NANOPARTICLE SYNTHESIS IN PULSED LOW TEMPERATURE DISCHARGES

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ABSTRACT

Silicon nitride powders with an average size as low as 7 nm are synthesized in a pulsed radio frequency glow discharge. The as-synthesized silicon nitride powder from a silane/ammonia plasma has a high hydrogen content and is sensitive to oxidation in air.

Post-plasma heating of the powder in a vacuum results in nitrogen loss, giving silicon-rich powder. In contrast, heat treatment at 800°C for 20 minutes in an ammonia atmosphere (200 Torr pressure) yields a hydrogen-free powder which is stable with respect to atmospheric oxidation.

Several approaches to synthesizing silicon carbide nano-size powders are presented. Experiments using silane/hydrocarbon plasmas produce particles with a high hydrogen content as demonstrated by Fourier transform infrared analysis. The hydrogen is present as both CH and SiH functionality. These powders are extremely air-sensitive. A second approach uses a gas mixture of methyltrichlorosilane and hydrogen. The particles have a low hydrogen content and resist oxidation. Particle morphology of the silicon carbide is more spherical and there is less agglomeration than is observed in the silicon nitride powder.

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. Thermal plasma techniques¹ in which precursors are atomized and allowed to condense in the afterglow have been highly successful for many materials including

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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 of SiCl_4 and NH_3 , laser pyrolysis of gaseous reagents, and thermal pyrolysis.

Almost a decade ago, Buss and Ho patented a process² 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 techniques³. 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 activity⁴. 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 and Bouchoule⁵ 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.

We applied the pulsed plasma technique to the synthesis of silicon nitride powder and achieved reasonable control of particle size as low as 7 nm⁶. The particles made in this way are rich in hydrogen-containing functionalities and the resulting powder is air-sensitive making subsequent handling difficult.

We report here the successful post-plasma heat treatment of the powders to render them air-insensitive. Also discussed are the results of applying 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.

EXPERIMENTAL

The plasma apparatus used to synthesize the nano-particles has been described previously⁶. Briefly, a vacuum chamber (base pressure 1 mTorr), is equipped with an electrode assembly consisting of a 15 cm diameter powered electrode, perforated with holes to allow gas flow in a showerhead configuration. The plasma region is enclosed by a grounded copper sheet with a grounded high transparency screen across the bottom.

The pumping port is located 15 cm beneath the electrode assembly, and is fitted with a single sheet of filter paper.

In a typical experiment, eg. gas flow 2 sccm SiH_4 , 12 sccm NH_3 , at 200 mTorr pressure, the plasma is pulsed with a square wave on/off cycle (0.1 second on/1.0 second off) for 100 periods. Particle morphology is determined from a transmission electron microscope (TEM) grid placed on the collection filter. By running the plasma for an hour, sufficient powder is accumulated to obtain Fourier transform infrared (FTIR) transmission spectra. 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.

The post-plasma heat treatment of powders is tested by venting the plasma apparatus with dry nitrogen. The powder is transferred with minimal air exposure to a second vacuum chamber and immediately evacuated. Powders are exposed to air for a maximum of 15 seconds. The powder is then heated in vacuum or in an ammonia atmosphere in a resistively heated tantalum crucible. FTIR spectroscopy is used to study the susceptibility of the powder to oxidation in air. A sample is placed in the spectrometer and spectra are periodically acquired. The

growth of silicon oxide is readily measurable at 1100 wavenumbers (cm^{-1}). The decomposition of the powder heated in vacuum is studied using thermogravimetric analysis with mass spectral analysis of the desorbing gas. Samples of powder weighing 100-200 mg are placed in an alumina crucible and the temperature is ramped at a rate of 10 $^{\circ}\text{C}/\text{min}$ with flowing argon as the carrier gas.

Experiments to study the synthesis of silicon carbide use several chemical approaches. Mixtures of silane and methane or ethylene produce powder over a wide range of plasma power (5-50 Watts). Particles are also generated from gas mixtures of argon and hydrogen containing MTS vapor.

RESULTS AND DISCUSSION

The silicon nitride powder synthesized in the pulsed rf glow discharge (0.1 second on-time, 10 sccm SiH_4 , 60 sccm NH_3) is rich in hydrogen³. The FTIR spectrum (Fig. 1a) shows strong absorptions at the SiH stretch (2100 cm^{-1}), and the NH stretch (3400 cm^{-1}) as well as the NH bending mode (1550 cm^{-1}). When exposed to ambient water vapor in the air, the SiH absorption decreases while the strong SiO absorption (1100 cm^{-1}) grows in as seen in the difference spectrum Fig 1b. Although the rate of oxidation can be slowed by storing the powder in a dry atmosphere, handling of the powder during preparation for sintering is difficult.

Thermogravimetric analysis (Fig 2) of the plasma synthesized powder shows that between 100 $^{\circ}\text{C}$ and 250 $^{\circ}\text{C}$, weakly bound ammonia desorbs. From 250 $^{\circ}\text{C}$ to 500 $^{\circ}\text{C}$, a second ammonia desorption occurs which may be associative recombination of NH_2 and H from different silicon sites. From about 250 $^{\circ}\text{C}$ to 900 $^{\circ}\text{C}$, 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 $^{\circ}\text{C}$, the powder ceases to evolve gas. The total weight loss is 8-10%.

Figure 1

Fig. 1. FTIR spectra of silicon nitride powder a) as synthesized, b) the difference spectrum after 48 minutes exposure to air.

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 nitrogen³, 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, 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

Figure 2

Fig. 2. TGA of plasma-generated silicon nitride powder. The weight loss curve is referred to the right. The mass spectral data for H_2 (solid curve) and NH_3 (dashed curve) are referred to the left.

that the extra loss of nitrogen may occur predominately from the near surface regions of the particles.

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. 3a) show the complete elimination of SiH functionality. This powder is resistant to oxidation (or hydrolysis) in atmosphere

Figure 3

Fig. 3. FTIR spectrum of silicon nitride powder after heating at 800 °C for 20 minutes. A) Fresh from oven, B) Difference spectrum after 24 hour air exposure.

(Fig. 3b); no detectable appearance of SiO functionality is observed after 3 days of atmosphere exposure.

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 (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. 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. 4b) shows significantly reduced CH and SiH features compared to Fig. 4a. A large feature at 3200 cm^{-1} is probably the result of adsorbed HCl.

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 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, $<100\text{ nm}$ 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.

Figure 4

Fig. 4. FTIR of powder from a continuous silane/methane plasma, 50/50 gas mixture, 30 Watts power.

CONCLUSIONS

The silicon nitride powders synthesized by pulsed rf plasma discharge can be stabilized with respect to air-oxidation by post-plasma heat treatment in an ammonia atmosphere at 800 °C. Heating the powder drives off the labile hydrogen, and the ammonia atmosphere prevents excessive loss of nitrogen. Particles can be generated from silane/hydrocarbon mixtures, but they are extremely sensitive to air oxidation. Particles from an MTS/H₂ plasma look promising as a precursor to silicon carbide.

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