

UNDERSTANDING AND CONTROLLING THE DEPOSITION OF ZINC OXIDE FROM AQUEOUS SOLUTION

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The fabrication of high surface area thin film materials, composed of nano- and micro- crystallites, is of great commercial and academic interest. Control of the size, shape and orientation of crystallites allows the creation of designer substrates for use in photoelectrochemical cells, catalysis and bio- and gas sensors.¹ The use of soft wet-chemical synthetic routes such as chemical bath deposition (CBD) and electrodeposition (ED) for large-scale production of these materials is of considerable current interest.²

An obstacle to widespread use of current solution deposition routes towards technologically important thin film materials is the need often to anneal/pyrolyse as-deposited films, in order to effect crystallization. Therefore there is considerable interest in developing novel synthetic procedures that provide high quality thin films materials at low temperatures.

Deposition of single crystalline thin films by solution methods is a relatively new and exciting development. For vapour-phase routes, it is accepted that atom-by-atom growth predominates and the formation of single crystalline films is dependent on mechanisms contingent on the presence, or otherwise, of lattice mismatch strain between the substrate and film. These mechanisms include atomic layer-by-layer growth and growth by island nucleation and coalescence. With a few notable exceptions,³ the mechanisms for solution deposition routes are less well understood

The classical models of crystal growth from solution describe initial formation of nuclei in a supersaturated solution followed by Ostwald ripening. The growth habit of solution-grown crystals is determined by two factors; the internal structure of the material in question and external conditions defined by experimental conditions, *e.g.* the nature and concentration of precursors, growth temperature, solution pH and the presence of impurities. Our studies on the CBD-ZnO system provide a model illustration of the outlined behaviour. Growth of zinc oxide thin films, comprising crystallites of a desired size and morphology, is facilitated by an understanding of the growth kinetics.

Recently the concept of "orientated attachment" has been developed to explain the growth of iron, titanium and zinc oxide crystallites. For the latter, anisotropic crystal growth of ZnO rods in solution resulted from coalescence of crystallographically orientated, preformed quasi-spherical ZnO nanoparticles formed in basic methanolic solutions.⁴ We have observed similar "orientated attachment" phenomena during our studies of thin film growth. Although the first reports of ZnO rod formation appeared over two decades ago, Andrés-Vergés and co-workers provided the first convincing reports of low temperature growth of ZnO microcolumns from solutions containing hexamethylenetetraamine (HMT).⁵ We have described a novel, two-step approach for

solution growth of highly orientated ZnO microcolumn arrays.⁶ The procedure involves deposition of ZnO template layers of the desired morphology and subsequent overgrowth of ZnO microcolumns on the templates. No additional annealing step is required; the quality of the as-deposited films was evidenced by room temperature lasing behaviour.⁷

In this presentation, various strategies for the deposition of ZnO will be considered. The modeling of solution equilibria will be described and factors controlling the morphology of as-deposited layers discussed. The potential for the use of such films in a wide range of applications will be outlined.

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