor applications, which otherwise show a very low sensitivity. This basic principle can be extended to a variety of materials (for example, electroceramics) provided that nanoscale particulate systems are available. Availability is still the limiting step in the application of these systems. Processing to films or other devices may be difficult but can be solved by using the particle-particle interaction control approach. Chemical synthesis allows the generation of multicomponent systems, for example, using the microemulsion route, since the introduction of dopants is very convenient by using this technique. Another possibility to obtain nanoscale films and to establish dopants in the grain boundaries is to use infiltration techniques. The appropriate phases can then be obtained by an additional firing. Owing to the relatively low-temperature sintering techniques with nanoscale ceramics, a variety of systems otherwise very difficult to process owing to their high sintering temperatures should be accessible for building up sensor systems. So far, the potential of these techniques has not been exploited sufficiently.

Another interesting system is the nanocomposite system, since it unifies optical transparency, solid-state properties, and properties related to the small particle sizes (eg, quantum confinement in semiconductors or plasmon resonances in metals) with large surface or interfacial areas. These properties provide interesting opportunities for various types of sensors. Summarizing, nanostructured materials open up a wide range for novel sensor applications owing to their large interfacial areas and the possibility of changing their optical or electronic properties with molecules contacting their surfaces.

In conclusion, one can say that the use of nanoparticles for sensors has a very interesting potential, but is still in its infancy.

## 9.5 References

- [1] Gleiter, H., *Nanocrystalline Materials*; Oxford: Pergamon Press, 1989.
- [2] Trusov, L. I., Lapowok, V. N., Novikov, V. I., in: *Properties and Application of Disperse Powders*; Kiev, Naukova Dumka, 1986, p. 98.
- [3] Winter, H., König, T. H. C. Starck Co., personal communication.
- [3] Matijevic, E., in: *Ultrastructure Processing of Advanced Ceramics*, Mackenzie, J. D., Ulrich, D. R. (eds.); New York: Wiley, 1988, p. 429.
- [5] Stern, O., *Z. Electrochem.*, (1924) 508.
- [6] Lange, F., in: *Proc. International Symposium on Molecular Level Designing of Ceramics, Nagoya, March 1991*; Nagoya: NEDO International Joint Research Project, 1991, p. 14.
- [7] Nabarro, F. R., in: *Report of Conference on Strength of Solids*; London: Physical Society, 1948, p. 75.
- [8] Coble, R. L., *J. Appl. Phys.*, **34** (1963) 1679.
- [9] Schmidt, H., Nass, R., Aslan, M., Schmitt, K.-P., Benthien, T., Albayrak, S., *J. Phys. (Paris), Colloq. C7*, **3** (1993) 1251.
- [10] Benthien, K., *Master's Thesis*, University of Saarland, Saarbrücken, 1993.
- [11] Osseo-Asare, K., Arriagada, F. J., in: *Ceramic Transactions, Vol. 12, Ceramic Powder Science III*, Messing, G. L., Hirano, S., Hausner, H. (eds.); Westerville, OH: American Ceramic Society, 1990, p. 3.
- [12] Ramamurthi, S. D., Xu, Z., Payne, D. A., *J. Am. Ceram. Soc.*, **73** (1990) 2760.
- [13] Nass, R., Burgard, D., Schmidt, H., in: *Proceedings of the 2nd European Conference on Sol-Gel Technology*, Nass, R., Schmidt, H., Vilminot, S. (eds.); Amsterdam: North-Holland, 1992, p. 243.
- [14] Burgard, D., *Master's Thesis*, University of Saarland, Saarbrücken, 1992.
- [15] Burgard, D., Kropf, C., Nass, R., Schmidt, H., in: *Proceedings of 1994 MRS Spring Meeting, Symposium "Better Ceramics Through Chemistry IV", April 1994, San Francisco; Mat. Res. Soc. Symp. Proc.*, in press.
- [16] Schmidt, H., in: *Proceedings of NATO ARV on Applications of Organometallic Chemistry in the Preparation and Processing of Advanced Materials, Cap d'Agde, France, September 1994*, in press.
- [17] Schmidt, H., Kasemann, R., Burkhart, T., Wagner, G., Arpac, E., Geiter, E., in: *ACS Symposium Series on Hybrid Organic-Inorganic Composites*, Mark, J. E., Bianconi, P. A., Lee, C. Y.-C. (eds.); Washington, DC: American Chemical Society, in press.
- [18] Schmidt, H., *J. Sol-Gel Sci. Technol.*, **1** (1994) 217.
- [19] Spanhel, L., Arpac, E., Schmidt, H., *J. Non-Cryst. Solids*, **147-148** (1992) 657.
- [20] Mennig, M., Schmitt, M., Burkhart, T., Becker, U., Jung, G., Schmidt, H., in: *SPIE Proceedings 2288, "Sol-Gel Optics III, July 1994, San Diego*, Mackenzie, J. D. (ed.), (1994) 130.
- [21] Mennig, M., Schmitt, M., Kutsch, B., Schmidt, H., in: *SPIE Proceedings 2288 "Sol-Gel Optics III", July 1994, San Diego*, Mackenzie, J. D. (ed.), (1994) 120.
- [22] Burkhart, T., Mennig, M., Schmidt, H., Licciulli, A., in: *Proceedings of 1994 MRS Spring Meeting, Symposium "Better Ceramics Through Chemistry IV", April 1994, San Francisco; Mat. Res. Soc. Symp. Proc.*, in press.
- [23] Mennig, M., Schmidt, H., Fink-Straube, C., *SPIE Proc.*, **1590** (1991) 152.
- [24] Mennig, M., Krug, H., Fink-Straube, C., Oliveira, P. W., Schmidt, H., *SPIE Proc.* **1758** (1992) 387.
- [25] Nass, R., personal communication, to be published.
- [26] Nass, R., Fischer, R., personal communication, to be published.
- [27] Nass, R., Schmidt, H., in: *Ceramic Powder Processing Science*, Hausner, H., Messing, G. L., Hirano, S. (eds.); Cologne: Deutsche Keramische Gesellschaft, Köln, 1989, p. 69.
- [28] Schmidt, H., in: *Ceramic Transactions, Vol. 22: Ceramic Powder Science IV*, Hirano, S., Messing, G. L., Hausner, H. (eds.) Westerville, OH: American Ceramic Society, 1991, p. 3.
- [29] Schmidt, H., in: *Extended Abstracts, Euroensors VII, Budapest, September 1993*, Technical University of Budapest, p. 327.
- [30] Nass, R., Albayrak, S., Aslan, M., Schmidt, H., in: *Proceedings of the International Conference "Ceramic Processing Science and Technology", September 11-14, 1994, Friedrichshafen/Bodensee, Germany*, in press.

- [31] Brinker, C. J., Scherer, G. W., *Sol-Gel Science*; Boston: Academic Press, 1990.
- [32] Schmidt, H., Nass, R., in: *Proc. Austceram '94*, Sorrell, C. C., Ruys, A. J. (eds.); *Int. Ceramic Monographs*, Vol. 1, No. 2, Sydney: Australasian Ceramic Society, 1994, p. 1065.
- [33] Henglein, A., *Top. Curr. Chem.*, **143** (1988) 115.
- [34] Fink-Straube, C., *PhD Thesis*, University of Saarland, Saarbrücken, 1994.
- [35] Oliveira, P. W., Krug, H., Künstle, H., Schmidt, H., in: *SPIE Proceedings 2288*, "Sol-Gel Optics III", July 1994, San Diego, Mackenzie, J. D. (eds.), (1994) 554.
- [36] Schmidt, H., Krug, H., Kasemann, R., Tiefensee, F., *SPIE Proc.*, **1590** (1991) 36.
- [37] Krug, H., Zeitz, B., Oliveira, P. W., Schmidt, H., in: *Proceedings 8th CIMTEC Congress, June 1994, Florence, Italy*, in press.