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Synthesis of Silicon Nitride Powder by Gas-phase Reaction

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Abstract

Amorphous silicon nitride powders consisting of isometric particles about 0·2 μm in size were precipitated from silane–ammonia–nitrogen mixtures heated to 600–1300°C. Without ammonia, elementary silicon with negligible nitrogen content was precipitated. At an ammonia/silane molar ratio of 4:3 to 3:1 powders with a decreasing content of free silicon were obtained. From mixtures rich in ammonia, white silicon nitride with a slight nitrogen hyperstoichiometry was precipitated. Unreacted silane in gases exiting from the reactor indicated that the conversion to silicon nitride was not full even at an ammonia/silane molar ratio of 30:1.

Amorphe, isometrische Si_3N_4-Pulver mit einer Korngröße von ca. 0·2 μm wurden aus SiH_4–NH_3–N_2 Atmosphären im Temperaturbereich von 600°C bis 1300°C abgeschieden. Ohne NH_3-Zugabe fand sich nur elementares Silizium ohne nennenswerten Stickstoffanteil. Bei NH_3/SiH_4-Verhältnissen von 4/3 bis 3 konnten Pulver mit abnehmendem Anteil an freiem Silizium erzeugt werden. Aus NH_3-reichen Gasmischungen ergaben sich weiße Si_3N_4-Pulver mit einem leichten Stickstoffüberschuß. Nicht verbrauchtes SiH_4, das am Abluftventil der Reaktionskammer austrat, zeigte, daß selbst bei einem NH_3/SiH_4-Verhältnis von 30 keine vollständige Umsetzung zu Si_3N_4 stattfand.

On a préparé des poudres de nitrure de silicium amorphe constituées de particules isométriques de 0·2 μm par précipitation de mélanges silane–ammoniaque–azote chauffés entre 600 et 1300°C. En l'absence d'ammoniaque, on observe une précipitation de silicium élémentaire à teneur en azote négligeable. Pour une fraction molaire ammoniaque/silane comprise entre 4/3 et 3, on a obtenu des poudres dont la teneur en silicium libre était décroissante. Les mélanges riches en ammoniaque conduisent à la précipitation d'un nitrure de silicium blanc présentant une légère sur-stoechiométrie. La présence à la sortie du réacteur de silane n'ayant pas réagi indique que la conversion en nitrure de silicium n'était pas totale, même pour des fractions molaires ammoniaque/silane comprises 30.

1 Introduction

Current research in silicon nitride based ceramics needs high-purity homogeneous powders with the following properties: low cationic impurity content ($<0·01$ mass%); low oxygen content (<2 mass%); phase composition >95 mass% α-phase; surface area $> 10\,m^2\,g^{-1}$, corresponding to a particle size $\ll 1\,\mu m$; narrow particle size distribution (close to monodisperse) and absence of aggregates.

The properties of synthesized silicon nitride are related to the method of preparation. The preparation and production methods can be divided according to the type of reaction as follows:

(1) Nitriding of powdered silicon[1,2] or silicide[3] by nitrogen or by ammonia.[4,5]
(2) Gas-phase reactions of silane[6] and its halogen derivatives.[7]
(3) Thermal decomposition of substances containing Si and N, e.g. silicon diimide, $Si(NH)_2$.[8,9]
(4) Carbothermal reduction and nitriding of silica.[10,11]

The products prepared by direct reaction between silicon and nitrogen need extensive milling to obtain high sinterability. Diversity in the particle form and wide particle size distribution are usually observed in milled powders. Nevertheless, other properties such as high surface area and relatively low oxygen content are attained by sophisticated technology.[2]

The carbothermal method provides for a great deal of control over particle size and morphology through the appropriate seeding by a fine α-silicon nitride powder.[10] However, the quality of this powder may be diminished by inherent impurity phases—silica and silicon carbide.

In the products obtained by thermal decomposition of the substances containing silicon, nitrogen, carbon and hydrogen, simultaneous formation of carbon and silicon carbide is critical.[12,13]

When halogenated silanes are used as the silicon source,[14,15] solid ammonium halogenides are formed as the by-products in addition to silicon nitride powder. The product is thus contaminated by relatively persistent halogen impurities, which may affect the properties of the silicon nitride ceramics.

At present, two methods are thought to satisfy all the requirements for a high-quality silicon nitride powder. They are the thermal decomposition of silicon diimide, which is commercially exploited, and the precipitation from the gas phase using silane as the silicon source.

Various gas-phase systems have been used for the preparation of silicon nitride: $SiCl_4$–NH_3,[7,16] SiH_4–NH_3,[6,16] $SiCl_4$–N_2–H_2,[17] SiF_4–NH_3,[18] SiH_2Cl_2–NH_3,[19] $SiBr_4$–NH_3.[20] These systems are frequently used for the deposition of thin films, mainly with the function of an electric isolation layer in integrated circuits. More recently, silicon nitride[6,21,22] powders were prepared by the gas-phase precipitation.

A specific case of the gas-phase precipitation of silicon nitride is the laser synthesis of silicon nitride.[23–26] Due to the short reaction times which can be achieved by laser excitation of the silane–ammonia mixture, the precipitated powders consist of extremely small particles (from 20 to 500 nm) with a narrow particle size distribution. High purity of the starting gases, a cold wall arrangement of the reactor and exclusion of any contact with air and moisture during the whole preparation route result in products with very low oxygen content. On the other hand, elementary silicon is easily coprecipitated in these conditions.

Prochazka & Greskovich[6] have prepared amorphous silicon nitride powders from a SiH_4–NH_3–Ar gas mixture within the temperature interval 500–900°C. The powders containing elementary silicon obtained at a molar ratio $NH_3/SiH_4 < 10$ crystallized to α-Si_3N_4 after thermal treatment at 1250–1350°C. In the region $NH_3/SiH_4 > 10$, cream-coloured powders with a composition close to the stoichiometry of Si_3N_4 were formed and their crystallization took place at about 1480°C. Analysis of the precipitated powders for oxygen content gave values around 2 wt% and the surface area of powders varied between 20 and 27 $m^2 g^{-1}$.

In the present paper, precipitation from SiH_4–N_2 and various SiH_4–NH_3–N_2 mixtures has been investigated on a laboratory scale. The influence of the maximum reaction temperature (from 600 to 1400°C), of the molar ratio of the reactants (SiH_4/NH_3) and of the total gas flow rate on the properties of the precipitate have been studied.

2 Experimental

Ammonia gas of technical purity (containing approx. 0·5 mass% H_2O) and electronic grade silane (15 mass% in nitrogen) were used for synthetic experiments. A schematic layout of the apparatus used is shown in Fig. 1. Ammonia gas was dried in two adsorption columns with predried potassium hydroxide. The rest of the water was captured in a subsequent vessel by metallic sodium distributed on silica glass wool. Mass flow meters and controllers working within ±2% absolute deviation from the selected value (supplied by Tesla Rožnov, CSFR) were used to keep constant flows of both gaseous reactants into the tube reactor during the whole reaction period. The maximum temperature of the reactor was measured by a calibrated Pt–PtRh10 thermocouple. The maximum temperature was kept constant in the region 600 to 1400°C with a deviation + 1·5°C from the selected temperature.

The reactor consisted of an alumina ceramic tube i.d. = 46 mm, length = 500 mm (Alsint 99·7% Al_2O_3 Haldenwanger Keramik, Berlin, FRG) placed verti-

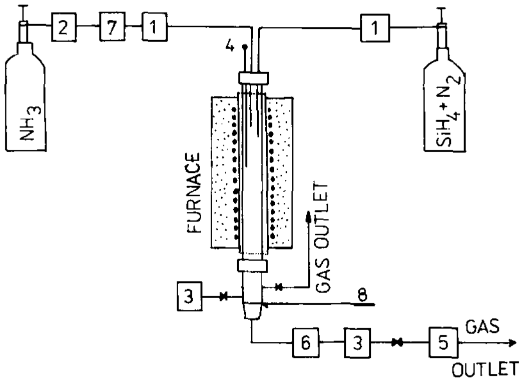

Fig. 1. Experimental layout for precipitation from a silane–nitrogen–ammonia gas mixture. 1, Mass flow meter; 2, drying column (KOH); 3, manometer; 4, thermocouple; 5, water-aspirator vacuum pump; 6, drying column (molecular sieve 4 Å); 7, drying column (Na); 8, glass frit.

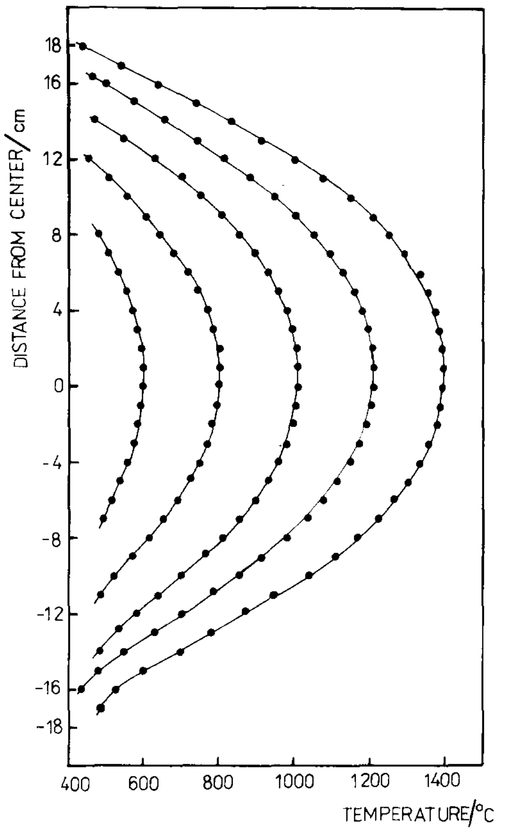

Fig. 2. Temperature distribution along the vertical axis of the tube reactor.

cally in a molybdenum wound resistance furnace. The vertical temperature distribution measured in the static state is shown in Fig. 2. These data together with the total gas flow through the reactor, which was varied between 47·5 and 400 cm^3 min^{-1} (all volumes are given at 22°C) make an estimation of the residence time of the reactants at various temperature possible if a piston flow is assumed.

In preliminary experiments various possibilities of gas inlet tube arrangement were tested, as is shown schematically in Fig. 3. In the case shown in Fig. 3(a) coprecipitation of elementary silicon caused by insufficient homogenization of the reaction mixture was observed. In the proximity of the silane inlet tube a relatively dense silicon layer was formed on the reactor walls. The arrangement in Fig. 3(b) led to a better homogenization of gaseous reactants. Under the same experimental conditions the analysis of precipitated silicon nitride showed a decreased silicon content and the area of the wall surface with a silicon deposit was diminished. Finally, the arrangement according to Fig. 3(c) provided a satisfactory mixing of gases before they reached the hot zone of the reactor for all silane and ammonia flows tested.

When the silane inlet tube was moved into the furnace and heated above 600°C an extensive decomposition of silane occurred and closing of the inlet tube by silicon deposits after a short time period was observed.

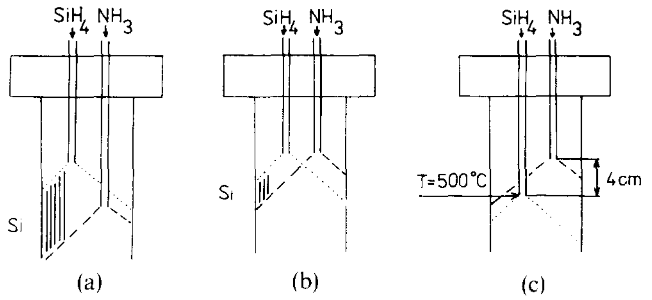

Fig. 3. Alternative gas inlet tube arrangements (see text).

After the reaction the precipitate was filtered from the mist with the help of a glass frit. A water-aspirator vacuum pump was used for back filtration and to keep the pressure in the reactor approximately constant at the level of about 105 kPa. This slight overpressure prevented contamination of the products by oxygen and moisture from the surrounding atmosphere during precipitation. In some experiments the gases leaving the reactor were caught in a cold finger cooled by liquid nitrogen.

The properties of the prepared powders were studied by X-ray diffraction analysis, thermal analysis, electron microscopy and IR spectroscopy. Exposure of the products to air atmosphere before analysis was minimized. Neutron activation analysis was used for determination of silicon and oxygen content and chemical analysis (Kjelldahl method) was used to determine the nitrogen content.

3 Results and Discussion

In preliminary experiments the potential for a SiH_4–N_2 mixture to form silicon nitride at 105 kPa between 600 and 1400°C was investigated. As shown in Table 1 the formation of elementary silicon prevailed at the total gas flow rate 400 cm^3 min^{-1} and the molar ratio $N_2/SiH_4 = 5{\cdot}51$. The content of nitrogen in the samples increased slightly with rising temperature of reaction but reached only

Table 1. Chemical composition of products precipitated from a silane–nitrogen mixture at a molar ratio $N_2/SiH_4 = 5{\cdot}51$ and a total gas flow rate 400 cm^3 min^{-1}

Product analysis	*Temperature (°C)*				
	600	*800*	*1 000*	*1 200*	*1 400*
N (mass%)	0·26	0·57	0·84	1·16	1·55
Si (mass%)	98·12	98·75	96·45	97·60	98·01
O (mass%)	2·08	1·72	1·92	2·12	1·86
Σ	100·46	101·04	99·21	100·88	101·42

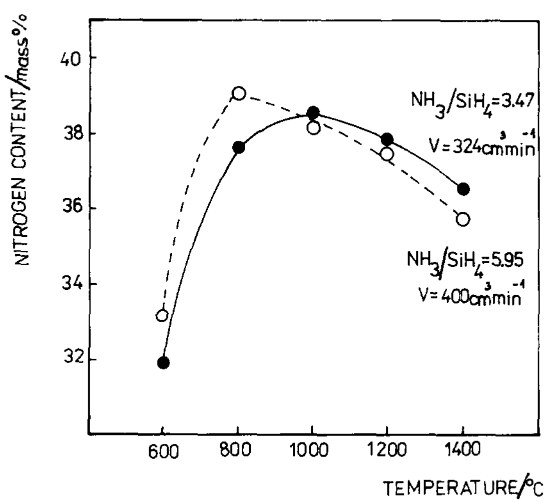

Fig. 4. Effect of the maximum reaction temperature on nitrogen content in precipitated products.

1·55 mass% at 1400°C. XRD analysis revealed silicon as the only crystalline phase in these products. Consequently, nitrogen approaches a role of an inert gas during silane ammonolysis in the SiH_4-NH_3-N_2 system.

In this study the following parameters affecting silicon nitride synthesis were studied:

(1) The maximum reaction temperature;
(2) The molar ratio of reactants SiH_4/NH_3;
(3) The total gas flow rate through the reactor.

From Fig. 4 it follows that the content of nitrogen in samples synthesized between 600 and 1000°C increased slightly. In IR spectra of the products prepared at 600°C (Fig. 5) a sharp intense absorption band at 2170 cm^{-1} was observed, which is characteristic for Si–H bonds.[6,27] Partial retention of Si–H bonds originating from silane leads to lowered nitrogen content values of low-temperature ammonolysis products. In the samples precipitated at 800°C and at higher temperatures the band at 2170 cm^{-1} was not observed and the nitrogen content approached Si_3N_4 stoichiometry. In some cases even hyperstoichiometry, i.e. values exceeding 40 mass% nitrogen, were found by chemical analysis. By heating these samples in Kjelldahl apparatus up to 200°C desorption of ammonia in an amount corresponding to nearly 1 mass% was observed.

A small decrease in the nitrogen content with increasing temperature in the interval from 800–1000°C to 1400°C is in agreement with presence of elementary silicon in these samples. Their colour varies with increasing reaction temperature from grey or light yellow through light brown to brown (see Tables 2 and 3). The colour of the products synthesized at 1400°C is nearly the same as that of silicon precipitated from the SiH_4–N_2 mixture in the preliminary experiments mentioned at the beginning of this section.

X-Ray phase analysis of the precipitates revealed partial crystallinity in the products synthesized at 1400°C. These contain 10 ± 5 mass% α-silicon nitride, while all those prepared at lower temperatures are amorphous from the viewpoint of X-ray diffraction. This observation is consistent with that of Prochazka & Greskovich,[6] who pointed out that

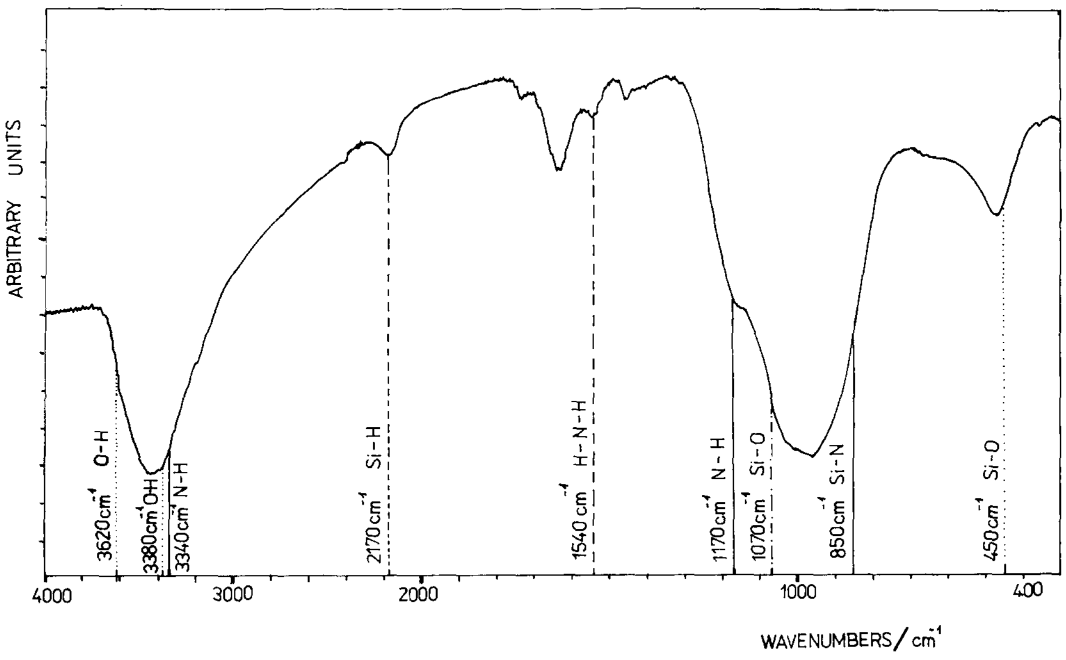

Fig. 5. IR spectra of the product synthesized at 600°C. Infrared peak assignments according to Brooks & Hess[27] and Prochazka & Greskovich.[6]

Table 2. Properties of products precipitated at constant ratios $NH_3/SiH_4 = 3{\cdot}45$ and $N_2/SiH_4 = 5{\cdot}51$ and a total gas flow rate 324 cm^3 min^{-1} at various reaction temperatures

Product characterization	*Temperature (°C)*				
	600	*800*	*1 000*	*1 200*	*1 400*
N (mass%)	31·94	37·58	38·51	37·80	36·53
Si (mass%)	63·68	61·20	58·86	59·19	62·42
O (mass%)	3·66	2·24	4·53	3·67	4·14
Σ	99·28	101·02	101·90	100·66	103·09
Colour	Yellow	Light yellow	Yellow–tan	Light tan	Tan

Table 3. Properties of products precipitated at constant molar ratios $NH_3/SiH_4 = 5{\cdot}95$ and $N_2/SiH_4 = 5{\cdot}51$ and a total gas flow rate 400 cm^3 min^{-1} at various reaction temperatures

Product characterization	*Temperature (°C)*				
	600	*800*	*1 000*	*1 200*	*1 400*
N (mass%)	33·15	39·41	38·13	37·04	33·53
Si (mass%)	63·91	59·22	61·29	59·83	65·05
O (mass%)	2·42	2·18	1·94	2·94	3·26
Σ	99·48	100·81	101·36	99·81	101·84
Colour	Light yellow	White	Cream–white	Light yellow	Light tan

amorphous silicon nitride powders containing elementary silicon crystallized between 1250 and 1350°C, while white powders without elementary silicon crystallized at 1480°C.

3.1 Effect of temperature

Experimental data on the effect of reaction temperature on properties of silicon nitride prepared are given in Tables 2 and 3.

From the material balance calculations of the synthetic process it follows that the yield, expressed as the number of moles Si in the solid product to that in the starting SiH_4, increases with the temperature of synthesis. This relation was not studied here in more detail, because of complicated evaluation of the amount of the precipitated product. Only a part of solid product (typically 40–60%) was collected on the filter, other varying amounts remained mainly on the colder walls of the reactor as a soft or a hard deposit. The gases leaving the reactor during experiments specified in Table 2 were condensed in a liquid nitrogen trap. Their analysis by means of mass spectrometry showed unreacted silane as the principal constituent besides ammonia.

Such a composition of the condensate was observed even at minimum total gas flow through the reactor, when the residence time of reacting gases within the hot zone is approximately 50 s. This indicates a departure from the equilibrium assemblage

$$Si_3N_{4(cryst.)} + N_2 + H_2$$

predicted by thermodynamic calculations.[28] Despite the fact that kinetic reasons cannot be excluded, more probably the different character of the solid products—a less stable amorphous silicon nitride compared to the crystalline phase assumed in calculations—is responsible for the partial conversion observed.

3.2 Effect of the ammonia/silane ratio

The effect of the molar ratio of the starting reactants on the formation of silicon nitride powder was studied at 800°C in the region $n(NH_3)/n(SiH_4)$ from 4/3 to 30. Total gas flow through the reactor was 400 cm^3 min^{-1} (see Table 4).

From Fig. 6 it follows that in samples prepared in

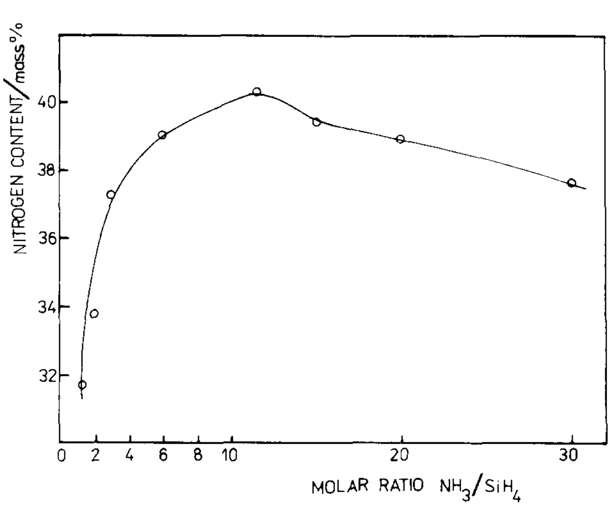

Fig. 6. Effect of the silane/ammonia molar ratio on nitrogen content in products precipitated at 800°C.

Table 4. Properties of products precipitated at a constant molar ratio N_2/SiH_4 = 5·51, total gas flow rate 400 cm^3 min^{-1} and temperature 800°C at various NH_3/SiH_4 molar ratios

Product characterization	*Molar ratio of NH_3/SiH_4*							
	4/3	*2*	*3*	*5·95*	*11·46*	*15*	*20*	*30*
N (mass%)	31·72	33·82	37·30	39·03	40·38	39·43	38·94	37·70
N (mass%) (200°C)	—	—	—	39·45	38·92	—	—	
Si (mass%)	65·96	65·37	59·82	59·68	58·07	57·75	56·41	58·28
O (mass%)	2·16	2·08	2·12	1·86	2·96	3·24	4·11	5·86
Σ	99·84	101·27	99·24	100·57	101·41	100·42	99·46	101·84
Colour	Cinnamon brown	Yellow–brown	Light yellow–brown	White	White	White	White	Light grey

Table 5. Properties of products precipitated at constant molar ratios NH_3/SiH_4 = 11·46 and N_2/SiH_4 = 5·51 and temperature 800°C at various total gas flow rate

Product characterization	*Total gas flow rate (cm^3 min^{-1})*				
	380	*285*	*190*	*95*	*47·5*
N (mass%)	40·38	39·45	38·96	39·48	36·18
Si (mass%)	57·60	59·84	57·74	60·22	62·88
O (mass%)	2·64	1·89	2·71	1·94	1·78
Σ	100·62	101·18	99·41	101·64	100·84
Colour	White	White	White	White	Light yellow

the interval from 4/3 to 11 the content of nitrogen increases from 31·7 to 40·3 mass%. Thus, a relatively high excess of ammonia is needed for the precipitation of nearly stoichiometric silicon nitride. Low molar ratio products are dark brown, indicating admixtures of elementary silicon. At higher ammonia/silane ratios, light cream or white products with an increased nitrogen content were precipitated.

A small decrease in the nitrogen content over the ratio ammonia/silane = 11·46 can be explained by an increased content of oxygen, most likely originating from traces of humidity which were not fully removed from the ammonia stream at relatively high flow rates through the drying columns.

The data in the present paper suggest that nearly pure silicon nitride powder without silicon admixture can also be precipitated at an ammonia/silane ratio tower than 10, but the reaction is not complete and gases after the reaction contain unreacted silane.

These results are somewhat distinct from those reported earlier by Prochazka & Greskovich[6] on the silane–ammonia–argon system. Quantitative conversion of silane to silicon nitride powder with a high nitrogen content was reported to occur only at an ammonia/silane ratio higher than 10.

3.3 Effect of total gas flow rate

Under an assumption of the piston flow the time of reactant contact at the synthesis temperature can be estimated from the total gas flow rate through the reactor. By its variation the effect of reaction time on properties of solid products can be indirectly estimated. This series of experiments made at a constant ammonia/silane molar ratio at 800°C showed little alteration of precipitate composition (Table 5, Fig. 7). Lowered nitrogen and increased silicon content in the sample precipitated at the minimum total gas flow rate used (47·5 cm^3 min^{-1}) was probably caused by erroneous metering of ammonia gas by the mass flow meter working at its limit of proportionality.

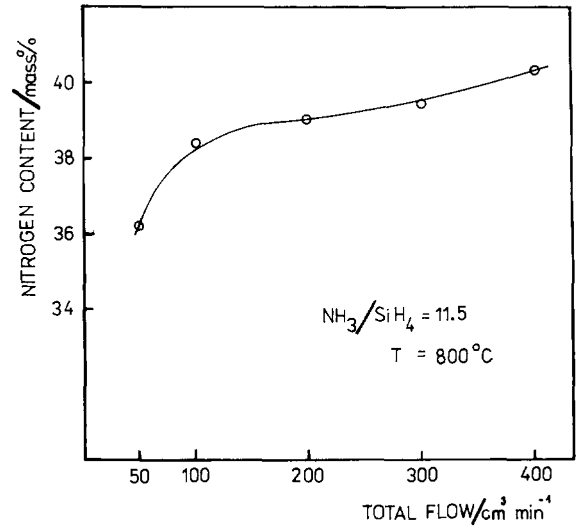

Fig. 7. Effect of the total gas flow rate on nitrogen content in products.

3.4 Effect of temperature on particle size and morphology

Silicon nitride powders synthesized at 800 and 1400°C (Table 2) are compared in Fig. 8. The powder synthesized at 800°C consists of primary particles with a size ranging from 0·05 to 0·2 μm. Non-aggregated discrete isometric particles as well as chain-like aggregates were observed. On the other hand, the particle size in the powder synthesized at 1400°C does not exceed 0·1 μm (Fig. 8(b)). This indicates relatively complicated relations among the nucleation rate, the growth rate and the temperature, or a mechanism involving decomposition of the larger particles formed at lower temperature, as suggested by Kato *et al.*[21]

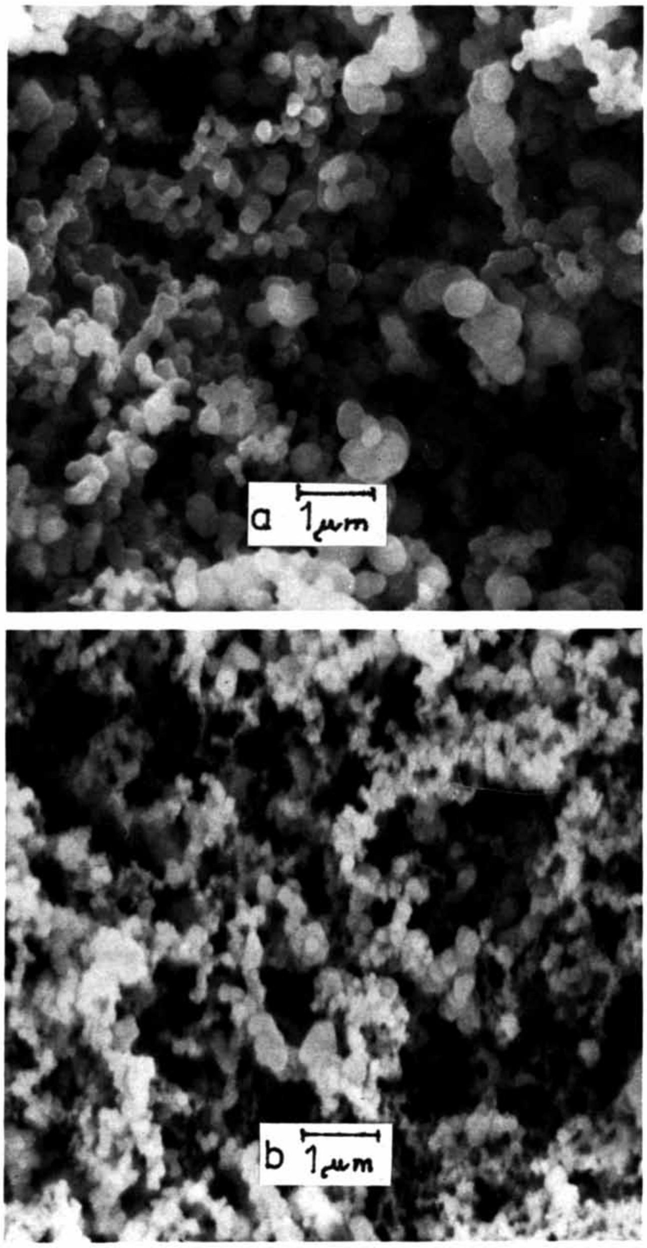

Fig. 8. SEM of powders synthesized at (a) 800°C and (b) 1400°C (see Table 2).

4 Conclusions

Amorphous silicon nitride powders consisting of isometric particles up to 0·2 μm in size were prepared by precipitation from silane–ammonia–nitrogen gas mixtures heated to 800–1300°C. White precipitates with a slight hyperstoichiometry (with a nitrogen content over 39·9 mass%) were filtered from the mist at an ammonia/silane ratio from 8 to 12 between 800 and 1000°C. By treatment at 200°C a desorption of ammonia was observed and the nitrogen content of the powder was found to decrease by about 1 mass%.

Powders prepared at 1400°C consisted of particles with a size of approximately 0·1 μm and were partially crystalline, containing about 10 mass% of α-silicon nitride.

An analysis of gases leaving the reactor showed the presence of silane within a whole interval of ammonia/silane ratios and total gas flow rates studied, which indicates that full silane to silicon nitride conversion was never achieved.

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