Chapter 8

Vapor Transport Model Development

The deposition efficiency and spatial thickness distribution of films created by Directed Vapor Deposition synthesis have been shown to be sensitive functions of the flow conditions in the system. To explore the origins of the effects reported in Chapters 5 and 7, a detailed model for vapor transport in the low vacuum gas jets encountered in DVD has been developed using a Monte Carlo (i.e. stochastic) method (Fig. 8.1). The goal of this work was to build a high fidelity model of the deposition process so that the role of the many process parameters could be assessed and understood. The approach began by applying the Direct Simulation Monte Carlo (DSMC) method of G. A. Bird [141] to calculate the velocity, pressure, and temperature field data for the carrier gas flow throughout the modeled region. As described in section 2.2.5., the DSMC technique seeks to predict the position and momentum of all particles in the fluid system by conducting a direct physical simulation of the fluid problem, rather than solving the possibly valid Navier-Stokes equations or the complex, but certainly applicable, Boltzmann equation. By tracking binary collisions between a subset of representative atoms for the system, the DSMC method replicates the behavior of the much larger number of atoms actually involved in the flowfield.

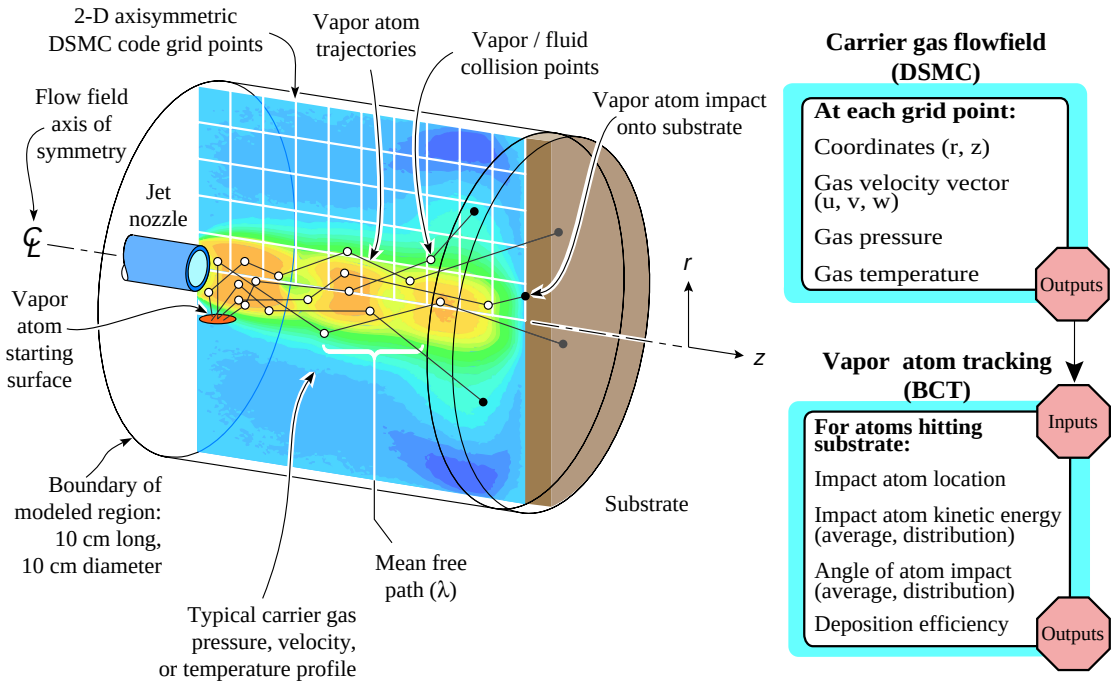

Figure 8.1 **Vapor transport modeling of DVD.** The modeling of this dissertation utilizes a Direct Simulation Monte Carlo (DSMC) code, shown here in a two dimensional axisymmetric configuration, to generate information about the carrier gas in the system. DSMC code outputs become the inputs to a bimolecular collision theory (BCT) model which determines vapor atom deposition information.

The output fields of the DSMC model are then used as the inputs to a biatomic collision theory (BCT) based model developed in this chapter to calculate the mean free path and velocity vector of individual vapor atoms contained in a carrier gas flow. By analyzing vapor atom trajectories with the BCT approach it is possible to calculate the vapor atom deposition efficiency, the spatial distribution of the film thickness, the impacting atom energy, and the impact angle of vapor atoms contacting the substrate. When combined with emerging microstructure models [29 - 33], these vapor transport model results help account for the experimental observations of a strong microstructure dependence upon

processing conditions [233]. The modeling approach is later used (Chapter 10) to drive design of an improved (second generation) DVD system.

8.1 Direct Simulation Monte Carlo (DSMC) Modeling of the Flowfield

8.1.1. Selection of discrete atom modeling method

As discussed at some length in Chapter 2 (section 2.2.5.), carrier gas flowfield properties can be analyzed using a continuum (Navier-Stokes equations) approach, a molecular (Boltzmann equation) approach, or a direct discrete atom simulation. The correct selection is determined by the “degree of rarefication” of the gas and the ease with which the applicable equations can be solved [141]. For moderately dense gases, the mean free path between atomic collisions is small compared with the size of physical objects in the system, continuum methods are valid approaches for the calculation of the flowfield, and solution of the Navier-Stokes equations can be accomplished using any number of commercially available CFD codes (e.g. Flow-3D from AEA-CFDS, Inc. [142]). At low gas densities atoms have much longer mean free paths and, as these distances approach the size of objects encountered by a flow, the continuum method breaks down. In this limit, flowfield properties can be obtained through an analysis of atomic collisions (i.e. either by solving the Boltzmann equation or by directly simulating the atomic collision problem [141].)

To determine the most appropriate modeling methodology for analysis of vapor transport during DVD, Knudsen numbers (equation (2.24)) were computed for the process conditions encountered in the experimental chapters of this dissertation. The decision was made to estimate Knudsen number at the nozzle throat for the selected conditions, using the noz-

zle diameter as the characteristic length substituted into equation (2.24). The numbers used for and the results of the calculations are shown in Table 8.1.

Table 8.1: Knudsen numbers for extreme experimental conditions

Mach Number	Gas Temperature (K)	Chamber Pressure (Pa/Torr)	Nozzle Diameter (cm)	Knudsen Number
1.45	300	27/0.2	1.27	0.01
1.95	300	540/4.0	1.27	0.0003

These numbers indicate that conditions *at the nozzle throat* can be modeled using any of the three methods listed above since only Knudsen numbers greater than about 0.1 preclude use of the Navier-Stokes equations. Still, as demonstrated in Chapter 4, the conditions in the DVD gas jet change rapidly as the gas travels through the processing chamber. For supersonic flow conditions, as soon as the carrier gas jet enters the chamber, it expands, and the pressure and temperature in the center of the jet decrease substantially, perhaps leading to free molecular flow (Kn > 0.1) in portions of the modeled volume where continuum techniques will not produce valid results. As Bird notes [234], “A Knudsen number of 0.1 has traditionally been quoted as the boundary between the continuum and transition regimes, but the characteristic dimension of complex flow fields may be specified in many different ways and the use of an ‘overall Knudsen number’ may be misleading.”

Because of uncertainties about the validity of the Navier-Stokes equations throughout the entire modeled volume and because of the difficulty of solving the Boltzmann equation, a discrete particle simulation method (e.g. DSMC) was chosen to simulate the carrier gas flow. Choice of this method for the initial carrier gas simulation also makes it easy to link the DSMC outputs in as the BCT model inputs for the vapor atom tracking portion of the DVD model. This choice of the DSMC method also makes possible modeling of any con-

ditions where the local Knudsen number reaches or surpasses the continuum limit of 0.1, (e.g. M = 1.45, chamber pressure = 6.6 Pa / 0.05 Torr), with the same code used for smaller Knudsen numbers. Finally, since the discrete atom DSMC method utilizes the same general solution techniques as those employed by the BCT model described in section 8.2, use of DSMC will facilitate the eventual integration of the two models into a comprehensive two (or more) component vapor transport model.

The validity of employing the Direct Simulation Monte Carlo method to model nozzle exhaust flows in low vacuum has been established in recent years by Boyd and others [149, 150, 151], where its primary use has been to understand the interaction of satellite rocket nozzle exhaust plumes with satellite components like solar arrays. The DSMC code used for this modeling work was obtained from Bird's recent book [141] and modified to the particular geometry and flow conditions of the DVD problem. The primary drawback to using the DSMC approach with Bird's code, designed to run on a single processor, is the significant length of time required to simulate high pressure process conditions. Use of a parallelized DSMC code could minimize this limitation [239]. Fig. 8.2 shows the computational sequence employed by Bird's DSMC code for flowfield data generation.

8.1.2. Adaptation of DSMC code to DVD

Modeling the carrier gas flow with the DSMC code (Appendix C) required the generation of a grid of points at which the pressure (P_c), velocity ($\mathbf{U}_c$), and temperature (T_c) of the carrier gas flow were recorded. The length and radial dimensions of the gridded region were based upon the DVD processing space employed for the experimental studies (Fig. 8.3), but, to simplify the modeling process, geometric asymmetries such as the crucible and scanning system were removed from the modeling configuration. This allowed a two-dimensional axisymmetric flow volume to be modeled using a rectangular mesh with a

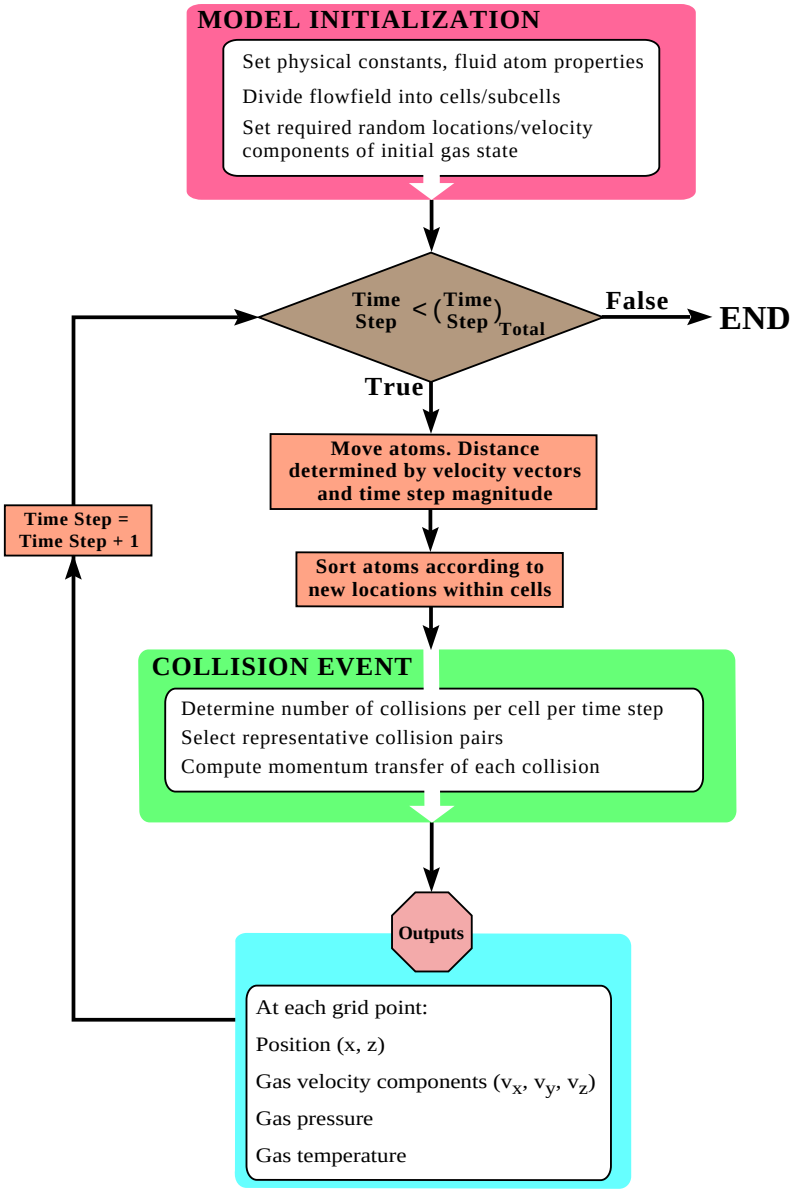

Figure 8.2 **A flowchart summary of Bird's DSMC code.** The computational sequence of G. A. Bird's Direct Simulation Monte Carlo code for modeling a two-dimensional axisymmetric flowfield.

line of symmetry about the flow's central (z) axis (Fig. 8.4). For all simulations, the spacing between adjacent gridpoints followed Bird's stipulation that cell dimensions, in flow

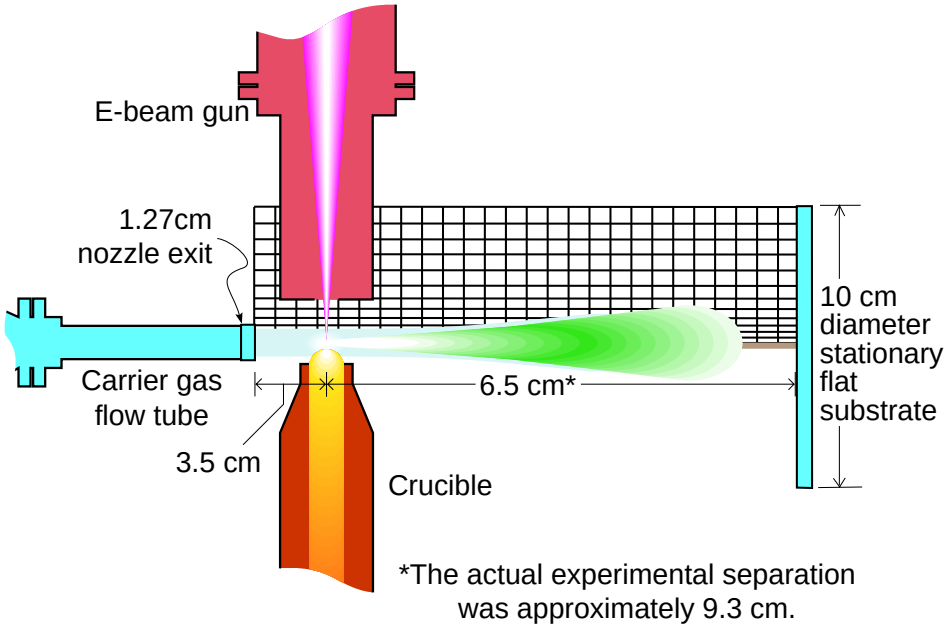

Figure 8.3 **An overlay of the DSMC modeling grid onto the experimental setup.** The locations of the primary DVD components used for the experimental deposition efficiency study define the relative positions of the nozzle, substrate, and crucible source for modeling.

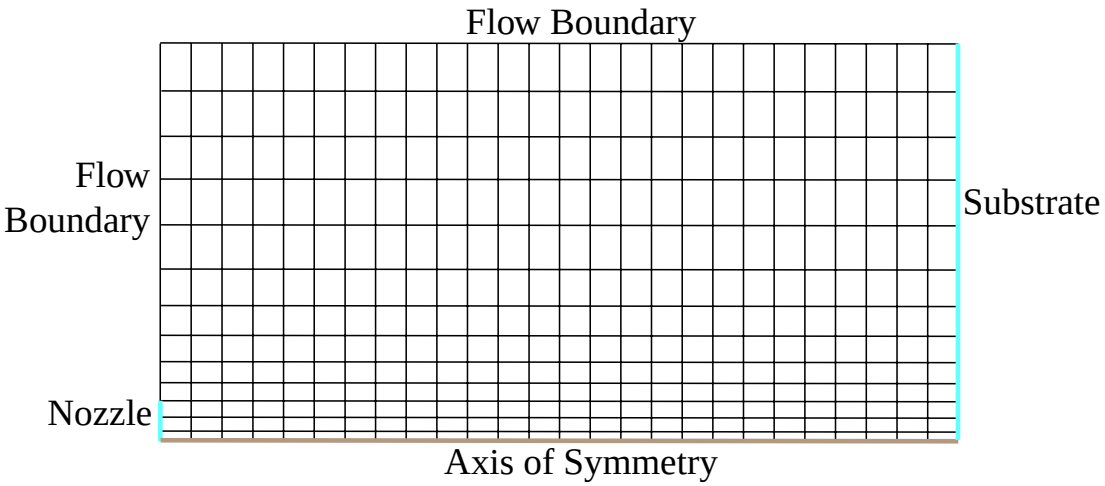

Figure 8.4 **Specifications for the DSMC modeling grid.** The basic DSMC grid configuration utilized for DVD calculations (10 cm long, 5 cm radial width).

regions with large macroscopic gradients, should be approximately one third the local mean free path, and time steps over which molecular motion and collisions are uncoupled conformed to Bird's suggestion that they be much less than the local mean collision time [141]. A greater density of gridpoints was placed along the main carrier gas flow line to capture the significant changes in pressure, velocity, and temperature when the flow accelerates out of the nozzle before slowing as it "senses" the substrate's presence and changes direction parallel to the substrate surface (e.g. Fig. 5.12 a)).

Unless noted otherwise, all simulations employed a nozzle radius of approximately 6.35 mm. One-dimensional isentropic[1] flow calculations of a compressible[2] fluid [116, 139] were used to determine the initial carrier gas pressure, velocity, and temperature at the nozzle exit since, as the gas passes from the mixing chamber into the nozzle, all three of these gas properties change. The magnitude of their change is dependent upon the fluid's ratio of specific heats and the Mach number of the flow. The validity of employing isentropic theory to establish initial conditions at the nozzle has been well established [150]. Fluid dynamics research has shown that for transonic (M = 1) or supersonic flow (M > 1), the velocity, pressure, and temperature conditions at the exit of the nozzle (i.e. the smallest cross-section through which carrier gas flows) always correspond to "choked" or Mach 1.0 conditions. This allows equations (2.19) and (2.20) to be used in combination with the following one-dimensional, isentropic flow equation to calculate the necessary input information [116, 139]:

$$\frac{T_o}{T_d} = 1 + \frac{\gamma - 1}{2} M^2. \tag{8.1}$$

In this equation:

[1] isentropic - entropy changes to not occur in the flow.
[2] compressible - density variations within the flow are nonnegligible.

T_o = Upstream temperature (K) and

T_d = Downstream temperature (K).

Thus, if the upstream (mixing chamber) temperature and pressure are 293 K and 667 Pa (5 Torr) respectively, equations (2.19), (2.20), and (8.1) indicate that the model inputs for the nozzle throat should be 220 K, 325 Pa (2.44 Torr), and 873 m/sec if a helium carrier gas is used. While these three equations can be used to predict the carrier gas pressure, velocity, and temperature at the throat and at some distance downstream, they do not describe the change in these properties accurately throughout the two-dimensional axisymmetric free-jet[1] expansion present in the DVD process. Thus the downstream flowfield's pressure, velocity, and temperature values must be determined using the DSMC code, with the one-dimensional isentropic flow values setting only the initial conditions at the nozzle throat.

For DSMC modeling of the DVD flowfield, Bird provides a large number of parameters which can be set to adapt his code to the particular problem under study. Within the main cells shown in Fig. 8.4, Bird's code allows subcells to be specified. The specification of these subcells helps to ensure that, when representative collision pairs are selected (Fig. 8.2), atoms as close to one another as possible are chosen for interaction. This helps to ensure that accurate results are generated by the code even if sharp velocity gradients exist across a single cell (e.g. in the vicinity of a Mach disk shock).

Bird's code also provides for the specification of radial weighting factors when conducting axisymmetric simulations such as the DVD simulations described here. Bird [141] explains that "The most severe practical problem associated with DSMC calculations for axially symmetric flows is the small fraction of the molecules that are located near to the axis. For example, if there are 50 equally spaced cells in the radial direction in uniform

[1] free jet - a gas flow expansion unconstrained by a diverging nozzle.