"Nanocrystalline Processing and Interface Engineering of Si_3N_4-based Ceramics"

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Reactor Construction and Modification

Construction and modification of the novel tubular flow reactor for the synthesis of nanocrystalline materials by thermal evaporation in a forced flux of gas has been an ongoing process over the past year. The first version of the reactor was used to synthesize nanocrystalline silicon (Si). The incoming gas flow rate is set with a mass flow controller. Helium (He) enters at one end of the reactor and flows over the resistively heated crucible where Si is evaporating. The silicon supply is continually replenished with a magnetically coupled loader. An IR pyrometer is used for temperature monitoring and control of the evaporation crucible. A pumping system consisting of a roots blower (booster pump) backed by a single-stage mechanical pump continuously removes the Si particles in the He gas stream from the growth zone over the evaporation source. The pressure in the reactor is controlled by a throttle valve with a capacitance manometer input. The particles entrained in the gas stream flow down the glass tube and are deposited on a liquid nitrogen cooled disc mounted parallel to the gas flow in the center of the collection chamber.

Other initial experiments used a flow of high purity N_2 as the carrier gas in an effort to produce Si_3N_4. However, this led to the formation of Si_3N_4 in the evaporation source as well. The silicon melt would solidify to Si_3N_4 and stop further evaporation. The next design allowed N_2 to be introduced just beyond the evaporation source. The idea was that the Si particles in the He gas stream would still be hot enough to lead to the dissociation of the N_2 and the formation of Si_3N_4. Because this did not work well, other techniques to produce a source of nitrogen radicals were examined. A microwave plasma processing approach was selected by which N_2 gas (introduced just beyond the evaporation source) is converted to atomic nitrogen by electron impact dissociation. The Si nanocrystallites, entrained in the He gas flow, will pass through this N_2 plasma and be nitrided on their way down the glass tube to the collection chamber. This microwave system (power supply, applicator, gas flow devices, cooling water, vacuum connections) has been designed and is currently being added to the existing reactor structure.

The first generation collection device establishes a perpendicular thermophoretic force with respect to the gas stream. In this approach, the substrate does not come in direct contact with the hot gas stream. The collected particles are then not affected by high temperatures which cause sintering or surface contamination. This device has been useful in establishing reactor operating characteristics, but is not a highly efficient collector. A second generation collection unit based on a filtration device is currently being designed. Given the temperature and contamination constraints, a metal filter will be utilized for this collection device. Additional significant modifications include those made to the evaporation power supply and crucible material to increase Si evaporation rates to ~10 g/hr

for uninterrupted periods of ≥ 45 minutes. A schematic of the tubular flow reactor incorporating these modifications is shown in Figure 1.

Reactor Characterization and Synthesis of Nanocrystalline Silicon

In order to characterize the tubular flow reactor's operation, the effect of reactor pressure and gas velocity on the particle size and morphology was examined [1]. The reactor was operated at pressures ranging from 0.5 mbar to 11.3 mbar. He gas velocities ranged from 12.5 to 40 m/s. The most typical operating conditions studied for this reactor were a pressure of 2 mbar and a gas velocity of 12.5 m/s. (All materials subsequently heat-treated were produced under these conditions.) Particle size and morphology characterizations were performed by transmission electron microscopy (TEM).

The as-synthesized material consists of spherical, crystalline particles. Figure 2 is a TEM micrograph of representative as-synthesized, crystalline Si particles ~7 nm in diameter. Their lattice fringes are clearly visible. The micrograph illustrates that nanocrystallites are effectively produced by this reactor design even at the higher evaporation rate. The powder removed from the reactor has a dark brown appearance from surface exposure to air. Shown in Figure 3 is a plot of particle size versus reactor pressure. The gas (particle) velocity was kept constant at 12.5 m/s for these experiments. By varying the pressure, average particle sizes ranging from 5.2 to 9.5 nm were obtained. The particle size increased with increasing reactor pressure due to confinement of the particles in the growth region above the evaporation source.

There was no significant difference in size or morphology of particles produced at gas velocities of 12.5, 15 and 25 m/s and a reactor pressure of 2 mbar. Discrete crystalline particles of ~6 nm were seen in these cases. At a gas velocity of 40 m/s, an amorphous film was deposited on the collection substrate. The product consisted of thin flakes of material rather than individual particles. This is likely due to the more rapid quench rate of the Si (on the order of 4.1×10^4 K/sec) and the fact that the Si atoms could not coalesce and order before they reached the liquid nitrogen cooled collector.

Silicon Nitridation

The as-prepared material has a B.E.T. surface area of 154.1 ± 1.6 m^2/g. Its high surface reactivity enabled nitridation and conversion to Si_3N_4 at relatively low temperatures. The as-prepared nanocrystalline Si was nitrided in both a thermal gravimetric analyzer (TGA) and a differential thermal analyzer (DTA) to follow nitridation and crystallization kinetics. Nitriding temperatures for conventional Si range from ~1200 °C to 1450 °C. Ultrafine Si powder of diameter 20-50 nm produced by other researchers by an arc-plasma method could be nitrided at 1100 °C if unexposed to air, or at 1200 °C if exposed to air. As shown in Figure 4, nitridation of our nanocrystalline Si was initiated at a low temperature of ~500 °C and was completed by ~1050 °C.

The as-prepared Si material is X-ray amorphous (see Figure 5a). The first evidence of X-ray crystallinity is found in a sample held at 1500 °C under N_2 gas flow for 30 minutes. The diffraction pattern indicated the formation of an α-Si_3N_4 phase in the sample. DTA reflects a major exothermic peak from 1490 °C to 1560 °C which may be attributed to crystallization of Si_3N_4. This suggests that the nitride formed between 500 °C and 1050 °C is amorphous. After an 1-hour hold at 1600 °C, the peaks for crystalline α-Si_3N_4 became well-defined (Figure 5b). This material has the typical grayish white color of α-Si_3N_4.

Y_2O_3 Sintering Additive

While sintering pure, ultrafine Si_3N_4, produced *in-situ* in the flow reactor, would be desirable, some amount of sintering additive may be required to provide liquid phase sintering. The strategy then involves minimizing the amount of oxide additives needed such that the high-temperature strength of Si_3N_4 will not be compromised. We believe nanocrystalline oxide additives may be a technique to accomplish this goal. Through chemical processing from 'reverse strike' of hydroxide precursors, nanocrystalline Y_2O_3 has been produced [2]. It was synthesized from Y_2O_3 powder dissolved in 4.0 N HNO_3. Precipitation is carried out by adding this acidic solution to a base solution of 2.5 N NH_4OH. The precipitates are then washed in ethanol, before drying and calcination in air at 600 °C, followed by ultrasonication. Vacuum heat treatments were also applied to preserve the ultrafine microstructure during the annealing process. The organic washes and ultrasonication are surface treatments that have been successfully used to break up interparticle bridging and hydrogen-bonding. The resulting Y_2O_3 powder is shown in Figure 6a. As a basis for comparison, one of the best commercially available Y_2O_3 (H.C. Starck Grade C) powders is shown at the same magnification in Figure 6b. Figure 7 is X-ray diffraction data also comparing these powders. In order to obtain a baseline for comparison of the nanocrystalline Si_3N_4 to be produced in the flow reactor, one of the best commercially available Japanese Si_3N_4 powders (UBE SN-E10) was characterized as well. TEM particle size and B.E.T. N_2 adsorption data are shown in Table 1 for several of the materials synthesized and/or examined during the past year.

TABLE 1

Material	Source	Particle Size	B.E.T. surface area
Si	tubular flow reactor	6 - 9 nm	154.1 ± 1.6 m^2/g
Y_2O_3	chemical precipitation	11 nm	92.7 ± 0.33 m^2/g
Y_2O_3	H.C. Starck Grade C	66 nm	15.5 ± 0.08 m^2/g
Si_3N_4	UBE SN-E10	113 nm	12.1 ± 0.02 m^2/g

Summary

A continuous tubular forced flow reactor has been constructed for a high production rate of nanocrystalline materials. Modifications to improve this apparatus are continuing. The effect of reactor parameters such as pressure and gas velocity on the particles produced was studied. Silicon nanocrystallites were produced with a high surface area (154 m^2/g) and were nitrided easily at low temperatures (1050 °C). Nanocrystalline Y_2O_3 with properties superior to commercially available powder was produced by a chemical precipitation method, and will be used as a sintering aid for the nanocrystalline Si_3N_4 to be synthesized with the tubular flow reactor equipped with the microwave plasma.

References

[1] D.T. Castro and J.Y. Ying, "Synthesis and Nitridation of Nanocrystalline Silicon Produced Via A Tubular Forced Flow Reactor," *Mater. Sci. Eng. A*, in press (see attached).

[2] T.A. Henderson, S. Lee, D.T. Castro and J.Y. Ying, "Chemical Precipitation and Surface Treatment of Nanocrystalline Y_2O_3," to be submitted to *J. Mater. Chem.*

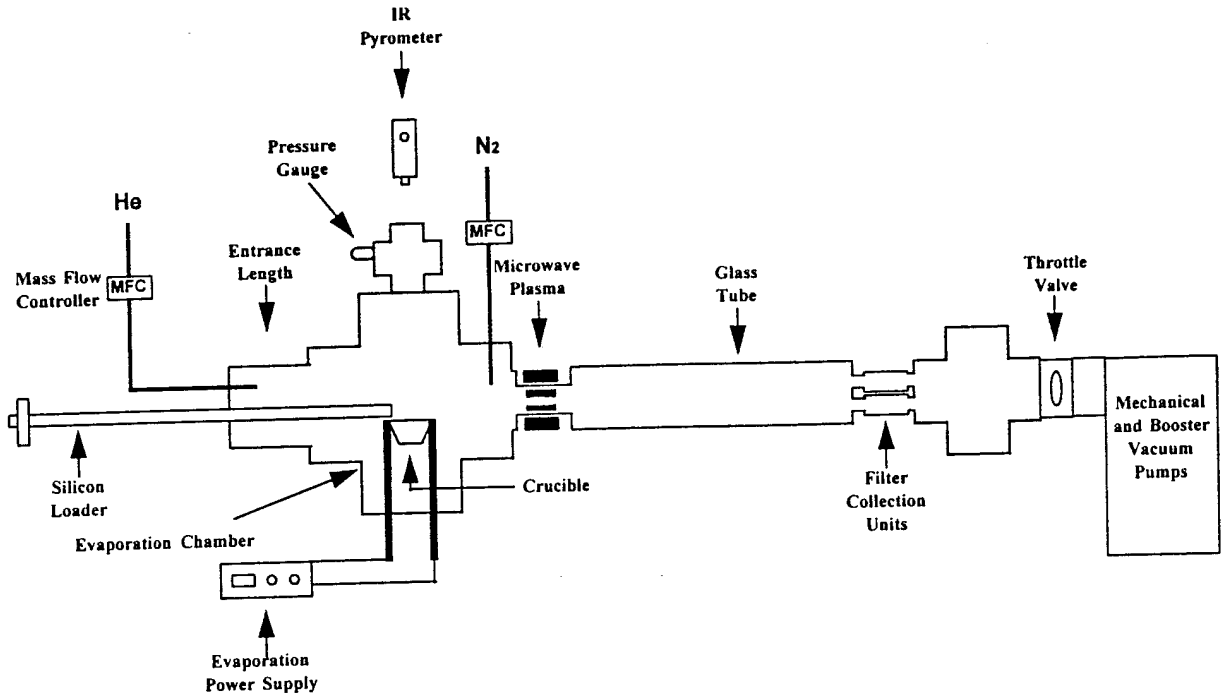

Figure 1: Schematic of modified tubular flow reactor.

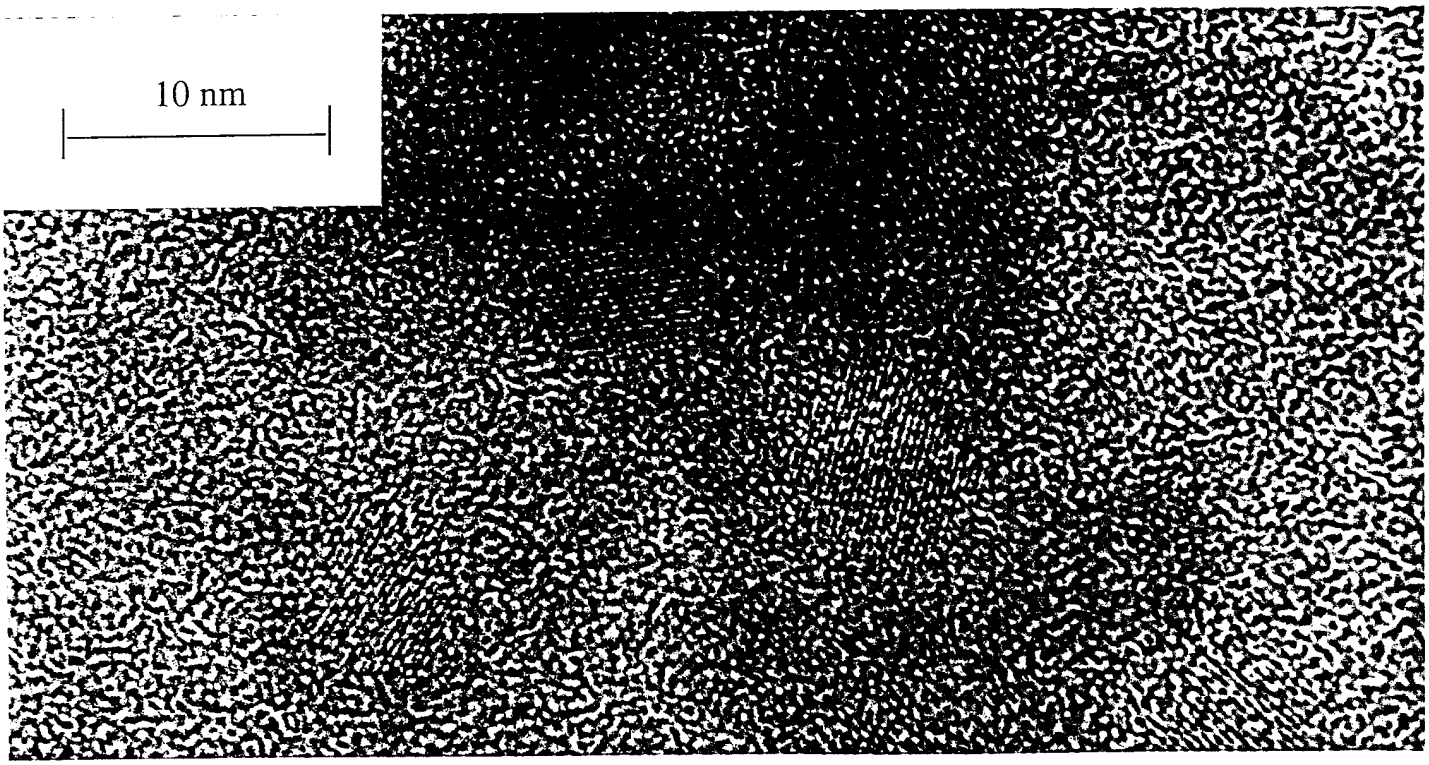

Figure 2: Nanocrystalline silicon particles produced at P = 7 mbar and gas velocity = 12.5 m/s.

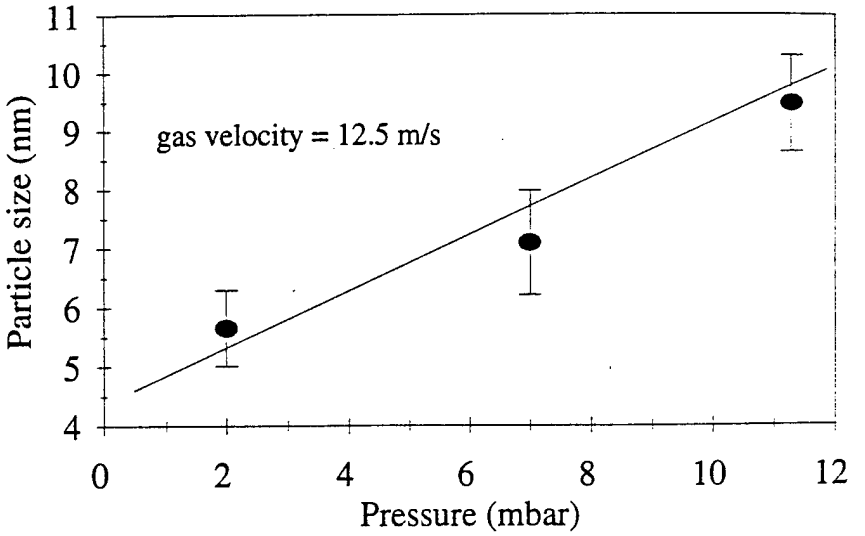

Figure 3: Particle size as a function of reactor pressure at a gas velocity of 12.5 m/s.

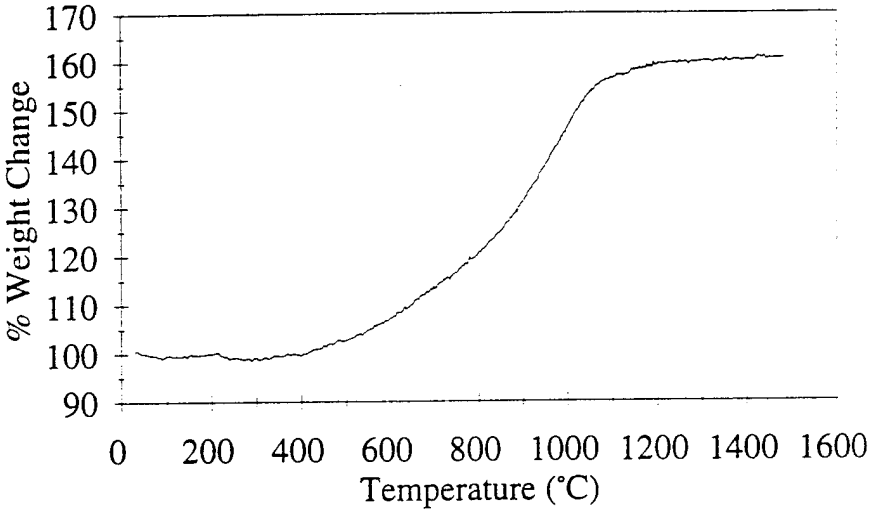

Figure 4: TGA data showing Si-to-Si_3N_4 conversion by 1050 °C.

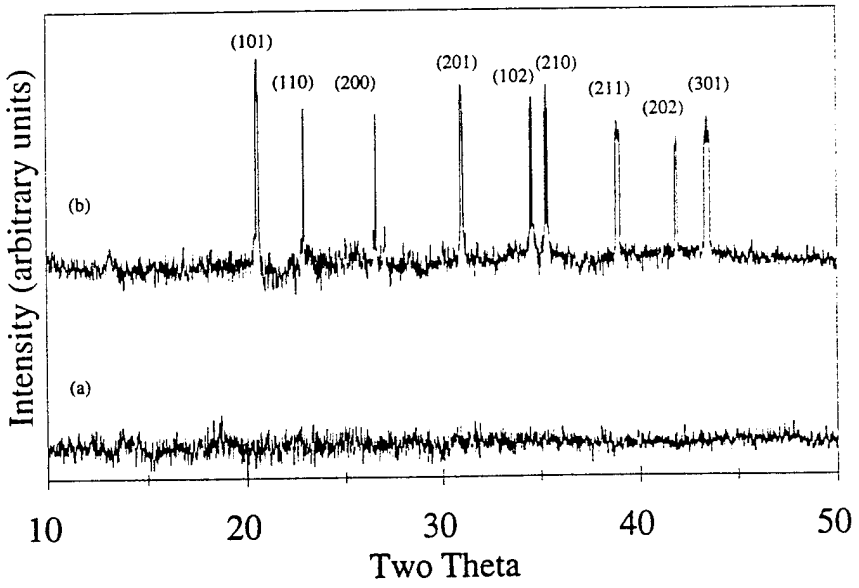

Figure 5: (a) XRD data showing that as-prepared material is X-ray amorphous. Following heat treatment at 1600 °C for 1 hour in a flowing nitrogen atmosphere, α-Si_3N_4 peaks (indexed) are well developed (b).

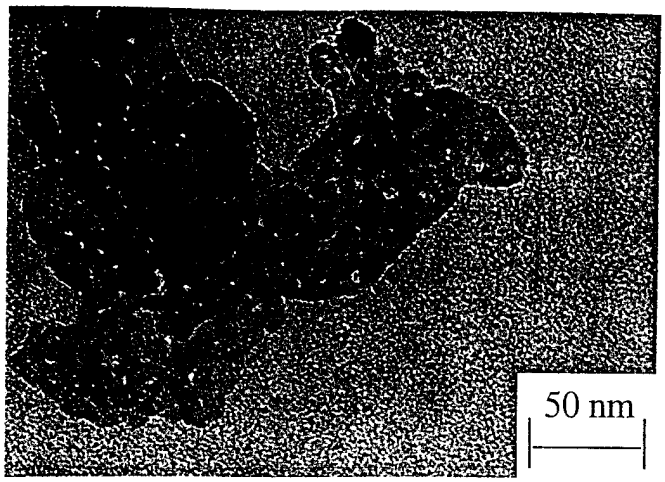

Figure 6a: Nanocrystalline Y_2O_3 produced via chemical precipitation. (Same magnification as Figure 6b).

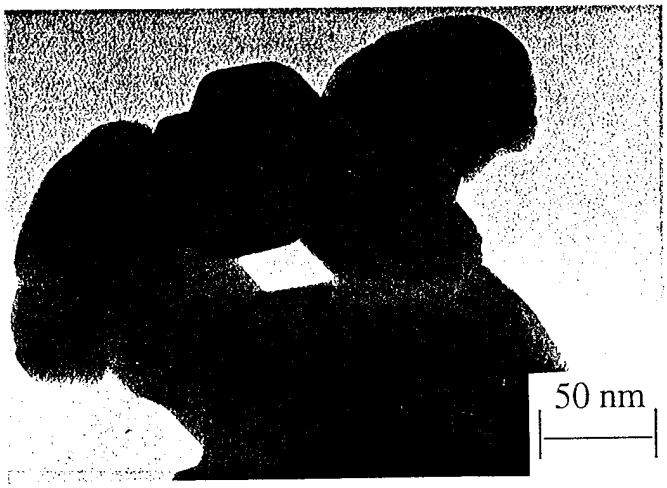

Figure 6b: Commercial Y_2O_3 (H.C. Starck Grade C). (Same magnification as Figure 6a).

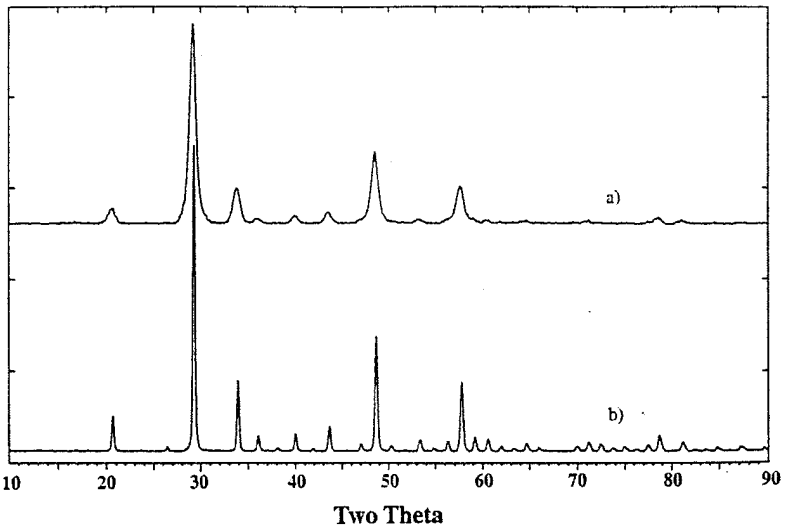

Figure 7: (a) XRD data of nanocrystalline Y_2O_3 produced via chemical precipitation. Crystallite size by XRD is 8.8 nm. (b) XRD data of commercial Y_2O_3 (H.C. Starck Grade C). Crystallite size by XRD is 73.3 nm.