Characteristics of Aerosol Assisted and Conventional Chemical Vapour Deposition of Metal Oxide Thin Films on Glass, with or without Noble Metal or $p$ Type Dopants

G. Walters, I. P. Parkin

*UCL, UK*

*gillian.walters@ucl.ac.uk*

**Abstract**

The characteristics and properties of aerosol assisted chemical vapour deposition (AACVD) and conventional atmospheric chemical vapour deposition (CVD) metal oxide thin films on glass substrates with or without Noble Metal or $p$ type dopants have been investigated and examined. Host metal oxide matrices including, ZnO, V$_x$O$_y$, and TiO$_2$ with various dopants are known to give specific physical and optical properties desired by many industries and have various potential properties e.g. thermochromic, electrochromic, photochromic and are known as ‘intelligent coatings’\(^1\). The AACVD synthesis technique was used singularly or in combination with CVD to achieve thin films on glass substrates either in static or dynamic situations with a range of temperatures (300-600 °C)\(^2\). The incorporation of dopants, if at all successful, was limited to small amounts in the horizontal AACVD technique alone and therefore a vertical AACVD/CVD combined synthesis was explored for a range of metal oxides and dopants. Computational fluid dynamics (CFD), Fluent™ software, was used to model the AACVD/CVD combination synthesis technique, to investigate flow, particle trajectory and droplet size properties, in particular the influence of velocity, evaporation, aerodynamic drag, and thermophoresis on flow and particles\(^3\).

1. **Introduction**

The effect of dopants on the colour, morphology, transmittance/reflectance and crystal lattice orientation are reported here using a range of analytical techniques such as UV-Vis spectroscopy, XRD, SEM, EDX, EDS. The influence of particle size (0.1 mm to sub micron) was investigated and found to be a fundamental to AACVD
nebulised droplets ability to reach the glass substrate surface and the main force of influence was found to be aerodynamic drag.

2. **Standard Reagents, Conditions and CFD Parameters**

Standard reagents and conditions used include: The host matrix precursor used for the formation of ZnO, VₓOₓ and TiO₂ AACVD films were Zn(acac)₂ and V(acac)₃ and titanium tetraisopropoxide (TTIP, 10 l/min) for CVD synthesis. The noble metal precursors selected for incorporation into AACVD films included HAuCl₄, Ag(acac), AgNO₃, Cu(acac)₂, Al(NO₃)₃ and for AACVD/CVD synthesis were HAuCl₄, AgNO₃, Cu(acac)₂, Al(NO₃)₃, Ga(acac)₃ and In(acac)₃. CFD Simulations: Gambit™ software was used to design various AACVD/CVD combination head 3D models with high resolution hybrid meshes (EquiAngle skew ≤ 0.9). Fluent™ (2ddp, 3ddp) software was used to model energy conservation, forces of drag, droplet trajectories (spherical model) and turbulent flow using the κ & ε Realizable³ model with/without the discrete thermophoretic model and evaporation for analysis (substrate surface: 600 ºC, solvent droplet: Methanol (MeOH) or water). Six AACVD/CVD vertical head designs, with one AACVD inlet and two CVD inlets were simulated in Fluent™ for flow characteristics, with various AACVD (4.32-17.39 m/s) and CVD (8.32-17.39 m/s) velocities, one head was assessed for particle trajectory from the AACVD inlet with/without discrete thermophoretic and evaporation models.

3. **Synthesis Results & Discussion**

The results from the static AACVD synthesis of undoped/ doped ZnO host matrix films were highly transparent clear films with visible transmission >85%². The Cu doped ZnO thin films were highly coloured and opaque. The undoped and Noble metal doped ZnO films had spherical morphology and the Al₂O₃/ZnO composite films had a range of morphologies (spherical to cubic)². The XRD patterns for both doped/undoped ZnO films (≤ 500 ºC) showed strong preferred (0 0 2) crystal lattice orientation, whereas all ZnO films (≥500 ºC) exhibited random crystal orientation for hexagonal ZnO². The Al₂O₃ dopant altered the preferred crystal orientation to (1 0 1)².
The results from the static AACVD synthesis of undoped/doped $V_xO_x$ ($V_2O_5$, EDX analysis) films deposited (350-450 °C) produced mainly transparent, highly coloured yellow-brown amorphous films with/without dopants, the Noble metal dopants caused a change in morphology of these films. The morphology of Au/Ag doped $V_xO_x$ films produced oblong nanoparticles (400 °C) increasing in spherical nature with increasing temperature (450 °C). CuO incorporation was successful and exhibited some interesting morphology from tubular ‘worm casts’ (350 °C) to spherical nanoparticles with increasing temperature (450 °C).

The results from the dynamic and static substrate samples of the AACVD/CVD synthesis doped/undoped TiO$_2$ thin films produced highly transparent clear films with visible transmission >85% at various temperatures (400-600 °C). The morphology of TiO$_2$ films were found to be influenced by the attempted addition of dopants but had no influence over the preferred anatase form of TiO$_2$. Control samples for dynamic films (400 °C) showed plate structures interspersed with smaller granular/spherical structures whereas the static films were more agglomerated in shape.

Plate like structures were seen for dynamic films with Au, Ag, CuO, Al, In, Ga and ZnO dopants (400, 450 °C), all dopants were below detection level, whereas spherical structures (100-800 nm) were observed for static films (400 °C) and one Au doped film exhibited uniform spherical structures (50–100 nm). Dynamic controls (600 °C) showed angular grains (100–150 nm). Static controls (600 °C) were agglomerated and angular in shape with larger embedded spear structures (400 nm). Al doped dynamic films (600 °C) produced angular needles with large embedded spear structures (250 nm). Au/Ag doped dynamic/ static films (600 °C) had angular structures (50-500 nm), static films also exhibited angular florets with increasing film thickness (4020–18750 Å, 402–1875 nm).

The influence of particle size (0.1–1.0 x 10$^{-4}$ mm) was investigated by CFD and found to be fundamental to the percentage (99-100%) of AACVD nebulised droplets (~0.04 mm) reaching the substrate surface. The main force of influence was aerodynamic drag. Change in the solvent (water, MeOH) or addition of the thermophoretic model
had no significant effect on the size of droplet required to hit the surface but addition of the evaporation model increased the droplet size (0.1 mm) required to hit the substrate by a factor of 10. A change in velocity of either the AACVD inlet or the CVD inlets did not appear to significantly affect the droplet size required to reach the substrate (further work required).

No ZnO, VₓOₓ and TiO₂ film synthesised by either synthesis technique had significant amounts of any dopants present, apart from CuO doped VₓOₓ films and nearly all dopants were below analytical detection level but the morphology and crystal orientation in particular cases, e.g. ZnO, was affected.

4. Further Work

Further investigation of the effect of velocity on droplet size required with turbulence models²,³,⁴,⁵ for both vertical AACVD/CVD head designs and the laboratory AACVD horizontal reaction chamber¹,².

Acknowledgements: EPSRC are thanked for an Eng. D. award to G.W. and I.P.P. Mr. Kevin Reeves, SEM, at UCL and Pilkington Technology Ltd, Analytical Group, Lathom, SEM, XRD are thanked for their help. The Royal Society/Wolfson Trust is thanked for a merit award to IPP.

References: