**Model based Prediction of Nanostructured Thin Film Morphology in an Aerosol Chemical
Vapor Deposition Process**

Tandeep S. Chadha^a, Mengmeng Yang^{a,b}, Kelsey Haddad^a, Vivek B. Shah^a, Shuiqing Li^b,
Pratim Biswas^{a,*}

^a Aerosol and Air Quality Research Laboratory
Department of Energy, Environmental & Chemical Engineering
Washington University in St. Louis
St. Louis, MO-63130, USA

^b Key Laboratory for Thermal Science and Power Engineering of Ministry of Education,
Department of Thermal Engineering
Tsinghua University
Beijing, China

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* To whom correspondence should be addressed:
Tel: +1-314-935-5548; Fax: +1-314-935-5464
E-mail address: pbiswas@wustl.edu

Abstract

The aerosol chemical vapor deposition (ACVD) process has been demonstrated as a promising approach to the single step synthesis of nanostructured metal oxide thin films. Multiple process parameters control the nanostructure morphology and the growth of thin films. This work focuses on utilizing a simulation based approach to understand the role of these parameters in governing the morphology of the thin film. A finite element based computational fluid dynamics model, coupled with a discrete-sectional aerosol model, and a boundary layer diffusion and sintering model has been formulated to predict the evolution of particle size distribution and the morphology of the synthesized nanostructured film. The morphology predicted by the model was validated by experimental observations. The model enables scale up and wider application of the ACVD process and can be extended to other gas phase deposition systems.

Keywords: Nanostructures, Chemical vapor deposition, Computational fluid dynamics, Modeling, Aerosol size distribution, Sintering

1 Introduction

Nanostructured thin films synthesis has attracted enormous interest in the past several decades due to their wide array of applications including solar photovoltaics[2-4], solar water-splitting [1, 5-11], CO₂ photoreduction [12, 13], and lithium-ion batteries [14]. Various approaches have been used to synthesize these nanostructured films, such as, thermal oxidation [15], vapor-liquid solid (VLS) growth [16], template-based synthesis [17], electrochemical methods [18] and gas phase methods [1, 19, 20]. Among these methods, gas phase synthesis such as flame aerosol deposition [19], particle-precipitation chemical vapor deposition (PP-CVD) [21], and aerosol chemical vapor deposition (ACVD) [22] present a rapid, scalable and low-cost method of synthesizing nanostructured thin films. These gas phase methods utilize the direct deposition and sintering of particles onto substrates to form the desired thin film morphology. Three predominant morphologies, namely, dense, columnar, and granular have been reported in the literature [1, 2, 23]. For applications in solar energy and energy storage, the columnar morphology has proven to be the most advantageous due to its oriented, single crystalline, one-dimensional structure, high surface area, and fast electron transfer[1, 2, 6, 14].

Increasing interest in the nanostructured thin films synthesized by the ACVD process and desire to scale-up the process for commercial application has prompted further research into understanding the effect of process parameters on the aerosol dynamics in the reactor and the synthesized morphology. While, the process is simple to operate, the intricate combination of fluid dynamics, heat transfer and aerosol dynamics needed to achieve control over the synthesized morphology is relatively complex. Understanding the relationship between process parameters and the morphology is crucial for scalability and commercial implementation of these processes. Efforts have been made to understand the factors that govern the morphology in such

processes. Thimsen and Biswas [19] studied the effect of precursor feed rate and the substrate temperature on the morphology, crystalline nature and photoactive performance of nanostructured TiO₂ thin films synthesized by a flame aerosol deposition process. The two parameters were linked to four characteristic times, the residence time (τ_{res}), the reaction time (τ_{rxn}), the collision time (τ_{col}) and the sintering time (τ_{sin}). Based on a qualitative comparison between these four characteristic times, three regimes in the deposition process were identified namely, chemical vapor deposition (CVD), individual particle deposition (IPD) and agglomerate particle deposition (APD), which yielded the three different morphologies stated above. An et. al. [1] utilized a similar empirical approach for understanding the link between the process parameters and the morphology in the aerosol chemical vapor deposition process (ACVD) utilizing the same characteristic times to identify three regimes — vapor only, vapor-particle mix and particle only regime. However, for the ACVD process, the process parameters often influence more than one characteristic time, making it difficult to correlate to the morphology of the synthesized films to characteristic times. As an example, increasing the substrate temperature leads to a decrease in τ_{rxn} , τ_{col} , and τ_{sin} but the effect on morphology would be dictated by the relative magnitude of decrease in each of these times, which cannot be determined by these qualitative approaches. This warrants the need for a quantitative approach, accounting for both the computational fluid dynamics (CFD) and the aerosol dynamics in the process.

Numerous studies have focused on coupling aerosol dynamics with CFD simulations for aerosol reactors [24, 25]. In order to do this coupling in a computationally efficient manner, approximations are often made on the CFD model and/or the aerosol dynamics model. Various aerosol dynamics models such as monodisperse, lognormal [26], modal [27], sectional [28], and discrete-sectional [29] have been developed to simulate aerosol dynamics in gas phase

reactors[30], as well as in atmospheric processes [31]. The selection of the aerosol dynamics model and the coupling depends on a number of factors that characterize the system being modeled. Grohen et. al. [32] and Schild et al. [24] applied mono-disperse aerosol dynamics models interfacing with the fluid mechanics to simulate the particle production in a flame spray pyrolysis reactor and a premixed aerosol reactor, respectively. The mono-disperse assumption reduces the number of aerosol dynamics equations on each discretized node to one, which substantially lowers the computational requirement. However, this simplification leads to inaccuracies in the particle size distribution. Prior literature for the ACVD process suggests that the particles depositing on the substrate are smaller than 5 nm. This makes the particle size information extremely critical and higher accuracies are desired, especially in the lower size range close to the nucleation size (0.49 nm).

In order to address the issue of computational time and desired accuracies in the aerosol size distribution, this work utilizes a COMSOL® multiphysics finite element simulation coupled one way to an aerosol dynamics model to simulate particle formation and growth in the reactor. The discrete sectional model (DSM) is chosen for the simulation of aerosol dynamics due to its molecular size resolution in the lower size range and the computational efficiency in the higher size range. Finally, the particle size distribution arriving at the boundary layer of the deposition substrate is correlated to the nanostructured morphology by simulating Brownian diffusion in the boundary layer and sintering on the substrate. The findings from the simulation have been validated by experimental results reported by An et. al [1] . The influence of process conditions on the particle size distribution and the resulting film morphology has been reported and an understanding of the governing parameters is developed.

2 Methods

2.1 Experimental process description

The ACVD process is specifically designed for the synthesis of nanostructured thin films while maintaining precise control over the morphology and the crystallinity of the thin films. The process originates from the flame aerosol deposition reactor but, it exhibits certain distinguishing features which will be described later. The process (Figure 1a) is comprised of three parts: the precursor feed system, the reaction chamber, and the control system. The precursor feed system contains a volatile precursor in a bubbler maintained at a constant temperature. Carrier gas (N_2) is bubbled through the volatile precursor to feed the precursor vapors into the reactor system via a feeder tube accompanied by an optional dilution system. The precursor reaction and aerosol dynamics occur in the reaction chamber, maintained at atmospheric pressure, as a result of the heat flux from the heated substrate. The aerosol is transported via mass convection to the heated substrate, where the vapor-particle mix is then deposited through Brownian diffusion in the boundary layer above the substrate. On the substrate, the vapors react and the particles sinter to form nanostructured thin films.

The control system provides real-time control over various process parameters in the precursor feed system and the reaction chamber, leading to consistent and reliable operation of the process. These process parameters include the carrier gas flow rate (Q_1), the precursor temperature (T_{wb}), the dilution gas flow rate (Q_2), and the dilution gas temperature (T_2) in the precursor feed system. For the modeling study, the above process parameters can be translated into three parameters namely, the initial precursor concentration (c_0), the total flow rate (Q_0), and the initial precursor feed flow temperature (T_0). In the reaction chamber, the process parameters controlled are the

substrate temperature (T_{s0}) and the feeder tube-substrate distance (h_0). In the present work, we investigate the influence of these five parameters (c_0 , Q_0 , T_0 , T_{s0} , and h_0) on the aerosol particle size distribution and the morphology of the synthesized nanostructured thin film. In most cases, since the columnar morphology is desired, the process parameters reported by An et al. for columnar morphology growth is chosen as the reference case (base set of parameters) and the effect of each parameter is studied[1]. The details of these simulation cases are listed in Table 1. Although, the system has previously been used to synthesize thin films of various metal-oxides, the present work focuses on the synthesis of TiO_2 using titanium tetraisopropoxide (TTIP) as the precursor.

2.2 Simulation of temperature and fluid flow

The fluid dynamics and heat transfer simulation, together with the mass transport are implemented using COMSOL®, a commercial finite element software designed for solving problems of multi-physics. The simulation domain is shown in Figure 1b simulated as a 2D axisymmetric geometry in COMSOL®. The equations for the heat transfer in the reactor components and the fluid phase along with the fluid flow and the mass transport of the vapor species are solved simultaneously at steady state using the heat transfer, laminar flow, and transport of diluted species physics in the package. The simulation zone is discretized using a free triangular mesh with a finer mesh for the zone between the end of the feeder tube and the substrate (defined as the refined zone). Corner and boundary layer refinement of the mesh is carried out for regions close to any surface. A laminar inflow boundary condition for the flow is used at the inlet of the reactor and a constant pressure boundary condition is used for the outflow. A no-slip boundary condition is applied to the flow interaction with the substrate. A convective

cooling boundary condition with external natural convection is applied to the outside wall of the glass chamber.

Outputs of the finite element simulation, including the velocity profile, the temperature profile and the reference vapor concentration are utilized as inputs to the aerosol dynamics model. This one-way coupling can be done under the assumption that the aerosols do not affect the fluid flow or the temperature profile within the reaction chamber. Further, since the Peclet number for particle transport is considerably high, in the range of 20 to 10^5 for particle sizes ranging from 0.4 to 20 nm in the temperature range under consideration, the diffusion of particles in the reaction chamber has been ignored. The discrete sectional model provides the solution for the temporal evolution of the aerosol size distribution and is performed using a Lagrangian approach along the velocity streamlines obtained from the CFD simulation. The simulation is done on different streamlines at varying radial distance from the axisymmetric axis upto the entrance of the substrate boundary layer, which is defined as the region above the substrate at which the radial velocity of the flow reaches 99% of the velocity magnitude[33]. The Peclet number for particle transport in the boundary layer tends to 0 and hence the above simulation scheme can no longer be applied. Instead, a different simulation scheme that only considers Brownian diffusion should be implemented to describe the boundary layer.

2.3 Implementation of aerosol dynamics

Various mechanisms participate in the particle size evolution, including the precursor decomposition, vapor nucleation, condensation, coagulation and surface growth. The aerosol dynamics simulated and the modeling approach for film morphology prediction is shown in Figure 2. These mechanisms are all considered in the aerosol dynamics equation [34]:

$$\begin{aligned}
& \frac{\partial n}{\partial t} + \frac{\partial(Gn)}{\partial v} + \frac{\partial(Sn)}{\partial v} - I(v^*)\delta(v - v^*) \\
& = \frac{1}{2} \int_0^v \beta(v-u, u)n(v-u, t)n(u, t)du - n(v, t) \int_0^\infty \beta(v, u)n(u, t)du
\end{aligned} \tag{1}$$

173 where n is the particle size distribution function, a function of particle size and time(t). The latter
 174 three terms on the left in Equation (1) represent the processes of condensation, surface growth,
 175 and nucleation respectively, while terms on the right side account for the coagulation process
 176 where $\beta(v, u)$ is the kinetic coefficient of coagulation of two particles of volume v and u . For
 177 TiO_2 particles originating from the thermal decomposition of TTIP, the molecular volume of
 178 $\text{TiO}_2(62.70 \text{ \AA}^3)$ exceeds the critical volume for nucleation ($31.42 \text{ \AA}^3$) and hence the formation
 179 rate of monomers can be directly calculated by the precursor decomposition rate, expressed
 180 by[35]:

$$R_g = k_g C_{TTIP}; k_g = 1.54 \times 10^6 [\text{s}^{-1}] \exp\left(-\frac{74.03 \left[\frac{\text{kJ}}{\text{mol}}\right]}{RT}\right) \tag{2}$$

181 where $R_g [\text{mol.m}^{-3}\text{s}^{-1}]$ is the TTIP decomposition rate, k_g is the reaction rate constant and C_{TTIP}
 182 $[\text{mol.m}^{-3}]$ is the concentration of the TTIP precursor in the gas phase. Surface growth is dictated
 183 by the reaction of TTIP on the TiO_2 surface, and the surface growth rate is expressed by[36]:

$$R_s = k_s A C_{TTIP}; k_s \approx 1 \times 10^{11} [\text{cm.s}^{-1}] \exp\left(-\frac{15155.16 [\text{K}]}{T}\right), \tag{3}$$

184

185 where $R_s [\text{mol.m}^{-3}\text{s}^{-1}]$ and k_s are the surface growth rate and reaction constant respectively, and A
 186 $[\text{cm}^2.\text{cm}^{-3}]$ is the surface area concentration of TiO_2 particles.

187 The discrete sectional method is a widely used approach for solving the aerosol general
 188 dynamics equation. The particle size distribution is discretized into several discrete sizes in the
 189 small size range and is sectionalized in the large size range. In this study, volume concentration
 190 is applied as the conserved aerosol moment, which is proven to produce the least numerical
 191 diffusion [37]. Based on the TTIP decomposition rate, surface growth rate and the aerosol
 192 dynamics equation (1), the DSM scheme proposed by Biswas et. al. [34], with modification to
 193 include surface growth, is used to calculate the change in aerosol moment for the discrete sizes
 194 and the sections. The number of discrete sizes is set to be 100, to better reflect the behavior of
 195 small TiO₂ clusters and to reduce the fluctuation brought by the transition from discrete sizes to
 196 sections. Therefore, the discrete sizes cover the volume from $v_{d,1}$ ($=v_1$) to $v_{d,100}$ ($=100v_1$), where
 197 v_1 is the volume of a TiO₂ monomer. The first section starts from $v_{s,1}$ ($=100.5v_1$) to $v_{s,2}$ ($=f_s v_{s,1}$),
 198 where f_s is the section spacing factor and is set at 1.08 in the simulations. The largest size
 199 covered by the sections is 20 nm.

200 Multiple size distributions are obtained at the substrate boundary layer depending on the
 201 streamline along which the simulation was performed. As discussed earlier, since the Peclet
 202 number is high, diffusion of the aerosols in the gas phase is neglected and hence it is assumed
 203 that no interaction takes place between the aerosols following different streamlines. The boundary
 204 layer can be divided into several annuluses based on the discretization of the space by the
 205 streamlines and the axisymmetric nature of the reaction chamber (Figure 3b inset). Since, the
 206 axial velocity of the flow in every annulus is known, the flow rate through each annulus can be
 207 calculated using equation (4):

$$Q_i = v_i \cdot A_i; \quad A_i = \left(\pi \left(r_i + \frac{\Delta r}{2} \right)^2 - \left(r_i - \frac{\Delta r}{2} \right)^2 \right) \quad (4)$$

where Q_i is the flow rate through the i^{th} annulus with flow velocity v_i and a radius r_i . Δr is the difference in radius of two consecutive annuluses. An average arrival particle size distribution was calculated based on the volumetric flow in each annulus represented by the corresponding streamline. The average size distribution is then used for modelling the particle deposition and sintering in the boundary layer.

The particles arriving at the boundary layer deposit on the substrate due to Brownian diffusion in the boundary layer. Unlike the flame deposition system, in the ACVD process thermophoresis will reduce the deposition flux. However, for simplicity, the effect of thermophoresis has been ignored since above the boundary layer, the axial flow velocity towards the substrate dominates. Zhang et. al.[33] have shown that the effect of thermophoresis for particles smaller than 2 nm can be ignored in the boundary layer of a flame reactor. The particle flux arriving on the substrate is calculated by solving the 1-D steady state diffusion of particles from the entrance of the boundary layer to the substrate. The particle size distribution obtained from the DSM model and zero number concentration at the substrate are the boundary conditions at the boundary layer entrance and the substrate surface, respectively. The arrival particle flux obtained is given by:

$$J(d_p) = \frac{N(d_p) \cdot D(d_p, T)}{L} \quad (5)$$

where $J(d_p)$ is the arrival flux ($\# \cdot m^{-2} \cdot s^{-1}$), $N(d_p)$ is the number concentration ($\# \cdot m^{-3}$) of the particles with size d_p calculated from the discrete sectional simulation, $D(d_p)$ is the diffusivity of the particle ($m^2 \cdot sec^{-1}$) reaching the substrate, and L is the thickness of the boundary layer (m). The viscosity of the fluid, the mean free path, and the particle diffusivity are calculated using the average temperature between the substrate and the entrance of the boundary layer. Using the arrival flux, a particle arrival rate in a 200 nm diameter cross-section (the typical diameter of a

single column in the nanostructured films) is calculated for each particle diameter. As the flux in equation (5) is based on a number concentration that is distributed as per the total discrete sizes and sections, a simple summation yields the total deposition flux. The total arrival flux of particle is calculated according to equation (6):

$$J_{tot} = \sum_{i=1}^{100} J(d_{p,i}) + \sum_{j=1}^{90} J(d_{p,j}) \quad (6)$$

where i represents the discrete sizes with particle diameter $d_{p,i}$ and j represents the sections with midpoint section diameter $d_{p,j}$. A characteristic time for particle arrival (τ_{arr}) is calculated as the inverse of the total particle arrival rate obtained from equation (6).

Once particles deposit on the substrate, they sinter with the already deposited particles. Using sintering theory proposed by Xing and Rosner [38] and the melting temperature data for TiO_2 reported by Lehtinen et. al [39], a sintering expression similar to one proposed by Tsantilis et. al [40], is derived for TiO_2 :

$$\tau_{sin}(d_p) = 3.01055 \times 10^{15} \left[\frac{\text{sec}}{\text{m.K}} \right] d_p^4 T \exp \left(\frac{3.4216 \times 10^4}{T} \left(1 - \frac{d_{pmin}}{d_p} \right) \right) \quad (7)$$

$$d_{pmin} = \left(\frac{4}{L \cdot \rho_s} \right) \left(\sigma_s - \sigma_l \left(\frac{\rho_s}{\rho_l} \right)^{\frac{2}{3}} \right) \quad (8)$$

where L is the latent heat of fusion per unit volume of solid, ρ_s and ρ_l are the solid and liquid phase densities, σ_s and σ_l are the solid and liquid surface tensions. The correction factor associated with the particle diameter in the exponential term of equation (8) accounts for the significantly low melting temperatures and viscous flow activation energies for small nanoparticles. As stated by Tsantilis et. al [40], the sintering of particles smaller than 1 nm (cluster of 15 molecules for TiO_2)

has been assumed to be instantaneous. Finally, an average sintering time, weighted by the number concentration, is calculated for the particle size distribution arriving at the substrate.

2.4 Experimental validation:

Real time particle size distribution measurements were carried out in the ACVD reactor by a scanning mobility particle sizer comprised of an electrostatic classifier (Model 3082, TSI Inc, MN) fitted with a nano differential mobility analyzer (Nano-DMA, Model 3085, TSI INC, MN), a nano-enhancer (Model 3777, TSI Inc, MN), and a condensation particle counter (Model 3772, TSI Inc, MN) capable of measuring particle size in the range of 1 - 30 nm. A sampling probe comprised of an 1/8inch tube with a hole drilled in the wall was placed on the substrate hot plate. A sampling flow of 0.4 lpm was taken from the reactor and diluted with filtered air, resulting in a dilution ratio of 20. The size distributions presented are corrected by the dilution ratio used. In order to confirm the model predictions of morphology, the effect of two process parameters, substrate temperature and feed inflow rate, was experimentally analyzed. Substrate temperature in the process was varied in the range of 400°C-600°C and the total flow rate was varied in the range 1.0-4.0 m³.s⁻¹. The morphology of the synthesized thin film was confirmed by scanning electron microscopy (SEM) (FESEM, NOVA NanoSEM 230, FEI Co).

3 Results and Discussion

3.1 CFD results for the reaction zone

The velocity and temperature profile obtained from the finite element simulations for the reference case is shown in Figure 3. Simulation results confirm the convective heating of the incoming gas flow as it reaches close to the substrate by the outgoing gas, which exits the reactor

through the spacing between the feeder tube and the quartz glass cover at the top of the reactor. The temperature in the feeder tube and the reaction chamber is fairly uniform and increases rapidly near the substrate.

The velocity streamlines in the reactor are shown in Figure 3c. The streamlines highlight the complex geometry of the ACVD reactor flow impinging on the substrate, turning radially and then back again due to the geometry of the outer quartz glass chamber. This causes a recirculation region in the reactor where prediction of aerosol dynamics is further complicated. Above the substrate, the velocity streamlines turn radially creating a stagnation region where diffusion is the dominant mechanism for particle transport to the substrate.

Figure 3d shows the velocity and temperature profile at the axisymmetric axis (center of the substrate). The boundary layer height is defined to be 0.06 mm above the substrate, where it is seen that the axial velocity is less than 1% of the velocity magnitude. The streamlines entering the boundary layer are shown in Figure 3c (right), along which the discrete sectional simulations are carried out. It is further observed that the temperature rises rapidly in the 0.7 mm region above the substrate, which indicates that the reaction and aerosol dynamics in this region play a major role in governing depositing particle size.

3.2 Simulation results for data in literature:

The process of particle diffusion, deposition, and sintering to yield a nanostructured thin film takes place in the substrate boundary layer. These processes depend on the particle size arriving at the boundary layer, the number concentration of the particles, and the temperature of the substrate. The simulated size distributions of particles arriving at the substrate boundary layer, obtained using the three sets of process parameters (Test 1, 4, 8) reported by An et al.[1], are

shown in Figure 4a. Each of the three cases represents either a dense, columnar or granular morphology, as defined by the previous study. It is observed that the morphology is correlated to the size distribution, with a shift towards the larger size corresponding to a transition of morphology from dense to columnar to granular. Further, it was observed that the particle flux arriving at the boundary layer increases significantly from 1.28×10^9 #/s for the dense film to 4.50×10^{10} #/s for the columnar film and 9.07×10^{10} #/s for the granular film. Thus, the larger size distribution, along with a higher particle flux arriving at the boundary layer, leads to a significant change in morphology. The model predicted results were confirmed by the experimental measurement of particle size distribution in the ACVD reactor (Figure 4b). Although the experimental measurements portray a larger particle size, possibly due to particle coagulation and growth in the sampling tube, the trends in number concentration are similar to the model predicted results. Overall, a significant increase in the total number concentration was observed in the columnar and granular case as compared to the dense case.

While surface reaction of the vapor on the substrate is the dominant growth mechanism, the morphology is governed by the presence of particles in the depositing mix. In order to quantitatively correlate the particle size distribution and flux arriving at the boundary layer to the film morphology, a characteristic time ratio (CTR) is defined as the ratio of the characteristic time for particle arrival (τ_{arr}) to the characteristic time for particle sintering (τ_{sin}). The τ_{sin} is an average sintering time for the different particle sizes weighted by the number concentration of the corresponding particle size. The CTR takes into account all factors governing the morphology of the thin film including, the particle size distribution, the particle arrival flux, and the sintering rate of the particles. A similar approach has been used previously by Lehtinen et al. to describe the onset of dendrite formation in TiO_2 particles as a result of coalescence and

sintering in the gas phase [39]. The values for the dense, columnar, and granular film was calculated to be 6.1×10^{25} , 4.8×10^1 , and 1.06×10^{-2} respectively. This agrees with the previous understanding that the dense morphology is a result of predominantly vapor deposition, extremely long particle deposition time and ultrafast sintering times; the columnar morphology is a result of comparable arrival times and sintering times leading to the arrival of the particle and near complete sintering with the existing structure allowing for the formation of a single crystal structure; and the granular morphology is a result of highly incomplete sintering leading to stacking of particles with identifiable grain boundaries[1].

3.3 The influence of process parameters on particle size distribution and morphology

As described earlier, the process of nanostructure thin film synthesis in the ACVD system can be divided into two stages. The first stage is particle formation and growth in the gas phase, followed by the second stage where particle deposition and film formation take place in the substrate boundary layer. The size distribution of the particles arriving at the substrate boundary layer, the final result of particle evolution in the gas phase and the initial condition for film formation in the latter stage, plays a connecting role in the relationship between the process parameters and the final film morphology. In order to achieve a controlled morphology, an understanding of the influence of process parameters on the arrival particle size distribution and the CTR is needed.

The arrival particle size distribution obtained from the coupled finite element – discrete sectional simulation is a result of the particle evolution process that is dictated by the complex combination of various aerosol dynamics occurring in the reaction chamber. In order to assess and explain the

influence of the ACVD process parameters on the final particle size, two governing factors are extracted from the CFD simulation results: the time averaged temperature (T_{avg}) and the residence time (t_{res}) of the aerosol. The residence time indicates the time for which aerosol dynamics have been ongoing in the reactor and thus determines the final particle size. In the present case, particle formation and growth predominantly takes place after the precursor gas exits the feeder tube, which was earlier defined as the refined zone in Figure 1b. Hence the residence time has been defined as the time it takes for the precursor gas to flow from the tube exit to the boundary layer surface ($t_{res} = \sum t_i$). The time averaged temperature can be used to evaluate the temperature history of the aerosol, which will determine the rate of aerosol dynamics. Due to the temporal nature of the aerosol dynamics, the temperature has been averaged on the time scale ($T_{avg} = \sum t_i T_i / t_{res}$). In the present case, similar to the residence time, the time averaged temperature history has been calculated for the refined zone. These two governing factors are used to explain the influence of ACVD process parameters on the particle size distribution arriving at the boundary layer.

Figure 5 shows the influence of substrate temperature. With an increase in the substrate temperature, the arrival particle size distribution shifts towards larger sizes and a higher number concentration. This trend is attributed to the rise of the time averaged particle temperature as the substrate temperature rises (Figure 5b). The residence time also appears to decrease slightly with an increase in substrate temperature. Trends of these two factors have opposing effects on the particle size distribution; however, the change in time averaged temperature dominates, leading to the aforementioned trend in the particle size distribution. In addition, we also note that the change in size distribution is more rapid as the substrate temperature rises. It reflects that the time averaged temperature has a nonlinear effect on the particle size distribution, which likely

originates from the exponential dependence of the rate of precursor decomposition on the temperature. The change in particle size distribution affects both the τ_{arr} and τ_{sin} since both these characteristic times are a function of the particle size. The change in substrate temperature also influences the τ_{sin} directly because sintering rate depends on the temperature of the substrate in addition to the particle size as shown in eq. (7). In addition, a continuous decrease in the CTR is observed with an increase in temperature (Figure 5c), which can be attributed to the increasing particle flux (decreasing τ_{arr}) accompanied by an increasing τ_{sin} seen for larger particles. The effect of substrate temperature was experimentally verified, as shown in Figure 5d, by synthesizing nanostructured thin films keeping all of the process parameters for columnar conditions but varying the substrate temperatures from 400°C-600°C. In all cases, a columnar morphology was observed by SEM, but the gradual transition from granular to columnar may not be visible through this characterization technique. Model predictions at 600°C are closer to the granular CTR while the morphology observed experimentally is columnar. This deviation is likely due to the effect of thermophoresis at higher temperatures on the depositing particle size distribution which have not been accounted for in the present work. Thermophoresis will reduce the deposition flux and at higher temperatures, due to higher temperature gradients, the effect is more pronounced. Branching of a few tall nanostructures was observed for the 400°C substrate temperature. This phenomenon of branching has been previously studied in detail and is a function of the thermal conductivity of the TiO₂ columns, which results in lower temperature at the tip of the column and hence lowers the sintering rate, resulting in the formation of branches[41].

The results of the effect of feeder-substrate distance are shown in Figure 6, which indicates that the arrival particle size distribution is only slightly affected by the feeder substrate distance. The

lack of any significant effect of this parameter occurs due to the strong opposition between the increase in time averaged particle temperature and the corresponding decrease in the residence time (Figure 6b). This also corresponds to a decrease in the τ_{arr}/τ_{sin} (Figure 6c), however this decrease is not thought to be significant enough to cause an observable change in the morphology.

The other three process parameters, Q_0 , T_0 and c_0 , are properties of the precursor flow, which is controlled by the precursor feed system. Figure 6a shows the influence of total flow rate on the arrival particle size distribution. In all cases, the precursor concentration was maintained constant at the reference value. Increase in the flow rate results in a decrease in the arrival particle size and the number concentration resulting in a left shift in the arrival particle size distribution (Figure 7a). This shift is a result of the decrease in both the time averaged temperature and residence time (Figure 7b). These two factors decelerate precursor decomposition and particle growth, and therefore the particle size and concentration drops sharply. This sharp drop is also reflected in a rapid decrease in the CTR, which allows the morphology to be changed just by changing the feed flow rate (Figure 7c). The effect of the total flow rate on the morphology of the synthesized nanostructure was also verified experimentally. Decreasing the total flow rate to $1.0 \text{ m}^3.\text{s}^{-1}$ causes the morphology to change from columnar to completely granular, which is in agreement with the simulation. Increasing the feed flow rate to $4.0 \text{ m}^3.\text{s}^{-1}$ causes the morphology to change to an irregular dense morphology, again in agreement with the simulation prediction.

Figure 8a presents the influence of initial precursor concentration on the arrival particle size distribution. Due to the low precursor concentration in the feed flow, the concentration of the precursor does not change the fluid flow and energy balance, and hence the time averaged temperature and residence time do not change with the initial precursor concentration. However,

the initial precursor concentration indeed has influence on the particle size distribution, which implies that initial precursor concentration also serves as an essential factor that governs particle evolution. Since the precursor decomposition reaction rate is first order with respect to the precursor, higher precursor concentration leads to a higher generation of TiO_2 monomers, and hence results in a higher number concentration and larger particle size, as shown by the simulation results. This effect is translated to the decrease in the CTR with increasing precursor concentration, which can be used to control the morphology of the thin film (Figure 8b).

Figure 9a shows the influence of feed inlet temperature on the arrival particle size distribution. The increase of feed inlet temperature leads to an increase of both the time averaged temperature and residence time (due to change in gas density) (Figure 9b). However, the change in time averaged temperature is again dominant in comparison to the residence time, so the influence of feed temperature is similar with that of the substrate temperature. However, the effect of the feed inlet temperature on the CTR is slightly different than the effect of substrate temperature. Since substrate temperature also influence surface sintering rates, the slope of the decrease in CTR changed at higher temperatures while the decrease in CTR for the precursor inlet temperature is more uniform. (Figure 9c).

In summary, the time averaged particle temperature, residence time and the initial precursor concentration are three essential factors that govern particle evolution, which could be used to explain and predict the influence of process parameters. Among the five process parameters, the increase of substrate temperature, initial precursor concentration, and feeding flow temperature promotes aerosol generation and growth, resulting in an increase in the arrival particle size and the total number concentration. Alternatively, increasing the feed flow rate has the opposite effect. All process parameters influence the morphology consistent with their influence on the

arrival particle size distribution. Interestingly, the feeder substrate distance has no significant effect on the arrival particle size distribution and hence the morphology of the thin film.

4 Conclusions:

A finite element based computational fluid dynamics model was used to simulate the temperature and velocity profile in the ACVD reaction, which was then coupled to a discrete sectional model to obtain the particle size distribution evolution. A characteristic time ratio (CTR), τ_{arr}/τ_{sin} was then calculated to predict the morphology of the nanostructured thin film. The effect of process parameters on the morphology was predicted and an understanding of these effects was developed based on the particle size distribution, the time averaged temperature, and the residence time in the reactor. The prediction of morphology obtained by the model was experimentally verified for two process parameters. The model provides key insights into the role of fluid and aerosol dynamics, and the ability to predict nanostructure morphology in the ACVD process. This could be used to provide a better control over the morphology of the synthesized films and help devise strategies to improve the throughput of the process for scaled-up production. Further, this modelling approach can be extended to other gas phases deposition processes such as the flame aerosol deposition process and the electrospray deposition process.

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Table 1: List of process parameters and their values used in the simulation study

Process Parameter	Simulation Range	Reference Value
Substrate Temperature (T_{s0})	300-700°C	450°C
Feeder Substrate Distance (h_0)	5-40 mm	20 mm
Feed Flow Rate (Q_0)	0.5×10^{-5} - $2.5 \times 10^{-5} \text{ m}^3 \cdot \text{s}^{-1}$	$1.83 \times 10^{-5} \text{ m}^3 \cdot \text{s}^{-1}$
Precursor Concentration (c_0)	1×10^{-3} - $1 \times 10^{-2} \text{ mol} \cdot \text{m}^{-3}$	$1.51 \times 10^{-3} \text{ mol} \cdot \text{m}^{-3}$
Feed Inlet Temperature (T_0)	20-100°C	35°C

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Figure 1: Schematic of the (a) ACVD process and (b) 2D axisymmetric setup of the ACVD reactor for the finite element modelling

Figure 2: Overview of aerosol dynamics simulated by the discrete sectional model, the Brownian dynamics model and the sintering model to predict film morphology synthesized by the ACVD process

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Figure 3: (a) Temperature,(b) velocity profile,(c) velocity streamlines depicting flow pattern in the ACVD reactor, and(d) velocity and temperature profile above the center of the substrate obtained from the finite element simulation

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Figure 4: (a) Simulated and (b) experimentally measured particle size distribution corresponding to the three different morphologies. Results reported are obtained from simulation and experiments performed at operating conditions described by An et. al[1]

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Figure 5: Effect of substrate temperature on (a) the particle size distribution (b) the time averaged temperature and (c) characteristic time ratio. The dotted lines indicate the value of the characteristic time ratio (τ_{arr}/τ_{sin}) for different morphologies observed experimentally by An et. al. [1] (d) SEM images depicting the morphology of the thin films synthesized at various temperatures

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Figure 6: Effect of feeder-substrate distance on (a) the particle size distribution (b) the time averaged temperature and (c) characteristic time ratio

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Figure 7: Effect of total inflow flow rate on (a) the particle size distribution, (b) the time averaged temperature, and (c) the characteristic time ratio with the SEM images for the corresponding experimental measurements.

Figure 8: Effect of precursor concentration in the inlet flow on (a) the particle size distribution and (b) the characteristic time ratio

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Figure 9: Effect of precursor inlet temperature on (a) the particle size distribution (b) the time averaged temperature and (c) the characteristic time ratio

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Graphical Abstract: