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Rf-plasma Synthesis of Nanosize Silicon Carbide and Nitride

Final Report

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Rf-plasma Synthesis of Nanosize Silicon Carbide and Nitride

FINAL REPORT

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Abstract

A pulsed rf plasma technique is capable of generating ceramic particles of 10 nanometer dimension. Experiments using silane/ammonia and trimethylchlorosilane/hydrogen gas mixtures show that both silicon nitride and silicon carbide powders can be synthesized with control of the average particle diameter from 7 to 200 nm. Large size dispersion and much agglomeration appear characteristic of the method, in contrast to results reported by another research group. The as-produced powders have a high hydrogen content and are air and moisture sensitive. Post-plasma treatment in a controlled atmosphere at elevated temperature (800 °C) eliminates the hydrogen and stabilizes the powder with respect to oxidation or hydrolysis.

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SUMMARY

This program explored the synthesis of nano-size powders of silicon nitride and silicon carbide by a novel pulsed-plasma technique. The method had been developed in France as a research tool to study the nucleation of silicon particles in silane discharges and it seemed plausible that it could be applied to other chemistries. Whereas a continuous low temperature rf plasma (13.56 MHz) of silane/ammonia mixtures gives silicon nitride particles with large average size (100-200 nm. diameter), the pulsed technique, applied to silicon, was shown to give small monodisperse particles with size controllable by plasma on-time.

In this program, silicon, silicon nitride and silicon carbide particles were successfully produced with average size as low as 7 nm. (0.007 μ) diameter. The as-synthesized powders have a high hydrogen content which imparts a strong sensitivity to oxidation by moist air. A post-plasma heat treatment of the powders renders them air-insensitive. The powders exhibit significant polydispersity which is not expected to negatively impact sintering, but there is also some fraction of apparently hard-agglomeration observed. The agglomeration mechanism is not well understood and sintering experiments will be needed to test the impact of this powder feature on macroscopic properties.

INTRODUCTION

There has been much effort in recent years to develop methods for producing materials with nanometer scale substructure. The desire is to control the macroscopic material properties such as toughness, elasticity and porosity by tailoring the microstructure. For ceramic materials, one approach is to synthesize nano-scale particles and develop methods for compressing and sintering these powders. A wide variety of approaches to manufacturing nano-particles of ceramics have been explored with various degrees of success[1]. Thermal plasma techniques[2] in which precursors are atomized and allowed to condense in the afterglow have been highly successful for many materials including metals and oxides. For thermal plasmas, however, the chemistry of the powder is typically controlled by thermodynamics and some compounds have been especially difficult to make including silicon nitride. Other approaches to synthesizing nano-particulate materials include direct nitridation of silicon, carbothermic reduction of silica, gas phase reaction[3] of $SiCl_4$ and NH_3, laser pyrolysis of gaseous reagents[4], and thermal pyrolysis[5].

Almost a decade ago, Buss and Ho patented a process[6] for synthesizing ultrafine particles of ceramic, metal and polymer materials in a low-temperature, non-thermal, radio frequency (rf) plasma. The method involves flowing gaseous precursors at low pressure through a glow discharge. Electron-molecule collisions in the plasma result in fragmentation of the starting gases into reactive free radicals which undergo complex gas-phase chemistry leading to particle nucleation. Properties of the powder were thoroughly characterized by a variety of techniques[7]. In particular, the average particle size and size-dispersion were found to be large, and only weakly controllable. The average particle size was typically 100-200 nm.

During the past decade, particle formation and transport in plasmas has become an area of intense interest and activity[8]. It has developed that these particles, occurring in the plasmas used to manufacture microelectronic devices, can result in serious loss of wafer yield. Stimulated by this economic urgency, many laboratories worldwide have begun investigating the mechanisms governing particle nucleation, growth, trapping and agglomeration. One important discovery by Boufendi et al.[9] in France was that by pulsing the rf plasma, very tight control of the particle size and dispersion was achieved in the case of silicon particles from silane.

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In this program, we have applied the pulsed plasma technique to the synthesis of silicon nitride powder and achieved reasonable control of particle size as low as 7 nm. The particles made in this way are rich in hydrogen-containing functionalities and the resulting powder is air-sensitive making subsequent handling difficult. We have found a successful post-plasma heat treatment of the powders which renders them air-insensitive.

We have also applied the pulsed plasma technique to the synthesis of silicon carbide particles. Several chemical approaches including silane/hydrocarbon plasmas and methyltrichlorosilane(MTS)/hydrogen plasmas are compared. The chemistry of the resulting powder is strongly affected by the choice of reagents. Particles synthesized from the MTS/H_2 plasmas was found to yield stable silicon carbide powder after heat treatment.

EXPERIMENTAL

Experiments are performed in a cubic aluminum chamber, 46 cm. length, mechanically pumped to the 1 mTorr base pressure range. A diagram of the electrode assembly and powder collection is shown in Figure 1. The plasma assembly consists of a 15 cm. diameter powered electrode, perforated with holes to allow gas flow in a showerhead configuration. The plasma region is enclosed on the sides by a grounded aluminum sheet with a grounded high transmission screen across the bottom. The distance from the powered electrode to the confining screen is 3 cm. The 15 cm. diameter pumping port is located beneath the electrode assembly (4-15 cm. distance), and is fitted with a single sheet of Whatman #1 filter paper. Transmission electron microscopy (TEM) is employed *ex situ* in order to study the size and morphology of the particles generated. To obtain samples, a TEM sample grid is placed beneath the plasma assembly on the filter paper.

A 10 mWatt helium-neon laser passes through the region beneath the plasma (or through holes in the electrode assembly wall). Laser light scattering from particles is observed by eye as a qualitative characterization of the process.
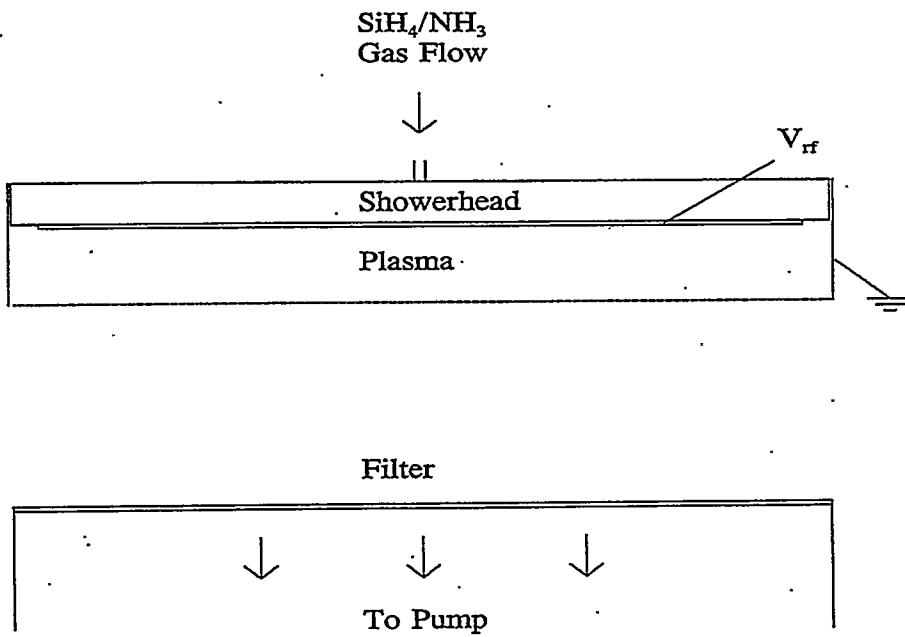
Figure 1. Schematic of the pulsed plasma apparatus.

Amorphous hydrogenated silicon particles are generated from silane/argon gas mixtures, typically, 1-2 sccm silane, 30 sccm argon, 200 mTorr pressure. Hydrogenated silicon nitride particles are produced in a silane/ammonia discharge, typically 10 sccm SiH_4, 60 sccm NH_3, 500 mTorr pressure. Silicon carbide particles are synthesized from a methyltrichlorosilane (MTS)/hydrogen plasma with a flow rate ratio of 1:10 and a pressure of 350 mTorr or from silane/methane or silane/ethylene mixtures.

In a typical experiment, gas flow is first established; then, the plasma is pulsed with a square-wave (100% amplitude modulation) for 100 periods. The TEM grid is then removed and analyzed. In order to obtain large quantities of powder for bulk analysis, the plasma is pulsed for several hours and the filter with accumulated powder is removed.

Experiments are conducted to verify that the flow is laminar. Flowing 10 sccm SiH_4 and 60 sccm NH_3, at 500 mTorr pressure, a continuous plasma is operated for 10 minutes. Black construction paper replaces the filter paper covering the 15 cm. diameter pump port and the pattern of white powder accumulated on the paper is readily visible.

RESULTS AND DISCUSSION

Silicon

In a study aimed at duplicating the experimental conditions of Boufendi et al[9], we investigated the formation of silicon particles in a silane/argon plasma. Using conditions similar to those of Ref. 9, (flowing 2 sccm SiH_4, 28 sccm Ar, at 200 mTorr pressure, 560 Volt rms.) we generate amorphous hydrogenated silicon particles. We find that the growth kinetics differ very markedly from those of the previous study. In Fig. 2 is shown the measured size distribution (obtained from analyzing the TEM photos) for silicon
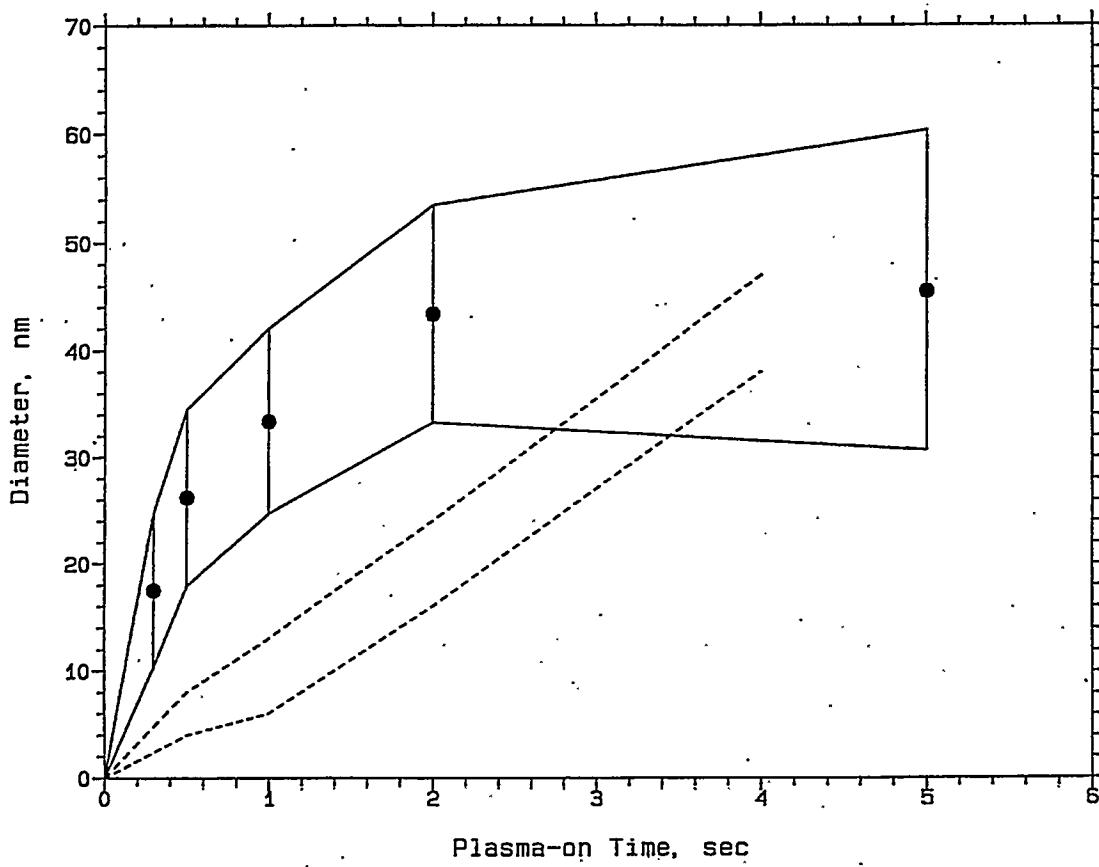
Figure 2. The size distribution of silicon particles, measured by TEM, from a pulsed rf discharge vs. plasma on-time. Solid lines are one standard deviation. Dashed lines are approximately the results for similar conditions from Ref. 9.

particles as a function of plasma-on time with the upper and lower solid line giving one standard deviation. Shown for comparison are dashed lines depicting the distribution obtained under

apparently similar conditions by Boufendi et al. We observe an initial rapid growth in particle diameter (70 nm/sec) which, for longer plasma on-periods, decreases to a slow growth rate (0.5 nm/sec) comparable to the growth rate of thin film silicon nitride on the walls. Growth rate of film on substrates placed on the screen is measured to be 0.3 nm/sec. In addition, the size dispersion is very large, in fact, with all sizes from zero to approximately twice the average diameter about equally represented. The very rapid growth phase followed by a marked slowing is similar to what was observed by Shiratani et. al. for growth of silicon in a Si/He discharge[10]. They postulate that the very rapid growth results from agglomeration of smaller particles although acknowledging that there are kinetic limitations to this agglomeration process.

We are unable at this time to resolve the discrepancy between our particle growth dynamics and those of Boufendi et al. We verified that the plasma off-time (from 1-10 sec., typically 2 seconds) played no role; the linear flow rate of gas under our conditions is 10 cm/sec, so that the particles should be swept from the plasma region in less than a second. The flow was demonstrated to be laminar by operating a continuous plasma of silane/ammonia and observing the pattern formed on black construction paper placed over the exit port 15 cm from the plasma-confining screen. The image of the screen was very well reproduced on the paper. It might seem surprising that the particles which are charged negative with respect to the plasma can surmount the potential barrier to pass through the screen. The particle experiences a combination of forces including fluid drag, ion drag, gravitational and, possibly, a thermophoretic force directed against the electrostatic barrier to passing the screen. The fluid drag, ion drag, thermophoretic force and particle charge all scale as the particle radius squared. Thus, particle growth should not greatly affect the force balance unless the particle mass became great enough that gravity begins playing a role. It seems more likely that the screen hole size, 1.4 mm, is large enough that there is a significantly lower barrier for a particle to pass through the center of the hole than near the wires themselves. Perhaps this electrostatic barrier is sufficiently reduced that the combination of forces is adequate to push the particle across. Actually, for laminar flow, an aerosol passing through a screen would not imprint the pattern, as the streamlines would close again very close to the wires. It is necessary to invoke electrostatic repulsion of the particles by the wires, pushing the particles out of their streamlines to imprint the pattern. In traveling 15 cm to the filter paper, small particles should diffuse out of their streamline erasing the pattern. We estimate that only

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particles larger than about 200 nm will remain in the streamline to carry the pattern to the paper. Thus it is only the agglomerates which are patterned on the paper.

No variation of pressure, flow, rf power, or gas mixture reduced the agglomeration or size dispersion noticeably. Although much effort was expended to match conditions of geometry, linear flow velocities, pressure and power, we were unable to observe the nearly monodisperse, unagglomerated silicon particle growth observed by Boufendi et al. Plasmas are, however, notoriously difficult to reproduce quantitatively in different laboratories. We are not actually able to confirm, at this time, that the plasma density, spatial uniformity, or temperature coincide with those of Boufendi et al. It has been suggested that the actual power density used by Boufendi is much lower than that used in our experiments, perhaps less than 1 Watt[11]

The silicon particles (Figure 3A) exhibit a structured surface morphology, with a roughness on the 5 nm scale, very similar to that reported by Boufendi et al. This surface texture
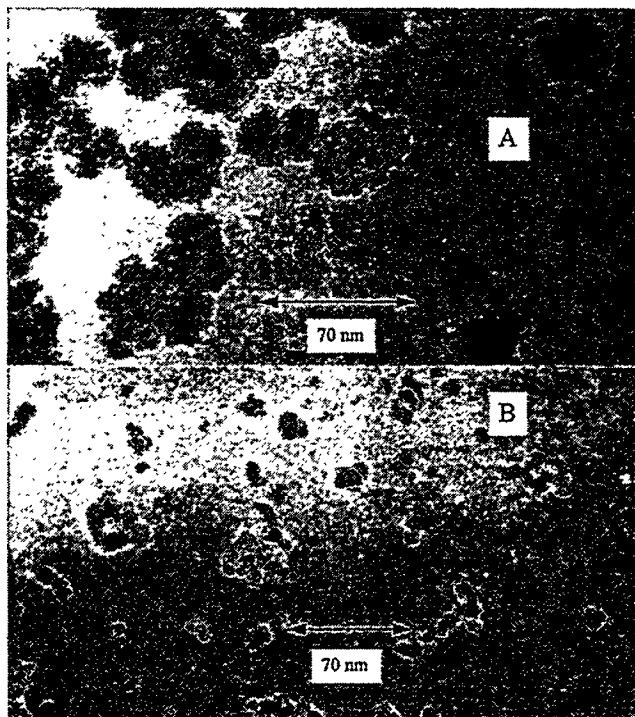

Figure 3. TEM photograph of particles generated in the pulsed plasma. A) Silicon 0.5 sec silane/argon plasma, B) Silicon nitride, 0.2 sec silane/ammonia plasma.

may result from a growth mechanism which consists of the agglomeration of 5 nm diameter particles as has been suggested. Alternatively, a molecular growth mechanism involving island

formation on the surfaces may lead to rough surface topography, including in the chemical vapor deposition of silicon[12]. It is also possible that the sub-structure of these particles is more elaborate than is apparent with our TEM resolution. The particles may even have a fractal type morphology as has been seen for other plasma-generated particles by Garscadden, Haaland, Ganguly and Williams[13,14].

Silicon Nitride

Particles are readily formed in a pulsed rf discharge of silane/ammonia gas mixtures. The chemistry of the particles appears consistent with our earlier observations using a continuous rf plasma[7]. Fourier transform infrared spectra (FTIR) (Figure 4) show strong SiH (2130 cm^{-1}) and NH absorptions (3360 cm^{-1} and 1550 cm^{-1}), confirming that the powder has a high hydrogen content. In the earlier work, the stoichiometry of the particles was found to depend on the silane to ammonia ratio in the inlet gases, and the color of the powder was indicative of the
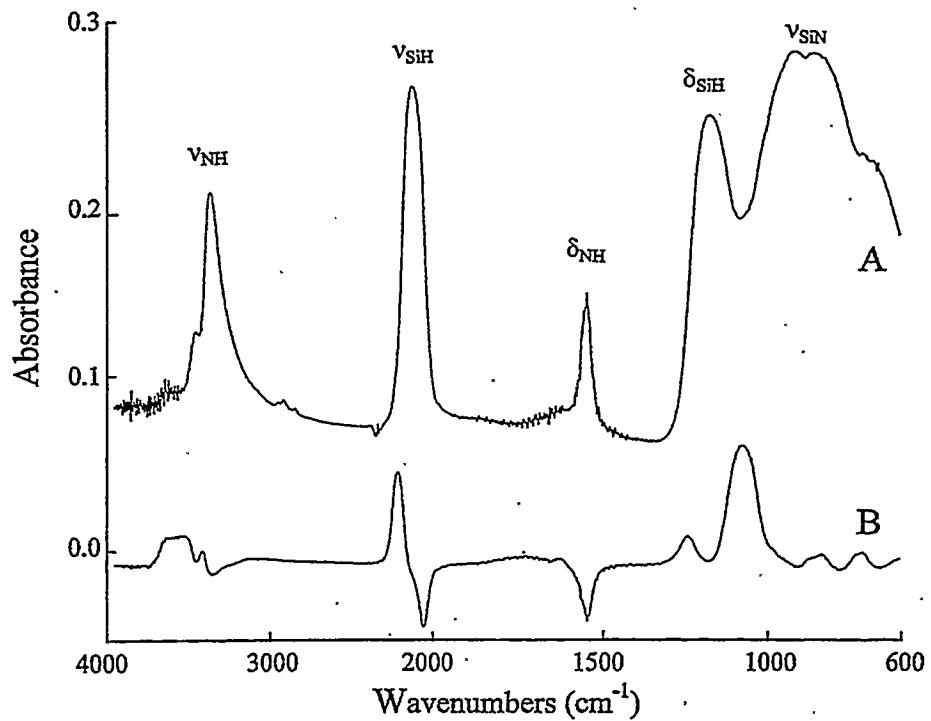

Figure 4. FTIR spectra of silicon nitride particles, 0.2 sec silane/ammonia plasma. A) Fresh powder from plasma. B) Difference spectrum of powder after 48 min. exposure to ambient air.

stoichiometry, varying from dark brown (pure silicon hydride) to white (SiN_2H_2). The powders

formed in a pulsed plasma with 6:1 ratio NH_3/SiH_4 are white corresponding to a stoichiometric

ratio of Si_3N_4 (i.e. the atomic ratio of Si/N is less than or equal to 0.75) but elemental analysis

has not been performed on these pulsed-plasma powders.

Fig 3B. is a TEM picture of silicon nitride particles formed with 100 cycles of a 0.2 sec-

on discharge. The average particle size determined from analysis of many TEM photos is 15 nm

diameter. It is clear that many particles have agglomerated into clusters or chains and that the

size dispersion is large. Similar pictures were analyzed for different plasma on-times and a

sample of the results is shown in Fig. 5. The average diameter is shown with a solid dot and is
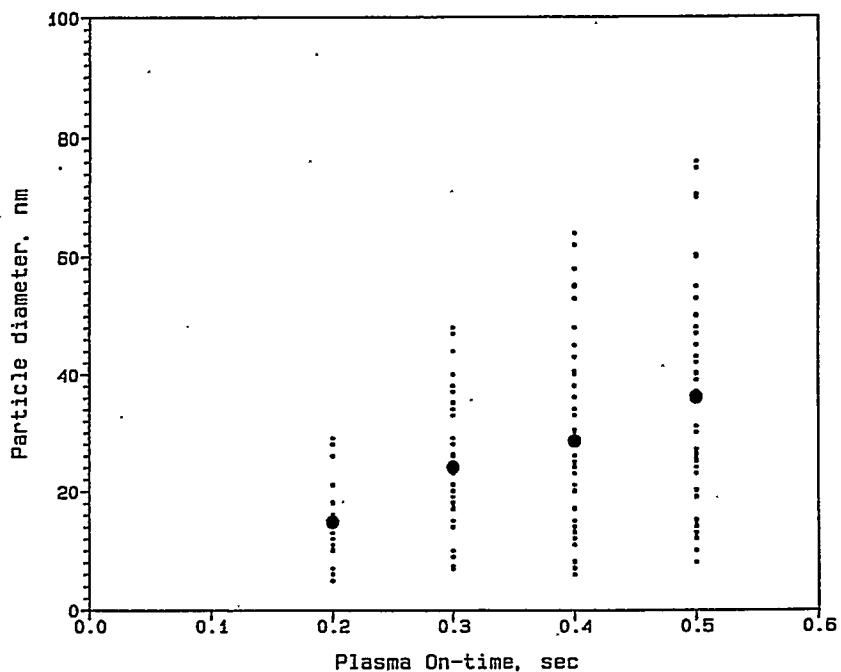
Figure 5. Silicon nitride particle size distribution for different plasma on-times. Large dot is the average diameter. Small dots are individual measurements.

seen to increase fairly linearly in time. The average particle grows at a rate (72 nm/sec)

comparable to the growth rate of silicon particles in the silane/argon plasma. At longer times,

not shown, the rate of growth slows similar to the behavior of silicon shown in Fig 2. In Fig. 5, a

point has been graphed for each measured particle to show the distribution of sizes. Clusters and

agglomerates are not included. It appears that particle nucleation is an ongoing phenomenon

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during the plasma-on period. All sizes of particles are approximately equally represented and the simplest model is that a particle may nucleate at any time and it then grows at a constant rate until the plasma is extinguished. The particles do not exhibit the rough surface morphology seen in the silicon particles. For all sizes from 5 nm to 200 nm diameter, the particles appear smooth with our TEM resolution. The particles are generally not spherical but have oblong or lumpy outlines which suggest agglomeration with continued growth of an overlayer.

The observed agglomeration of particles is potentially detrimental to the goal of producing high density ceramic material. It is generally expected that hard agglomeration into complex shapes will seriously degrade the ability to obtain close packing. It is important to establish the physical mechanisms leading to agglomeration. An isolated body suspended in a plasma acquires a negative potential relative to the plasma. We would expect that the negatively charged particles should repel each other and remain separated. For very small particles, the charge will be sufficiently small that random fluctuations will lead to occasional neutralization. There is much evidence in our TEM photos for agglomeration occurring at all sizes of particles, including 100 nm diameter where charge accumulation should be too large (hundreds of charges) to allow random neutralization. When the plasma is extinguished, though, the particles may be neutralized by the residual ions and could agglomerate through collisions.

Close inspection of the agglomerates seen in TEM photographs reveals that some are very strongly fused as if significant material growth has occurred after association of the particles. This would seem to point to a mechanism of agglomeration in the plasma itself at least for some particles. The smooth appearance of the particle surface might suggest melting and neck-formation by mass transport. The temperature of the gas and ions in the plasma is, however, very low, probably less than 50 °C. The particle is presumably nucleating and growing by highly exothermic reaction of radicals which might heat the growing particle faster than it can radiate. If the particle were to exceed 1000 °C (still well below the melting point), however, it would desorb the bound hydrogen, in conflict with the post-plasma FTIR results. Thus, particle melting should be discounted.

When laser light scattering is monitored either in the bulk of the plasma, or beneath the electrode assembly (with and without the lower screen), no particles are observed during the on-cycle. A sudden appearance of light scattering occurs only in the instant after the plasma is

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extinguished. The individual particles below 100 nm do not scatter enough laser light to be visible by this technique, thus it appears that a burst of agglomeration occurs after the plasma is turned off.

Silicon nitride particles generated by the pulsed plasma technique are found to be very air sensitive. When a freshly synthesized sample is placed in the FTIR and monitored hourly, the SiH bonds are seen to decrease while the SiO bonds increase. In Figure 4B is seen the difference spectrum for powder exposed to ambient air for 48 min. The oxide absorption at 1075 cm^{-1} has grown while the NH (1550 and 3360 cm^{-1}) and SiH (2130 cm^{-1}) absorptions have been altered. The SiH$_n$ peak appears to have shifted as if some SiH groups (~2070 cm^{-1}) have been preferentially removed with growth of other SiH$_n$ functionalities (2230 cm^{-1}). It is more difficult to assign these absorptions than is possible with amorphous silicon[15], because the presence of nitrogen and oxygen will alter the bonding characteristics of the SiH functionalities. The time constant for growth of the oxide is strongly dependent on humidity. The powder synthesized by the pulsed plasma technique (mean diameter 15 nm) was found to oxidize significantly faster (greater than a factor of 2) than the powder from a continuous plasma (mean diameter 150 nm). This is presumably because the rate is dependent on the surface area to volume ratio which is an order of magnitude larger for the small particles.

For purposes of powder handling in studying the sintering properties, the air sensitivity is inconvenient. Experiments were conducted to explore the chemistry of the particles under post-plasma heat treatment. Thermogravimetric analysis (Fig 6) of the plasma synthesized powder shows that between 100 °C and 250 °C, weakly bound ammonia desorbs. From 250 °C to 500 °C, a second ammonia desorption occurs which may be associative recombination of NH$_2$ and H from different silicon sites. From about 250 °C to 900 °C, H$_2$ gas desorbs (but note that there is some contribution to the mass 2 signal from cracking of ammonia which has not been corrected). Above about 900 °C, the powder ceases to evolve gas. The total weight loss is 8-10%.

When gram quantities of pulsed plasma synthesized silicon nitride are heated to 800 °C for 20 minutes, the powder changes from pure white to a deep brown. This color is characteristic of silicon-enriched powder. Although the powder is synthesized stoichiometrically rich in nitrogen[3], it is apparent that excessive nitrogen is evolved during heating in vacuo and silicon-rich powder results. This color change was only observed for the powder from pulsed plasmas,

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with 15 nm or less average diameter. The larger particles, averaging 150 nm, from a continuous discharge remained white on heating in vacuo. This suggests that the extra loss of nitrogen may occur predominately from the near surface regions of the particles.
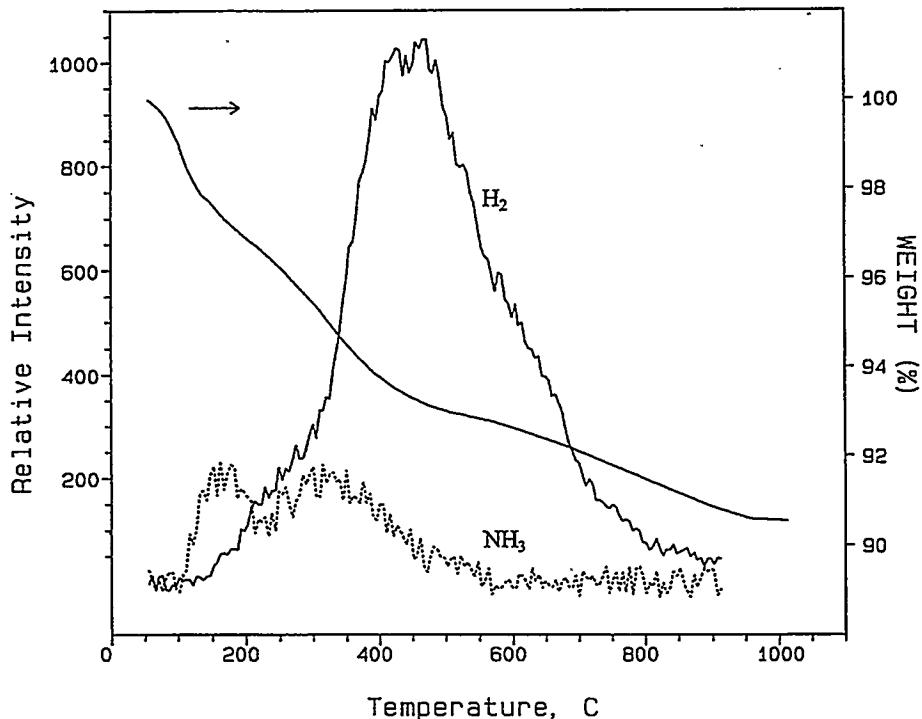

Figure 6. Thermogravimetric analysis of silicon nitride powder (right axis) from a pulsed plasma (0.2 sec plasma on time). Mass spectrometer analysis (left axis) of evolved gas: NH_3 (17 amu.) and H_2 (2 amu.).

The freshly synthesized nano-powder is heated at 800 °C in various pressures of ammonia. At an ammonia pressure of 200 Torr or above, the powder retains its white color. FTIR spectra of these heat-treated samples (Fig. 7a) show the complete elimination of SiH functionality. This powder is resistant to oxidation (or hydrolysis) in atmosphere (Fig. 7b); no detectable appearance of SiO functionality is observed after 3 days of atmosphere exposure.

Silicon Carbide

We apply the rf plasma technique to the synthesis of silicon carbide using gas mixtures of silane and methane in analogy with the successful silicon nitride technique. Powder is readily generated from such mixture over a wide range of gas mixtures (10-90% silane) and rf powers

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(5-50 Watts). The powders formed are extremely sensitive to air-oxidation, making it difficult to obtain FTIR spectra without significant oxide formation. In fact, on venting the plasma apparatus to air, the powder spontaneously combusted in some instances. The FTIR spectrum (Fig. 4a) shows very significant content of SiH (2100 cm^{-1}), and CH$_n$ (2900 cm^{-1}), functionality.
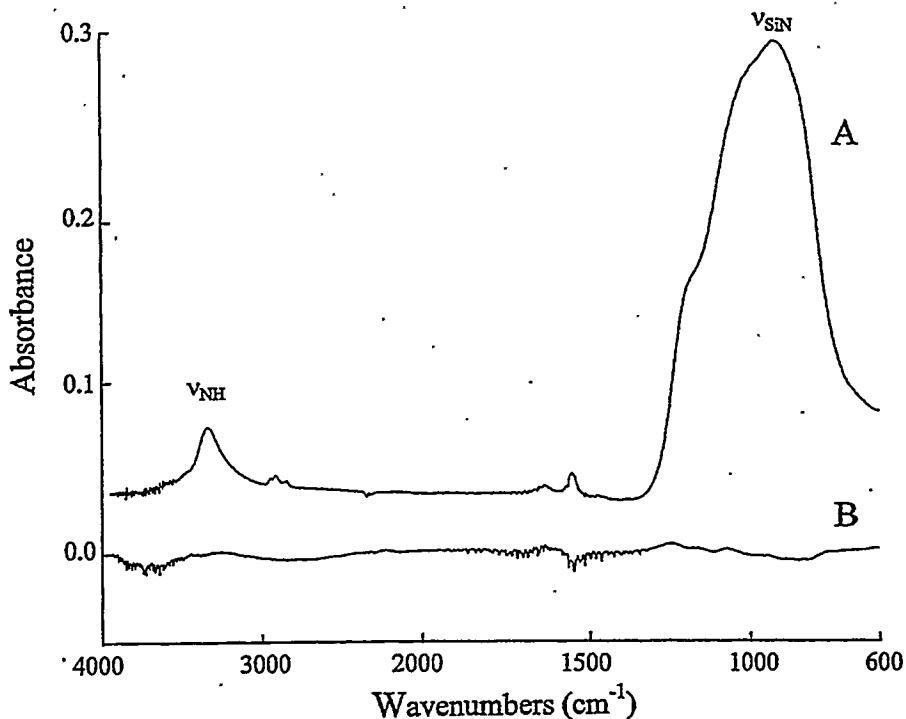

Figure 7. FTIR spectra of heat-treated silicon nitride particles, 0.2 sec silane/ammonia plasma, 800 °C, 20 min., ammonia atmosphere. A) Freshly heat-treated powder. B) Difference spectrum of powder after 24 hour exposure to ambient air.

Powder generated from silane/ethylene gas mixtures is indistinguishable from silane/methane mixtures.

Powder is also produced from plasmas containing gas mixtures of MTS and hydrogen, with or without added argon. The FTIR spectrum (Fig. 8b) shows significantly reduced CH and SiH features compared to Fig. 8a. A large feature at 3200 cm^{-1} is probably the result of adsorbed HCl.
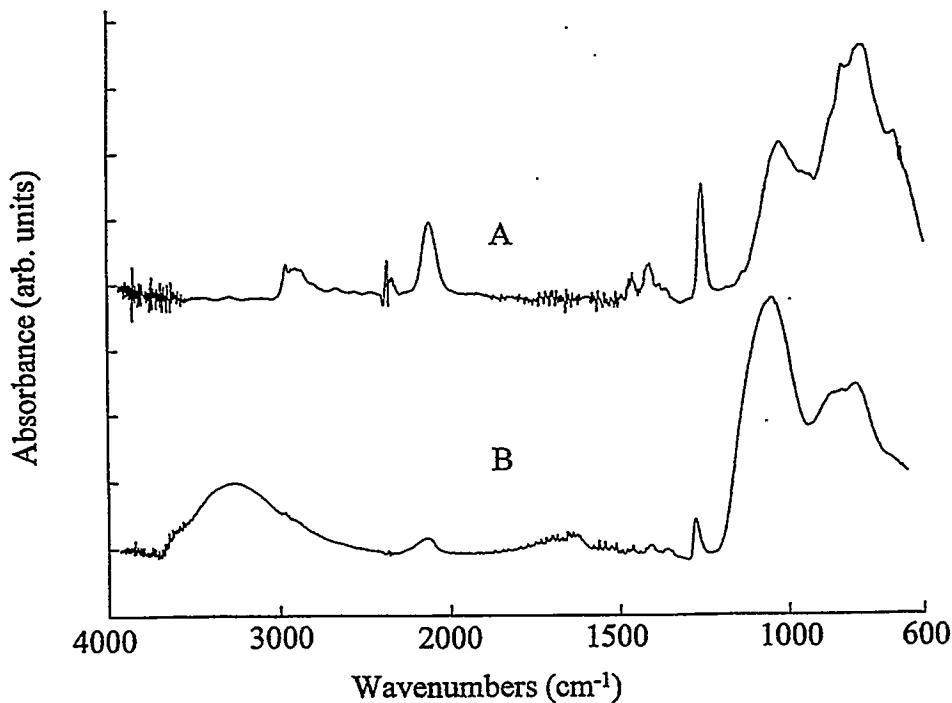
Figure 8. FTIR spectra of silicon carbide particles. A) From silane/methane plasma. B) From MTS/hydrogen plasma.

The hydrogenated SiC powder as synthesized in the plasma readily oxidizes in ambient air, similar to the behavior of the silicon nitride. Heat treatment of the powder in an inert, argon, atmosphere, at 800 °C for 20 minutes is sufficient to eliminate the hydrogen-containing functionalities and render the powder resistant to oxidation. The FTIR spectra of SiC before and after heat treatment are shown in Fig 9.

Particle morphology of the MTS/H_2 powders is studied with TEM of samples produced from the pulsed plasmas. The morphology is similar to that of silicon nitride, roughly spherical particles with a significant fraction of the mass occurring in large agglomerates. A larger fraction of individual particles exhibit spherical shape, and the degree of hard agglomeration of SiC particles appears to be reduced relative to silicon nitride, but experiments are underway to
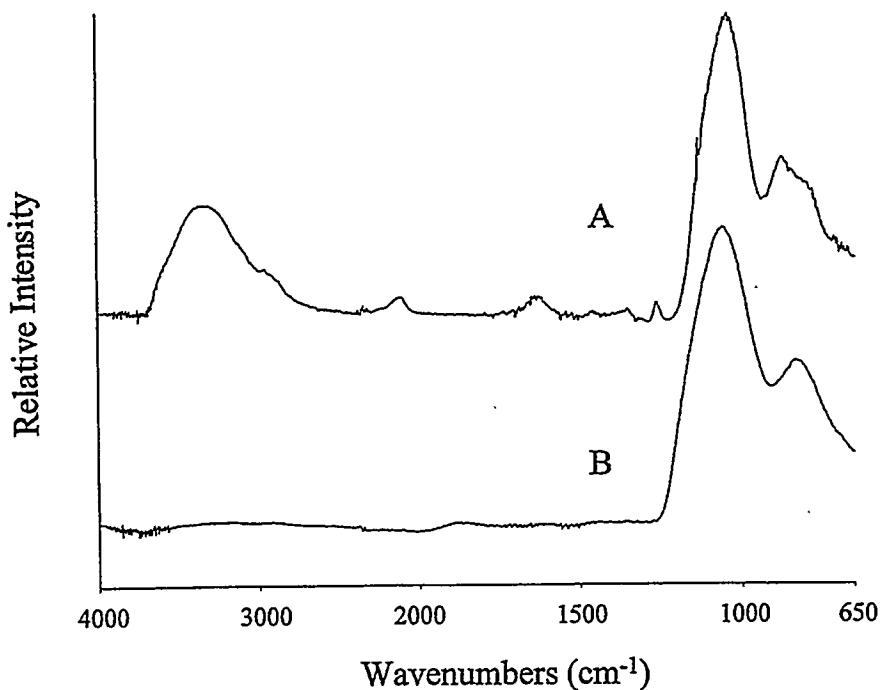
Figure 9. FTIR spectra of silicon carbide particles. A) From MTS/hydrogen plasma. B) After baking at 800 °C-20 min.

investigate potential sampling bias. The fluid flow in the plasma apparatus is laminar through the showerhead and through the collection filter. Calculations suggest that the small particles, <100 nm diameter, will be significantly depleted by diffusion to the walls compared to the larger particles and agglomerates. TEM grids placed on the plasma walls appear to confirm this, collecting relatively more of the smaller particles. Large agglomerates are, however, also observed on these wall-mounted TEM grids. Since the fluid flow should prevent the more massive agglomerates from reaching the walls, it is probable that the agglomerates on the sidewalls grow in place by charge dipole induced attraction of incoming small particles at the surface.

The particle morphology of the silicon carbide is similar to the smooth and spherical fluorocarbon particles previously reported[16]. It is clear that the mechanisms of particle growth differ for each of the chemistries and much work remains to sort out the connection between chemistry and morphology.

CONCLUSIONS

The pulsed rf plasma technique using silane/ammonia gas mixtures is capable of generating silicon nitride particles in the ten nanometer size range. Large size dispersion and much agglomeration are always observed. Similar agglomeration is observed for silicon particles grown from silane/argon mixtures. The distribution of particle sizes for initial growth to approximately 80 nm suggests a mechanism of continuous nucleation with linear radial growth. Some agglomerates appear to be formed by association in the plasma while laser light scattering shows a burst of agglomeration immediately after the plasma is extinguished. Plasma generated silicon nitride particles are sensitive to hydrolysis by water vapor in air but can be stabilized by post-plasma heat treatment in ammonia. The kinetics of oxidation and thermal loss of hydrogen/nitrogen show strong particle size differences.

Silicon carbide particles can be generated in a MTS/H2 plasma and have morphologies and air sensitivity similar but not identical to the nitride. SiC can also be synthesized from silane/hydrocarbon mixtures but powders are found to be highly reactive.

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