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Direct simulation Monte Carlo modeling of metal vapor flows in application to thin film deposition

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Thin films of metal for electronics, nano/microelectromechanical systems and optical coatings are often prepared by various vacuum deposition techniques. Modeling such metal vapor flows using methods such as the direct simulation Monte Carlo (DSMC) can aid in the design and analysis of deposition systems and accelerate development of films with desired properties. The determination of suitable variable hard sphere (VHS) molecular model parameters for DSMC simulations using measured growth rate distribution is demonstrated with aluminum vapor as an example. Axisymmetric DSMC simulations using a VHS model corresponding to a reference diameter of 0.8 *nm* and a viscosity-temperature exponent of 1 are shown to agree well with available experimental data. The model is then used in two-dimensional DSMC simulations to study the interaction of plumes from multiple sources. An expression for substrate mass flux assuming no interaction between sources agrees well with DSMC simulations for a mass flow rate of 0.1 *g/min* corresponding to a Knudsen number (*Kn*) of about 0.1. The non-additive interaction of plumes at a higher flow rate of 1 *g/min* corresponding to a *Kn* of about 0.01 results in a higher mass flux non-uniformity in the DSMC simulations which is not captured by the simplified analytical expression.

1. Introduction

Thin film deposition processes [1] for various metallic and semiconductor elements are used to obtain materials with desirable optical, electrical, magnetic, chemical, mechanical, or thermal properties. Optical applications of thin films include reflective and antireflective coatings, magnetic memory discs, and optical waveguides. On the other hand, integated circuits are comprised of thin films of insulators, conductors and semiconductors deposited using similar techniques. Thin films are also used in sensors [2] such as thin film thermocouple (TFTC), thin film strain gauge (TFSG) for use in aerospace applications. Lei et al. [3] describe a TFSG based on an alloy of palladium-13 wt% chromium (PdCr) as well as a TFTC based on platinum-13% rhodium (Pt13Rh) and platinum (Pt) for high temperature applications such as gas turbine engines. Additionally, deposited layers of metals and metal oxides are also used in the fabrication of nanostructures such as nanowires and nanobelts due to their favorable physical, electronic and chemical sensing properties [4].

A number of thin film deposition techniques are based on assembly of solid-state structures from the vapor phase. A common factor of all these techniques is that they use energy, thermal or electric, to convert the material to be deposited from bulk form to vapor phase and condense it to form thin films after transport to a substrate. Techniques which involve no chemical reactions are referred to as physical vapor deposition (PVD) processes. In some cases, there could be chemical reactions either in the gas phase or at the substrate location in which case the methods are broadly classified as chemical vapor deposition (CVD) techniques. Physical vapor deposition techniques include thermal evaporation, molecular beam epitaxy (MBE), electron beam physical vapor deposition (EBPVD), and ion-assisted techniques such as sputtering.

In a thermal evaporation, the energy for conversion to vapor phase is supplied usually by resistive heating. An EBPVD system heats the material to be deposited by a high energy electron beam. This helps to attain much higher temperatures sufficient for evaporation of metals such as *Ni* that cannot be deposited using thermal evaporation. The electrons produced using thermionic or field emission are deflected to the deposition source using magnetic fields. Sputtering is a PVD technique that is quite different from the techniques described above. In sputtering, the target material to be deposited is bombarded by ions thereby leading to the ejection of

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neutral atoms which are then transported from the target to the substrate. The sputtering technique uses both direct current (DC) and radio frequency (RF) plasmas to generate ions. The DC magnetron sputtering is another technique that is advantageous for a number of applications. Using a magnetron allows the plasma to be sustained at much lower pressures compared to DC and RF discharge plasmas.

There are several advantages and disadvantages for the various PVD techniques as summarized in Table 1 and the use of a particular deposition method is strongly dependent on the application. For example, EBPVD allows a greater control over the microstructure of the deposited thin films whereas, being a line-of-sight approach, it is not suitable for deposition on complex geometries with corners and fine features. Also, the energy of atoms reaching the substrate location are lower at about 0.1 *eV* compared to the atoms that reach the substrate in a sputter deposition (between 1 and 10 *eV*). However, sputtering deposition techniques require larger pressures than EBPVD and thermal evaporation to ignite the plasma that supplies the ions. The increase in pressure directly contributes to more collisions in the gas phase when the vapor is trasnsported from the target to the substrate decreasing the line-of-sight nature of the sputtering technique which could be disadvantageous for a few applications.

For applications involving thin films and nanostructures of metals, predictive modeling is important. This work deals with one aspect of modeling thin film deposition processes, namely the vapor transport from the source to the substrate using direct simulation Monte Carlo (DSMC) simulations. Since most of the deposition processes occur at low pressures or ultra-high vacuum (UHV), the cost of repeating experiments for optimizing deposition conditions is very high. Also, modeling is one of the tools available to understand microscopic growth processes that play a significant role in determining the properties of the synthesized nanostructures or thin films. Since the deposition process involves an interplay of many different processes, it requires a multiphysics approach to be able to capture all the relevant physics. For example, even a thermal evaporation process involves melting the solid, evaporation to vapor state, transport of the vapor from the source to the substrate, growth at the substrate and solidifaction. Due to a combination of various physical processes, the modeling framework for thin film deposition and nanostructure growth typically consists of various modules that can deal with different steps.

The low pressure vapor transport is best handled using the DSMC method [5]. DSMC is a stochastic approach that is widely used to solve the Boltzmann equation for applications in various nonequilibrium flows such as those encountered in vacuum technology, hypersonic flight and microscale gas flows. Accurate predictions of the vapor transport process from the source to the substrate depends on the various models fed into the DSMC method including interaction between molecules and atoms in the gas-phase as well as gas–solid interaction. The DSMC method, provides as an output, the number flux and energy distribution of the atoms at the substrate location which plays a strong role in the growth process.

The growth process on the substrate can be modeled using the Kinetic Monte Carlo (KMC) method [6]. The quantities of interest obtained at a specific location on the substrate, from the DSMC method, are inputs to the KMC method. The KMC method then simulates the growth taking into account various processes such as adsorption, surface diffusion, desorption and surface reactions if necessary. The KMC method can predict the grain structure of the deposited thin films which is directly related to their mechanical and thermal properties.

The main goal of this paper is to demonstrate the calibration of DSMC molecular model parameters by comparison with thickness distribution measurements using aluminum as an example. The calibrated model is then used to study coevaporation from multiple sources typically encountered in large scale depositions and the influence of plume interactions on the thickness distribution of the deposited thin films. The remainder of the paper is organized as follows. Section 2 reviews molecular models for gases with specific emphasis on unique features of metal vapors, Section 3 presents the results and discussion and Section 4 summarizes the conclusions.

2. Molecular models for metal vapors

One of the most important parameters required to perform a DSMC simulation is the molecular model that specifies the interaction between atoms and molecules. Molecular models can be broadly categorized into models that account only for the repulsive interaction between molecules and models that account for the long range attraction as well as short range repulsion between molecules. There are a wide range of purely repulsive models such as the hard sphere (HS) [12], variable hard sphere (VHS) [13], variable soft sphere (VSS) [14], generalized hard sphere (GHS) [15] and generalized soft sphere (GSS) [16] that have been used in the past with the VHS model being the most widely used model due its computational efficiency and capability to reproduce the viscosity of various molecules using two parameters - the reference diameter (d_{ref}), and the viscosity-temperature exponent (ω). Among realistic attractive-repulsive potentials, the Lennard–Jones (LJ) intermolecular potential [17] is well established and is known to provide an accurate representation of the interaction between molecules for moderate relative energies typically encountered in vacuum deposition processes. LJ intermolecular potential has been used in rarefied flow simulations in the past [18–20] even if not as commonly as the VHS model. While the VHS model reproduces only the viscosity variation with temperature,

Table 1
Summary of various deposition techniques for thin films and nanostructures.

Deposition technique	Advantages	Limitations	References
EBPVD	Wide range of growth rates, smooth surfaces, flexible substrate temperatures and applicable for any material, Higher growth rates compared to other techniques like thermal evaporation	Line-of-sight process and cannot be used to coat complicated geometries, lower kinetic energy (∼0.1 *eV*) of atoms/molecules at substrate compared to ion-assisted methods	[7]
Thermal evaporation	Less expensive equipments and simple setup	Cannot achieve very high temperatures limiting its use to certain materials	[8]
MBE	Clean growth environment, compatible with other deposition methods, atomically smooth surfaces possible	Less suitable for large scale production, lower deposition rates compared to other methods	[9]
Sputtering (DC, RF, magnetron)	Higher kinetic energy (few *eV*) of atoms/molecules at substrate, not line-of-sight making it useful for complicated geometries	Higher pressure required to sustain the plasma, rough microstructure	[10, 11]