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Final Report for Grant No. DOE/DE-FG02-98ER14909
"Experimental and Modeling Studies of Nanometer Aerosol Filtration"

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The primary objective of this grant is to perform a fundamental study of filtration of nanoparticles, and to obtain filtration knowledge necessary to design particle collection devices/systems for nanoparticle processing and for preventing nanoparticle emissions into the environment.

In the past 3.5 years, DOE funding for this project has supported the publication of 2 Ph.D. Theses, 5 journal articles (published or submitted), 2 conference proceedings and 1 patent application. A copy of each of these publications is attached in the appendix. Below is a complete list of these publications:

Publications Attributable to the Present Grant

1. Sato, S., Chen, D. R. and D. Y. H. Pui (2002) Molecular Dynamics Study of Nanoparticle Collision with a Surface - Implication to Nanoparticle Filtration. Submitted to *Journal of Aerosol Science*.
2. Chen, D. R. and David Y. H. Pui (2000) Generation of High Concentration Nanoparticles for Filtration Studies. Proceedings of the Eighteenth Symposium on Energy Engineering Sciences, May 15-16, 2000, Argonne National Laboratory, Argonne, IL.
3. Sato, S., D.R. Chen and D. Y.H. Pui (2002) Nanoparticle Filtration: Molecular Dynamics Simulation. Proceedings of the Twentieth Symposium on Energy Engineering Sciences, May 20-21, 2002, Argonne National Laboratory, Argonne, IL.
4. Lee, Poshin, Chen, D. -R. and Pui, D.Y.H. (2002) Experimental Study of a Nanoparticle Virtual Impactor. Submitted to *Journal of Aerosol Science*.
5. Sato, S., Chen, D.-R. and Pui, D. Y. H. (2002) A Novel Method for Producing Spatially Uniform Aerosols in a Low Pressure Environment. *Aerosol Sci. Technol.* **36**, 145-153.
6. Sato, S., Chen, D.-R. and Pui, D. Y. H. (2002) Particle Transport at Low Pressure: Particle Deposition in a Tube with an Abrupt Contraction. *J. Aerosol Sci.* **33**, 659-671.
7. Sato, S., Chen, D.-R. and Pui, D. Y. H. (2002) Particle Transport at Low Pressure: Deposition in Bends of a Circular Cross Section. *Accepted for Publication in Aerosol Sci. Technol.*

8. Sato, Shintaro (2001) Particle Transport at Low Pressure and Nanoparticle Collision with a Surface. Ph.D. Thesis, Mechanical Engineering Department, University of Minnesota. (May 2001).
9. Lee, Poshin (2002) Experimental Study of a Nanoparticle Virtual Impactor. Ph.D. Thesis, Mechanical Engineering Department, University of Minnesota. (June 2002).

U.S. Patent Application Publication:

10. David Y. H. Pui and Da-Ren Chen, "High Mass Throughput Particle Generation Using Multiple Nozzle Spraying," US 2002/0007869 A1, Jan 24, 2002.

The research covered a wide area relevant to Nanoparticle Filtration, under the following main topics: 1) Nanoparticle Filtration and Molecular Dynamics Simulation, 2) Modeling and Development of a Nanoparticle Virtual Impactor for Nanoparticle Classification, 3) Particle Transport under Low Pressure Conditions, 4) Development of a High Throughput Nanoparticle Generator. A number of novel tools and numerical models have been developed under the DOE support. Their utility and impact are expected to extend well beyond nanoparticle filtration.

1. Nanoparticle Filtration and Molecular Dynamics Simulation [1, 2, 3]

Nanoparticle filtration is important in the recovery of nanoparticle powders from materials synthesis processes, and for preventing nanoparticle emissions in the environment as well as for protecting workers against exposure to nanoparticles. Theories have shown that the penetration of nanoparticles through the filters would increase due to thermal rebound between the nanoparticles and filter collection surface.

The filtration efficiency of nanoparticles was first investigated experimentally [2]. A model screen filter was used for the particle penetration study. Silver nanoparticles in the size range of 3 to 20 nm were generated as test aerosols and the penetration of these particles through the model filter was measured. To study the electrostatic effect, penetration of neutralized and singly charged particles were measured and compared with Cheng and Yeh's theory. The experimental penetration deviates from Cheng and Yeh's theory for particles smaller than 10 nm. The experimental penetration is lower than that predicted from theory. This is in the opposite direction of thermal rebound effect. The lower penetration has been attributed to the enhanced collection of the charged particles by the metal screen due to electrostatic effect.

Additional measurements were performed at elevated temperature of 50-80°C. Increased penetration is observed for particles smaller than 5 nm and at elevated temperature of 80°C, suggesting the possibility of thermal rebound between the nanoparticles and the screen filter.

In order to gain fundamental understanding of the thermal rebound processes, a molecular dynamics simulation was performed [1, 3]. The MDS will help to identify the appropriate pairs of particle/surface and experimental conditions, e.g., high temperature or low pressure, to further investigate thermal rebound. Silver, nickel and silica particles were tested against their collisions with a silver surface. The energy loss mechanisms of the colliding nanoparticles were also investigated. Losses to the surface and the rotational degree of freedom were found to be important. Particle and surface hardness, particle shape, and particle size all affect the energy loss mechanisms. The results indicate that nanoparticles with thermal energy at room temperature are unlikely to bounce off a surface even when a very weak interaction potential between the particle and the surface is assumed. It suggests that thermal rebound is not likely to be a serious problem in nanoparticle filtration at the room temperature conditions. The effect of particle and surface temperatures on nanoparticle rebound has not been explored in this study. At the elevated temperature, the thermal energy of the nanoparticle and/or surface will increase. It will thus increase the probability of nanoparticle bounce. It is recommended that future studies be focused on high temperature conditions.

2. Modeling and Development of a Nanoparticle Virtual Impactor for Nanoparticle Classification [4, 9]

A number of novel tools and numerical models have been developed under the present DOE support. They include the High Throughput Nanoparticle Generator (Section 4), the Flow Distributor for producing spatially uniform aerosols in a low pressure environment (Section 3), the Molecular Dynamics Simulation Model to study particle bounce (Section 1), and the Supersonic Flow Model to study nanoparticle impaction (Section 2). Their utility and impact are expected to extend well beyond nanoparticle filtration.

In the Nanoparticle Virtual Impactor study, we are interested in using the inertial means to accelerate nanoparticles for impaction study. The numerical model helps to identify important parameters for accelerating the nanoparticles. We are particularly interested in studying the “virtual” impaction principle in that the nanoparticles are impacted into a receiving tube. The device will be useful to classify and sizing nanoparticles for many high-tech applications.

The collection/classification of nanoparticles using impaction principle often requires accelerating the velocity of the carrier gas into the transonic or supersonic flow regime. To study the application feasibility a virtual impactor has been constructed and its performance under different operational conditions has been studied. Our experimental result shows that the virtual impactor has a 50% cutoff size ranging from 15 to 60 nm under varying the operation conditions. Further, the cutoff size of 60 nm can be obtained at the impactor chamber pressure of 3.0×10^4 Pa. The pressure is much higher than those with single-nozzle solid-stage impactors. Design parameters have also been investigated experimentally. They include the separation distance between the collection probe and acceleration nozzle, the pressure ratio of the upstream and downstream chambers, the diameter ratio of the collection probe and nozzle, the flow ratio of the

minor and total flows, different total mass flow rates and the operation pressure. The experimental data was scaled with the Stokes number in this study. The performance of the virtual impactor can then be estimated with the measured operation variables. A significant finding in the parametric study is that the optimal diameter ratio of collection probe to nozzle is around 1.8 when a critical orifice is used, which is different from the value of 1.4 recommended by previous studies when using virtual impactors for submicron particle applications.

A modification based on studies of the prototype virtual impactor mentioned previously has been performed. The replaceable cone shape nozzle, interchangeable collection probe tip, and different outlet positions were implemented into this modification. Results show that the internal loss particle inside the chamber can be greatly reduced, and by using different throat sizes of cone shape nozzle, collection efficiencies can be higher than in the previous design. Different collection probe designs with porous metal as the collection surface were also studied.

A numerical model was also established to predict the performance characteristics of this virtual impactor. The model consists of (1) calculation of the flow field by solving the compressible Navier-Stokes equations with non-structured grid schemes and (2) limiting particle tracking by solving the trajectory equation with the inclusion of compressible flow drag force. Results show good agreement between the model prediction and experiment data. The model has been used for the optimization of this nanoparticle virtual impactor, and assists in interpreting the experimental data.

3. Particle Transport under Low Pressure Conditions [5, 6, 7, 8]

Transport and deposition processes, e.g., filtration and transport losses, in the nanoparticle size range often occur in the transition and free molecule regimes, depending on the Knudsen number, Kn . Kn is defined as the ratio of the mean free path of gas molecules λ , to the particle radius a , i.e., $Kn = \lambda/a$. Because of the small particle radius in the nanoparticle size range, these processes often occur in the transition ($Kn = 1$) and free molecule ($Kn \gg 1$) regimes. Since λ is inversely proportional to pressure, nanoparticle transport processes can thus be studied under low pressure conditions.

Many practical applications require understanding particle transport at low pressure. Most of the semiconductor manufacturing processes are performed under low pressure, e.g., chemical vapor deposition (CVD), physical vapor deposition and etching. The deposition rate of contaminant particles on semiconductor wafers increases at low pressure due to the reduced drag force on the particles. Therefore, understanding particle transport at low pressure is important in avoiding unwanted particles deposition onto the wafers and in improving the product yields.

Although many quantitative studies on particle behavior or transport have been performed at atmospheric pressure, those at low pressure are very limited. This is partly due to the difficulty in preparing test aerosols at low pressure. One possible method is to produce test aerosols with a known diameter and composition at atmospheric pressure

and to introduce them to vacuum systems through an orifice or capillary. This simple method, however, was found to have a serious problem: the spatial distribution of the aerosols thus introduced to the vacuum chambers is non-uniform in general. In some cases, the particles are actually highly localized. In other cases, aerosol jets produced by the orifice do not disappear, even after a long distance. This difficulty has been a significant obstacle to conducting fundamental studies under low-pressure conditions.

We have established a method [5] that can produce spatially uniform test aerosols at pressures as low as 0.1 Torr. The method utilizes counter-flow configuration where two critical orifices are opposed to each other in a low pressure chamber for turbulent mixing. With this aerosol injection apparatus, it is possible to perform *quantitative* studies on particle transport at low pressure. The inertial deposition of fine particles in a tube with an abrupt contraction [6] and that in a bend of a circular cross section [7] were selected as topics for such transport studies. Numerical simulations for particle trajectories were also performed for comparison. These fundamental studies are an important step towards conducting transport studies in more complex systems, i.e., nanoparticle filtration in the transition and free molecule regimes, in the future.

4. Development of a High Throughput Nanoparticle Generator [2, 10]

A high concentration nanoparticle generator has been developed with high mass-throughput. The generator produces monodisperse aerosols of high concentration in the size range of 3 nm to 1 μ m. It will be useful to challenge high efficiency filter to obtain accurate penetration values. Additional beneficial applications will include the production of industrial quantity of nanoparticles for pharmaceutical and materials sectors.

A multiple-nozzle arrangement of electrospray has been developed to produce high mass-throughput of nanoparticles. Electrospray has been used to produce nanoparticles from solutions or colloidal suspensions. It is capable of producing particles 10-100 times smaller than the conventional pneumatic atomization technique. This will allow the product materials to have 100-10,000 times larger specific surface area than those produced from the conventional technique, for a given quantity of spray solution. The increased surface forms the basis of enabling technology for several important applications, e.g., fast response and high bioavailability for drug products.

One limiting factor in deploying the electrospraying technique is that a single spray-nozzle dispenses only a small quantity of solution in μ l/min. A major challenge will be to increase the mass-throughput from the sprayer. We have successfully implemented a multiple-nozzle electrospray that will allow 1,000 to 10,000 times higher mass throughput rate than the single-nozzle electrospray.

A U.S. Patent Application, US 2002/0007869 A1 [10], "High Mass Throughput Particle Generation using Multiple Nozzle Spraying," was published and the decision by the examiner's office is now pending. The patent application has been credited to the present DOE grant. A copy of the patent application is attached.

Appendix

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