

Novel low temperature solution deposition of perpendicularly orientated rods of ZnO: substrate effects and evidence of the importance of counter-ions in the control of crystallite growth

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Perpendicularly orientated ZnO rods have been grown on thin ZnO templates, from aqueous solutions of zinc acetate and hexamethylenetetraamine (HMT); growth along the *c*-axis of the ZnO crystallites is promoted by the presence of acetate in the bath.

Zinc oxide possesses structural, electrical and optical properties that make it useful for a diverse range of technological applications. It is a n-type semiconductor (direct bandgap of 3.35 eV at RT¹) and crystallises in the wurtzite (HCP structure) with zinc atoms occupying half of the tetrahedral sites. Polycrystalline thin films of ZnO have been employed in SAW devices, optical waveguides, transparent conducting electrodes and as window layers in chalcopyrite based solar cells.² Nanophase zinc oxide has recently become of interest as an alternative to the TiO₂ nanostructured electrode in Grätzel-type photocells.³

There has been considerable interest in using single crystal ZnO as an alternative material to GaN within semiconductor quantum well based lasers. Several groups have demonstrated UV lasing of epitaxial ZnO films grown on sapphire substrates.⁴ Techniques such as RF sputtering, MBE, CVD and pulse laser deposition have been used for the deposition of epitaxial films of ZnO.⁵ However, growth techniques are usually expensive and the choice of substrate is restricted.

Until recently, wet-chemical routes such as electrodeposition⁶ and chemical bath deposition⁷ have been generally unappreciated. However because of an increasing interest in developing low-temperature routes towards ordered films of aligned crystallites on substrates,⁸ these methods are receiving more attention. These procedures have involved deposition of material on to an existing template, *e.g.* a single crystal, in order to exploit an epitaxial relationship between the desired phase and target substrate. Consequently these are restricted to specific material–substrate combinations. A potentially more general approach, involving control of the interfacial tension of an aqueous solution based system, has been described for growth of highly orientated metal oxide microcrystallites.⁹ The concept is based on the principle that homogeneous nucleation of a solid phase has a higher activation energy than heterogeneous nucleation and growth. Hence growth occurs at lower levels of supersaturation on a substrate than in homogeneous solution. We have been motivated to investigate this concept further, extending our general CBD studies of compound semiconductor materials.¹⁰

In this communication, we describe a new approach for the low temperature solution growth of ZnO rods on TO-glass substrates. The approach has potential to be extended to a wide range of metal oxides and substrates. In contrast to reports in the literature, the formation of ZnO rods was found to be sensitive to the nature of the substrate.⁹ Previously we have demonstrated control of ZnO crystallite morphology *via* tailoring of bath chemistry.¹¹ These factors led us to develop a novel, simple two-step approach to the growth of highly orientated films.

The procedure involves (1) formation of a CBD ZnO template layer of the desired morphology (obtained *via* judicious choice of ligand and counter-ion) and (2) subsequent growth of acicular rods on these templates. Control of the

density of the ZnO rod arrays is achieved through the first step; dimensionality and crystallinity are tailored *via* the second step. In a typical experiment,[†] a ZnO template layer (~500 nm) was deposited by CBD on TO-glass. Based on our earlier studies,¹¹ the zinc nitrate–triethanolamine (TEA) system was chosen in order to give dense, highly crystalline films (Fig. 1(a)) with particulate size controlled by deposition time. There is evidence that the lateral dimensions of the rods appear to be constrained by the crystallite size of the ZnO template. Micrographs of ZnO rods collected from baths (Fig. 1(b)) and grown on template films (Fig. 1(c)) under identical conditions clearly shows the substrate effect. XRD patterns from films were indexed to crystalline ZnO. Although XRD data from the template and rods are superimposable there is clear evidence for preferred orientation in the [002] direction, consistent with growth of *c*-orientated ZnO rods (Fig. 2).

The rationale behind the second step derives from the need to impede the propensity of ZnO crystallites to undergo basal twinning¹² and to enhance the crystallinity and growth of ZnO rods. A range of bath chemistries have been investigated, the best results were obtained for heated aqueous solutions containing zinc acetate, HMT (hexamethylenetetraamine) and additional chloride ion (the latter appears to impede twinning). The role of acetate is equivocal, we note that the optimum solution pH for ZnO rod deposition is close to the pK_a (4.73¹³) of the conjugate acid. Moreover, studies on single crystals of ZnO have shown that carboxylate chemisorption behaviour differs markedly on polar *c* and non-polar *a* faces, on the latter a bidentate configuration is adopted.¹⁴ Most recent reports indicate that adsorption occurs only on terrace defects on *c*-faces of ZnO crystals.¹⁵ We suggest that similar phenomena are implicated during the growth kinetics of our ZnO rods, better rods are obtained from acetate precursors (Fig. 1(c) *vs.* (d)). We have also performed additional studies using different zinc carboxylates and similar results were obtained; these will be described elsewhere.

The significance of the current investigation is threefold. First of all, we have demonstrated a novel and simple low temperature route to the formation of thin films of highly orientated ZnO rods. Secondly, the use of a ZnO template film of desired morphology allows tailoring of the surface density of these rods. Finally, we have shown that the choice of ligand and counter-ion in the deposition bath exert a strong effect on the quality of the ZnO rods. These films have potential for use in quantum well semiconductor lasers. Further studies on different metal oxides are planned.

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Notes and references

[†] *Experimental:* ZnO template layers were deposited from aqueous baths (pH = 11.0; 75 °C) containing zinc nitrate (0.018 mol dm⁻³) and triethanolamine (0.072 mol dm⁻³) on glass microscope slides and TO-glass (Hartford, USA). Substrates were cleaned by a standard procedure. ZnO rods were grown over a period of 1 h from solutions (pH = 5.0, adjusted by

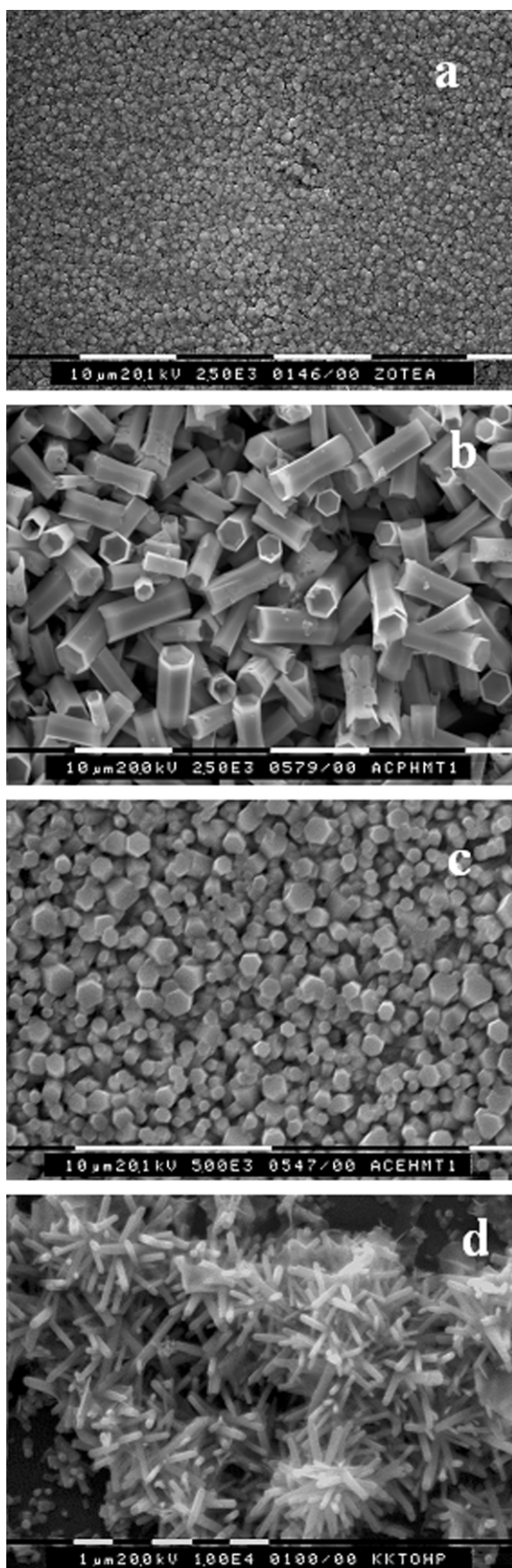


Fig. 1 Scanning electron micrographs of ZnO materials. (a) ZnO template film on TO-glass from TEA-zinc nitrate bath; (b) ZnO rods formed from zinc acetate-HMT bath in the absence of substrate; (c) ZnO rods formed on ZnO template as in (b); (d) ZnO rods deposited directly on TO-glass by method described by Vayssieres *et. al.*,⁹ using high pH and zinc nitrate. Films are less homogeneous and ordered.

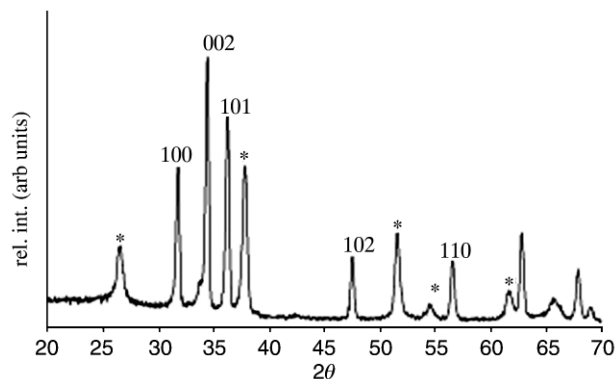


Fig. 2 X-Ray diffractogram of ZnO film, composed of buffer layer and rods, as given in Fig. 1(c). Peaks indexed as zincite (JCPDS 36-1451). ZnO films exhibit preferential orientation in the [002] direction, consistent with growth along the *c*-axis of the developing ZnO crystallites. *Reflections assigned to TO-glass substrate.

dropwise addition of conc. HCl; 90 °C) containing zinc acetate (0.005 mol dm⁻³) and hexamethylenetetraamine (HMT; 0.005 mol dm⁻³). After an induction period of ~0.5 h, the bath develops a milky appearance and growth of ZnO rods occurs. Samples were washed in DI water and allowed to dry in air before characterisation. *Characterisation*: scanning electron micrographs were obtained using a Philips 525 SEM. Samples were gold coated prior to analysis. X-Ray diffraction studies were performed using Cu-K α radiation (40 kV; graphite monochromated) on a Philips X'Pert Materials Diffractometer (MPD). Measurements were taken using a glancing angle incidence detector (3°) for 2 θ values over 10–80° (steps of 0.04°; count time 2 s). Electronic absorption spectra were obtained with a Helios β Thermospectronic spectrophotometer. For direct bandgap semiconductors, extrapolation of linear plots of α^2 vs. $h\nu$ allows determination of the optical bandgap.

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