

Surface Structure of Commercial Si_3N_4 Powders Analyzed by X-Ray Photoelectron Spectroscopy (XPS)

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市販窒化ケイ素粉末表面構造のX線光電子分光(XPS)による解析

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Surface structures of seven different commercial Si_3N_4 powders were investigated by X-ray photoelectron spectroscopy (XPS). The evaluated powders were produced by three different methods: diimide precipitation, carbothermal reduction and nitridation of silicon using different nitriding media with final treatments. The XPS spectra of all as received powders show $\text{Si}2\text{p}$, $\text{C}1\text{s}$, $\text{N}1\text{s}$ and $\text{O}1\text{s}$ signals after 0, 5 and 10 s etching periods. Tetrahedral structures $\text{Si}-\text{XYZW}$ with different atoms (Si ; H ; N ; O) or groups (NH ; NH_2 ; OH) in XYZ and W , from here after substituted by them, were observed for all as received commercial Si_3N_4 powders. For five out of the seven Si_3N_4 powders, the two main tetrahedra present on the most outer surface layer are $\text{Si}-\text{SiSiN}(\text{OH})$, and tetrahedra containing O ; $\text{Si}-\text{O}(\text{NNN})$; SiSiH ; SiNN ; NNO . The two powders produced by nitridation of silicon with HF acid washing in the final treatment present $\text{Si}-\text{SiSiN}(\text{NH}_2)$ and tetrahedra containing OH ; $\text{Si}-\text{SiN}(\text{Si}; \text{N})(\text{OH})$. The powder produced by carbothermal reduction process using NH_3 (g) presents the highest fraction of O containing tetrahedra. For all powders after 5 and 10 s etching periods, the main structure changed to NH_2 ; $\text{Si}-\text{SiN}(\text{H}; \text{Si})(\text{NH}_2)$ and NH groups containing configurations $\text{Si}-\text{SiN}(\text{Si}; \text{N})(\text{NH})$, respectively. The surface of Si_3N_4 powders of any production method does not have structure close to SiO_2 , $\text{Si}_2\text{N}_2\text{O}$ or an intermediate between them as commonly accepted.

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1. Introduction

Silicon nitride (Si_3N_4) components are one of non-oxide ceramic materials that are stable under normal atmospheric conditions and have gained a lot of interest in the past 20 years. Their specific assembly of excellent (chemical, physical, thermal and mechanical) material properties has generated interest in their use as a high temperature structural material.¹⁾ The structures and properties of ceramic components depend directly on the density, uniformity and rheological properties of the green compacts from which they are sintered. Surface characterization of ceramic raw powders should be conducted before forming green bodies. It is very important to prepare well-disperse primary particles in order to form dense ceramic bodies.²⁾ The mechanical properties of Si_3N_4 based ceramic bodies are largely controlled by the phases formed on the grain boundaries during sintering.³⁾ A major technical issue in the processing of these ceramic materials is the sinterability of the silicon nitride starting powders. It has been stated that the sinterability is determined by the formation of the oxide layers on the surface of the powder particles at the sintering temperature.⁴⁾ Many research works have been focused on the optimization of the kind and amount of sintering additives, which form molten silicate phase and allow densification by liquid-phase sintering mechanism. Besides the selection of additives and sintering conditions, physical and chemical properties of Si_3N_4 ceramics are strongly influenced by the characteristics of the starting Si_3N_4 powder surfaces.

The surface of silicon nitride powders has been character-

ized by different surface analytical techniques. Several authors using different analytical techniques; XPS,⁵⁾ SIMS,⁶⁾ ESCA⁷⁾ and HF dissolution,⁸⁾ concluded that the surface layer of silicon nitride powders has a composition closer to SiO_2 or $\text{Si}_2\text{N}_2\text{O}$ or an intermediate between them. The existence of a nonstoichiometric SiN_x phase has also been detected by XPS analysis.^{9),10)} FTIR studies have the capability to detect hydrogen-related species as an advantage compared to electron microscopy. This technique has been applied in many works to specify the kinds of surface groups present on the surface of Si_3N_4 powders. Surface groups, such as SiNH_2 , Si_2NH , SiOH , SiH and SiH_2 have been reported.^{11)–20)}

Commercial Si_3N_4 powders were analyzed by temperature programmed desorption mass spectrometry (TPDMS). H_2 , H_2O , NH_3 and N_2 desorbed from all powders but the proportions were different for each powder. It was concluded that the surface of Si_3N_4 powders is different from the surface of silica in the kinds and quantities of desorbed molecules.^{21)–23)} Recently, Si-H absorption bands of commercial Si_3N_4 powders linked to tetrahedral units with different atoms (Si ; H ; N ; O) and groups (NH_2 ; NH ; OH) configurations have been reported.²⁴⁾

In the present work the XPS spectral characteristics of seven commercial Si_3N_4 powders are investigated.

2. Experimental

X-ray photoelectron spectroscopy (XPS) spectra of seven commercial Si_3N_4 powders, produced by different processes as shown in **Table 1**, were obtained using a XPS instrument (JEOL JPS-100SX). The X-rays used to bombard the sample were monochromatic $\text{MgK}\alpha$ rays with energy of 1253.6 eV.

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Table 1. Production Processes and Specifications of the Seven Commercial Silicon Nitride (Si_3N_4) Powders and Their Nomenclature

Nomenclature	Oxygen content/mass%	Specific surface area/ m^2g^{-1}	Synthesis method	Nitridation media
A1	1.05	10.2	Silicon diimide precipitation	$\text{NH}_3(\text{l})$
A2	0.98	9.2		$\text{NH}_3(\text{g})$
B1	1.88	11.6	Carbothermal reduction and nitridation	N_2
B2	2.45	6.5		$\text{NH}_3(\text{g})$
C4**	0.66	8.5	Nitridation of silicon	N_2
C5*	0.83	3.9		$\text{N}_2 + \text{H}_2$
C6**	0.78	11.6		$\text{N}_2 + \text{H}_2$

* Crushed

** Crushed and washed by HF acid and water

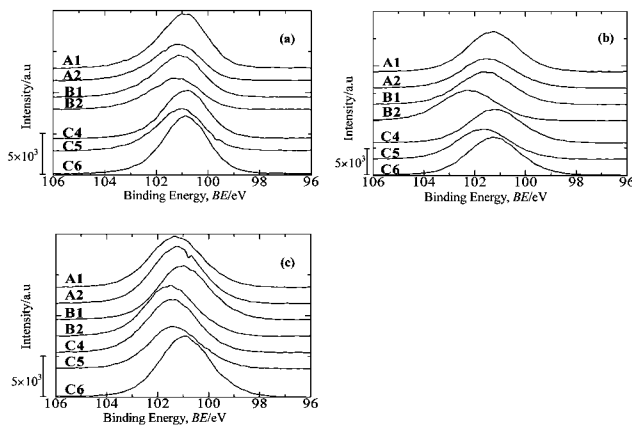


Fig. 1. XPS spectra of $\text{Si}2\text{p}$ signals for all Si_3N_4 powders at 0 s (a), 5 s (b) and 10 s (c) etching time. Symbols correspond to the powders nomenclature shown in Table 1. All powders show $\text{Si}2\text{p}$ signal but peak intensities and binding energies are different for each powder.

The vacuum in the analysis chamber was 2×10^{-7} Pa. A narrow scan resolution of 0.1 eV was used. The adventitious $\text{C}1\text{s}$ peak, arising from traces of hydrocarbon in the spectrometer, was used as a reference for evaluating the peak positions because of static charging of samples. The $\text{C}1\text{s}$ peak position was observed together with other peaks ($\text{Si}2\text{p}$, $\text{N}1\text{s}$ and $\text{O}1\text{s}$) of the spectrum, and the $\text{C}1\text{s}$ line at $\text{B.E.} = 284.6$ eV was fixed 5).

Ar-ion etching was also applied for different periods (0; 5 and 10 s) at 1.7 kV ion energy, 15 mA current and pressure of 2×10^{-2} Pa. The spectral signals were deconvoluted using a Jandel peak separation with Gaussian shape.^{25),26)} The peak area data of the fittings with the highest F-statistic were used for quantification.

3. Results and discussions

The XPS spectra for $\text{Si}2\text{p}$ (106–96 eV), $\text{C}1\text{s}$ (290–280 eV), $\text{N}1\text{s}$ (402–392 eV) and $\text{O}1\text{s}$ (538–528 eV) signals for all powders at 0 s (a), 5 s (b) and 10 s (c) etching periods are shown in Figs. 1, 2, 3 and 4, respectively. The XPS spectra of all as received Si_3N_4 powders show $\text{Si}2\text{p}$, $\text{C}1\text{s}$, $\text{N}1\text{s}$ and $\text{O}1\text{s}$ signals, but peak intensities and binding energies are different for each powder. The signals seen in the figures have been referenced to the adventitious $\text{C}1\text{s}$ line, arising from traces of hydrocarbons in the spectrometer. In the $\text{Si}2\text{p}$ signal, the positions of

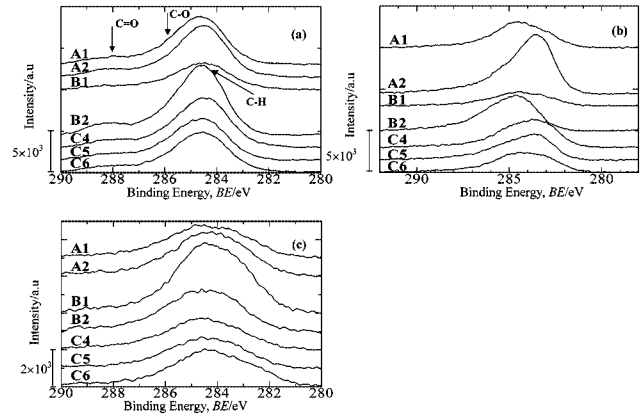


Fig. 2. XPS spectra of $\text{C}1\text{s}$ signals for all Si_3N_4 powders at 0 s (a), 5 s (b) and 10 s (c) etching time. Symbols correspond to the powders nomenclature shown in Table 1. The observed C bonds correspond to $\text{C}=\text{O}$, $\text{C}-\text{O}$ and $\text{C}-\text{H}$.

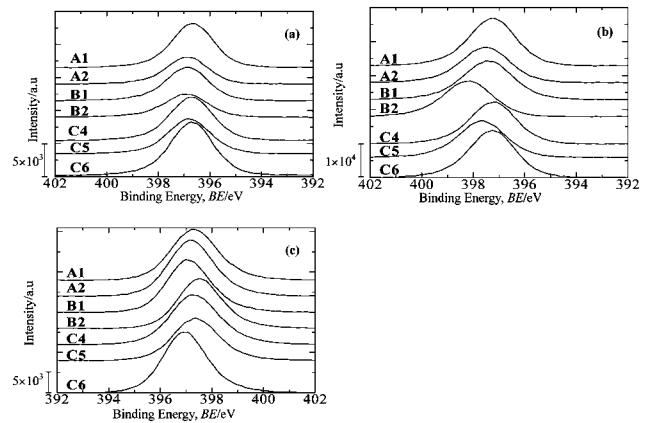


Fig. 3. XPS spectra of $\text{N}1\text{s}$ signals for all Si_3N_4 powders at 0 s (a), 5 s (b) and 10 s (c) etching time. Symbols correspond to the powders nomenclature shown in Table 1.

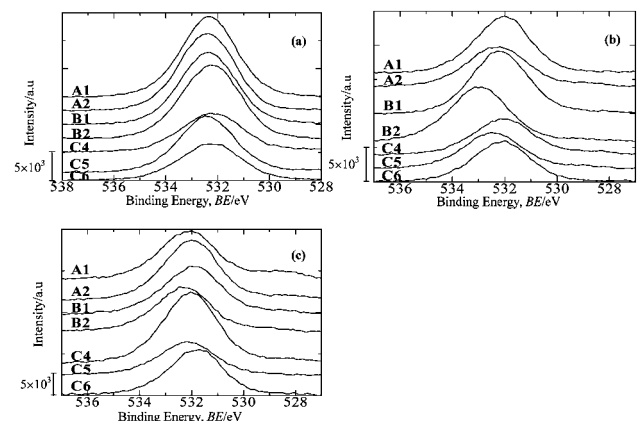


Fig. 4. XPS spectra of $\text{O}1\text{s}$ signals for all Si_3N_4 powders at 0 s (a), 5 s (b) and 10 s (c) etching time. Symbols correspond to the powders nomenclature shown in Table 1.

the band maximum are slightly different among the powders between etching periods. The maximum is at around 101.6

Table 2. Binding Energies and Corresponding Configurations. The Data of Configurations That Include O and H Atoms as well as OH, NH₂ and NH Groups Marked with an * were Estimated by the Present Authors as Explained in the Text. The Ones Calculated by Miyazaki et al. are also Included²⁶⁾

Configurations	Binding Energy, BE/eV	Configurations	Binding Energy, BE/eV
Si-SiSiSiSi	99.4	Si-SiNN(NH ₂)*	101.8
Si-SiSiSiC	99.5	Si-SiNNO*	102
Si-SiSiCC	99.7	Si-SiNN(OH)*	102.1
Si-SiSiSiN	99.9	Si-SiSiH(NH)*	102.2
Si-CCCC	100.1	Si-SiSiO*	102.2
Si-SiSiSi(NH)*	100.4	Si-SiNNH*	102.3
Si-CCCN	100.5	Si-SiSiH(NH ₂)*	102.4
Si-SiSiSiO*	100.8	Si-SiSiHO*	102.6
Si-SiSiNN	100.5	Si-NNNO*	102.6
Si-SiSiN(NH)*	101	Si-NNN(OH)*	102.7
Si-SiSiSiH*	101.1	Si-NNNH*	102.9
Si-SiSiNN	101.1	Si-NNO(NH)*	103
Si-SiSiN(NH ₂)*	101.2	Si-NNO(NH ₂)*	103.3
Si-SiSiN(OH)*	101.5	Si-NNOO*	103.4
Si-SiNN(NH)*	101.6	Si-NNO(OH)*	103.6
Si-NNNN	101.7	Si-NNOO*	104.2

* Estimated by the present authors

eV–101 eV and has been assigned to Si–N bonds.^{10),25)} The Si–N bond binding energy variation is due to differences of silicon near-neighbour atoms as it will be discussed in details later. The maximum of the N1s signals for all the powders is located in the range 397.1–397.5 eV, and assigned to N–SiSiSi bonds.^{3),26),27)} The O1s signal is in the range 530.5–533.8 eV. Contributions from O–Si, O–C and O–H bonds or even absorbed metal oxide impurities can overlap in this range.^{3),28),29)} It is therefore difficult to separate them, because their binding energies are close. O–N bonds have been reported to have a binding energy in the range 399.7–402.8 eV.^{27),30)} None of the powders show a considerable peak in this range.

Miyazaki et al. reported a linear relation between the binding energy of the Si–N bond for different tetrahedron containing Si, N and C atoms and the sum of the electronegativities of the atoms in the tetrahedra.²⁵⁾ We estimated the Si–N binding energy in tetrahedra containing other combinations including H and O atoms as well as NH, NH₂ and OH groups for different configurations using the correlation of these authors and the corresponding sum of the electro negativities of the elements and/or groups. The results are shown in **Table 2**. It was assumed that the proportions of tetrahedra with more than two H atoms or NH, NH₂, OH groups were very small and could be neglected.³¹⁾ The Pauling's electronegativity used for each atom was as follows: Si = 1.8, H = 2.1, C = 2.5, N = 3 and O = 3.5.²⁵⁾

The spectra of Si2p signal shown in Fig. 1 were deconvoluted using a Jandel peak fit and analysis software. The results of the fitting with the highest F-statistic are shown in **Figs. 5(a)**, **(b)** and **(c)** corresponding to etching time periods 0, 5 and 10 seconds. The binding energies obtained from the peak separation of the spectra for all powders and possible assignments for tetrahedral configurations are listed in **Table 3**. The highest intensity peak obtained for each powder is underlined.

Table 3 indicates that for five out of the seven powders the highest intensity peak has a binding energy around 101.5 eV assigned to a Si–SiSiN(OH) tetrahedral configuration. Exceptions are the two powders produced by direct nitridation of silicon with HF acid washing as final treatment (C4 and C6)

where the highest intensity peak has a binding energy of 101.2 eV assigned to a Si–SiSiN(NH₂) tetrahedra. Only the powder produced by carbothermal reduction process using N₂ as nitridation media (B1) shows tetrahedra that includes two O atoms as neighbors of the Si–N bond. After 5 second etching time, all powders show the highest intensity peak corresponding to NH₂ group containing tetrahedra. For the powder produced by carbothermal reduction method using NH₃ (g) as nitriding media (B2) the highest intensity peak is located at a binding energy of 102.3 eV assigned to Si–SiSiH(NH₂) tetrahedral configuration. For the other powders the highest peak is located at around 101.2 eV corresponding to Si–SiSiN(NH₂) configuration. Si–C bonding was obtained in A and C powders located at around 99.5 eV. Other peaks in the range of 101.9–104.3 eV were assigned to oxygen bond to silicon (Si–O) observed for six powders but not for the powder produced by nitridation of silicon using a mixture of N₂ + H₂ as nitriding media with acid washing (C6) which shows OH instead of O. After 10 second etching time, for five out of seven powders the highest intensity peak has a binding energy around 101.5 eV assigned to a Si–SiNN(NH) tetrahedral configuration. Exceptions are, the powder produced by carbothermal reduction process using N₂ as nitridation media (B1) and the one produced by direct nitridation of silicon using a mixture of N₂ + H₂ as nitriding media with HF acid washing as final treatment (C6) where the highest intensity peak has a binding energy of 101.1 eV assigned to a Si–SiSiN(NH) tetrahedra. OH group containing configurations were observed in the powder produced by silicon diimide precipitation using NH₃ (l) as nitridation media (A1) and the powder produced by carbothermal reduction process using N₂ as nitridation media (B1) corresponding to Si–SiNN(OH) at 102.2 eV. The powders that were washed in further treatment (C4 and C6) show tetrahedra containing two N atoms and one O atom around 102.5 eV.

The assignment of all components in the Si2p signal as described above agrees with the N1s and C1, O1s signals. The relations shown in **Figs. 6(a)** and **(b)** may be taken as a confirmation of the tetrahedral assignments.

The tetrahedral configurations listed in Table 3 containing OH, NH₂, O, NH or Si and N bond to silicon were grouped as follows: OH; Si–SiN(Si; N)(OH), NH₂; Si–SiSi(N; H)(NH₂), O; Si–O(NNN; SiSiH; SiNN; NNO; NOO), NH; Si–SiN(Si; N)(NH) and Si, N; Si–SiSiSi(Si; N). **Figure 7** shows the fractions of each group for each powder obtained using the summation of intensities obtained from the deconvoluted spectra. In the most outer layer of all A, all B and C5 powders the largest configuration contains OH as Si–SiSiN(OH) and the second; O as SiO(NNN; SiSiH; SiNN; NNO) configurations. For the two powders that were washed (C4 & C6) the largest contains NH₂ as Si–SiSiN(NH₂) and the second; OH as SiSiN(Si; N)(OH) configurations respectively. The powder produced by carbothermal reduction process using NH₃(g) as nitridation media shows the largest intensity fraction of O containing configurations, meanwhile the one using N₂ (B1) shows the largest of OH configurations at the most outer surface. After 5 s etching time, for six powders, the main component contains NH₂ group in Si–SiSi(N; H)(NH₂) configurations. The powder produced by carbothermal reduction method using N₂ as nitriding media (B1) shows the highest intensity component corresponding to the oxygen containing configuration; Si–SiNNO. The powder produced by nitridation of silicon using a mixture of N₂ + H₂ as nitriding media with acid washing (C6) shows the highest intensity of NH₂ group containing configuration Si–SiSiN(NH₂) and in-

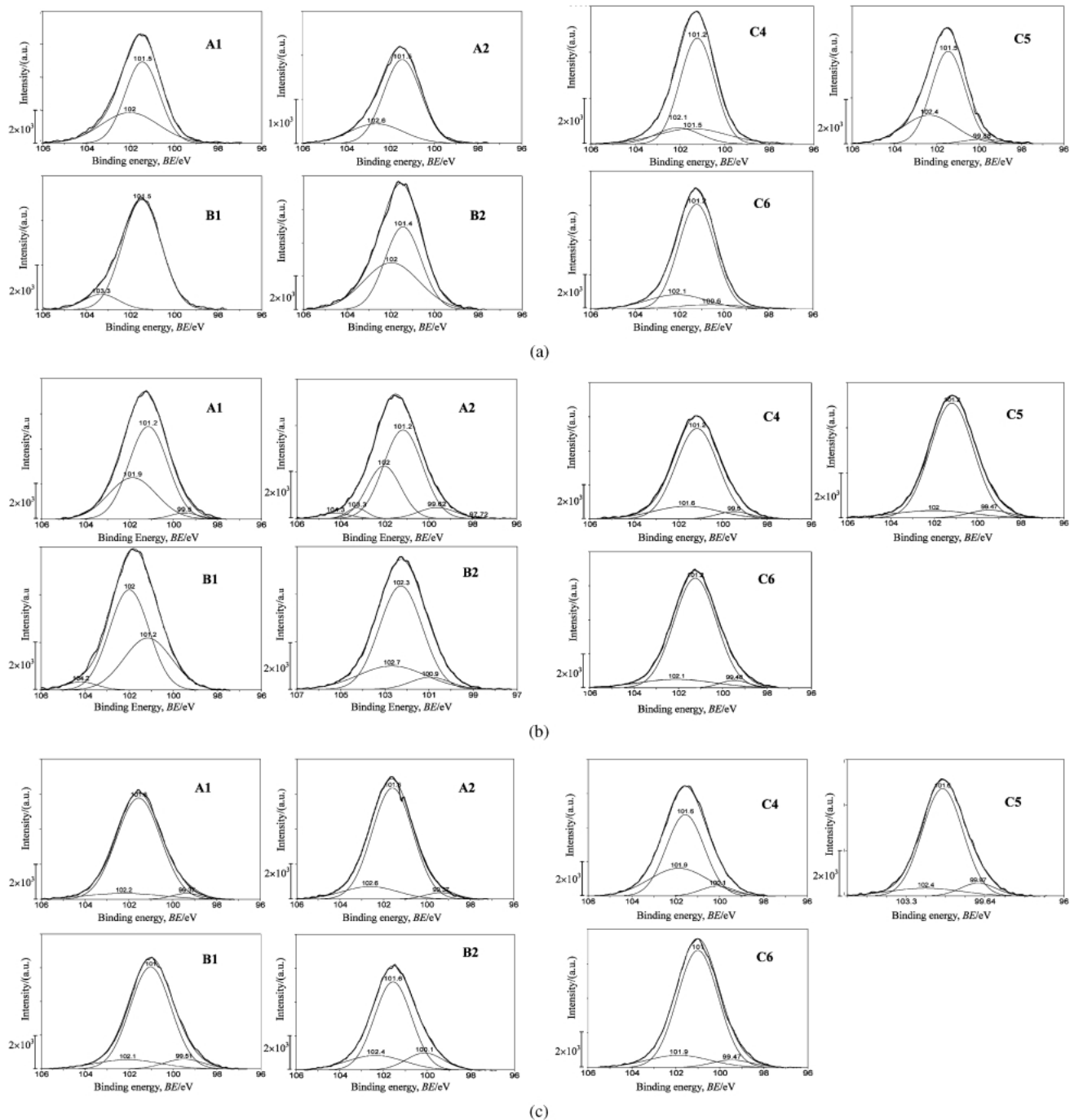


Fig. 5. Deconvolution of Si2p signal for all powders at 0 s (a), 5 s (b) and 10 s (c) etching time. Symbols correspond to the powders nomenclature shown in Table 1.

stead of O configurations as the other six powders do, presents OH configuration. After 10 s etching time, for all the powders the main component contains NH group. For five out of seven powders, the second component contains O atom, meanwhile, the powder produced by silicon diimide precipitation using NH_3 (I) as nitriding media (A1) and carbothermal reduction method using N_2 as nitriding media (B1) show OH groups containing configurations instead of O configurations.

The powders using NH_3 as nitriding media in the production process (A and B2) show similar O, NH_x containing configurations and intensity fractions. The powder produced by the same production process of powder B2, carbothermal reduc-

tion method but using N_2 instead of NH_3 as nitriding media shows different intensity fractions, especially at 5 second etching period the O containing configurations intensity fraction is very high. The powder that was not washed (C5) in further treatment shows O containing configurations at most outer layer but the two powders that were washed (C4 and C6) do not. The washed powders are the only ones that show NH_2 configurations in the most outer layer. By washing with acid oxygen was removed and generated NH_2 configurations. NH groups exist more inside of the surface for all the powders in agreement with the TPDMS findings.²³⁾

The intensity fraction of NH_2 containing configurations

Table 3. Observed Binding Energies from Deconvoluted Spectra and Their Assignments for All Si_3N_4 Powders for 0, 5 and 10 s Etching Periods. Without Etching the Highest Intensity Peaks, Underline, Correspond to Si-SiSiN(OH) for Five Powders and Si-SiSiN(NH_2) for the Two Powders Produced by Nitridation of Silicon and Washed by Acid. For All Powders after 5 and 10 s Etching Periods Correspond to NH_2 Groups Si-SiSi(N; H) (NH_2) and NH Groups Si-SiN(Si; N) (NH) Containing Configurations, respectively. Tetrahedra Containing O; Si-O (NNN; SiSiH; SiNN; NNO; NOO) Configurations are also Observed

Production process	Diimide precipitation						Carbothermal reduction						Direct nitridation of silicon								
Powder (Nitriding media) Washed by HF (*)	A1 (NH ₃ l)			A2 (NH ₃ g)			B1 (N ₂)			B2 (NH ₃ g)			C4 (N ₂) *			C5 (N ₂ + H ₂)			C6 (N ₂ + H ₂) *		
Etching periods/sec	0	5	10	0	5	10	0	5	10	0	5	10	0	5	10	0	5	10	0	5	10
XYZW	Binding energy, BE/eV																				
SiSiSiSi	99.4			99.4																	
SiSiSiC	99.5			99.6			99.5						99.5			99.5			99.5 99.5		
SiSiSiN										100.1			100.1			99.9 100					
SiSiNN																			100.6		
SiSiN(NH)							<u>101</u>			100.9									<u>101</u>		
SiSiN(NH ₂)	<u>101.2</u>			<u>101.2</u>			<u>101.3</u>						<u>101.2</u> <u>101.2</u>			<u>101.2</u>			<u>101.2</u> <u>101.3</u>		
SiSiN(OH)	<u>101.5</u>			<u>101.5</u>			<u>101.4</u>			<u>101.4</u>			101.5			<u>101.5</u>					
SiNN(NH)				<u>101.6</u>			<u>101.6</u>						<u>101.6</u>			<u>101.6</u>					
SiNN(OH)				102.2			102.1						102.1						102.1 102.1		
SiSiH(NH ₂)										<u>102.3</u>											
SiNNO	102						102			102			101.9 101.9			102			101.9		
SiSiHO										102.4						102.4 102.4					
NNNO				102.6 102.6						102.7											
NNOO				103.3			103.3														
NOOO				104.3																	

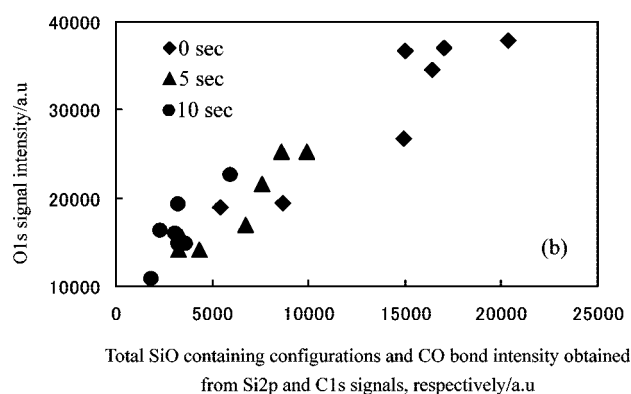
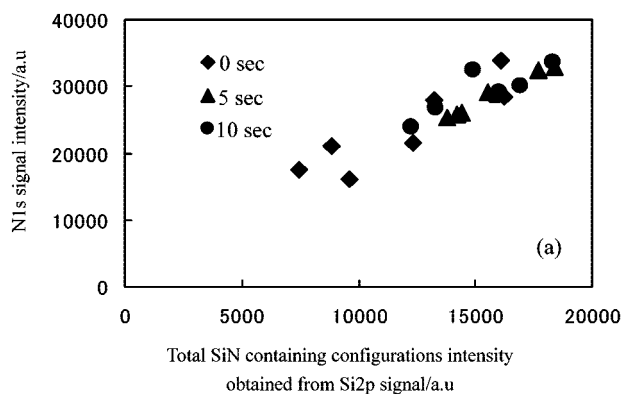


Fig. 6. Agreement between signals; Si2p and N1s (a), Si2p, C1s and O1s (b), for all powders at 0, 5 and 10 s etching time. All observed N atoms are bonded to Si and all observed O atoms are bonded to Si and C atoms. All configurations are described in this section.

$[\text{NH}_2]/(\text{OH} + \text{NH}_2)$ obtained from the deconvoluted XPS spectra as listed in Table 3 at 0 and 5 s etching time (this work) and the fraction of NH_3 desorbed molecules $[\text{NH}_3]/(\text{NH}_3 + \text{H}_2\text{O})$ from TPDMS measurement²¹⁾ are in good agreement as shown in Fig. 8.

Figure 9 shows that the $\text{OH}/(\text{NH}_x + \text{OH})$ containing configurations intensity fraction obtained from the deconvoluted spectra from 0 to 10 s etching time correlates well with the $\text{OH}/(\text{NH}_x + \text{OH})$ absorbance intensity fraction obtained from DRIFT (diffuse reflectance infrared Fourier transform spectroscopy) (data from Ref. 32).

4. Summary

Tetrahedral structures Si-XYZW with different atoms or groups were observed for all as received commercial Si_3N_4 powders.

For five out of the seven Si_3N_4 powders the two main tetrahedra present on the most outer surface layer are Si-SiSiN(OH) and tetrahedra containing O; Si-O(NNN; SiSiH; SiNN; NNO). The two powders produced by nitridation of silicon with HF acid washing in the final treatment (C4 and C6) present Si-SiSiN(NH_2) and tetrahedra containing OH; Si-SiN(Si; N) (OH). The powder produced by carbothermal

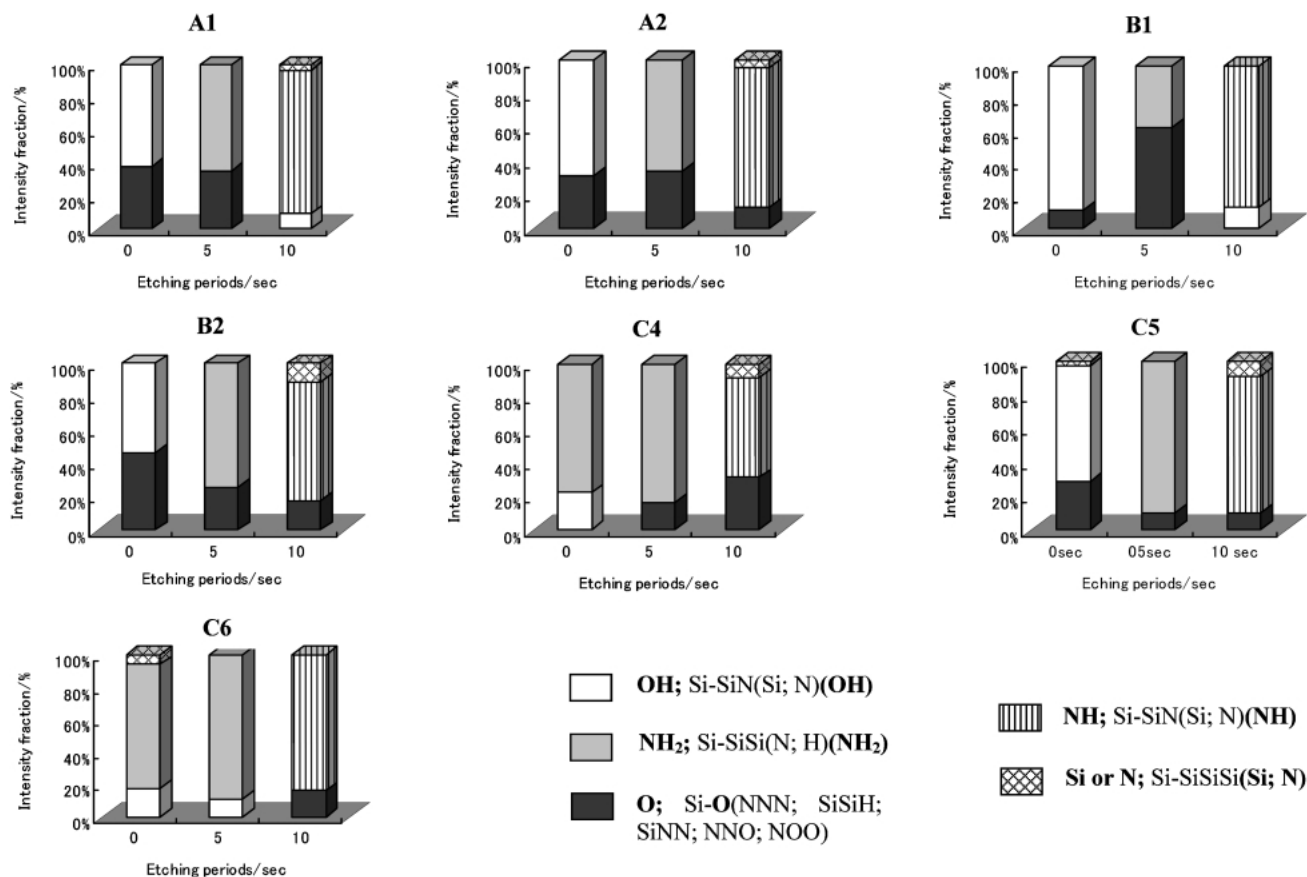


Fig. 7. Fractions of tetrahedra containing OH, NH_2 , O, NH and Si; N. For five out of the seven Si_3N_4 powders (A, B and C5) the two main tetrahedra present on the most outer surface layer are $\text{Si-SiSiN}(\text{OH})$ and tetrahedra containing O. The two powders produced by nitridation of silicon with HF acid washing in the final treatment (C4 and C6) present $\text{Si-SiSiN}(\text{NH}_2)$ and tetrahedral containing OH. For all powders after 5 and 10 s etching periods, the main structure changed to NH_2 ; $\text{Si-SiN}(\text{H}; \text{Si})(\text{NH}_2)$ and NH groups containing configurations $\text{Si-SiN}(\text{Si}; \text{N})(\text{NH})$, respectively.

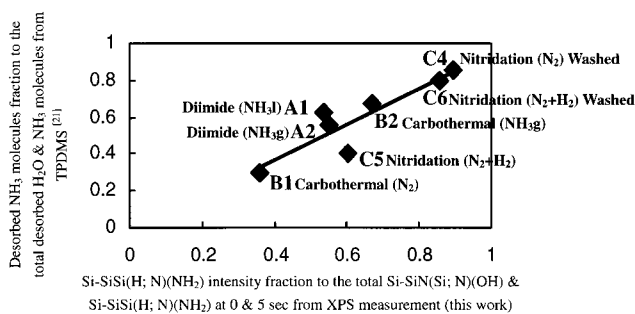


Fig. 8. Agreement between two methods XPS (this work) and TPDMS.^[21] The powder produced by carbothermal reduction process using N_2 as nitridation media (B1) shows the lowest fraction of NH_2 containing tetrahedra. Symbols correspond to the powders nomenclature shown in Table 1. Production process, nitriding media and further treatment are also indicated.

reduction process using NH_3 (g) presents the highest fraction of O containing tetrahedra.

After 5 s etching the composition of the powder produced by nitridation of silicon using a mixture of $\text{N}_2 + \text{H}_2$ as nitriding media with acid washing (C6) does not considerable change but for the other powders is different. Instead of $\text{Si-SiSiN}(\text{OH})$ all powders present $\text{Si-SiSiN}(\text{NH}_2)$ tetrahedra and the proportion of tetrahedra with O increased for B1, decreased

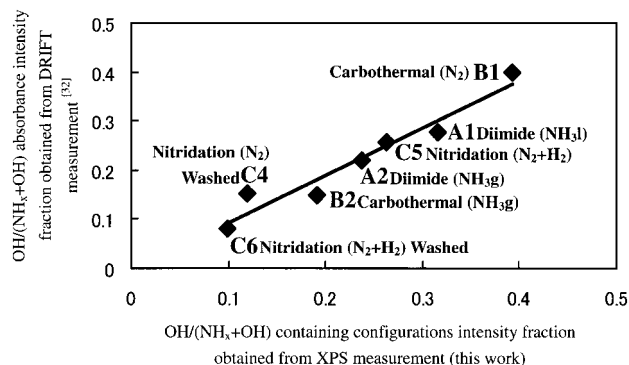


Fig. 9. Absorbance intensity fraction of OH groups measured by DRIFT^[32] correlates with the intensity fraction of OH groups containing configurations from 0 to 10 s etching time obtained from XPS measurement (this work). Symbols correspond to the powders nomenclature shown in Table 1. Production process, nitriding media and further treatment are also indicated.

for B2 & C5 and almost did not change for the A1 and A2 powders.

The composition of all powders changed after 10 s etching. Instead of NH_2 groups configuration as at 5 s etching they show NH groups configurations $\text{Si-SiN}(\text{Si}; \text{N})(\text{NH})$. All powders show O or OH containing tetrahedra, including C6.

In the washed powders, C4 and C6, the tetrahedra are different than for the other powders.

5. Conclusions

Seven commercial Si_3N_4 powders were investigated by XPS and compared to previous works. The following conclusions were revealed:

(1) The surface of Si_3N_4 powders for any production method can not be regarded as having a composition close to SiO_2 , $\text{Si}_2\text{N}_2\text{O}$ or an intermediate form between them as commonly accepted.

(2) The surface structure of all the powders is a mixture of Si-XYZW tetrahedra with different atoms (Si; H; N; O) and groups (OH; NH; NH_2) configurations that bond to the same silicon.

(3) The results are in agreement with our previous FTIR^{(24), (32)} and TPDMS^{(21)–(23)} studies.

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