SiH_x Absorbance Bands in Si₃N₄ Powder Surfaces Analyzed by Diffuse Reflectance Infrared Fourier Transform Spectroscopy

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窒化ケイ素粉末表面のSiH_x吸収バンドの拡散反射フーリエ変換赤外線分光による解析

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The SiH_x stretching absorbance region (2300–2000 cm⁻¹) of seven different commercial Si₃N₄ powders was investigated by diffused reflectance infrared Fourier transform (DRIFT) spectroscopy. The powders evaluated were produced by three different methods: diimide precipitation, carbothermal reduction and nitridation of silicon using different nitriding media and final treatments. SiH groups were detected in all powders. The results show the presence of H-SiXYZ tetrahedral units. XYZ can be different atoms or groups (Si, H, N, O, NH, NH₂ or OH) that bond to the same silicon atom. The H-Si bands were classified considering the backbonded atoms of the H-Si into four main tetrahedral by fixing the XY atoms and several possibilities for Z as follows: silicon-based; H-SiSi (Z=Si, NH, H or O), nitride-based; H-SiSiN (Z=NH₂ or O), oxynitride-based; H-SiNO (Z=N, NH or NH₂) and silica-based; H-SiOO (Z=NH₂, OH, O or H) tetrahedral configurations. The proportions of these tetrahedral units are different for each powder. The powder produced by the carbothermal reduction process using N₂ as nitriding media presents the largest fraction of H-Si groups linked to silica-based tetrahedral units. For the other six powders the largest fraction of H-Si groups is linked to silicon-based tetrahedral units.

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1. Introduction

Fourier transform infrared (FT-IR) spectroscopy is a very useful technique for the analysis of powders and films that provides structural bonding information including H atoms. SiH_x groups have been observed in the IR spectra of different Si related materials and films. Each material shows SiH absorption bands at different wavenumbers because the vibration frequency depends on the effective electronegativity sum of the atoms that form the local environment of the Si atom. The lowest frequency has been reported at 2000 cm⁻¹ in amorphous Si (here after a-Si) films^{1,2)} and the highest at 2300 cm⁻¹ for molecular hydrogen chemisorbed on highly dehydrated silica.³⁾ In an amorphous silicon nitride (Si₃N₄) film the SiH band stretching frequency has been observed at 2160 cm⁻¹.⁴⁾ In amorphous Si₃N₄ powders the SiH stretching vibration shifted from 2130 cm⁻¹ to 2174 cm⁻¹ by increasing the SiH₄/NH₃ ratio in the production process.⁵⁾ By increasing the [N]/[Si] ratio in a-SiN:H alloys the stretching vibration frequencies of SiH bonds wavenumber change from 2010 cm⁻¹ to 2172 cm⁻¹. These values are in agreement with the values calculated by the chemical induction model for H-SiSiSiSi and H-SiNNN configurations, respectively.⁶⁾ Viard et al. calculated the frequency of Si-H bonds considering H-SiXYZ tetrahedrals with XYZ corresponding to Si, N, and O atoms or OH, NH, NH₂ groups in different configurations that compared well with the experimental results obtained for a-SiO_xN_y:H films.⁷⁾ The SiH stretching and bending absorbance frequencies in hydrogenated silicon sub-oxides (a-SiO_x:H alloys systems) have been investigated by infrared absorption spectroscopy as a function of the [O]/

[Si] ratio of the suboxide matrix itself; *r*. It was shown that the frequency of the SiH bond depends not only on the sum of the electronegativity of the nearest neighbor atoms of the local environment (H-SiSi_{3-n}O_n with *n* = 0 to 3), but also on the average electronegativity of the host SiO_r network.⁸⁾ The chemisorption of molecular hydrogen on highly dehydrated silica showed the presence of =SiH₂ groups with stretching vibration at 2287–2300 cm⁻¹.³⁾ In the present work the infrared spectral characteristics of seven commercial Si₃N₄ powders in the Si-H stretching vibration region are investigated.

2. Experimental

Diffused reflectance infrared Fourier transform (DRIFT) spectra of seven commercial Si₃N₄ powders, produced by different processes as shown in **Table 1**, were obtained using a Shimadzu FT-IR 8300 spectrometer equipped with a TGS (Triglycine Sulfate) detector and data processing software. The spectra were measured in the 400–4000 cm⁻¹ region at 4 cm⁻¹ resolution and 256 scan-

Table 1. Production Processes and Specifications of the Seven Commercial Silicon Nitride (Si₃N₄) Powders

Nomenclature	Oxygen content/mass%	Specific surface area/m ² g ⁻¹	Synthesis method	Nitridation media
A1	1.05	10.2	Silicon diimide precipitation	NH ₃ (l)
A2	0.98	9.2		NH ₃ (g)
B1	1.88	11.6	Carbothermal reduction and nitridation	N ₂
B2	2.45	6.5		NH ₃ (g)
C4**	0.66	8.5	Nitridation of silicon	N ₂
C5*	0.83	3.9		N ₂ + H ₂
C6**	0.78	11.6		N ₂ + H ₂

* Crushed

** Crushed and washed by HF acid and water

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Fig. 1. Common scale DRIFT spectra of the seven different Si₃N₄ powders in the SiH stretching band frequency region. Symbols correspond to the powders nomenclature shown in Table 1. All powders show H-Si bands.

ning times in dry air atmosphere. For each powder seven spectra were obtained for different samples, and then averaged. The DRIFT spectra were recorded using a diffused reflectance accessory and macro sample cup.

An Al mirror was used to obtain the background spectra. The samples and background spectra were collected in power mode and stored as single beam spectra for further processing. The spectral bands were separated using a Jandel peak separation and analysis software in log(1/R) units.

3. Results and discussions

The DRIFT spectra in the SiH_x stretching region (2300–2000 cm⁻¹) obtained for the seven Si₃N₄ 100% powder samples is shown in Fig. 1. The figure shows that SiH_x absorbance bands are present in all powders, but the spectral patterns are not identical. The absorbance band at wave numbers lower than 2200 cm⁻¹ is similar in all powders. In contrast, the biggest difference is observed in the higher wave numbers bands.

The spectra shown in Fig. 1 were deconvoluted using a Jandel peak fit and analysis software. The results are shown in Fig. 2. The wave numbers obtained from the peak separation of the spectra for all powders and possible assignments for the other three neighbor atoms of the H-Si in the tetrahedral configuration are listed in Table 2. The highest intensity peak obtained for each powder is underlined. For all powders, except for the powder produced by the carbothermal reduction method using N₂ as nitridation media (B1), the highest absorbance peak has a frequency of about 2102 cm⁻¹ assigned to a H-SiSiSiO tetrahedral configuration. In the case of the B1 powder the band observed at 2266 cm⁻¹ assigned to a H-SiOOO configuration is slightly higher. All powders except the B1 powder show the presence of H-SiSiN(NH₂) tetrahedral configurations. This powder presents the lowest NH₂ groups content.^{9,10} Only two powders the one produced by the carbothermal reduction process using NH₃ gas as nitridation media (B2) and the one produced by direct nitridation of silicon using a mixture of N₂ + H₂ as nitridation media without final acid washing treatment (C5) show tetrahedral configurations which include NO as neighbor atoms of the H-Si group as seen in Table 2. In addition powder B2 and all the powders produced by the direct nitridation of silicon method (C powders) show a band at about 2286 cm⁻¹. A similar band has been observed for chemisorbed molecular hydrogen on highly dehydrated silica and assigned to H₂Si group.³

The H-Si bands listed in Table 2 can be classified consider-

Table 2. Wavenumbers of the SiH Stretching Bands Obtained by Deconvoluting the Spectra Shown in Fig. 2 and Possible Neighbor Atoms Configurations Assignments. The Highest Intensity Peak of Each Powder is Underlined

H-Si bands wave numbers, ν/cm ⁻¹							Neighbor atoms configurations of the H-SiXYZ tetrahedral
A1	A2	B1	B2	C4	C5	C6	
2013	2013	2013	2012	2013	2013	2013	SiSiSi ^[7]
2062	2062	2061	2061	2061	2061	2061	SiSi(NH) ^[7]
2087	2088	2085	2086	2086	2086	2086	SiSiH ^[7]
<u>2102</u>	<u>2104</u>	2103	<u>2100</u>	<u>2101</u>	<u>2103</u>	<u>2102</u>	SiSiO ^[7]
2121	2122		2119	2120	2122	2122	SiN(NH ₂) ^[7]
2162	2160	2160	2160	2160	2160	2160	SiON ^[7]
			2205				NN(OH) ^[7]
					2210		NO(NH ₂) ^[7]
			2214				NO(NH) ^[7]
			2235				NON ^[7]
			2225	2225	2224		OO(NH ₂) ^[7]
			2243	2245	2247		OO(OH) ^[7]
2268	2267	<u>2266</u>	2267	2267	2270	2267	OOO ^[7]
			2288	2282	2286	2281	OOH ^[3]

ing the backbone atoms of the H-Si into four main H-SiXYZ tetrahedral configurations by fixing the XY atoms and several possibilities for Z as follows: silicon-based; H-SiSiSi(Z = Si, NH, H or O), nitride-based; H-SiSiN(Z = NH₂ or O), oxynitride-based; H-SiNO(Z = N, NH or NH₂) and silica-based; H-SiOO(Z = NH₂, OH, O or H).

The summation of absorbance intensity fractions obtained from the deconvoluted spectra for the bands within each group are shown in Fig. 3. The proportions of different configurations vary among the powders but the largest fraction observed for all powders corresponds to H-SiSiSi(Si; NH; H; O) configurations. The powder produced by the diimide precipitation process using NH₃ gas as nitriding media (A2) shows the highest fraction of all powders (83.6%) which is similar to the powder produced by the direct nitridation process using a mixture of N₂ + H₂ as nitriding media with HF acid washing as final treatment (C6), (81.9%). For the Si₃N₄ powder produced by the carbothermal reduction process using N₂ as nitridation media (B1) the intensity fraction is the lowest (48.1%) and comparable to the H-SiOO(NH₂; OH; O; H) (50.8%) which is slightly higher as previously stated. This is the largest H-SiOO(NH₂; OH; O; H) configuration absorbance fraction of all powders mean while the powder produced by the diimide precipitation process using NH₃ gas as nitriding media (A2) shows the lowest (2.9%). The powder produced by the diimide precipitation process using NH₃ liquid as nitriding media (A1) presents the highest fraction of H-SiSiN(NH₂; O) configurations (18.6%). For the diimide precipitation process the use of NH₃ gas (A2) instead of liquid (A1) as nitriding media results in an enhancement of Si rich tetrahedral configurations. The same is observed for the carbothermal process when NH₃ gas (B2) is used instead of N₂ (B1). In the case of the direct nitridation of silicon process the final acid treatment considerably reduces the presence of O rich configurations if powder C5 that is not washed is compared with powder C6 that is acid washed.

The absorbance intensity fractions of each H-Si band are shown in Figs. 4(a), (b), (c) and (d) for SiSi(Si; NH; H; O), SiN(NH₂; O), NO(N; NH; NH₂) and OO(NH₂; OH; O; H) back bond configura-

Fig. 2. Deconvolution of the spectra shown in Fig. 1. The results show the presence of tetrahedral with various atoms Si, H, N, O or groups OH, NH, NH₂ that bond to the same silicon. The wavenumbers and possible assignments are listed in Table 2. Symbols correspond to the powders nomenclature shown in Table 1. Production methods and nitriding media are also indicated.

tions, respectively. Figure 4(a) indicates that the largest fraction for all powders corresponds to the SiSiO configuration, followed by the SiSiH. In the case of tetrahedral containing SiN the powders produced by the diimide precipitation process A1 and A2 present the highest absorbance intensity fractions of all powders. For all powders except the powder produced by the carbothermal reduction process using N₂ as nitriding media (B1) the highest fraction corresponds to the SiN(NH₂) backbone configuration as seen in Fig. 4(b). NO based configurations are observed only in powders B2 and C5 and the fractions are very small Fig. 4(c). Within the OO configurations the powder produced by the carbothermal reduction process using N₂ as nitriding media (B1) and

the two powders produced by the silicon diimide precipitation method (A1 and A2) show only the H-SiOOO tetrahedral units. On the other hand, the other powders show a large proportion of H-SiOOH tetrahedral as seen in Fig. 4(d).

Table 3 presents a summary, which includes only the three major tetrahedral configurations for each powder. From this table it is observed that two powders, A2 and C6, even though are produced by two different starting materials, Si(NH₂) and Si and using two different nitriding media, present a close distribution of tetrahedral configurations, meanwhile the powders produced by the same process and the same starting material SiO₂, B1 and B2, but using a different nitriding media have very different tetrahedral config-

Fig. 3. Absorbance intensity fraction of four SiSi(Si; NH; H; O), SiN(NH₂; O), NO(NH₂; NH; N) and OO(NH₂; OH; O; H) groups of tetrahedral configurations for all powders. The largest intensity observed for all powders is in SiSi(Si; NH; H; O) except for the powder produced by the carbothermal reduction process using N₂ nitriding media (B1) which shows comparable fraction in the OO(NH₂; OH; O; H) configurations.

urations. In the case of the direct nitridation process there are two factors affecting the composition of the surface, one is the use of N₂ + H₂ mixture instead of N₂ and the second is the washing by HF as final treatment. The powder produced with the mixture of N₂ + H₂ and washed by HF acid (C6) does not show a substantial amount of silica based tetrahedral units meanwhile the other two powders, C5 that is not washed by acid and C4 that was produced using only N₂ do.

All powders, except the powder produced by the carbothermal reduction process using N₂ as nitriding media (B1), present H-Si groups linked to Si rich rather than O rich tetrahedral units. The use of hydrogen in the form of ammonia, H₂ gas mixed with N₂ or as an acid final treatment seems to reduce the oxygen content of the surface layer where the H-Si groups are present.

4. Summary and conclusions

H-Si absorbance bands were identified and quantified by DRIFT for seven commercial Si₃N₄ powders. The wave numbers of the H-Si absorption bands obtained by deconvolution of the spectra show the presence of tetrahedral units with different atoms

Fig. 4. Absorbance intensity fraction of different neighbor atoms configurations in each group for all powders. The combination of H-SiXYZ tetrahedral with different configurations and proportion are different in each powder. These differences relate to the production process, nitridation media and further treatment.

Table 3. Absorbance Intensity Fraction (%) of the Three Main H-SiXYZ Tetrahedral Configurations Obtained from Fig. 4 for All the Powders

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) *
Tetrahedral unit	%						
H-SiSiSiO	47	57	24	54	41	35	54
H-SiSiSiH	20	22	17				21
H-SiSiN(NH ₂)	13	11		10	9		8
H-SiOOH				12	19	12	
H-SiOO(OH)						14	
H-SiOOO			51				

(O, N, Si, H) and groups (NH, NH₂, OH) configurations, which bond to the same silicon atom (Table 2).

All powders except the powder produced by the carbothermal reduction process using N₂ as nitriding media (B1) present the largest fraction H–Si groups linked to Si rich rather than to O rich tetrahedral units (Table 3).

The use of hydrogen in the form of ammonia, added to N₂ or as an acid final treatment appears to reduce the oxygen content of the surface layer where the H–Si groups are present.

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References

- 1) Fameli, G., Della Sala, D., Roca, F. and Gerardi, C., *J. Non-Cryst. Solids*, Vol. 198–200, pp. 69–72 (1996).
- 2) Miyoshi, Y., Yashida, Y., Miyozaki, S. and Hirose, M., *J. Non-Cryst. Solids*, Vol. 198–200, pp. 1029–1033 (1996).
- 3) Morterra, C. and Low, M. J. D., *Chemical Communications*, pp. 1491–1493 (1968).
- 4) Luongo, J. P., *Applied Spectroscopy*, Vol. 38, pp. 195–199 (1984).
- 5) Ho, P., Buss, Richard J. and Loehman, R. E., *J. Mater. Res.*, Vol. 4, pp. 873–881 (1989).
- 6) Aivazov, A. A., Budaruan, B. G. and Stryahilev, D. A., *J. Non-Cryst. Solids*, Vol. 167, pp. 185–191 (1994).
- 7) Viard, J., Beche, E., Durand, J. and Berjoan, R., *J. Eur. Ceram. Soc.*, Vol. 17, pp. 2029–2032 (1997).
- 8) Tsu, D. V., Lucovsky, G. and Davidson, B. N., *Physical Review B*, Vol. 40, pp. 1795–1805 (1989).
- 9) Hien, T. T. T., Ishizaki, Ch. and Ishizaki, K., *J. Ceram. Soc. Japan*, Vol. 111, pp. 28–32 (2003).
- 10) Nakamatsu, T., Ishizaki, Ch. and Ishizaki, K., “Ceramic Engineering and Science Proceedings,” Vol. 19, Am. Ceram. Soc. (1998) pp. 3–10.