AACVD of metal oxides: from precursor synthesis to TCOs and photocatalysts

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Current research involves developing processes towards sustainable and inexpensive high quality transparent conducting oxide (TCO) films on float glass. In particular replacement materials for Indium Tin Oxide (ITO) are being developed. These materials are used in low-e window coatings (>£5B pa), computers, phones and photovoltaic devices. Indium is listed as a critical element- available in limited amounts often in unstable geopolitical areas. Tin metal has had the biggest rise in price of any metal consecutively in the last four years (valued at >£30K per ton) and indium is seen as one of the most difficult to source elements. We have been developing sustainable upscaled routes to TCO materials from precursors containing earth abundant elements (titanium, aluminium, zinc) with equivalent or better figures of merit to existing TCOs. Our method uses Aerosol assisted chemical vapour deposition (AACVD) to develop large scale coatings [1].

Compared to conventional CVD, the AACVD method uses aerosol droplets to transport precursors, with the aid of inert carrier gases. Therefore, in AACVD volatility is no longer crucial and this allows for a wider choice of precursors being available for use and can lead to high quality films at low cost [2]. The most basic requirements for precursors of materials are solubility (for solution based CVD, e.g. aerosol-assisted (AA)CVD) and volatility (for low pressure (LP)CVD and atmospheric pressure (AP)CVD). For CVD precursors, besides appropriate volatility, they should exhibit stable vapour pressures, and cleanly decompose to the desired product at useful substrate temperatures. In addition to favourable and stable vapour pressure characteristics, a CVD precursor must also have appropriate reactivity for the desired film growth process. Precursors that satisfy all of these requirements are limited and our research involves the investigation of alternative precursors and deposition technologies in order to improve the functional properties of the resulting films. At present the majority of examples of precursors to metal oxides are alkoxide or β-diketonate complexes. β-ketoimines are a relatively under-investigated and potentially valuable class of ligand for the formation of volatile precursors for the deposition of these oxides. Thermal properties of such complexes can be fine-tuned by thoughtful alteration of the various substituents on the ligand, in particular through functionalisation of the imino residue to incorporate additional donor atoms to occupy coordination sites on the metal centre, preventing oligomerisation of precursor molecules. AACVD is a solution-based method, which alleviates the need for volatile precursors, the main requirement being the solubility of the precursor in the chosen solvent. We describe the synthesis of metal oxide and composite thin films, using a range of precursors, by AACVD - a low cost, tuneable and scalable technique. The synthesis, structures, thermal properties and AACVD application of a range of novel precursors, including zinc, gallium and indium β-ketoiminate and β-ketonate complexes are described. Synthesis of the precursors is possible via various routes, affording products of high purity in good yields [3]. Of particular note is the successful stabilisation of rare gallium hydride and trimeric Zn-O species (Figure 1). CVD studies show the potential for this class of compounds for application in metal oxide thin film deposition. The functional properties of the films have been investigated, including their use as transparent conducting oxides and photocatalysts [4].

The development of a new combinatorial AACVD (cAACVD) rig allowed for the deposition of films with graded composition, which in turn gave a greater degree of control over the resulting stoichiometry of the film afforded. Thin films of graded composition can be achieved by allowing two separate solutions of precursors, e.g. one for Ga and one for In, to enter from opposite sides of the reactor. This creates a gradient in the, for example Ga:In ratio present in the precursor mix horizontally across the substrate and therefore a range of deposition conditions are achieved in a single experiment. These techniques have been extended to photocatalytic SnO_2:TiO_2 and N:Nb:TiO_2 films [5].

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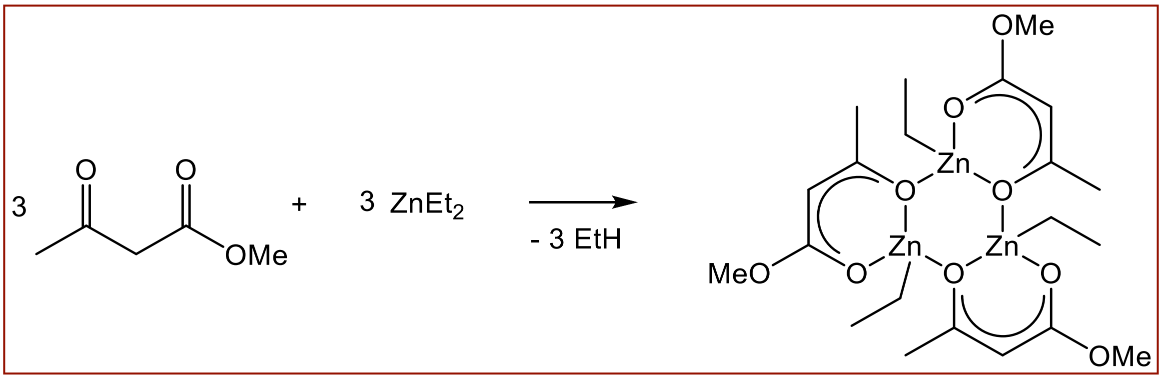

Figure 1. Synthesis of trimeric Zn β-ketonate. Ligand selection of bidentate *β*-diketonates was shown to be key to isolating a cyclic trimer.

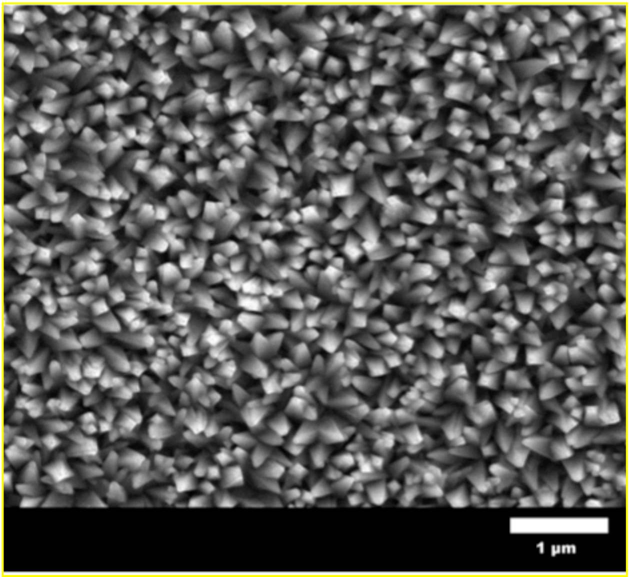

Figure 2. SEM of TiO_2/SnO_2 composite film deposited via AACVD.