

# Influence of polyvinyl pyrrolidone on the formation and properties of ZnO thin films in chemical bath deposition

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## Abstract

Thin films consisting of ZnO nanoparticles were prepared by solvolysis from solutions of zinc acetate, polyvinyl pyrrolidone (PVP) and sodium hydroxide in 2-propanol at temperatures of 328 K. Uniform, photoluminescent films with homogeneous surface coverage were obtained on silicon wafers modified with SO<sub>3</sub>-H terminated self-assembled monolayers (SAMs). High resolution transmission electron micrographs and the corresponding electron diffraction patterns in combination with X-ray Photoelectron Spectroscopy revealed that nanocrystalline wurtzite-type ZnO is present in the films.

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## 1. Introduction

For the deposition of ceramic thin films from aqueous solutions a variety of reaction procedures were developed in the last years, such as Chemical Bath Deposition (CBD), which refers to the thermohydrolysis (or “forced hydrolysis”) of metal salts for the fabrication of oxidic films [1,2]. The work concerning the deposition of ZnO was recently summarized [3]. A number of variations in the reaction solutions were investigated, however, the formation of ZnO thin films via these techniques encounter the same difficulties, i.e. these films often consist of micrometer-sized crystals. Therefore careful control of the reaction conditions is necessary to ensure acceptable adherence and surface roughness [3,4]. Further problems arise, when lateral nano-

structuring of such films must be achieved [5]. Other attempts to control the morphology of ZnO thin films investigated the influence of the substrate. Self-assembled monolayers (SAMs) with various functionalities and chain lengths were employed. Yet only the above-mentioned typical micrometer-sized hexagonal columns were synthesized [4,6].

A possible alternate approach to make the CBD process more applicable could be the employment of growth controlling additives, which are already widely applied in the synthesis of ZnO powders [7]. Of particular interest are soluble polymers, which are known to inhibit the growth of distinct planes of zincite crystals and are able to stabilize spherical nanoparticles [8]. Therefore anionic graft-copolymers based on polyacrylic acid were used to grow uniform ZnO/polymer films, which consisted of nanosized particles showing no anisotropic crystal growth [9–11]. Anionic surface coverage, however, drastically reduces the photoluminescence of ZnO colloids [12].

Polyvinyl pyrrolidone (PVP) [13] and polyethylene glycol (PEG) [14] are additives that were employed for the preparation of diluted suspensions of spherical and rod-

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like ZnO nanoparticles in 2-propanol. Interestingly PVP-capped ZnO nanoparticles (ZnO/PVP) even show enhanced photoluminescence in comparison to ZnO particles without organic modification grown under the same conditions [11]. The work presented here describes the preparation and characterization of ZnO thin films synthesized by the solvolysis of zinc salts in the presence of PVP.

## 2. Experimental

### 2.1. Substrate preparation

Silicon slides of  $10 \times 10$  mm were cleaned and oxidized in piranha solution (70 vol.% conc.  $\text{H}_2\text{SO}_4$  and 30 vol.% of 30 wt.%  $\text{H}_2\text{O}_2$ ) and washed abundantly with distilled water afterwards. The silicon substrates were then dipped into a solution of bicyclohexyl containing 1 vol.% of trichlorosilylhexadecane thioacetate under inert atmosphere. To convert the thioacetate into a sulfonate functionality, the wafers were immersed in a suspension of potassium hydrogenmopersulfate (the procedure was published in detail [15]).

### 2.2. Film deposition

0.110 g (0.5 mmol)  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  was dissolved in 20 mL of 2-propanol containing 0.6% distilled water under vigorous stirring at 328 K. The solution was diluted to a total volume of 40 ml, followed by chilling to 273 K. 3.0 g (0.3 mmol) PVP (Aldrich K15,  $M_w \sim 10,000$ ) was added and dissolved at room temperature with the help of ultrasound. Finally 8 mL of a solution of 0.11 M NaOH in 2-propanol containing 3.3% distilled water (pellets of sodium hydroxide were dissolved firstly in water, then 2-propanol was added at 328 K) were added dropwise under continuous stirring by using a peristaltic pump. Afterwards the solution was placed in an ultrasonic bath for 10 min.

The sulfonate functionalized substrates were immersed in 10 ml aliquots of the deposition solution, covered and then placed in an oil bath at 328 K. The solution was exchanged every 1.5 h. Total deposition times were 4.5 h. Finally, the samples were washed with distilled water, dried in a stream of dry argon.

Although the adherence was not quantified, it should be noted that the films can be subjected to a standard preparation for TEM cross-section micrographs. Further a simple tape-peel test with commercial adhesive tape and ultrasonication in water could not remove the films.

### 2.3. Film characterization

**TEM:** Transmission electron microscope (TEM) images of the ZnO films were obtained by using a JEM 4000FX microscope (acceleration voltage 400 kV). Cross-sectional specimens used for TEM examination were prepared

according to the method by Strecker et al. [16]. **SEM:** The obtained ZnO films were characterized by scanning electron microscopy (SEM) (JSM-6300F at 3 kV). The film thickness was measured by the cross-section image of SEM and the structure properties of the films. **PL:** Photoluminescence (PL) spectra were collected with an excitation wavelength of 326 nm at room temperature using a FluoroMax-3 spectrofluorometer (Jobin-Yvon). Appropriate filters were installed in the excitation light path to avoid stray light (interference filter, maximum aperture at 326 nm) and in the emission light path (long-wave pass, 340 nm for 350–410 nm and 370 nm for 372–724 nm range, respectively) to avoid second-order contributions. **XPS:** X-ray Photoelectron Spectra (XPS) were recorded using a Thermo VG Thetaprobe system employing monochromatic incident Al  $K\alpha$  radiation ( $h\nu = 1486.68$  eV; spot size 400  $\mu\text{m}$ ). Energy calibration, removal of contaminations and charge compensation during the measurements was carried out according to established procedures [17]. Detailed spectra of the Zn 2p spin-orbit doublet and the O 1s and C 1s photoelectrons lines were measured with a pass-energy of 100 eV and a step size of 0.1 eV. Charge correction of the BE scale of the Shirley-background-corrected XPS spectra was performed by referencing the resolved C 1s main peak to the corresponding value for adventitious carbon of 284.8 eV.

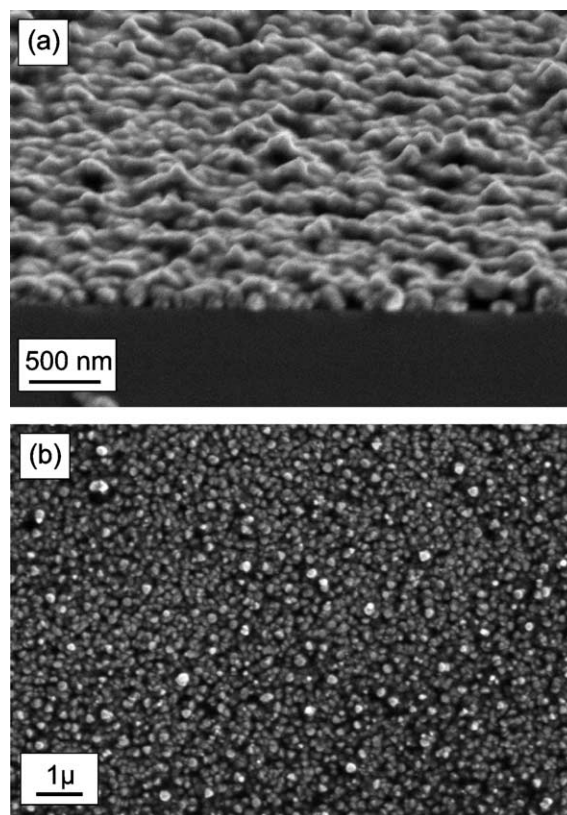


Fig. 1. SEM micrographs of films deposited on  $\text{SO}_3\text{H}$ -functionalized silicon wafers: (a) cross section and (b) top view.

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