

Simulations of Reactor Efficiency for Pulsed Pressure Chemical Vapor Deposition (PP-CVD)

Hadley M. Cave, Susan P. Krumdieck and Mark C. Jermy

Department of Mechanical Engineering, University of Canterbury, Private Bag 4800, Christchurch 8020, New Zealand

Abstract. Pulsed Pressure Chemical Vapor Deposition (PP-CVD) is a method for the processing of thin films which presents some unique challenges to flow modeling techniques. In this process a timed pulse of a dilute gaseous precursor is released through an orifice into a continuously evacuated reactor volume. In this paper, the Direct Simulation Monte Carlo (DSMC) method is used to model the unsteady flow field of carrier gas through a representative PP-CVD reactor. The Pulsed Injection Efficiency Simulation (PIES) model is then used to track the movement of precursor particles through the carrier gas stream. The simulations show that the injection phase produces a highly uniform distribution of precursor particles throughout the reactor volume. During the pump-down phase, these particles diffuse to the substrate due to random molecular walk at a rate which greatly exceeds the reactor evacuation rate. The result is precursor conversion efficiencies exceeding 90% and highly uniform film deposition. A number of steady flow reactors operating at similar pressures were also simulated as a point of comparison. Although computational constraints prevent the simulation of actual PP-CVD reactors by DSMC, the method clearly demonstrates the physical mechanisms resulting in high precursor conversion efficiencies and film thickness uniformity observed during experimental studies of the reactors.

Keywords: Pulsed Pressure Chemical Vapor Deposition (PP-CVD), Direct Simulation Monte Carlo (DSMC)

PACS: 05.10.Ln, 47.45.-n, 81.15.Gh

INTRODUCTION

Over the past several decades, chemical vapor deposition (CVD) has become an increasingly important process for the manufacture of thin film materials. These materials have importance in such diverse applications as electronics, bio-technology and optics. As thin film technology has advanced, new types of CVD processes have been developed to manufacture these films [1].

The motivation for this work is the patented Pulsed Pressure CVD (PP-CVD) process developed by Raj *et al.* [2]. Like other CVD processes, deposition occurs via the thermal decomposition of the precursor on a heated substrate, however unlike other processes the precursor is delivered in an unsteady manner whereby timed pulses of precursor are released into a continuously evacuated reactor volume. The technique has been successfully used by Krumdieck *et al.* to deposit films of titania and yttria-stabilized zirconia from liquid metal-organic precursors delivered into the reactor as liquid droplets via an ultrasonic nozzle [3, 4].

Figure 1 shows a functional schematic of a PP-CVD reactor, along with a plot of the reactor pressure during operation. For gaseous precursors, during the injection phase ($0 < t < t_i$) a solenoid valve is opened which releases the precursor in the high pressure source vessel into the reactor volume at pressure P_{min} . When the valve closes at $t = t_i$ the reactor is at its maximum pressure of P_{max} . During the pump-down period ($t_i < t < t_p$) the reactor is evacuated by the vacuum pump and the reactor pressure during this phase is given by:

$$P(t) = P_{min} + (P_{max} - P_{min}) \exp\left(-\frac{t}{\tau_R}\right) \quad (1)$$

where τ_R is the reactor pump-down constant which can be determined experimentally by fitting the exponential function to the measured pressure profile [5].

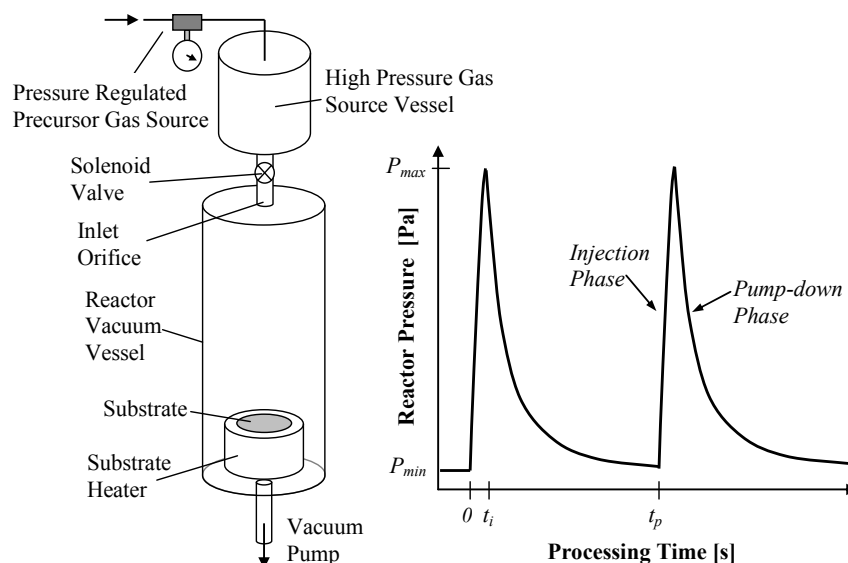


FIGURE 1. Functional schematic of a Pulsed Pressure Chemical Vapor Deposition (PP-CVD) reactor with a plot of the reactor pressure during operation.

Experimental studies and a phenomenological model of PP-CVD by Krumdieck and Raj have reported that during the deposition of titania, the conversion efficiency of the TTIP precursor into solid film exceeds 90% under certain operating conditions [3, 6, 7]. Efficiencies this high have not been reported in conventional CVD processing.

Previous work by the authors, including a study of the injection phase using computational fluid dynamics (CFD), has shown that during the PP-CVD injection phase the scale of macroscopic property gradients is of the order of the mean free path and the continuum description of gas dynamics becomes invalid. The preferred technique for modeling such flows is the Direct Simulation Monte Carlo (DSMC) technique [8]. Here the movement and collisions of a large number of test particles are decoupled over a time step which is a fraction of the mean collision time. The technique is well established and has been used to simulate flow applications as diverse as high altitude aerodynamics [9], micro-thrusters for space applications [10] and steady flow CVD [11].

Modeling of the PP-CVD process using DSMC presents some significant challenges. The wide range of flow densities and the unsteady nature of the process, along with the relatively long cycle time, mean that modeling the entire process using the DSMC technique requires significant computational expense, even given the 2D axisymmetric nature of the flow. This problem is exacerbated by the low concentration of the precursor molecules meaning a large number of particles must be simulated to maintain accuracy. A technique used to overcome a similar problem is the stochastic biatomic collision theory (BCT) method developed by Groves to model the Directed Vapor Deposition (DVD) of copper [12]. Here the paths of a large number of reactant molecules are tracked individually through a steady background gas field generated using DSMC. The technique assumes the concentration of reactant molecules is low enough that there is negligible interaction between them.

REACTOR SIMULATIONS

Simulation Method and Model Development

The technique used to model the transport of precursor is loosely based on the BCT method but is adapted for unsteady flow. This technique, known as the Pulsed Injection Efficiency Simulation (PIES) method, utilises the variable soft sphere (VSS) model developed by Koura and Matsumoto [13] to simulate the collision of precursor particles with molecules in the carrier gas field. In this way the movement of the test particles through the reactor volume is decoupled from collision events in much the same way as the DSMC method, while allowing the use of readily available collision parameters.

The carrier gas flow field is simulated using Bird's "DS2V" DSMC code until the jet structure has collapsed to an approximately stationary uniform flow field within time $t = 2t_i$. An axisymmetric DSMC background flow field

TABLE 1. Simulation parameters

Reactor Height, h	200 mm	Supply Pressure, P_S	100 & 1000 Pa
Reactor Diameter, d_R	100 mm	Supply Temperature, T_S	293 K
Substrate Diameter, d_S	75 mm	Pulse Pressure Range, $P_{min} \rightarrow P_{max}$	$1 \rightarrow 10$ Pa
Inlet Orifice Diameter, d_i	10 mm	Reactor Evacuation Rate	0.05 m ³ /s
Substrate Temperature, T_{sub}	800 K	Precursor Particles Simulated	~10,000
Wall Temperature, T_W	300 K	Precursor Particle Types	He, Ne, Ar, Kr, Xe

is used, however the tracking of particles using the PIES model is carried out in three-dimensions.

The unsteady nature of the simulations results in a relatively high statistical scatter in the flow field especially near the reactor's axis of symmetry and this statistical noise becomes unacceptably large after the jet structure collapses. For this reason, and to reduce the computational expense of the simulations, the flow field is assumed to be of uniform density with negligible bulk flow and a pressure given by equation (1) for $t \geq 2t_i$. A more complete description of the PIES technique and details of the validation procedures are given by Cave *et al.* [14].

There are a number of limitations in the model which prevent simulation of actual PP-CVD systems at the present time. Constraints on actuator valve speed and vacuum pump capacity mean actual PP-CVD reactors have injection times of the order of 0.1s and pump-down times of the order of 10s. In order to reduce the enormous computational expense of simulating such a system, a hypothetical reactor was modeled with a short injection time (and hence a large inlet orifice) and a rapid pump-down rate. Additionally, there are few VSS parameters presently available for the complex metalorganic precursor molecules used in most PP-CVD deposition experiments. For this reason the reactor was modeled with a helium carrier gas and using noble gas particles as the "precursor".

The parameters for the simulations are listed in Table 1. Although no direct experimental data is available for this system, these parameters satisfy the experimentally derived operating parameters of Krumdieck *et al.* [15] and thus the simulations are expected to demonstrate the physical mechanisms behind PP-CVD reactor operation.

PP-CVD Simulation Results

The PIES model was used to track each particle through the helium carrier gas flow field until it was removed from the reactor or came into contact with the substrate and was deposited. Figure 2 shows the Mach 1 contour generated using the DS2V code along with precursor particle positions for argon precursor near the beginning and end of the injection phase for the $P_S = 100$ Pa ($t_i = 3.2$ ms) and $P_S = 1000$ Pa ($t_i = 0.32$ ms) cases. Here the precursor molecule positions have been projected onto the zero-azimuth plane.

Figure 3a gives the precursor conversion efficiency results for the $P_S = 100$ Pa and $P_S = 1000$ Pa cases for each precursor type. The efficiency was calculated by comparing the number of particles removed from the reactor to the number deposited.

Figure 3b shows film thickness profiles and deposition uniformity values for argon precursor for each of the supply pressure cases. Uniformity was determined statistically by recording the number of particles impacting per

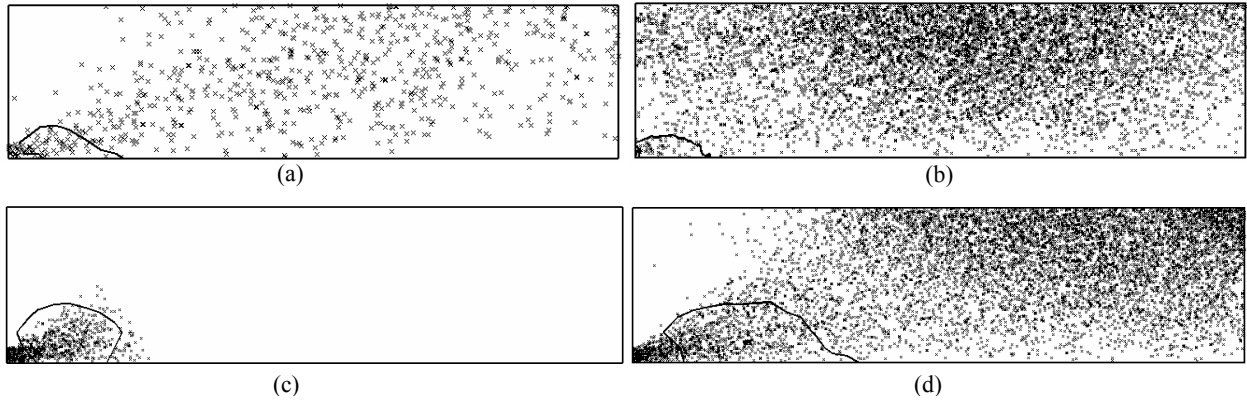


FIGURE 2. Mach 1 contours and argon "precursor" particle positions during the injection phase for a) $P_S = 100$ Pa at $t = 0.24$ ms, b) $P_S = 100$ Pa at $t = 3.1$ ms, c) $P_S = 1000$ Pa at $t = 0.024$ ms and d) $P_S = 1000$ Pa at $t = 0.31$ ms.

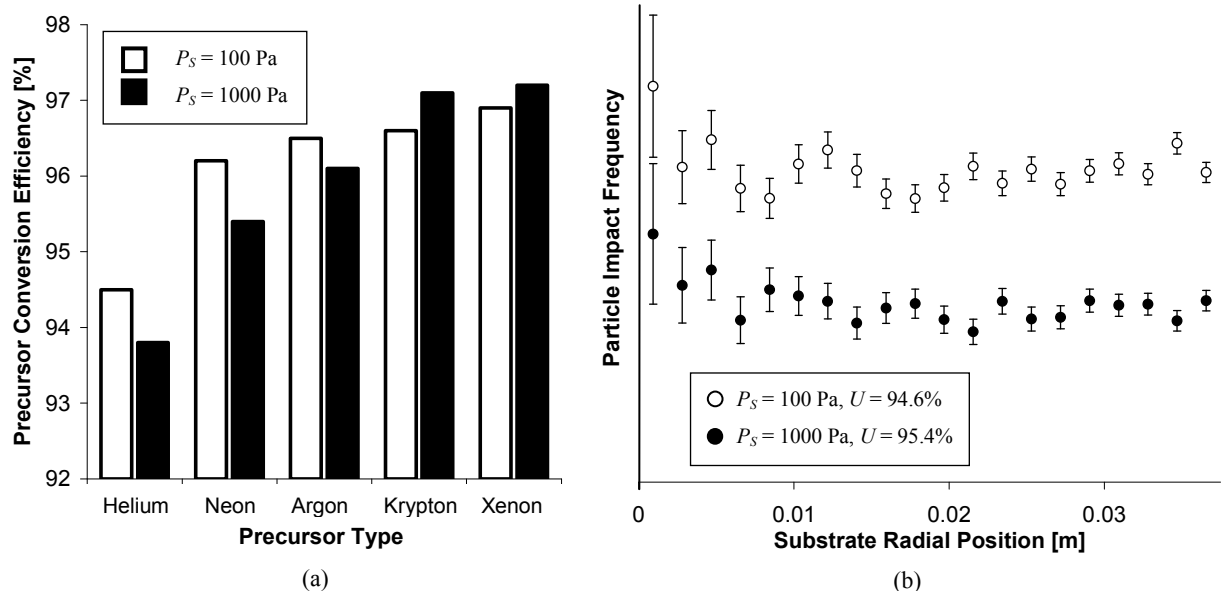


FIGURE 3. a) PP-CVD reactor efficiency for various precursors at different supply pressures and b) argon precursor film thickness profiles for the two different cases (profiles spaced for clarity).

unit area N' over M annular sampling areas and comparing this value to the mean deposition rate over the whole substrate using equation (2). In every case uniformity exceeded 85% and generally was more than 90%.

$$U = \left(1 - \frac{\sum_{i=1}^M |N' - \bar{N}|}{\sum_{i=1}^M N'} \right) \cdot 100\% \quad (2)$$

Comparison with Steady Flow Reactors

As a point of comparison, a number of steady flow reactors were also simulated. Here the supply pressure was set to either $P_s = 100$ Pa or $P_s = 1000$ Pa and the reactor pressure P_R was varied by adjusting the reactor evacuation rate. In each case the carrier gas was helium. Figure 4a shows the conversion efficiency for each precursor type for the two different supply pressure cases and several supply pressure to reactor pressure ratios. Figure 4b shows film thickness profiles and deposition uniformity values for two typical steady flow reactor cases. The uniformity depended on flow structure and precursor mass. Where the jet structure dispersed above the substrate, uniformity exceeded 90% in some cases however where the jet impinged on the substrate uniformity generally was below 50%.

DISCUSSION

The DSMC flow field simulations show that the region of highly supersonic flow upstream of the Mach disc expands rapidly during the initial part of the expansion and then contracts to a quasi-steady jet structure as the reactor pressure rises. After the inlet orifice closes at $t = t_i$, the jet structure collapses resulting in an approximately uniform flow field by $t = 2t_i$. The PIES model shows that this unsteady expansion process results in a highly uniform distribution of precursor particles downstream of the region of influence of the jet structure.

During the injection phase, a fraction of the particles arrive at the substrate because of the significant axial momentum imparted by the expansion process. Heavier precursor particles are scattered less by collisions with the carrier gas particles hence the fraction arriving during the injection phase is proportional to the precursor mass. This accounts for the increase in reactor efficiency as the precursor particles increase in mass. Longer injection times also

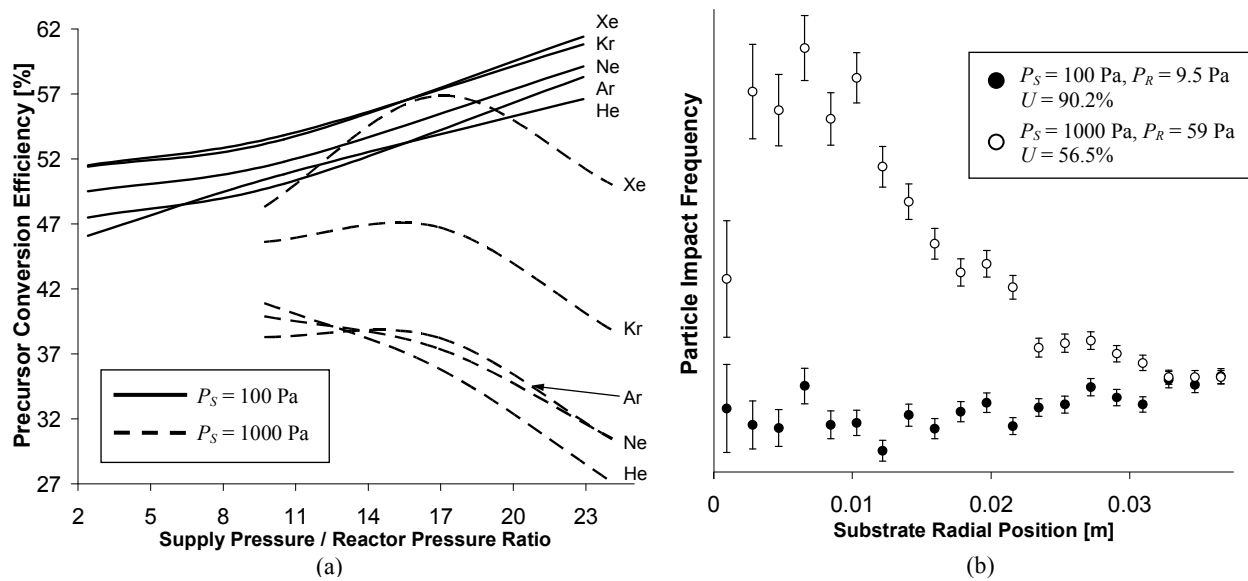


FIGURE 4. a) Steady flow reactor efficiency for various precursor gases at different supply pressures and b) examples of argon precursor film thickness profiles for two different cases (profiles spaced for clarity).

increase the fraction of particles arriving at the substrate during the injection phase.

After the jet structure collapses at the conclusion of the injection phase there is negligible bulk flow in the reactor volume and the precursor particles move to the substrate primarily via random molecular walk. The rate at which this diffusion process occurs is considerably higher than the rate at which particles can be removed from the reactor by the vacuum pump resulting in high precursor conversion efficiencies.

The uniform distribution of precursor particles at the end of the injection phase and the lack of significant bulk flow structures within the reactor also account for the high film deposition uniformity. Since precursor particles move to the substrate via random walk, there are no regions of high precursor concentration near the substrate and the resultant film profile is consequently of uniform thickness. It is expected that long injection times would decrease the uniformity of the films due to the development of quasi-steady bulk flow structures within the reactor. Heavier precursor particles would exacerbate this because of their high axial momentum and low scattering during the injection phase. The simulations demonstrated this to some extent, however this effect was offset by the slightly higher deposition rates towards the edge of the substrate due to the influence of the pump outlet, so the results are not entirely conclusive.

The results clearly illustrate potential advantages over steady flow reactors. In the steady flow case, bulk flow effects are always significant and consequently a large proportion of precursor particles are convected out of the reactor volume before they can diffuse to the deposition surface. Deposition uniformity was found to be poor especially when the steady jet structure impinged upon the substrate. The high momentum of heavy particles close to the jet's axis resulted in a film which was thicker towards the centre of the substrate and thin toward the substrate edges where precursor particles had to diffuse in a direction approximately normal to the bulk flow direction to reach the deposition surface. Steady flow reactors with jet structures which had dispersed well above the substrate had film uniformities equivalent to PP-CVD reactors, however precursor conversion efficiency was always inferior.

The limitations in the modeling method have not permitted the simulation of actual PP-CVD reactor systems meaning there is no corresponding experimental data to fully validate the results. However, the results are consistent with experimental studies which show that uniform deposition can be achieved when the injection time is as short as possible (to evenly distribute precursor particles in the reactor) and pump-down times should be relatively long (so that reactor bulk flow is negligible) [15]. Additionally, the predicted efficiencies are consistent with those achieved experimentally [3, 6, 7].

FUTURE WORK

The aim of the simulations was to investigate the physical mechanisms governing PP-CVD reactor efficiency and deposition uniformity as a first step in the simulation of actual reactors and the design of reactors for specific applications. The results presented in this paper have revealed a great deal about the PP-CVD process, however

there are a number of limitations which prevent it being used to simulate actual reactors including the relatively long process time scale and high supply pressure. The authors plan to collaborate with a research group to use hybrid continuum-DSMC, parallel DSMC or Model Boltzmann Equation (MBE) methods to simulate a more realistic flow field. The authors intend to use these simulation techniques, in combination with surface chemistry models, to investigate the capability of PP-CVD to deposit uniform films on substrates with complex shapes.

Some work is also required to incorporate a droplet evaporation model into the method and to calculate collision parameters for complex liquid metal-organic precursors so that reactors utilising liquid precursor delivery via an ultrasonic nozzle can be simulated.

Each of these tasks requires additional experimental work to validate the results of the simulations. The authors intend to deposit a diamond film from a methane / hydrogen mixture on a substrate in the vicinity of a hot wire in order to validate the gas precursor simulations, and further experiments will be carried out with metal-organic precursors to validate the model incorporating the droplet model.

CONCLUSIONS

In this paper, the DSMC technique was used to simulate the unsteady carrier gas flow field in a PP-CVD reactor. The PIES model was then used to track the paths of dilute precursor particles through this flow field. The simulations have revealed a great deal about the physical mechanisms governing the PP-CVD process. The rapid injection of the precursor into the reactor results in a highly uniform distribution of precursor particles which then diffuse to the substrate via random molecular walk during the pump-down phase. This leads to both high precursor conversion efficiencies and good film thickness uniformity, results which are consistent with experimental deposition data. The results also highlight the potential advantages over conventional steady flow reactors, which have low efficiencies and require careful design to achieve acceptable film uniformity.

ACKNOWLEDGMENTS

This research was conducted as part of Hadley Cave's PhD project under the sponsorship of the Tertiary Education Commission (Te Amorangi Matauranga Matua) Top Achiever Doctoral Scholarship scheme. The work was also supported by the Royal Society of New Zealand Marsden Fund Grant UOC203 and a University of Canterbury internal research grant.

The contributions of Dr. Maxim Lebedev, Asdis Kristinsdottir, Silviu Baluti, Joo-Young Lee, Raphael Albert Leonid Marcus and Ady Peled are gratefully acknowledged. We are grateful to Profs. J.-S. Wu and J.-C. Huang for their useful discussions on this research. We would also like to thank Prof. Graeme Bird for making modifications to his excellent DS2V software which enabled us to carry out the flow field simulations.

REFERENCES

- 1 M. Ohring, *Materials Science of Thin Films*, Academic Press, San Diego, 2002.
- 2 V. Versteeg, C.T. Avedisian and R. Raj, U.S. Patent No. 5,451,260 (13 April 1994).
- 3 S.P. Krumdieck and R. Raj, *J. Am. Ceram. Soc.* **82**(6), 1605-1607 (1999).
- 4 S.P. Krumdieck, O. Sbaizero, A. Bullert et al., *J. Am. Ceram. Soc.* **85**(11), 2873-2875 (2002).
- 5 S.P. Krumdieck and R. Raj, *Chem. Vap. Deposition* **7**(2), 85-90 (2001).
- 6 S.P. Krumdieck, *Acta Mater.* **49**, 583-588 (2001).
- 7 S.P. Krumdieck and R. Raj, *Surf. Coat. Technol.* **141**, 7-14 (2001).
- 8 G.A. Bird, *Molecular Gas Dynamics and the Direct Simulation of Gas Flows*, Oxford University Press, Oxford, 1994.
- 9 G.J. LeBeau and F.E. Lumpkin, *Comput. Methods Appl. Mech. Engrg.* **191**, 595-609 (2001).
- 10 I.D. Boyd, Y. Jafry and J.V. Beukel, *J. Spacecraft Rockets* **31**(2), 271-277 (1994).
- 11 H.A. Al-Mohssen and N.G. Hadjiconstantinou, *J. Comput. Phys.* **198**, 617-627 (2004).
- 12 J.F. Groves, "Directed Vapor Deposition", Ph.D. Thesis, University of Virginia, 1998.
- 13 K. Koura and H. Matsumoto, *Phys. Fluids A* **3**, 2459-2465 (1991).
- 14 H.M. Cave, S.P. Krumdieck and M.C. Jermy, accepted for presentation at: Process Intensification and Process Innovation II, Christchurch (New Zealand), September 2006.
- 15 S.P. Krumdieck, J.-Y. Lee and H. Raatz, *Electrochem. Soc. Proc.* **8**, 179-185 (2003).