MONTE CARLO MODELING OF ATOM TRANSPORT DURING DIRECTED VAPOR DEPOSITION

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ABSTRACT

Atomic vapor transport has been investigated in the low vacuum (5 - 100 Pa) supersonic gas jets encountered in directed vapor deposition processes using a combination of Direct Simulation Monte Carlo (DSMC) techniques and a bimolecular collision model. The DSMC code generates the velocity vector, pressure, and temperature field for the carrier gas flow. This data is used as an input to a bimolecular collision model of atomic vapor transport in the flow. In the collision model, calculation of directed momentum loss cross-sections allows the location of carrier gas/vapor atom collisions to be deduced, and the vapor atom velocity vectors for individual vapor atoms to be tracked from source to substrate. For atoms arriving at the substrate, the impact location and velocity vector are obtained, making possible calculation of deposition efficiency, film thickness, adatom energy, and impact angle. These are the key inputs for simulations of resulting film microstructure/morphology evolution. Preliminary results for atomic transport of Cu vapor in supersonic He flows compare favorably with previously reported experimental observations.

INTRODUCTION

The quality of materials synthesized via physical vapor deposition processes depends upon their defect populations and microstructure. Recent studies have revealed that many process variables affect a film’s structure, including [1]:

1. The elemental composition of the depositing vapor.
2. The growth temperature.
3. The substrate material, cleanliness, crystallinity, and orientation.
4. The rate of deposition.
5. The kinetic energy of the atoms landing on the substrate.
6. The angle of incidence of the vapor atoms.
7. The nature of the background gas environment.

These material quality concerns are still an issue for many relatively mature deposition technologies (e.g. electron beam evaporation, sputtering, reactive/activated reactive evaporation, and ion plating). They are of central importance in the development of new, less expensive technologies like Directed Vapor Deposition (DVD) [2] and Jet Vapor Deposition™ (JVD™) [3]. By capturing vapor in a carrier gas stream, focussing it, and directing it onto a substrate, DVD (Fig. 1) and JVD™ afford the opportunity to vary important processing conditions widely and to use expensive metal, ceramic, and semiconducting source materials efficiently [4, 5].

The need to understand and optimize DVD and JVD™ processes has motivated interest in the analysis of vapor transport and deposition. Here vapor transport from source to substrate is analyzed for the DVD process using a combination of a Direct Simulation Monte Carlo (DSMC) technique, to describe the carrier gas flow, and a bimolecular collision analysis, to track the vapor atoms entrained in the carrier gas flow. The model outputs include thickness distribution, deposition efficiency and adatom energy and impact angle. The latter two outputs are the inputs of Monte Carlo/Molecular Dynamics models of film microstructure development [6-8], and thus development of this model will enable the eventual linking of processing method/conditions to film morphology/microstructure in DVD™ systems.
EXPERIMENTAL

The DVD system and the results of initial experiments conducted with it have been described elsewhere [4]. For modeling, it is important to recognize that the system utilizes a simple converging nozzle to produce an underexpanded axisymmetric free jet which accelerates to supersonic velocities upon entering the processing chamber (Fig. 2). Visual observations of the DVD carrier gas jet structure are possible due to excitation and ionization of both the evaporant and its carrier gas jet by the electron beam. The general structure of the jet from nozzle to substrate has been experimentally verified through visual observations and conforms to that described in the literature for similar nozzle configurations and pressure ratios [9, 10].

MODELING APPROACH

Direct Simulation Monte Carlo (DSMC)

The analysis has modeled the representative volume of Fig. 3. The accuracy of the DSMC method for simulating free jet expansions into low vacuum has been established [11]. The two-dimensional axisymmetric DSMC code used for this modeling work was obtained from [12]. It was modified to the particular geometry and flow conditions of this problem. The carrier gas was helium, and the relevant gas parameters were obtained from [12]. Grid dimensions followed Bird’s stipulation that cell dimensions, in flow regions with large macroscopic gradients, should be approximately one third the local mean free path, and time steps over which molecular motion and collisions were uncoupled conformed to Bird’s suggestion that they be much less than the local mean collision time [12]. The modeled volume measured 0.10 m in length and 0.05 m in radius with a nozzle radius of 0.0064 m. Isentropic flow calculations [13] determined the initial carrier gas pressure, velocity, and temperature at the nozzle throat. The validity of employing isentropic theory for this purpose has been established [11]. Five sets of flow conditions were
Figure 2  Upon leaving the nozzle, the carrier gas accelerates to supersonic velocity before slowing abruptly at the Mach disk. Depending upon the source-to-substrate distance, the flow may reaccelerate to supersonic velocities one or more times before being slowed by additional shocks. Finally, the substrate generates a wall shock which decreases carrier gas velocity in the axial direction to zero. The vapor atom velocity vector will be affected significantly by this carrier gas stream structure.

Figure 3  The DSMC code generates carrier gas flow field pressure, velocity vector, and temperature data at each grid point. This data provides the information necessary to calculate the mean free path and velocity vector of vapor atoms traveling through the flow.

simulated. A mixing chamber/processing chamber pressure ratio of 7.75 was analyzed since this was experimentally achievable over a wide range of chamber pressures. Isentropic theory indicates that this pressure ratio results in a Mach 1.95 flow. Five background chamber pressures (6.67, 13.3, 26.7, 53.3, and 93.3 Pa) were examined. The number of atoms simulated for each run was about 400,000. The flow field simulations were run on a 16 node IBM SP2 computer.
Bimolecular Collision Theory

A bimolecular collision technique was used to track the paths of neutral vapor atoms in a neutral, monoelemental carrier gas from source to substrate (or out of the modeled volume). During transport, vapor atoms collide with individual carrier gas atoms at intervals determined from mean free path calculations. Each collision event is treated as an elastic, momentum transferring event which changes the velocity vector of the vapor atom. The flow chart of Fig. 4 lays out the computational bimolecular collision model and its outputs.

Experiments have shown that the angular density, $I(\theta)$, of vapor atoms leaving a high-vacuum e-beam evaporant surface can be described by [14]:

$$I(\theta) = I_o \cos^n \theta$$

(1)

where $I_o$ = Normal vapor density (atoms/sec),
$n$ = 2, 3, 4, or more, and
$\theta$ = Angle from the normal to the vapor emitting surface.
In the vapor transport model, the initial direction of travel for individual atoms of copper conforms to a distribution in which \( n = 4 \).

The vapor atom source was placed a quarter of the distance from the nozzle to the substrate and 0.03 m below the modeled volume centerline with the crucible oriented as shown in Fig. 3. The emitted atom energy distribution from an electron beam heated surface has an average value of about 0.2 eV for Cu [14]. Atoms of this energy were launched from the source and allowed to propagate until they collided with a first carrier gas atom. Bird [12] and McDaniel [15] have both shown that the point at which such a collision occurs can be determined from the atom’s mean free path (\( \lambda \)) in a gas whose velocity distribution follows a Maxwell-Boltzmann distribution:

\[
\lambda = \frac{RT}{\sqrt{2}PN_A\sigma_d}
\]

(2)

where

- \( R \) = Universal gas constant (8.3145 J/(mol K)),
- \( T \) = Average carrier gas temperature along vapor atom’s path of travel (K),
- \( P \) = Average carrier gas pressure along vapor atom’s path of travel (Pa),
- \( N_A \) = Avogadro’s number (6.0221x10^{23} atoms/mol), and
- \( \sigma_d \) = Directed momentum loss cross-section for the specific gas/vapor combination.

For the problem under study, \( T, P \) and the carrier gas velocity (\( \mathbf{U} \)) vary along the vapor atom’s path of travel with variation of \( \mathbf{U} \) leading to \( \sigma_d \) variation with position in the flow. To account for these changes in the calculation of \( \lambda \), it was necessary to sample \( T, P \), and \( \mathbf{U} \) at discrete points along the vapor atom trajectory and compute average mean free path values. While \( T \) and \( P \) can be obtained directly from the DSMC code, the directed momentum loss cross-section (\( \sigma_d \)) must be separately computed [17, 18]. Here, classical two-body collision concepts were used [16]. The final calculated cross-section depends upon the relative kinetic energy of the two atom’s involved in a scattering event (\( E \)), an impact parameter (\( b \)), the center of mass scattering angle (\( \chi \)), and the angular differential cross-section (\( \sigma(\chi) \)).

When a vapor atom/carry g gas atom collision occurs, a molecular dynamics method can be used to compute momentum transfer [17, 18-20]. For the bimolecular collision model developed here, the universal potential of Ziegler et al. was used [21]. This repulsive potential fits theoretically generated potentials to laboratory data for randomly chosen atom pair interactions. Compared with other potentials (e.g. Moliere, Lenz-Jensen, and C-Kr), the universal potential produces better agreement between theory and experiment (standard deviation = 5%) [21].

While the output of the DSMC code provides an average carrier gas velocity value at each grid point, the atoms in the real carrier gas flow possess a distribution of velocities approximately described by a Maxwell-Boltzmann (normal) distribution [22]:

\[
\phi = n \left( \frac{m_c}{2\pi kT_c} \right)^{\frac{3}{2}} \exp \left( -\frac{m_c [(U_{\|} - U_c)^2 + U_\perp^2]}{2kT_c} \right)
\]

(3)

where

- \( \phi \) = Magnitude of the normal distribution for a given value of \( U_c \),
- \( n \) = Carrier gas atom number density (atoms/m^3),
- \( U_{\|} \) = Carrier gas velocity parallel to primary flow, and
- \( U_\perp \) = Carrier gas velocity perpendicular to primary flow.

Using the distribution function of equation (3), average velocity values of the carrier gas flow field can be distributed to create a more accurate description of vapor atom / carrier gas interactions. To generate deposited vapor distribution, efficiency, angle of impact, and energy of impact
information for the various processing conditions, the flow field data for each DSMC run was read into the bimolecular collision model, and the trajectories of 10,000 copper atoms were followed.

RESULTS AND DISCUSSION

DSMC modeling of the Mach 1.95 free jet flows revealed that, while the initial zone of silence and Mach disk were present for all conditions simulated, a second or third shock became evident only as the chamber pressure increased. The axial flow velocity vector for helium with a 26.7 Pa chamber pressure is shown in Fig. 5. The location of the shock structure is similar to DSMC results reported elsewhere [11].

![Graph showing shock locations and substrate](https://example.com/graph.png)

Figure 5  In this graph of axial flow velocity, a Mach disk and second normal are visible as the carrier gas expands and accelerates into the lower pressure processing chamber (26.7 Pa) before slowing to zero at the substrate wall. The nozzle diameter is 0.0064 m.

The average position, impact angle, adatom energy and deposition efficiency for the atom tracking simulations are summarized in Table 1. The center of the region of deposition moved downwards from near the top towards the bottom of the substrate as the chamber pressure increased, similar to experimental observations [4]. The spatial distribution of material on the substrate is shown in Fig. 6. The distributions of adatom energies and impact angles are shown in Fig. 7. The lower deposition energies and higher impact angles at low chamber pressures are due to the absence of the second and third shock regions which accelerate the vapor atoms into the substrate before they are deflected into the wall jet. After reaching a peak deposition energy or

<table>
<thead>
<tr>
<th>Chamber Pressure (Pa)</th>
<th>Vertical Position* (m)</th>
<th>Impact Angle (degrees)</th>
<th>Adatom Energy (eV)</th>
<th>Deposition Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.67</td>
<td>0.0353</td>
<td>24.9</td>
<td>0.092</td>
<td>10.36</td>
</tr>
<tr>
<td>13.3</td>
<td>0.0288</td>
<td>24.4</td>
<td>0.115</td>
<td>53.62</td>
</tr>
<tr>
<td>26.7</td>
<td>-0.0045</td>
<td>22.6</td>
<td>0.125</td>
<td>88.94</td>
</tr>
<tr>
<td>53.3</td>
<td>-0.0160</td>
<td>30.6</td>
<td>0.111</td>
<td>86.32</td>
</tr>
<tr>
<td>93.3</td>
<td>-0.0222</td>
<td>36.8</td>
<td>0.101</td>
<td>85.44</td>
</tr>
</tbody>
</table>

* Above or below the centerline of substrate
Figure 6  While the general shape of the vapor distribution for all simulations mirrored that shown here for the 26.7 Pa run, the location of the vapor concentration moved down the substrate as the chamber pressure increased.

Figure 7  a) Angular distribution for atom tracking simulations b) Adatom energy distribution for atom tracking simulations.

minimum impact angle, further chamber pressure increases result in a decrease in adatom energy and corresponding increase in impact angle as the atoms are more successfully turned into the wall jet by the higher gas density [4].

The deposition efficiency results exhibit a maximum at a chamber pressure of 26.7 Pa. This appears to follow a similar trend to that observed experimentally [4]. At low chamber pressures, the momentum transfer of the small number of carrier gas / vapor atom collisions is insufficient to redirect the vapor atoms to the substrate. At intermediate chamber pressures the vapor hits near the center of the substrate. As the chamber pressure increases further, the average deposition position of the vapor atoms steadily moves towards the bottom of the substrate, and deposition effi-
ciency decreases as vapor atoms are captured in the wall jet and carried beyond the bottom edge of the substrate [4].

CONCLUSIONS

The effect of a free jet expansion upon atomistic vapor transport has been studied using a DSMC method in combination with bimolecular collision theory. The vapor deposition efficiency, distribution, adatom energy, and impact angle strongly depend upon the chamber pressure. This is linked to changes in the shock structure of the free jet expansion. Deposition efficiency and distribution trends mirrored those observed experimentally. This modeling method appears to be a promising technique for understanding vapor transport in various physical vapor deposition technologies and for optimizing the design of such systems.

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REFERENCES