

# Atmospheric ageing of nanosized silicon nitride powders

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Ambient oxidation of nanosized silicon nitride powder produced by the vapour phase reaction of silicon tetrachloride and ammonia has been studied in this work. Aliquots of the powder were stored in argon gas, in dry air and in air of 80% humidity, and changes in the bulk and surface properties were investigated against the ageing time. The powder samples were characterised by wet chemical analysis, XPS, TG-MS, FTIR, XRD and TEM methods. No significant changes were detected on storage in argon gas for 90 days. However, in samples stored in dry air and humid air, remarkable oxidation and formation of N–H species were found. The particulate powder tends to agglomerate in both dry and humid air, and this results in changes in the particle size and morphology. The nanosized silicon nitride powders therefore should be processed by excluding their contact with the oxygen and moisture containing ambient atmosphere.

## Introduction

Silicon nitride powders produced in high temperature thermal plasmas by the vapour phase reaction of silicon tetrachloride and ammonia have many interesting properties including high purity, mainly amorphous microstructure and a mean particle size in the nanometer range.<sup>1,2</sup> No hard agglomerates are formed in these powders. They are characterised by high chemical reactivity and sintering activity. Thus, these powders are favourable precursors of advanced silicon nitride ceramics with good mechanical properties.<sup>3</sup>

Studies on the sintering of silicon nitride powders to dense ceramic bodies have shown the importance of surface composition: the nature and amount of sintering aids depended on the surface oxygen content of the powders.<sup>3,4</sup> A surface oxygen layer is known to be present in all silicon nitride powders. The vapour phase synthesis results in nanosized, amorphous silicon nitride powders with a high specific surface area and, therefore, relatively high oxygen content. These powders are susceptible to further oxidation when contacted with oxygen and moisture on storage and processing.

Danforth *et al.*<sup>5</sup> detected a remarkable increase of the surface oxygen content during the ambient oxidation of laser synthesized, very fine silicon nitride powders. Oxidation was attributed to the adsorption of water from the air by the surface amino (N–H) groups. Similar results were published by Li *et al.*<sup>6</sup> on the basis of diffuse reflectance infrared Fourier transform (DRIFT) spectra. The higher the surface N–H concentration of silicon nitride powder, the more extensive was the oxidation observed. They established a rather complex surface structure for the laser synthesized silicon nitride powders subjected to atmospheric ageing, including amino, hydroxy and silanol groups, adsorbed CO<sub>2</sub> and a complex surface compound consisting of Si, N, C and H. To avoid oxidation Li *et al.*<sup>6</sup> proposed the removal of surface amino groups, *e.g.* by annealing.

Up to now no systematic study has been published on the ambient oxidation of silicon nitride powders synthesized in thermal plasmas. The aim of this paper is to report a study on the ageing behaviour of particulate powders during storage under different contacting atmospheric conditions. Special

emphasis has been placed on the surface chemical properties and microstructure.

## Experimental

The silicon nitride powder studied in this work was produced by the vapour phase reaction of SiCl<sub>4</sub> and NH<sub>3</sub> in a RF thermal plasma reactor under conditions given previously.<sup>1</sup> To remove the NH<sub>4</sub>Cl by-product formed due to the excess of NH<sub>3</sub> in the plasma synthesis, the as-synthesized powder was treated in argon gas at 400 °C for 1 h. The resulting powder was predominantly amorphous with a crystalline phase content of about 20%, as was determined by FTIR and XRD investigations.<sup>3</sup>

Behaviour of the particulate powder on atmospheric ageing was studied by storing aliquots (≈2 g each) in a dry argon atmosphere, in dry air, and in air of 80% relative humidity for different periods of time (3–540 days). Changes in the bulk and surface chemical compositions and microstructure were investigated against the ageing time.

The bulk nitrogen content was determined by wet chemical analysis, while the oxygen content was measured by the gas extraction method (LECO TC-436).

The surface chemical composition was analysed using a KRATOS XSAM 800 X-ray photoelectron spectrometer in fixed retarding ratio mode (FRR=20) using MgK<sub>α1,2</sub> (1253.6 eV) excitation. The MultiQuant<sup>7</sup> program was used for the quantification of the XPS spectra and to calculate the layer thickness. The thickness of the surface SiO<sub>2</sub> layer was calculated from the O 1s line intensity by assuming that the sample consists of uniform spheres of 40 nm diameter.

The thermal behaviour of silicon nitride powders was studied by a computer controlled TG-MS system consisting of a Perkin-Elmer TGS-2 thermobalance and a Hiden-Hall 2/301 mass spectrometer. Samples of 2–4 mg were heated in an argon carrier gas at 20 °C min<sup>-1</sup> up to 500 °C. A portion of the volatile products was introduced into the ion source of the mass spectrometer. The MS intensities of selected ions were monitored and normalised by reference to the intensity of <sup>38</sup>Ar.

The FTIR spectra were recorded using a Perkin-Elmer 1710

instrument using a DTGS detector, a Perkin-Elmer DRIFT accessory and microsampling. The silicon nitride powders were measured in KBr-diluted form at 4% concentration. The as-formed nitride specimens were mixed with ground KBr. Spectroscopic grade KBr was used as the reference material. The spectra were recorded from 4400 to 400  $\text{cm}^{-1}$  by averaging 200 scans at 4  $\text{cm}^{-1}$  resolution.

The crystalline phases were identified by X-ray diffraction (XRD) using a Guinier–Hagg focusing camera and  $\text{CuK}\alpha_1$  radiation. The relative amounts of  $\alpha$ - and  $\beta$ - $\text{Si}_3\text{N}_4$  phases were determined from the XRD patterns using the Gazzara and Messier method.<sup>8</sup> The  $\alpha$ - $\text{Si}_3\text{N}_4/\beta$ - $\text{Si}_3\text{N}_4$  ratio was calculated from the averaged intensities using the formula proposed by Camuscu *et al.*<sup>9</sup>

Morphological changes due to ageing were studied by transmission electron microscopy (TEM, TESLA BS540).

## Results and discussion

The bulk and surface compositions of silicon nitride samples subjected to ageing are summarised in Table 1. The starting powder (SN-0) is characterised by nearly theoretical bulk nitrogen content and rather high oxygen content. Our previous investigations revealed that about 95% of the total oxygen content of particulate silicon nitride powder was concentrated near to the surface of particles<sup>3</sup> which indicated post-synthesis oxidation in the thermal plasma reactor.

In fact, neither the bulk nor the surface composition changed on storage of SN-0 in argon gas for 90 days (Table 1: SN-90 Ar).

However, for samples stored in dry air the oxygen content increased considerably against the time (Table 1: SN-3 DA to SN-540 DA). It is remarkable that the surface chemical composition changed to a greater extent than the bulk composition. In 540 days the bulk oxygen content rose by a factor of 2.2, while the surface oxygen content increased by a factor of 2.9, the latter indicating favoured oxidation of the uppermost surface layer.

The Cl 2p peak in the XPS spectra is centred at 199.0 eV which corresponds to chlorine in Si–Cl bonds, residual from the  $\text{SiCl}_4$  reactant. The oxidation was coupled to a decrease in surface chlorine content. Some traces of water vapour are to be found in the dry air also. Thus, formation of HCl and/or  $\text{NH}_4\text{Cl}$  is very probable on the surface of particles. These compounds are volatilised partly during the ageing process, partly under the conditions of the XPS analysis.

There is always an outermost hydrocarbon-type layer on the surface of samples studied by XPS. In the silicon nitride powders studied in this work the thickness of the surface hydrocarbon layer was about 200 pm, and it hardly changed with the ageing time. This carbon layer is the consequence of

unavoidable contamination during manipulation of powders, because the UHV base pressure in the analysis chamber was lower than  $1 \times 10^{-10}$  MPa. There was a surface oxide ( $\text{SiO}_2$ ) layer below the hydrocarbon layer, and its thickness increased on ageing. The original  $\text{SiO}_2$  layer thickness of 300 pm corresponded to about one monolayer of  $\text{SiO}_2$  with a  $\text{SiO}_4$  tetrahedron size of 265 pm. This increased by a factor of 3.6 on storage in dry air for 540 days (Table 2).

Similar trends were observed for samples stored in air of 80% humidity (Tables 1 and 2: SN-3 HA to SN-540 HA). However, the relevant changes were more significant in the latter case. In 540 days the bulk oxygen content increased by a factor of 6.5 while the increase in surface oxygen content was 5.7. These values and the more than thirteen-fold growth of the thickness of the surface  $\text{SiO}_2$  layer (Table 2) indicate that oxidation in humid air is not restricted to the uppermost surface layer, but it extends to the bulk as well. For samples SN-90 HA and SN-540 HA the actual values of layer thickness should be regarded as indicative only, due to the limitation of the model used for the calculations. However, they properly reflect the trends of changes.

The decrease of chlorine content was more extensive in humid air as compared to that in dry air. Adsorption of water vapour on the surface of silicon nitride grains clearly enhanced the formation of  $\text{NH}_4\text{Cl}$ .

Plotting  $\text{SiO}_2$  layer thickness against ageing time (Fig. 1) suggests different stages of surface oxidation depending on the particle size of the silicon nitride grains. Previous XRD investigations revealed that the starting powder of this work (SN-0) consisted of  $\approx 80\%$  amorphous material and  $\approx 20\%$  crystalline phase, mostly  $\alpha$ - $\text{Si}_3\text{N}_4$ .<sup>3,10</sup> On the basis of BET measurements the average grain size of the amorphous fraction was 35 nm, while that of crystalline particles was 75 nm as calculated from the X-ray line profile analysis.<sup>10</sup> Thus, the form

**Table 2** Thickness of surface  $\text{SiO}_2$  layer

Powder	$\text{SiO}_2$ layer thickness/pm
SN-0 <sup>a</sup>	300
SN-90 Ar <sup>b</sup>	300
SN-3 DA <sup>c</sup>	350
SN-7 DA <sup>c</sup>	450
SN-30 DA <sup>c</sup>	560
SN-90 DA <sup>c</sup>	590
SN-540 DA <sup>c</sup>	1090
SN-3 HA <sup>d</sup>	1040
SN-7 HA <sup>d</sup>	1130
SN-30 HA <sup>d</sup>	1330
SN-90 HA <sup>d</sup>	2700
SN-540 HA <sup>d</sup>	4000

<sup>a</sup>Starting powder. <sup>b</sup>Stored in argon. <sup>c</sup>Stored in dry air. <sup>d</sup>Stored in air of 80% humidity.

**Table 1** Bulk and surface chemical compositions of silicon nitride samples stored in different conditions for 0, 3, 7, 30, 90 and 540 days

Powder	Bulk composition (mol%)		Surface composition (mol%)			
	N	O	Si	N	O	Cl
SN-0 <sup>a</sup>	37.4	2.3	55.0	31.0	7.9	6.1
SN-90 Ar <sup>b</sup>	37.5	2.2	55.0	31.1	7.8	6.1
SN-3 DA <sup>c</sup>	37.4	2.3	54.6	30.4	9.3	5.6
SN-7 DA <sup>c</sup>	37.2	2.5	51.7	29.1	12.9	6.4
SN-30 DA <sup>c</sup>	36.6	3.9	51.2	29.6	16.3	2.9
SN-90 DA <sup>c</sup>	36.1	4.8	52.1	28.2	15.9	3.8
SN-540 DA <sup>c</sup>	36.0	5.0	52.0	22.7	23.2	2.0
SN-3 HA <sup>d</sup>	36.6	3.1	52.4	23.0	22.7	1.9
SN-7 HA <sup>d</sup>	35.9	3.9	52.0	22.5	24.1	1.4
SN-30 HA <sup>d</sup>	33.0	7.8	51.6	20.4	26.8	1.2
SN-90 HA <sup>d</sup>	30.6	13.3	49.5	11.9	37.9	0.7
SN-540 HA <sup>d</sup>	29.5	15.0	47.8	5.8	45.7	0.7

<sup>a</sup>Starting powder. <sup>b</sup>Stored in argon. <sup>c</sup>Stored in dry air. <sup>d</sup>Stored in air of 80% humidity.

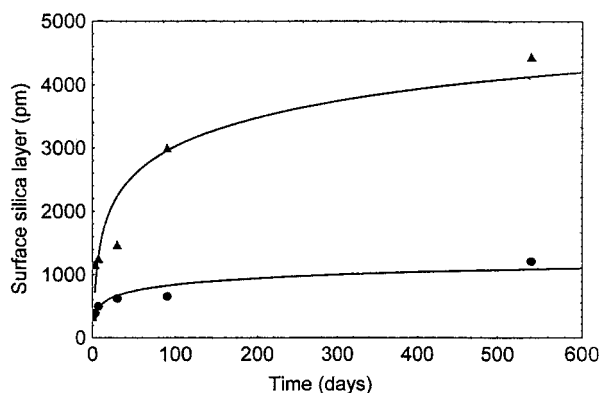


Fig. 1 The surface silica layer thickness as plotted against the ageing time (●) in dry air, (▲) in air of 80% humidity.

of the curves in Fig. 1 can be explained as follows: the ageing process starts with the rapid oxidation of smaller amorphous grains of higher reactivity. It leads to the formation of a thicker and thicker surface oxide layer which slows down the oxidation process: instead of a gas–solid reaction, the diffusion of oxygen through the surface SiO<sub>2</sub> layer becomes the rate controlling step. For longer periods of time the larger crystalline grains of lower reactivity are oxidized as well.

The chemical states of surface silicon were determined by band synthesis through peak fitting of the relevant Si 2p signal envelopes of the XPS spectra. In the peak fitting the binding energies of pure substances were regarded and the FWHM of  $1.8 \pm 0.1$  eV was adjusted to the setting of the XPS equipment.

In one particular case the Si 2p envelope was fitted by four Gaussian components centred at 103.7, 102.8, 101.7 and 100.5 eV. The four components corresponded to Si–O, O–Si–N, Si–N and Si–Si–N bonds (Figs. 2(a)–(c)). The higher the (oxygen + moisture) content of the ambient gas, the greater the proportion of Si–O bonds in the solid samples. In the sample stored in argon gas for 90 days 6.3% of the silicon content was found in Si–O bonds (Fig. 2(a)), while for the sample stored in air of 80% humidity for 540 days (Fig. 2(c)) the proportion of Si–O bonded silicon was nearly 80%. The O 1s peak in the XPS spectra, however, was symmetrical, and gave no evidence for more than one oxygen species. This does not necessarily mean a single oxygen state, because the spectral resolution of the XPS equipment used in this work was greater than the difference between the binding energies of the Si–O and O–Si–N-type oxygen species.

Changes in the surface composition can not be attributed to oxidation only. Most probably nitrogen-containing volatile compounds were also formed during storage either in dry or in humid air. From the XPS investigations no direct evidence was obtained for the formation of such compounds. TG-MS investigation of samples SN-90 Ar, SN-540 DA and SN-540 HA (Fig. 3), however, supports the above assumption. The MS ion intensity plots in Fig. 3 indicate minor amounts of NH<sub>3</sub> ( $m/z=16$ ) with three local maxima at 165, 270 and 340 °C. Based on previous studies of plasma synthesized silicon nitride nanopowders the maxima can be assigned to desorption of NH<sub>3</sub> and sublimation of NH<sub>4</sub>Cl.<sup>3,11</sup>

The TG curves in Fig. 3 suggest that the mass loss detected in the temperature range from 20 to 500 °C mostly occurred below 200 °C. Hence, it was due to the volatilisation of adsorbed water, contribution of other species to the actual mass loss was negligible. There was a total mass loss of 0.2% for the sample stored in argon gas, while for the sample stored in humid air a mass loss of 2.2% was measured.

In the XPS investigations the great majority of information was obtained from a surface layer of  $\approx 3$  nm thickness. The depth of analysis was greater by about one order of magnitude in the FTIR measurements. The mean particle size of silicon nitride samples

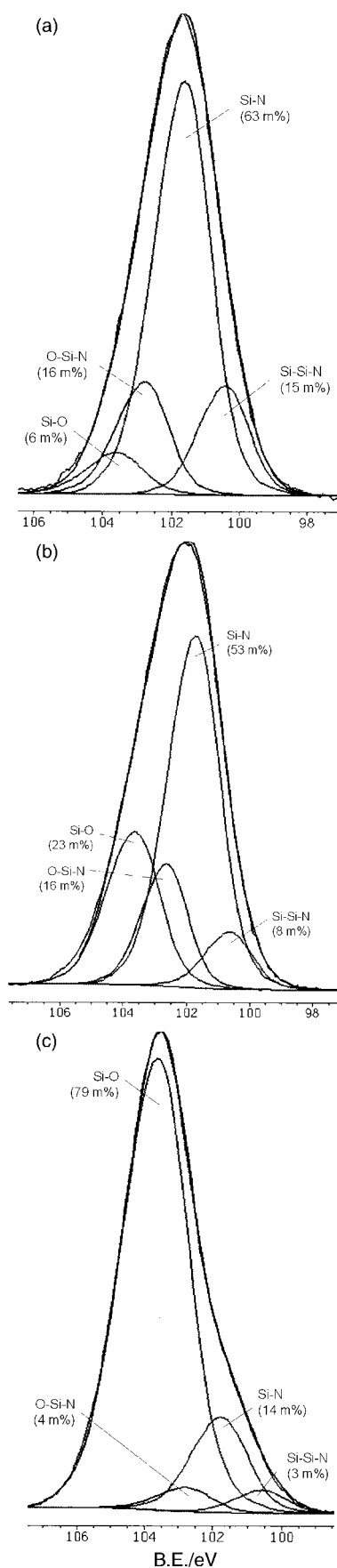


Fig. 2 Deconvolution of the Si 2p signal envelope: (a) SN-90 Ar, (b) SN-540 DA, (c) SN-540 HA.

was in the range of 40–80 nm in this work; therefore the FTIR investigations provided information on the bulk rather than on the surface properties of particulate powders.

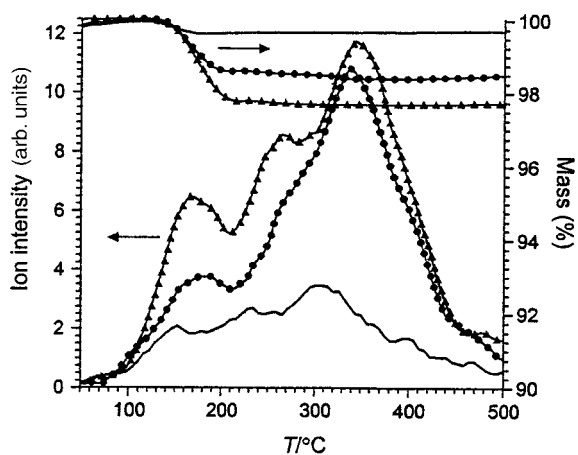


Fig. 3 TG and MS ( $m/z = 16$ ) plots of samples subjected to ageing: (—) SN-90 Ar, (●) SN-540 DA, (▲) SN-540 HA.

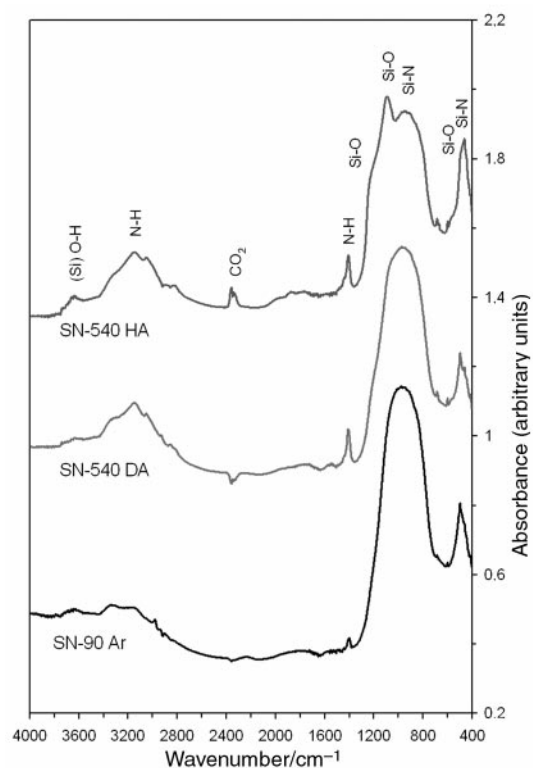


Fig. 4 FTIR spectra of samples subjected to ageing.

The DRIFT spectra of samples SN-90 Ar, SN-540 DA and SN-540 HA are shown in Fig. 4. A remarkable growth of the absorption intensity at 3720, 3360, 2360, 1400 and 1090  $\text{cm}^{-1}$  was detected with the (oxygen+moisture) content of the

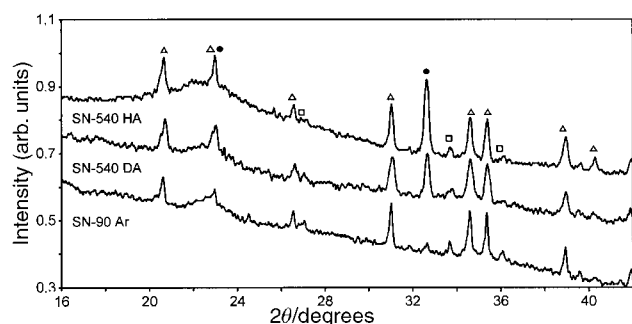


Fig. 5 X-Ray diffractograms of samples subjected to ageing: (Δ)  $\alpha$ - $\text{Si}_3\text{N}_4$ , (□)  $\beta$ - $\text{Si}_3\text{N}_4$ , (●)  $\text{NH}_4\text{Cl}$ .

ambient atmosphere. The absorption at 3720  $\text{cm}^{-1}$  corresponds to the stretching vibration of silanol groups, while the absorption at 3360  $\text{cm}^{-1}$  is due to the overlap of N-H stretching vibrations and H-O vibrations.<sup>12</sup> The absorption at 1090  $\text{cm}^{-1}$  is assigned to Si-O-Si stretching vibrations. The increase of the intensity of the above absorption bands is

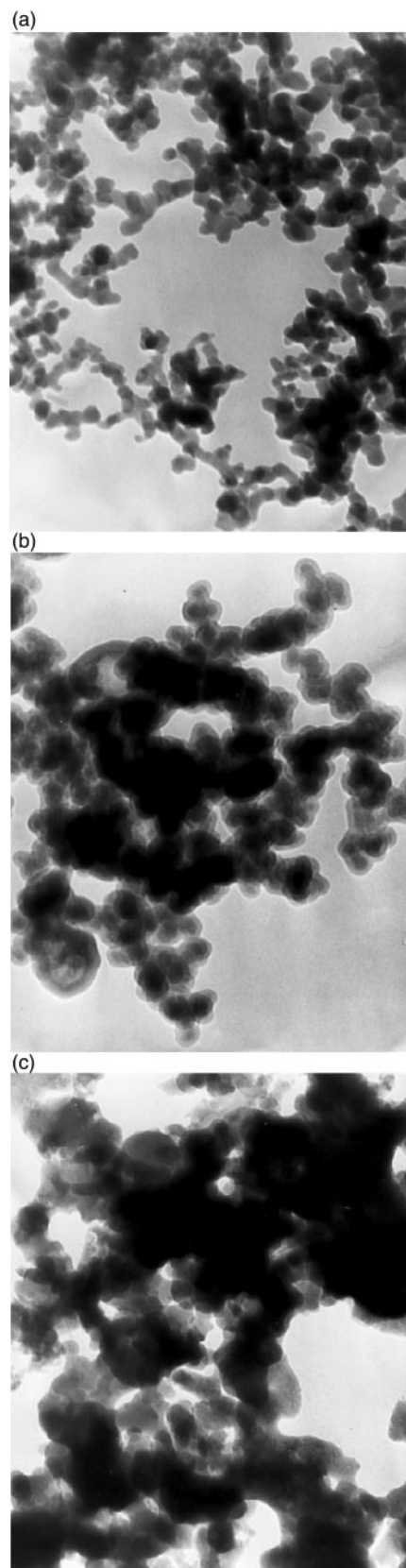


Fig. 6 TEM micrographs of samples subjected to ageing (magnification: 99000 $\times$ ): (a) SN-90 Ar, (b) SN-540 DA, (c) SN-540 HA.

**Table 3** Changes in the  $\alpha$ -Si<sub>3</sub>N<sub>4</sub>/ $\beta$ -Si<sub>3</sub>N<sub>4</sub> ratio on ageing

Powder	$\alpha/\beta$ ratio
SN-90 Ar <sup>a</sup>	7.3 ± 0.7
SN-540 DA <sup>b</sup>	9.3 ± 0.7
SN-540 HA <sup>c</sup>	10.2 ± 0.7

<sup>a</sup>Stored in argon. <sup>b</sup>Stored in dry air. <sup>c</sup>Stored in air of 80% humidity.

indicative of oxidation and formation of silanol groups in the sample stored in air of 80% humidity for 540 days (Fig. 4: SN-540 HA). In this sample even the absorption intensity at 460 cm<sup>-1</sup> (Si–N deformation mode) was higher than that of the sample stored in an argon atmosphere. This indicates a chemical environment of higher oxygen content, *i.e.* it furnishes further proof of oxidation. The FTIR investigation also confirmed that the sample stored in humid air for 540 days was much more oxidized than the sample stored in dry air for the same period of time (Fig. 4).

The appearance of higher absorption intensities at 3360 cm<sup>-1</sup> (N–H and O–H vibrations) and at 1400 cm<sup>-1</sup> (N–H deformation mode) in sample SN-540 HA confirms the findings above on the formation of volatile nitrogen containing compounds with the moisture content of the ambient atmosphere. The increase of NH<sub>4</sub>Cl reflections in the X-ray diffractograms (Fig. 5) with the (oxygen+moisture) content of the ambient atmosphere gave further evidence of the formation of N–H-type species on ageing.

No conclusion can be drawn from Fig. 5 on changes in the amorphous silicon nitride content of particulate powders. However, the  $\alpha/\beta$ -Si<sub>3</sub>N<sub>4</sub> ratio changed with the composition of ambient atmosphere (Table 3). Most probably some crystalline  $\beta$ -Si<sub>3</sub>N<sub>4</sub> transformed to amorphous species following ageing for 540 days.

The TEM micrographs (Figs. 6(a)–(c)) indicate remarkable morphological changes on ageing. The particle size of the original sample (Fig. 6(a)) increased: the silicon nitride grains stuck together on storage in both dry and humid air (Fig. 6(b) and (c)). In the sample stored in air of 80% humidity the water adsorption was so significant that large agglomerates were formed in which the grains were bonded with adsorbed surface water (Fig. 6(c)).

## Conclusions

Atmospheric ageing of nanosized silicon nitride powders produced in a thermal plasma reactor by the vapour phase reaction of silicon tetrachloride and ammonia results in substantial changes in the surface and bulk properties. The higher the (oxygen+moisture) content of the ambient atmosphere, the more profound are the changes taking place.

Oxidation on storage leads to the formation and dominance of an Si–O type surface layer accompanied by a decrease in the concentration of surface Si–N, O–Si–N and Si–Si–N species. The starting silicon nitride powder is covered by about one monolayer of SiO<sub>2</sub>. In dry air the surface coverage rises to about two SiO<sub>2</sub> monolayers in 30 days, and to about four monolayers in 540 days. In air of 80% humidity the surface SiO<sub>2</sub> coverage rapidly increases and consists of four mono-

layers in three days, and five monolayers in 30 days. In this work the presence of 80% humidity in the ambient atmosphere accelerated the early stages of oxidation by a factor of three, as compared to the behaviour in dry air.

Different stages of oxidation are found, depending on the particle size of the silicon nitride grains. In the early stages of this process the small, amorphous grains are oxidized. This is followed by the oxidation of larger crystalline grains in the latter stages of ageing.

Oxidation was accompanied by the formation of Si–O–H and N–H species, as was concluded from the FTIR investigations. In addition, TG-MS and XRD measurements indicated that the N–H type species were NH<sub>3</sub> and NH<sub>4</sub>Cl, respectively.

The above findings along with the analyses of chemical composition made clear that the chemical and structural changes in particulate powders were not restricted to the uppermost surface layer, but they involved the inner part of grains as well.

The nanosized silicon nitride particles tend to agglomerate on ageing in both dry and humid air which leads to changes in grain size and morphology.

The nanosized, thermal plasma silicon nitride powder requires special care on storage and handling. In order to avoid extensive oxidation of as-synthesized powder, this should be processed and stored by excluding oxygen and moisture.

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