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Supersonic Nanocrystal Deposition for Nanostructured Materials

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ABSTRACT

We experimentally demonstrate the large scale production and controlled collection of metal and semiconductor nanocrystals by laser ablation of microparticles entrained at high density in a flowing aerosol. For silver, produced nanocrystals exhibit bimodal, log-normal size distributions. Mean particle sizes are controlled from 3-16 nm by varying the type and pressure of carrier gas as well as laser fluence. For collection, a micronozzle orifice ($d = 200\ \mu\text{m}$) accelerates nanocrystals through a sonic jet into a vacuum chamber for deposition onto a room temperature substrate. We describe two regimes of deposition that depend on the nanocrystal's energy per atom on impact. Soft landings ($E \ll 1\ \text{eV/atom}$) preserve the individual particle properties such as size and shape. Low energy impactation is demonstrated for CdSe in an argon carrier gas. The CdSe nanoclusters remain crystalline upon deposition and display visible photoluminescence. At higher particle impactation velocities ($E \sim 0.3\ \text{eV/atom}$) nanocrystals exhibit the onset of self sintering upon impact. At high number densities, adherent, conductive lines are formed from deposited silver nanocrystals. Line widths of $33\ \mu\text{m}$ FWHM are directly written onto substrates using a $200\ \mu\text{m}$ diameter nozzle.

INTRODUCTION

Cluster beam methods have been gaining increasing attention for the formation of nanoscale systems.^[1] These techniques have the ability to produce and deposit both individual nanocrystals as well as thin and thick films directly from the nanocrystal jet^[2]. Traditionally, however, cluster beam techniques have faced a trade off between controlling the properties of the individual deposited nanoclusters or producing significant quantities of materials. Recently our group has reported a technique known as laser ablation of microparticles (LAM)^[3] which is capable of controlling the size of the nanocrystals at production rates of grams per hour. Here we demonstrate the use of this system for deposition of individual nanocrystals and their assembly into nanocrystalline thick films.

Smalley and co-workers first demonstrated laser ablation followed by supersonic expansion of the vapor to form nanoclusters with controllable properties.^[4] Particle deposition using an orifice as small as $200\ \mu\text{m}$ was described by Hayashi and co-workers^[5] for depositing metal nanoparticles. This work first demonstrated the ability of gas jet deposition for producing nanostructured patterns. Recently, supersonic deposition of nanoparticles has been developed

extensively by Girshick and co-workers.^[6-7] Their technique involves the aerodynamic focusing of nanoparticles formed in a thermal plasma into a collimated beam that supersonically impacts onto a substrate. By aerodynamic focusing, they are able to deposit macroscopic quantities of nanoparticles in a controllable manner. Though their results are quite good, the production technique lacks fine nanoparticle control and the collection technique is hindered by the use of a large nozzle (~2 mm) that requires an increased pumping capacity as well as a series of aerodynamic lenses to collimate the nanoparticle beam to sub-millimeter dimensions. The LAM technique coupled with a sonic micronozzle combines the advantage of fine nanocrystal control exhibited by laser ablation with the large quantities inherent to many aerosol processes and the controllable direct deposition of sub-millimeter patterns.

This system has been tested with silver for its applicability to conductive nanostructures and CdSe for its potential as a tunable optical device element. Previous work has characterized the nanocrystals produced by ablation of silver microparticles. In addition to silver and cadmium selenide, several other materials are being tested for various applications. Functional materials such as Terfinol-D yield adherent nanostructured thick films with magnetostrictive properties. Soft impaction of silicon and gallium nitride nanocrystals are being studied for use in nonlinear optical nanocomposites.

SOURCE NANOCRYSTALS

The LAM system consists of a generator producing an aerosol of micron sized feedstock microparticles which are ablated by a pulsed excimer laser forming an aerosol of nanocrystals.³ Previously, we have characterized this nanocrystal generator for the production of silver nanoparticles in argon, nitrogen and helium at various pressures^[8]. Pressure was found to be an excellent parameter for tuning the size distributions to a desired mean size in the range from 6-20 nm (Fig. 1a). More detailed studies of the size distributions for silver nanocrystals showed that they exhibit bimodality with a mode due to the laser induced shock wave, at small sizes (3-6 nm) and a second surface evaporation mode at larger sizes (11-16 nm)^[9]. The mass in the distribution displayed a striking shift from the surface mode to the shock mode with increasing laser fluence as seen in Fig. 1b,c.

The produced nanocrystals are sonically accelerated into a vacuum chamber for deposition onto a solid substrate. In this work we have studied the collection sub-system by utilizing a micronozzle and two different carrier gases with greatly different expansion velocities. Of special note is the compatibility of the LAM process with the use of micronozzles for collection. As discussed by Di Fonzo et al.^[6] micro-expansion nozzles produce narrow beams of nanoparticles, however, due to their small diameter often become clogged. Our system has not encountered this difficulty when using nozzles as small as 150 microns, even at large deposition rates. It is believed that two factors are responsible for the large, continuous throughputs. First, we use a co-axial sheath gas to reduce radial diffusion of the aerosol. A skimmer is adjusted to accept the nanoparticle flow plus a fixed amount of the sheath gas flow to buffer the nanoparticles from the walls of the expansion nozzle. Second, LAM produces nanoparticles that are charged, thus preventing coalescence of the small particles into larger agglomerates that may cause material build up around the edges of the nozzle leading to blockage of the flow.

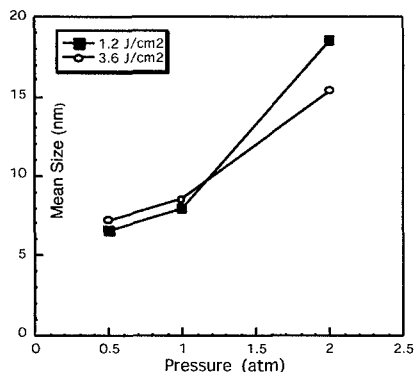
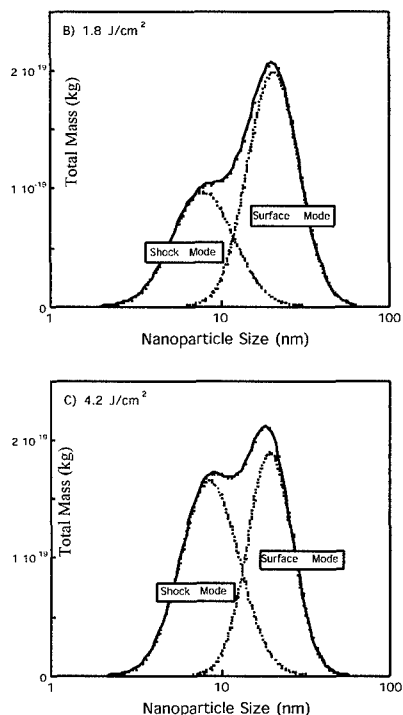


Figure 1. Size analysis for silver nanoparticles produced in the LAM process: a) Mean size versus gas pressure at varying laser fluences. Control of bimodal nanoparticle mass distributions using laser fluence b) 1.8 J/cm² and c) 4.2 J/cm².



RESULTS AND DISCUSSION

Particle Deposition

Soft landings of the produced nanocrystals are required to retain their individual properties such as size and shape. Hard impact leads to particle agglomeration and low temperature coalescence into materials with enhanced mechanical and electrical properties due to the nano-scale grain sizes. For a given substrate and cluster type, the kinetic energy per atom determines the fate of the cluster on impact. Simulations of Hsieh et al.^[10] indicate that clusters with energy much less than 1 eV per atom show little deformation on impact while near this energy significant deformation and compaction occurs.

Our nanocluster beam expands through the micro-orifice nozzle into a low pressure chamber with a pressure ratio of 10⁴. The rarefied gas flow accelerates to the limiting choked-flow velocity (He: $v_c = 760$ m/s; Ar: $v_c = 240$ m/s). Particles in this flow accelerate to the gas velocity within seven relaxation times^[11] which corresponds to ~ 1-2 nozzle diameters for particles of 10 nm or less. The distance required for particle acceleration is less than 400 μ m, well within our typical

collection distances of 1-3 mm. Therefore, we can expect the nanoclusters will impact onto the substrate surface with a kinetic energy given to good accuracy by the mass of the cluster and the velocity of the choked flow of gas through the micronozzle.

To adjust this velocity through our thin plate nozzle we have two options: increase the carrier gas stagnation temperature or use different carrier gases. Higher temperatures produce faster jets through an increase in the average kinetic energy of the gas molecules in the carrier gas. In this work we demonstrate soft and hard impaction through the use of different carrier gases. The average velocity of an ideal gas is inversely proportional to the molecular mass. A low molecular weight gas such as helium will have a high gas velocity ($v_c = 760$ m/s) whereas heavier molecules such as argon have a lower average velocity ($v_c = 240$ m/s). For materials like silver and cadmium selenide in argon the kinetic energy per atom is limited to 0.03 eV/atom while for helium it is up to 0.3 eV/atom. Therefore materials deposited from a helium jet have kinetic energy that is a significant fraction of the cluster binding energy and will compact on the substrate. On the other hand, materials deposited in argon are expected to land softly.

Soft Landings (CdSe nanocrystals in Argon)

For application as quantum dots, nanocrystals must retain their size and shape upon impaction. In addition, no defects should be generated within the nanocrystals during deposition. As discussed above, CdSe nanocrystals in an argon carrier gas impact the substrate with no more than 0.03 eV/atom, well below the binding energy of the crystal. Figure 2 demonstrates that the nanoparticles were non-agglomerated, spheroidal and remained crystalline upon impact. Note that the nanocrystal density on the surface can be controllably deposited in a fractional monolayer by adjusting the number density of feedstock in the carrier gas and the raster speed of the substrate underneath the jet. Visible luminescence was observed from CdSe nanocrystals deposited onto quartz substrates.

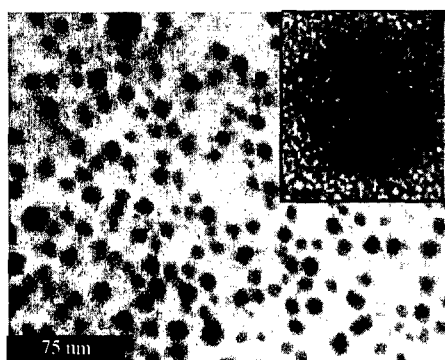


Figure 2. Cadmium Selenide nanocrystals deposited at low kinetic energy in argon carrier gas. The main TEM micrograph shows the overall size distribution and the inset shows a single crystalline 8 nm diameter CdSe nanocrystal.

Hard Impacts (Ag nanocrystals in Helium)

To demonstrate hard impaction of clusters, we ablated silver microparticles and deposited the resultant nanoclusters onto a room temperature substrate. At large velocities, the nanocrystals sintered together on the substrate as a continuous adherent film.^[12] Preliminary conductivity measurements as well as cross-sectional SEM imaging of these films support the conclusion that the nanocrystals form dense, sintered compacts. By employing a micronozzle for the expansion and by using a small substrate-nozzle distance ($\sim 1\text{mm}$), the width of the nanocrystal jet at the substrate can be minimized. Figure 3 shows an optical micrograph of silver nanocrystals deposited on a translated silicon wafer to controllably write lines. The height profiles of these lines can easily be made in the $10 - 100\text{ }\mu\text{m}$ range with widths of less than $80\text{ }\mu\text{m}$ FWHM. The diffuse edges of the lines are due to Brownian diffusion within the jet. To achieve sharp edged lines, a stencil mask can be used^[13]. It should be noted that these lines are less than half the nozzle diameter demonstrating the effectiveness of the sheath gas both at reducing radial particle diffusion in the jet and the ability to aerodynamically focus the jet.

These films are robust and adherent when deposited on silicon wafers from a helium jet. No indication of scratch off is noted when the film is measured with the sharp profilometer scribe. This demonstrates qualitatively the onset of sintering even at room temperature. Observations of the microstructure within the deposited silver lines revealed a variation in grain structure with impaction energy. At lower cluster energies, the films were nanostructured and exhibit numerous small voids with coarsening of grains. For higher energies, better compaction was seen with fewer voids and a grain structure approaching the bulk. Films impacted from the helium jet at large deposition energies ($\sim 0.3\text{ eV/atom}$) had improved conductivity as compared to silver films deposited in argon.

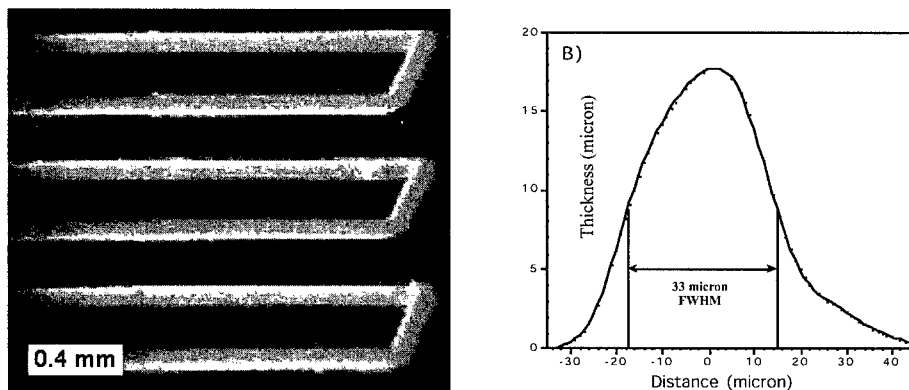


Figure 3. Adherent and conductive silver lines that were directly written from silver nanocrystals in a helium jet. A) Optical micrograph of a serpentine test pattern, B) Profilometer scan of a line with 33 μm FWHM and 80 μm base width.

CONCLUSIONS AND FUTURE WORK

We have demonstrated soft impaction of CdSe nanocrystals in an argon jet and hard impaction of Ag nanocrystals in a helium jet. Aerodynamically focused silver nanoparticle jets are capable of writing patterns of narrow conductive lines with good adhesion to the substrate. Currently we are studying the variation of conductivity and film microstructure with particle kinetic energy. Luminescence studies of semiconductor nanocrystal quantum dots are underway to determine the fraction of fluorescing particles and their quantum yield. To incorporate these particles into functional optoelectronic nanocomposites, we have constructed a system which allows nanocrystal deposition as described above followed by thin film passivation with a larger band gap material by ion beam sputtering or pulsed laser deposition.

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