Laser Vapor Phase Synthesis of Submicron Silicon and Silicon Nitride Powders from Halogenated Silanes

R. A. BAUER, R. SMULDERS, E. R. GEUS, P. J. VAN DER PUT,
J. G. M. BECHT, AND J. SCHOONMAN

Delft University of Technology
Department of Inorganic and Physical Chemistry
Laboratory of Inorganic Chemistry
P.O. Box 5045
2600 GA Delft, The Netherlands

In the state of the art laser synthesis process for silicon, silicon nitride, and silicon carbide, silane is used as a gaseous reactant. In order to replace SiH_4 by chlorinated silanes we have studied the laser synthesis of Si_3N_4 from mixtures of SiH_2Cl_2 and NH_3 , and SiCl_4 and NH_3 using a 150 W cw CO_2 -laser. At room temperature chlorinated silanes readily react with NH_3 to form $\text{Si}(\text{NH})_2$. A laser reactor was developed in which the reactant gases were mixed in the laser beam, thus preventing the formation of $\text{Si}(\text{NH})_2$. A concentric N_2 gas stream was utilized to guide the ceramic powders into a high-temperature electrostatic precipitator in which Si_3N_4 was separated from the waste product NH_4Cl . A major problem in utilizing chlorinated silanes is their poor absorption of the CO_2 -laser radiation ($10.6\ \mu\text{m}$). SF_6 has been explored for use as an inert sensitizer.

Particle sizes of the amorphous powders were of submicron dimensions, spherical and nearly monodisperse. The sizes of the particles were studied by TEM and BET analysis. The powders were analyzed by IR-spectroscopy, X-ray fluorescence, XRD, and EDX.

Introduction

Recent interest in high temperature structural ceramics has led to the development of chemical vapor precipitation (CVP) techniques for the formation of a variety of high quality oxidic and nonoxidic ceramic powders. Usually thermally activated CVP is used. Haggerty et al.¹⁻⁵ have developed laser-CVP for the synthesis of ultrafine ceramic powders, in particular of Si, SiC, and Si_3N_4 . Characteristic of the laser-driven gas phase synthesis process is a well-defined reaction zone which facilitates a considerable degree of control over composition and size, as well as size distribution of the product powders. In the laser-CVP of Si, SiC, and Si_3N_4 , silane is invariably used as the silicon reactant, while in the traditional thermally activated CVP of powders and thin films of Si_3N_4 , chlorinated silanes (i.e. SiH_2Cl_2 and SiCl_4) are employed frequently.^{6,7}

Silane absorbs the radiation of a CO_2 -laser ($10.6\ \mu\text{m}$) very efficiently. With increasing number of chlorine atoms the absorption of $10.6\ \mu\text{m}$ radiation by chlorinated silanes decreases, the absorptivity of silicon tetrachloride being virtually zero. The utilization of chlorinated silanes in laser-CVP, therefore, requires an inert sensitizer.

Recent work indicates that the synthesis of equiaxed submicron powders of amorphous Si_3N_4 with a narrow size distribution is feasible using thermally activated CVP.⁷ We have extended this research to the use of chlorinated silanes in the laser-CVP of Si and Si_3N_4 powders. Particular emphasis was focused on the role of SF_6 as a sensitizer for the production of powders in the systems SiH_2Cl_2 , $\text{SiH}_2\text{Cl}_2\text{-NH}_3$, and $\text{SiCl}_4\text{-NH}_3\text{-H}_2/\text{N}_2$. In the latter two systems, NH_4Cl is formed as a solid by-product. In order to separate the aerosol particles of Si_3N_4 , a high temperature electrostatic precipitator has been developed. Chlorinated silanes react at ambient temperatures with NH_3 to form silicon diimides. To avoid this reaction a laser reactor was equipped with a specially designed nozzle.

Experimental Aspects

Reactants

Reactants for silicon and silicon nitride by laser vapor precipitation (L-CVP) were dichlorosilane, SiH_2Cl_2 (Air Products, 97% dichlorosilane, 3% other chlorosilanes); silicon tetrachloride, SiCl_4 (Janssen Chimica, 99.8%); and ammonia, NH_3 (Air Products, 99.999%). An inert sensitizer was sulphur hexafluoride, SF_6 (Airproducts, 99.97%). The flow carrier gases N_2 and H_2 were purified by a copper (BASF, R 3-11) and palladium (BASF, R 0-20) catalyst, respectively, and a zeolite (DOW, A4).

The liquid reactant SiCl_4 (bp = 57 °C) was evaporated into a reflux condenser. The flow and partial pressure were regulated by controlling the carrier gas flow through the condenser; the condenser temperature was regulated by a constant temperature bath (Tamson, TLC 3).

Laser-CVP

The selection of the present reactants for the synthesis of Si_3N_4 implies the room temperature formation of silicon diimide, $\text{Si}(\text{NH})_2$, unless precautions are taken in the nozzle design. In addition, ammonium chloride is a by-product, requiring adequate separation of Si_3N_4 .

A schematic drawing of the stainless steel reactor is presented in Fig. 1. The two KCl windows were flushed with N_2 (28 l/h). The reactor was operated at atmospheric pressure. An industrial 150 W cw CO_2 -laser (Electrox, PB 2000), radiating at 10.6 μm , was partially focused with a ZnSe lens (focal length, 30 cm) in an orthogonal stream of reactants.

Three types of nozzles were examined for this experiment. Figure 2 shows their schematics. Best results were obtained by using nozzle 2(C); the other types caused premixing and hence solid imide formation before heating by the laser radiation.

The brightness temperature was monitored by a one-color optical pyrometer (Heimann, KS81) having an optical window of 0.7 to 1.2 μm , and a measuring spot diameter of 1.5 mm.

The reaction products were confined to a small well-defined reaction zone by a concentric N_2 gas stream (156 L/h). This gas stream was also employed to feed the products into a horizontal electrostatic precipitator (ESP). A schematic picture of the employed ESP is given in Fig. 3. The potential of the central wire electrode was set at about +20 KV, while the external cylindrical counter electrode was grounded. The wire electrode was encapsulated in a quartz tube in order to prevent corrosion by the reaction product gas stream. The temperature of the ESP furnace was kept at 750 °C. The temperature of the wire electrode did not exceed

400 °C, due to a cooling effect of the reaction product gas stream.

The powders were analyzed using IR-spectroscopy, EDX, and X-ray fluorescence and characterized by XRD, and electron diffraction on the TEM. Particle sizes were estimated from TEM micrographs, while equivalent spherical diameters (ESD) were calculated from BET surfaces using methane as adsorbing gas.

Results and Discussion

Silicon and silicon nitride powders were made at atmospheric pressure either by direct laser excitation of dichlorosilane or by indirect laser excitation of SiH_2Cl_2 or SiCl_4 using SF_6 as a sensitizer. The process conditions and results of our experiments with SiH_2Cl_2 and SiCl_4 are summarized in Tables I and II, respectively.

Silicon Particle Formation

The reactant was SiH_2Cl_2 . A yellow, thermal flame developed in the reactor due to laser excitation and decomposition of SiH_2Cl_2 followed by nucleation of elemental silicon. Dark brown powders of amorphous silicon were produced, which were fairly monodisperse. The mean particle diameter was 50 nm. The product contained small amounts of chlorine impurities and the yield related to SiH_2Cl_2 was virtually 100% (1.7 g/h Si). A few minutes after starting the deposition experiments, the reaction flame stabilized and long production times could be maintained. The capacity of the electrostatic collector limited the experiments to one hour.

Sausa and Ronn have shown that dichlorosilane at low pressures dissociates by excitation with a tuned pulsed CO_2 laser.⁸ As shown above, dichlorosilane is clearly capable of absorbing sufficient power from a nontuned cw industrial laser to produce ultrafine silicon powders at atmospheric pressures.

Silicon Nitride Particle Formation by Direct Laser Excitation of SiH_2Cl_2 and Reaction with NH_3

When ammonia was added to dichlorosilane in the reactor, a yellow-white thermal flame developed having a temperature which was higher than in the case of silicon production under similar reaction conditions. Amorphous silicon nitride was obtained as shown by the characteristic absorption band (950 cm^{-1}) in the infrared spectra. These spectra also showed that the product was slightly contaminated by small amounts of both NH_4Cl and imides (absorption bands at 2900 cm^{-1} and 1200 cm^{-1}). The average particle diameter of the tan-colored Si_3N_4 powder was 30 nm which is below the value obtainable by thermally activated CVP.⁷ Transmission electron micrographs showed the particles to be moderately agglomerated as shown in Fig. 4. The synthesis of silicon nitride powder by laser CVP in a continuous flow reactor using halogenated silane reactants has not been reported before.

Silicon Nitride Powder Formation Using SiH_2Cl_2 and NH_3 as Reactants and SF_6 as Sensitizer

SF_6 is a well-known sensitizer used in laser chemistry.⁹ We have studied the effects of increasing SF_6 concentration on silicon nitride powder production (Table I). At SF_6 flow rates below 0.4 L/h, no changes in flame character were observed. However, at an SF_6 flux of 1 L/h a blue fluorescence was seen beyond the reaction flame core. Similar fluorescence has been observed by other authors¹¹⁻¹³ and ascribed to fluorescence of sulphur particles formed during decomposition of laser-excited SF_6 in the presence of hydrogen or hydrogen containing compounds.¹² This latter

observation is corroborated by the presence of minor amounts of sulphur in the present silicon nitride, as determined by XRD in preliminary experiments. The mean Si_3N_4 particle size was insensitive to SF_6 flow rates. Particles were amorphous and contained slightly more than the usual amounts of imides and NH_4Cl .

Experiments Using SiCl_4 and NH_3 as Reactants and SF_6 as Sensitizer

Our efforts to produce silicon nitride by SF_6 sensitized laser excitation of SiCl_4 under the conditions mentioned in Table II yielded white powders. These powders spread through the reactor instead of leaving through the exhaust funnel. This caused production runs to be terminated prematurely. The thermal characteristics of the laser spot were quite different from those observed in Si_3N_4 formation using SiH_2Cl_2 as reactant. In addition to SF_6 , the presence of molecular hydrogen was noticed to be necessary for the formation of the characteristic blue sulphur fluorescence. The presence of SF_6 turns out to be essential for energy absorption as well, since imide aerosol formation without SF_6 will not show a thermal flame on laser excitation. However, if hydrogen is replaced by nitrogen, a white-yellow thermal emission is observed instead of the blue sulphur fluorescence of decomposing SF_6 . Hence molecular hydrogen seems to quench thermal emission and to stimulate SF_6 decomposition.

These preliminary experiments with SiCl_4 show that although SF_6 can be used as a sensitizer, the reaction conditions need to be more carefully controlled than in the case of dichlorosilane decomposition.

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Table I. Process Conditions and Powder Characteristics for SiH_2Cl_2 as Reactant

	SI	SN1	SN5	SN2	SN3	SN4	SN7
Flows (L/h)							
SiH_2Cl_2	2	2	2	2	2	2	2
NH_3		7	5	5	7	5	5
SF_6			0.1	0.2	0.4	1	0.1
Power density (KW/cm ²)	5	5	5	5	5	5	4
Average gas velocity at center outlet (cm/s)	71	71	74	78	85	106	74
Product	Si	Si_3N_4	Si_3N_4	Si_3N_4	Si_3N_4	Si_3N_4	Si_3N_4
BET, surface (m ² /g)	50.5	56.9	69.2	45.2	67.6	48.4	
Equivalent diameter, BET (nm)	51.2	33.2	27.3	41.8	27.9	39.0	
Diameter TEM (nm)	40-60	20-40	20-30	10-60	10-30	20-30	15-30
Color	brown	light brown	white	tan	tan	tan	white
Crystallinity*	c, a	a	a	c [†] , a	a	a	a
Agglomeration grade [‡]	M	M	S	W	S	VS	M
Amount of sulphur (EDX) [§]	n	n	m	m	m	s	m
Amount of NH_4Cl (IR)		m	m	n	m	m	m
Amount of imide (IR)		m	s	m	s	s	s
Amount of oxide (IR)	s	m	m	m	m	s	m

*c=polycrystalline, a=amorphous.

[†]crystalline particles were silicon.

[‡]N=none, W=weak, M=moderate, S=strong, VS=very strong.

[§]n=not detected, m=minor, s=substantial.

Table II. Process Conditions for SiCl_4 as Reactant

	SN8	SN9
Flows (L/h)		
SiCl_4	2	2
carrier gas H_2	2	
N_2		2
NH_3	7	7
SF_6	0-2	1
visual observation	blue fluorescence	thermal emission

Fig. 1. Schematic of the laser reactor.

Fig. 2. Schematic of the nozzle systems with different reactant gas outlets: (1) N_2 , (2) NH_3 , (3) $\text{SiH}_2\text{Cl}_2/\text{SiCl}_4$, H_2/N_2 , and SF_6 .

Fig. 3. Schematic of the high temperature electrostatic precipitator (ESP).

Fig. 4. TEM photograph of Si_3N_4 particles.