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Silicon Nitride and Oxide Powder Surface Characterization by TPD

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Abstract

Surfaces of silicon nitride powders produced by three different production processes were analyzed by temperature programmed desorption (TPD) technique. The main desorbed species detected in the temperature range 40–1300°C are H_2, H_2O, NH_3 *and* N_2 *from* Si_3N_4 *and* Si_2N_2O *powders, and* H_2 *and* H_2O *with small amounts of* N_2 *from SiO,* SiO_2*(am and c). Powders SiO and* SiO_2*(am) show much larger desorption quantities than the other powders investigated. The distributions of desorbed species fractions reflect the production process and nitridation media. Powders produced using* N_2 *are strongly affected by the final treatment. Heating in air produces a powder with large amount of –OH groups (B1), meanwhile acid and water washings reduce the –OH groups and increase* $-NH_2$ *and =NH groups (C5, C6). For a powder using* $NH_3(g)+CH_4$ *as nitridation media, the heat treatment in air does not seem to increase –OH (B2), however shows similar desorption distribution to the powder using* $NH_3(g)$ *as nitridation media, but produced by a different method (A2). The use of* $NH_3(l)$ *appears to enhance the formation of surface groups which evolve as* NH_3 *and* N_2*, with respect to the use of* $NH_3(g)$ *(A1). © 1998 Elsevier Science Limited. All rights reserved*

1 Introduction

Raw powder surface of silicon nitride is well known to govern manufacturing and properties of final products, e.g. for mixing behavior (sometimes colloidal mixing) with additives,[1] fluidity,[2] and sintering behavior and mechanical strength.[3,4] The surface states of silicon nitride and oxynitride powders have been characterized by a lot of surface analytical techniques. Fourier transform infrared spectroscopy (FT–IR) studies,[5,6] have been applied to specify the kinds of surface groups such as $SiNH_2$, Si_2NH, SiOH, SiH and SiH_2 as shown in Fig. 1, and electron spectroscopic analysis (e.g. Ref. 7) for the relative quantification of bondings between silicon and oxygen or nitrogen. Temperature programmed desorption (TPD) technique is a well established analytical method for qualitative and quantitative analysis by observing desorbed molecules and its activation temperature for catalysts. Another advantage of TPD is the higher sensitivity for hydrogen and hydrogenated species compare to electron spectroscopy.

According to Kawamoto,[8] UHV type TPD have been firstly applied to evaluate powder surfaces of Si_3N_4, in 1989. Eleven types of commercial Si_3N_4 powders, which are two diimide precipitate powders, two carbothermal nitride powders and seven direct nitride Si_3N_4 powders commonly used, were evaluated by TPD from room temperature to 1000 K. A topic of their analysis is that the amount of H_2O desorption linearly increases as the oxygen content of Si_3N_4 powders increases. Another topic of Kawamoto's dissertation is that the bulk oxygen content of Si_3N_4 powders were also evaluated by extracting surface oxygen of the Si_3N_4 powders in aqueous environment. It is also reported that an aqueous environment causes to increase fluidity of commercial Si_3N_4 powders.[9] Kawamoto proposed reaction mechanism of the surface groups on the Si_3N_4 powders surfaces during heating, using the surface groups on Si_3N_4 powders reported by Ramis *et al.*[5] He could not conduct precise quantification of surface species on Si_3N_4 powders, since background m/e 28 spectrum remained and their TPD apparatus could not achieve high enough temperatures to observe

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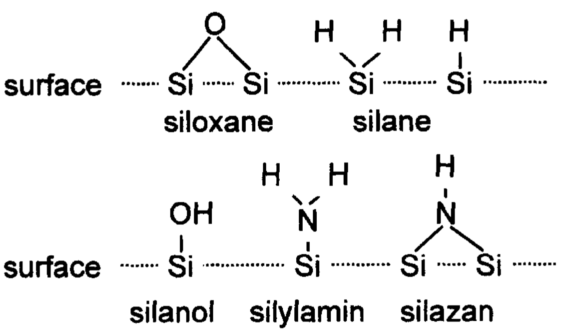


Fig. 1. Surface groups on Si_3N_4 and Si_2N_2O powders, identified by FT-IR. Reported by Ramis *et al.*[5] and Busca *et al.*[6]

complete desorption. Improving the heating system in the TPD apparatus, Si_3N_4 powder surfaces are analyzed up to 1450°C, which is a high enough temperature to discuss complete desorption before decomposition.

2 Experimental Procedure

Seven commercial Si_3N_4 powders produced by three kinds of production process commonly used are investigated in this report. Detailed production processes are shown in Table 1, and nomenclatures and powders used are same as Kawamoto's study except A1 which was replace with the powder synthesized in a different lot. Powders A1 and A2 were produced by the silicon diimide precipitation process. Powder A1 was synthesized by using liquid ammonia (NH_3), and A_2 was by gaseous NH_3. Powder B1 was synthesized by carbothermal reduction process using nitrogen (N_2) gas and carbon, and B2 by NH_3 and methane (CH_4). Powders C4 to C6 were synthesized by direct nitridation process of silicon using N_2(g) for C4, N_2(g) and H_2(g) mixture (9:1) for C5 and C6. Powders C4 to C6 were crushed after nitridation, and C4 and C6 were washed by acid and water to remove contamination during milling. Four kinds of silicon oxide powders, silicon monoxide (SiO), amorphous and crystalline (quartz) silicon dioxide [SiO_2 (am) and (c), respectively] and silicon oxynitride (Si_2N_2O), are examined for comparisons with the raw Si_3N_4 and for investigations of the surface oxide layers.

The SiO, SiO_2 (am) and SiO_2 (c) powders used are commercial products of Aldrich Chemical Company Inc., Nakarai Chemicals Ltd., and Soekawa Chemicals, respectively. Ube Industries, Ltd specially manufactured the Si_2N_2O powder. It was synthesized by the reaction between silicon dioxide powder (Merk Co.) and silicon nitride powder (Ube). The silicon nitride powder used to synthesize the oxynitride, is amorphous and produced by silicon diimide precipitation. The two raw materials are reacted at 1900 K in nitrogen gas for one hour. The specific surface areas (SSA) of all powders were measured by BET isothermal adsorption technique.

About 15 mg of powder sample is placed in a molybdenum capsule of 3 mm in diameter and 10 mm in height. Each sample is initially located in a chamber pre-evacuated to 10^{-5} Pa, and transferred into an ultra-high vacuum chamber under 10^{-6} Pa, and heated up to 1450°C at a constant heating rate of 20 K min^{-1}. During the heating of the sample powders, the partial pressures of desorbed gases which are generated by the reactions and desorbed from powder surfaces are measured by a quadrupole mass spectrometer. Thus, TPD spectra of the powders were obtained.

Obtained partial pressure spectra is converted into desorption rate, r_d, which is the number of desorbed molecules per unit surface area per unit time. Considering ideal gas flow eqn (1) is obtained,

$$r_d(t) = \frac{S}{AkT}P(t) \qquad (1)$$

where S is pumping speed, A the surface area of the sample, k Boltzmann constant, T the temperature

Table 1. Production processes for Si_3N_4 powders used in this study

Synthesis method		*Chemical reaction*	*Sample nomenclature*	*O (mass%)*	*SSA (m^2g^{-1})*	*Normalized O content (mass% SSA^{-1})*
Silicon diimide precipitation	NH_3 (l or g)	$3SiCl_4 + 6NH_3 \rightarrow 3Si(NH)_2 + 4NH_4Cl$	A1(l)	1·05	10·2	0·10
		$3Si(NH)_2 \rightarrow Si_3N_4(am) + 2NH_3$	A2(g)	0·98	9·2	0·11
		$Si_3N_4(am) \rightarrow Si_3N_4(c)$ (heat treatment in N_2)				
Carbothermal reduction	N_2	$3SiO_2 + 6C + 2N_2 \rightarrow Si_3N_4 + 6CO$ heat treatment in air	B1	1·88	11·6	0·16
	NH_3	$3SiO_2 + 6CH_4 + 4NH_3 \rightarrow Si_3N_4 + 6CO + 18H_2$ heat treatment in air	B2	2·45	6·5	0·38
Nitridation of silicon	N_2	$3Si + 2N_2 \rightarrow Si_3N_4$	C4	0·66	8·5	0·08
		crushing	C5[a]	0·83	3·9	0·21
		washing by acid and water (C4, C6)	C6[a]	0·78	11·0	0·07

l, Liquid; g, gas; am, amorphous; c, crystal.

[a] N_2 and H_2 (10%) mixture gas is used.

in the vacuum chamber, P the partial pressure of the species in the chamber by desorption and t is time.[10]

Thus, the number of desorbed molecules, n, is obtained by integrating the desorption rate and time as:

$$n = \int_{t\min}^{t\max} r_d(t)\mathrm{d}t = \frac{S}{AkT}\int_{t\min}^{t\max} P(t)\mathrm{d}t \qquad (2)$$

Obtained TPD spectra consist of several different desorption stages, e.g. different bonding energy or different surface species. Therefore the temperature and quantity of desorption of each stage may reflect the surface of the powder. For this purpose, obtained TPD spectra are resolved into primary spectra, which are approximated to Lorentzian. Davidon–Fletcher–Powell (DFP) method is used for convergent calculation.[11]

3 Results

Sample temperature and partial pressure of the desorbed gases whose masses are 2, 12, 14, 15, 16, 17, 18, 27, 28, 29, 32 and 44 as fragments of hydrogen (H_2), ammonia (NH_3), water (H_2O), carbon monoxide (CO), nitrogen (N_2), oxygen (O_2), silicon (Si), and silicon monoxide (SiO) molecules are recorded. Obtained partial pressures are normalized into desorption rates (the number of desorbed molecules per unit time and unit area) by eqn (1). The partial pressures of major desorbed species, H_2, NH_3, H_2O and N_2 molecules are calculated with their cracking patterns[12] and relative sensitivity of the mass spectrometer. Processed TPD spectra from Si_3N_4 powders and oxide powders as reference are shown in Figs 2 and 3, respectively. The total number of desorbed molecules per unit surface area is also calculated by integrating the desorption rate by eqn (2). The total numbers of H_2, NH_3, H_2O and N_2 up to 1300°C for all the Si_3N_4 powders investigated, as well as those of the oxides are shown in Fig. 4. Fractions of desorbed molecules H_2, NH_3 and H_2O to the total of the three are shown in Fig. 5 as a three phase diagram.

4 Discussion

Possible desorption reactions to account for the observed H_2O, NH_3 and H_2 desorption patterns of the Si_3N_4 powders are summarized and listed in Table 2. This task is an extension of the reactions previously proposed by Saito.[13] In addition, the reaction, $SiONH_4^+ + SiOH \rightarrow Si_2O + H_2O + NH_3$, proposed by Kawamoto[7] may take place as the lowest temperature reaction in this table.

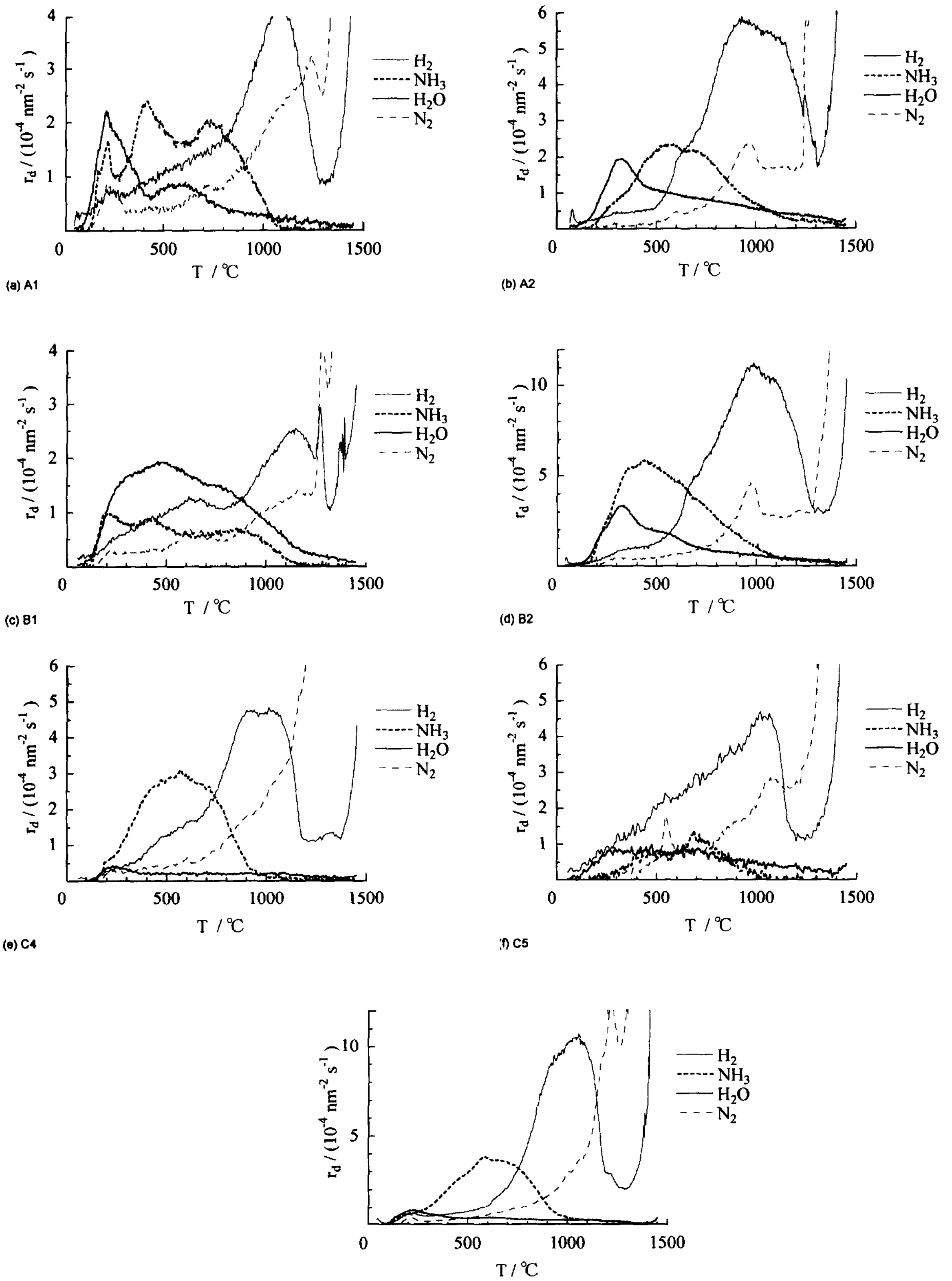
4.1 H_2 desorption

The large quantity of H_2 desorption compared to the one of H_2O observed for the SiO powder may be explained by the secondary ion mass spectroscopy (SIMS) study of water adsorbed states on bare silicon and native silicon oxide using heavy water by Yabumoto *et al.*[14] The result shows deuterium concentration on bare Si is 1 digit higher than native oxide, even though the shapes of spectra are similar to each other. The SiO powder which has high silicon concentration and probably many dangling bonds due to its meta-stableness may have a lot of SiH species in its surface and bulk. In our TPD experiment, H_2 desorption spectrum from examined SiO powder has 4 major peaks at 212, 400, 541 and 803°C. Considering that reported H_2 desorption spectra from hydrogen terminated Si show wide peaks around 400–500°C,[15] the observed peaks of the H_2 TPD spectrum from the examined SiO powder at around 200°C might be generated from SiH_2, the 400°C peak from vicinal SiH, the 541°C from isolated SiH and the 803°C from SiH in the bulk. Therefore H_2 desorption involving SiH_2 or SiH may occur around these temperatures and the peaks at higher temperatures may involve, e.g. cleavage of O–H or N–H bonds. The H_2 desorption from Si_3N_4 powder may involve at least SiH, SiOH, $SiNH_2$ and Si_2NH, however we could not specify the reactions for each temperature. Probably the reactions relate to the density of surface groups at each temperature and further investigation is necessary with other analytical techniques.

4.2 H_2O desorption

H_2O desorption from hydroxylated silica, $2SiOH \rightarrow Si_2O + H_2O\uparrow$, is well known. SiO_2(am), SiO_2(c) and SiO powders show high desorption peaks below 400°C in agreement with a desorption temperature around 170–400°C.[16] Up to around 1100°C, at which H_2O desorption from SiO_2(c) almost finishes, isolated SiOH groups generate H_2O continuously. However large quantity of total desorbed H_2O from SiO_2(am) powder, 5·4 H_2O from 10·8 SiOH, is much larger than the theoretical number (4–6·7 SiOH groups/nm^{-2} for fully hydroxylated SiO_2[17]), which suggests the participation of underlying molecules(e.g. buried surface groups or surface groups in micro pores which N_2 gas can not penetrate during BET surface area measurement) in their desorption especially around 950°C.

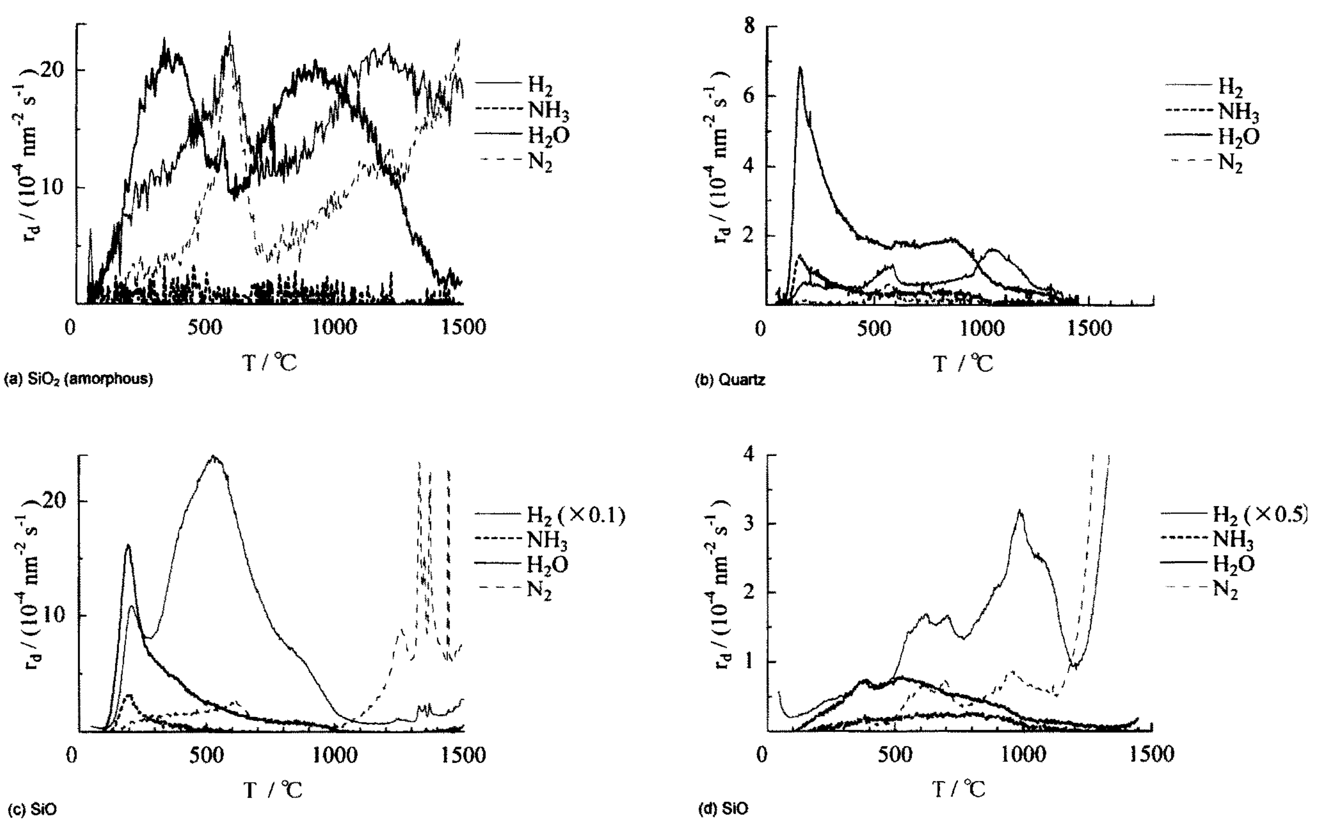
SiH groups are involved in the H_2O desorption in the condensation reaction with SiOH. From a



(a) A1 (b) A2 (c) B1 (d) B2 (e) C4 (f) C5

Fig. 2. (a)–(g) Processed TPD spectra from Si_3N_4 powders. Obtained partial pressure is converted to numbers of desorbed molecules by eqn (2) with cracking patterns and relative sensitivity of mass spectrometer. Thus desorption rate, rd is calculated for each species. Please note the difference of ordinates which are normalized by SSA. All Si_3N_4 powders show appearance of $^{29}Si^+$ intensity around 1300°C, which might be the result of a part of surface decomposition. Further study for this decomposition phenomenon will be reported elsewhere.

study of NH_3 nitridation of SiO_2 by Brow and Pantano,[18] the reactions between $SiNH_2$ and SiOH, and Si_2NH and SiOH produce H_2O. In the reactions to desorb H_2O, SiOH performs still important role, however $-NH_2$ and $=NH$ surface groups should be involved. The temperature for each reaction is not specified, however, the reactions can be ordered with respect to temperature considering Brow's work and condensation change of $SiNH_2$ to Si_3–N via Si_2NH as the temperature



(a) SiO_2 (amorphous) (b) Quartz (c) SiO (d) SiO

Fig. 3. (a)–(d) Processed TPD spectra from silicon oxide powders. NH_3 desorption spectra do not appear in SiO_2 (am and c) and SiO due to no nitrogen in their components. The H_2 and H_2O desorption rates from SiO_2(am) powder and H2 from SiO powder are much higher than those from other powders.

increases. Kawamoto studied the same powder, Powder A1, but from a different synthesis lot. This author reported a rapid increase of $NH_4{}^+$ concentration in the water during aqueous washing. Interpreting this result together with his TPD analysis, Kawamoto proposed the presence of $SiONH_4{}^+$ surface groups.[8] In our TPD analyses, a very similar feature in Powder A1, the sharp H_2O and NH_3 desorption at low temperature (around 200°C) at the same time, may be from the following reaction proposed by Kawamoto:

$$SiONH_4^+ + SiOH \rightarrow Si_2O + H_2O + NH_3 \qquad (3)$$

which desorbs both of H_2O and NH_3 at the same time.

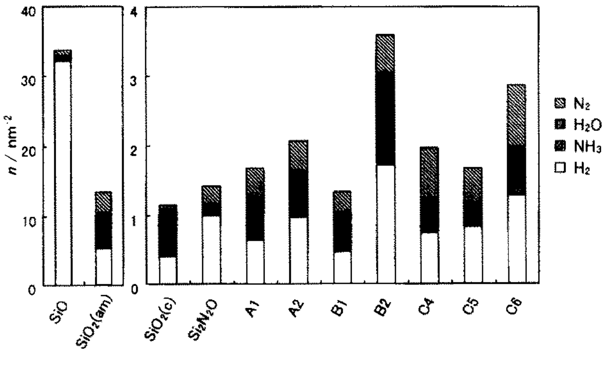


Fig. 4. Total quantity of each desorbed species.

4.3 NH_3 desorption

NH_3 is mainly produced by the reactions between $2SiNH_2$, or $SiNH_2$ and SiNH groups. The former reaction (between $2SiNH_2$) occurs at lower temperature than the latter reaction. Therefore Powders

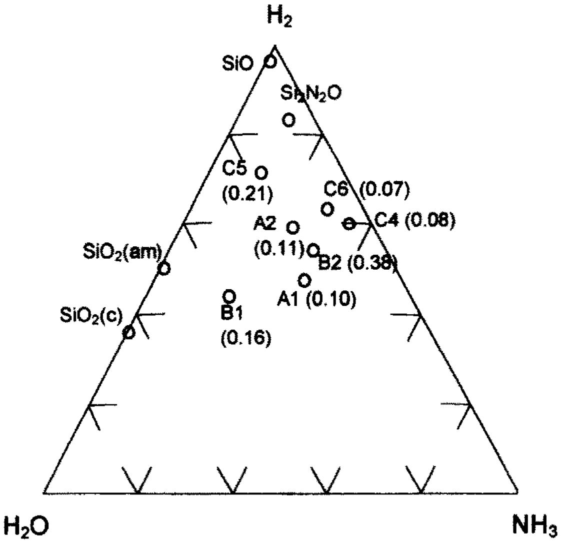


Fig. 5. Fraction of each desorbed species to the total of desorbed H_2, H_2O and NH_3 molecules. The numbers indicated in brackets after sample nomenclatures are the normalized oxygen content by SSA (mass%/m^2 g^{-1}). Normalized oxygen content can not explain the fractions of desorbed species independently. However similarity in the same nitridation media in production process can be found by the location within the triangle (see text).

Table 2. Proposed desorption reactions for H_2O, NH_3 and H_2 modified Saito's proposal.[13] In addition, the reaction, $SiONH_4^+ + SiOH \rightarrow Si_2O + H_2O + NH_3$, proposed by Kawamoto[7] may take place as the lowest temperature reaction in this table

Desorbed species		*H_2O*		*NH_3*		*H_2*		*N_2*	
		Reactants	*Products*	*Reactants*	*Products*	*Reactants*	*Products*	*Reactants*	*Products*
Temperature range (°C)	Increasing temperature	2SiOH	Si_2O	$2SiNH_2$	Si_2NH	$2SiH_2$	2SiH		
		$SiNH_2 + SiOH$	Si_2NH						
		SiOH + SiH	$2Si^+$	$SiNH_2 + SiH$	$2Si^+$	$SiH + Si_2NH$	$Si^+Si_2N^+$		
		$SiOH + Si_2NH$	$Si^+ + Si_2N^+$	$SiNH_2 + Si_2NH$	$Si^+Si_2N^+$	2SiH	$2Si^+$		
		(From isolated)		(From isolated)		(From isloated)			
		2SiOH	Si_2O	$SiNH_2 + Si_2NH$	$Si^+Si_2N^+$	2SiH	$Si^+Si_2N^+$	$2Si_2N^+$	4Si
		$SiOH + Si_2NH$	$Si^+ + Si_2N^+$			$SiH + Si_2NH$	$Si^+ + Si_2N^+$		

B1, B2 and C5 [A1 should be eliminated due to different reaction eqn (3)] which start to desorb NH_3 at low temperature may have more $SiNH_2$ groups than Si_2NH compare to other powders. SiH groups are also involved in the NH_3 desorption in the condensation reaction with $SiNH_2$.

4.4 Quantification and qualification

The main desorbed species detected by TPD analysis in the temperature range 40–1300°C are H_2, H_2O, NH_3 and N_2 from Si_3N_4 and Si_2N_2O powders, and H_2 and H_2O with small amounts of N_2 from SiO, SiO_2(am and c).

Quantities of desorbed H_2, NH_3, H_2O and H_2 molecules from each powder are shown in Fig. 4. Total desorbed molecules from SiO and SiO_2(am) powders are much larger than other powders and very far from the desorption behaviors showing by other powders. Due to much more H_2O desorption from SiO_2(c) powder than Si_2N_2O and Si_3N_4 powders and presence of NH_3 desorption from Si_2N_2O and Si_3N_4 showed, obviously it is understood that Si_3N_4 powder surfaces are not completely oxidized or hydroxylated. Fraction of each desorbed species to the total quantity of desorbed H_2, H_2O and NH_3 molecules is plotted in Fig. 5. The numbers indicated in brackets after sample nomenclatures are the normalized oxygen content by SSA ($mass\%/m^2\,g^{-1}$). Normalized oxygen content can not explain the fractions of desorbed species, especially for H_2O, independently. The location on the triangle relates to oxygen related surface groups and hydrogen related groups. However the amount of desorbed NH_3 more relates to surface $-NH_2$ groups than total $-NH_2$ and $=NH$ groups.

To include all nitrogen related surface groups, total quantity of desorbed N_2 is added to total quantity of desorbed NH_3, and the desorption species fractions to the total desorbed H_2, H_2O and $NH_3 + N_2$ are plotted in Fig. 6. SiO shows the largest H_2 desorption fraction among all of the powders investigated (0·95) followed by Si_2N_2O (0·7). SiO_2(c) shows the largest H_2O desorption fraction (0·61) followed by SiO_2(am) (0·40).

The distributions of desorbed species fractions for the Si_3N_4 powders investigated appear to be more closely related to the nitridation media used in the production process and final treatment than the starting material itself, for instance Powders A2 and B2 using NH_3(g) as nitridation media but produced by two different nitridation methods show more similar distributions of desorbed species than B1 and B2, which are produced by the same method but use different nitridation agents [N_2 + C and NH_3(g) + CH_4, respectively]. The effect of final treatment is observed as follows.

Powders B1 and C4 use N_2 as nitridation media, but the final treatments are different. B1 is heat treated in air, meanwhile C4 is crushed, and washed by acid and water. The heat treatment apparently produces a large amount of –OH in Powder B1, and the washing of C4 reduces the amount of –OH if we compare with powder C5, which is not subjected to washing.

The use of NH_3(l) (A1) appears to enhance the formation of surface groups which evolve as NH_3 and N_2, with respect to the use of NH_3(g) which appears to produce more H_2 related surface groups as reflected by the results of A2 and B2 with respect to A1.

The TPD spectra of Si_3N_4 and Si_2N_2O powders are much more broad than those of SiO, SiO_2(am) and SiO_2(c) indicating a much more complex array

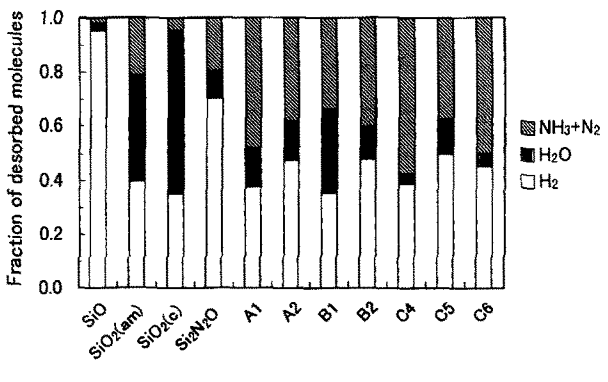


Fig. 6. Molecular fractions of each desorbed species to the total desorbed H_2, NH_3, H_2O and N_2. Total desorbed NH_3 and N_2 are added to account for the –NH and $=NH_2$.

of surface groups and desorption reactions among them. Possible reactions which may explain the desorption of the species recorded were presented in Table 2. However specific temperature assignment for each reaction were not possible with the present spectra, and further investigation is needed.

Total desorbed molecules from SiO and SiO_2(am) powders are much larger than the theoretical number of site (4–6·7 SiOH/nm^{-2} for fully hydroxylated SiO_2[17]), which suggests the participation of underlying molecules (e.g. buried surface groups or surface groups in micro pores which N_2 gas can not penetrate during BET surface area measurement) in their desorption. Due to much more H_2O desorption from SiO_2(c) powder than Si_2N_2O and Si_3N_4 powders and presence of NH_3 desorption from Si_2N_2O and Si_3N_4 showed, obviously it is understood that Si_3N_4 powder surfaces are not completely oxidized or hydroxylated.

5 Conclusions

TPD spectra from Si_3N_4 powders provide much information on the surface groups of raw powders, i.e. types and quantity of surface groups. The main desorbed species detected by TPD analysis of Si_3N_4 and Si_2N_2O powders in the temperature range 40–1300°C are H_2, H_2O, NH_3 and N_2. The main desorbed species from SiO, SiO_2(am), SiO_2(c) are H_2 and H_2O with small amounts of N_2. The SiO and SiO_2(am) shows much larger quantity of desorption compare to other powders.

The desorbed molecular fractions reflect the production process and nitridation media. In the case of the powders using N_2 as nitridation media, heat treatment in air increases –OH, and the acid and aqueous washings decrease –OH and increase =NH/–NH_2 groups. In the case of powder using $NH_3(g) + CH_4$ as nitridation media, the heat treatment in air does not increase –OH, however shows similar desorption distribution to the powder using same nitridation media, NH_3(g), but produced by different method. The use of NH_3(l) appears to enhance the formation of surface groups which evolve as NH_3 and N_2, with respect to the use of NH_3(g).

Due to the low heating rate used in our experiment, compared to the rates use in general TPD experiments for catalysis, the obtained spectra are very broad and made peaks separation difficult. New spectra are needed with an optimized heating rate to separate the peaks properly and differentiate all the different desorption mechanisms.

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