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TITLE: RF PLASMA SYNTHESIS OF ULTRAFINE, ULTRAPURE SILICON CARBIDE POWDER

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RF PLASMA SYNTHESIS OF ULTRAFINE, ULTRAPURE SILICON CARBIDE POWDER

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SUMMARY

Ultrafine, ultrapure silicon carbide powder has been produced by reaction of silane and methane in a high temperature rf plasma. Preliminary studies include the effect of gas composition and of power (plasma temperature) on the stoichiometry of the powder. The carbon-to-silicon ratio of the powder was varied from 1.0 to 1.9 by changing the process conditions. The powder has a BET surface area of $101 \text{ m}^2/\text{g}$, which is equivalent to a particle diameter of 18.5 nm. A particle size in the range of 10 to 20 nm was measured by transmission electron microscopy. X-ray diffraction results indicate a domain size of 7.5 nm and a crystal structure of beta (cubic) silicon carbide. Spectrographic analysis shows that metallic impurities are lower than high quality grade commercial powder. Because of the high surface area, the powder must be stored and processed in an inert atmosphere to prevent severe contamination with oxygen.

1. INTRODUCTION

Ultrafine, ultrapure silicon carbide powder offers a new approach to obtaining dense, fine-grained materials with improved properties. By taking advantage of the surface energy available from the high surface area of these powders, we hope to be able

to consolidate them at lower temperatures and without the sintering aids necessary for conventional powders.

The ultrafine powders were obtained by reaction of silane with methane in the tail flame of an rf plasma. Similar silicon carbide powders have been made previously by Stroke,[1,2] and methods for making various refractory powders in rf plasmas have been reviewed by Hamblyn and Reuben.[3] Earlier work with plasmas was done by Audsley and Bayley[4] who studied the oxidation of silicon tetrachloride in an argon/oxygen plasma and by Dundas and Thorpe[5] who described the production of titanium oxide by oxidation of the chloride in an rf plasma.

Ultrafine titanium nitride was produced by Yoshida, et al.[6] by passing powdered titanium through an argon/nitrogen plasma, and Kagawa et al.[7] made ultrafine magnesium oxide by spraying an aqueous solution into an rf plasma. Silicon, silicon nitride, and silicon carbide powders with characteristics similar to the present rf plasma silicon carbide powder have been synthesized at MIT using a laser-assisted CVD approach.[8-12] The advantage of an rf plasma is that it provides a very clean system with little contamination of the product, contrary to an arc plasma where electrode erosion often leads to significant contamination.

The prevalent designs of rf plasma systems include a water- and gas-cooled quartz containment vessel surrounding the plasma,

and quite often a nonsymmetric condition develops resulting in meltdown of the quartz vessel. A new design has been developed at Los Alamos that has solved this overheating problem and has opened the way for further advances in the use of rf plasma for high temperature processing.

2. APPARATUS

The plasma system used for these studies has been described elsewhere.[13] It consists of a plasma tube and associated rf power generator, a reaction chamber, a cooldown chamber, and a powder collection system.

Briefly, the plasma tube is a new design using the concept of a transformer. Several heavy-walled, water-cooled copper fingers are inserted inside a quartz mantle. They transmit power from the surrounding rf coil to the contained plasma and their chevron cross section is such that they overlap each other and prevent direct radiation from the plasma to the quartz mantle. Thus, the mantle remains cool. Also, the absence of ionizing radiation around the coil suppresses troublesome arcing that often occurs between turns or between the coil and the mantle.

Argon flows down through the plasma to help stabilize the plasma and to provide a tail flame at the bottom of the plasma tube. Reactant gases are introduced into the tail flame radially

through four orthogonally positioned orifices located in the reaction chamber at the bottom of the plasma tube. Mixtures of argon, silane, methane, and hydrogen comprise the reactant gas.

In this high temperature region, the silane and methane are decomposed, and upon very rapid cooling, the gas becomes supersaturated and silicon carbide is precipitated. The cooling rate is believed to be so high that the number density of nuclei is large and particle growth is limited, producing ultrafine powder.

Below the reaction chamber is a water-cooled, cooldown chamber where the gas/powder mixture is cooled to ambient temperature before entering the powder collection system.

The powders are collected in two cyclone separators connected in series. Although the particle size is too small (10-20 nm) to be separated by a cyclone, there is enough agglomeration to permit efficient separation and collection. About 45% of the powder deposits on the walls of the reaction and cooldown chambers, about 45% is separated and collected in the cyclones, and the remainder is lost in the exhaust. Production rates of 100 g/hr have been achieved; however, this rate is limited by the gas control and metering system and is not necessarily the limit for the plasma tube.

3. RESULTS AND DISCUSSION

Ultrafine, ultrapure silicon carbide powder was made by radial injection of silane, methane, and hydrogen into the tail flame of the plasma. We have studied the effects of gas composition and rf power on the chemical composition of the powder and have evaluated the particle size and crystal structure of the powder.

The composition of the powder can be varied over a wide range from excess silicon to excess carbon. This is accomplished by adjustments in the feed gas composition and/or rf power. Table 1 lists the power and gas flows for several different conditions. The plasma argon is used to sustain the plasma and to provide the tail flame. The process argon is used as a diluent for the process gas which is injected into the plasma tail flame. In the first three runs at power levels between 15 and 19 kW, the only change made was in the silane flow rate. Chemical analyses of Runs 1 and 2 were not made but the color comparison of Runs 1, 2, and 3 clearly showed the differences. Run 1 was a dark tan color, Run 2 black, and Run 3 dark gray. X-ray diffraction of powder from Run 1 gave patterns for silicon as well as beta silicon carbide, and visual examination of Run 1 at 50x showed some spherical particles that were not present in the other two runs. We believe these spheres to be silicon. The excess carbon in Run 2 did not

Table 1.

PROCESS VARIABLES AND POWDER COMPOSITION

Run No.	Power kW	Plasma Ar	Process Gas Flow (SLPM)				Powder Composition C/Si Ratio
			Process Ar	Hydrogen	Methane	Silane	
1	15	22	4.5	5.3	1.0	.65	Excess Si
2	15	22	4.5	5.3	1.0	.21	Excess C
3	19	22	4.5	5.3	1.0	.41	1.1
4	18	34	4.5	5.3	2.3	.65	1.0
5	33	34	4.5	5.3	1.0	.41	1.9
6	20	34	4.5	0	5.9	1.64	1.1

produce an x-ray pattern and is presumably amorphous. All three runs contained beta silicon carbide as the major constituent. The chemical analysis of Run 3 showed that the carbon-to-silicon ratio was 1.1 or very nearly stoichiometric.

In Run 4, the plasma argon was increased simultaneously with an increase in both methane and silane. This change produced a carbon-to-silicon ratio of 1.0 at the same power level as the first three runs.

In Run 5, the power level and plasma argon flow were increased, but the other gas flows were the same as Run 3. Here the carbon-to-silicon ratio in the powder increased to 1.9, almost doubling that of Run 3. While these data are certainly not conclusive, they suggest that higher power levels increase the carbon activity in the gas providing more carbon for incorporation into the powder.

We have observed that hydrogen in the feed gas lowers the temperature of the tail flame considerably. This is illustrated by the observation that with only plasma and process argon flowing, a visible tail flame extends into the reaction chamber approximately 100 mm. The introduction of only half of the hydrogen used in these experiments will quench the visible part of the tail flame, a clear indication of a large drop in temperature. It is not surprising then that a change in power will have a major effect on the reactions in the tail flame because of temperature changes.

Hydrogen was not included in Run 6. With its elimination it was anticipated that higher flow rates of methane and silane could be used since the tail flame temperature would be hotter than before. This was indeed the case. The flow rate of both gases was increased by a factor of 2.5 over those used in run 4, with little change in the stoichiometry.

Particle size of the powder was determined by transmission electron microscopy. Figure 1 is a photomicrograph of some of those particles showing a size range of 10 to 20 nm. The chain-like agglomeration is characteristic of particles in this size range,[14] although the manner in which the individual particles are bonded together is not yet known. These sizes are consistent with a BET surface area measurement of $101 \text{ m}^2/\text{g}$, which is equivalent to a particle diameter of 18.5 nm.

X-ray diffraction results indicate a crystal structure of beta silicon carbide (cubic form) with a domain size of 7.5 nm. The cubic structure is interesting and may shed some light on the actual conditions leading to its formation. It is known that the beta form is obtained in the presence of excess silicon even when heated above 3100 K.[15] In most other environments one of the alpha prototypes (hexagonal)[15] is the stable structure. It would appear then that during the nucleation and growth period, conditions exist such that the activity of silicon is higher than carbon and the excess silicon catalyzes

the formation of the beta structure. These conditions only need be momentary because the residence time in the high temperature environment is so short. Since in our experiments the carbon concentration in the gas is higher than the silicon, the activity of carbon relative to silicon will increase as precipitation progresses and this would tend to increase the amount of carbon in the product. It is possible, therefore, to have excess silicon during the initial stage of particle nucleation and growth and excess carbon during the final, lower temperature stage.

One of our objectives in doing this work was to produce ultrapure silicon carbide. Spectrographic analysis of these powders shows that the impurity levels are well below those of high quality commercial powders. Table 2 lists the impurities of powder made at Los Alamos compared to an H. C. Starck Company Grade B-10 silicon carbide powder. With the exception of zinc, all impurities are present at concentrations lower than in the commercial powder. Elements not listed are below detectable limits.

As with most high-surface area and chemically active materials, oxygen contamination is a problem. The oxygen content of these powders as sampled in the process and maintained in an argon atmosphere is less than 0.5 per cent by

Table 2.

IMPURITY COMPOSITION OF THE POWDER COMPARED WITH COMMERCIAL POWDER

Element*	CVD Powder	Commercial** Powder
B	<10 ppm	200 ppm
Al	10	800
Ca	5	50
Ti	<3	50
Cr	<10	20
Fe	<10	300
Cu	20	40
Zn	100	<30
Ag	5	<1
W	<300	1000
O	<1%	Unknown

* Elements not shown are below detectable limits for both powders.

** H. C. Starck Company - Grade B-10

weight. Various exposures to air can increase that to 3.0 per cent. Consequently, special handling procedures are required to maintain a low oxygen content.

4. CONCLUSIONS

Ultrafine, ultrapure silicon carbide powder has been made by reaction of silane with methane in the tail flame of an rf plasma. This confirms earlier work but in a plasma system that is very reliable and that overcomes the overheating problems of conventional systems.

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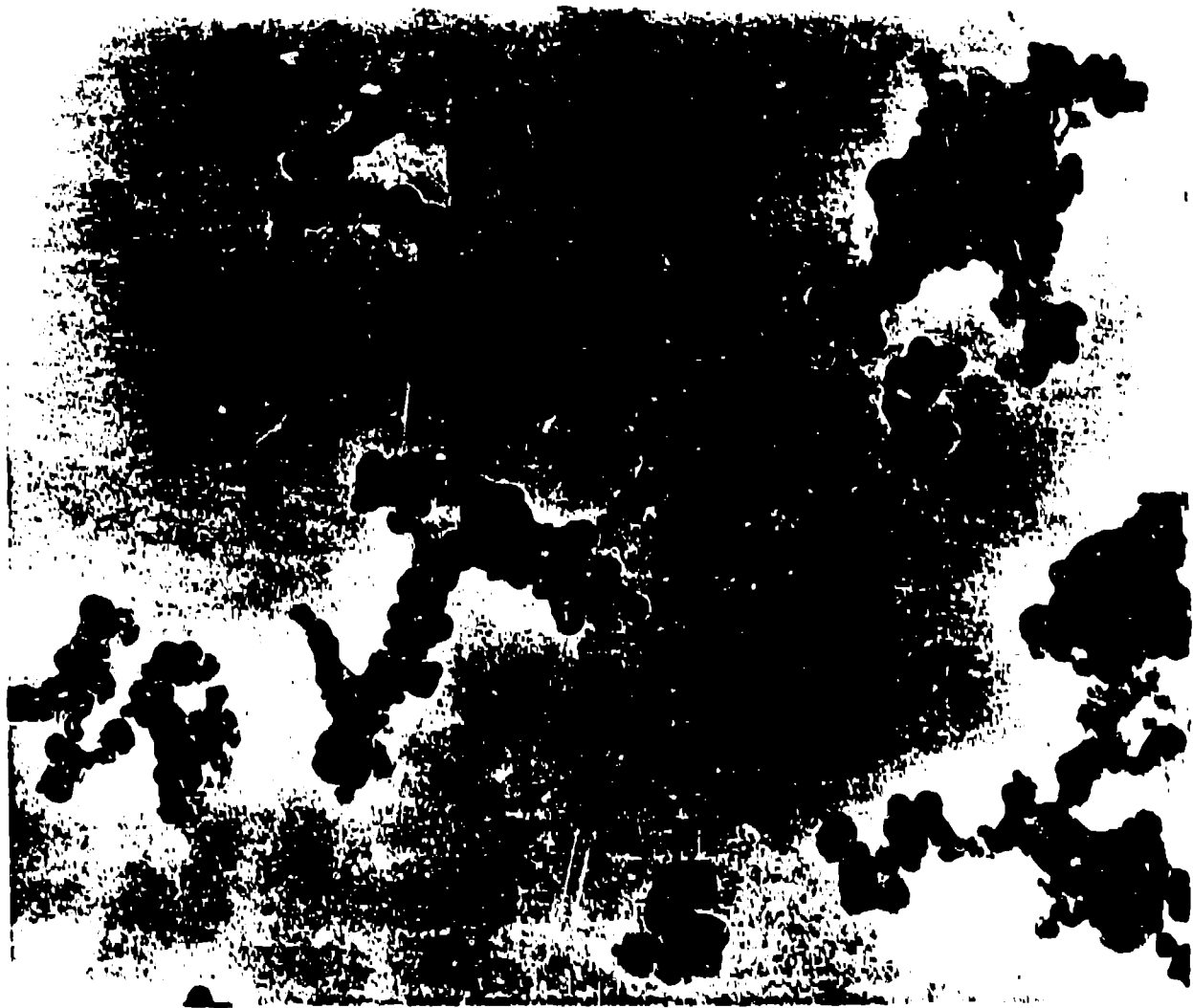
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FIGURE CAPTION

Fig. 1. TEM of Silicon Carbide Powder



— 1000 Å