FOCUSED BEAM DEPOSITION OF PLASMA-SYNTHESIZED NANOPARTICLES

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Abstract

We have developed a method for producing narrow particle beams based on aerodynamic focusing of nanoparticles that are synthesized in a plasma expansion. An argon-hydrogen plasma generated by a DC torch is expanded through a nozzle from an upstream pressure in the sub-atmospheric range to a downstream pressure around 300 Pa. Gaseous reactants are injected into the plasma just upstream of the nozzle. The rapid expansion drives particle nucleation. An aerodynamic lens assembly [1], consisting of a series of disks with coaxial orifices, is positioned downstream of the nozzle. By design the lens assembly focuses particles within a specified size range to a collimated beam whose dimensions are on the order of tens of microns. This particle beam can then be used to write patterns on a computer-translated substrate, or can be shuttered and used in conjunction with techniques such as micro-molding to fabricate or coat MEMS parts.

When the focused beam deposits on a stationary substrate a high-aspect-ratio “tower” is produced. In preliminary experiments [2] we demonstrated focused beam deposition of such towers, consisting of either SiC, Ti or TiC particles. The concept of depositing two-dimensional micropatterns was also demonstrated, by manually translating the substrate. In the present paper we report further experimental results of focused particle beam deposition. Detailed numerical models were developed of several aspects of the process, including a model of flow and individual particle trajectories in the lens assembly; a model that predicts the distribution of particles by solving the aerosol general dynamic equation for an ensemble of particles, including the effect of radial diffusion; and an approximate model for the evolution of the deposit cross-section profile produced by impacting particle beams.

Introduction

Narrow beams of nanoparticles can potentially be used in conjunction with standard microfabrication techniques to create superior components for microelectromechanical systems.

Fig. 1... Overall schematic of experimental apparatus. “Substrate 1” is used for deposition of continuous films. “Substrate 2” is used for focused particle beam deposition of patterned microstructures.
(MEMS). Because these deposits would be inherently nanostructured, they may offer superior friction- and wear-resistance, which are currently crucial limitations for MEMS parts such as miniature gears for micro-transmissions and electrodes for micro-electro-discharge machining.

Previously, we reported a method for depositing nanostructured films, known as “hypersonic plasma particle deposition” (HPPD) [3]. We also reported a modification to the HPPD process which can produce high-definition structures [2]. In this paper we focus on the high-definition system and present results of further experiments and numerical simulations of the various aspects of the process.

Experimental
The experimental set-up is shown schematically in Fig. 1. The experimental apparatus and the operating conditions are described in detail elsewhere [4]. In short, in the HPPD process, a direct current (DC) plasma torch operating at ~10 kW power is used to generate the plasma with a flow of 30 slm of argon and 7.5 slm of hydrogen during typical operating conditions. The reactant feed gases (typically 50 sccm of SiCl4/TiCl4 and 250 sccm of CH4) are injected radially through injection ports located downstream of the plasma arc generator. The temperatures in the plasma at the injection ring location are high enough to dissociate these gaseous reactants almost completely into their elemental forms. The resulting gas-vapor mixture is then quenched through a converging nozzle leading to supersaturation of reactant vapor and subsequent nucleation of particles. The particle-laden flow exits the nozzle and expands supersonically to the substrate resulting in continuous film formation by inertial impaction.

In a modification to the HPPD process, the deposition substrate is replaced by an aerodynamic lens assembly [1]. The nucleated particles are collimated to a narrow beam using the aerodynamic lenses. Micropatterns are formed by inertial deposition of these nanoparticles on the substrate. This paper presents some of the experimental results showing deposit structures as well as theoretical modeling of particle trajectories and a model for predicting the shape of the deposited structure.

Numerical Method
The behavior of particles in the aerodynamic lens assembly is governed by the flow of the carrier gas. A two-dimensional axisymmetric model was developed to characterize the carrier gas flow. The conservation equations were solved for steady, laminar, compressible flow using the commercially available software CFD-ACE [5]. Two approaches were followed to characterize the particle behavior inside the aerodynamic lens assembly. A Lagrangian approach was used to track particles and included the effects of viscous drag but neglected Brownian diffusion. To study the effect of Brownian diffusion inside the aerodynamic lens assembly, a particle population balance equation (GDE) [6] was solved using the moment method.

In the Lagrangian approach, the equations for the motion of particles were formulated based on the drag in the free molecule regime. The particle motion is governed by equations (1) and (2).

\[
\frac{d\vec{x}}{dt} = \vec{v} \tag{1}
\]

\[
\frac{d\vec{v}}{dt} = \frac{3}{4} \frac{\rho_s}{\rho_p d_p} C_d |\vec{u} - \vec{v}| (\vec{u} - \vec{v}) \tag{2}
\]
where \( \vec{x} \) represents the particle position, \( \vec{u} \) and \( \vec{v} \) represent the fluid and particle velocity, respectively, \( C_d \) is the drag coefficient, \( \rho_g \) and \( \rho_p \) are gas and particle densities, respectively, and \( d_p \) is the particle diameter. The equation set was solved using a fourth order Runge-Kutta scheme.

The \( k^{th} \) moment of the particle size distribution is defined by \( M_k = \int_0^{\infty} v_p^k n(v_p,t)dv_p \), where \( v_p \) is particle volume and \( n(v_p,t) \) is the particle size distribution function. The time evolution of the \( k^{th} \) moment can be obtained by multiplying both sides of the aerosol GDE by \( v_p \) and by integrating over the particle size range. The result can be written as

\[
\frac{\partial M_k}{\partial t} = [\dot{M}_k]_{\text{coagulation}} + [\dot{M}_k]_{\text{diffusion}} + [\dot{M}_k]_{\text{convection}}
\]

For the present problem, the particle concentrations were assumed to be small, consistent with typical conditions inside the lens assembly, such that coagulation was not significant. The second term on the right-hand side of Eq. (3) represents particle motion by Brownian diffusion and can be expressed as

\[
[\dot{M}_k]_{\text{diffusion}} = \int_0^{\infty} v_p^k \nabla \cdot (D(v_p) \nabla n(v_p))dv_p
\]

where \( D \) is the particle diffusion coefficient. The expression for \( D \) is modified following the procedure of Lee and Liu [7], by representing the particle diffusion coefficient by:

\[
D = \frac{k_B T}{3\pi \mu} \left( \frac{\pi}{6v_p} \right)^{\frac{1}{3}} + 3.314\lambda \left( \frac{\pi}{6v_p} \right)^{\frac{2}{3}}
\]

where \( T \) is the gas temperature, \( \mu \) is the gas viscosity, \( \lambda \) is the gas mean free path, and \( k_B \) is the Boltzmann constant. The convection term in Eq. (3) can be written as [8]

\[
[\dot{M}_k]_{\text{convection}} = \int_0^{\infty} v_p^k \nabla \left( \vec{u} \cdot \nabla \vec{u} \right)n(v_p)dv_p
\]

where \( \tau \) is the particle relaxation time expressed as \( \tau = \rho_p d_p^2 C_c / 18 \mu \), where \( C_c \) is the Cunningham slip correction factor.

The non-integer moments resulting due to the dependence of diffusion coefficient and relaxation time on the particle diameter in the above equations can be expressed in terms of the first three integer moments, \( M_0, M_1 \) and \( M_2 \), by assuming a lognormal size distribution function of the general form

\[
n(v_p,t) = \frac{N}{3\sqrt{2\pi} \ln \sigma_g} \exp \left\{ -\frac{\ln^2(v_p / \bar{v}_g)}{18\ln^2 \sigma_g} \right\} \frac{1}{v_p},
\]

where \( N \) is the total particle concentration. The geometric mean particle volume, \( \bar{v}_g \), and the geometric standard deviation, \( \sigma_g \), can also be expressed in terms of the first three moments by

\[
\bar{v}_g = \frac{M_2}{M_0^{\frac{3}{2}} M_1^{\frac{1}{2}}}, \quad \text{and}
\]

\[
\ln^2 \sigma_g = \frac{1}{9} \ln \left( \frac{M_0 M_2}{M_1^2} \right)
\]

Finally, the \( k^{th} \) moment is related to \( \bar{v}_g, \sigma_g, \text{and} M_0 \) by
\[ M_k = M_0 \nu_k t \exp\left(\frac{9}{2} k^2 \ln^2 \sigma_k \right) \] (10)

One thus needs to solve only for the first three moments of Eq. (3), i.e. \( k = 0, 1 \) and 2, to obtain the value of any arbitrary moment.

**Results and Discussion**

**Experimental.** Figure 2 shows a SEM micrograph of a titanium tower grown by collimating the nanoparticles and depositing them on a substrate located 4 mm downstream of the exit of the aerodynamic lens assembly. The height of this structure is about 0.36 mm and the structure was grown over a period of 10 minutes. The base diameter of the tower (150 \( \mu \text{m} \)) is smaller by a factor of 10, while the diameter corresponding to half-width of the tower (30 \( \mu \text{m} \)) is smaller by a factor of 60 compared to the diameter of the critical nozzle (1.85 mm). This fact is important in continuous production of microstructures while avoiding clogging of the nozzle.

**Flow Modeling and Particle Trajectories.** The lens assembly used for the numerical calculations consists of five lenses in series, each with an orifice diameter of 2.26 mm, and spaced 47 mm apart. The lens assembly terminates with a critical orifice 1.85 mm in diameter at the downstream end. The pressure is about 345 Pa at the inlet and about 1.0 Pa in the chamber downstream of the assembly.

![Fig. 2 Scanning electron micrograph of a titanium tower deposited on a stationary substrate](image)

![Fig. 3 Predicted gas streamlines (top) and trajectories of 20-nm SiC particles (bottom), for aerodynamic lens assembly with same geometry and conditions as in experiments.](image)

Figure 3 shows the predictions of a numerical simulation for both the gas streamlines and trajectories of 20 nm spherical silicon carbide particles. As can be seen from Fig. 3, the gas contracts as it passes through the orifice and re-expands. Very small particles behave like gas molecules and nearly follow the gas streamlines. Very large particles are accelerated to the centerline, but due to their larger inertia, they continue their motion and are projected past the axis and end up on a streamline farther away from the axis than the one on which they originated. On passing through subsequent lenses, these particles are lost to the walls of the lens assembly. Intermediate size particles are accelerated to the center by the gas, but due to the balance between the inertia and driving gas drag force, they terminate their radial motion on a streamline that is closer to the flow axis than the one on which they originated. As these particles traverse through the
lens system, they are brought closer to the axis, and exit the lens assembly as a tightly collimated beam.

**Numerical Solution of the General Dynamic Equation.** The general dynamic equation was solved using the moments method for three cases, (i) initially monodisperse particles with diameter of 10 nm, (ii) initially monodisperse particles with diameter of 20 nm, and (iii) initially polydisperse particles with a geometric volume mean diameter of 20 nm and a geometric standard deviation of 1.5. In each case, the effect of Brownian diffusion on the particle distribution is included. The Stokes drag term was neglected and particles were assumed to be convected with the local flow velocity. As a result these calculations do not show the aerodynamic focusing effect, but are instead intended to isolate the effect of Brownian diffusion.

![Fig. 4 Radial profiles of concentrations for particles of 10 nm and 20 nm in the aerodynamic lens assembly at different axial locations.](image1)

![Fig. 5 Radial profiles of normalized geometric mean diameter at four different axial locations for an initially polydisperse aerosol traversing through the lens assembly under the influence of Brownian diffusion.](image2)

Figure 4 compares the radial profiles of particle concentrations for the particles with initially monodisperse distribution of 10 nm and 20 nm. The comparison is made at two axial locations, 9.5 mm upstream of the second and the fifth lens, hereafter referred to as axial location 1 and 2, respectively. The concentrations for both particle classes are assumed to be the same at the inlet of the lens assembly. As can be seen from Fig. 4, the particle concentrations decrease as we go farther away from the axis of the lens assembly. This is due to the loss of particles to the walls of the tube by Brownian diffusion. Also to be observed is the fact that the particles of 10 nm diameter are lost preferentially compared to the particles of 20 nm diameter. As we go further downstream axially, the particle loss has increased significantly. The ratio of total particle flux to that of the flux at the inlet decreases from 0.63 to 0.36 from axial location 1 to 2 for the particles of 10 nm diameter. The corresponding decrease for the particles of 20 nm diameter is from 0.78 to 0.58. This shows that Brownian diffusion is an important factor governing the particle trajectories and beam width as they travel through the lens assembly.

Figure 5 shows the radial profiles of mean particle diameter at various axial locations for initially polydisperse particles with a geometric volumetric mean diameter of 20 nm and a geometric standard deviation of 1.5. As seen there, the particle size distribution shifts to larger particles, with the ratio of mean diameter at subsequent downstream axial locations to the mean diameter at the inlet, always greater than 1. Furthermore, this ratio is higher farther away from the axis. This is due to the preferential loss of small particles to the walls of the lens assembly by Brownian diffusion.
Deposit Cross-Section Profile. A simple theoretical model was developed to predict the profile of the deposit cross-section as the particles impact and deposit on the substrate. The model assumes that the radial velocity distribution for the particle at the exit of the critical orifice due to Brownian motion can be approximated by a Maxwell-Boltzmann distribution. Furthermore, since the particles exit the nozzle to a low background pressure (~1 Pa), subsequent collisions with gas molecules would be rare and one can safely assume that the radial component of the particle velocity is frozen as it exits the critical nozzle. This gives a radial spread in the particle distribution and due to the form of the Maxwell-Boltzmann velocity distribution, it is easily seen that the particle concentration profile is given by a normal (Gaussian) distribution with the center of the distribution at the flow axis. The model assumes that the particles deposit on the substrate with a weight based on the radial spread of the particle distribution calculated at the location of the substrate. Figure 6 shows a comparison of the shape of the predicted structure to that of the actual tower where the predicted structure is allowed to grow in height equal to the height of the experimentally grown structure. The slight discrepancy observed can be attributed to the particle bounce and glace which are not taken into account in the model. More particles would bounce and glance off the inclined surface of the tower, resulting in the tower deviating from the Gaussian and becoming thinner as it grows in height.

Conclusions
We have successfully demonstrated the feasibility of producing high aspect ratio nanocrystalline microstructures both experimentally and theoretically. It is also shown that Brownian diffusion plays an important role in determining the width of the collimated beam especially for smaller particles. Currently work is in progress at growing well-defined micropatterns by implementing computer-controlled rastering of the substrate. In the numerical simulations, Stokes drag term is being added to the general dynamic equation to predict the width of the particle beam as it exits the aerodynamic lens assembly.

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References