Highly Porous Film Synthesis by Single-Step Direct Aerosol Deposition

David K. PHAM \(^1\), Nils HORNIG \(^1\), Udo FRITSCHING \(^3\) and Lutz MÄDLER \(^1\)*

Received 10 May 2010
Accepted 18 May 2010

Abstract – With the fabrication and processing of films produced by conventional liquid-phase deposition methods, the obtained film porosities are often limited due to the need of post-deposition heat treatment steps. This may lead to collapse of microstructures and detrimentally affect the open morphology of porous films. A novel alternative production method therefore is single-step, gas-phase aerosol deposition. This method has been shown to produce films with estimated porosities of up to 98%, validated in numerical simulations. The key to synthesize highly porous films through this approach is the successful generation of nanoparticle aggregates, ensuring high specific surface area. Particle production is to be assisted by thermophoretic deposition for loose packings while maintaining a cooled substrate to hinder possible film sintering. Highly porous films have found challenging applications e.g. in gas sensing, and as a consequence, much work has focused on characterizing porous film properties and understanding the diffusion and gas transport through porous structures.

Key Words: Porous Film Synthesis, Aerosol Deposition, Flame Spray Pyrolysis, Flame Aerosol Reactor, Laser Ablation, Nanostructured Films, Nanoparticle Aggregates.

1. Introduction

With the recent advances in solid-state film synthesis, the fabrication of films with porosities greater than 95% is possible \(^1\) - \(^3\). Such films fit the needs of gas sensing particularly well due to high specific surface areas, which enhance sensor response from the abundant gas-to-surface interaction sites, and percolating structures that maintain suitable electrical conductivity. Although applications in fields such as fuel cells \(^4\), \(^5\), catalysis \(^6\), and photovoltaics \(^7\) are promising, this review will highlight the use of highly porous films for the example of gas sensing applications.

As outlined in Fig. 1, conventional film synthesis is a straightforward process that consists of several key steps, including dispersion preparation, liquid-phase deposition, and heat treatment \(^8\) - \(^15\). During dispersion preparation through suspension of preprocessed powders in solvents \(^8\), \(^12\), \(^16\) and wet-chemical techniques, such as sol-gel \(^9\), \(^10\), dispersants and binding agents are commonly used to ensure uniform deposition as well as film stability and substrate adhesion. Film deposition is carried out by a number of processes: spin-coating \(^11\), screen-printing \(^8\), or doctor-blading \(^12\) - \(^15\), for instance. After the removal of solvents and additives by heat treatment, resulting films typically show granular, porous structures, as seen in Fig. 2. However, undesired interactions between solvents, additives, and dispersed particles in combination with particle sintering can cause the formation of macroscopic surface cracks and the partial collapse of film structure \(^8\), \(^12\), \(^13\). Consequently, it is often a challenge to produce highly porous film structures through conventional liquid-phase deposition.

A state-of-the-art alternative to conventional film synthesis, which circumvents the previously mentioned issues surrounding liquid-phase deposition, is direct aerosol deposition \(^1\), \(^5\), \(^17\) - \(^19\). This approach is a single-step, gas-phase deposition process from precursors to solid aerosols to stable films. Depending on the mechanism of deposition and aerosol growth dynamics, films with various microstructures, both dense and porous, are fully attainable. It is important to note that direct aerosol deposition processes not only offer the advantage of continuous, single-
Fig. 1  Solid-state films can be synthesized through conventional liquid-phase or single-step gas-phase deposition methods. Conventional methods consist of dispersion preparation through wet-chemical techniques or preprocessed powder suspension, followed by film patterning and heat treatment for solvent removal. Single-step methods entail the generation of solid aerosols or gas/vapor plumes and their direct deposition from the gas phase. One of the key advantages of single-step methods is the lack of a heat treatment step.

Fig. 2  Films made by conventional liquid-phase deposition have a granular, loosely packed structure, as a result of interactions between solvents, binders, and particle constituents during post-deposition heat treatment. SEM images of doctor-bladed ZnO films.

step operation but also tunable film structures with corresponding functionalities. As seen in Fig. 3, gas/vapor deposition, commonly referred to as chemical or physical vapor deposition (CVD/PVD), depending on the means of gas/vapor generation, is traditionally limited to dense, single-crystal film fabrication. However, modifications to CVD and PVD processes, resulting in the formation of solid aerosols, can also be used to synthesize porous films.

To better describe the synthesis of films made by direct aerosol deposition and the characterization of such films, experimental as well as simulated findings of the most common direct deposition methods will be reviewed. In particular, the specific conditions and process parameters necessary for highly porous film synthesis will be stressed due the immense promise offered by stable film structures with extremely high specific surface area.

2. Direct Aerosol Deposition

In this review, direct aerosol deposition will refer to any process that generates a solid aerosol for deposition onto a desired substrate surface, forming a stable film without post-deposition treatment. As a whole, direct aerosol deposition includes a range of aerosol generation methods coupled with controlled deposition. From aerosolized commercial powders, films have been synthesized by passing the entrained particles through an accelerating nozzle for deposition by impaction. Similar films have also been made with nanometer-sized grains and
pores by the laser ablation of microparticles (LAM) that generated nanoparticle aerosols also deposited by impaction. Following laser ablation of solid material targets, inert gas condensation of the generated vapor plume has been able to produce films of varying porosities depending on the chamber pressure. With liquid precursors, as in combustion chemical vapor deposition (CCVD) or flame spray pyrolysis (FSP), the atomization step is controlled by gaseous flow used to create droplets as well as transport the dispersed materials to the reaction stage. Because of the high temperatures available in the heated reactors of CCVD or self-sustaining flames of FSP, sprayed liquid droplets are vaporized into a supersaturated plume leading to the generation of solid aerosols by homogeneous nucleation of primary particles. Further gas-phase growth dynamics and post-deposition surface diffusion or particle sintering are controllable to some extent with proper temperature management of the reactor and substrate surface. Similar to FSP processes, flame aerosol reactor (FLAR) systems also take advantage of a flame to provide enough energy for conversion of gaseous precursors to product aerosols before deposition.

2.1 Deposition Velocity

In order to describe the differences in deposition mechanisms, the non-dimensional Peclet number will be used:

\[
Pe = \frac{Lv}{D}
\]

where \( L \) is the characteristic length, such as particle radius, \( v \) is the particle velocity, and \( D \) is the particle diffusivity. When \( Pe \) is large, the velocity term dominates and deposition is tending toward the ‘ballistic limit’. On the other hand, for low \( Pe \), the diffusion term dominates and this is considered to be in the ‘diffusion limit’. In addition to purely diffusional transport, other low-velocity deposition processes include thermophoresis, which is observed when particles in high temperature environments migrate toward regions at lower temperatures with a rate dependent on the temperature gradient. As compared to thermophoretic deposition that has achieved films up to 98 % porosity, ballistic deposition by impaction at velocities ranging from 100 – 1000 m/s has produced more compact structures with densities at 60 – 80 % of the bulk material. The resulting film-to-substrate adhesion was proven to be quite strong through scratch tests on 3 \( \mu \)m films made by supersonic impaction of nanoparticles from LAM and ultrasonic treatment on 8 \( \mu \)m films made by the aerosol deposition method (ADM). As seen in Fig. 4, dense films made by impaction can offer higher specific surface areas by increasing surface roughness. This was achieved when ceramic materials...
with high hardness values impacted previously deposited layers, leading to the evolution of craters \(^2\).

### 2.2 Growth Dynamics

For diffusion and/or thermophoresis limited deposition at small Pe numbers, particle growth dynamics is a key factor in determining film structure. The size and shape of deposited particles, aggregates, defined as strongly bonded groups of particles through the development of sintering necks, or agglomerates, weakly bonded groups of particles and/or aggregates, essentially depend on the initial aerosol particle concentration and the temperature environment \(^3\).

#### 2.2.1 Initial Particle Concentration

As seen in Fig. 5, porous films made by pulsed laser ablation deposition show the effect of particle concentration without the influence of temperature on film morphology \(^1\). With a KrF excimer laser in nitrogen at room temperature, Ga\(_2\)O\(_3\) films were made consisting of nanoparticles between 10 – 500 nm \(^1\). For various chamber pressures between 1 – 100 Torr, resulting film structures were shown to change noticeably. In Fig. 5(a) at a chamber pressure of 1 Torr, the Ga\(_2\)O\(_3\) film has a granular, columnar-like structure, but in Fig. 5(c) at 10 Torr, the Ga\(_2\)O\(_3\) film structure has been altered into a lace-like, random packing. Because pulsed laser ablation provides only localized heating for the initial vapor plume generation, changes in film morphology were solely attributed to the degree of particle agglomeration, which is promoted at higher chamber pressures due to longer particle residence times in the concentrated plume environment.

![Fig. 5](image)

**Fig. 5** Particles deposited from the gas-phase at lower concentrations have a granular, more compact structure whereas lace-like, loosely packed structure result at higher concentrations. FE-SEM images of Ga\(_2\)O\(_3\) films made of nanoparticles between 10 and 500 nm from pulsed laser ablation deposition at various chamber pressures (a) 1 Torr (b) 5 Torr (c) 10 Torr (d) 100 Torr \(^1\).

#### 2.2.2 Particle Temperature History

The effect of temperature management on aerosol growth dynamics has been previously studied in detail \(^1,3\)\(^1\). To summarize, the relative rates between particle collisions, sintering, and coalescence compete to determine film structure, where sintering refers to the development of strong bonds between particles in contact and coalescence occurs when particles combine to form a larger particle. Because initial particle concentrations are typically high, particle collisions are unavoidable. For the case of coalescence rates higher than the rate of particle collisions, singular particles are deposited since any agglomerates will merge to form larger isolated particles \(^1\)\(^1\)\(^1\). The resulting granular, columnar-like film morphology can be seen in Fig. 6, where TiO\(_2\) films were made by FLAR deposition. In these studies, even though substrate temperatures were at 910 K, deposited particles with a diameter of about 8 nm by TEM analysis experienced negligible sintering with film crystal sizes of 9 nm as derived from XRD analysis. In contrast, smaller particles, \(~ 4.5\) nm by TEM, showed higher sintering rates after deposition, where crystals were found to grow to 47 nm and consequently, the film structure densified. In CCVD, the effect of various substrate temperatures was explored for the deposition of 70 % SSC and 30 % SDC films \(^5\). As seen in Fig. 7, grain sizes increased with increased substrate temperatures from 800 – 1400 \(^\circ\)C and the overall structure became denser with less abundant but larger pores.

When the rate of coalescence is lower than the collision rate, aggregation of primary particles becomes more apparent. Through FSP, highly porous films were produced with estimated porosities of 98 % by deposition of particle aggregates \(^1\). This is achieved by the fast flame quenching that takes place within the atmospheric conditions of the reactor setup, which serves to entrain

![Fig. 6](image)

**Fig. 6** Films made by aerosol deposition of singular particles have a granular, columnar structure. SEM image of TiO\(_2\) film made of 10 nm particles by FLAR \(^7\).
surrounding air and quickly dilute the aerosol with cold gas slowing coalescence. Additionally, a water-cooled substrate is used to ensure limited particle sintering after deposition. Pt-doped SnO$_2$ films made by FSP can be seen in Fig. 8. Note the similarities between Fig. 5(c) and 8, where both methods were able to successfully deposit particle aggregates with nanometer grain sizes leading to highly porous film structures. Although such highly porous films are stable and have been used as gas sensors, one concern is the low film-to-substrate adhesion due to the limited particle contacts to the substrate surface. For improved adhesion, FSP-made films have been annealed by exposure to particle-free xylene flames providing a temperature estimated at 1000 $^\circ$C. The film densification appeared to be uniform, and improvement to substrate adhesion was shown through impinging N$_2$ and water jet tests. The porosity was reduced to 62 %, and in Fig. 9 the morphology can be seen to be cauliflower-like with columnar structure.

2.3 Film Patterning

Due to the directionality of impactation deposition, film patterning of aerosols at high velocities is a fairly straightforward process. However, for diffusional or thermophoretic deposition, constrained lift-off masking techniques have been used effectively to deposit films in specific designs. Through FSP routes, multi-layer films have also been produced without any significant damage to bottom layers.

3. Simulated Generation and Characterization of Porous Films made by Direct Aerosol Deposition

Although the fabrication of solid-state films through direct aerosol deposition has become reality, the formal char-
acterization of such films with quantitative assessments of microstructure and physical properties is currently lacking. Namely for highly porous films, simulation models provide much needed insight where experimental exploration is currently too complex or demanding. In particular, the simulation of gas, heat, and momentum transport through these films can determine their effective functionality in such applications as gas sensing or catalysis.

3.1 Structural Features
Films made by the direct deposition of singular particles have been previously modeled through Brownian dynamic simulations \(^{38,39}\). In these studies, the deposited aerosol was assumed to be dilute near the substrate such that particle-particle interactions in the gas-phase could be considered negligible; appropriately, sequential particle release with periodic boundary conditions was employed. The inclusion of van der Waals forces in addition to purely diffusive forces noticeably changed film morphology, where structures with lower fractal dimension and more open structures resulted due to the attractive interactions between particles in the bulk and already deposited particles. Particle velocity through convective transport also considerably affected film structure, which clearly increased in packing density and fractal dimension as the velocity was increased. Similarly, increased gas temperatures as well as increased temperature gradients without particle sintering resulted in more compact structures with higher mean particle coordination numbers and higher packing densities. When particle sintering was taken into account, the fractal dimension appeared to tend towards the ballistic limit of 3 whereas the fractal dimension of films that did not undergo sintering became roughly constant at 2.65. From these works, it can be concluded that van der Waals forces play a significant role in particle deposition, deposition velocity is key to the development of the deposit structure, and sintering can contribute to structure densification.

Direct deposition of nanoparticle aggregates has been modeled by the sequential release of agglomerates, appropriately assuming that the aerosol is dilute during deposition to such an extent that no particle-particle interactions dominate in the aerosol phase \(^{40}\). The transport of the agglomerates toward the substrate was described by the Langevin equation of motion incorporating thermophoretic forces. It was found that simulated agglomerates with fractal dimension of 1.8 that comprised of 20 primary particles with diameters of 10 nm produced films with porosities of 98.9 %, corresponding with the estimated 98.2 % from experiments. In addition to film porosity, the simulation also found a comparable film thickness of 19 \(\mu\)m to the observed experimental film thickness of 30 \(\mu\)m. The significance of thermophoresis in the direct deposition of agglomerates was validated when 100 K temperature difference was introduced, where the deposition rate increased by a factor of 7.5 with a film porosity change of approximately 0.1 %.

3.2 Physical Properties
In addition to porosity, particle coordination number has been shown to be an important parameter in defining porous film structure. A three-dimensional representation of nanocrystalline TiO\(_2\) films was generated by a random packing of spheres to investigate the change in particle coordination number with porosity \(^{41}\). At 60 % film porosity, simulated and experimental pore size distributions compared well, where the simulated particle coordination number was 4. The coordination numbers were predicted to range from 6.6 to 2.8 for porosities of 40 % to 80 %, respectively, which confirms the decrease in interparticle contacts with increased porosity. The study suggests that a particle coordination number of 4 is sufficient for unconstrained electron transport for application in solar cells or gas sensing, for example. Further work on the electrical conductivity of porous films has been explored through nanoparticle aggregate film simulations similar to Mädler, et al. 2006 \(^{42}\). The shortest conducting pathways through the structure as well as the number of conducting pathways were determined in order to find the overall film conductance. It was found that the conductivity of the films increased with increasing film packing density regardless of aggregate size. Overall, this model gives insight into film features that can be optimized to improve electrical conductivity.

Young’s modulus of nanoparticle-based TiO\(_2\) porous films was investigated using a Monte Carlo approach with a continuum method \(^{43}\). The film is simulated by sequentially depositing aggregates, assuming the surrounding gas is air and the particle concentration is dilute without particle-particle interactions. Bonding between aggregates is defined by van der Waals interactions and bonds between particles within an aggregate are defined as strong chemical bonds. This distinction is used to represent the mechanical behavior of the deposited nanoparticle networks as a jointed truss model. The simulated films had porosities of 94 % for 17 nm particles in an aggregate of 15 particles, which is comparable to previous simulation studies as well as experimental findings. By decreasing primary particle size the Young’s modulus increased due to the increase in surface-to-volume ratio. But by increasing the aggregate size the Young’s modulus only increased nominally and with an increase in film porosity,
3.3 Transport Mechanisms through Porous Structures

In general, porous structures appear in a broad range of length-scales for both pore and particle diameters. Depending on the Knudsen number:

\[ Kn = \frac{\lambda}{L} \]

where \( \lambda \) is the molecular mean free path and \( L \) as a characteristic length for molecular movement, e.g. pore diameter, the diffusion regime can appear either as Knudsen diffusion for \( Kn > 1 \) or bulk diffusion for \( Kn < 0.01 \) (see Fig. 10). The transient regime between \( 1 < Kn < 0.01 \) incorporates both Knudsen and bulk diffusion. As for gas transport in the Knudsen regime, transport mechanisms are no longer dominated though intermolecular collisions but rather by collisions to spatial boundaries, e.g. pore walls. In the case of \( Kn < 0.01 \) the transport mechanisms of heat and mass are treated as a continuum, and intermolecular collisions are not considered. In this regime, several works on the transport mechanisms in porous structures have been published.

In the continuum regime, the flow through porous layers was performed e.g. spheres and cylinders through numerical models \( 44 \sim 46 \). Momentum and heat transfer phenomena were also simulated for fluidized spherical particles and fixed bed reactors \( 47 \sim 50 \), open-pore ceramic structures \( 51 \), fibrous porous media \( 52 \) and porous membranes \( 53 \). These studies used computational fluid dynamics (CFD) for the determination of general flow characteristics or heat and mass profiles inside porous structures. In addition, validation of results obtained by simulation techniques through experimental investigations was reported. Conclusively, for relatively large geometries modeled as continuum, exact validations of the described CFD models could be achieved.

Regarding the Knudsen flow regime, work has been done on the modeling and simulation of diffusive transport mechanisms. For modeling transport phenomena through porous structures on molecular length scales, selective gas separation \( 53 \) as well as mass transfer and adsorption kinetics of pore diffusion have been simulated numerically \( 54 \). In this particular work, the importance of pore diffusion amongst other transport phenomena, i.e. viscous flow and surface diffusion, is highlighted. Furthermore, in the Knudsen regime, Monte-Carlo tracer methods are often used for high-resolution descriptions of interacting molecules with closed boundaries or among themselves. With this technique, the movement of molecules and diffusive transport of single particles was described as in catalysts or adsorbents, respectively \( 55, 56 \).

The models for describing continuum and Knudsen region are found to be identical, while simulation transport in the transient region at \( 1 < Kn < 0.01 \) pressure diffusion, slip flow and diffusion slip have to be considered \( 57, 58 \).

For the characterisation of gas transport mechanisms in highly porous layers made of nanoparticle aggregates, the mean free path of the molecules at ambient temperature and pressure is estimated as 65 nm and pore length roughly estimated from SEM pictures are on the order of 20 – 100 nm. Assuming both the pore length and mean free path of the molecules the Knudsen number can be roughly denoted as \( Kn > 1 \) and the characterisation of gas transport mechanisms can be performed by numerical simulation techniques, like Monte-Carlo tracer method.

Moreover, porous layers have been simulated with effective gas diffusion coefficients predicted \( 59 \sim 61 \). Finite-element-based methods were used to simulate random-distributed porous solids with varying porosities between 0 – 100 % and different particle coordination numbers \( 60 \). The effective gas diffusion coefficients were predicted from these simulations assuming Fick diffusion. For a particular coordination number, it was shown that a threshold exists where the effective diffusivity increases non-linearly with porosity, and beyond that threshold the diffusivity’s dependence on porosity becomes quasi-linear. In another study, the residence time of gas diffusing in simulated silica gel sphere packing with a porosity of 45 % was determined \( 59 \). The residence time was

![Fig. 10](image-url) For the simulation of momentum, heat, and mass transfer through a representative complex porous structure (left), the length scales over which the transport mechanisms are modeled are of great importance, either (I) bulk diffusion which is mainly simulated through CFD techniques or (II) Knudsen diffusion which is mainly simulated through Monte Carlo modeling methods \( 56 \) (modified).
calculated in the Knudsen approximation and a linear dependence of the residence time on the layer thickness was found. The effect of molecule-solid interaction on the overall diffusivity in porous layers has also been investigated \(^{61}\).

4. Conclusions and Outlook

Direct aerosol deposition, a state-of-the-art, single-step approach for solid-state porous film synthesis, has been summarized both with experimental findings and simulated validations and assessments. Direct aerosol deposition methods offer the benefit of tunable film morphologies with the key process parameters being deposition velocity and particle temperature history. Under conditions for nanoparticle aggregate deposition without particle sintering after deposition, highly porous films estimated at 98% porosity have been fabricated. Numerical simulation studies have been used to confirm the growth mechanism of such highly porous structures as well as to describe physical film properties, such as electrical conductivity and mechanical elasticity. Gas transport through porous layers has also been simulated, where numerical methods have been explored for the Knudsen flow regime that is of interest in highly porous films.

Acknowledgements

This work was supported by the German Research Foundation (DFG: MA 3333/2-1 and Research Training Group 1375 “Nonmetallic Porous Structures for Physical-Chemical Functions” at the University of Bremen). The authors would like to acknowledge Katharina Groffmann (University of Tübingen) for providing electron microscopy images presented in this review.

References

34 ) Schulz, H., Mäddler, L., Strobel, R., Jossen, R., Pratsinis, S. E. and


