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Growth of thin ZnO films from aqueous solutions in the presence of PMAA-graft-PEO copolymers

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Abstract

The deposition of homogeneous and adherent ZnO films on Si wafers by thermohydrolysis of zinc salts in aqueous solution is reported. Using a graft copolymer (polymethacrylic acid partially grafted with polyethyleneoxide side chains) homogeneous films of nanosized particles on Si wafers with self-assembled monolayers (SAMs) were obtained. The addition of the polyelectrolyte is necessary to suppress the formation of undesired, larger zincite crystals, which form inevitably otherwise. Films grown at different growth rates were characterized by atomic force microscopy (AFM) and scanning electron microscopy (SEM). Films that were obtained at high growth rates exhibit canyon-like morphology, whereas low growth rates yield uniform films with low surface roughness. According to X-ray Photoelectron Spectroscopy (XPS) a part of the polymer remains attached to the precipitated particles and can be removed by pyrolysis at about 723 K.

Keywords: Electron microscopy; Spectroscopy; Thin films; ZnO

1. Introduction

The deposition of ceramic thin films from aqueous solution at low temperatures is an emerging field of research. Thermohydrolysis (or “forced hydrolysis”) of soluble metal compounds is a variation of Chemical Bath Deposition (CBD),[1] which is suitable for the synthesis of metal oxide thin films. More “bioinspired” routes use substrates which are modified with organic compounds, so-called self-assembled monolayers (SAMs), that can improve the film deposition.[1,2]

The deposition of ZnO by CBD (static or liquid flow) however encounters several difficulties. Films of ZnO grown by thermohydrolytic reactions on silica glass or mica consist mainly of agglomerations of larger micron-sized crystals, therefore they exhibit a rather high surface roughness and their adherence is difficult to control.[3,4]

A possible solution might be the employment of polymers, which inhibit the growth of the zincite crystals and are able to stabilize spherical nanoparticles.

Block copolymers like polyethylene oxide-block-polymethacrylic acid (PEO-block-PMAA) were introduced by Wegner an co-workers to control the morphology of ZnO in bulk precipitation.[5,6]

Homopolymers like polyvinylpyrrolidone have also been used for growth modifcation.[7,8] PEO-block-PMAA copolymers have the advantage that the length of both the PEO and the PMAA moiety can be adjusted, which serves to control the influence of the polymer on the growth of the ZnO.

Recently, we reported an improved route for the formation of ZnO thin films by CBD. Adherent Films of nanosized particles on Si wafers were formed by addition of polymethacrylic acid grafted with polyethylene oxide side chains, $P(MAA_{0.66}\text{-co-}(MAA\text{-}EO_{20})_{0.33})_{70}$.[9]

In the present paper we provide a description of the growth mechanism and the effect of the growth rate on the film morphology.

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2. Experimental

2.1. Film deposition

Surface functionalization was achieved by dipping hydroxylated silicon p-type {001} wafers into a 4 mM solution of freshly distilled γ-mercaptopropyltrimethoxysilane in dry toluene under argon atmosphere. Such samples are denoted here as 'SAM coated', although no densely packed and highly ordered SAMs are obtained by the use of such short-chain hydrocarbons.

It was found, that higher concentrations of the surfactant or the use of undried or even protic solvents, such as ethanol, lead to the deposition of witish stains on the silicon wafers, which presumably consist of oligomeric silanes.[10] No uniform formation of ZnO films was observed on such stained wafers.

In this paper two compositions of deposition solutions will be discussed, which contain the same amount of zinc salts and copolymer, poly[methacrylic acid-co-(methacrylic acid-graft-polyethylene oxide)] $\mathrm{P(MAA_{0.50}\text{-}co\text{-}(MAA\text{-}EO_{20})_{0.50})_{70}}$ ($M_n = 20.000\ \mathrm{g\cdot mol^{-1}}$), but differ in the amount of hexamethylenetetramine (HMTA) added.

These will be denoted here as *ZnO-h* (80 mM $\mathrm{ZnCl_2\cdot 6\,H_2O}$, 20 mM $\mathrm{Zn(CH_3COO)_2\cdot 2\,H_2O}$, 4000 ppm copolymer and 2.5 mM HMTA) and *ZnO-l* (80 mM $\mathrm{ZnCl_2\cdot 6\,H_2O}$, 20 mM $\mathrm{Zn(CH_3COO)_2\cdot 2\,H_2O}$, 4000 ppm copolymer and 2.0 mM HMTA).

The components were mixed according to the sequence published earlier.[9]

The substrates were immersed in 10 ml aliquots of the deposition solution, covered and placed in an oil bath at 353 K. The solution was exchanged every 1.5 h. Total deposition times were 4.5–7.5 h. For the composition *ZnO-h*, the starting pH was 6.3 and then 6.5–6.6 after the deposition, whereas for *ZnO-l* the pH started at 6.2 and was 6.4–6.5 afterwards.

Annealed samples were obtained by heating at 723 K for 30 min in air (heating rate 10 K/h, cooling rate 40 K/h).

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

2.2. Film characterization

XPS: VGA ThetaProbe instrument using Mg K_α source (1253.6 eV). The energy scale was calibrated for the maximum intensity of the Ag $3d_{5/2}$ peak of pure silver at 368. 25 eV. Multi-region spectra were recorded at 37° take-off angle and 53° detection angle relative to the surface normal. The carbon peak at 285 eV was used as a reference to correct for charging effects.

Atomic force microscopy: Digital Instruments Nanoscope III applying tapping mode with silicon cantilevers. Scanning electron microscopy: Zeiss DSM 982 Gemini at 1.7 kV.

The thickness of the films was determined by carefully scratching the film with a sharp needle and measuring the depth of the scratch at five locations by means of AFM. The estimated error for the thickness is below 5%.[11]

3. Results and discussion

Thermohydrolytic reactions can be speeded up by the addition of base generating agents like HMTA. Thus, the only purpose of HMTA in this work is to increase slowly the pH of the reaction solution. No influence of HMTA on the morphology of ZnO crystals was observed in bulk precipitation experiments under comparable conditions.[3,6,9]

Adherent films were obtained from solutions of *ZnO-h* as well as from *ZnO-l*. As expected, the addition of the higher amount of HMTA in *ZnO-h* leads to higher growth rates (Fig. 1). Growth rates with *ZnO-h* are about 20 nm/h and almost constant after 3 h. Films from *ZnO-l* grow much slower. The growth rate increases steadily and reaches about 7 nm/h after 7.5 h. ("Growth rate" as discussed here means simply the ratio of film thickness and deposition time.)

At even lower concentrations of HMTA than in *ZnO-l*, no significant film formation was observed (<10 nm after 7.5 h). If higher concentrations of HMTA than in *ZnO-h* were employed, the reaction solution rapidly turned turbid and only deposits of loosely adherent, withish flakes were obtained, i.e. no film of nanoscale particles is formed in this case.

These observations indicate that the degree of supersaturation of the reaction solution must be carefully

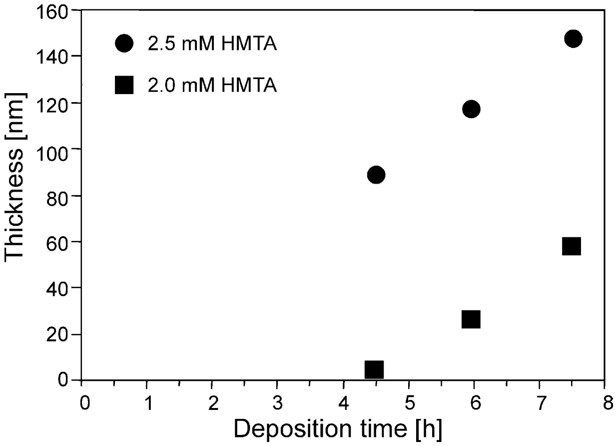


Fig. 1. Comparison of the achieved thickness from solutions containing 100 mM [Zn], 4000 ppm copolymer in addition to 2.5 mM HMTA—*ZnO-h* (circles) or 2 mM HMTA—*ZnO-l* (squares).

controlled in order to achieve an optimal film growth. Too low supersaturation leads to no significant film growth. Whereas at levels of too high supersaturation bulk precipitation will occur in the solution. The presence of the particles in the solution will then inhibit the film growth. On the substrate only sedimentation can be observed.

The investigations presented here, also show a drastic effect of the growth rate on the film morphology.

Although the starting solutions *ZnO-h* and *ZnO-l* differ only slightly in the amount of HMTA, the resulting films exhibit very different morphologies. Films grown from *ZnO-h* exibit canyon-like features (Figs. 2a and 3a). The voids are regularly distributed over the whole surface. The depth varies, whereby the deepest voids are in the order of the film thickness. The film shown in Fig. 2a has a thickness of 153 nm after 7.5 h and a roughness (RMS) of 26.28 nm.

In contrast films from *ZnO-l* do not show the above-mentioned voids (Figs. 2b and 3b). The films are uniform and have a comparably low surface roughness. The film presented in Fig. 2b has a thickness of 57 nm after 7.5 h and a RMS value of 4.18 nm.

XPS spectra of as-deposited and calcined samples from *ZnO-h* were recorded to determine the chemical composition of the films. Since peaks from the silicon wafer were visible in the survey spectra (Fig. 4a), contributions to the O 1s peak from the amorphous intermediate silica layer, which was generated by the hydroxylation of the Si-wafer, were expected, therefore the Zn 2p peaks were analysed.

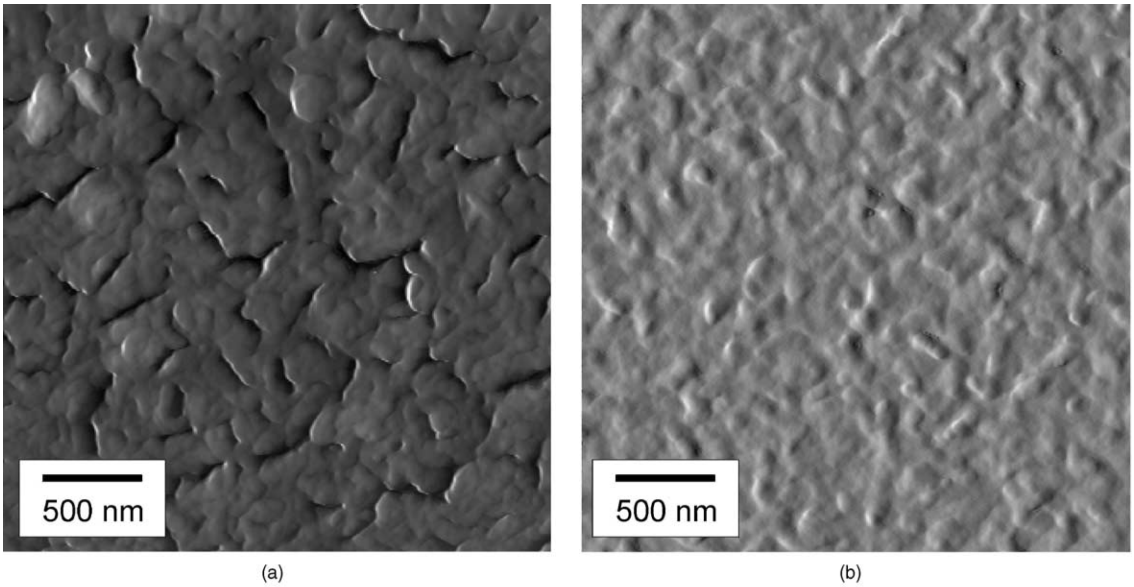
The Zn $2p_{3/2}$ peaks shifts to 1022.5 eV after calcination, which is a characteristic value for ZnO thin films. In the as-deposited sample the $Zn2p_{3/2}$ peak is present at about 1023.5 eV, indicating coordination of the copolymer to a part of the zinc in the film.[12] The corresponding peaks for simple zinc carboxylates though would be found at significantly higher energies (typically >1026 eV).[13]

This is in accordance with earlier investigations, which suggest that at the rather high copolymer concentrations used in these investigations, a part of the polymer is incorporated in the film.[9,13] In a related experiment it was shown by thermogravimetric measurements, that polyacrylic acid, which was used as a dispersant for the preparation of green bodies via slip casting, was removed from ZnO ceramics by calcination in air at temperatures above 723 K.[14]

No significant difference in the positions of the Zn $2p_{3/2}$ peaks in *ZnO-l* and *ZnO-h* was observed, which suggests that the same compound is present in both films.

4. Conclusions

Although the role of the copolymer is not completely understood, some aspects were described by several authors. The first stage in the formation of ZnO particles in the presence of the investigated polyelectrolytes is the formation of nanoparticles. These nanoparticles are initially fixed in a polyelectrolyte network in an amorphous or metastable form. At polymer concentrations below a critical threshold, the initial nanoparticles are dissolved and crystallize in the thermodynamically stable forms. This can then lead to the formation of larger crystals, which can also exhibit micrometer dimensions. At sufficiently high polymer concentrations



(a) (b)

Fig. 2. AFM image of as-deposited film grown after 8 h on SH-modified Si-wafer from a solution containing 100 mM [Zn], 4000 ppm copolymer and (a) 2.5 mM HMTA—*ZnO-h* (Z = 247.5 nm) and (b) 2 mM HMTA—*ZnO-l* (Z = 40.6 nm).

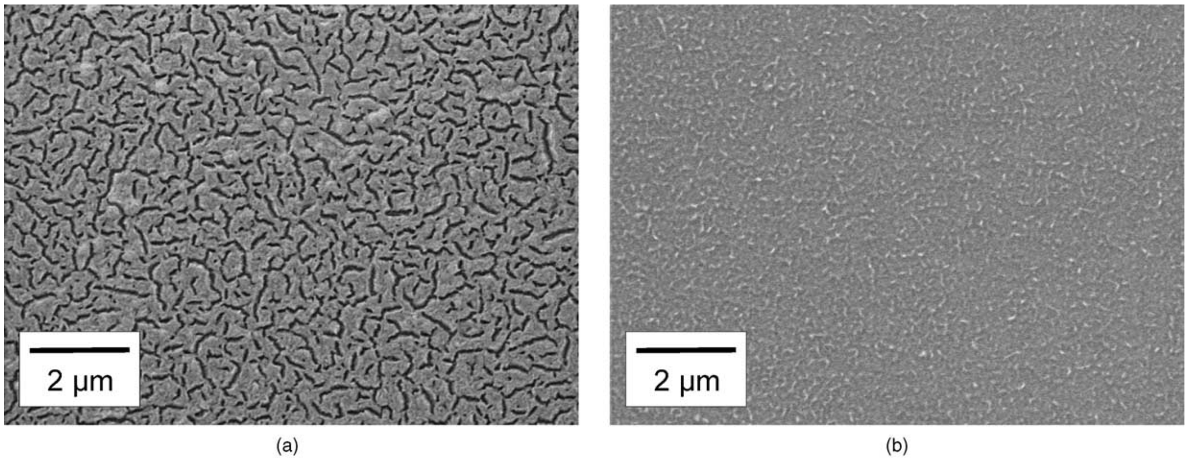


Fig. 3. SEM micrographs of as-deposited film grown on SH-modified wafers in 8 h from a solution containing 100 mM [Zn], 4000 ppm copolymer and (a) 2.5 mM HMTA *(ZnO-h)* and (b) 2 mM HMTA *(ZnO-l)*.

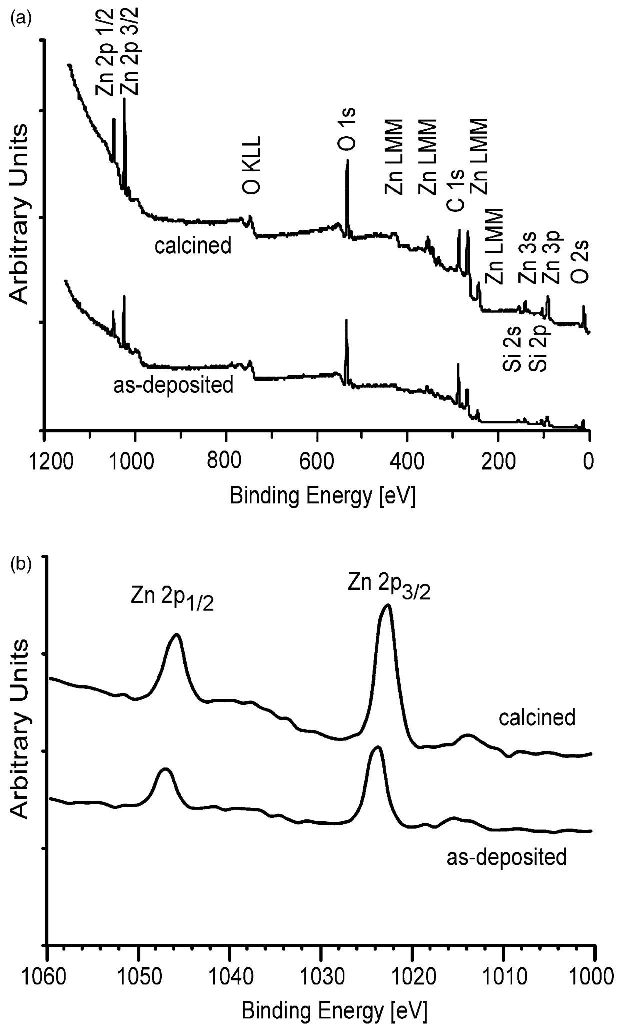


Fig. 4. XPS spectra (*ZnO-h*; deposition time 6 h); (a) survey (Mg K_α-source) of an as-deposited and a calcined sample, (b) Zn2p1/2 and 2p3/2 peaks before and after calcinations at 723 K.

however these particles do not change further and are trapped in the copolymer matrix.[12,15]

Since the polymer concentrations used in the present film formation investigations are higher than those which were used by other authors for the precipitation of powders (0–250 ppm), the stabilization of nanoscale particles is to be expected. Further, the current investigations show, that such particles are suitable building units for thin films.

The influence of the growth rate on the film morphology is remarkable. From the observations the following model is proposed.

The wafer will be partially occupied by ZnO/copolymer particles shortly after the onset of the thermohydrolytic reaction. Particles from the solution can then attach either to the wafer or the already deposited ZnO/copolymer particles. At high growth rates the film thickens quickly, but parts of the wafer remain uncovered, i.e. the canyon-like features are observed. Whereas low growth rates yield complete coverage of the wafer and allow uniform growth.

This might suggest, that the interactions of the ZnO/copolymer particles among themselves are slightly more favorable than interactions between the ZnO/copolymer particles and the SAM-modified surface of the wafer.

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