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Plasma coating of nanoparticles in the presence of an external electric field

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Film deposition onto nanoparticles by low-pressure plasma in the presence of an external electric field is studied numerically. The plasma discharge fluid model along with surface deposition and heating models for nanoparticles, as well as a dynamics model considering the motion of nanoparticles, are employed for this study. The results of the simulation show that applying external field during the process increases the uniformity of the film deposited onto nanoparticles and leads to that nanoparticles grow in a spherical shape. Increase in film uniformity and particles sphericity is related to particle dynamics that is controlled by parameters of the external field like frequency and amplitude. The results of this work can be helpful to produce spherical core-shell nanoparticles in nanomaterial industry.

1. Introduction

With increasing application of nanotechnology in industry, nanostructures with unique chemical and physical properties have attracted the attention of a growing number of researchers from various disciplines in recent years. As, recently, synthesis of nanostructures such as nanofibers, nanotubes, and nanoparticles from different materials have been an interesting area for many scientific research groups [1–5]. Because of their shape and properties, nanoparticles produced from various materials like the metal oxide, carbon black, magnetite, polymers or pigments have found a variety of applications in fields such as the optic, electronic, paint, biotechnology, cosmetic, blending or recycling of plastics, etc. [6,7]. A practical and very efficient method to create nanoparticles with new properties is the surface coating of nanopowders with other materials, resulting core-shell nanomaterials. Surface coating can alter or adjust the surface characteristics like wettability, adhesion, hydrophilicity, hydrophobicity, flowability, printability, dissolution and corrosion resistance [8–19]. Coated nanopowders have been exploited in a wide spectrum of applications such as emitters in field emission display panels [20], nanocapsules in controlled drug delivery systems [21], abrasives produced by deposition of diamond-like carbon layers [22], photocatalyst for water decontamination [13], and solid fuels for combustion [23]. Many methods can be employed to the coating of nanopowders, such as the magnetron sputtering, electron beam evaporation, sol-gel, gas-condensation process, and plasma enhanced chemical vapor deposition [24,25]. Plasma enhanced chemical vapor deposition, PECVD, is preferred to the other methods due to its numerous advantages such as low temperature of processing, high selectivity among deposition precursors, excellent purity control compared to liquid-phase processing, the resistance of particles against aggregation due to the high degree of charging, and wide range of chemistries that can be conducted.

Recently, by using capacitively coupled plasma reactor, Cao and Matsoukas have conducted experiments to study the coating of micro and nanoparticles in isopropanol/Ar plasma [8,9]. Their results revealed that the thickness of film growth onto particles is a linear function of the process time and the deposition rate depends on the particle size. Also, nonuniformity in the deposited film onto particles was seen in conjunction with this technique, resulting nonspherical growth of nanoparticles. A dependency of the film nonuniformity on the particle size was also observed, as films on small particles had poor uniformity and small particles in comparison with large particles lost their initial sphericity remarkably. To validate these experimental results, by using a kinetic model, Rovagnati and Mashayek studied the plasma deposition over dust particles in both isotropic and drifting plasmas. They showed that when the particles are immersed in an isotropic plasma, the deposited film retains intact the initial sphericity of particle. Whereas, if the particles are considered to levitate in the (pre) sheath formed around the lower electrode of the discharge the film grows in a nonuniform manner similar to experimental observations of references [8,9]. In the second case, the good

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resemblance with the film topography observed experimentally suggested that the main source of the film nonuniformity is due to the contribution of ions which move along a preferential direction. In other words, the intrinsic nonhomogeneous nature of plasma near bottom electrode was considered to be the cause of nonuniform deposition onto particle surface, which becomes more evident when particles are exposed to the plasma for a longer duration to obtain thicker layers.

The above reports imply that in a plasma discharge due to non-zero directed ion flux near the bottom electrode where the particles are trapped by balance between the electric, neutral drag, ion drag, and gravitational forces [26–29], distinct parts of the particle surface do not receive same ion flux, as part of particle surface facing the plasma center collect more ion flux than the opposite side. Since the ions play an important role in the film growth both via ion stitching of the adsorbed species and direct-ion incorporation it results in nonuniformity of deposited film [30]. Therefore, it can be inducted that with the rotation of nanoparticles during plasma coating process one can increase the film uniformity and maintain initial sphericity of particles. In this way averaged deposition rate during a specific time will be same for each part of particle surface and the deposited film will be uniform. Therefore, to tackle the nonuniformity problem, this work is devoted to studying of plasma coating of nanoparticles in the presence of an external electric field that can rotate nanoparticles during the growth process. To this end, we utilize a one-dimensional multi-fluid plasma model for simulation of capacitively coupled Methane plasma discharge. When plasma reaches to steady state the spherical nanoparticles with no electric charge are injected from the upper electrode into the discharge. To determine the position of nanoparticles a linear dynamics model including electric field, gravity, neural drag, and ion drags forces is considered. The deposition rate in different parts of nanoparticle surface is determined by the surface deposition model, while the particles temperature is adopted by particle heating model. For rotation of nanoparticles, we apply an external circularly polarized electric field that interacts with particles through their non-zero electric dipole moments. In following section one-dimensional methane discharge model used in this work is introduced. Section 3 describes dynamics of nanoparticles injected into plasma and introduces the considered external electric field. Surface deposition and particle heating models used in this work are summarized in Section 4. The results of the numerical simulation are presented and discussed in Sec. 5. Then the paper is concluded in Sec. 6 with a summary of main findings.

2. Methane plasma discharge model

In this work, the one-dimensional multi-fluid approach developed by Nienhuis et al. [31] is utilized to model Methane discharge created between two horizontal parallel plates. This fluid model is described by the balance equations for the densities and drift-diffusion expression for the fluxes of the various species. The set of fluid equations also contains Poisson equation for electrostatic potential and energy equation for the electron. No ion energy equation is considered because it is assumed that the ion temperature is equal to that of the neutral gas such that they are in thermal equilibrium. Also, since the ions cannot give the instantaneous response to an alteration of the actual electric field, in ion balance equations an effective electric field is replaced. The source terms for the density balance equations are dependent to rate coefficients of chemical reactions that occur between different species. Also, in order to allow the influence of the mass flow, the gas inlet and pumping are taken into account in the model by considering the additional sink and source terms in the density balance equations of the neutrals. Detailed kinetic electrochemical reactions in Methane plasma has been extracted from reference [32]. The model takes into account 20 different species including electrons, neutrals, and positive ions. The considered reactions are 27 electron-neutral reactions, 7 ion-neutral reactions, and 12 neutral–neutral reactions. The reaction rate coefficients of the ion-neutral and neutral–neutral reactions are used from the literature, while local electron collision rates and electron transport coefficients are interpolated from look-up tables. The look-up tables are created by Boltzmann equation solver [33] that gives the electron transport and reaction rate coefficients as a function of electron average energy. The time-dependent discharge characteristics change only along the Z axis (i.e., the direction normal to the plates). The voltage of upper plate is fixed to zero (anode electrode) while the lower plate is biased (cathode electrode) by a periodic voltage with rf frequency. In the model, the amplitude of the potential is changed gradually until the dissipated power (i.e., the power given the charged species by ohmic heating) equals the electric power, which is an input parameter in this model. The spatial discretization of the equations is made by the Sharfetter–Gummel exponential approach [34] and for time evolution a fully implicit method is employed. The electron density is set to zero on the electrodes. Since the ion flux incident on the electrodes has only a drift component, their density gradient is fixed to zero when the electric field is directed towards the electrode. The boundary conditions for the equations of neutrals are related to the plasma-wall interaction. In the model, the electron transport and Poisson equations are solved simultaneously to avoid numerical instabilities and errors. Newton's iteration method is used to solve the resulting set of nonlinear equations. Meanwhile, the convergence criterion is defined such that the relative difference in the discharge parameters between two successive rf cycles is less than 10^{-6}.

3. Dynamics of nanoparticle immersed in plasma

This section gives a detailed description of linear dynamics of nanoparticles injected into plasma discharge and of interaction between an external circularly polarized electric field and non-spherical charged particles.

3.1. Linear dynamics

Position and velocity of nanoparticles injected into discharge is determined by following momentum equation:

$$m_p \frac{dv_p}{dt} = -q_p \frac{d\phi}{dz} + m_p g + F_{id} + F_{nd}, \tag{1}$$

where $m_p = \frac{4}{3}\pi r_p^3 \rho_p$ is the mass, v_p is the particle speed, q_p is the electric charge, and r_p and ρ_p are the radius and mass density of the nanoparticles. The terms in the right hand denotes respectively to electric, gravitational, neutral drag, and ion drag forces [26–28]. The nanoparticle charge q_p is determined by the electron and ion currents reaching to particle surface:

$$\frac{dq_p}{dt} = \sum_i I_i - I_e, \tag{2}$$

where electron and ion currents are given by [35,36]:

$$I_e = e\pi r_p^2 n_e(z(t)) \left(\frac{8k_B T_e}{\pi m_e}\right)^{1/2} \exp(eq_p/4\pi\epsilon_0 r_p k_B T_e), \tag{3}$$

and

$$I_i = e\pi r_p^2 \tfrac{1}{2} n_i(z(t)) v_{th,i} \left(\sqrt{\pi}(\bar{u_i} + \tfrac{1-2\bar{\Phi}_p}{2\bar{u_i}})\mathrm{erf}(\bar{u_i}) + \exp(-\bar{u_i}^2)\right). \tag{4}$$

Here $n_e(z(t))$ and $n_e(z(t))$ are electron and ion density in the position of nanoparticle, erf is the error function, and $\bar{u_i} =$

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