The use of Additives to Control the Morphology of Thin Films Synthesized Using Aerosol Assisted Chemical Vapour Deposition

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Abstract

This paper identifies and discusses the use of additives to control the morphology of nanoscale crystalline zinc oxide films, grown using AACVD, principally from a solution of zinc acetate in methanol. We will discuss the use of both positively charged additives such as tetramethylammonium bromide and cetyltrimethylammonium bromide as well as negatively charged additives like sodium dodecylsulphate. Additives such as these, combined with other experimental parameters such as deposition time, have allowed us to control the size of the particles (from 100 to 400 nm in diameter), their orientation, and the regularity of their shape, from rough edged plates to well defined hexagons. We will show that the additives can be used to control morphology consistently over a temperature range of 250-400°C, and that this technique can be applied generally to a number of additives and solvents.

Keywords: zinc oxide; aerosol assisted chemical vapour deposition; structure directing additives; morphology

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1. Introduction – shape control in zinc oxide particles

In this paper we present our recent findings on the use of additives in Aerosol Assisted (AA)-CVD to control the morphology and orientation of crystallites in zinc oxide films. It has been widely established that it is both possible and desirable to control the morphology of zinc oxide particles by synthesis from solution - using techniques such as hydrothermal synthesis and chemical bath deposition. In these routes of crystallization structure directing additives (SDAs) are used, along with other experimental parameters such as reaction time and concentration, to control the shape and size of zinc oxide particles, allowing generation of needles and plates, as well as more complex hierarchical and branched structures (Zhang et al., 2006, Zhang et al., 2008, Liu et al., 2009). A selection of images of these different microstructures have been collated in a previous publication (Liu et al., 2011). This control is attributed, to a first approximation, to the SDAs binding or capping specific crystallographic faces of zinc oxide, and therefore encouraging growth from other faces (Meagley and Garcia, 2012, Tian et al., 2003). Use of different SDAs or successive use then allows controlled growth of the crystallites.

The ability to control zinc oxide particle shape is desirable - particularly in a thin film - because many reports have shown that the functional properties of the material depend heavily on the morphology. Examples include a fivefold increase in photocatalysis for plate-like ZnO compared to rod-like (McLaren et al., 2009), and in photocatalytic degradation of dyes it has been shown that morphology can be more important even than the surface area for catalytic activity (Ali et al., 2010). When used in dye sensitized solar cells vertically aligned nanorods were found to double light conversion efficiency compared to granular particles (Sharma et al., 2011), and in a second study a tenfold increase was found using aligned nanorods (Zhang et al., 2008).

Although there are clear benefits to shape and orientation control, and it is routinely possible to influence these in zinc oxide grown from solution, until now it has not been possible to gain a similar level of control using a vapour deposition route. This is a handicap given the many advantages of CVD routes such as scalability and low cost. However our research has recently found that SDAs can be used in AACVD to

![Figure 1. SEM images of zinc oxide films formed using zinc acetate in methanol with (a) no additive; (b) 1 mol. eq. of cetyltrimethylammonium bromide; (c) 1 mol. eq. tetraoctylammonium bromide; (d) 1 mol. eq. tetramethylammonium bromide; (e) 1 mol. eq. sodium dodecylsulphate.](image-url)
influence morphology and microstructure in thin films.

In aerosol assisted CVD the film precursor is supplied via a solution mist; because of this we identified that, unlike more traditional CVD routes, there is the opportunity to introduce an SDA that can interact with the precursor or nucleating crystal to control or influence morphology. In our initial communication (McNally et al., 2012), we made use of the surfactant cetyltrimethylammonium bromide (CTAB) as an additive in the deposition of zinc oxide films from a solution of zinc acetate in methanol. This work found that a concentration of CTAB as low as 4 mM was sufficient to cause significant changes in the morphology of the film. Without the additive the film formed irregular sized and roughly shaped platelets, with almost random crystallographic orientation; in contrast, with the addition of CTAB the film formed regular hexagonal platelets of consistent size with a strong orientation of their 0001 axis perpendicular to the substrate. Further, we were able to control the extent of the orientation by variation of the concentration of the additive. A representative SEM image showing the morphology of zinc oxide without additive can be found in figure 1(a), while that found using CTAB as an additive can be found in figure 1(b).

In this paper we will present our most recent results on the use of different additives, solvents and precursors in AACVD to control morphology. We will also speculate on the mechanism through which the effect is occurring.

2. Experimental notes

Unless otherwise stated all films were synthesized from a solution of 0.5 g of zinc acetate dissolved in 35 ml of methanol, (giving a zinc acetate concentration of 78 mM) using argon as a carrier gas at a rate of 1 L min⁻¹. The depositions were carried out at 350°C, and any additive present was used at 78 mM, an equal concentration to the zinc acetate.

In each case the film morphology was identified using a field emission scanning electron microscope and crystallographic orientation identified using X-ray diffraction. Diffraction patterns were modelled using Rietveld refinement in conjunction with the spherical harmonic approach to take account of preferred orientation (VonDreele, 1997). This generates a quantitative measure of the preferred orientation, the texture or $J$ factor, where $J = 1$ indicates random orientation and increasing values of $J$ indicate increasing texture in the film.

3. Results and Discussion

3.1. Effect of additive on structure

In our preliminary work we made use of the surfactant CTAB, which contains an ammonium group that is capable of binding to the charged 0001 surface of the crystallites, and this would be the traditional explanation for morphological control in growth from solution. However, compared with the more simple solvent routes in which SDAs are used in the shape control of zinc oxide crystals, the AACVD system is more complex. In solvent routes the principal interaction is considered to be binding of the additive to crystallite faces during particle growth. This may be the case for AACVD, but then the question arises; does this occur in the aerosol droplets, the vapour phase or at the heated substrate? There is also the possibility that CTAB is acting as a surfactant and affects the surface energy or stability of the aerosol droplets, again changing the crystal growth conditions and affecting the particle shape. It is also worth noting that at the temperatures used in this synthesis, 350°C, the additive CTAB has been shown to decompose, principally to trimethylamine, and N,N-dimethylhexadecylamine, amongst other by-products (Goworek et al., 2009). It is possible therefore, that decomposition products of the additive also play a role in the control of the microstructure.
Further experiments have been carried out using the related additives of tetramethylammonium bromide (TMAB) and tetraoctylammonium bromide (TOAB). These generate similar morphologies to CTAB, and can be seen in figure 1(c) for TOAB, and figure 1(d) for TMAB. In the case of TOAB the film morphology shows less regular shape control, the hexagonal plates have somewhat more ragged edges, but greater orientation control than with CTAB. The platelets more consistently stack on top of each other, and there is much greater 0001 texture, with a J-factor of 8.0 compared with 3.2 for the CTAB film. In contrast TMAB appears to show a ‘weaker’ effect; a texture factor of 2.4 and although distinct platelets are still observable, they appear more variable in size, from 100 to 400 nm, and less regular in shape than those found with CTAB, (although more regular and hexagonal than with TOAB).

To contrast the ammonium additives, experiments were also carried out with sodium dodecylsulphate, a negatively charged additive. The resultant morphology can be seen in figure 1(e) where it can be observed that this additive produces a film with extremely regularly shaped hexagonal platelets, with a consistent size and strong orientation of the 0001 direction perpendicular to the substrate ($J = 4.1$).

The tests on different additives indicate that shape control is not a unique property of CTAB as an additive. They show that it is more general, and that distinct plate-like morphologies can also be made using both cationic and anionic SDAs. The results also indicate that the exact morphology can be altered by the choice of additive, as although similar each SDA generated different variations in microstructure.

### 3.2. Effect of temperature, concentration, solvent and precursor

The majority of the depositions were carried out for this work at 350°C. However, we also carried out a number of tests to determine if temperature played a significant factor in controlling the microstructure. To do this a standard reaction using 0.5 g of zinc acetate and 0.2 g of CTAB in 35 ml of methanol was repeated at temperatures from 150°C to 450°C at 50°C intervals. Below 250°C no deposition occurred, this seems to be below the necessary decomposition temperature for zinc acetate to form zinc oxide. From 250°C to 400°C the same microstructure and orientation were found, but at 450°C the microstructure reverted to that found when no additive was used. This indicates that there is an effective temperature ‘window’ in which the additive can be used, but that within this range a consistent microstructure can be generated, dependant on additive and concentration but independent of the temperature.
In order to test the effect of variation in concentration, CTAB was again used as the model system. A series of experiments were run using 0.5 g of zinc acetate with a range of different amounts of CTAB as additive, dissolved in 17.5, 35 or 70 ml of methanol, to sequentially dilute the precursor-additive solution, while maintaining the ratio between zinc precursor and additive. Figure 2 shows the resulting microstructures for the three different dilutions, for a zinc acetate to CTAB ratio of 2:1 or 0.5 molar equivalents of CTAB. These images show that for all three films the zinc oxide forms as individual hexagonal platelets, but perhaps counter-intuitively that the size of these increased with decreasing concentration from 250 nm to 500 nm in diameter. The X-ray diffraction analysis also showed a consistent increase in amount of preferred orientation with texture factors rising from 1.7 to 3.5 to finally 5.4 for the most dilute system using 70 ml of methanol.

The exact reason for this inverse relationship between reagent concentration and particle size is still unclear, but it should be noted that the greater volume of solution used extends the deposition time - it takes
longer to transfer the solution via aerosol mist - and that the increased platelet size could be related to Ostwald ripening with increased deposition time. Further experiments to resolve this are on-going.

A further test of the generality of additives to control microstructure was carried out by changing the precursor. This test was carried out using zinc acetylacetonate as an alternative zinc oxide precursor. Zn(acac)\textsubscript{2} has poor solubility in methanol so a solvent change was also necessary, to ethanol. The morphology observed using zinc acetylacetonate in ethanol can be seen in figure 4(a), where there appear to be clusters of stacked platelets, with irregular shape, and that these clusters pack together with little selective orientation between them. The addition of CTAB does change this morphology, to one in which the platelets can be seen more independently, giving a rougher overall surface. The change in microstructure is less profound than that observed with zinc acetate, but still definitely present.

The results in our presentation at EUROCVD 19 will show that additives can be used to control the microstructure in zinc oxide films. We will discuss the relationship between the additive used, the experimental parameters and the observed microstructure, and how this can be used to control morphology and properties in thin films.

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