Chapter 2

Background

As noted in section 1.3 of the previous chapter, the core motivation for this dissertation’s research has been a desire to discover an improved method for the deposition of refractory elements, compounds, and alloys rapidly, efficiently, and with little contamination. As the previous chapter also noted, Storer [21] has suggested that an economically feasible method for depositing such film structures onto complex shapes could be some type of non-line-of-sight coating technique. When attempting to identify a vapor deposition method which meets all of these requirements, the desired process capabilities do not appear to be available in one existing technology.

Sputtering deposits material slowly (~1 µm/min [12] versus 1 mm/min for e-beam systems [11]). Sputtering rates are generally low due to the difficulty of sustaining the intense plasma discharge density necessary for higher rate deposition [12]. Standard e-beam technology generates low deposition efficiencies (only line-of-sight deposition) when coating small cross-section substrates like continuous fibers to be used in metal matrix composites. Non-line-of-sight coating does not occur in e-beam systems because evaporation in these systems almost always occurs in high vacuum (pressures less than $10^{-1}$ Pa / $10^{-3}$ Pa).
where material transfer occurs by collisionless, line-of-sight atomistic transport [11]. Resistive flash evaporators generally evaporate refractory materials slowly [12], and in these systems there is a risk of vapor stream contamination. Contact between a refractory evaporant source material (e.g. molybdenum) and an equally high melting point resistive heating target (e.g. tungsten) has a high probability of introducing both source material and heating target into the vapor stream. The apparent inability of any of these techniques to combine all of the desired processing abilities described in Chapter 1 has motivated thought about previously unconsidered material synthesis pathways.

This chapter examines the possibilities of modifying the desirable high rate electron beam evaporation tool so that it can perform uncontaminated line and non-line-of-sight material synthesis as efficiently as possible. In general, the process of vapor phase material synthesis consists of five steps:

1. Vapor creation.
2. Vapor transport.
3. Vapor adsorption onto the substrate.
5. Adatom movement by bulk diffusion through the growing film lattice to final positions.

Within the framework of these five steps, this chapter reviews the state-of-the-art of electron beam material synthesis and assesses its presently understood ability to synthesize engineering materials from the vapor phase.

---

1 133.3 Pa = 1 Torr, 1 atmosphere = 760 Torr = 101,300 Pa, space vacuum = $10^{-12}$ Torr
This examination of vapor phase material synthesis is generally limited to e-beam processing due to the complexity of the physical processes involved in producing vapor with an e-beam and due to the distinctly different manner in which other, less desirable, PVD techniques like sputtering produce their vapor (i.e. less desirable for the specific applications focussed upon in this research). This chapter examines current experimental and theoretical understanding of how to enhance an e-beam system’s vapor atom deposition distribution, efficiency, angle, energy, and form (monatomic or cluster). Finally, a brief examination of known relationships between processing parameters and final film microstructures at the end of this chapter illustrates why, if a new system can be invented, a uniquely configured e-beam system could provide vapor phase material processing engineers with an ability to synthesize unique engineering products by changing vapor transport, and thus vapor deposition, characteristics from those of a conventional e-beam PVD system.

2.1 Vapor Creation Using an Electron Beam Gun

When reliable vacuum pumping technology in the 1940’s first made it possible to achieve vacuums at or below the milliTorr range (~0.10 Pa), scientists made use of the resulting long electron mean free paths to generate electron beams that evaporated elements, alloys, and compounds for engineering material synthesis. Use of e-beams has been extensive over the ensuing years in part because of their ability to evaporate and deposit a large variety of materials rapidly, cleanly, and with a minimum consumption of energy [11].

2.1.1. Pure metal / metal alloy processing

E-beam systems have demonstrated an ability to evaporate and deposit not only easy to process pure elements like aluminum, zinc, gold, and silver but also more difficult to pro-
cess low vapor pressure elements like molybdenum, tungsten, and carbon, and highly reactive elements such as niobium, titanium, and tantalum [37]. E-beam systems evaporate and deposit all of these elements by cleanly bringing the heat source (electrons) directly into contact with the source material, often contained as a “skull” melt inside a water-cooled crucible (Fig. 2.1). A crucible is frequently used to contain the source material because it maintains solid source material (a “skull”) between the crucible wall and the molten evaporant pool, preventing vapor source contamination from the crucible.

Researchers have also demonstrated that alloys with a vapor pressure ratio as high as 1000:1 between their elements can be e-beam evaporated from a single crucible source and deposited with the correct chemical composition [38, 39]. This ability is crucial to the fabrication of materials for the MMC aerospace application described in Chapter 1 (e.g. deposition of Ti_xMo_{(1-x)}, (Ti_2Al)_xNb_{(1-x)}, or Ti-6wt%Al-4wt%V) [20, 21, 38, 39]. For alloys with elements having a greater vapor pressure ratio, lower melting point (and higher activity) material can be wire fed into a pool of the more refractory material [20] or separate element evaporation from adjacent crucible sources can be employed [11, 37]. When separate crucible evaporation is employed, alloys are created by mixing atomic fluxes as shown in Fig. 2.1.

E-beam processing of pure elements and alloys does present challenges to those attempting to control deposition characteristics precisely. During single crucible alloy processing, the initial vapor stream is rich in the more volatile component(s) of the feed-stock due to differences in evaporation rate for elements in the alloy. Langmuir [11] has provided a general relationship between an element’s evaporation rate, given as a mass flux, and its molecular weight, vapor pressure, and temperature:

\[ a \propto P_s \left( \frac{W}{T_v} \right)^{1/2} \]  \hspace{1cm} (2.1)
Chapter 2. Background

where 
\[ a = \text{Specific evaporation rate (kg/(m}^2\text{ sec)),} \]
\[ P_s = \text{Saturated vapor pressure at a temperature } T_v \text{ (Pa) [2],} \]
\[ W = \text{Molecular weight of the evaporant (kg/mol), and} \]
\[ T_v = \text{Absolute temperature of the evaporant (K).} \]

Not only do elements initially leave the crucible at different rates due to differences in vapor pressure but also, for some length of time thereafter, the compositions of the melt pool and vapor stream continue to change until the compositions of the solid rod stock and the molten pool reach a stable equilibrium (i.e. until the rate at which vapor constituents A and B leave the molten pool equals the rate at which they are introduced from the solid) [11, 12]. Reaching this equilibrium state adds significantly to the processing cycle time.

Figure 2.1 **Multicrucible e-beam deposition.** Material in region (AB) can create an alloy that is approximately of the correct composition if the substrate is translated.
(potentially hours), wastes valuable source material, and decreases system flexibility [11, 40]. While multiple crucible evaporation can sidestep this time dependent composition fluctuation, alloy processing from multiple crucibles in a high-vacuum e-beam system creates a stoichiometrically correct deposit only in that region above the crucibles where the vapor clouds of the neighboring crucibles intersect [11]. As a result, significant amounts of expensive vapor can be wasted (Fig. 2.1). Even in this region, small compositional differences exist as a result of variation in the vapor density distribution from the e-beam source and vapor collisions between species A and B which lead to different rates of interdiffusion [11]. Substrate translation is usually employed to reduce compositional gradations across the film surface.

In addition to vapor flux composition distributions which vary with time or position, all e-beam systems exhibit a vapor spatial density distribution which is nonuniform and dependent upon numerous process variables [39, 41]. It has been reported throughout the literature that atoms ejected from an e-beam target take on a distribution described by [12]:

\[ I(\theta) = I_o \cos^n \theta \]  

where \( I(\theta) \) = Vapor stream density in a direction \( \theta \) degrees from the normal to the vapor emitting surface,

\( I_o \) = Vapor stream density for \( \theta = 0 \), and

\( n \) = 2, 3, 4, or more.

While the vapor stream emerging from a planar surface element takes on a \( \cos \theta \) distribution (where \( n = 1 \)) [2], numerous authors note that e-beam vapor streams rarely exhibit this simple cosine vapor distribution for various reasons as described in Fig. 2.2 [11, 2, 42]. In addition to the influences shown in Fig. 2.2, e-beam vapor stream distributions also
depend upon the e-beam scanning cycle employed (rate and pattern) and the specific material evaporated [11, 38].

2.1.2. Compound processing

In addition to an ability to deposit pure elements and alloys, e-beam systems have demonstrated a reasonable ability to create material from compound sources. For compounds which are poor conductors of electricity and heat, some combination of reduced e-beam.

Figure 2.2  **Vapor distribution in an e-beam system.** Several factors can combine to modify an e-beam evaporator’s vapor flux distribution [11].

2.1.2. *Compound processing*

In addition to an ability to deposit pure elements and alloys, e-beam systems have demonstrated a reasonable ability to create material from compound sources. For compounds which are poor conductors of electricity and heat, some combination of reduced e-beam.
power densities (below $2 \times 10^7$ W/m$^2$) [1], specialized e-beam scan patterns [1], and partially dense source materials (e.g. 60% dense yttria-stabilized zirconia for TBC applications [43]) are usually necessary to prevent source material cracking and generate a controlled vapor stream. When working with complex compound source materials like yttria-stabilized zirconia, vapor pressure problems can arise that are similar to those described for single crucible alloy evaporation.

A more common problem during compound evaporation is dissociation of the constituent elements, an event which precludes stoichiometrically correct film creation unless the lost elements are replaced during deposition [11]. While some compounds exhibit minimal dissociation with little of the gaseous element being removed by the process chamber vacuum pump [11, 15], most require introduction of additional reactive gas into the work chamber for useful RE or ARE deposition [2, 11, 15, 37, 44, 45]. RE allows compounds to reform during deposition by introducing reactive species into the processing chamber and raising the chamber pressure as high as 1 Pa ($\sim 10^{-2}$ Torr). A primary drawback of RE for dense film synthesis is vapor atom thermalization\(^1\) leading to film porosity due to reduced adatom kinetic energy [11, 15]. Vapor atom thermalization during reactive evaporation has motivated development of ARE in which plasma-enhanced reactivity of the gas environment makes possible a decrease in reactive gas pressure, a corresponding reduction in gas/vapor collisions, and a minimization of vapor atom thermalization [11, 15].

2.1.3. Vacuum regime

E-beam material synthesis has occurred almost exclusively in chamber pressures below 10 Pa ($\sim 10^{-1}$ Torr). However, recent material processing efforts by Eastman, Halpern, and

---

\(^1\) thermalization- a change in the velocity and energy of an atom towards the average velocity and energy of the surrounding gas as the result of momentum transferring atomic collisions.
others [46, 47] have demonstrated that useful vapor phase materials can be created at higher chamber pressures. Eastman et al. have used e-beam evaporation to create nanophase $\gamma$-$\text{Al}_2\text{O}_3$ clusters with a mean grain size of 2.5 nm in a 1 Torr (~$10^{-2}$ Pa) oxygen rich environment while Halpern et al. have deposited resistively-evaporated gold by transporting vapor to a substrate in a helium gas jet at chamber pressures around 1 Torr.

Despite the work of Eastman and the development of RE and ARE processes for compound production which have utilized e-beam systems with chamber pressures up to 1 Pa (~$10^{-2}$ Torr), many researchers believe that e-beam film synthesis in reduced vacuum is not viable. This mindset has developed as a result of certain widely accepted “rules of e-beam processing.” The literature [11, 18, 37] generally states that e-beam vapor-phase processing must occur in high vacuum because:

- Operating an e-beam gun with pressures greater than $1\times10^{-2}$ Pa (~$10^{-4}$ Torr) in the electron generating workspace can result in dielectric breakdown of the reduced vacuum environment and high voltage arcing (i.e. shorting) between the negatively charged filament and nearby portions of the gun maintained at different electrical potentials. Thus, energy for source evaporation is instead transferred to the gun, potentially damaging it and preventing low vacuum e-beam processing [11].

- The tungsten filaments which generate electrons in many e-beam evaporation systems degrade rapidly in low vacuum or atmospheric pressure. Thus, if the vacuum in the filament workspace is poor, electron emission from the filament generates ions which bombard and erode the filament, preventing low vacuum processing [48].

- If the entire system’s pressure exceeds $1\times10^{-2}$ Pa, e-beam energy dissipation occurs via gas scattering in the gun and process chamber, and the energy is unavailable for material evaporation, making low vacuum e-beam processing unfeasible [11, 49].

- Conducting film synthesis in a low vacuum environment leads to vapor atom thermalization and poor quality deposit microstructures [11].
• Operating in high vacuum has often been considered necessary to avoid contamination [11, 50]. This belief has led to the development of long process cycles in which the chamber is evacuated below $10^{-2}$ Pa, the chamber and its internal fixtures are heated to “bake-out” contaminants prior to deposition, and deposition occurs at a pressure low enough to ensure few evaporant atoms react with contaminant particles. It has also produced processing rules stating that “for pure films a pressure/deposition rate ratio of $< 10^{-7}$ Torr/Å/sec [$10^{-5}$ Pa/Å/sec] must be achieved” [51].

Although many researchers have deemed e-beam vapor phase material synthesis in reduced vacuum impractical [11, 12, 37], other researchers have demonstrated the feasibility of low vacuum / atmospheric e-beam material processing.

The need to weld thick steel plates for ships and submarines and a desire to use e-beams to induce chemical reactions has motivated research into methods of conducting e-beam material processing at pressures above $10^{-2}$ Pa, even in open atmosphere [11]. These applications have led to the development of e-beam guns employing either transparent thin foil windows or differentially pumped gun sections to decouple the high vacuum e-beam generating space from the low vacuum / atmospheric processing region [11, 52 - 56]. While 25 µm thick electron “transparent” windows of Ti or Al work in e-beam guns employing high accelerating voltages (i.e. > 30 kV) and low power densities, an open unimpeded path from filament to target is required for high current density welding systems [53]. During the 1960’s, systems with such electron pathways were perfected in which electrons could be generated in a $10^{-5}$ Pa workspace evacuated by one pump, passed through two separately pumped gun segments at $10^{-2}$ Pa and 1 Pa, and used to weld metal parts at atmospheric pressure. While these welders occasionally experienced filament erosion or high voltage breakdowns resulting from sudden pressure rises in the filament workspace (due to vapor bursts from the workpiece), they have demonstrated the feasibility of low vacuum / atmospheric material processing [11].
E-beam operation under reduced vacuum or atmospheric conditions has also been improved by maximizing beam propagation through the gas environment in the gun and processing chamber. Fundamental investigations of e-beam / gas interactions by Boedecker, et al., Arata, and others [11, 49, 57] have revealed that the most important factors affecting beam propagation are the beam path length through the increased pressure, the e-beam’s accelerating voltage, and the molecular weight of the gas through which the beam propagates. Thus, when processing material under low vacuum or atmospheric pressure, beam propagation can be maximized by passing the e-beam into the elevated pressure regime close to the target and by decreasing the scattering cross-section of the gas in the processing chamber (i.e. by using a high e-beam accelerating voltage and a low molecular weight gas in the processing chamber) [48, 49].

2.2 Vapor Transport

After atomistic vapor has been created with a PVD tool like an electron beam gun, vapor transport to the substrate occurs either as a result of the vapor creation process itself (e.g. thermal evaporation energy) or can be effected by various external means acting upon the individual vapor atoms (e.g. interaction with electric or magnetic fields or as the result of collisions with gas atoms in the chamber). Indeed, the particular method and process conditions used to generate the vapor stream have been shown to influence significantly the spatial distribution, angle of incidence, kinetic energy, deposition efficiency, and form (e.g. monatomic or multatom clusters) of vapor atoms reaching a substrate. Process-induced modifications of these parameters critically affect film growth (section 2.3).
2.2.1. High vacuum vapor transport

Often, the inherent characteristics of a high vacuum e-beam vapor stream (e.g. deposition efficiency and spatial, angular, and energy distribution) do not coincide with the optimal vapor stream characteristics desired for an application.

2.2.1.1 Spatial distribution

As section 2.1.1. explained, the vapor distribution from an e-beam source can be described by equation (2.2) in which \( n = 2, 3, 4 \) or more. This diverging, nonuniform vapor distribution can cause material processing difficulties in some applications. For instance, when coating fibers, the vapor stream of e-beam systems (Fig. 2.3) leads to significant variation of the material deposition rate on neighboring fibers. The magnitude of this nonuniform coating (onto flat substrates) has been described using the following equation [11]:

\[
\frac{d_s}{d_{so}} = \frac{1}{\left[1 + \left(\frac{r_s}{h_v}\right)^{2(n+3)/2}\right]^{1/(n+3/2)}}
\]

(2.3)

where:  

\( d_s \) = Local film thickness on a flat substrate,

\( d_{so} \) = Film thickness directly above vapor source,

\( r_s \) = Distance from midpoint of substrate,

\( h_v \) = Source to substrate separation distance, and

\( n \) = Exponent as used in equation (2.2).

In the fiber coating application, nonuniform vapor deposition is generally undesirable and could result in improper fiber spacing in a consolidated composite material (Fig. 1.2).
2.2.1.2 Angular distribution

For all substrate surfaces, the diverging vapor streams of Figs. 2.1 - 2.3 lead to variation in the angle of vapor deposition with lateral position and with source-to-substrate separation. When coating large substrates with variable surface topologies (e.g., trenches and vias on 200 - 300 mm semiconductor wafers), this leads to an angular deposition which can prevent proper coating of non-line-of-sight surfaces [58].

2.2.1.3 Kinetic energy

During a thermal material synthesis process like e-beam evaporation, as energy is introduced into a liquid, some fraction of the atoms in the melt gain enough vibrational kinetic energy to escape into the vapor phase.
energy to overcome the intermolecular forces binding them to the liquid. Atoms leaving an e-beam melt generally have 0.1 - 0.2 eV of kinetic energy [59] and a tight energy distribution [60]. In the literature, the magnitude of the evaporation induced kinetic energy is generally related to the material’s vaporization temperature by the following Boltzmann temperature equation [11, 2, 61]:

\[ E = \frac{3}{2} k T_v = \frac{1}{2} m v^2 \]  \hspace{1cm} (2.4)

where  \( E \)  = Kinetic energy of the evaporated atoms (J),  
\( k \)  = Boltzmann’s constant (1.381 x 10^{-23} J/K), and  
\( T_v \)  = Vaporization temperature of the source (K).

Although it is not initially apparent why this relationship should be true, Maissel and Glang [2] have provided a semirigorous proof of equation (2.4). They explain that the speed \( c \) of any atom is comprised of three components \( u, v, \) and \( w \) perpendicular to each other. For an ensemble of atoms in a volume with different speeds, the mean square velocity of all \( N \) molecules is:

\[ \frac{-2}{u} = \frac{\sum u^2}{N} \]  \hspace{1cm} (2.5)

and the mean-square speed of those molecules is:

\[ c^2 = \frac{\sum c^2}{N} = \frac{-2}{u} + v^2 + w^2 \]  \hspace{1cm} (2.6)
Kennard [62] and Parker [63] have demonstrated that, within a volume $V$, molecules with a mass $m$ and a velocity $u$ exert a pressure:

$$P = \frac{N}{V} m u^2$$  \hspace{1cm} (2.7)$$
on a flat surface perpendicular to the direction of $u$. If the velocities in different directions are assumed to be uniformly distributed, then:

$$\frac{1}{u^2} = \frac{1}{3} \frac{1}{c^2}$$  \hspace{1cm} (2.8)$$

Substituting equation (2.7) into equation (2.8) yields:

$$P = \frac{N}{3V} m c^2$$  \hspace{1cm} (2.9)$$

Given the Universal Gas Law, an expression for the relationship between gas temperature and velocity can now be written:

$$\frac{1}{3} m c^2 = kT$$  \hspace{1cm} (2.10)$$

Multiplying equation (2.10) by 3/2 gives an expression for kinetic energy and also equation (2.4).

More recently, Asano et al. [59] have demonstrated experimentally that actual atom velocities are frequently above the level suggested by the basic relation of equation (2.4). In a study of uranium, titanium, and copper mean atomic velocities, Asano et al. found that the mean velocity of each atom type exceeded the predicted thermal mean velocity. Uranium’s velocity was 2.1 times greater than predicted by equation (2.4) while titanium’s was 1.6 and copper’s 1.3. Interestingly, Asano et al. concluded that the increase in velocity was the result of electronic excited state energy to kinetic energy conversion during adiabatic
expansion away from the molten vapor source. (The exchange of excited state energy for kinetic energy has been demonstrated elsewhere during atomic collisions between alkali metals [64].) Asano et al. [59] explained that the increase in velocity was less substantial for copper due to its smaller number of possible excited states.

Whether the adatom energies in thermal evaporation systems are 0.2 eV or 1.3, 1.6, or 2.1 times that level, Thornton [65, 66, 67, 68] has experimentally demonstrated that substantially more energy per atom must be introduced into a growing vapor phase deposited material (> 0.5 eV) to generate dense microstructures at low substrate temperatures. Zhou et al. have used molecular dynamic modeling methods to illustrate this same requirement [31]. As section 2.2.2.3 will discuss, this energy requirement has led to the development of various methods of adatom energy enhancement so that useful films can be created for dense film applications.

2.2.1.4 Deposition efficiency

Frequently, applications require that vapor be deposited only in select locations (e.g., into the vias of semiconductor wafers and onto fibers for continuous fiber reinforced metal matrix composite creation). In their most basic configurations, high-vacuum e-beam (and sputtering) systems lack the ability to redirect their vapor stream after it leaves the source with a \( \cos^\theta \) distribution. As a result, deposition into the deep trenches and vias which are a part of newer semiconductor devices is becoming increasingly difficult. Rossnagel et al. and Yang et al. have recently studied ways to tailor vapor stream angular distributions for the most efficient filling of electrical conduits on semiconductor devices [36, 54, 58, 69, 70]. The need to deposit materials efficiently in selected locations is also observed during line-of-sight fiber coating in high vacuum e-beam systems. Such systems often intersect little more than 5% of the total vapor stream (c.f. Fig. 2.3), allowing the rest of the highly refined, expensive matrix material to deposit uselessly onto the walls of the chamber.
2.2.2. Modification of vapor transport characteristics

Because the inherent characteristics of a high vacuum e-beam vapor stream sometimes do not generate desired material properties, researchers have developed ways to modify various aspects of the vapor stream [71].

2.2.2.1 Spatial distribution

Since the 1970's, researchers have investigated ways to modify vapor distributions to produce a more uniform vapor stream and to enhance non-line-of-site coating. One of the more successful methods for varying the vapor stream distribution in e-beam systems has been to raise the background processing chamber pressure above \(10^{-2}\) Pa (~10\(^{-4}\) Torr). Investigations by Beale and Grossklaus [44, 72] revealed that raising argon pressures to 0.1 Pa decreased the exponent for their \(\cos^n\theta\) distribution from 8 to 5.5, indicating that higher chamber pressure led to a less focussed, more uniform coating. Interestingly, experimental investigations by Erikson et al. [73, 74] showed that, at argon pressures of 1x10\(^{-4}\) Pa and higher, vapor focussing in their system became increasingly pronounced as chamber pressure rose (Fig. 2.4). While researchers generally agree that vapor distribution changes with varying gas pressure are the result of atomic collisions [11], the particular cause of vapor stream defocussing and then focussing with increasing chamber pressure has not been explained. In Erikson’s system, vapor atom clustering could have changed the effective mass of the vapor particles being scattered, decreasing their rate of lateral diffusion and increasing the focus of their final deposit. Alternatively, higher vapor pressures resulting from the elevated e-beam powers of Erikson’s study could have caused a more significant surface deformation of the source material and thereby generated a more focussed initial vapor stream (c.f. Fig. 2.2).
Another method investigated for vapor spatial density distribution variation has been substrate biasing. Erikson [73] reported that this did not change the distribution of vapor deposited from an ionized vapor cloud, and Krutenat [75] suggests that substrate biasing in combination with a plasma discharge between source and substrate led to “randomization” of the vapor stream and non-line-of-sight coating. The scattered depositions observed by Erikson and Krutenat are most probably the result of vapor/gas collisions between source and substrate with substrate biasing contributing little to vapor redirection. Although substrate biasing does not appear to affect vapor direction, Rossnagel et al. have shown that unbalanced magnetrons in sputtering systems are capable of affecting the distribution of vapor traveling from sputtering target to substrate [36, 54, 58, 70].

**Figure 2.4  Background gas pressure modifies vapor density distribution.** Results from Erikson’s study of medium vacuum e-beam deposition show an increase in vapor focus as argon chamber pressure is increased from 4 to 50 x 10^{-5} Pa. (Evaporation rate = 32 g/min. Source-to-substrate distance = 32.4 cm) [73]
2.2.2.2 Angular distribution

In sputtering systems, researchers have changed the angular distribution of vapor through the use of collimators and unbalanced magnetrons. Collimation [76] places a physical filter between source and substrate to allow passage of only the fraction of atoms traveling nearly normal to the substrate. While collimation facilitates microelectronic trench and via filling, it is slow and inefficient [76]. Use of an unbalanced magnetron, which forces charged sputtered particles to travel along electromagnetic field lines, has proven more useful as a means for efficiently modifying vapor distributions [58, 61]. In sputtering systems, Rossnagel and others [70] have successfully used electrostatic collimation to manipulate the ionized vapor flux angular distribution for more efficient trench filling.

2.2.2.3 Kinetic energy

In sputtering, cathodic arc, and certain RE/ARE e-beam systems negative bias voltages of 50 - 300 V are frequently applied to substrates to increase the energy of the incident charged species [12, 16, 18, 77]. Mattox [16] and others [78] realized in electron beam systems that interaction of the e-beam with the gas in the chamber created an ionized plasma of vapor atoms and chamber gas atoms. By applying a negative electrical bias (~100 V) to the deposition substrate, both ionized gas and vapor atoms could be accelerated towards the substrate as part of an “ion plating” process, imparting kinetic energies of 10-10,000 eV to depositing atoms [16]. Kinetic energies of this magnitude lead to significant film densification, the removal of some atoms deposited via sputtering, and the introduction of disorder into the growing film unless significant substrate heating is permitted.

2.2.2.4 Deposition efficiency

Limited studies have shown that PVD processing with moderate background chamber pressures can lead to significant non-line-of-sight deposition and, for certain system configurations, an increase in deposition efficiency [44, 79]. For flat substrate coating studies,
Bunshah and colleagues [44] reported an overall decrease in deposition efficiency with increasing chamber pressure, but, for substrates with surfaces not in the line-of-sight of the source, they noted that non-line-of-sight coating efficiencies could be enhanced by:

- Changing the mass of the scattering gas introduced into the chamber. Bunshah noted that, for a given chamber pressure, the amount of non-line-of-sight coating increases as the mass of the scattering gas molecule approaches that of the evaporant.

- Increasing the pressure of the scattering gas in the chamber. Introducing gas into the chamber increased non-line-of-sight coating, and higher chamber pressures resulted in more non-line-of-sight coating.

Bunshah and colleagues offered no physical insight into the root cause of these trends except to say that they were dictated by simple momentum exchange principles between gas and vapor atoms.

In a study of deposition onto fibrous substrates from a metal vapor laden Jet Vapor Deposition\textsuperscript{TM} inert gas stream, Hill [79] noted that the mass capture efficiency of the fibers was greater than the cross-sectional area occupied by the fibers. Hill attempted to explain his observations using a continuum-based vapor diffusion model designed to predict lateral diffusion of vapor atoms across carrier gas streamlines. While Hill only explored copper deposition in a helium chamber pressure of 4 Torr, he suggested that the magnitude of non-line-of-sight coating could be varied with changes to the carrier gas stream velocity (i.e. Mach number). Highest deposition efficiencies were reached at Mach numbers of 1.0 - 1.2 with decreasing deposition efficiency at higher and lower Mach numbers.

2.2.2.5 Evaporated material form

Material processing in medium or high vacuum with e-beam systems most often generates individual atoms of material which deposit on various substrates to form a multitude of important film products [11, 12, 37, 61]. While atomistic vapor is the most common mate-
rial form desired by those employing e-beam systems, some researchers have demonstrated that slight modifications to the PVD environment can lead to the formation of significant numbers of vapor clusters (agglomerations of atoms) [46, 50, 79-89]. As noted in Fig. 2.2, extremely high evaporation rates in conventional e-beam systems can lead to the formation of a virtual vapor source above the source material surface. In this region the density of vapor atoms is high enough to lead to vapor/vapor atom collisions, redistributing the vapor stream and in some cases leading to vapor cluster formation [11]. The results of Erikson [73] (section 2.2.2.1) also emphasize the important effects of clustering upon the material creation characteristics of a vapor deposition system.

Even when vapor densities are not extremely high, vapor atom cluster formation has been reported to be common in low vacuum processing environments [90, 91], suggesting that the background chamber gas plays a role in cluster formation. As Steinwandel and Hoeschele explain [92], the cluster nucleation process occurs via a series of steps in which individual atoms (A) and some other atomistic or molecular species (M) collide:

\[ A + A + M \leftrightarrow A_2 + M^* \]  \hspace{1cm} (2.11)

\[ A_2 + A + M \leftrightarrow A_3 + M^* \]  \hspace{1cm} (2.12)

\[ A_{n-1} + A + M \leftrightarrow A_n + M^* \]  \hspace{1cm} (2.13)

After the collision event the third species often becomes energized by the collision event (M*). Steinwandel and Hoeschele point out that “The reaction sequence [equations (2.11) - (2.13)] is frequently formulated without the three-body collision partner M. However, it should be noticed that three-body collisions are required due to the conservation laws of momentum, and energy for elementary reactions.” In the low vacuum environment, the third body will frequently be a background gas atom rather than a third vapor atom.
When attempting to describe cluster formation, numerous authors have taken a thermodynamic approach [86-88, 93-95] while others have pursued a kinetic activity explanation [96-100]. Study of the numerical results generated to date by both methods indicates that current kinetic models provide more reasonable predictions of experimental cluster formation results. Steinwandel and Hoeschele summarize [92]:

The classical [thermodynamic] theory of homogeneous nucleation is inadequate in order to describe the nucleation behavior of metal vapors at all degrees of supersaturation that could be realized experimentally. Nucleation appears to be a problem of elementary reaction kinetics in conjunction with a proper statistical thermodynamics formulation for stability criterions of small clusters.

The exact reaction kinetics and stability criterion appropriate to a particular system under study depend upon the characteristics of the system. For instance, as Smirnov and Strizhev note [100]: “The character of clustering is different for neutral and weakly ionized atomic beams. Ions of an atomic beam are nuclei of condensation, and the presence of charged atomic particles in an atomic beam is responsible for condensation of atoms.”

In a recent study of Jet Vapor Deposition™, a low vacuum vapor deposition technique, Hill [79] has calculated the probability of cluster formation for different processing conditions using a reaction kinetics approach and has used those results to delineate experimentally observed microstructures created during the coating of fibers. Hill calculated the importance of cluster formation by first determining the equilibrium concentration of unstable metal vapor dimer (i.e., prior to collision with a third body):

\[
[Cu_2^*] = \frac{[Cu]^2}{2} \left( \frac{4}{3} \pi (\sigma_{Cu}^3 - \sigma_{rCu}^3) \right)
\]

where \([Cu_2^*] = \text{Concentration of unstable dimers (dimers/m}^3)\),

\([Cu] = \text{Concentration of metal monomer (atoms/m}^3)\),
\( \sigma_{aCu} \) = Activity radius of a copper atom (m), and 
\( \sigma_{rCu} \) = Hard sphere radius of copper atom (m).

Hill then indicated that the rate of stable dimer formation could be derived from:

\[
Z_{Cu_2-He} = [He][Cu_2^*] \pi \left( \frac{\sigma_{aCu_2} + \sigma_{rHe}}{2} \right)^2 \left( \frac{8kT}{\pi \mu} \right)^{1/2}
\]  (2.15)

in which 
\( Z_{Cu2-He} \) = Volume collision frequency (collisions/m\(^3\)/sec) 
\( [He] \) = Concentration of background gas (atoms/m\(^3\)), 
\( \sigma_{aCu2} \) = Activity radius for the unstable dimer (m), 
\( \sigma_{rHe} \) = Hard sphere radius of a helium atom (m), and 
\( \mu \) = Reduced mass of collision, defined as \( 1/\mu = 1/\mu_{Cu} + 1/\mu_{He} \) (kg).

Stable dimer formation then makes possible the formation of larger clusters (N + 1 atoms) at a rate given by [79]:

\[
Z_{Cu_N-Cu} = [Cu][Cu_N] \pi \left( \frac{\sigma_{aCu_N} + \sigma_{rCu}}{2} \right)^2 \left( \frac{8kT}{\pi \mu} \right)^{1/2}.
\]  (2.16)

Assuming a sticking coefficient of one, the growth rate of a N-mer will be the collision rate seen by an individual N-mer [79]:

\[
\frac{dN}{dt} = \frac{Z_{Cu_N-Cu}}{[Cu_N]} = [Cu] \pi \left( \frac{\sigma_{aCu_N} + \sigma_{aCu}}{2} \right)^2 \left( \frac{8kT}{\pi \mu} \right)^{1/2}
\]  (2.17)

where \( 1/\mu = 1/\mu_{CuN} + 1/\mu_{Cu} \).
Finally, for a given set of processing conditions and a time of flight ($\tau$) for the metal atoms from source to substrate, Hill suggests that the average size of clusters ($N_{av}$) in a system is given by [79]:

$$N_{av} = \frac{1}{\tau} \int_{0}^{\tau} N(t) \, d\tau.$$  \hspace{1cm} (2.18)

While Hill has theoretically examined cluster formation rates, others like Dugdale [50] have experimentally explored how vapor phase nucleation of particle clusters affects film structure and has uncovered methods for avoiding cluster formation. Dugdale [50, 84] and others [46] have found that evaporation in low vacuum with an ambient temperature gas in the chamber can lead to homogeneous nucleation of vapor clusters and “the precipitation of powders which form friable and porous columnar structures” [50]. The parameters which determine when such structures appear include the evaporant material used, the evaporation rate, the specific ambient gas and pressure, the geometry of the system, and the temperature of the substrate [50]. Substrate heating alone does not eliminate the effects of vapor phase cluster nucleation upon microstructure. Further exploration by Dugdale [84] revealed however that the apparent effects of vapor phase cluster nucleation could be significantly reduced by heating the gas in the vacuum chamber as high as 600°C.

Dugdale [84] explained that chamber gas and vapor atom heating should theoretically decrease the vapor atom concentration, should increase the radius of a thermodynamically stable cluster [86], and should thus decrease the number of clusters which form. (The dependence of cluster formation rate upon temperature and vapor atom concentration has been examined in some detail elsewhere [86-88].) Dugdale concluded by reporting a reduction in cluster concentration as a result of heating the gas and vapor in his deposition chamber. This significantly changed film microstructure, from porous to dense columns.
While he did not suggest a physical explanation for the microstructural change, it is not difficult to envision that low energy cluster deposits form a porous material structure while individual atoms at a higher temperature create a denser microstructure (Fig. 2.5).

**Figure 2.5**  The effect of clustering upon deposited film morphology. A hypothetical comparison between the film structure formed during low energy cluster deposition and higher energy individual atom deposition.

2.2.3. Jet Vapor Deposition$^\text{TM}$

During the 1980’s a new method was invented for creating films in a reduced vacuum and for manipulating vapor stream characteristics (i.e. distribution, energy, angle, efficiency, and form) during transport from source to substrate [47, 85]. Jet Vapor Deposition$^\text{TM}$ (JVD$^\text{TM}$) used a nozzle and gas jet to transport atoms or clusters of atoms to a substrate for deposition. This technique represents an extension of the technology of high pressure ratio molecular beam separators to a lower pressure ratio regime [101-110].

JVD$^\text{TM}$ often employs either a thermal evaporation source (a resistively heated wire) or another non-electron-beam heating source in combination with an inert gas jet to create
vapor atoms, to accelerate those atoms from their thermally induced velocities, to concentrate the vapor stream through a spray nozzle, and to deposit the adatoms onto a substrate in a low vacuum (~ $10^{-2}$ Pa) (Fig. 2.6) [9, 10, 12]. JVD\textsuperscript{TM} employs vapor atom collisions with a carrier gas flowing towards the nozzle exit to redirect the vapor and reshape the vapor’s density distribution. Using a pressure drop into the chamber to accelerate the entire flow, the JVD\textsuperscript{TM} method then makes use of the inertial momentum of the vapor atoms to create a focussed deposit since, for a critical range of pressures, many of the vapor atoms cannot be turned into the wall jet by atomic collisions with the carrier gas before contacting the substrate (Fig. 2.6).

Figure 2.6  \textbf{Molecular beam deposition.} Once vapor atoms are accelerated through a nozzle, they can either impinge upon the substrate or be deflected into the wall jet. The pressure ratios shown are representative of those employed in a JVD\textsuperscript{TM} system [12, 79].

with a carrier gas flowing towards the nozzle exit to redirect the vapor and reshape the vapor’s density distribution. Using a pressure drop into the chamber to accelerate the entire flow, the JVD\textsuperscript{TM} method then makes use of the inertial momentum of the vapor atoms to create a focussed deposit since, for a critical range of pressures, many of the vapor atoms cannot be turned into the wall jet by atomic collisions with the carrier gas before contacting the substrate (Fig. 2.6).
Reported results from deposits created with molecular beam separators and JVD\textsuperscript{TM} processes suggest that they could have a unique ability to vary vapor atom spatial, angular, and energy distributions as well as deposition efficiencies and vapor atom forms [47, 80, 83, 101-112]. Though not reporting exact distribution information, JVD\textsuperscript{TM} results indicate that, by using a high molecular weight vapor atom / low molecular weight carrier gas combination (e.g. gold / helium), focussed, highly efficient, highly nonuniform deposits can be created on stationary substrates [47]. While reporting focussed, high deposition efficiencies for gold on flat substrates (95\%), Halpern et al. [47] and others [113, 114] do not provide information on the exact vapor atom spatial, angular, or energy distributions during transport and deposition. Hill [79] does present limited fiber coating deposition distribution data for the JVD\textsuperscript{TM} process with basic continuum-based model explanations for the observed experimental results. In other modeling work related to the JVD\textsuperscript{TM} process, de la Mora et al. [115] and Marple et al. [104] use continuum fluid flow concepts such as Stokes number and drag coefficient to examine the influence of vapor cluster mass upon deposition efficiency. Little in-depth analysis appears to be available in the literature though for a complete assessment of the rapid material synthesis abilities of these low pressure molecular beam systems.

In addition to an ability to affect vapor atom deposition efficiency and distribution, molecular beam separators and the JVD\textsuperscript{TM} process could have the ability to increase adatom kinetic energy by passing the vapor through a nozzle. First order estimates of the maximum velocity attainable through use of a nozzle can be determined using one-dimensional equations for isentropic flow of a compressible fluid [116]. The important governing relationships between pressure, temperature, Mach number, and jet velocity are given by:

\[ \frac{P_o}{P_d} = \left[ 1 + \frac{\gamma - 1}{2} M^2 \right]^{\gamma/\gamma - 1} \]  

(2.19)
and

\[ U = M \sqrt{\gamma R_s T} \]  \hspace{1cm} (2.20)

where

- \( P_o \) = Upstream pressure before the nozzle (Pa),
- \( P_d \) = Downstream pressure at the nozzle or in the chamber (Pa),
- \( \gamma \) = Ratio of specific heats (5/3 for helium and argon),
- \( M \) = Flow’s Mach number,
- \( U \) = Carrier gas stream speed (m/sec),
- \( T \) = Absolute temperature (K), and
- \( R_s \) = Specific gas constant (2077 J/(kg K) for helium, 208.1 J/(kg K) for argon).

2.2.4. Supersonic gas jet structure

While equations (2.19) and (2.20) give an upper bound to vapor atom velocity and kinetic energy exiting a molecular beam nozzle, multidimensional shock waves further downstream in low vacuum supersonic gas jets slow the carrier gas from supersonic velocities as the gas and vapor travel toward the substrate [117], making vapor atom velocity and position prediction with these one-dimensional equations impossible (Fig. 2.7). Two of the most important features of a supersonic nozzle expansion are the so-called zone of silence, where the gas flow accelerates to supersonic velocities, and a Mach disk, at which the gas flow rapidly decelerates to velocities below Mach 1 (Fig. 2.7). In addition to these structures, Adamson and Nicholls and others [117, 118] note that when a supersonic jet exits into a low vacuum (above a pressure of ~1 Pa), weak secondary shock structures can be present downstream of the sharply defined Mach disk.
The initial, expanding zone of silence is formed when the “high” pressure gas in the nozzle enters the chamber and expands in an attempt to match the lower background pressure found in the processing chamber. In many instances in which the background pressure is high enough to allow for a continuum description of atomic interaction, the nozzle exhaust overexpands, creating a lower pressure in the zone of silence than that found in the surrounding chamber. As a result, the background pressure forces the overexpanded barrel shock to narrow.

Figure 2.7 **Structure of a continuum free-jet.** The general structure of a continuum free-jet expansion has been well characterized [117-120]. The structure shown here is considered to be continuum-based since its existence requires a high enough density and collision frequency to allow for the definition of density and equilibrium temperature within the length scale of the apparatus [118].
At some point downstream, the compression waves surrounding the barrel shock coalesce to generate a diamond shock or a Mach disk shock if the pressure ratio \( \left( \frac{P_o}{P_d} \right) \) is significantly above the level necessary to generate supersonic flow (2.05 for helium and argon). Depending upon the pressure in the processing chamber, this expansion and contraction sequence can be repeated as the jet attempts to reach equilibrium with the surrounding gas. Subsequent shock waves beyond the initial Mach disk are of decreasing strength as viscous effects dissipate the jet’s energy [117]. While the zone of silence represents the primary region of supersonic flow, the repeated expansions of the jet downstream can create small additional regions of supersonic flow. The final major feature of the flow is the wall jet. Once the gas flow interacts with the substrate, the speed of the gas jet toward the substrate slows dramatically, a concave wall shock forms, and the gas is forced parallel to the substrate [120]. In sum, the idea of using a carrier gas stream to facilitate vapor deposition appears intriguing, but the technique is not well characterized or understood.

Interaction of the vapor atoms and carrier gas with the substrate undoubtedly decreases the adatom velocity component directed toward the substrate as the vapor atoms are redirected into the wall jet (c.f. Fig. 2.6). While the correlation between velocity and kinetic energy for vapor atoms of selected mass is simple \( E = \frac{1}{2}mv^2 \), little experimental or theoretical work has been done to determine the actual velocity of adatoms reaching the surface in a vapor deposition system utilizing a nozzle and gas jet.

2.2.5. Vapor transport modeling

Because of the development of low and medium vacuum technologies such as diode sputtering and JVD™, theoretical understanding of vapor transport for materials processing has become a point of focus in recent years. Numerous researchers have investigated vapor transport issues in these systems and have realized that modifications to initial
vapor stream characteristics result from collisions with gas atoms in the processing chamber which affect vapor deposition properties of the system (e.g. depositing atom energy, angle, and distribution) [121-137]. To understand the significance of vapor transport effects upon material deposition characteristics and to optimize the design of vapor deposition systems operating in medium or low vacuum, researchers have three primary avenues along which to investigate the phenomena: solution of the Navier-Stokes equations, solution of the Boltzmann equation, or direct physical simulation of the gas flow.

The Navier-Stokes equations [116] are a set of partial differential equations that represent the equations of motion governing a fluid continuum. While in actuality a fluid flow represents collision events between the individual atoms of a gas or liquid flow, under many conditions the Navier-Stokes equations allow the properties to be defined and solved for in a continuum (average) sense. One form of the Navier-Stokes equations is shown below in Einstein’s tensor notation [138]:

\[
\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x_j} \rho u_j = 0 \tag{2.21}
\]

\[
\rho \frac{\partial u_i}{\partial t} + \rho u_i \frac{\partial u_i}{\partial x_j} = -\frac{\partial P}{\partial x_i} + \frac{\partial}{\partial x_j} \sigma_{ji} \tag{2.22}
\]

\[
\rho \frac{\partial H}{\partial t} + \rho u_i \frac{\partial H}{\partial x_j} = \frac{\partial P}{\partial t} + \frac{\partial}{\partial x_j} (\sigma_{ji} u_i - q_j) \tag{2.23}
\]

where

- \( t \) = Time (sec),
- \( x_i \) = Position (m),
- \( u_i \) = Velocity (m/sec),
- \( \rho \) = Density (g/cm\(^3\)).
\[ \begin{align*}
P &= \text{Pressure (Pa)}, \\
H &= \text{Total enthalpy (kJ)}, \\
\sigma_{ji} &= \text{Viscous stress tensor (Pa), and} \\
qu &= \text{Heat flux (W)}. \\
\end{align*} \]

Whether or not it is appropriate to use the Navier-Stokes equations to analyze a fluid flow problem is determined through calculation of the dimensionless Knudsen number (Kn) of a flowfield \cite{116}:

\[ (Kn) = \frac{\lambda}{L} \]  \hspace{1cm} (2.24)

where \( \lambda = \text{Mean free path (m), and} \)

\[ L = \text{Characteristic dimension of the modeled geometry (e.g. source to substrate separation) (m)}. \]

As laid out by John \cite{139} and Shames \cite{140}, a Knudsen number greater than 0.1 represents the transition to free molecular flow at which point a Boltzmann equation solution or discrete atom simulation must be employed rather than the continuum Navier-Stokes equations. To estimate the validity of continuum based computations, a quick calculation of \( \lambda \) can be made using the following equation \cite{126, 141}:

\[ \lambda \equiv \frac{1}{\pi d^2 n} \]  \hspace{1cm} (2.25)

where \( d = \text{Gas atom hard-sphere diameter (m), and} \)

\[ n = \text{Gas atom number density (atoms/m}^3). \]
While several researchers have used the Navier-Stokes equations to examine vapor transport for materials synthesis [112, 125, 142] there are drawbacks to use of these equations. First, the continuum method does not provide information about individual atoms as desired for simulations of film growth [29-33]. Second, the Navier-Stokes equations which most commercial continuum codes employ often have difficulty capturing the phenomena associated with vapor transport at many of the rarefied processing pressures utilized [116, 139]. As Shames notes [140]:

The continuum breaks down when the mean free path of the molecules is of the same order of magnitude as the smallest significant length in the problem [e.g., nozzle diameter in a JVD™ system]. Under such circumstances we may no longer detect meaningful, gross manifestations of molecules. The action of each molecule or group of molecules is then of significance and must be treated accordingly.

In a slightly different explanation Bird [141] goes on to note that the Navier-Stokes equations can no longer be used once it becomes impossible to relate average values of appropriate molecular quantities such as shear stresses and heat fluxes to macroscopic quantities such as pressure, temperature, and velocity. According to Bird [141]:

More specifically, the transport terms in the Navier-Stokes equations of continuum gas dynamics fail when gradients of the macroscopic variables become so steep that their scale length is of the same order as the average distance travelled by the molecules between collisions, or mean free path.

An alternative to the use of the Navier-Stokes equations is solution of the older Boltzmann equation dating from 1872 which can be used to describe molecular behavior in a fluid
over a much wider range of Knudsen numbers, from Kn less than 0.001 to Kn greater than 100 [141]. The Boltzmann equation is shown below [143]:

\[
\frac{\partial f}{\partial t} + u_j \frac{\partial f}{\partial x_j} + F_j \frac{\partial f}{\partial u_j} = \frac{\partial f}{\partial t}
\]  

(2.26)

where  
- \( f \) = Velocity distribution function of a gas,  
- \( u \) = A single atom’s velocity function, and  
- \( F \) = Some external force acting upon the gas atom at time \( t \).

(The right side of the equation represents the change in the velocity-distribution function for the total gas with time as the result of binary collision encounters (\( e \)) at a fixed point. Chapman and Cowling [143] provide a thorough explanation of the origin of this equation.) The major drawback to using the Boltzmann equation for analysis of vapor transport has been the difficulty of obtaining solutions to the complex equation. A notable exception is the Chapman-Enskog solution of the Boltzmann equation for “a restricted set of problems in which the distribution function \( f \) is perturbed by a small amount from the equilibrium Maxwellian” distribution [141]. Solutions such as Chapman-Enskog will not always be valid in material processing systems where gas atom velocities are far from Maxwellian, e.g. supersonic gas expansion from a nozzle.

To attack problems of this type, researchers have turned to direct physical simulations of the gas flow in which computers are used to calculate the interaction of many thousands or even millions of representative atoms as they collide with one another or interact with boundaries in simulated physical space. Solutions for both steady and unsteady state problems are obtained by averaging over many small time steps. Some of the most recent vapor transport material processing modeling efforts of this type have been produced by Elsing, Knotek and others [121-124] in which vapor transport in diode sputtering has been
simulated. While providing a hint of the type of adatom deposition energy and angle information which can be produced by direct physical simulations of vapor transport, these initial efforts have been limited.

Proper theoretical description of the individual collision processes requires the use of interatomic potentials, energy dependent atomic cross-sections, and classical mechanics describing the collision of two bodies moving in three dimensions [58, 126-136, 144]. Elsing, Knotek, and others [121-124] have not employed any of these basic concepts in their models. In addition, their sputtering results assume that the gas atoms are stationary during collisions with energetic vapor atoms. Finally, they base their adatom energy and angular distribution conclusions upon the simulation of a limited number of atoms (~100), a number too small to eliminate statistical fluctuations from the results [137]. Simulation of just 100 atoms by Elsing and Knotek highlights one of the primary drawbacks to stochastic modeling of individual atom collisions, the computational expense of trying to track the many moles of atoms actually involved in vapor transport.

One of the more fully developed methods of direct physical simulation of thousands or millions of atoms in a gas flow is the Directed Simulation Monte Carlo (DSMC) method originally developed by G.A. Bird [141]. This method has been used extensively in recent years and has built a solid reputation as a modeling tool through comparisons of model results with independent laboratory experiments [120, 141, 148-151] for a number of engineering problems, including vapor transport [147, 148]. While providing reasonable accuracy, the DSMC method tries to minimize the computational expense of direct physical simulations by making certain approximations such as the use of variable hard sphere (VHS) and variable soft sphere (VSS) estimates of atomic dimensions rather than more accurate, but computationally expensive, estimates of energy dependent atomic cross-sections [141]. There are some indications that these estimates lead to discrepancies between
model and experiment [152, 153]. Bird [141] discusses that the problem with the VHS approximation is that “this scattering law is not realistic and that the cross-section is independent of the relative translational energy \( E = \frac{1}{2}mv^2 \) in the collision. Other than at extremely low temperatures, the effective cross-section of real molecules decreases as \( c_r \) [velocity] and \( E_t \) increase.” Bird also notes that even when the more sophisticated VSS model is invoked “the diameter varies in the same way as the VHS model, but the deflection angle is...” given somewhat more accurately.

In general though, use of the general DSMC method to model low vacuum vapor transport could provide a vital link between current understanding of vapor creation and general vapor deposition characteristics in this environment. Indeed it is probably the preferred method of simulation for studying the vapor transport problem due to its reliance upon a direct physical simulation of the problem, an approach valid at all mean free path lengths encountered in medium or low vacuum vapor transport. Reliance upon continuum methods could introduce severe uncertainty into results. The flow structure shown in Fig. 2.7 not only has significant changes in Mach number associated with various portions of the gas flow but also large changes in pressure and mean free path [110, 118]. While continuum equations could be valid in one portion of the flowfield, they could be quite inaccurate in others. Reliance upon DSMC methods, based on discrete particle concepts valid across the entire important range of Knudsen numbers, appears to be justified. Accurate prediction of deposition distributions, energies, impact angles, efficiencies, and forms with DSMC methods could provide accurate input to molecular dynamics and Monte Carlo simulations of vapor adsorption and diffusion on a substrate for the design of engineering structures [29-33].
2.3 Vapor Adsorption and Diffusion on a Substrate

The ultimate motivation for creating and transporting vapor to a substrate is the formation of useful engineering products from the vapor phase. Extensive research to date [12, 29-33, 61, 68, 154-182] has already provided great insight into what vapor creation and transport based processing parameters affect vapor phase material structural development. Although microstructure formation will not be a focal point of this dissertation’s research, the generation of desired, useful microstructure is ultimately the reason for developing a system which can manipulate vapor atom transport characteristics.

The desire to create films repeatedly and economically and to understand how the entire deposition process determines the film microstructure and properties has led researchers to explore film growth through experiments [12, 68, 154-173] and computer-aided modeling [29-33, 61, 174-183]. Much of this work has focussed upon understanding what determines the occurrence of point, linear, and planar defects during film nucleation and growth, the presence of chemical imperfections, and the formation of amorphous, polycrystalline, or single crystal deposits - all critical microstructural variables affecting the final physical properties of films in engineering applications. Many of the contributors to Bunshah’s book note [12] agree that the most important factors affecting vapor phase material growth are:

- Elemental composition of the depositing atoms [156],
- Film growth temperature [66, 155],
- Deposit thickness [65],
- Substrate material [1], cleanliness [183], crystallinity [1], and orientation [1, 61],
- Rate of deposition [66, 174],
- Kinetic energy of the atoms landing on the substrate [30, 179],
• Angle of incidence of the vapor atoms [76, 154], and
• Presence and nature of a surrounding gas phase [66, 159, 162, 163, 165, 169, 171-173].

As these parameters have been identified, efforts have focussed upon the development of processing roadmaps which can aid engineers as they design film synthesis equipment by showing the influence of the various parameters upon microstructure (e.g. Figs. 2.8 and 2.9). Both figures show how several of the factors listed above affect film microstructure.

Figure 2.8  *Thornton’s zone diagram*. Experimental study of sputtering (e.g. Ti, Cr, Fe, Cu, Mo and Al) revealed repeatable microstructural trends - improving material quality with higher temperature and lower chamber gas pressure [66].

The underlying cause of a significant portion of the reported microstructure variation appears to be the directed energy of the adatoms. In Fig. 2.8, as chamber pressure increases, vapor atom thermalization becomes greater, and, as Zhou et al. [31] explain, adatoms depositing with lower energies and at normal incidence have a limited ability to
move across the film surface to form a dense microstructure. Similarly, decreasing the substrate temperature makes less energy available to depositing adatoms. As a result, their ability to jump from one site on the surface to another is minimized, again leading to a more porous structure.

Both Figs. 2.8 and 2.9 highlight the dramatic changes which can be made to material structure as deposition parameters are varied. Experimental and modeling work to date has allowed many of the basic, important process-property relations to be uncovered and many significant vapor phase film processing technologies to be developed which can manipulate the important process parameters to create film products. While current technology based on this general understanding of deposition is capable of producing highly

Figure 2.9 **Vacancy concentration as a function of adatom energy.** Two dimensional molecular dynamics modeling, using an embedded atom method to describe interatomic interactions, reveals a lattice site vacancy concentration dependence upon incident Ni adatom energy; deposition rate = 10 nm/ns [31].
engineered films, most researchers acknowledge that process capabilities must evolve and that process models of vapor creation, transport, and deposition, beyond the level of general film growth roadmaps, must be developed and employed during film synthesis to attain tomorrow’s more stringent specifications.

Indeed, some researchers believe vapor creation, transport, and deposition models will have to be incorporated into closed-loop, real-time process control systems (e.g. Intelligent Processing of Materials (IPM) [184, 185]) which utilize in-situ sensors throughout the process to ensure quality film creation. The work of Yang, Zhou, Johnson, and Wadley [29-33] to model deposition phenomenon represents an effort to move beyond general roadmaps and towards material design tools and eventually closed-loop control.

2.4 Summary

The preceding examination of electron beam film synthesis illustrates that e-beam systems have a strong ability to process a great number of elements, alloys, and compounds. At the same time, study of e-beam vapor deposition distributions, efficiencies, angles, and energies reveals that, for certain applications, an ability to chose the desired range of these parameters for different applications could enhance the attractiveness of electron beam systems to material processors.