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SYNTHESIS OF SILICON NITRIDE POWDERS IN PULSED RF PLASMAS

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ABSTRACT

Nanometer size silicon nitride particles are synthesized using a pulsed radio frequency plasma technique. The plasma is modulated with a square-wave on/off cycle of varying period to control size and morphology and to deduce the growth kinetics. *In situ* laser light scattering and *ex situ* particle analysis are used to study the nucleation and growth. For SiH_4/Ar plasmas which nucleate silicon particles, an initial extremely rapid growth phase is followed by a slower growth rate, approaching the rate of thin film deposition on adjacent flat surfaces. In SiH_4/NH_3 plasmas, silicon nitride particle size can be tightly controlled by adjusting the plasma-on time. The size dispersion of the particles is large and is consistent with a process of continual nucleation during the plasma-on period. Our observed polydispersity differs dramatically from that reported from other laboratories.

INTRODUCTION

It has been recognized for many years that silicon nitride has excellent high temperature structural properties such as high strength and low weight which would make it ideal for many applications such as engine parts. Unfortunately, the low temperature properties of hardness and brittleness make manufacturing processes difficult. It is known that materials formed from nanometer size subunits can exhibit improved macroscopic properties such as enhanced ductility or superplasticity. Also, in order to obtain the optimum properties, it is important to achieve microstructural and chemical homogeneity with minimal defects in a nearly fully dense ceramic. This is facilitated by starting with fine-particle-size powders that have low impurity content.

Obtaining the ultrafine powders that are needed for exploratory research as well as manufacture has proven to be a problem. A variety

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of techniques are currently used to produce commercial silicon nitride powders[1]. These include direct nitridation of silicon, carbothermic reduction of silica and gas-phase reaction of $SiCl_4$ and NH_3. Several other gas-phase processes have been reported including the thermal pyrolysis of silane and ammonia[2] and laser pyrolysis of gaseous reactants[3]. Each of these processes has limitations in the morphology, size distribution, and chemical purity of the product.

In 1988, Buss and Ho patented a process[4] for synthesizing ultrafine particles of silicon nitride and other materials in a 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. Particles leaving the plasma are collected by filtering the gases pumped from the reactor. The technique is capable of generating gram quantities of silicon nitride powder in a few hours of operation in a laboratory reactor. Properties of the powder were well characterized by a variety of techniques[5].

During the past decade, particle formation and transport in plasmas has become an area of intense interest and activity[6]. 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 particularly important achievement was reported by Boufendi and coworkers[7] in France in 1992. They studied formation of silicon particles in a silane/argon plasma by pulsing the plasma on for a short time and collecting the particles for electron microscopy. Remarkably, they found a linear rate of particle growth to the 40 nm size with a very narrow size dispersion. They postulated an initial stage of the plasma in which nucleation occurs, producing a high density of 5 nm size particles followed by a no-nucleation stage in which these smaller particles associated into the observed clusters.

We report here experiments aimed at applying this pulsed plasma approach to the synthesis of nano-size silicon nitride powders. Part of the work entails reproducing experiments of the French group with silane/argon to confirm the technique. Some striking differences in particle growth rates and size dispersion are reported. Applying the pulsed plasma technique to the silicon nitride system, we have demonstrated control of average particle size but with persistent size dispersion and agglomeration.

EXPERIMENTAL

A diagram of the apparatus is shown in Fig. 1. The plasma

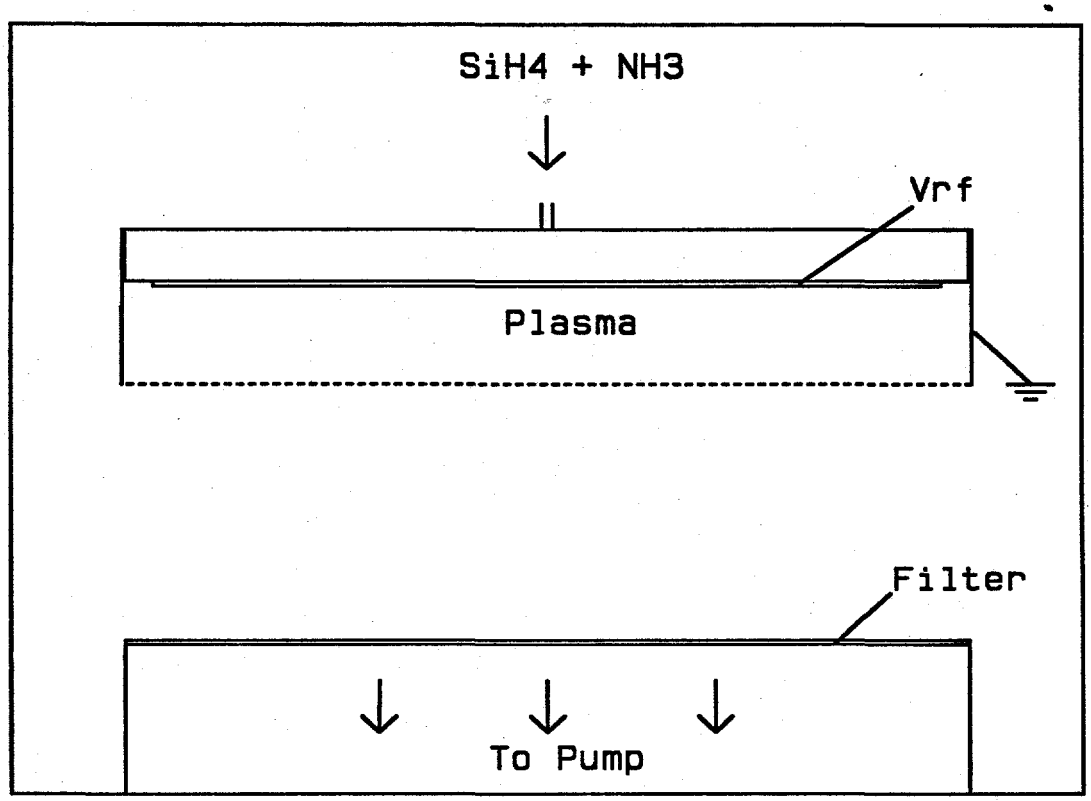

Fig. 1. Diagram of pulsed rf plasma apparatus.

electrode assembly consists of a 15 cm diameter powered electrode, perforated with holes to allow gas delivery in showerhead configuration. The plasma region is enclosed by a grounded aluminum sheet with a grounded high transmission screen across the bottom. The pumping port is located 4 cm beneath the electrode assembly, and is fitted with a single sheet of Whatman #1 filter paper. In order to study the size and morphology of the particles generated, transmission electron microscopy (TEM) was employed *ex situ*. To obtain samples, a TEM sample grid was placed beneath the plasma assembly on the filter paper.

A 10 mWatt helium-neon laser passed through the region beneath the plasma (or through holes in the electrode assembly wall). Laser light scattering from particles was observed by eye as a qualitative characterization of the process.

In a typical experiment, gas flow was first established (eg. 2 sccm SiH_4, 12 sccm NH_3, at 200 mTorr pressure); then the plasma was pulsed with a square wave on/off cycle for 100 periods. The TEM grid was then removed and analyzed. In order to obtain large quantities of powder for bulk analysis, the plasma was pulsed for several hours and the filter with accumulated powder was removed.

RESULTS AND DISCUSSION

Silicon

In a study aimed at duplicating the experimental conditions of Boufendi et al, we investigated the formation of silicon particles in a silane/argon plasma. We find that the growth kinetics differ very markedly from those of the French group. In Fig. 2 is shown the measured size distribution for silicon 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 which, for longer plasma on-periods, decreases to a slow growth rate. In addition,

the size dispersion is very large, in fact, with all sizes from zero to approximately twice the average diameter represented. We are unable at this time to resolve the discrepancy between our particle growth

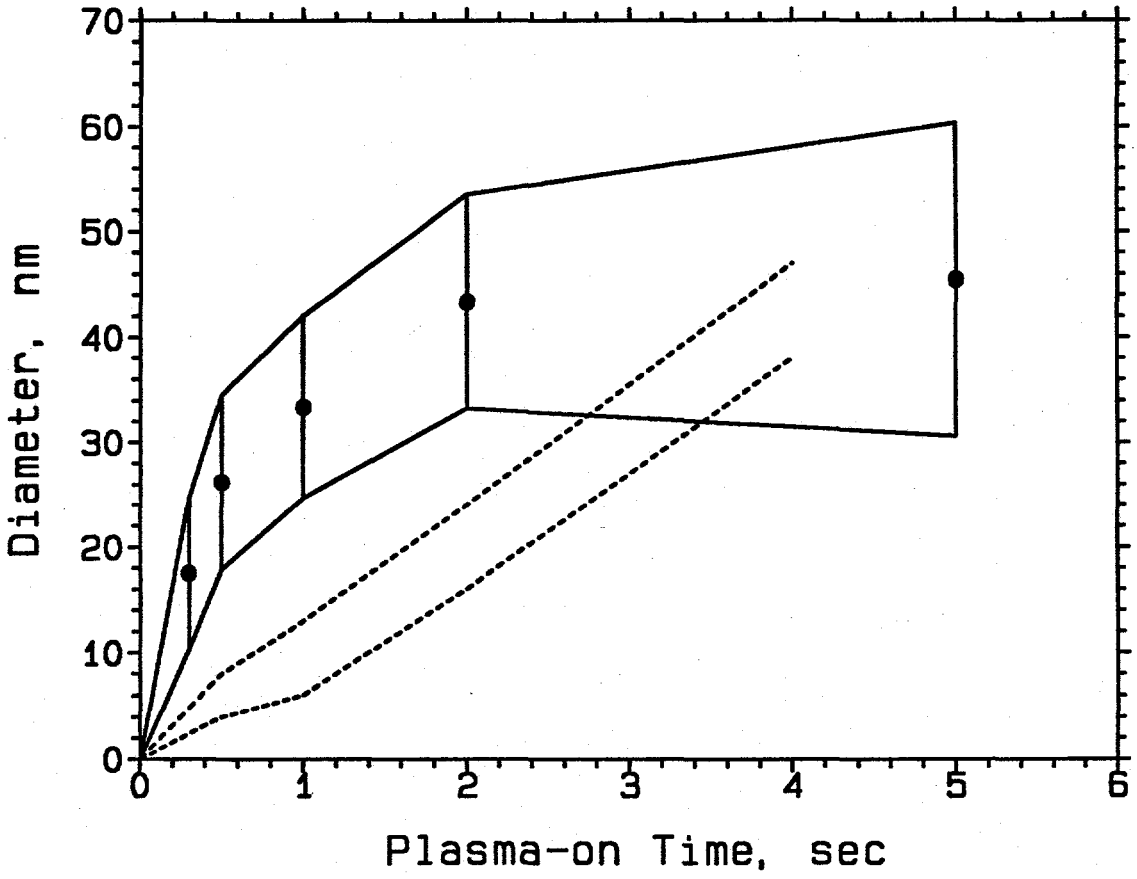

Fig. 2. Silicon particle size distributions obtained from a pulsed silane/argon plasma. Dashed lines show the data of Ref. 7.

dynamics and those of Boufendi et al. Great effort was expended to match conditions of geometry, linear flow velocities, pressure and power. 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 truly coincide with those of Boufendi et al.

Silicon Nitride

Pulsed rf plasmas of silane/ammonia gas mixtures successfully generated nano-size particles. The chemistry of the particles appears consistent with our earlier observations using a continuous rf plasma[5]. Fourier transform infrared spectra (FTIR) show strong SiH (2100 cm^{-1}) and NH absorptions (3400 cm^{-1}), confirming that the powder has a high hydrogen content. The color of the powder is very slightly off-white. In the earlier work we noted a strong correlation between the particle stoichiometry and color, with the silicon-rich particles being highly colored. The powders formed in a pulsed plasma have a color associated with a stoichiometric ratio of Si/N, but elemental analysis has not yet been performed.

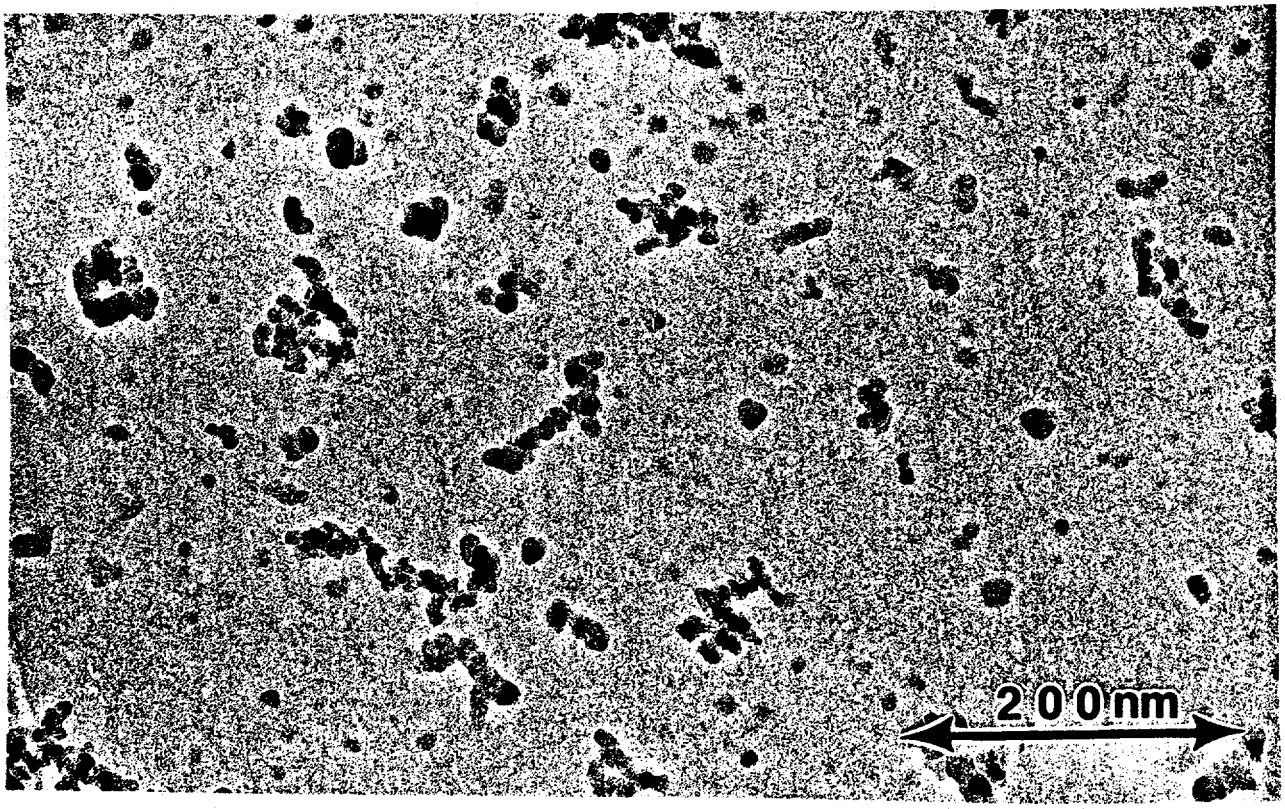

Fig. 3. TEM of particles from a SiH_4/NH_3 plasma pulsed on for 0.25 sec.

Fig 3. is a TEM picture of silicon nitride particles formed with 100 cycles of a 0.25 sec-on/ 2.0 sec-off 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. 4. The average diameter is shown with a solid dot and is seen to increase fairly linearly in time. A point has been graphed for each measured particle to show the distribution of sizes. Clusters and agglomerates were not included. It is apparent that

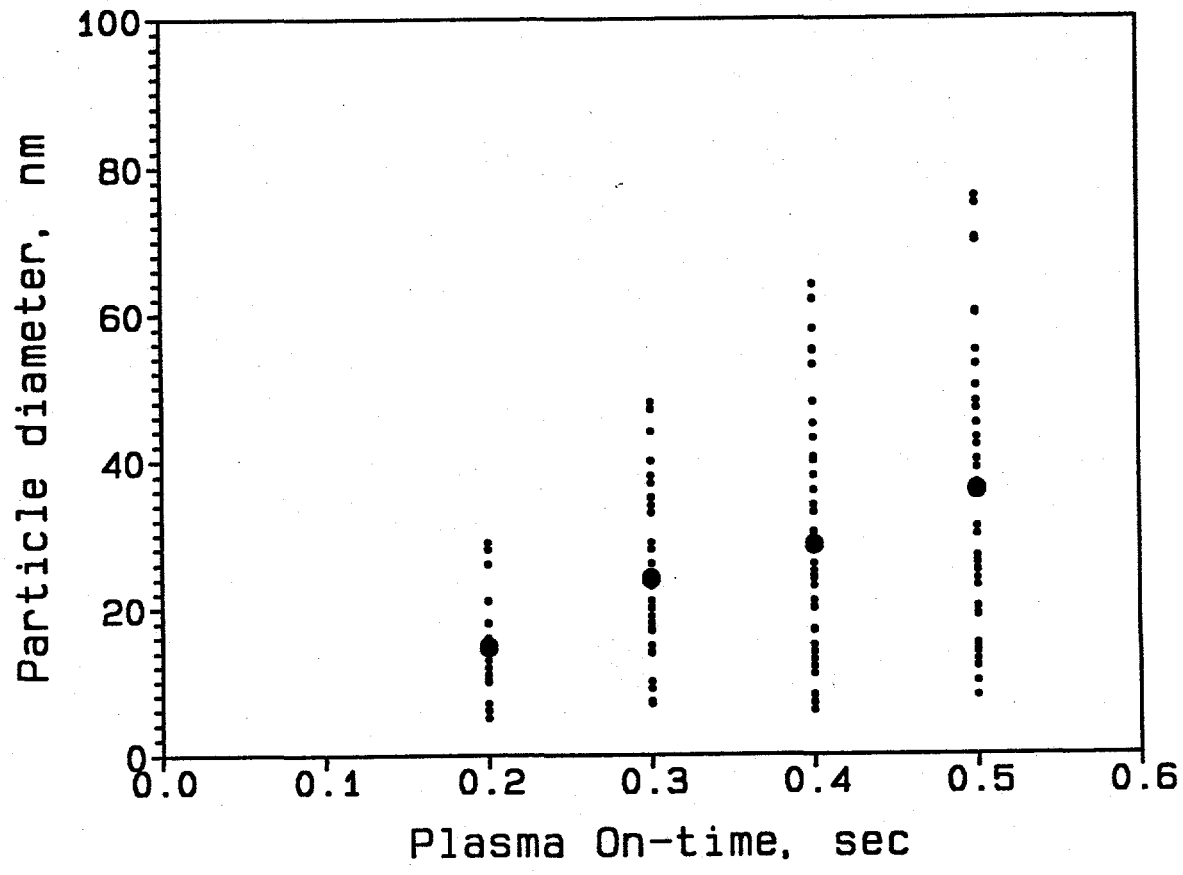

Fig. 4. Particle size distributions from a SiH_4/NH_3 plasma, large dot is the mean diameter.

particle nucleation is an ongoing phenomenon 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 observed agglomeration of particles is potentially detrimental to the ultimate 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 because the electron velocity greatly exceeds that of the positive ions. We would expect that the negatively charged particulates should repel each other and remain separated. This would only break down when the particle mass becomes very large. 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 fuzed 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, however, it would desorb the bound hydrogen, in conflict with the post-plasma FTIR results. Thus, particle melting should be discounted.

One additional observation is relevent. When laser light scattering was monitored either in the bulk of the plasma, or beneath the electrode assembly (with and without the lower screen), no particles were observed during the on-cycle. A sudden appearance of light scattering occurred only in the instant after the plasma was extinguished. The individual particles below about 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. More studies are underway to identify the processes leading to agglomeration.

CONCLUSIONS

The pulsed rf plasma technique is capable of generating silicon nitride powder with controlled average size in the 10 nm size regime. Large size dispersion and some degree of agglomeration are always observed. Compaction and sintering studies will be needed to evaluate these particles as precursor candidates for superior silicon nitride ceramics.

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