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Molecular Models for DSMC Simulations of Metal Vapor Deposition

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Abstract. The direct simulation Monte Carlo (DSMC) method is applied here to model the electron-beam (e-beam) physical vapor deposition of copper thin films. A suitable molecular model for copper-copper interactions have been determined based on comparisons with experiments for a 2D slit source. The model for atomic copper vapor is then used in axi-symmetric DSMC simulations for analysis of a typical e-beam metal deposition system with a cup crucible. The dimensional and non-dimensional mass fluxes obtained are compared for two different deposition configurations with non-uniformity as high as 40 % predicted from the simulations.

Keywords: direct simulation Monte Carlo; vacuum technology; thin-film deposition

1. INTRODUCTION

Metallic thin-film materials are widely used in manufacture of integrated circuits, micro-electro-mechanical systems and composites. Chemical vapor deposition (CVD), plasma-enhanced CVD (PE-CVD) and electron beam physical vapor deposition (EBPVD) are some of the most widely used deposition techniques for metals. The metal thin film properties such as the grain size, residual stress and film thickness depend strongly on the vapor flows formed during the deposition. A description of the metal vapor flow based on non-equilibrium kinetic theory of gases is required to predict the resultant spatial variation of parameters such as incidence angle and energy that play a key role in determining the film properties.

Accurate modeling of vapor flows using the DSMC technique requires the specification of a suitable molecular model for the vapor of interest. Such collision models are usually based on the measurements of transport properties such as coefficient of viscosity or thermal conductivity of the gas phase of a substance. However, such measurements are difficult to perform for non-volatile materials such as metal vapors. The main goal of this work is to evaluate various molecular models for metal vapors of interest, determine suitable models for use in DSMC simulations of vacuum thin-film deposition processes, and apply it to a vacuum deposition system of practical interest using a typical commercially available EBPVD system.

The remainder of the paper is organized as follows. Section 2 briefly describes molecular models relevant to this work. Section 3 discusses the DSMC simulation conditions. Results and discussion are presented in Section 4 with Section 5 reserved for conclusions.

2. MOLECULAR MODELS FOR METAL VAPORS

One of the most important inputs to a DSMC simulation is the molecular model that specifies the interaction between the simulated molecules. The most commonly used molecular models in DSMC including the hard sphere (HS) and Variable Hard Sphere (VHS) models neglect the large range attractive force that exists between molecules. The variation of viscosity as a function of temperature for the VHS model is given by the form

$$\mu = \mu_{\text{ref}} \left(\frac{T}{T_{\text{ref}}} \right)^{\omega} \tag{1}$$

where μ_{ref} is the viscosity at the reference temperature T_{ref}. The mean free path, λ, for the VHS model is given by[1]

$$\lambda = \frac{1}{\sqrt{2}\pi n d_{ref}^2 (T_{\text{ref}}/T)^{\alpha}} \tag{2}$$

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where $\alpha = \omega - 0.5$. The HS model is a special case of the VHS model and corresponds to ω = 0.5 or α = 0.0. The most widely used model that accounts for the attractive component of the force between molecules is the Lennard Jones potential model[2]. The Lennard-Jones potential describes intermolecular interaction in the form

$$U = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{3}$$

where, U is the potential energy, ε the depth of the potential well and σ the distance at which the inter-molecular potential is zero. For copper-copper interaction, parameters of Lennard-Jones(LJ) potential based on experimental data on cohesive energy at room temperatures are reported [3] as $\sigma = 2.277 \times 10^{-10}$ m and $\varepsilon = 0.415$ eV. The LJ potential parameters obtained using the empirical correlations of Bird *et.al*[4] are given by[5] $\sigma = 2.242 \times 10^{-10}$ m and $\varepsilon = 0.281$ eV. The two LJ potential parameter sets are used to calculate the variation of viscosity as a function of temperature given by[6, 7]

$$\mu = \frac{5}{8\sigma^2}\sqrt{\frac{mkT}{4\pi}}\frac{V}{W^{(2)}(2)} \tag{4}$$

where V and $W^{(2)}(2)$ are functions of kT/ε tabulated [6, 7]. Fan *et.al* suggest molecular models for various metal vapors including copper and the suggested VHS parameters are given by d_{ref} = 0.6271 nm, ω = 0.849, and T_{ref} = 2000 K. Figure 1 compares the variation of viscosity as a function of temperature obtained using the LJ potential parameters with the variation obtained using various VHS and HS molecular models. Models 1, 2, and 6 have been suggested in previous works[8, 9, 10] while models 4, and 5 agree well with the viscosity variation predicted by the two LJ models.

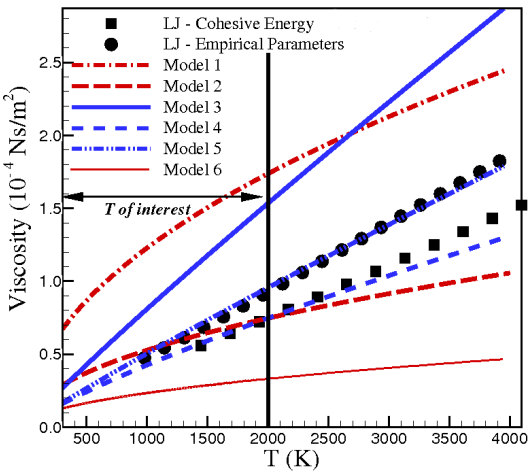

FIGURE 1. Comparison of variation of viscosity as a function of temperature for two Lennard-Jones potential models and various VHS and HS models used in previous computational studies of atomic copper vapor.

3. DSMC SIMULATION PARAMETERS AND FLOW CONDITIONS

The DSMC simulations presented here correspond to the experimental conditions of the electron-beam deposition of copper[11]. Figure 2 shows a schematic of the geometry. The equilibrium mass flux of vapor effusing from the source is entirely determined by the jet temperature and is given by $m_f = n\bar{c}/4$[1] where n is the saturation number density and $\bar{c}$ is the average velocity.

In our DSMC simulations, we have the jet temperature and hence the mass flow rate as a free parameter for reasons described in detail in [5]. The DSMC simulations presented in this work were performed using the 3D version

of the SMILE[12] software system and consider six molecular models as tabulated in Table 1. The details of the DSMC simulation parameters used in the simulations are given in [5]. DSMC simulations were performed for various molecular models and jet temperatures. Varying the molecular model changes the Knudsen number (Kn) and varying the jet temperature results in different mass flow rates and hence different Knudsen numbers.

TABLE 1. Summary of molecular models used in DSMC simulations

Model No.	Model Type	d_{ref} (nm)	T_{ref} (K)	α
1	HS	0.234	300	0.000
2	HS	0.357	300	0.000
3	VHS	0.450	300	0.420
4	VHS	0.550	300	0.310
5	VHS	0.570	300	0.420
6	VHS	0.627	2000	0.349

4. RESULTS AND DISCUSSION

4.1. Comparison with Experiments

Three-dimensional DSMC simulations of metal vapor flow from the e-beam system shown schematically in Fig. 2 were performed for various molecular models and source temperatures. The atomic copper vapor flow field computed for a source temperature of 1860 K using model 4 is shown in Fig. 2. The density contours are shown here for the three planes normal to the x, y and z axes respectively.

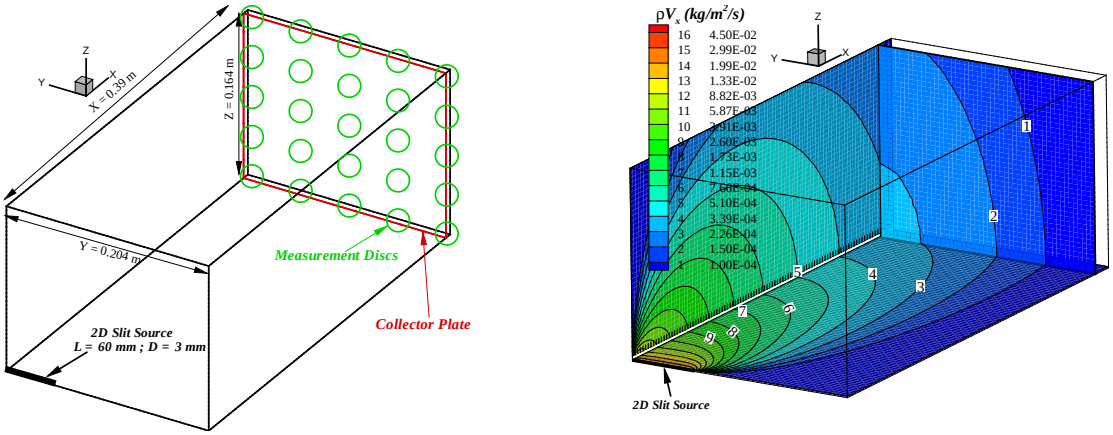

FIGURE 2. (Left) Schematic of the experimental set-up/computational domain for DSMC simulations and (right) Contours of mass flux on three slices of the three-dimensional flow field for a source temperature of 1860 K obtained from DSMC simulations using model 4.

For a DSMC simulation to give reliable predictions of the deposition process, it is needed that dimensional mass fluxes from the simulations agree with experiments. The agreement of non-dimensional mass fluxes alone is not sufficient because the non-dimensional quantities would lead to a good agreement as long as the Knudsen number of the simulations agrees well with the experiments. Figure 3 shows the comparison of dimensional and non-dimensional mass flux at various locations on the collector plate for the experiments and DSMC simulations performed using different molecular models corresponding to one of the deposition conditions in [11].

For these simulations the temperature of the slit source was chosen such that the Knudsen number of all the DSMC simulations considered for a given case in the experimental data were the same. This Kn was chosen by performing a number of DSMC simulations for various Kn and comparing the non-dimensional mass flux profiles with those obtained from the experiments. For Case 2, the Kn of the simulations shown is approximately 0.098. This can be clearly seen in the comparison of the non-dimensional mass flux profiles in which the profiles for the various DSMC simulations and the experiment agree extremely well. However, the dimensional mass flux profiles for the various

DSMC simulations are significantly different and only the DSMC simulation performed using molecular model 3 agrees well with the experiments. A similar trend was shown for other experimental conditions corresponding to various *Kn* numbers with model 3 leading to very good agreement between DSMC simulations[5] and the experiments.

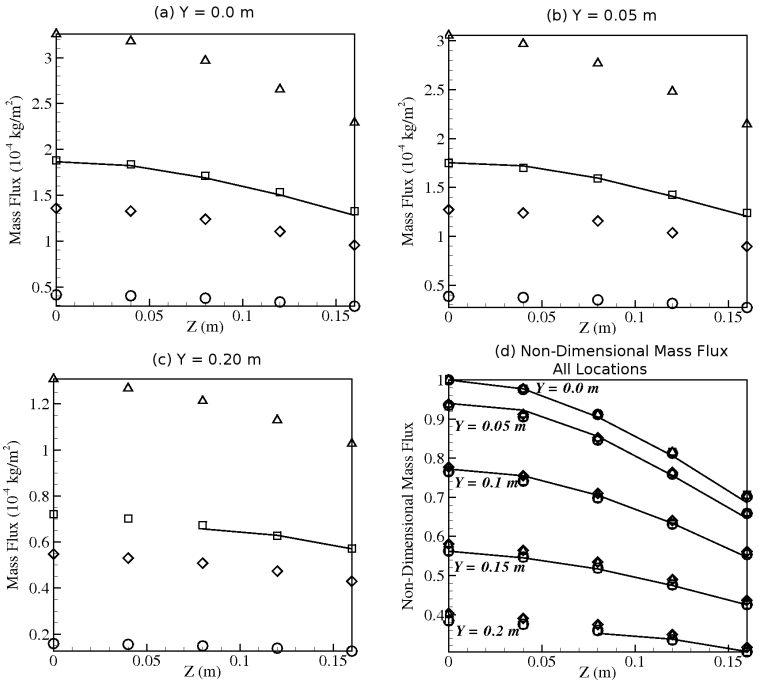

FIGURE 3. Comparison of DSMC simulations and Experiments. Δ - Model 1 ; ♢ - Model 2 ; □ - Model 3 ; ○ - Model 4 ; ∇ - Model 5 ; ◁ - Model 6 ; Solid line - Measurements.

4.2. Application to EBPVD system with a cup crucible

The molecular model corresponding to model 3 was used to simulate thin film deposition of copper using the cup-shaped *EVCFABEB-13* Fabmate crucible and an EBPVD system manufactured by Kurt J. Lesker company. A schematic of the deposition setup as used in Birck Nanotechnology center at Purdue is shown in Fig. 4.

The copper vapor expanding from the source is deposited on a 0.3048 *m* (12 *in*) substrate placed at a distance of about 0.3556 *m* (14 *in*) from the source exit plane. The electron-beam is used to heat the copper in the source which then expands into vaccum to be deposited on the substrate. Also shown in Fig. 4 is the geometry of the cup crucible *EVCFABEB-13*. The dimensions for the cup crucible are given by A=0.03759 *m*, B = 0.017 *m*, C = 0.003175 *m*, $D = 15^\circ$ with a total volume of 8.2 *cc*. The exit diameter of the source is 0.03124 *m*.

The *EVCFABEB-13* cup crucible was modeled using the axisymmetric version of SMILE and two different deposition conditions were considered. The first case had the source filled up to the brim wih copper pellets whereas the second case considered a half-filled source. The situation in which the source is half-filled commonly occurs in small scale depositions where a given deposition does not utilise all the copper in the filled source. The temperature was fixed at 1800 *K* corresponding to $Kn = 0.07$ based on the exit diameter of the source.

Figure 5 shows the number density and Knudsen number contours for deposition using both the filled and half-filled sources. A *Kn* of about 0.07 at the source location increases to 10 at a distance of 0.25 *m* from the source exit. Figure 6 shows the dimensional and non-dimensional mass flux profiles for both the filled and half-filled cases. The non-dimensional mass flux profiles do not vary significantly for the maximum angle of about 23° considered in our DSMC simulations. However, the dimensional mass flux decreases by about 20 % at the axis for the half-filled source. Figure 6 also compares the non-dimensional mass flux predicted by the cosine law for free-molecular flow.

The non-dimensional mass flux using a cosine law has been obtained by taking into account the different radial distances of various points on the substrate from the source location. The non-dimensional mass flux profile with these

corrections is given by $\cos^4\theta$. The deviation of the non-dimensional mass flux from cosine law can be attributed to the *Kn* of 0.07 which corresponds to the transitional regime with the presence of significant collisional region near the source exit.

The general consequence of depositing thin films using a half-filled crucible is to decrease the dimensional mass flux at the substrate location whereas the non-uniformity of the deposited films remains the same for both the cases. The decrease in dimensional mass flux implies that to deposit a film of the same thickness it takes longer when the source is half-filled compared to when the source is fully filled. The DSMC simulations predict a non-uniformity about 40 % for the thin films deposited using the cup crucible.

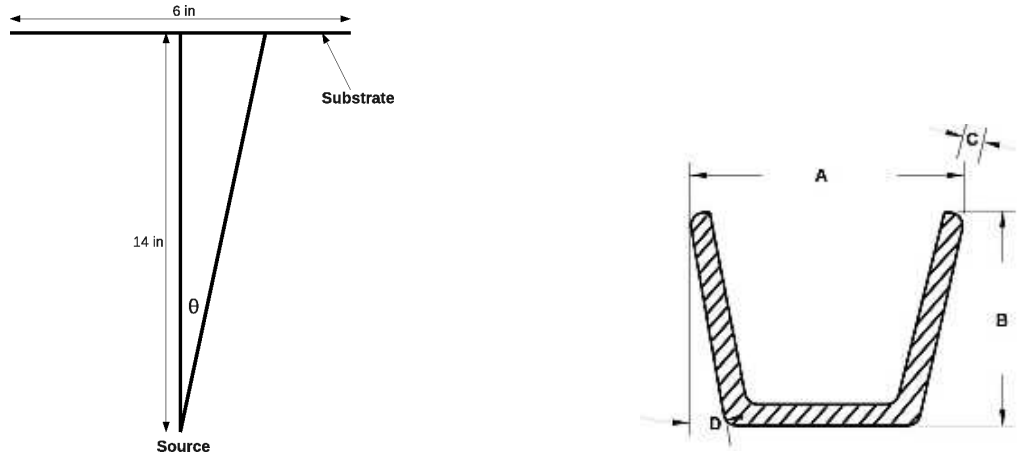

FIGURE 4. Schematic of deposition set-up as used in the Birck Nanotechnology Center at Purdue and the *EVCFABEB-13* cup crucible (*Source : www.ulet.co.kr - Unlimited Enhanced Technology*).

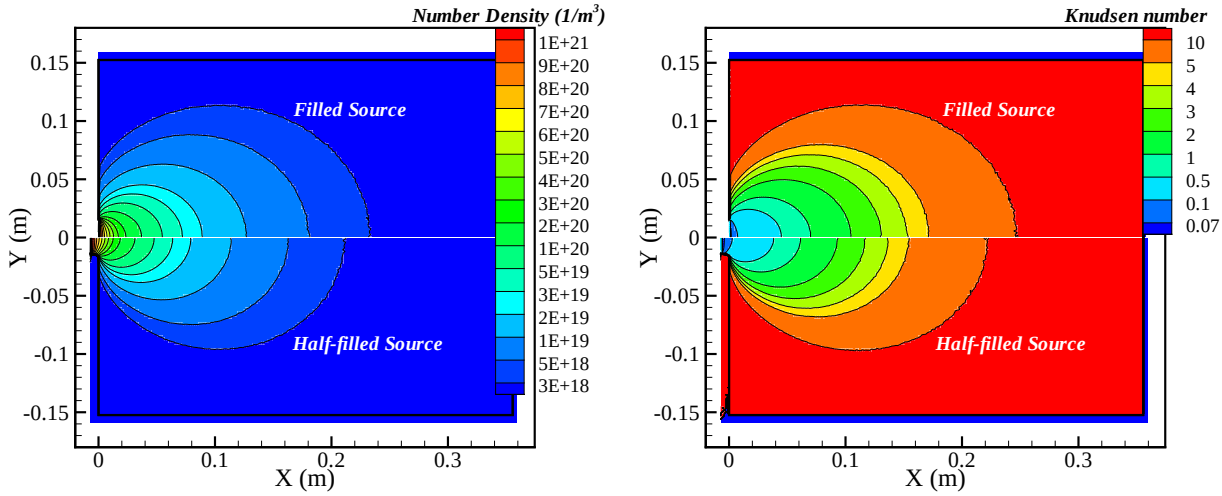

FIGURE 5. Comparison of number density and Knudsen number contours for the filled and half-filled cup crucible.

5. CONCLUSIONS

DSMC simulations were performed for the electron-beam physical vapor deposition of copper thin films to determine a suitable molecular model for copper vapor. Predictions for the non-dimensional and dimensional mass fluxes obtained using various variable hard sphere (VHS) models were compared with published experimental data. A VHS model with a higher effective viscosity than the Lennard-Jones models leads to a very good agreement with

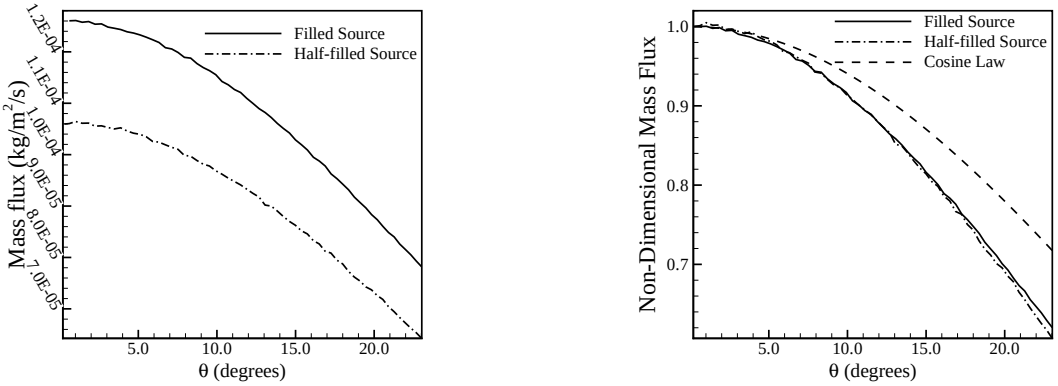

FIGURE 6. Comparison of dimensional and non-dimensional mass fluxes for the filled and half-filled *EVCFABEB-13* source.

measurements. The parameters of the model are given by a reference diameter d_{ref} = 0.45 *nm*, an exponent α = 0.42 and a reference temperature of T_{ref} = 300 *K*. The VHS molecular model determined for copper is be used in axi-symmetric DSMC simulations of a practical EBPVD vacuum deposition system using *EVCFABEB-13* source. The simulations were performed for two different configurations in which the source was either filled or half-filled. While the non-dimensional mass flux profiles remain the same for the two different configurations, the dimensional mass flux decreases by about 20 % for the half-filled source. The non-dimensional mass flux profile for both configurations indicate a non-uniformity of about 40 %.

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