Chapter 4: Microhollow Cathode Discharge Operating Conditions Impact on Nanoparticle Size Production

"There's plenty of room at the bottom." — R. Feynman

4.1. Introduction

Nanoparticles have emerged as a principle component in many fields of research, ranging from heterogeneous catalysis[1] to aerosol science[2] to biology.[3] The aspects of nanoparticles that enable these applications are the ratio of surface area to volume and/or the quantum confinement effect of the nanoparticles. The actual particle size is invariably one of the most important factors in determining the resultant optical, magnetic, and/or catalytic properties.

The desire to control precisely particle size has led to many synthesis techniques, including liquid and aerosol methods. Liquid methods have improved substantially in their ability to generate monodisperse distributions,[*4-5*] but at the difficulty associated with using surfactants to cap and to control the growth process may not be desirable. Aerosol methods are favorable in this regard as collection can proceed independent of synthesis and the capping material can be selected.[*6*]

A microhollow cathode discharge (MHCD) was recently demonstrated to generate an aerosol of silicon nanoparticles from silane.[*7*] The size of nanoparticles produced was measured *in situ* using a standard aerosol technique with a Radial

Differential Mobility Analyzer (RDMA) to be in the 3 to 5 nm size range. The only variable reported to affect the nanoparticle size was the concentration of silane passed through the discharge.

The RDMA was capable of the size measurements, but was not ideal since it was not designed to measure particle size below 8 nm.[*8*] A new RDMA (i.e., the nano-RDMA) has recently been reported that is fully capable of making size measurements in the 1 to 12 nm size range.[*9*] In this section, particle size measurements made using a nano-RDMA will be reported from the synthesis of nanoparticles. The effect on particle size of the following parameters will be reported: (1) silane concentration, (2) plasma flow rate, (3) plasma current, and (4) germanium concentration (no silane).

4.2. Experimental Method

The size of nanoparticles produced using a MHCD were determined using the setup shown in figure 4.1. The MHCD was constructed as previously reported.[*7*] Briefly, the discharge consisted of two electrodes where one was a stainless steel (SS) capillary (cathode, I. D. ≈ 180 μm, length 15 mm) and the other was a SS tube (anode, O. D. ≈ 3 mm). The two electrodes are maintained at a fixed separation of 1 mm. Between the electrodes the discharge was sustained using a high voltage power supply with a current-limiting resistor in series. The electrodes were enclosed inside a glass tube (O. D. ≈ 12 mm) using UltraTorr and Swagelok fittings.

Three separate gas streams controlled with mass flow controllers were delivered to the MHCD. Two gas streams (an ultrahigh purity argon and the other 20 ppm silane in argon or 21 ppm germane in argon) were passed through the capillary. This stream passed directly through the most intense portion of the plasma that was located inside of

the capillary. The third stream was introduced in the gap between the electrodes where the afterglow of the discharge was visible. This stream served to dilute the particle stream emerging from the capillary. The combined stream with a total flow rate of 600 standard cubic centimeters per minute (sccm) passed through the anode that is connected to the nano-RDMA for *in situ* particle size analysis. The flow rate through the capillary was maintained at 150 sccm for the experiments studying the effects of plasma power and hydrogen concentration. For the experiments varying the flow rate through the capillary, the concentration of silane was maintained constant at 3 parts per million (ppm).

The nano-RDMA used for these measurements was the first version. It was operated in voltage stepping mode for all experiments using a 10 standard liters per minute (SLM) nitrogen sheath flow rate. Stepping mode consisted of setting the voltage on the nano-RDMA and waiting two seconds while this voltage stabilized. The current produced by the charged particles transmitted through the nano-RDMA was measured with a home-built Faraday cup electrometer sensitive to ±1 fA.

The particle composition of the germanium nanoparticles was confirmed through depositing directly from the discharge on a silicon wafer that was cleaned with hydrofluoric acid (the composition of silicon nanoparticles was confirmed in the previous report[*7*]). In this configuration, the wafer was positioned so that it rested on the anode on top of a holder that allowed the gas flow to exit through holes drilled through the radius, as shown in figure 4.2. After exposing the sample to air, the sample was analyzed using energy dispersive spectroscopy (EDS) in a scanning electron microscope (SEM).

4.3. Results and Discussion

The results for experiments varying plasma current are presented first. In figure. 4.3, the particle size distributions measured for various current levels is presented. Except for the lowest current (i.e., 2.5 mA), the distributions were approximately identical. This indicates a saturation type behavior in plasma current. The plasma current was closely associated with input power as the voltage between the electrodes varies slightly with current. Beyond a certain power input, the MHCD did not require additional power to decompose the gaseous precursor. Due to these data, the MHCD was operated typically using plasma currents of 7.5 mA.

Operating with the lowest power impacted the heating in the discharge and the energy distribution of the electrons. The plasma absorbed less power and did not experience as much joule heating, lowering the neutral gas temperature of the discharge. At the same time, the plasma density was lower, resulting in fewer available energetic electrons to further ionize neutral species and to break apart molecules. Due to these two effects at low power, it is likely that less precursor was decomposed and therefore the result was smaller nanoparticles.

The results for different silane concentrations were repeated as well using the range-appropriate nano-RDMA. As shown in figure 4.4, the size distributions revealed a similar trend of increasing particle mobility diameter with increasing precursor concentration, but the measured distributions were narrower than previously reported due to the better resolution of the nano-RDMA. The size distributions broadened and increased in concentration of particles produced with increasing concentration as well, as reported previously. The concentrations measured here are similar to those reported

previously. The final observation made using the nano-RDMA was that particles smaller than 2.5 nm were found for concentrations less than 3 ppm.

The third parameter investigated was the effect of the flow rate through the capillary on particle size production, demonstrated in figure 4.5. It was found that the flow rate through capillary does not affect particle size produced. This result was somewhat peculiar as the different flow rates should correspond to different residence times in the discharge. It is important to note that flow rate through the capillary is most likely not directly related to residence time, as the plasma volume inside the capillary could expand or contract depending on the actual flow rate. The flow rate through the plasma did not appear to affect the concentration of particles produced either despite a greater amount of precursor (same concentration) passing through the discharge. To fully explain this result would require simulations of the process that led to particle formation as well as the particle dynamics in and after the discharge. A possible explanation for this result is due to particle loss. With the same precursor concentration, the discharge nucleated particles of identical size for each of the flow rates tested. At the higher capillary flow rates, the flow rate of the argon stream introduced in the afterglow portion was lower. With the gas emerging from the capillary expanding and the lower flow rate mixing in the afterglow, more particle deposition could occur at the anode. The lower sheath flow rate would decrease the buffer thickness that particles would have to travel to deposit on the anode.

The final variable investigated for its affect on particle size production was germane concentration in the discharge, shown in figure 4.6. The particle size increased and the size distribution broadened with increasing amounts of germane introduced into

the flow through the capillary. The germanium nanoparticle size produced was larger than the silicon nanoparticle produced with similar precursor concentrations. The difference could partially be attributed to bond length, but could also be due to a difference in growth kinetics.

The maximum concentration of germane that could be introduced into the discharge for extended periods of time was 4 ppm. This was lower than the limit for silane (5 ppm). Using high concentrations of precursor caused material to deposit inside the capillary, increasing the pressure upstream of the capillary. The capillary would eventually clog completely, extinguishing the microplasma and requiring installation of a new capillary.

The identity of the germanium nanoparticles were confirmed through collecting the nanoparticles on a silicon substrate and measuring the energy dispersive spectra (EDS) in a SEM, as shown in figure 4.7. The spectra confirmed the presence of germanium, but also included silicon, oxygen, and carbon from the substrate. No metallic impurities from the capillary were observed. The lack of metallic impurities was a significant observation given the results associated with sputtering of the capillary (chapter 5). This suggested that a gaseous precursor introduced into the microplasma inhibited sputtering. The same material that caused the capillary to clog at high precursor concentrations most likely deposits on the capillary walls, coating the surface and preventing the sputtering of the metallic electrode.

4.4. Summary

The effect of three important parameters (plasma power, flow rate, and gas composition) on particle size produced was measured. The mean particle size and

standard geometric deviation increased with silane concentration passed through the discharge, but the size distributions were narrower than previously reported due to the improved resolution of the nano-RDMA. A threshold plasma current is needed for the discharge to form particles with identical sizes while the flow rate through the capillary did not affect the particle size produced or number concentration. Introducing germane into the discharge resulted in the production of germanium nanoparticles and did not produce additional sputtered material.

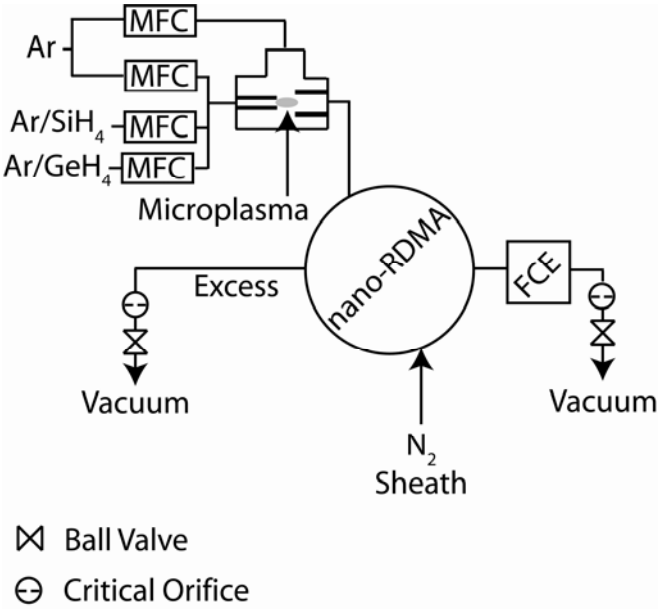

Figure 4.1. Schematic of Microplasma.

Schematic of experimental set up used to measure the effect of the microplasma operating conditions on nanoparticle production.

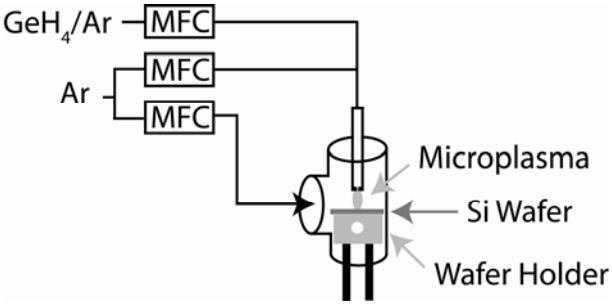

Figure 4.2. Schematic of Microplasma Deposition.

Schematic of experimental setup used to collect germanium nanoparticles. The silicon wafer was positioned on a holder constructed of aluminum.

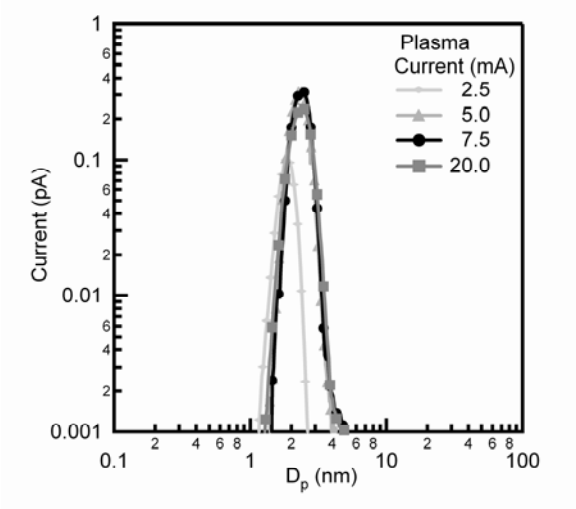

Figure 4.3. Size Distribution for Different Plasma Currents.

Silicon nanoparticle size distribution produced using the microplasma at different currents. The microplasma was operated with 3 ppm of silane and the total flow rate through the capillary was 150 sccm.

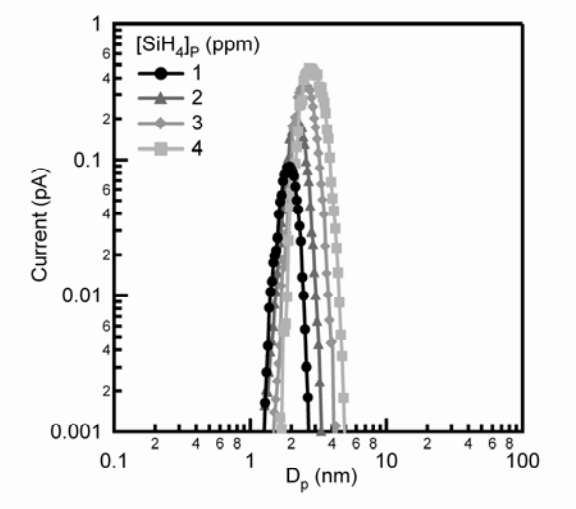

Figure 4.4. Size Distribution for Different Silane Concentrations.

Silicon nanoparticle size distribution produced from a single microplasma with different concentrations introduced into the microplasma. The plasma current was 7.5 mA and the total flow rate through the capillary was 150 sccm.

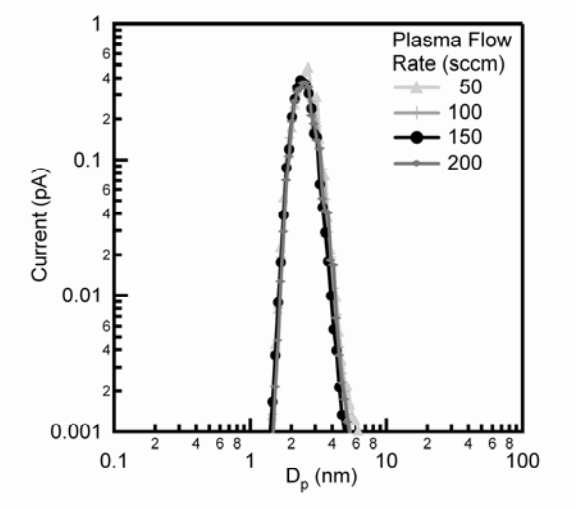

Figure 4.5. Size Distribution for Different Plasma Flow Rates.

Silicon nanoparticle size distribution produced using a microplasma with different flow rates through the capillary. The silane concentration was 3 ppm and the plasma current was 7.5 mA.

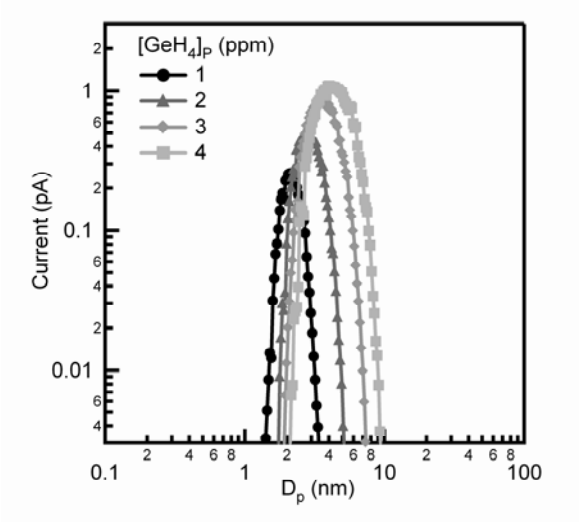

Figure 4.6. Size Distribution of Germanium Nanoparticles.

Germanium nanoparticle size distribution produced using a microplasma with different precursor concentrations flowing through the capillary. The total flow rate through the capillary was 150 sccm and the plasma was operated with a current of 7.5 mA.

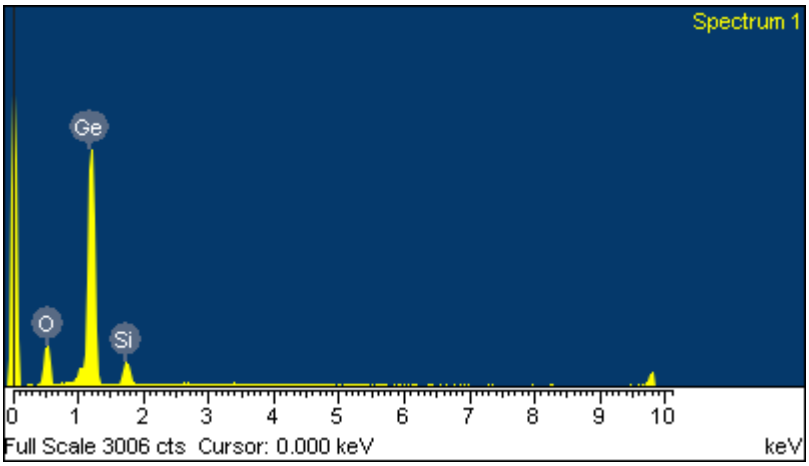

Figure 4.7. EDS of Germanium Nanoparticles.

EDS of germanium nanoparticles deposited on a silicon wafer. No evidence of iron was observed.

References

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