

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

Public Reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimates or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188,) Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE Jan 15, 2007	3. REPORT TYPE AND DATES COVERED Final Report: March 1, 2005 – Dec 30, 2006	
4. TITLE AND SUBTITLE Development of Focus-Free SERS Substrate Assembly			5. FUNDING NUMBERS C-W911NF-05-1-0040	
6. AUTHOR(S) Richard Mu			8. PERFORMING ORGANIZATION REPORT NUMBER NITI-ARO-MR-03-05	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Nami Innovation & Technology Inc. 9474 Smithson Lane Brentwood, TN 37027			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-221				
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.				
12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release, unlimited.			12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Summary Ion beam irradiation has been used to develop microlens arrays for focus-free SERS substrate assembly development. Pulsed electron-beam deposition by ablating Ag target provides further understanding of the PED technique. Under low pressure and lighter mass of backing gas, a smooth thin film can be formed. The increase of molecular mass of the backing gas will result in nanoparticle formation. PED is a powerful technique for materials fabrication and SERS substrate fabrication. All results do indicate the potential for SERS based spectral sensing development but more work is required to further developments. The original proposal was proposed and funded was a 2-year project, funding was cut for the second year. Thus, we can only demonstrate the feasibility is solid.				
14. SUBJECT TERMS Metal and Semiconductor Nanocrystals, SERS, Nanoparticle Fabrication, Pulsed Electron-beamdeposition (PED)			15. NUMBER OF PAGES 13 pages	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OR REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION ON THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT SAR	

Part I. Formation of Microsphere Assembly on A Substrate

1. Deposition of 0.5 and 1 μm Silica and Polystyrene Microspheres on Optical Slides and SiO_2 Substrates

We have found very effective way of depositing submicron spheres, especially polystyrene spheres on mica surfaces with convective paintbrush deposition technique on freshly cleaved mica surface, as illustrated in figures 1 & 2. Several mm sized self-assembled monolayer of 200 nm spheres can be obtained. When the micron-sized silica spheres were used, self-assembly formation is limited with only the convective paintbrush approach. It is partly due to gravity since the sedimentation of the silica microsphere is fairly fast. In fact, we have found that we can make quasi-close packed microspheres on optical slide or silica substrate with the combination of simple deposition and convective paintbrush approach. The later will help to eliminate the multilayer formation. Due to the large size, we have also tried to immerse the microsphere deposited substrate back to solvent and some of the microspheres were removed easily by the solvent due to the poor binding due in part to weakness of the microsphere-substrate interaction and microsphere – microsphere interaction. Therefore, as we actively improve the quality of the microsphere deposition on glass substrate, we also made efforts to address the binding problem.

2. Development of SiO_2 Sol-Gel Nanocoating Strategy

Sol-gel nanocoating approach was designed to address two critical issues for microlens development: 1) sol-gel nanocoating will allow us to uniformly modify the different kinds of optically transparent substrate surfaces which enable us to use single technique to fabricate

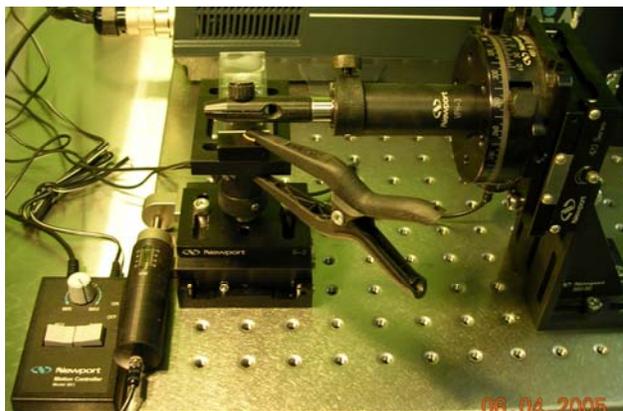


Figure 1 Convective paintbrush experimental setup.

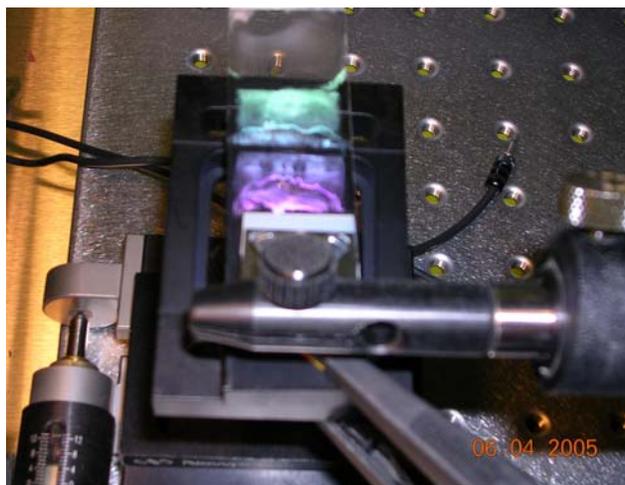


Figure 2 An example of 1 micron silica sphere deposited on an optical slide. The collar is the result of diffraction.

microlens array, and 2) SiO_2 based nanocoating will also serve as a binding layer to immobilize the deposited microspheres on a substrate surface so that the large cracking, as illustrated in figure 3, will be eliminated. It is believed that these large cracks are created as the result of polymer bead shrinkage upon drying.

(A little side track) Figure 4 is an illustration that we can use the self-assembled nanosphere as a template to fabricate spatially ordered nanostructures on a substrate surface. This technique will be further explored when we start to fabricate SERS substrate late of the program.

After fairly thorough literature search along with a undergraduate student: Ms. Erika Perez, we have decided to take SiO_2 sol-gel approach to carry out nano-coating experiment. The project will become one of the undergraduate student's participating NSF funded summer program in my group at Fisk University. The experiment will be carried out in my Fisk laboratory where the proper facilities are available. The detailed experiment outline has been prepared on the next page. Ms. Perez will give a short presentation on June 9 as her summer project.

Title of her project: **Inorganic Nanocoating Objectives**

- To explore the use of inorganic precursors in a series of hydrolysis and condensation reactions to create a quality three dimensional molecular network (such as, sol-gel) that has specific properties to tailor nano-surface chemistry of organic and inorganic substrates in general.
- More specifically, to develop a controllable procedure allowing systematically modifying the substrate surfaces at nanoscale with pure silica sol, as an example, to change the wettability of both organic and inorganic surfaces for the advancement of our silica nanosphere lithography technology.

Precursors

(Tetraethoxysilane (TEOS), Ethanol, and Hydrochloric Acid)

- *The structure and molar ratio of the precursors greatly influences the structure of the deposited film.*

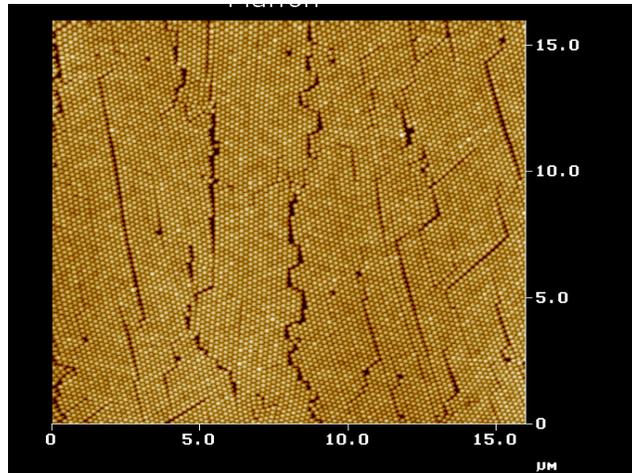


Figure 3 AFM images of 200 nm polystyrene beads formed on a Mica surface.

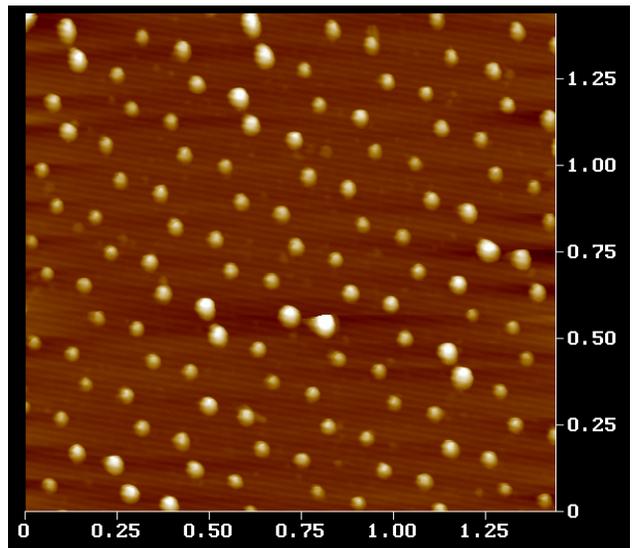


Figure 4 An AFM image of Au nanostructure fabricated on Mica surface with the help of

- Tetraethoxysilane/Tetraethylorthosilicate ($\text{Si}(\text{OC}_2\text{H}_5)_4$) – undergoes hydrolysis (the alkoxide group is replaced by a hydroxyl group.) and provides a molecule that can undergo condensation and hence polymerization can occur.
- Ethanol - adjust the viscosity of the sol, therefore controlling kinetics (how fast) of the gelatin taking place.
- Hydrochloric acid - serves as a catalyst for the hydrolysis and condensation reactions.

Nano-coating Process

- Dip-coating procedure is illustrated in figure 5. The substrate to be coated is mounted on to a clip that is

Desired Outcome and Applications

- Development of an experimental protocol for silica nano-coating
- Establishment of conditions which allows the systematic change of nano-surface chemistry, which includes the controls of film thickness, roughness, uniformity, and wettability
- With an example of silica sol, we will investigate wetting property changes from partial wetting to complete wetting to improve the effectiveness of the nanosphere lithography.



Figure 5 Dip-coating setup in Nanoscale Materials and Sensors lab

3. Other Related Activities

1. Given a talk on “how to obtain support from federal government agencies” Fisk faculty Retreat (May 5, 2005).
2. Participated NSF-Major Instrument in Chemistry” proposal writing and contributed a section on “NMR Investigation of Molecular Diffusion Dynamics and Adsorbate-Adsorbent Interactions in Nanostructured Materials” (May 15, 2005)
3. There are minimum two abstracts in process to be submitted to MRS Fall Meeting which micro- and nanosphere patterning technique is employed for ZnO nanostructure fabrication.

Part II: Ion Beam Modification for Microlens Array Fabrication

1. 10 MeV Pt⁴⁺ ion Irradiation of Silica Microspheres on Optical Slides

In order to controllably change the focal length of self-assembled microlens array, we have proposed to use ion beam irradiation to change the shape of the microlens from nearly perfect microspheres to oblate shape. By doing so, the focal length of the microlens array will be increased. The proper control can also decrease the commonly existed spherical aberration, etc.

In our first try reported in previous monthly report, the use of He ions at 1MeV to irradiate the polybeads failed to show the shape change. It may be due to the relatively low energy loss for small ions, which failed to cause the densification of the polybeads along the ion travel direction. As a result, we have observed no shape changes for He irradiated polybeads on silicon wafer. TRIM calculation, then has been done to use highly charged Pt ions to irradiate silica spheres. From the TRIM calculation, 10 MeV Pt ions should be able to penetrate through 1 micron sized silica sphere as shown in figures 1&2. Figure 1 illustrates trajectory of the ions as they penetrate into the silica beads, while figure 2 illustrates the ion distributions once the ions lose their energy and stopped in the silica materials. The real experiment has been carried out and the SEM images were taken. As illustrated in figure 3, the Pt ion irradiation indeed showed shape modification. The aspect ratio change from 1:1 before the ion irradiation to ~ 2:3 ratio after 10 MeV Pt irradiation. Currently, no high magnification has been conducted due to the limitation of the SEM system available. Further study is underway to obtain possible qualitative results.

Figure 4 illustrates a large view of the oblate shaped silica after high energy ion bombardment. The modification seems to be uniform in very large scale.

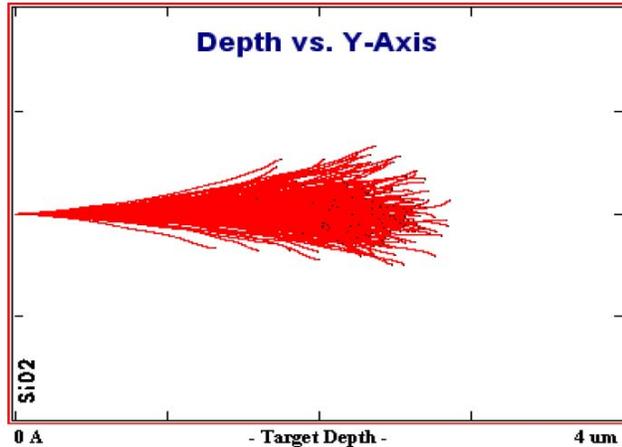


Figure 1 TRIM calculation of penetration depth of 10 MeV Pt ions implanted into silica matrix.

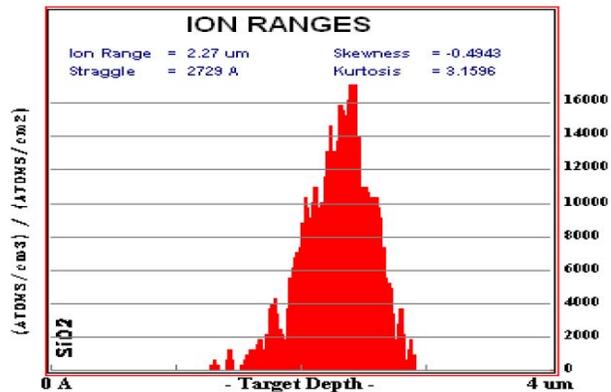


Figure 2 Ion stopping range to ensure the employed ions having high enough energy capable of penetrating through a 1-micron sized silica sphere.

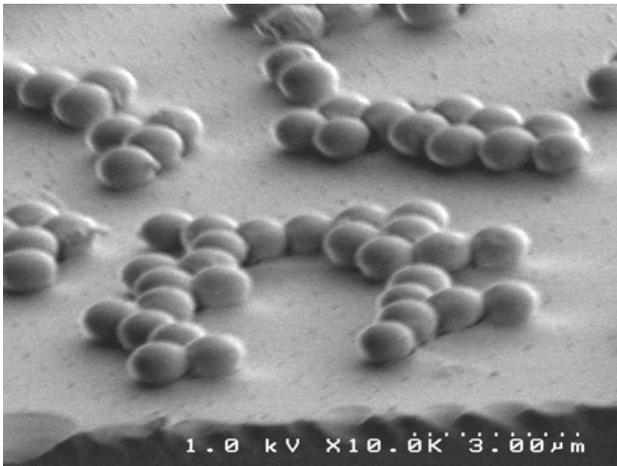


Figure 3. A SEM image of 1-micron silica spheres after irradiated with 10 MeV Pt ions. Clearly, the shape of 1 micron sized silica beads changed from a spherical to oblate shape.

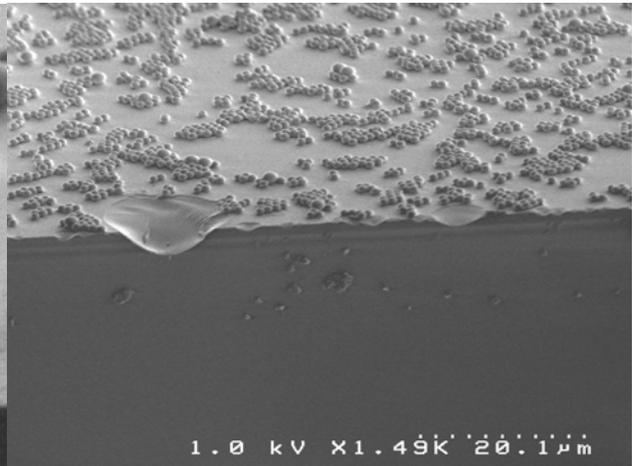


Figure 4 A low resolution of SEM image to show a uniform shape modification occurred demonstrating the feasibility of employing the technique for microlens fabrication.

II. Fabrication of Metal Nanoparticles (Gold or Silver) with Pulsed Laser and its Size Control

In order to obtain optimized SERS substrate, it is important to get pure metal nanos free from other contaminants as in the case of solution chemistry, efforts were made to develop an experimental strategy to control the particle size. Figure 5 has shown that a long time irradiation of Au nanos in water can indeed change the surface plasma absorption intensity and peak position suggesting the size change of the Au nanos.

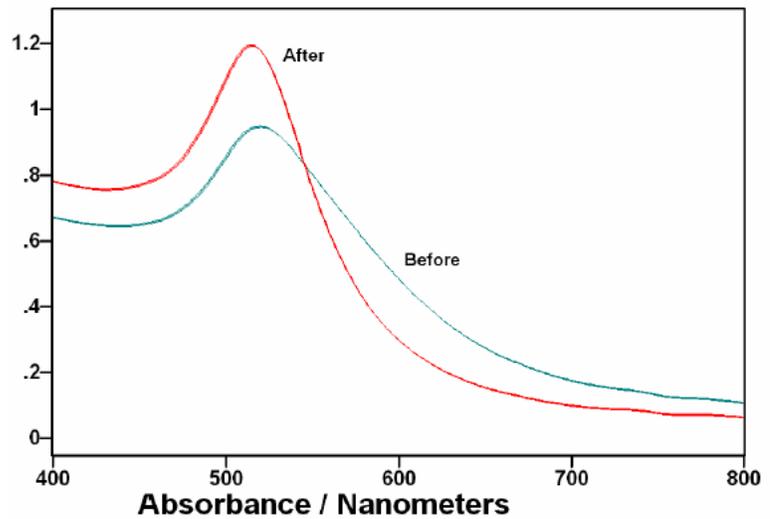


Figure 5 Optical absorption of Au nanos fabricated in water before and after pulsed laser irradiation.

Part III:

Development of New Nanoparticle Fabrication Techniques with an Excellent Size and Surface Chemistry Control for Spectral Sensing

1. Introduction

Surface-enhanced Raman scattering (SERS) technique may have a great potential to be a powerful analytical tool of determining chemical information for molecules on or in the vicinity of nano-sized metallic particle coated substrates.¹⁻¹⁷ Enhancement of optical processes near the surfaces of noble metal NCs opens exciting new possibilities for highly sensitive imaging with high spatial resolutions. In general, there are two traditional operational mechanisms to describe the overall SERS effect: electromagnetic (EM) and chemical (CHEM) enhancement mechanisms. EM enhancement is the amplification of laser fields due to surface plasmon resonances in the metal NCs where the adsorbed molecules to be investigated residing. CHEM enhancement results from electronic resonance/charge transfer between a molecule and a metal surface, which leads to an increase in the polarizability of the molecule.²⁻⁵ Enhancements as large as a factor of $>10^{13}$ have been reported for Raman scattering of dye molecules adsorbed onto the surface of silver NCs, enabling chemically specific detection and measurement of single molecules. Since these large enhancement values occur only within ~ 10 nm of the metal NC surface, enhanced optical processes possess spatial resolutions of the order of the NC size. This powerful combination of high sensitivity and high resolution can be exploited in applications including detection of biological and chemical warfare agents, real time imaging of biological processes in living cells, and measurement of the optical properties of single semiconductor NCs. However, the many reports have shown time and time again that SERS technique suffers severely from the reliability and reproducibility problems, which has hampered the SERS technology for commercial utilization.

2. The CHEM and EM Effects:

- Variation of “CHEM Effect” from system to system. Once the SERS substrate is fabricated, the choice of metal nanoparticles, Ag, Au or other metals and the supporting substrate, have already determined. The nano-surface chemistry of the SERS substrate is fixed. Thus, the possible chemical bonding or nature of the interactions of the metal nanoparticles and supporting substrate with the probed molecules has been decided. Therefore, the surface selectivity of the probed molecules on metal nanoparticle and supporting substrate surfaces can be extremely important: *site selectivity and specificity*. In order to multigate the site selectivity from the supporting substrate, one would have to avoid using 2D structure.
- Spatial variation of optical near field distribution and number of *hot spot* – “nonlinear optical near field effects” called “EM Effect”. Number of theoretical modeling and experiments has demonstrated that the spatial distribution of the nonlinear optical near field *near* the metal nanoparticles is highly dependent on the size, shape, particle density, and configuration of the metal nanoparticle clusters. It is also true that the strongest optical field is *not on the surface of metal nanoparticles. It is rather in the vicinity of the surface*. Therefore, directly adsorbed probed molecules on the metal surface are not guaranteed to have the maximum SERS signal. A small spacer might be useful to enhance the EM effect.

3. Experimental Approaches Addressing the Reliability and Reproducibility Problem

We have initiated two ways to address the problem: one is to develop the technology to produce exactly the same 3D nanostructure in large scale. And the other is to achieve statistically equivalent nanostructure assembly in 3D. That is, within the SERS sampling volume, all possible configurations of metal clusters are included. The former is nice but it is technologically limited and very difficult to achieve. The later is relatively easy to fabricate and more economical. Thus, we would like to initiate the following research efforts in next 12 months: 1) fabrication of metal nanoparticles with pulsed laser ablation in controlled environment and in solution, 2) tailoring the nanoparticle surface chemistry during and after the nanoparticle fabrication, and 3) development of a new light trapping microstructure for SERS signal enhancement.

4. Sample Preparation

In order to obtain spot size, silver (Ag) thin film on optical glass was used as ablation target. The film deposition was done with the help of electron beam evaporation system in our lab. The optical glass was first cut into 10 x10 mm in size. Then the substrate was cleaned with acetone and then methanol in a sonicator. The substrates were then blew dried with dry nitrogen gas before they were amount on to a sample holder for silver film deposition in the e-beam chamber. The film thickness was measured with the help of thickness monitor. A typical deposition rate was 0.2 nm per second. A total of a 50 nm silver film was deposited on the glass substrates to be used for ablation experiments.

5. Pulsed Electron-beam Deposition of Silver on Silicon Substrates

1" diameter x 0.125" silver target from Lesker Company was used for silver deposition on to Si wafer. The Si wafer was cut into 4x4 mm² and went through a simple cleaning process. That is, acetone, methanol and then high pressure pure nitrogen blew dry before amount on to a sample holder, as illustrated in figure 2. In figure 2, the estimated plume center was also marked on the substrate, which provide a reference point for analyses. A total of eight samples were amount on the holder for each run. The location was indexed as A1, A2, and A3 for the top row. B2 and B3 in the middle row and C1, C2, and C3 were the bottom row.

In this study, two types of gas, He and Ar

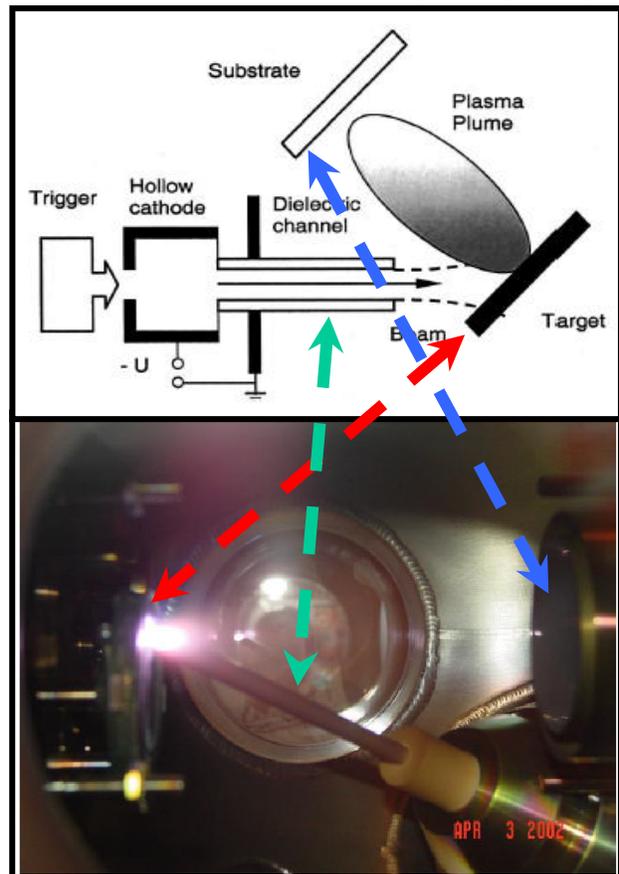


Figure 1 A general lay out of the ablation experiment with a commercial channel-spark source (top). A photograph of e-beam chamber during the ablation (Bottom).

were used at pressure of 11, 13, 15, and 17 m torr and the e-beam charge potential of 11, 13, 15, and 17 keV.

6. Sample Characterization

To estimate the spot size ablated by pulsed electron beam, a high resolution HP scanner was used to acquire the image and image analysis software was used to calculate the spot size. Six spots were averaged to obtain a data point. The atomic force microscope (AFM) used in this study is a Nanoscope III (Digital Instruments, Santa Barbara, CA). Tapping mode AFM was employed to image the thin solid film surface under ambient conditions. The reason we used tapping mode AFM technique over the contact mode AFM is the easiness to minimize the tip-sample interactions which may lead to physical damage or modifications to the sample surface. The typical scan sizes were 1 and 5 μm^2 . The scan rate was about 1 Hz. A simple statistical image was carried out first to gain a general information about each sample before a few good images were recorded.

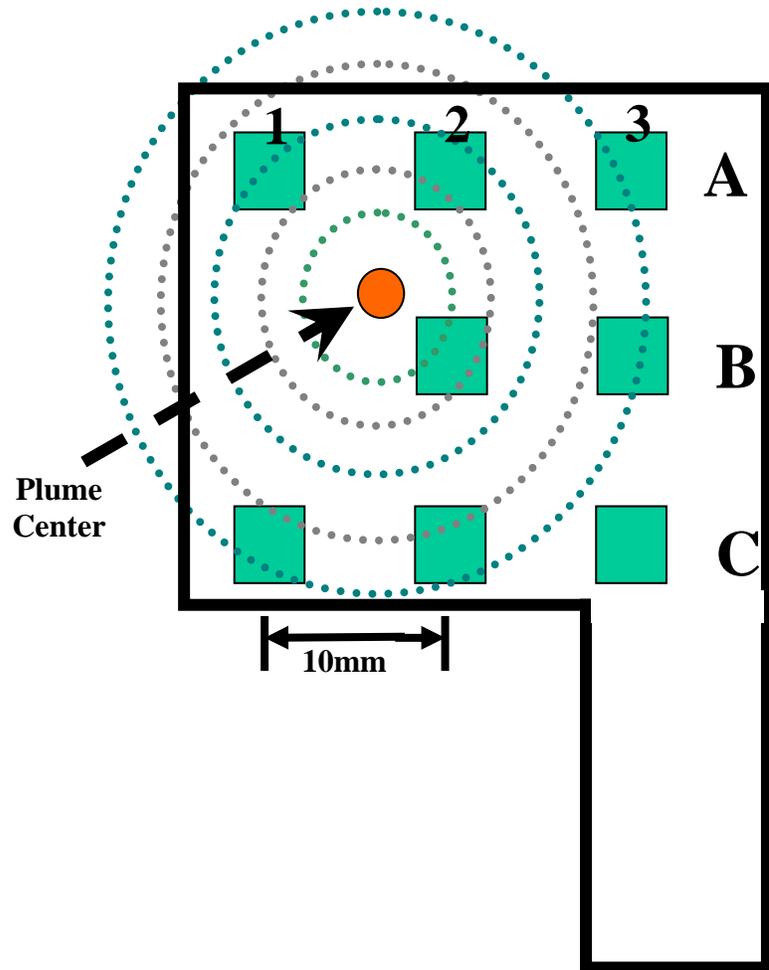


Figure 2 A layout of the Substrate Holder. The dotted circle indicates the ablated plume location with respected to the substrate

7. Pulsed Electron-beam Deposition of Ag on Si Surface

Since our primary goal of the research effort is to obtain optimized experimental parameters of PED system to be used for nano materials fabrication, in this section, efforts were made to understand the deposition process and try to answer the questions like: *where was the ablated material was deposited on the substrate? How was the material deposited? Is it a film, nanoparticles, or both forms? How did the backing gases affect the film or particle formation? And what about charging potential?*

Figures 3 and 4 represent two sets of AFM images sampled from a total of 16 samples (each set contains 8 samples) as illustrated in figure 2 in the experimental section. Figure 3 displays the sample fabricated under Ar backing gas while figure 4 illustrate the samples with He as the backing gas. Under the Ar gas, it is clear that the deposited materials are largely nanoparticles.

Higher particle density and larger size is located near B2 location suggesting the center of the plume is near B2. when He was used as backing gas, the sample surface was very smooth illustrated in figure 4. Few particles were observed indicating that a film might have been deposited.

As discussed in the introduction, when the target material is heated by pulsed electron beam, the irradiated area can reach very high temperature surpassing the boiling point of the material. Depending the electron penetration depth (related to charging potential) and spot size, certain amount of material will evaporate with very fast rate, which lead to the plume formation. Due to the fact that some of the evaporated materials may be in both ionized and neutral forms, the plume is often called plume plasma. As the plume expands into the chamber, it will collide with the gas present in the chamber and create plume-gas interface. The backing gas then serve as the confining medium preventing "free" expansion of the plume. Depending the strength of the confinement (type of gas and pressure in the chamber), the pressure inside the plume will increase and the speed of the plume expansion will also slow down. In fact, the material that was evaporated first will be slowed down in early time through the collision with backing gas molecules. The later evaporated species will collide with the slowed species. The collisions among the ablated species will lead to nanoparticle formation. The reason that the sample B2 has larger and denser particles is that 1) the forward plume species were slowed more effectively and 2) more material was evaporated in the forward direction. As a result, the center of the plume should form larger particles and more material deposited on the substrate. As expected, the samples that away from the center plume contain fewer and smaller particles shown in figure 11. The film formation under He gas can be understood due to the much lighter mass of the Helium with respect to Argon, which leads to weaker plume confinement. Therefore, very small particles or clusters are formed. Once these small particles and clusters arrived on substrate surface, the instability and remaining kinetic energy will lead to film formation.

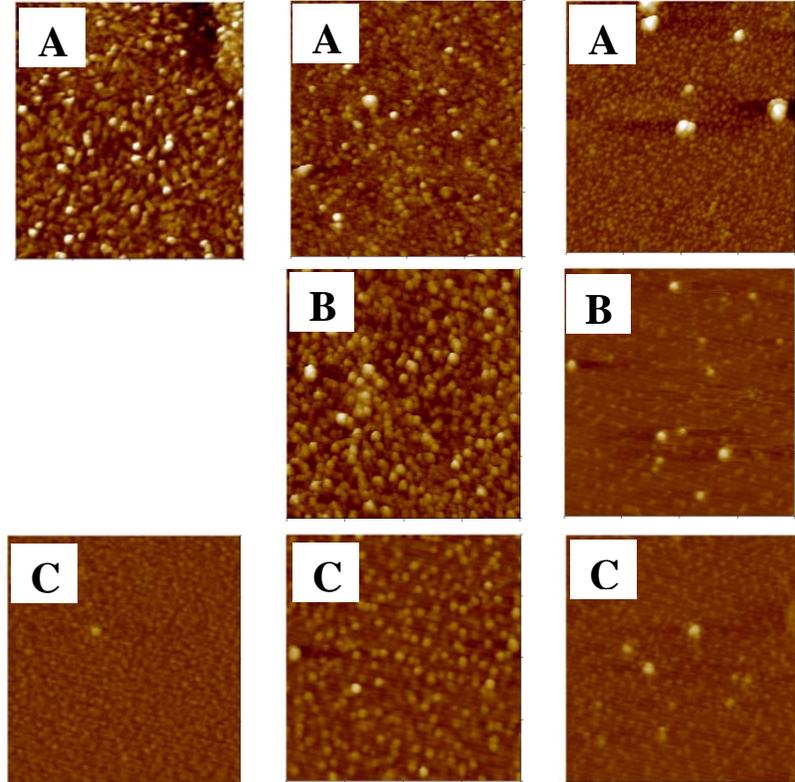


Figure 3 AFM images of Ag deposited Si substrates under Ar backing gas at a pressure of 13 mtorr

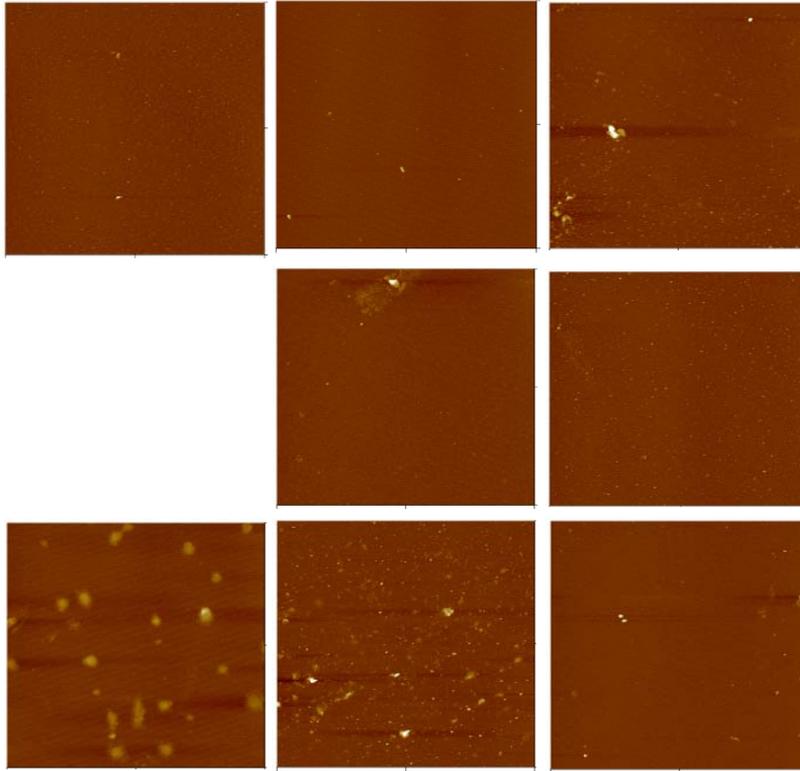


Figure4 AFM images of Ag deposited Si substrates under He backing gas at a pressure of 13 mtorr

Summary

Pulsed electron-beam deposition by ablating Ag target provides further understanding of the PED technique. Under low pressure and lighter mass of backing gas, a smooth thin film can be formed. The increase of molecular mass of the backing gas will result in nanoparticle formation. The interplay of charging potential, backing gas pressure, and types of gas molecules provides wide fabrication choices for materials fabrication. Thus, PED is a powerful technique for materials fabrication.

References

1. R. Stark, J. Christiansen, K. Frank, F. Mucke and M. Stetter, *IEEE Trans. on Plasma Sci.* **23**, 258 (1995)
2. M. Hobel, J. Geerk, G. Linker, C. Shultheiss, *Appl. Phys. Lett.* **56**, 973 (1990)
3. M. Nistor *et al*, *Appl. Surf. Sci.* **247**, 169 (2005)
4. H.L. Porter, C. Mion, A.L. Cai, X. Zhang, J.F. Muth, *Mat. Sci. & Engineering B*, **119**, 210 (2005)
5. R.J. Choudhary *et al*, *Appl. Phys. Lett.* **84**, 1483 (2004)
6. D.B. Chrisey and G.K. Hubler (eds.) “*Pulsed Laser Deposition of Thin Films*,” John Wiley & Sons (1994).
7. J.C. Miller and R.F. Haglund (eds.) “*Laser Ablation and Deposition*,” Academic Press (1998).
8. for examples: E. Fogarassy, D.B. Geohegan, and M. Stuke (eds.) “*Laser Ablation-Mechanisms and Applications*,” European Mater. Res. Soc, Symp. Proc. 55 (1996); J.C. Miller and D.B. Geohegan (eds.) “*Second International Conference on Laser Ablation*,” AIP Conf. Proc. 288, Amer. Inst. Of Physics, New York (1993).
9. Mikhail Strikovski and K.S. Harshvardhan, *Appl. Phys. Lett.* **82**, 853 (2003)
10. Stanley Humphries, Jr., *Charged Particle Beams*, John Wiley & Sons, 211 (1990)
11. PEBS-20 Manual and datasheets