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Numerical investigation of the film uniformity during the surface coating of charged nanoparticles in a low pressure plasma reactor

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ABSTRACT

The uniformity of film deposition on charged nanoparticles, trapped near the sheath of a capacitively coupled plasma reactor, is studied by numerical simulation of the multi-fluid plasma equations, surface deposition processes, and nanoparticle heating effects. It is found that the anisotropy in the ion flux onto the powered electrode may be hold responsible for the film nonuniformity. The nonuniformity increases with increasing of the particle radius, although small particles lose sphericity faster than the large particles. Because of the electron temperature dependence of the deposition rate and the incident ion flux, higher electron temperatures lead to more nonuniform film deposition. However, the uniformity is improved and the sphericity is restored by the increase in the background gas pressure and/or temperature.

1. Introduction

Nanopowders, including carbon black, magnetite, metal oxide, pigment or polymers find applications in various fields such as: electronics, paints, cosmetics, bio-technology, recycling or blending of plastics, etc. However, nanopowders need an adequate surface treatment in order to acquire new surface properties required in different applications. Surface coating of nanopowders with other materials in low temperature plasma discharges is a very efficient and practical method to alter or modify the surface properties like adhesion, hydrophobicity, hydrophilicity, printability, wettability, flowability, disolution and corrosion resistance [1–12]. Coated nanopowders have been used in a broad spectrum of applications such as nanocapsules in controlled drug delivery systems [13], emitters in field emission display panels [14], solid fuels for combustion [15], photocatalyst for water decontamination [4], and abrasives produced by deposition of diamond like carbon layers [16].

The dynamics of trapped nanoparticles is determined by the balance between the electric, ion drag, neutral drag, thermophoretic, and gravitational forces [17–21]. The electric charge of the nanoparticle is an important parameter which is calculated from the balance of the electron and ion currents to the nanoparticle surface. Due to much larger mobility of the electrons, particles located near the plasma sheath are normally negatively charged. The electrostatic force is generally directed towards the bulk plasma, whereas all the other forces tend to expel nanoparticles from the reactor. Since the particle charge capacity is directly proportional to its radius, particles with different radii will be trapped at different positions.

Recently a lot of research works have been devoted to the study of plasma coating of nano and micron-sized particles. Kersten et al. [22] employed dc magnetron sputtering to investigate the possibility for coating of iron microparticle with compact aluminum layers. They found the growth rate of aluminum layers in the order of 1 nm/s which satisfies the requirement of industrial applications well. Yarin et al. employed a multi-fluid reaction model for thin film coating of nanoparticles by amorphous carbon layer in a CH_4/H_2 plasma [23]. They showed that the growth rate increases with increasing of the pressure but is independent of the particle size. Mangolini and Kortshagen developed a numerical model to describe the energy balance of nanoparticles in a nonthermal plasma [24]. Their results showed that for small particles with radius of a few nanomaters, the surface temperature can far exceed the background gas temperature. Maurer and Kersten used an energy balance model to estimate the energy fluxes towards a nanoparticle immersed in Ar/H_2 plasma [25]. The results showed that the nanoparticle surface temperature can exceed the gas temperature due to the heat released in the plasma–surface interaction processes and the main source of the heat is the electron–ion recombination on the nanoparticle surface. Cao and Matsoukas used a capacitively coupled plasma reactor to investigate the coating of micro and nanoparticles in isopropanol/Ar plasma [11,12]. Their results showed that the film thickness is a linear function of the

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deposition time and also the growth rate depends on the particle size. Thick films on the particles have poor uniformity and lead to nonspherical particle growth. Also a dependence of the deposition nonuniformity on the particle size, was observed. The nonsphericity of the deposited film for the small particles was generally high.

Following our previous works on the study of nanoparticle coating in low pressure plasmas [26,27], this work is aimed to investigate the experimentally observed film nonuniformity and its dependence on the ambient plasma parameters. To this end, we employ a one-dimensional multi-fluid description along with the surface deposition and nanoparticle heating models to study the deposition kinetics in a methane plasma discharge. Spherical nanoparticles with no electric charge are introduced from the top electrode into the discharge. Then the nanoparticle charge is calculated from the balance of the electron and ion currents and their equilibrium position is determined by numerical solutions of the corresponding fluid equations. The deposition flux onto the nanoparticle surface is obtained from the surface deposition model, while the surface temperature is determined by the nanoparticle heating model. It is assumed that the deposition time is much larger than the characteristic time of the particle motion, such that the particles are always in local equilibrium.

2. Methane plasma discharge model

A one-dimensional multi-fluid model is used to simulate the discharge created between two horizontal parallel plates [28]. The time dependent discharge characteristics vary only along the direction normal to the plates (i.e., z axis). This fluid model is described by the balance equations for the species densities and drift-diffusion expression for the fluxes of the various species. The balance equations are coupled to the Poisson equation for the calculation of the electric field. By solving these equations one finds the behavior in space and time of the particle densities and of the electric potential (and other plasma characteristics) during one rf-cycle of the periodic steady state discharge.

The energy balance equations are disregarded in this model. It is assumed that the electrons have constant temperature and the ions have nearly the same energy as the neutrals. The validity of the isothermal approximation, used in this simulation, is justified by comparing the energy relaxation length with the system dimension. In low pressure plasma discharges, the deposited electromagnetic energy is mainly coupled to the electrons. On the other hand, due to inefficient energy transfer from electrons to the ions and neutrals, the plasma is not in thermal equilibrium and the electron temperature T_e greatly exceeds the ion and neutral temperatures T_i and $T_{\rm gas}$, respectively. Generally, T_e varies over a narrow range between 1 and 6 eV, whereas T_i and $T_{\rm gas}$ are at most a few times room temperature. It is also noted that the energy relaxation length varies as $\lambda_\varepsilon = (\lambda_m \lambda_{\rm inel}/3)^{1/2}$ with the total mean free path for the momentum transfer λ_m, and the mean free path for inelastic energy loss processes $\lambda_{\rm inel}$. For the electron temperature to be uniform in a gas discharge of typical dimension 10 cm, the pressure should be smaller than 600 mTorr which is generally satisfied in low pressure processing plasmas, including the present work.

In this work, we focus on the CH_4/H_2 plasma. The model considers 20 different species including electrons, neutrals, and positive ions [29]. Detailed kinetic electrochemical reactions in such a plasma has been presented in our previous work, table II [26]. All species obey the continuity across the discharge:

$$\frac{dn_j}{dt} + \frac{d\Gamma_j}{dz} = \omega_j, \tag{1}$$

where Γ_j is the net flux of species j at z, and ω_j is the reaction source term which accounts for all reactions creating and destroying that species. The reaction source term for each species is calculated from table III of Ref. [26]. The drift-diffusion expression for fluxes are obtained from

$$\Gamma_j = -D_j \frac{dn_j}{dz} \pm \mu_j n_j \frac{d\phi}{dz}, \tag{2}$$

where n_j is the concentration of species j at z and D_j and μ_j are the diffusion and mobility coefficients of the species j, respectively [30,31]. The set of fluid equations is completed with Poisson equation for electrostatic potential:

$$\frac{d^2\phi}{dz^2} = -\frac{e}{\epsilon_0}\left[\sum_{j=\rm ion} n_j - n_e\right], \tag{3}$$

where the summation on the right-hand side is over all ion species. The upper plate is grounded (anode electrode) while the lower plate is powered (cathode electrode) by a periodic voltage with rf frequency $\nu_{\rm rf}$:

$$V = V_{\rm rf} \sin(2\pi \nu_{\rm rf} t). \tag{4}$$

The ion velocity is extracted from the ion flux by using

$$v_i = \Gamma_i / n_i. \tag{5}$$

This velocity includes both drift and diffusion of the ions.

3. Particle coating model

This section provides a detailed description of the nanoparticle coating model, consisting of the nanoparticle dynamics, surface deposition, and nanoparticle heating modules, and used to predict the deposition flux onto the particle surface.

3.1. Nanoparticle dynamics

The dynamics of a nanoparticle injected into the plasma is governed by the electric, ion drag, neutral drag, and gravitational forces [17–20]. The nanoparticle motion is described by the momentum equation:

$$m_p \frac{dv_p}{dt} = -q_p \frac{d\phi}{dz} + m_p g + F_{id} + F_{nd}, \tag{6}$$

where $m_p = \frac{4}{3}\pi r_p^3 \rho_p$ is the mass, v_p is the speed, q_p is the electric charge, and ρ_p and r_p are the mass density and radius of the nanoparticles. For the ion drag F_{id} we use the expression by Trubnikov [18], which spans a large range of pressures and densities and gives more accurate results compared to the other theories [19], especially at low pressures

$$F_{id} = 2\pi n_i m_i v_{si} v_i b_{\pi/2}^2 \ln\left(\frac{b_{\pi/2}^2 + \lambda_{De}^2}{b_{\pi/2}^2}\right). \tag{7}$$

Here, $v_{si} = \left(\tilde{v}_i^2 + 8k_{\rm B}T_i/\pi m_i\right)^{1/2}$ is the mean ion speed, $\tilde{v}_i = v_i - v_p$ is the directed ion speed relative to a particle moving with velocity v_p, $b_{\pi/2} = eq_p/\left(4\pi\varepsilon_0 m_i v_{si}^2\right)$ is the impact radius corresponding to a 90° deflection, and $\lambda_{De} = (\varepsilon_0 k_{\rm B} T_e / n_{0e} e^2)^{1/2}$ is the electron Debye length. The neutral drag force F_{nd} is given by the Epstein expression [20]

$$F_{nd} = -\frac{4}{3}\pi r_p^2 m_n n_n v_{\rm thn} v_p, \tag{8}$$

with $v_d \ll v_{\rm thn}$, and $v_{\rm thn} = \sqrt{8k_{\rm B}T_{\rm gas}/\pi m_n}$ is the thermal speed of the neutrals. The nanoparticle charge q_p is determined by the electron and ion currents towards particle surface:

$$\frac{dq_p}{dt} = \sum_i I_i - I_e. \tag{9}$$