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Hypersonic Plasma Particle Deposition—A Hybrid between Plasma Spraying and Vapor Deposition

J. Hafiz, R. Mukherjee, X. Wang, P.H. McMurry, J.V.R. Heberlein, and S.L. Girshick

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In the hypersonic plasma particle deposition process, vapor phase reactants are injected into a plasma and rapidly quenched in a supersonic nozzle, leading to nucleation of nanosize particles. These particles impact a substrate at high velocity, forming a coating with grain sizes of 10 to 40 nm. As previously reported, coatings of a variety of materials have been obtained, including silicon, silicon carbide, titanium carbide and nitride, and composites of these, all deposited at very high rates. Recent studies have shown that slight modifications of the process can result in nanosize structures consisting of single crystal silicon nanowires covered with nanoparticles. These nanowires are believed to grow in a vapor deposition process, catalyzed by the presence of titanium in the underlying nanoparticle film. However, simultaneously nanoparticles are nucleated in the nozzle and deposited on the nanowires, leading to structures that are the result of a plasma chemical vapor deposition (CVD) process combined with a nanoparticle spray process. The combination of these two process paths opens new dimensions in the nanophase materials processing area.

Keywords aerodynamic lens, nanoparticle impaction, nanostructured coatings, nanowires, thermal plasma

1. Introduction

Thermal spraying by plasmas or flames is a widespread, highly developed technology for applying coatings for wear resistance as well as for other applications such as thermal barriers and corrosion resistance. A major drawback to this process is the coarseness of the coating microstructure, which essentially retains the grain size of the powder injected into the torch. Consequently, it is very difficult to deposit nanostructured coatings using traditional thermal spraying. For synthesizing nanostructured coatings, the authors' group at the University of Minnesota has developed a process called hypersonic plasma particle deposition (HPPD), which takes advantage of the flexibility and high-rate deposition capabilities of a thermal plasma while keeping the grain structures in the nanometer range (Ref 1, 2). The authors' process produces nanoparticles by injecting gas phase reactants into a reactive thermal plasma that is expanded into a low-pressure chamber via a convergent boron nitride nozzle. The high-temperature (~4000 K) in the injection region of the nozzle dissociates the gas-phase reactants (for instance $SiCl_4$ + CH_4 for producing SiC deposits) into their elemental constituents. Expansion through the nozzle results in supersaturation of the reactant vapors and consequent nucleation of particles. A substrate is placed 20 mm downstream of the nozzle in the low-pressure chamber (at ~267 Pa versus ~60 kPa in the injection region). This distance is smaller than the calculated Mach disk location, resulting in hypersonic velocities at impact due to underexpansion of the flow. This leads to the formation of dense, hard nanoparticulate films. Short residence times inhibit particle growth, and most particles remain between 10 to 40 nm in diameter.

The HPPD system has been used to synthesize nanoparticles of various substances from the system (Si,Ti,C,N), including Si, SiC, Ti, TiC, multilayered Ti/TiC, and Si-Ti-N composites. Chloride vapors of Si and Ti are injected using a bubbler system, with flow rates in the range 10 to 150 sccm. Carbon and nitrogen are introduced using methane and ammonia, respectively. This paper reports the analysis of nanostructured films and patterns deposited by inertial impaction with the HPPD process. Moreover, the synthesis of nanoparticle-covered nanowires is also examined.

2. Experimental Setup

Figure 1 shows a schematic of the experimental system. The plasma is generated by a direct-current (dc) arc, operating at ~200 A current and ~8 kW power. The main plasma gases are argon, at a flow rate of 30 to 35 sLm, and either hydrogen or nitrogen, at a flow rate of 2 to 6 sLm.

In situ particle size distribution measurements were performed using a sampling probe interfaced to an extraction/dilution system in series with a scanning electrical mobility spectrometer (SEMS). The SEMS system measures particle size distributions based on mobility diameters. Details of the sampling system are presented elsewhere (Ref 3). During measure-

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J. Hafiz, R. Mukherjee, X. Wang, P.H. McMurry, J.V.R. Heberlein, and **S.L. Girshick,** Dept. of Mechanical Engineering, University of Minnesota, 111 Church St. SE, Minneapolis, MN 55455. Contact e-mail: jhafiz@me.umn.edu.

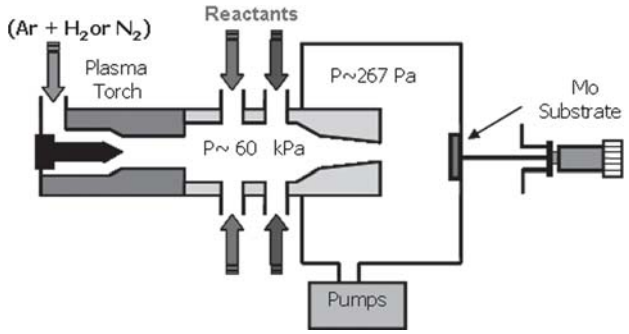

Fig. 1 HPPD system

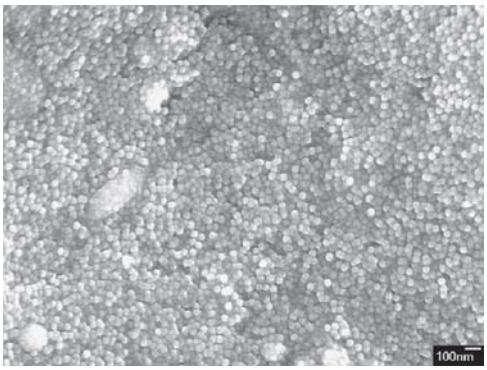

Fig. 2 SEM image of Ti-Si nanoparticle film

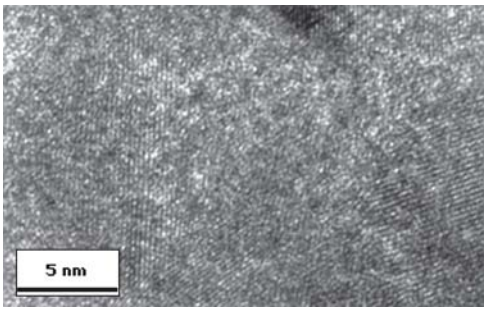

Fig. 3 TEM image of a Si-Ti-N film

ments, the molybdenum (Mo) substrate was removed and replaced with the sampling probe. The probe was placed 20 mm away from the nozzle, corresponding to the substrate standoff distance for film deposition (Fig. 1).

The hypersonically deposited nanostructures were investigated using various characterization tools. X-ray diffraction (XRD) spectra were obtained with a Bruker AXS microdiffractometer (CuKα). X-ray photoelectron spectroscopy (XPS) was carried out with a PHI-5400 model equipped with an Al x-ray source. Scanning electron microscopy (SEM) was performed with a JEOL 6500 field emission gun (FEG) microscope equipped with an energy-dispersive spectrometer. Transmission electron microscopy (TEM) was performed using a JEOL 2010 FEG TEM. Samples from the coatings were prepared for TEM analysis using the focused ion beam (FIB) milling technique (Ref 4). Using a FEI Strata DB235 FIB, electron transparent cross sections of the coatings were prepared.

3. Results and Discussion

3.1 Nanostructured Coatings

The nanostructured nature of HPPD synthesized coatings can clearly be seen in Fig. 2, which shows a Ti-Si coating synthesized by flowing $TiCl_4$ and $SiCl_4$ as reactants for 2 min. As can be seen the particles are fairly monodisperse, with most particles having a diameter in the range 30 to 40 nm.

The HPPD system has been used to synthesize SiC coatings with hardness values as high as 38 GPa (Ref 2). Recently, the authors have primarily focused on the Si-Ti-N system due to its potential applications for hard coatings (Ref 5).

3.1.1 Si-Ti-N Coatings. Si-Ti-N nanostructured films have shown good promise as candidates for high hardness and friction resistance applications. The authors have synthesized Si-Ti-N coatings of 10 to 50 μm thickness on molybdenum substrates at deposition rates of 2 to 30 μm/min, with hardness values up to 28 GPa. During deposition, substrate temperatures ranged from 400 to 1000 °C (all substrate temperatures quoted refer to the deposition surface). Substrate temperature was found to be an important parameter governing the quality of the film. High substrate temperatures (>750 °C) yielded denser, harder, and more crystalline films, while films deposited around 400 °C tended to be highly porous.

For microstructural characterization the authors prepared a TEM sample synthesized with an Ar + N_2 mixture by FIB milling. The corresponding TEM image highlights lattice fringes of nanocrystallites that appear to be embedded in an amorphous matrix (Fig. 3). A series of tilt experiments on a TEM need to be performed to verify the existence of the amorphous matrix. However, based on information from additional characterization (XRD and XPS), the authors believe that the matrix is amorphous. The average fringe spacing of the embedded crystallites was measured to be 0.2119 nm, closely corresponding to the (200) phase of TiN, which has a lattice spacing of 0.212 nm. XPS results indicate that the amorphous matrix consists of Si_3N_4. The presence of TiN crystallites in the film is also highlighted by the XRD spectrum of the film (Fig. 4), which shows only crystalline TiN.

In situ size distribution measurements were performed to characterize the impacting particles that form the authors' coatings. The authors' measurements show that the mode of the size distribution lies in the range 10 to 15 nm with a number mean diameter of 13 nm (Fig. 5). In addition to the near real-time SEMS measurements, crystallite size was also determined from broadening of the Bragg reflections obtained from XRD measurements of the coatings. The WA method was used for this analysis, as researchers have found it to be more accurate than other methods when dealing with grain sizes in the nanometer range (Ref 6). Crystallite size determined from the broadening of TiN reflections for the Ar + N_2 case showed the mean size to equal 14.9 nm, corresponding well with the SEMS measurements. It is interesting to note that the mode of the distribution from the SEMS data and the mean size from XRD peak broad-

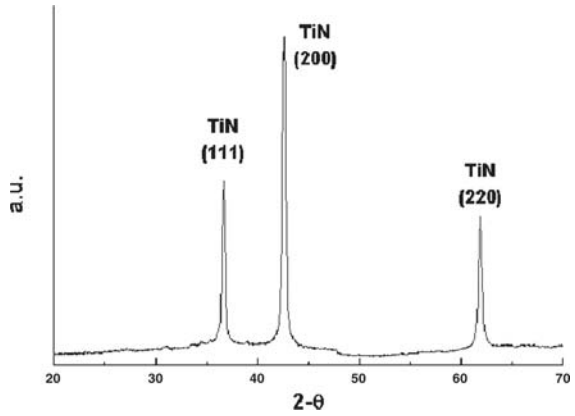

Fig. 4 XRD spectrum showing crystalline TiN

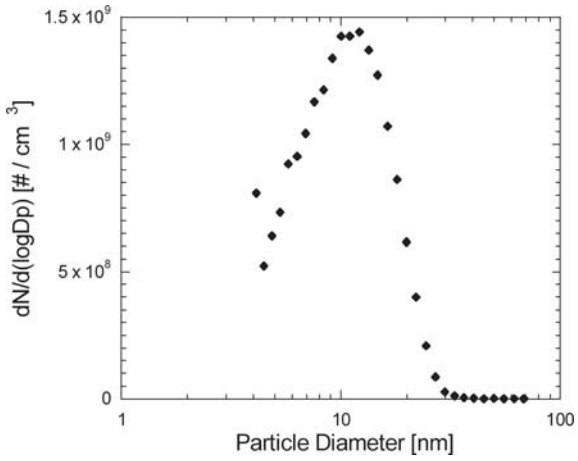

Fig. 5 Particle size distribution measured by the SEMS system

ening were similar, even though the SEMS measures all synthesized particles, whereas the WA analysis provided information only concerning crystalline TiN in the deposited film. The results indicate that for the deposition conditions examined, the size distribution of the TiN crystallites may be representative of the overall grain size distribution in the film.

Si-Ti-N film hardness values measured up to 28 GPa. Typical growth rates are one to three orders of magnitude higher than that of conventional chemical vapor deposition (CVD) processes, which comprise the primary method for synthesizing similar films. Improving the hardness of the Si-Ti-N coatings may require decreasing the size of the TiN crystallites. The construction of hard nanocomposite coatings is based on the synthesis of TiN nanocrystallites in the range of 3 to 10 nm surrounded by an amorphous matrix of Si_3N_4. Additionally, the ideal separation between the TiN nanocrystals should be about one monolayer of Si_3N_4 to attain high hardness (Ref 7). At these conditions, both dislocations and incoherent stress relaxation are hindered, resulting in superhardness. The authors' coatings show larger crystallite sizes (>10 nm), sufficient for the formation and propagation of dislocations. This may restrict the hardness that is achieved with their coatings, unless deposition conditions can be modified so as to reduce particle sizes.

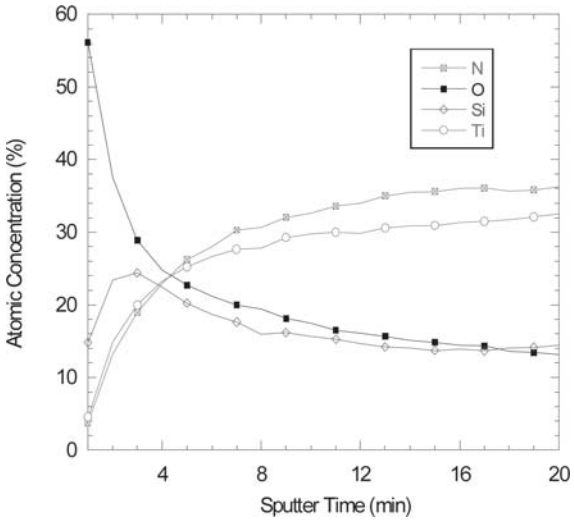

Fig. 6 Auger depth profile of a Si-Ti-N film

Another reason for the moderate hardness value of the Si-Ti-N coatings may be the presence of oxygen throughout the coatings. Recent results have suggested that oxygen content >1% results in a maximum hardness of Si-Ti-N coatings of ~30 GPa (Ref 8), which is approximately the hardness the authors have achieved. To calculate the amount of oxygen in the sample they measured the atomic concentration of all elements present as a function of sputter time using Auger emission spectroscopy. Figure 6 shows the corresponding Auger depth profile. Each element was monitored simultaneously during data acquisition. As can be observed, oxygen levels are high initially due to the formation of a native oxide layer. However, even after sputtering for 20 min the oxygen concentration in the film is well over 10%. The authors are currently working to decrease the amount of oxygen diffused throughout the sample.

3.2 Focused Nanoparticle Beam Deposition

For depositing nanostructured patterns, the molybdenum substrate was removed and replaced with an aerodynamic lens assembly (Ref 9, 10), located approximately 1 m downstream of the nozzle. Nanoparticles from the nozzle are collimated into a tight beam using an aerodynamic lens assembly consisting of a set of thin-plate orifices mounted inside a cylinder. The lens assembly used here focuses 10 to 100 nm particles into a collimated beam with a diameter of a few tens of microns. A critical orifice is placed at the end of the cylinder, beyond which the flow undergoes another expansion. The focused nanoparticles are then deposited at room temperature onto a motion-controlled substrate to form micropatterns or structures, with feature sizes down to a few tens of microns (Ref 11).

The authors have conducted a number of experiments in which either SiC, Si-Ti-N, or Ti particles were deposited using aerodynamic focusing. Figure 7 shows a high aspect ratio nanostructured Ti tower synthesized with the lens system. The authors are currently studying micromolding of microelectromechanical system (MEMS) devices by filling micromachined silicon molds with the nanoparticle beams. Figure 8 shows a

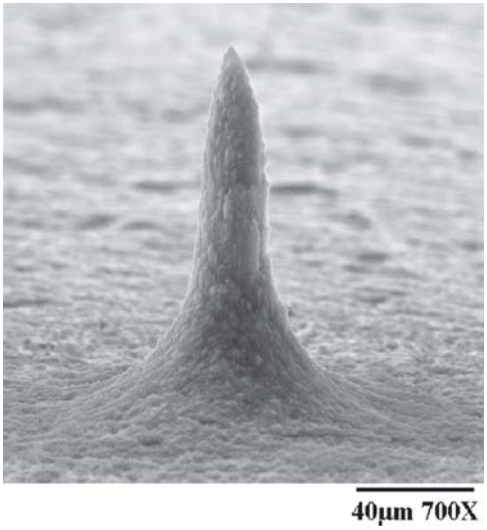

Fig. 7 A high aspect ratio nanostructured Ti tower

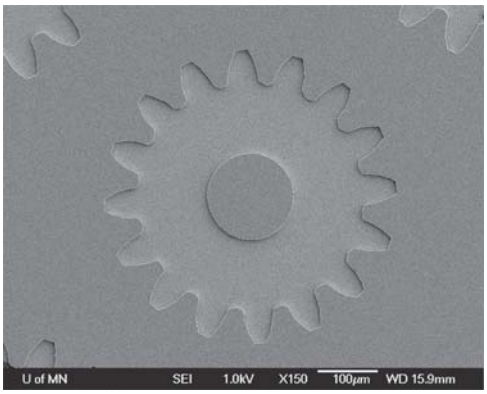

Fig. 8 Micromachined silicon gear mold

silicon gear mold fabricated using standard microfabrication techniques, while Fig. 9 shows the cross section of a gear filled with SiC nanoparticles using the focused nanoparticle beam.

3.3 Nanoparticle-Coated Nanowires

Hybrid nanostructures consisting of nanotubes or nanowires that are coated with nanoparticles are of interest for a variety of potential applications, including catalysis, sensors, electronic devices, magnetics, optics, and others. Through a slight modification of their deposition process, the authors have been able to synthesize such a hybrid structure, consisting of nanowires densely coated with nanoparticles. To their knowledge, coating of nanowires with nanoparticles that bombard the nanowires from the gas phase has not previously been reported.

For the nanowire synthesis experiments the plasma was generated by the arc operating at 200 A current and ~8 kW power input. The main plasma gases were argon, at a flow rate of 30 sLm, and hydrogen, at 2 to 3 sLm. A two-step process was used. In the first step, which lasted for 2 min, vapors of $SiCl_4$ and $TiCl_4$ were coinjected into the plasma at flow rates of 20 and 40 sccm,

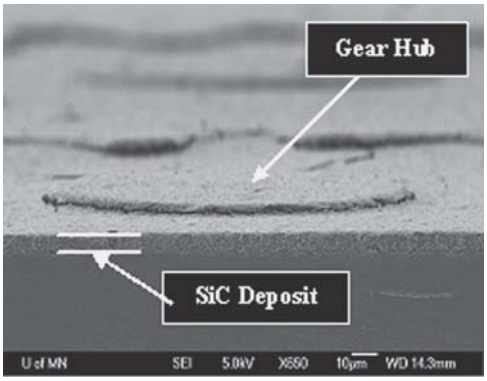

Fig. 9 Cross section of mold filled by a layer of SiC nanoparticles from the focused nanoparticle beam

respectively. In the second step of the process, with the $TiCl_4$ flow switched off and the $SiCl_4$ flow rate doubled, a dense array of randomly oriented nanowires grew on top of the Ti-Si nanoparticle film, as seen in Fig. 10. The nanowire deposit covered ~1.5 cm^2 of the substrate. Calculated mass deposition rates of the nanowires equal approximately 1 mg/h. Figure 11 shows a high-resolution SEM image of a single nanowire, which is seen to be densely coated with nanoparticles whose diameters appear to lie in the range ~5 to 25 nm and to have a faceted catalyst particle at its tip.

The authors believe that the nanowires are synthesized due to a combination of nanoparticle impaction and CVD. In HPPD, nanoparticles nucleate in the nozzle expansion and bombard the substrate by hypersonic impaction, producing nanoparticle films as shown in Fig. 2. At the same time, the gas phase environment adjacent to the substrate may be conducive to CVD. For the operating conditions of these experiments, a stationary bow shock lies ~2 mm above the substrate, where the hypersonic free jet has expanded to approximately Mach 8. Numerical modeling (Ref 12) predicts that the gas is cold in the hypersonic flow just upstream of the shock, but past the shock the temperature rapidly recovers almost to its stagnation value, that is, to the ~4000 K value at the inlet of the expansion nozzle, before dropping to the substrate temperature, in these experiments ~1230 K. Thus the temperature at the edge of the fluid boundary layer above the substrate is quite high, and the temperature gradient is extremely steep. If reactant species are not completely consumed by gas-to-particle conversion upstream of the shock, then under these conditions one would expect the substrate to be exposed to high fluxes of monoatomic reactant vapor, which would be expected to be an active growth species for nanowire growth if suitable catalyst particles are present.

4. Summary and Conclusions

Hypersonic plasma particle deposition is a novel method for generating and depositing nanoparticles to form nanocrystalline films, patterns, and structures. Unlike most thermal spray methods, the particles that are sprayed are directly nucleated from gaseous precursors, eliminating the need for powder feeding and producing films that are inherently nanostructured. Si-Ti-N

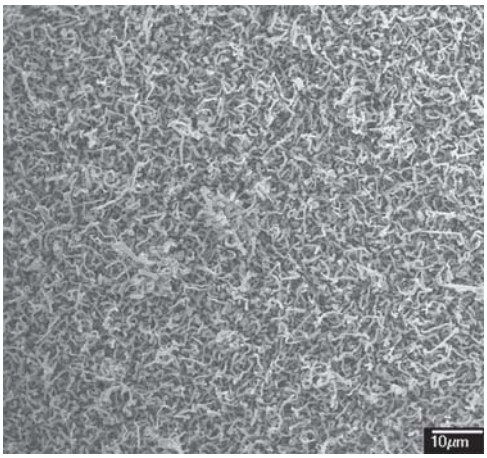

Fig. 10 Low-resolution SEM micrograph showing high-density coverage of nanowires

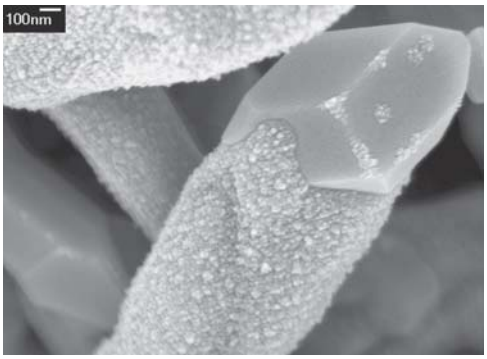

Fig. 11 High-resolution SEM micrograph showing nanoparticle covered nanowires with faceted catalyst

films were deposited at rates as high as about 30 μm/min, with measured hardness values as high as 28 GPa. Aerodynamic focusing was used to generate nanoparticle beams, which were then used to deposit towers and to fill three-dimensional gear molds. A slight modification to the deposition method resulted in the reproducible growth of nanoparticle-covered nanowires. The synthesis of such structures is thought to be the result of nanoparticle impaction in combination with CVD.

Acknowledgments

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References

1. S.L. Girshick, J.V.R. Heberlein, P.H. McMurry, W.W. Gerberich, D.I. Iordanoglou, N.P. Rao, A. Gidwani, N. Tymiak, F.D. Fonzo, M.H. Fan, Hypersonic Plasma Particle Deposition of Nanocrystalline Coatings, *Innovative Processing of Films and Nanocrystalline Powders,* K.L. Choy, Ed., Imperial College Press (London), 2002, p 165-191
2. N.P. Rao, N. Tymiak, J. Blum, A. Neuman, H.J. Lee, S.L. Girshick, P.H. McMurry, and J. Heberlein, Hypersonic Plasma Particle Deposition of Nanostructured Silicon and Silicon Carbide, *J. Aerosol Sci.,* 1998, **29,** p 707-720
3. X. Wang, J. Hafiz, R. Mukherjee, T. Renault, J. Heberlein, S.L. Girshick, and P.H. McMurry, System for In-situ Characterization of Nanoparticles Synthesized in a Thermal Plasma Process, *Plasma Chem. Plasma Process.,* 2005, **25,** p 439-453
4. S. Nakahara, Recent Developments in a TEM Specimen Preparation Technique Using FIB for Semiconductor Devices, *Surf. Coat. Technol.,* 2003, **169-170,** p 721-727
5. S. Veprek and A.S. Argon, Mechanical Properties of Superhard Nanocomposites, *Surf. Coat. Technol.,* 2001, **146-147,** p 175-182
6. A. Niederhofer, P. Nesladek, H.-D. Mannling, K. Moto, S. Veprek, and M. Jilek, Structural Properties, Internal Stress and Thermal Stability of nc-TiN/a-Si_3N_4, nc-TiN/$TiSi_x$ and nc-$(Ti_{1-y}Al_ySi_x)N$ Superhard Nanocomposite Coatings Reaching the Hardness of Diamond, *Surf. Coat. Technol.,* 1999, **120-121,** p 173-178
7. S. Veprek and M. Jilek, Super and Ultrahard Nanocomposite Coatings: Generic Concept for their Preparation, Properties and Industrial Applications, *Vacuum,* 2002, **67,** p 443-449
8. M. Dayan, M. Shengli, X. Kewei, and S. Veprek, Effect of Oxygen and Chlorine on Nano-structured TiN/Si_3N_4 Film Hardness, *Mater. Lett.,* 2005, **59,** p 838-841
9. P. Liu, P.J. Ziemann, D.B. Kittelson, and P.H. McMurry, Generating Particle Beams of Controlled Dimensions and Divergence I. Theory of Particle Motion in Aerodynamic Lenses and Nozzle Expansions, *Aerosol Sci. Technol.,* 1995, **22,** p 293-313
10. P. Liu, P.J. Ziemann, D.B. Kittelson, and P.H. McMurry, Generating Particle Beams of Controlled Dimensions and Divergence II. Experimental Evaluation of Particle Motion in Aerodynamic Lenses and Nozzle Expansions, *Aerosol Sci. Technol.,* 1995, **22,** p 314-324
11. F.D. Fonzo, A. Gidwani, M.H. Fan, D. Neumann, D.I. Iordanoglou, J.V.R. Heberlein, P.H. McMurry, S.L. Girshick, N. Tymiak, W.W. Gerberich, et al., Focused Nanoparticle Beam Deposition of Patterned Microstructures, *Appl. Phys. Lett.,* 2000, **77,** p 910-912
12. A. Gidwani, "Studies of Flow and Particle Transport in Hypersonic Plasma Particle Deposition and Aerodynamic Focusing," Ph.D. Thesis, University of Minnesota, Minneapolis, MN 2003