

Studies on Atmospheric Ageing of Nanosized Silicon Nitride Powders

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Abstract Ageing of nanosized silicon nitride powder produced by the vapor phase reaction of silicon tetrachloride and ammonia has been studied in argon gas, in dry air and in air of 80% humidity, respectively, for 3 to 540 days. No remarkable changes were observed either in the bulk or the surface properties on storage in argon gas for 90 days. However, samples stored in dry air and humid air, respectively, exhibited remarkable oxidation and formation of N-H species. It was proved that nanosized silicon nitride powders should be stored and processed in oxygen-free conditions.

Introduction

Silicon nitride powders produced in high temperature thermal plasmas by the vapor phase reaction of silicon tetrachloride and ammonia have interesting properties including high chemical purity, amorphous microstructure and mean particle size in the nanometer range [1,2]. These powders are suitable raw materials of advanced silicon nitride ceramics [3]. 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 powders [3,4].

It is known that Si_3N_4 powders are susceptible to oxidation when contacted with oxygen or water vapor on storage and processing. Danforth [5] detected a remarkable increase of surface oxygen content of laser-synthesized silicon nitride powders under ambient conditions. It was attributed to the adsorption of water by the surface amino (N-H) groups. Similar results were published by Li [6]. The higher was the surface N-H concentration of the Si_3N_4 powder, the more oxidation was observed. A rather complex surface structure including amino-, hydroxy- and silanol-groups, adsorbed CO_2 and a complex surface compound consisting of Si, N, C and H was proposed for the laser synthesized Si_3N_4 powders subjected to atmospheric ageing.

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 on the ageing behavior of particular powders when stored under atmospheric conditions.

Experimental

Silicon nitride powder studied in this work was produced by the vapor phase reaction of SiCl_4 and NH_3 in a radiofrequency thermal plasma reactor as described previously [1]. To remove the NH_4Cl by-product formed due to excessive NH_3 , the as-synthesized powder was annealed in argon gas at 400°C for 1 hour. The resulting powder was predominantly amorphous with a crystalline phase content of about 20%, as it was determined by FTIR and XRD investigations [3].

Behavior of particular powder on atmospheric ageing was studied by storing its aliquot portions (≈ 2 g each) in dry argon atmosphere, in dry air, and in air of 80% relative humidity, respectively, for 3 to 540 days. Changes in the bulk and surface chemical compositions and microstructure were investigated against ageing time.

The bulk nitrogen content was determined by wet chemical analysis, while the oxygen content was measured by gas extraction (LECO TC-436). The surface chemical composition was analyzed by a KRATOS XSAM 800 X-ray photoelectron spectrometer. The MultiQuant [7] program was used for the quantification of XPS spectra and to calculate the surface layer thickness. The FTIR spectra were recorded by a Perkin-Elmer 1710 instrument using a DTGS detector, a Perkin-Elmer DRIFT accessory and micro sampling. XRD patterns were used to calculate the relative amounts of α -Si₃N₄ and β -Si₃N₄ phases [8], and the α -Si₃N₄/ β -Si₃N₄ ratio [9].

Results and discussion

Bulk and surface compositions of silicon nitride samples subjected to ageing for different periods of time are shown in Table 1. The starting powder (SN-0) is characterized by nearly theoretical bulk nitrogen content and rather high oxygen content. Our previous investigations revealed that about 95% of the total oxygen content of SN-0 was concentrated near to the surface [3]. It refers to post-synthesis oxidation.

Actually, neither the bulk, nor the surface composition changed on storage of SN-0 in argon gas for 90 days (Table 1, SN-90Ar). However, for samples stored in dry air the oxygen content increased considerably against the time (Table 1, SN-3DA - SN-540DA). The surface chemical composition changed in a greater extent as compared to the bulk one. In 540 days the bulk oxygen content increased by a factor of 2.2, while the surface oxygen content got higher by a factor of 2.9. Similar tendencies as above were observed for samples stored in air of 80% relative humidity (Tables 1 and 2, SN-3HA - SN-540HA). However, the changes were more significant in the latter case. Our data confirms previous findings on preferred oxidation of the uppermost surface of particles.

Thickness of the surface oxide layer was calculated from the O 1s line intensities of XPS spectra [7]. The sample was assumed to consist of uniform spheres of 40 nm in diameter. It was found that the thickness of the surface oxide (SiO₂) definitely increased on ageing. For the starting SN-0 powder thickness of the SiO₂ layer was 300 pm (Table 1). It corresponds to about one monolayer of SiO₂ with a SiO₄ tetrahedron size of 265 pm. On storage in dry air for 540 days thickness of the SiO₂ layer increased by a factor of 3.6, while on storage in humid air by a factor of 5.7 (Table 1).

Table 1. Bulk and surface chemical compositions of silicon nitride samples before and after ageing

Powder No.	Bulk composition [m/m %]		Surface composition [m/m %]				Surface SiO ₂ layer [pm]
	N	O	Si	N	O	Cl	
SN-0 ¹	37.4	2.3	55.0	31.0	7.9	6.1	300
SN-90Ar ²	37.5	2.2	55.0	31.1	7.8	6.1	300
SN-3DA ³	37.4	2.3	54.6	30.4	9.3	5.6	350
SN-7DA ³	37.2	2.5	51.7	29.1	12.9	6.4	450
SN-30DA ³	36.6	3.9	51.2	29.6	16.3	2.9	560
SN-90DA ³	36.1	4.8	52.1	28.2	15.9	3.8	590
SN-540DA ³	36.0	5.0	52.0	22.7	23.2	2.0	1090
SN-3HA ⁴	36.6	3.1	52.4	23.0	22.7	1.9	1040
SN-7HA ⁴	35.9	3.9	52.0	22.5	24.1	1.4	1130
SN-30HA ⁴	33.0	7.8	51.6	20.4	26.8	1.2	1330
SN-90HA ⁴	30.6	13.3	49.5	11.9	37.9	0.7	2700
SN-540HA ⁴	29.5	15.0	47.8	5.8	45.7	0.7	4000

¹ starting powder, ² stored in argon, ³ stored in dry air, ⁴ stored in air of 80% relative humidity

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. The Si 2p envelope was fitted by four Gaus-

sian components centered 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, respectively (Figs. 1(a)-(c)). The higher was the (oxygen + moisture) content of the ambient gas, the greater was the share of Si-O bond in the samples. For sample stored in argon gas for 90 days 6.3% of the silicon content was found in Si-O bond (Fig. 1(a)), while for sample stored in air of 80% relative humidity for 540 days (Fig. 1(c)) share of oxygen-bonded silicon was nearly 80%.

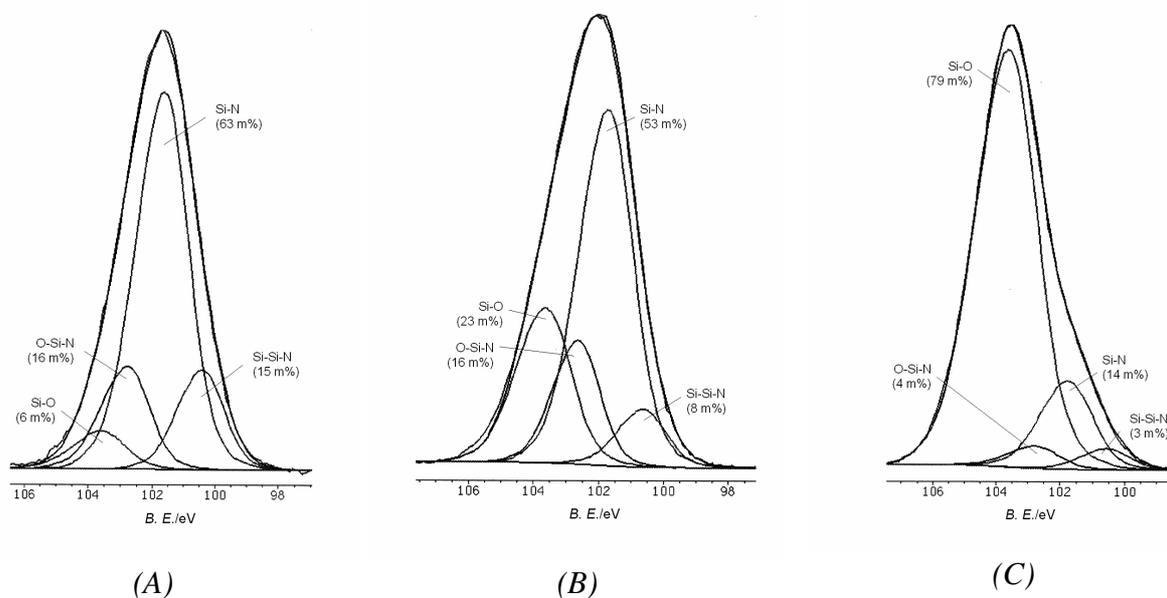


Figure 1. Deconvolution of the Si 2p signal envelope: (a) SN-90 Ar (b) SN-540 DA (c) SN-540 HA

In XPS analysis the vast majority of information is obtained from a surface layer of ≈ 3 nm thickness. However, in FTIR measurements the depth of analysis is greater by about one order of magnitude. The mean particle size of silicon nitride samples was in the range of 40-80 nm in this work. Thus, from FTIR investigations we get information rather on the bulk, than on the surface properties of particular powders.

In the DRIFT spectra (Fig. 2), a remarkable growth of absorption intensities at 3720, 3360, 2360, 1400 and 1090 cm^{-1} , respectively, was detected with the (oxygen + water vapor) content of the ambient atmosphere. The absorption at 3720 cm^{-1} corresponds to the stretching vibration of silanol groups, while the absorption at 3360 cm^{-1} is the overlap of N-H stretching vibrations and H-O vibrations [10]. The absorption at 1090 cm^{-1} is assigned to Si-O-Si stretching vibrations. Increase of the intensity of the above absorption bands refers to oxidation and formation of silanol groups in sample stored in air of 80% relative humidity for 540 days (Fig. 2, SN-540HA). In this sample even the absorption intensity at 460 cm^{-1} (Si-N deformation mode) was bigger as compared to sample stored in argon atmosphere (Fig. 2, SN-90Ar). It refers to a chemical environment of higher oxygen content i.e. it furnishes further proof of oxidation.

According to XRD measurements, the α -Si₃N₄/ β -Si₃N₄ ratio increased from 7.3 to 9.3 (SN-540DA) and 10.2 (SN-540HA), respectively. Most probably, some crystalline β -Si₃N₄ transformed to amorphous material in 540 days.

Conclusions

Atmospheric ageing of nanosized silicon nitride powders produced in RF thermal plasma conditions by the vapor phase reaction of silicon tetrachloride and ammonia results in substantial changes in

the surface and bulk properties. The higher is the (oxygen + water vapor) content of ambient atmosphere, the more profound changes are taking place.

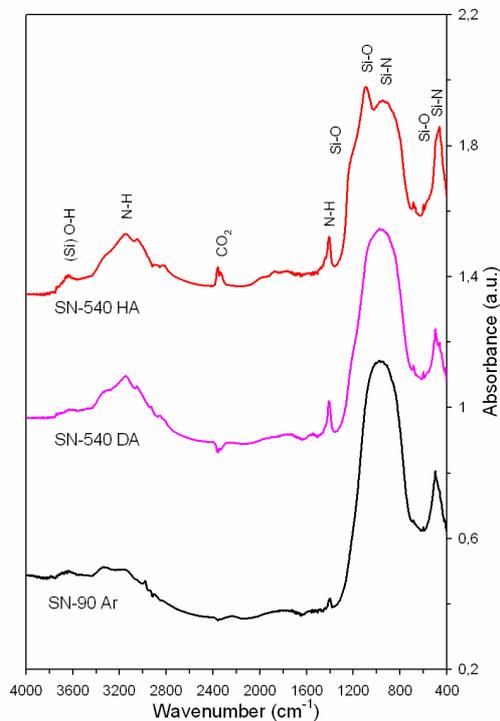


Figure 2. FTIR spectra of samples stored for 540 days

Oxidation on storage results in the formation of a Si-O type surface layer accompanied by a decrease in the concentration of surface Si-N, O-Si-N and Si-Si-N species. Surface of silicon nitride powder as-annealed is covered by a SiO₂ monolayer.

It was proved that the nanosized silicon nitride powder produced in thermal plasma conditions requires special care on storage and handling. In order to avoid extensive oxidation, it should be stored and processed by excluding its contact both with oxygen and moisture.

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