

Water-based wet chemical synthesis of (doped) ZnO nanostructures

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Abstract Looking at its vast range of applications, nanostructured ZnO can be considered as a key technological material. Simple and ecological production techniques for this and other nanostructured materials can boost the detection of their unusual properties. In this context water-based wet chemical synthesis routes for nanostructured ZnO are explored in this study. The advantages and disadvantages of controlled double-jet precipitation, microemulsion preparation, hydrothermal synthesis and an aqueous solution-gel route are described for the formation of (doped) ZnO nanoparticles. The influence of the synthesis parameters on the particle size, size distribution and degree of agglomeration of the particles is reported. Thin films are prepared by chemical solution deposition from aqueous solution. The heat treatment profile and the precursor composition are seen to largely control the density, the grain size and the degree of preferential *c*-axis orientation.

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1. Introduction

ZnO has received broad attention in materials research, due to its outstanding versatile properties, ease of preparation and low cost. A vast range of applications make nanostructured ZnO a key technological material; e.g. it is used as a phosphor material, in varistors, in surface acoustic wave devices, in gas sensors, as transparent conducting oxide, as UV-absorber in sunscreens and recently as alternative for TiO₂ in dye-sensitized solar cells [1].

Wet chemical routes for the synthesis of nanostructures (materials with at least one dimension in the nanometer scale) are a valuable alternative to conventional processing and gas phase synthesis, with known commercial applications [2]. Water-based chemical methods offer numerous advantages like being environmentally benign, using cheap and easy to handle starting products and low cost, uncomplicated equipment, while requiring only a low energy input. Moreover they allow the easy tailoring of synthesis parameters throughout the whole process, which may be exploited to achieve a more precise control of composition, shape and size of the resulting material.

Since the synthesis route determines the later properties of the material, the preparation method chosen is a very important issue when designing ZnO for a specific application. For example, rests of metal salts used as reactants may remain on the particles interfering with e.g. the electrical properties; a more hydrophilic or hydrophobic surface can be created thus affecting the later options for solvent choice when dispersing the material, etc.

In this paper some results from our research group concerning the synthesis of ZnO nanoparticles and nanofilms from aqueous solution are reported.

2. Synthesis of ZnO nanoparticles

ZnO nanoparticles can be prepared in different ways from aqueous solution: hydrothermal [3–5], precipitation [5–7] and microemulsion [8] routes have been reported. Depending on the experimental conditions, these simple wet chemical routes result in ZnO nanoparticles in all kinds of morphologies from spherical to rodlike, ellipsoidal, etc. [3, 4, 7]. Apart from the size, other important issues are the particle size distribution and the degree of agglomeration. Monodispersed particles are required in most applications, while a prerequisite to utilize nanoparticles is that they can be deagglomerated to the greatest extent and remain stable in colloidal suspension.

In our group different water-based solution routes for the preparation of ZnO nanoparticles have been applied as exemplified in the next paragraphs.

2.1. Controlled double-jet precipitation (CDJP)

Methods able to produce monodispersed particles from solution are based on a good control over the kinetics of nucleation and growth. When a base is simply dropped in a metal salt solution, local inhomogeneities in pH value and concentration of base exist leading to the broadening of the size distribution of the precipitated particles. A narrow size distribution can be obtained by using e.g. “forced hydrolysis” or thermohydrolysis methods [5, 6] where a thermally unstable compound is introduced that decomposes on heating creating a basic environment, homogeneously throughout the solution. However, these forced hydrolysis methods can only be used for low concentrations and they require long processing times (several hours/days of aging). To generate larger quantities of uniform particles in shorter times, the controlled double-jet precipitation technique—originating from photographic industry—was recently employed [7].

The feasibility of an optimized CDJP route for the synthesis of ZnO nanoparticles at a relatively low temperature of 70°C was demonstrated in [9]. Starting from ZnCl₂ and NaOH aqueous solutions in a 1:2 molar ratio it is possible to form nanoparticles of pure ZnO when the reactants are added in a double-jet set-up with heating jacket at 70°C. However, the resulting 20–30 nm nanoparticles tend to agglomerate in ellipsoidal particles with sizes of a few 100 nm [9]. The degree of agglomeration of the nanoparticles can be reduced by optimizing the experimental set-up and/or by the addition (in the reactor or afterwards) of dispersants like trisodi-

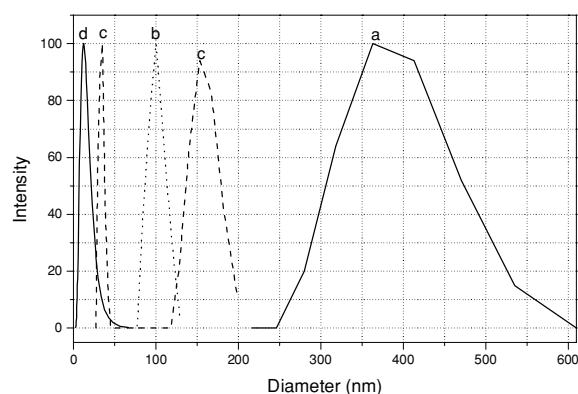


Fig. 1 PCS analysis of (a) ZnO particles precipitated in an optimized CDJP set-up at 70°C, (b) the same particles after addition of sodium phosphate or (c) sodium pyrophosphate; (d) ZnO particles in a microemulsion

um phosphate or sodium pyrophosphate, as demonstrated by the PCS (photon correlation spectroscopy) analysis shown in Fig. 1a–c.

2.2. Microemulsion synthesis

Another route to synthesize ZnO nanoparticles is by using water-in-oil microemulsions. In this way the reaction environment is restricted to the aqueous cores that function both as nanoreactors and as particle agglomeration barriers. The dimensions of the nanoreactors (and thus of the resulting nanoparticles) are very uniform and can be modulated in the range from a few nm to about 50 nm by various parameters, particularly the ratio [water]/[surfactant].

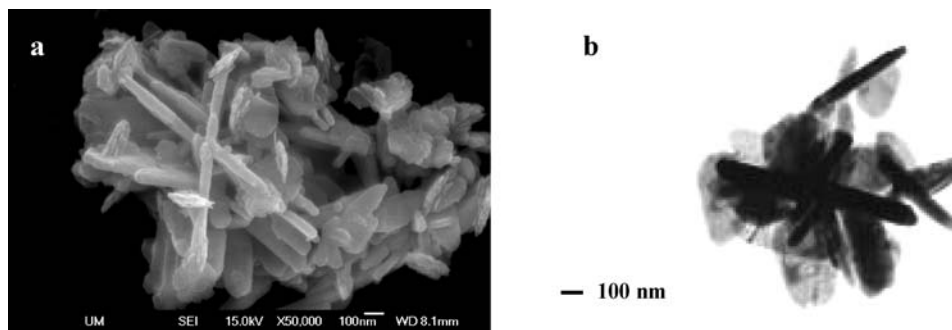
When an AOT (sodium bis (2-ethylhexyl) sulfosuccinate, 1.3 M)—heptane (25 ml)—ZnCl₂ (0.25 M) microemulsion is mixed with an AOT (1.3 M)—heptane (25 ml)—NaOH (0.50 M) microemulsion at 70°C, ZnO nanoparticles are formed in the aqueous cores of the microemulsion upon colliding of the nanodroplets. PCS analysis (Fig. 1d) of the microemulsion shows that the ZnO particles in the cores of the microemulsion are approximately 12 nm with a narrow size distribution. However, when the particles are recovered from the microemulsion by extraction with acetone, the particles agglomerate severely, unless a fraction of the surfactant remains on the particles. Again, deagglomerating dispersants are required to obtain a stable sol of the nanoparticles.

2.3. Hydrothermal synthesis

Hydrothermal methods are also frequently reported to produce ZnO nanoforms with various morphologies.

For example hydrothermal treatment of a washed precipitate of Zn(OH)₂—formed by mixing ZnCl₂ and NaOH solutions with molar ratio 1:2—in the presence of hexamethylenetetramine is seen (Fig. 2) to produce a mixture of

Fig. 2 SEM (a) and TEM (b) images of ZnO needles and plates prepared by hydrothermal treatment ($160^{\circ}\text{C} - 6\text{ h}$ in pressure bomb) of an aqueous dispersion of a $\text{Zn}(\text{OH})_2$ precipitate (obtained from mixing of 0.5 M ZnCl_2 and 1 M NaOH solution and washing) in the presence of 0.01 mol hexamethylenetetramine



needle- and platelike ZnO particles. The degree of agglomeration can be improved by ultrasonic treatment. To deagglomerate the particles it is also possible to add dispersants in the hydrothermal reactor (as long as they keep their structure during the hydrothermal treatment) or after the hydrothermal treatment. For example in Fig. 3 a hydrothermally treated $\text{Zn}(\text{OH})_2$ precipitate is seen to be deagglomerated by the addition of sodium pyrophosphate.

2.4. Aqueous solution-gel synthesis

Another synthesis route extensively studied in our group is a so-called aqueous solution-gel route, a special case of the more general sol-gel routes. The aqueous solution-gel route combines the advantages of economical and ecological benign solvents and metal salts with the more general advantage of sol-gel synthesis, i.e. the composition homogeneity of the end product [10]. The route has already proven its success for the production of various multimetal oxides [11–13]. The chelating ligands added completely prevent the hydrolysis and condensation of the metal ions. For, this hydrolysis and condensation are likely to occur in aqueous solution when high valent metal ions are present. After solvent evaporation a glasslike amorphous gel is aimed at, retaining the homogeneous molecular mix of the species in the solution. In the

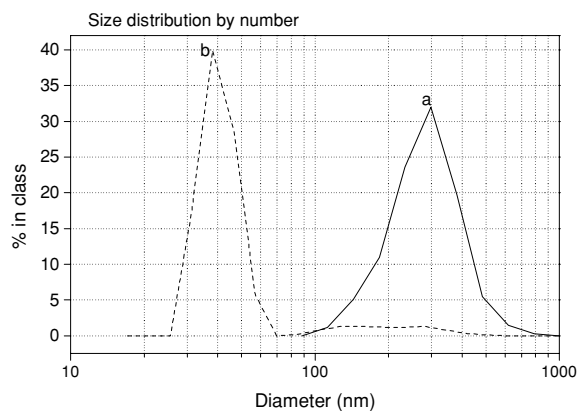


Fig. 3 PCS analysis of a hydrothermally ($200^{\circ}\text{C} - 30\text{ min}$) treated $\text{Zn}(\text{OH})_2$ precipitate – obtained by abrupt mixing of $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (0.5 M) and NH_3 (1 M) – without (a) and with (b) sodium pyrophosphate added afterwards as a dispersant

next step the homogeneous gel is calcined in order to obtain the desired oxide phase.

Besides being a successful method to synthesize homogeneous multimetal oxides, the aqueous solution-gel method has been applied to produce nanoparticles [14, 15]. In [15] doped ZnO nanoparticles have been prepared by this route. Starting from a solution of zinc acetate dihydrate, citric acid as the complexant and ammonia as the base (i.e. *precursor I*), a solid glassy gel is obtained that is calcined to a fine, crystalline ZnO nanopowder, as demonstrated in Fig. 4. The starting products are selected both based on their ability to form an amorphous gel and on the fact that they contain elements that can be easily removed during thermal treatment.

2.4.1. Importance of the monophasic character of the gel

Optimal gelation conditions imply a.o. the prevention of early precipitation. While, in case of multimetal oxide synthesis, precipitation during gelation must be avoided to prevent metal segregation from the homogeneous precursor solution, it is seen that, in case of nanopowder fabrication, the monophasic character of the amorphous precursor gel is required to ensure the monodispersity of the particles. When a too low ratio of citric acid: Zn is used (e.g. $0.66:1$), an amorphous precursor gel with very small ($<100\text{ nm}$ needle-like) particles in it is obtained [15]—as detected by

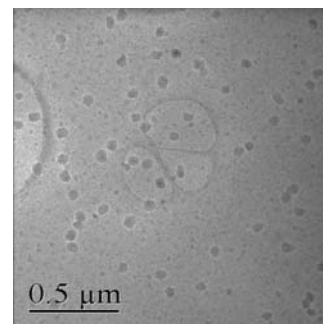


Fig. 4 Cryogenic TEM picture of an aqueous dispersion of ZnO prepared by the aqueous solution-gel method showing the individual crystals

cryogenic-TEM. Calcination of this gel leads to a product with nanoparticles but also larger submicron particles; a result of the existence of different species in the precursor gel, which decompose at different temperatures and show different growth kinetics. Only nanoparticles are obtained when an optimized citric acid: Zn ratio (i.e. 1:1) is used.

2.4.2. Heat treatment of the gel

In order to remove the citric acid—ammonia matrix the gel is calcined. From complementary analysis by HT-XRD (high temperature—X-ray diffraction), TGA (thermogravimetric analysis) and FTIR (IR spectroscopy) of the gel, it can be concluded that ZnO crystallizes as zincite below 400°C (when heated in dry air at 10°C/min), that is, before the gel matrix is completely decomposed (at 430°C when heated in dry air at 10°C/min) [15]. This information can be related to the structure of the gel. Indeed it is seen that Zn²⁺ is not only coordinated with the carboxylate groups, but also with the α -hydroxy group of the citrate. As soon as the α -hydroxy group decoordinates, Zn²⁺ can start to crystallize as the oxide. Moreover, it is assumed this α -hydroxy group is oxygen donating, since the oxide phase is even formed when the gel is heated in inert (but otherwise identical) conditions. However, in order to remove the rest of the organic matrix, further heating (to at least 430°C when heating in dry air at 10°C/min) is necessary.

2.4.3. Size control and morphology of the aqueous solution-gel prepared particles

The temperature at which the precursor is calcined determines the average particle size. When the precursor gel is heated up in dry air at 10°C/min including a 15 min. isothermal period at the calcination temperature, the average particle size (of more than 200 particles) as analyzed by TEM ranges from 23 nm at 430°C to 175 nm at 870°C. A linear relation between the logarithm of the particle size and the reciprocal (calcination) temperature enables one to tune the particle size to the desired value between these limits [15].

Since the particles are formed from a gellike structure that needs to decompose before and during the formation of the oxide particles, the calcination atmosphere has a profound influence on the final product. When the calcination is done in inert circumstances (N₂ – 500°C), the obtained particles are identical in size and phase. However, the product still contains remaining organic species, which cannot be removed oxidatively like in dry air. When the precursor gel is decomposed in pure oxygen, the sample heated at 430°C contains pure zincite phase. But in this case two different kinds of particles are found: particles comparable to dry air decomposition experiments with similar size, but also needlelike particles with width <100 nm and variable length (1D nanowires): see Fig. 5. Their formation is connected to the final decomposition step of the gel that occurs explosively in pure oxygen, reaching very high temperatures. Some of these nanowires are composed of individual nanoparticles as can be seen clearly in the TEM image in Fig. 5(a), while others appear as single crystals as proven by DF-TEM analysis.

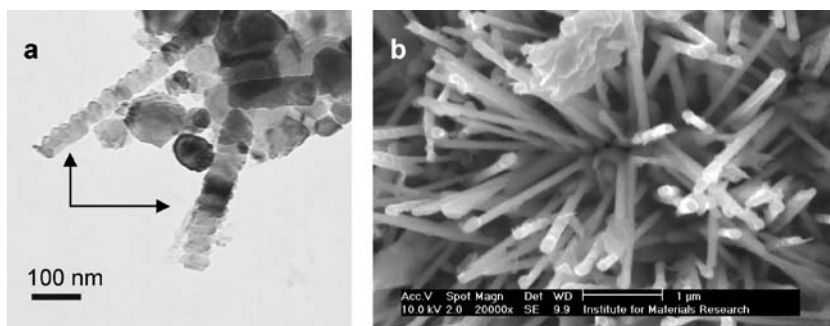
2.4.4. Al³⁺-doped ZnO nanoparticles by aqueous solution-gel synthesis

The aqueous solution-gel method is ideally suited to dope materials with even very small amounts of the dopant, since the dopant can simply be introduced in the aqueous precursor solution. The ZnO nanoparticles obtained from the aqueous solution-gel synthesis are doped with Al³⁺ to improve the conductivity properties. Al(NO₃)₃-citrate (in a 1:1 Al : citric acid molar ratio and pH adapted to 8.5 by ammonia) solutions were added to the Zn precursor. As expected, the size of the Al-doped ZnO particles decreased with increasing amounts of Al³⁺ (from 23 nm to 5 nm for 5% doping), as shown by Fig. 6.

2.5. Conclusion: ZnO nanoparticle synthesis by wet chemical routes

In conclusion it can be stated that several simple wet chemical routes can be applied for the synthesis of nanoparticles.

Fig. 5 TEM (a) and SEM (b) images of ZnO nanowires formed by calcination of the precursor in 100% O₂ atmosphere at 430°C



To obtain monodispersed particles, the kinetics of nucleation and growth should be controlled very well, as illustrated for the CDJP method. Another option is to limit the reaction environment to nanodimensions as done in the microemulsion method.

Although a thermal treatment is required in the solution-gel synthesis process, it is still possible to obtain nanoparticles. The calcination temperature can even be used to tailor the size of the nanoparticles. Also the aqueous solution-gel synthesis is very well suited to easily prepare doped materials with even very low dopant levels.

When a dispersion or sol of nanoparticles is required, colloidal deagglomeration methods have to be applied, creating a sterical or electrostatic repulsion force on the nanoparticles to counterforce their attraction. This can be done during the synthesis, by incorporating a dispersant in the synthesis route, or afterwards when the particles have already formed. In some cases no dispersant is required, e.g. when remaining ions from the reactants are adsorbed on the particles giving them a specific charge, high enough to provide electrostatic stabilization.

3. Synthesis of thin films

Thin films can be prepared in several ways by wet chemical methods. From solution it is possible to nucleate and grow the oxide on a substrate by hydrothermal [16] or sol-gel techniques, possibly in combination with chemical solution deposition (CSD) methods. While hydrothermal methods require only a low temperature, they are not generally applicable for the preparation of homogeneous multimetal oxides. The sol-gel method can guarantee the compositional homogeneity, however thermal treatments are required to remove the gel matrix and form the desired phase, which might be a problem for temperature sensitive substrates. For these temperature sensitive substrates a better option is to prepare the thin film by deposition of a dispersion of nanoparticles that are previously synthesized.

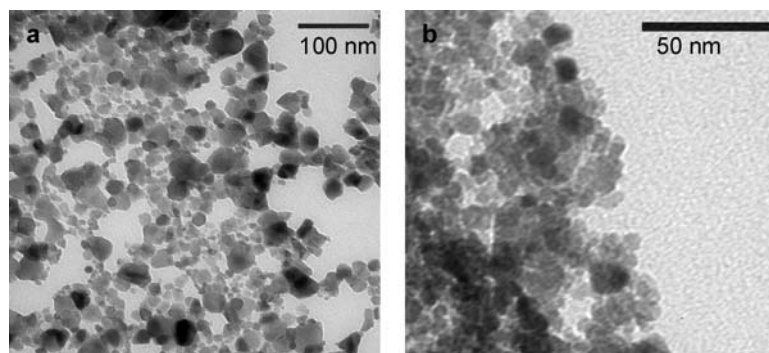
Chemical solution deposition by spincoating is usually carried out with alcoholic precursors. The general toxicity, moisture sensitivity and high cost of the starting products (usually alkoxides in organic solvents) however demand the use of aqueous solutions in an environmentally justified preparation method. Water-based methods for preparation of ZnO films by CSD are scarce in literature. The biggest obstacle for their development is most probably the poor affinity of the substrates for water. Instead of adding organic species to the aqueous solution to enhance the wetting, our approach is to increase the hydrophilicity of the substrate by a chemical cleaning procedure, described in [17].

3.1. Aqueous precursor solution for chemical solution deposition

The same aqueous precursor as mentioned in 2.4 (*precursor 1*) can also be used to deposit a thin film by chemical solution deposition (spincoating) on a cleaned Si/SiO₂ substrate, followed by a thermal treatment (annealing at 500°C) [18]. A smooth crystalline ZnO film with grains of about 20 nm and thickness of max. 20 nm is obtained. However, using this precursor it is not possible to do multiple depositions, since the first layer dissolves again when the second is deposited, due to the amphoteric character of ZnO. Therefore a new precursor with a neutral pH value is developed (*precursor 2*) [19] starting from ZnO instead of zinc acetate and using ethylenediamine as a base, which also serves as viscosity regulator. Thermal analysis of precursor 2 after gelation shows that the final decomposition temperature amounts to about 500°C and that in contrast with precursor 1, ZnO does not crystallize before the gel is completely decomposed. After spincoating of the aqueous precursor on cleaned glass or Si/SiO₂ substrates and after thermal treatment, involving a drying and preheating step of the individual layers and a final annealing step, a crystalline ZnO film with grains of 20–50 nm can be prepared from this precursor; see Fig. 7.

It is possible to regulate the oxide film thickness by changing the concentration of the precursor (from 6 to 55 nm for

Fig. 6 BF-TEM images of 0.5% (a) and 5% (b) Al³⁺-doped ZnO nanoparticles showing the decrease in particle size with increasing dopant level



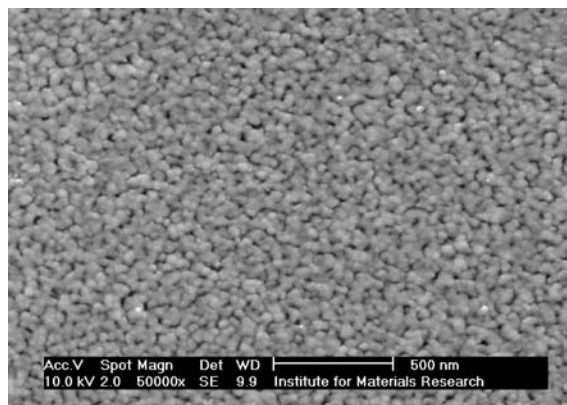


Fig. 7 SEM SE image of 4 layers of ZnO prepared by spincoating (3000 rpm, 30'') the aqueous precursor 2 (1 M), followed by a drying step (300°C, 45'') and a preheating step (550°C, 5') of the individual layers and a final annealing step (550°C, 60')

0.37 and 1.0 M) and by performing multiple depositions. The preheating of the individual layers after each deposition is a prerequisite to be able to do multiple depositions.

The features of the ZnO films are largely influenced by the preparation conditions, as will be demonstrated in the next sections.

3.2. Density and grain size of the ZnO film obtained from deposition of the aqueous precursor

Since the film is formed by decomposition of a gel precursor consisting of Zn species surrounded by an (organic) matrix, a lot of gases are released during the thermal treatment and the density of the films is influenced by the heat treatment. To gain dense films the preheating of the individual layers should be done at a temperature close to the final decomposition temperature of the precursor (around 500–550°C). In this way the matrix is removed completely after each deposition and slowly enough not to introduce too much pores in the film [19].

The grain size of the ZnO particles is also largely influenced by the thermal treatment. The grain size is smallest with preheating and final annealing temperatures around the

decomposition temperature of the precursor, i.e. when “mild” crystallization conditions apply. An increase of the preheating or annealing temperatures to values around 600°C and higher brings about a large increase of the grain size [19]. Since the small grains are seen to be incorporated in the larger grains, these higher preheating and/or annealing temperatures also imply that more porosity is present in the film.

3.3. Orientation of the ZnO film deposited from aqueous precursor

The orientation of a film is determined mostly by the substrate used (lattice matching) and the applied deposition technique and temperature. For the multilayer ZnO thin films deposited on a Si/SiO₂ substrate a preferential *c*-axis orientation is observed [19]. The degree of preferential *c*-axis orientation is influenced by the applied thermal treatment profile. For example, the degree of preferential *c*-axis orientation is higher when crystallizing the individual layers at preheating temperatures higher than the final decomposition temperature of the precursor ($\geq 500^\circ\text{C}$). This can be explained by again considering the gas development during the final annealing step, which is much less in case the preheating temperatures are higher than the precursor decomposition temperature, leading to less disturbance of the film during the later annealing step.

Also the annealing process has a large influence: it is observed that the degree of preferential *c*-axis orientation increases when higher annealing temperatures or longer annealing times are used. However, as shown higher, these conditions also imply larger grains and pores in the film, which is not always desired.

Next to the thermal treatment the individual layer thickness is seen to be the principal parameter influencing the degree of preferential *c*-axis. When the individual layer thickness is varied by using precursors with different [Zn²⁺] concentrations (while the total gel film thickness is equal upon deposition), it is observed that the degree of preferential *c*-axis orientation increases significantly when the individual layer thickness decreases. This can be

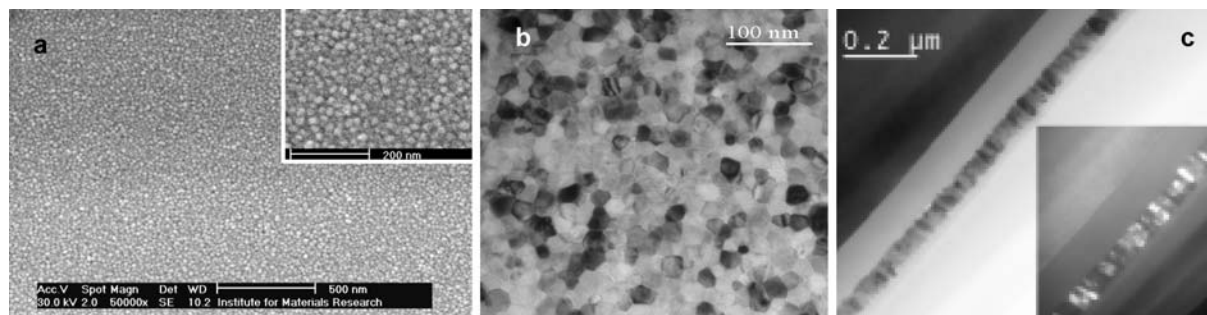


Fig. 8 ZnO film prepared from deposition by spincoating (3000 rpm, 30'') of 27 layers of precursor 3 (0.1 M), dried (300°C, 45''), preheated (450°C, 90'') and annealed (500°C, 60'')

visualized in TEM pictures of cross-section samples of the films [19]: a film of 21 layers of 5 nm consists of more or less columnar grains pointing throughout the film, while a film formed by depositing 2 layers of 50 nm consists of many small crystals (polycrystalline film) and no columnar grains.

Even thinner films would possibly lead to a higher preferential orientation, however the reactivity of the precursor solution towards the underlying calcined layers is still too high to allow thinner layers to be deposited. To decrease the reactivity, the precursor 2 (mentioned in 3.1) was modified by addition of extra ZnO, so that the solution is completely saturated in Zn^{2+} , the precursor is unreactive and thinner individual layers can be deposited [20]. The thermal analysis of this *precursor 3* shows a lower organic content than precursor 2, implying less gas development when the film is thermally treated, and a lower final decomposition temperature: 440°C vs. 500°C. All these differences can be related to the properties of the ZnO films obtained. SEM (Fig. 8a) and TEM (Fig. 8b) analyses show a very uniform and dense film with low grain size (20–25 nm). In TEM images of a cross section (Fig. 8c) of a film columnar crystals are seen, and indeed XRD analysis shows a very high degree of *c*-axis orientation.

3.4. Al^{3+} -doped ZnO films synthesized by deposition from aqueous solution

These Al-doped ZnO films are used for applications as transparent conductive oxide (TCO). To dope the oxide with different concentrations of Al, a separate Al-citrate precursor is used. The films show a minimal resistivity of $\sim 5 \times 10^{-3} \Omega \text{ cm}$ for the films doped with the lowest amount of Al^{3+} (0.5%) [20]. This is comparable to other literature values. Transmission spectra between 200 and 1000 nm show that a film of 300 nm (20 layers) allows the transmission of about 90% of the light, which can be considered as highly transparent.

3.5. Conclusion: ZnO thin films prepared by deposition from aqueous solution

Although water-based methods for the deposition of ZnO films are rarely observed in literature, it is possible to prepare a ZnO film from a purely aqueous solution. The same precursor as for the preparation of ZnO nanoparticles can be used for this purpose, however for multilayer deposition a precursor with a more neutral pH value and an intermediate preheating are required. The density and grain size of the film can be adapted by varying the thermal treatment profile, i.e. by regulating the gas development arising from the decomposition of the gel matrix. The films show a preferential *c*-axis

orientation that can be increased by varying the thermal treatment profile, the individual layer thickness or the precursor composition. Also Al^{3+} -doped ZnO films were prepared that offer both a good conductivity and a transparency of >90%.

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