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Preparation of Fine Amorphous Silicon Nitride Powder in the System SiH_4–Ar–NH_3

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Abstract

Amorphous silicon nitride powders have been prepared in a tube reactor in the system silane–argon–ammonia in the temperature range 500–1100°C. The powders prepared at 500°C show the presence of elementary silicon. The powders prepared above 650°C are near stoichiometric in composition, isometric in morphology and the particle size distribution is in the range of 0·05–0·2 μm. The powders prepared at 1100°C are nearly monodispersive, having the particle size 0·1 μm. The influence of molar ratio of ammonia to silane shows that silicon nitride powder of near stoichiometric composition can be prepared above 11·62 and below this ratio the powders contain elementary silicon. The change in total gas flow rate shows that below 300 cm^3 min^{-1} the powders again contain elementary silicon and with further increase in flow rate the powders are near stoichiometric at 400 cm^3 min^{-1} and little hyperstoichiometric in nitrogen content at and above the flow rate of 500 cm^3 min^{-1}. Surface characterization by X-ray photoelectron spectroscopy indicates that most of the oxygen is confined on the surface and is present in the form of SiO_2.

1 Introduction

Silicon nitride based ceramics are well recognized as the material of the next generation, suitable for high temperature structural applications. Although there is a fast development in achieving superior high temperature mechanical properties, bending strength up to 950 MPa and fracture toughness 7·5 $MPa.m^{1/2}$,[1] however there are still opportunities left to improve these properties. It is commonly accepted that to prepare good quality ceramics the powder should have the following properties: low cationic impurity (< 2 wt%), low oxygen (< 2 wt%), > 95 wt% α phase content and average particle size in the range of 1 μm and close to monodispersive. Generally silicon nitride powders are prepared in four different ways: 1. nitriding of powdered silicon by nitrogen or ammonia; 2. silicon diimide, $Si(NH)_2$ decomposition; 3. carbothermal reduction and nitridation of silica; 4. gas phase reaction of silane or its halogen derivatives with nitrogen or ammonia.[2] Besides the described methods which are used in an industrial scale, there are several other synthesis methods which are under development at present, e.g. plasma synthesis, laser induced reaction etc.. The impurity contents are inherent to the method of preparation. The last mentioned method is usually applied in the deposition of thin coatings by chemical vapor deposition. Nevertheless, recently a lot of attention has been paid to prepare high quality silicon nitride powders from the gas phase reaction route.[3–8] There are three different ways in which the gas phase reactions are carried out: 1. laser induced reaction; 2. R.F. plasma synthesis;[5–8] 3. electrically heated reaction tube.[4] Each system has its own advantages and disadvantages. However, the powders prepared by the last technique are submicron and isometric. Addition of 20 wt% of this amorphous powder to the commercial powder (H. C. Stark, LC12 S) leads to the homogeneous nucleation of β-Si_3N_4, resulting in fine microstructure and improved mechanical property of sintered body.[9,10] The various gas phase systems in the deposition of thin coatings by chemical vapor deposition for application in electronics are: $SiCl_4$–NH_3, SiH_4–NH_3, $SiCl_4$–N_2–H_2, SiF_4–NH_3, SiH_2Cl_2–NH_3, $SiBr_4$–NH_3. But recently some work has been carried out to prepare ultra-fine nitride powders in the system SiH_4–N_2–NH_3[4] and SiH_4–Ar–NH_3.[3]

The main aim of the present work is to study extensively the influence of different parameters

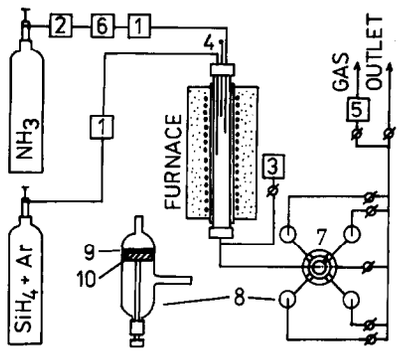

Fig. 1. Experimental set-up for the synthesis of silicon nitride from a silane–argon–ammonia gas mixture: 1. mass flow meter; 2. drying column (KOH); 3. manometer; 4. thermocouple; 5. rotary vacuum pump; 6. drying column (Na); 7. sample collector–distributor; 8. sample collecting chamber; 9. glass frit; 10. powder stripper.

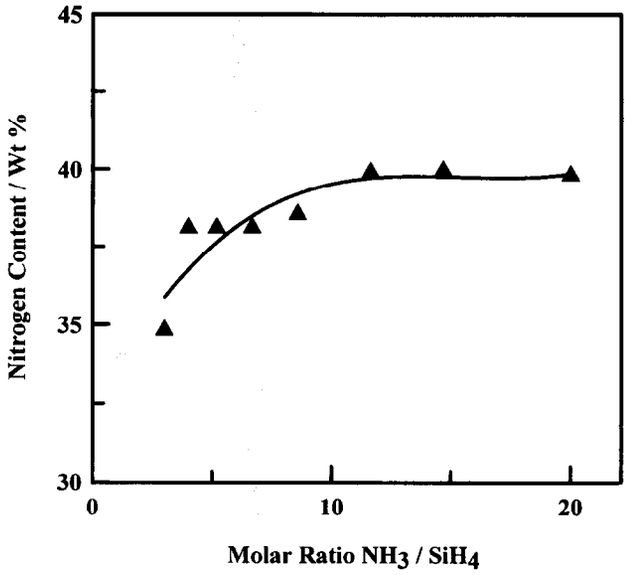

Fig. 2. The change of nitrogen content of powders against ammonia/silane molar ratio prepared at 650°C.

such as temperature, ratio of NH_3 to SiH_4, flow rate of the total gas and influence of the carrier gas Ar with respect to N_2 on the particle size, morphology and the quality of the product in the system SiH_4–Ar–NH_3.

2 Experimental

Ammonia gas of technical purity (99·5%), electronic grade silane (15 wt% in argon) and argon (purity 99·5%) were used for the experiment. The details of the experimental set up of the hot wall reactor is described in an earlier publication.[4] The reactor dimensions are as follows: internal diameter = 46 mm and length = 500 mm. There was a little modification made in the sample collector to improve the collection efficiency and avoid choking of the glass frit. In the present experiments a new multiple sample collector was designed with the mechanical scrubber and rotary valve to get multiple number of samples synthesized in different conditions in one run. The schematic description of the apparatus is given in Fig. 1. The first set of experiments were carried out by varying the mole ratio of NH_3 to SiH_4 (r) in the range of 3–20 keeping the total flow of gas across the reactor at 400 cm^3 min^{-1} and temperature of reaction at 650°C. In the second set of experiments the total gas flow varied in the range of 200–600 cm^3 min^{-1} simultaneously maintaining the ratio of NH_3 to SiH_4 at 11·62 and reaction temperature at 650°C. In the third set of experiments r was constant at 11·62 and the total flow of gas increased from 400–1000 cm^3 min^{-1} by the introduction of argon stepwise and keeping the reaction temperature at 650°C. The last set of experiments were carried out in the temperature range between 500–1100°C at fixed ratio of NH_3 to SiH_4 at 11·62. In all the experiments the pressure of the reactor was kept at 110 kPa.

The properties of the powders were studied by XRD analysis, SEM, FTIR spectroscopy. The elemental analysis of silicon was done by neutron activation analysis, oxygen by LECO TC-136 and nitrogen by titrimetric method (Kjelldahl method). The surface composition of the powders were analyzed by XPS.[11]

3 Results and Discussion

In the earlier study,[4] it was revealed that in the system SiH_4–N_2–NH_3, nitrogen acts merely as a carrier gas, since in the system SiH_4–N_2 on Si_3N_4 formation was observed up to 1400°C. The molar ratio of NH_3 to SiH_4 of about 11, temperature at 650°C and total gas flow rate of 400 cm^3 min^{-1}

Table 1. Chemical composition of the products prepared at various mole ratios NH_3/SiH_4 at a constant temperature of 650°C and a flow rate of 400 cm^3 min^{-1}

r	*3*	*4*	*5·18*	*6·66*	*8·57*	*11·62*	*14·66*	*20*
N (wt%)	34·81	38·09	38·06	38·0	38·53	39·89	39·95	39·88
O (wt%)	1·31	1·51	1·47	2·44	1·19	1·43	2·23	6·91
Si (wt%)	65·13	58·92	59·57	59·53	59·43	59·39	60·13	51·88
Σ	101·1	98·52	99·1	99·97	99·15	100·71	102·3	98·67
Colour	Brown	Light brown	Light brown	White	White	White	White	White

were suggested as the optimum conditions for the production of amorphous silicon nitride powder of near stoichiometric composition in the system SiH_4–N_2–NH_3. On the basis of these results the conditions for the present experiments were chosen.

3.1 Influence of NH_3/SiH_4 ratio, (r)

The effect of the molar ratio of ammonia to silane was studied in the range from 3–20 at a constant temperature of 650°C and total flow rate of gases at 400 cm^3 min^{-1} across the reactor. The characteristics of the products are given in Table 1.

From the nitrogen content analysis it is observed that at lower r value the nitrogen content is below the stoichiometric composition (39·96 wt% of N_2) of silicon nitride. When the r value is 11·62 and above, the products contain the stoichiometric amount of nitrogen. The trend in nitrogen content with the change in molar ratio is plotted in Fig. 2. It can be seen that for the synthesis of nearly stoichiometric silicon nitride powder a relatively excess amount of ammonia is required. Low molar ratio products are brown to light brown in colour indicating the presence of elementary silicon. As the r value is increased to 11·62 and above, the products are white and near stoichiometric in composition. However, when a high excess amount of ammonia is present, the product is a little hyperstoichiometric in nitrogen content. In the present experiments, no decrease in the nitrogen content was observed by increasing the molar ratio (r) above 11, which was distinctly observed in the previous work in the system SiH_4–N_2–NH_3.[4] The present result is in agreement with the earlier results:[3,4] that near stoichiometric silicon nitride can be prepared at a molar ratio of ammonia to silane 11. SEM studies of the powders show that powders prepared at a lower molar ratio (r), i.e. 3 and 4, are agglomerated. The particles have a tendency to agglomerate and form necks and rings.

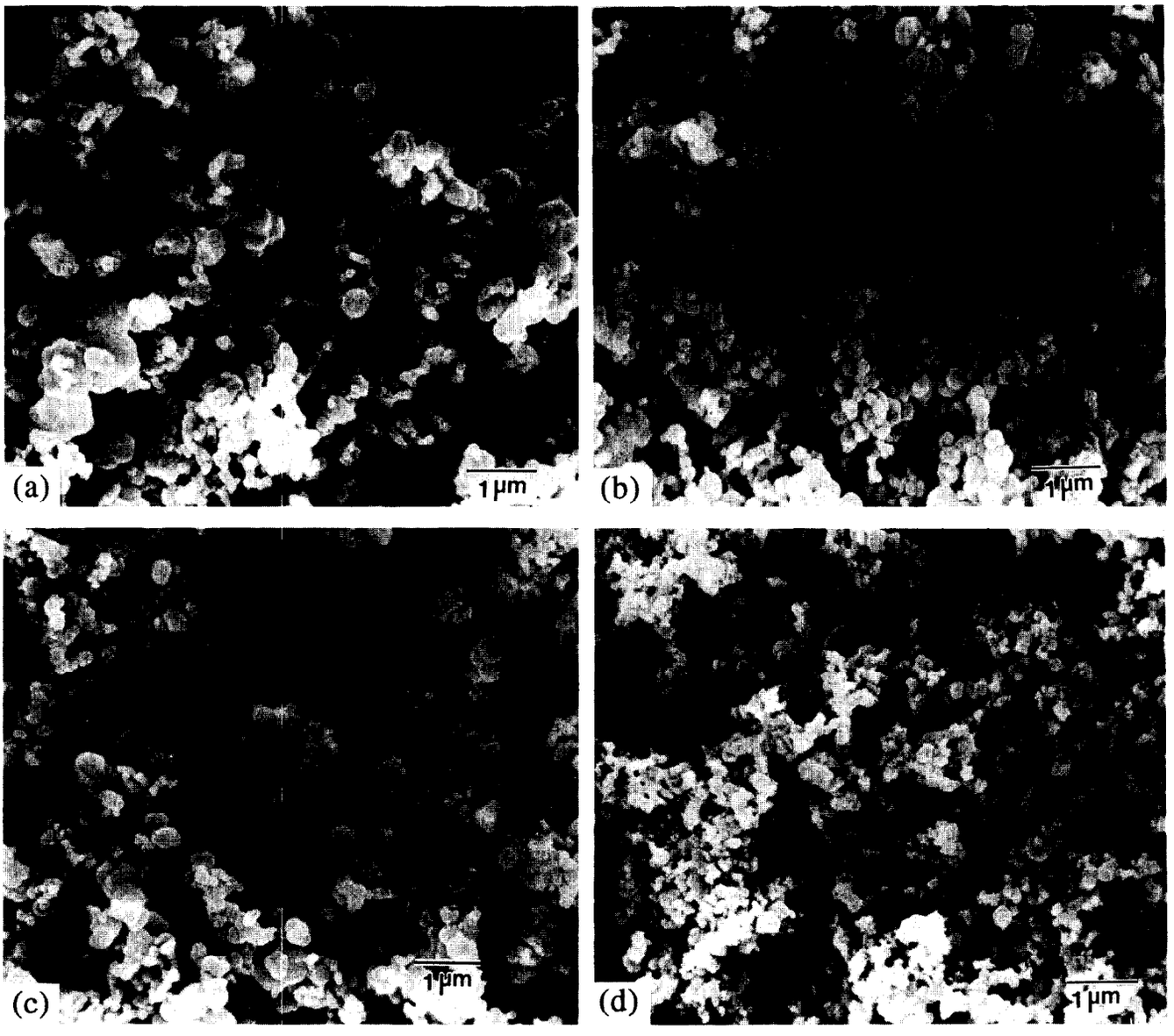

Fig. 3. SEM photographs of powders: (a) prepared at 650°C, total gas flow rate 400 cm^3 min^{-1} and ammonia/silane ratio = 11·62; (b) at 650°C, total gas flow rate 400 cm^3 min^{-1} and ammonia/silane = 20; (c) at 650°C, total gas flow rate 600 cm^3 min^{-1} and ammonia/silane ratio = 11·62; (d) at 1100°C, total gas flow rate 400 cm^3 min^{-1} and ammonia/silane ratio = 11·62.

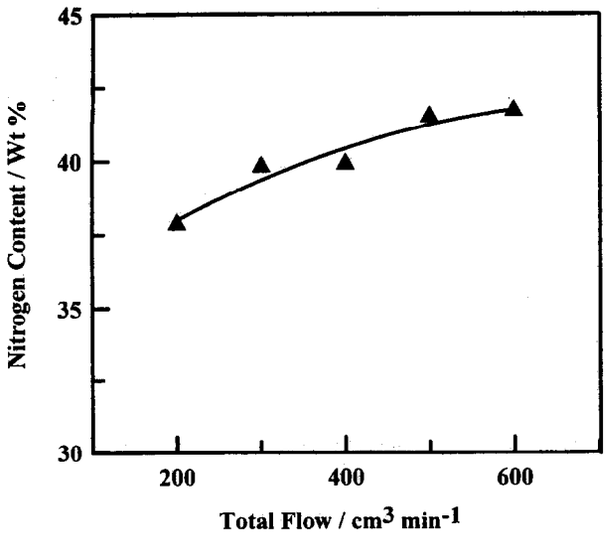

Fig. 4. The change of nitrogen content against total gas flow rate at 650°C and ammonia/silane = 11·62.

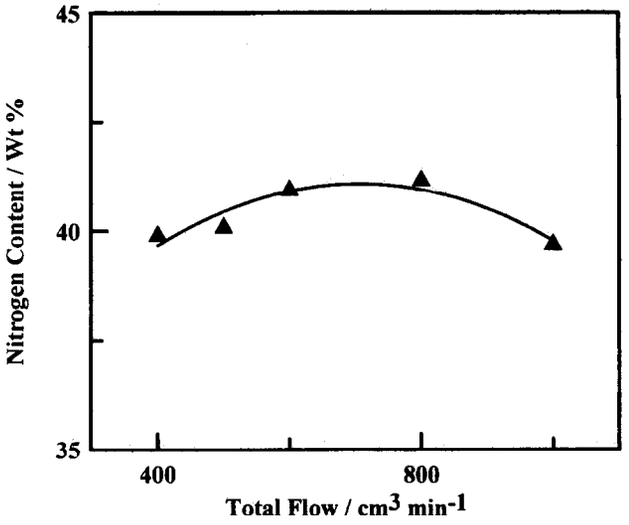

Fig. 5. The change of nitrogen content against total gas flow rate by the addition of argon to 400 cm^3 min^{-1} of the original gas mixture at 650°C and ammonia/silane ratio = 11·62.

At molar ratio of 5·18 and 6·66 the products are less agglomerated. At a further increase of molar ratio, the size of particles are in the range of 0·05–0·2 μm and practically without agglomeration. An SEM photograph of a product at molar ratio 11·62 is shown in Fig. 3(a). There is no large change in the particle size and morphology with further change in the molar ratio up to 20, which can be observed from Fig. 3(b).

Considering the stoichiometry in composition and quality of the product the powder prepared at r = 11·62, seems to be the optimum. So these synthesis conditions have been adopted as the basis for the next experiments.

3.2 Influence of total gas flow rate

In order to investigate the effect of the total flow rate of gases across the reactor, the temperature and molar ratio of ammonia to silane (r) were kept constant at 650°C and 11·62 respectively and the total flow rate, i.e. NH_3 (g) + SiH_4 (g) was varied from 200–600 cm^3 min^{-1}. The characteristics of the powders are presented in Table 2. The nitrogen content is plotted against the flow rate in Fig. 4. Increase of the flow rate above 300 cm^3 min^{-1} increased the nitrogen content gradually above the stoichiometric composition. When the total flow rate is 200 cm^3 min^{-1}, the nitrogen content is well below the stoichiometry. In this case the elementary silicon was increased and the colour of the product was light brown. This indicates that at a lower total gas flow, the rate of formation of elementary silicon is promoted. On the other hand, its recombination with ammonia leading to the formation of silicon nitride is limited at lower temperatures.

SEM observation shows, Fig. 3(c), that a finer product was obtained at a higher flow rate of 600 cm^3 min^{-1} (compare Fig. 3(a) and (c)). This fact is also confirmed by the specific surface area measurement by BET: the product prepared at 400 cm^3 min^{-1}, shown in Fig. 3(a) has a specific surface area of 12 m^2 g^{-1} whilst the product prepared at 600 cm^3 min^{-1}, shown in Fig. 3(c) has a specific area of 14 m^2 g^{-1}. The particle size distribution of this finer product is narrow and varies in the range from 0·05 to 0·2 μm.

In another series of experiments, the total gas flow rate has been increased by the addition of argon stepwise to the original total flow of gas 400 cm^3 min^{-1} of NH_3(g) + SiH_4(g) + Ar(g) to 1000 cm^3 min^{-1} keeping temperature at 650°C and the molar ratio of ammonia to silane at 11·62.

Table 2. Chemical composition of the products at various total gas flow rates and at constant molar ratio of NH_3/SiH_4 = 11.62, T = 650°C

Total gas flow rate (cm^3 min^{-1})	*200*	*300*	*400*	*500*	*600*
N (wt%)	37·85	39·80	39·89	41·49	41·70
O (wt%)	7·57	2·08	1·43	3·03	3·85
Si (wt%)	52·87	56·75	59·39	52·85	51·20
Σ	98·29	98·63	100·71	97·37	96·75
Colour	Light brown	White	White	White	White

Table 3. Chemical composition of products at various total gas flow rate of carrier gas (Ar) and constant molar ratio of NH_3/SiH_4 = 11·62, T = 650°C (The total gas flow rate was changed by the addition of argon to the original total flow of 400 cm^3 min^{-1})

Total gas flow rate (cm^3 min^{-1})	*400*	*500*	*600*	*800*	*1000*
N (wt%)	39·89	40·07	40·93	41·15	39·69
O (wt%)	1·43	2·34	1·98	2·25	1·60
Si (wt%)	59·39	57·31	57·96	56·60	60·39
Σ	100·7	99·72	100·8	100	101·7
Colour	White	White	White	White	White

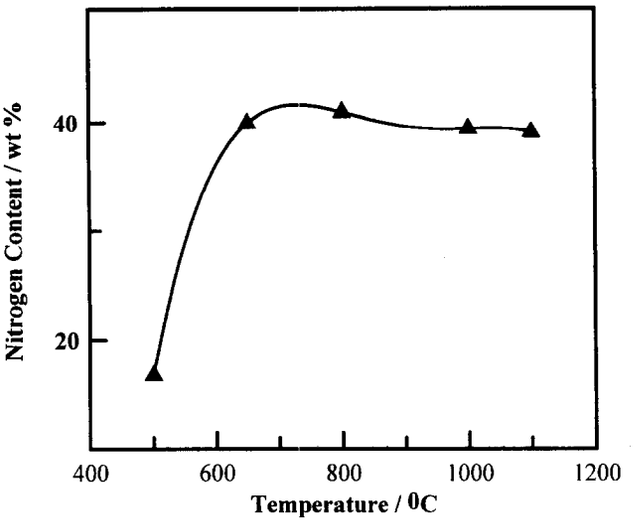

Fig. 6. The change of nitrogen content against temperature of synthesis at total gas flow rate 400 cm^3 min^{-1} and ammonia/silane = 11·62.

The chemical composition of the products are given in the Table 3, and the change of nitrogen content with respect to the total flow rate is shown in Fig. 5. From these results, it is obvious that with an increase in the flow rate there is a slight tendency to increase the nitrogen content up to 800 cm^3 min^{-1}.

3.3 Influence of temperature

For this series of experiments, the total gas flow rate was kept at 400 cm^3 min^{-1} and the mole ratio of ammonia to silane at 11·62. The chemical composition and characteristics of the products prepared in the temperature range between 500 and 1100°C are given in Table 4 and the dependence of nitrogen content on the temperature is shown in Fig. 6. From Table 4 and Fig. 6 it is clear that silicon nitride of near stoichiometric composition can be prepared at and above 650°C. At 500°C the product contains only 16·79 wt% of nitrogen and a proportionately higher amount of silicon. It seems that 650°C is the critical temperature for the formation of silicon nitride in this system. Below this temperature there is a tendency of the formation of elementary silicon. From the thermodynamic analysis (Table 5), it is obvious that the enthalpy of reaction 1 is negative, that means silicon nitride should have formed at this temperature without elementary silicon. The fact that elementary silicon is present in the product at 500°C is due to kinetic reasons. At this temperature, the decomposition rate of silane is higher than the recombination of elementary silicon to silicon nitride.

Table 5. Thermodynamic data of the different reactions

Reactions	ΔG *at 700 K* *kcal/mol*	ΔG *at 900 K* *kcal/mol*
1. 3 SiH_4 + 4 NH_3 → Si_3N_4 + 12 H_2	−212·65	−232·90
2. SiH_4 → Si + 2 H_2	−21·29	−25·97
3. 3 Si + 4 NH_3 → Si_3N_4 + 6 H_2	−148·78	−154·98

Table 6. Surface chemical composition of powders as determined by XPS (in at%)

Total gas flow rate (cm^3 min^{-1})	*Si*	*N*	*O*	*C*	*N/Si*	*O/Si*
200	28·42	24·87	38·47	8·24	0·88	1·40
300	27·44	28·69	33·13	10·74	1·05	1·20
400	28·45	26·21	38·79	6·55	0·92	1·36
500	28·39	26·60	36·48	8·52	0·94	1·28
600	28·09	24·50	39·70	7·71	0·87	1·41

The product prepared at 650°C is not agglomerated and the particles are isometric with the size from 0·05 to 0·2 μm, Fig. 3(a). On the other hand with an increase of the reaction temperature, the refinement of the product was observed. At 1100°C, superfine almost monodispersive isometric powder was prepared with the particle size ranging from 0·05 to 0·1 μm, Fig. 3(d)

The formation of finer powders at higher temperatures is most probably due to the creation of more nucleation centers. The powders are still mainly amorphous at 1100°C with partial crystallization, at about 5–10%.

4 XPS studies

According to the wide scan spectra registered for the samples prepared at 650°C r = 11·62 and with varying total gas flow rates from 200 to 600 cm^3 min^{-1}, Si, N, O and C could be detected on the surface (The characteristics of the powders are presented in Table 2). As an example the wide scan spectra of samples prepared at 400 cm^3 min^{-1} is presented in Fig. 7. The surface chemical composition and the N/Si and O/Si atomic ratios were calculated from the relevant wide scan spectra and

Table 4. Chemical composition of the products prepared at a constant molar ratio NH_3/SiH_4 of 11·62 and total gas flow rate of 400 cm^3 min^{-1} at various reaction temperatures

Temperature (°C)	*500*	*650*	*800*	*1000*	*1100*
N (wt%)	16·79	39·89	40·90	39·36	39·04
O (wt%)	2·13	1·43	1·83	1·41	1·22
Si (wt%)	80·50	59·39	58·58	59·49	59·30
Σ	99·5	100·71	101·31	100·26	99·56
Colour	Brown	White	White	White	Light tan

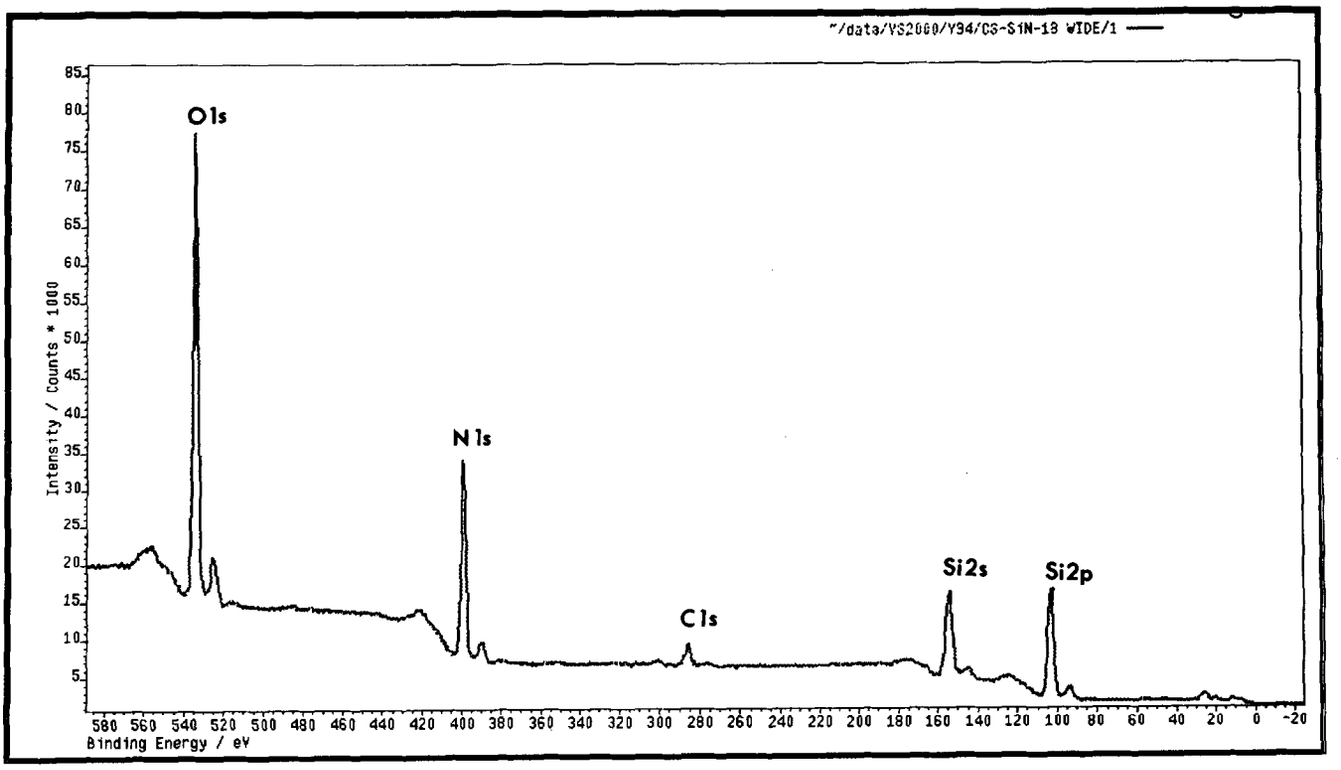

Fig. 7. Wide scan XPS spectrum of the powder prepared at 650°C, total gas flow rate 400 cm^3 min^{-1} and ammonia/silane ratio = 11·62.

summerized in Table 6. It is evident that all samples are characterized by a high surface oxygen content. In addition the tendencies in the changes of the bulk and surface compositions against the total flow rate of gases are similar (see Tables 2 and 6).

Deconvolution of the Si 2*p* peak (Fig. 8) refers to the simultaneous presence of Si–N and Si–O bonds. So most of the oxygen on the surface is present in the form of SiO_2.

5 Conclusions

Effects of the NH_3/SiH_4 molar ratio, total gas flow rate and reaction temperature on the properties of

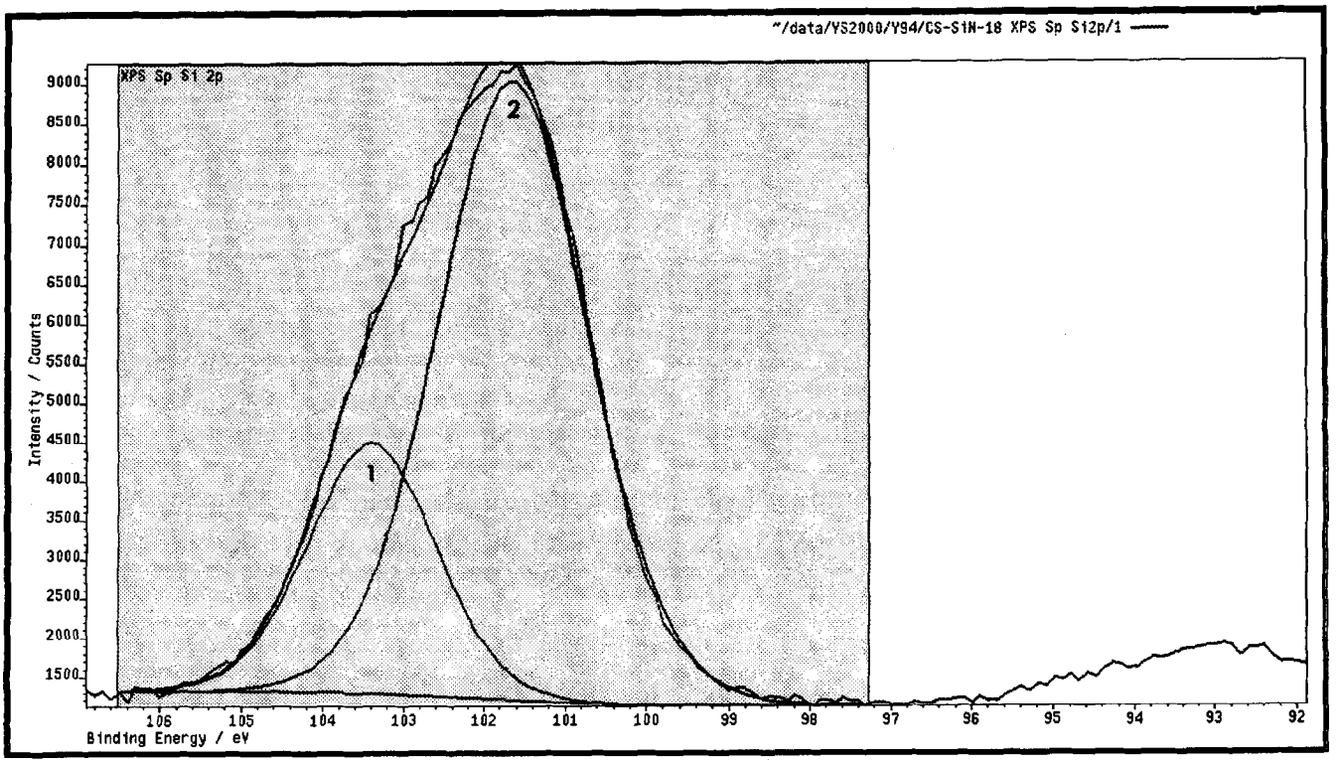

Fig. 8. Deconvolution of Si 2*p* peak; peak 1 corresponds to Si–O; peak 2 to Si–N bonds.

Si_3N_4 powders prepared in the system SiH_4–NH_3–Ar in a tube reactor have been investigated. It was found that for the formation of a stoichiometric silicon nitride powder, the NH_3/SiH_4 molar ratio should be kept at about 11. The total gas flow rate above 400 cm^3 min^{-1} creates more finer fractions of the powder without changing the morphology of the particles. However, powders of hyperstoichiometric in nitrogen content are being formed at higher flow rates. The temperature of synthesis has a substantial influence both on the nitrogen content as well as the mean particle size of the products. The optimum conditions for the preparation of nanosized, isometric, mainly amorphous silicon nitride powders in the given system are: NH_3/SiH_4 molar ratio = 11·62, total flow rate = 400 cm^3 min^{-1}, temperature 650°C.

Acknowledgements

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