CHEMICAL VAPOR PRECIPITATION OF SILICON NITRIDE POWDERS WITH A TUNABLE CO₂ LASER


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Silicon nitride powders were synthesized by laser excitation of the gaseous reactants dichlorosilane and ammonia. Average particle size, degree of agglomeration, particle morphology and chemical composition, are related to the type of chemical reaction during formation which changes with the geometry of the gas introduction nozzles in the reactor.

INTRODUCTION

For covalently bonded ceramics which do not sinter easily such as the nitrides, carbides, and borides, control of powder composition, structure, particle size, size distribution, and degree of agglomeration is decisive for the quality of the sintered ceramic product. Very small submicron particles are particularly interesting. These can be produced by gas phase synthesis which affords easy control through process parameters such as gas composition, pressure, temperature and gas flow rates. Many materials and pigments such as silica, titania and carbon powders are routinely made from gaseous reactants. If laser radiation is used for thermal excitation, rather than conventional conductive heating, very high heating and cooling rates are achieved and gases can be selectively excited in a mixture by choosing the laser
frequency to match the absorption bands of the reactants. Laser power and frequency are additional process control variables.

Submicron silicon nitride powders have been synthesized by means of Laser-Chemical Vapor Precipitation (L-CVP) using silane and ammonia [1] and from the more cost-effective chlorinated silicon compounds using an untuned IR-laser [2]. In the present paper the results of our recent work on the deposition of fine silicon nitride powders using laser excitation of dichlorosilane (SiH2Cl2) and ammonia (NH3) is presented. By means of a tunable CO2 laser the two reactants could be separately excited. The process of preheating one of the reactants before introducing the other precursor for reaction was compared with excitation of either reactant in a gas mixture.

Besides particle size, agglomeration should be controlled for ceramic application. The combination of average cluster size determined with Sedimentation Field Flow Fractionation (SFFF) and primary particle size as determined from transmission electron micrographs permits estimation of the degree of agglomeration of the particle clusters as reported elsewhere in more detail [3].

EXPERIMENTAL PROCEDURES

The powder formation process is carried out at atmospheric pressure. Figure 1 shows a schematic of the reactor. The central SiH2Cl2-nozzle has an internal diameter of 1 mm and the four adjustable side nozzles for ammonia 0.4 mm. These nozzles inject the reactants in the laser beam spot where the silicon nitride particles form. The laser beam was focused by zinc selenide optics to a spot having a diameter of 1.5 mm. The reaction process conditions that were varied were precursor gas mixing and laser excitation sequence. By varying the point of NH3 introduction into the laser excited dichlorosilane, the powder characteristics could be changed. The submicron particles were electrostatically removed from the aerosol at elevated temperatures in order to separate them from volatile ammonium chloride which is a waste product of the reaction. The 150 W CO2 laser from Edinburgh Instruments (type PL 6) was tuned to output the 10P20 line ($\lambda = 10.6 \, \mu m$) for selective excitation of dichlorosilane. The 9R30 line ($\lambda = 9.2 \, \mu m$) was used
to excite ammonia. The ammonia flow rate was 110 sccm and the dichlorosilane flow 53 sccm. The residence time of the gas in the visible laser flame (above the ammonia introduction point) was estimated to be 20 ms. The silicon nitride production rate under these
conditions was approximately 1 g/h.
The powders were removed from the precipitator in an inert atmosphere glove box to prevent oxidation. Primary particle sizes were determined from transmission electron micrographs while the average degree of agglomeration n was derived from the cluster size, determined by SFFF as follows. The powder was suspended in a dilute aqueous ammonia solution (0.002 M), these suspensions were ultrasonically dispersed over a 10 minute period before injection into the Dupont SF^3 analyzer. Figure 2 shows a transmission electron micrograph of a cluster of monosized primary silicon nitride particles obtained by laser CVP.
<table>
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<th>Sample number</th>
<th>h NH₃ exc.</th>
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Meaning of symbols used: h (column 2) indicates height of NH₃ injection; the asterisk in column 3 indicates which powders were made using selective NH₃ excitation; the number in column 4 gives the relative amount (in arbitrary units) of fibrous particles in the powder deposit if present; column 5 gives the weight ratio of silicon to nitrogen in the powders (theoretically 1.5 for stoichiometric Silicon nitride); in columns 6 and 7 particle diameters in nm are given as determined with transmission electron microscopy and gas adsorption (BET) respectively; column 8 gives the average number of primary particles in the clusters as determined from SFF size measurements [3].

The composition of the powders was determined by chemical analysis for silicon by Inductively Coupled Plasma, and nitrogen by ammonia titration using conductivity [4]. The flame temperature was monitored by a two-colour pyrometer which permitted measurement of the temperature distribution in the flame.
RESULTS

The results are summarized in table 1. There are three regimes of reaction process parameters producing different powder characteristics. The samples in the lower third of table 1 (number 11 to 15) were obtained by laser excitation of either reactant in a gas mixture. The highly agglomerated powders obtained in this premixed regime had a high nitrogen content and a composition close to the stoichiometric value. The particles were dense as shown by the similar values of their TEM and BET determined diameters. If ammonia was excited in this regime, the powders were invariably white, whereas those obtained with selective dichlorosilane excitation had a tan colour. This however, was their only difference, the other characteristics were quite similar. This color change was not accompanied by a significant difference in the Si/N ratio.

The samples produced in the postmixed regime (numbered 1 to 5 in table 1) were produced by excitation of dichlorosilane with injection of cold ammonia gas into the laser generated flame. These powders were brown to tan colored, had an excess of elementary silicon as shown by chemical analysis, a low degree of agglomeration and large porous particles. The samples numbered 6 to 10 were produced in a transition regime and consisted of a mixture of whiskers and large distorted porous particles also with an excess of silicon. The flame temperature at the ammonia introduction point (this point of the flame invariably had the highest temperature) was 2400°C in the premixed and intermediate regimes. In the postmixed regime the maximum flame temperature was 1500°C.

DISCUSSION

The mechanism of silicon nitride formation has been studied by Morosanu et al. [5]. The characteristics of the powders made in the premixed regime are consistent with their reactions. Because of rapid energy equilibration at atmospheric pressure, the results are not expected to be heavily dependent on the choice of reactant excited by the laser.

The proposed overall reactions [5] are:

\[ \text{SiH}_2\text{Cl}_2 \quad \rightarrow \quad \text{SiCl}_2 \quad \rightarrow \quad \text{SiNH} \quad \rightarrow \quad \text{Si}_3\text{N}_4 \]
The chemically undetectable but visually surmised excess of silicon in the dichlorosilane excitation experiment is probably the result of a higher concentration of the intermediate product SiCl₂, producing traces of silicon by reduction.

The reactions of silicon nitride formation in the postmixed regime is expected to be quite different because dichlorosilane is excited and decomposed to silicon before it is allowed to react with ammonia. Silicon droplets form which increase in size upon colliding. Hence the large size of the primary particles as seen in the electron micrographs. Exposure of the hot silicon mist to ammonia results in growth of a solid surface crust of silicon nitride on the surface of the silicon droplets and irregularly shaped large porous particles obtain, usually incompletely converted to the nitride. In several cases in the transition regime, carrot-like particles form, which is usually an indication of a Vapor-Liquid-Solid (VLS) mechanism. A simultaneous growth of solid silicon nitride and liquid silicon drops probably occurs which explains the observed morphology.

The formation reaction consistent with the observed morphology in the transition and the postmixed regimes is:

\[ \text{SiH}_2\text{Cl}_2 \quad \text{**} \quad \text{Si(l)} \quad \text{**} \quad \text{Si}_3\text{N}_4(s) \]

The observed excess of silicon is the result of a residence time of the particles in the laser flame which is too short for complete reaction of silicon to silicon nitride.

CONCLUSIONS

The characteristics of silicon nitride powders produced by Laser Chemical Vapor Precipitation from dichlorosilane and ammonia are largely determined by which is done first: mixing of the precursor gases or laser excitation.

Very pure, highly agglomerated powders with monosized
dense amorphous particles result from excitation of either reactant in a gas mixture. Incompletely nitrided porous precipitates containing large irregularly shaped particles having a low degree of agglomeration are the result of postmixing ammonia into an aerosol of liquid silicon particles obtained by laser decomposition of dichlorosilane.

REFERENCES


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