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Analysis of SiH and SiN vibrational absorption in amorphous SiN_x:H films in terms of a charge-transfer model

S. Hasegawa, L. He, Y. Amano, and T. Inokuma
Department of Electronics, Faculty of Technology, Kanazawa University, Kanazawa 920, Japan

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Amorphous SiN_x:H films were deposited at 300 °C by rf glow discharge of SiH_4-NH_3 mixtures, and the SiH and SiN stretching absorption were investigated as a function of the N content x. From the x dependence of the absorption intensity, the bonding structure was decomposed into five bonding units without H atoms and those with H atoms, on the basis of *a modified random-bonding model.* For each bonding unit, *the oscillator strength of the SiH absorption* and the SiH and SiN bond lengths were estimated from the values of the additional partial charge on the Si, N, and H atoms by using Sanderson's model. The peak wave numbers of the SiH and SiN absorptions were calculated by linking them to their respective bond-length values, a procedure which is based on an assumption that the force constant will be mainly controlled by the bond length. The effective SiH and SiN peak wave numbers for a given value of x, obtained as a statistical average of the calculated ones for individual bonding units, agreed well with the experimentally determined values. Also, peak shifts of the SiH absorption for various bonding units and those of the SiN absorption due to incorporation of SiH, SiN, and NH bonds are discussed in terms of the above charge-transfer model.

I. INTRODUCTION

Amorphous SiN_x:H (a-SiN_x:H) films deposited by plasma-enhanced chemical vapor deposition (PECVD) have attracted growing interest because of their potential for wide application in microelectronics, for example, as insulators in thin-film transistors[1–3] and in passivation layers.[4] Incorporated N atoms are bonded to three Si atoms for a relatively low N content (x in SiN_x) range,[5–7] and N atoms with two Si atoms and one H atoms as nearest neighbors occur at higher x.[8–10] Since these structural changes complexly affect the electronic and optical properties of the films, an understanding of the chemical bonding properties as a function of x becomes necessary. The chemical bonding structure can be examined by means of vibrational absorption[8–19] and photoemission[5–7,20] techniques.

The stretching absorption from SiN bonds occurs at 800–890 cm^{-1}.[9,15] In the case of N-ion-implanted SiN_x films, it has been reported that the main absorption for low x is a broad line with its peak between 750 and 800 cm^{-1},[12] and two separated lines at 766 and 963 cm^{-1}.[17] However, the films having high x displayed three separated lines at 845, 890, and 930 cm^{-1}.[14] Furthermore, pyrolytic Si_3N_4 films displayed a single broad line centered around 880 cm^{-1}.[11] In PECVD SiN_x:H films, including a few at. % nitrogen, formed at deposition temperature T_d as low as 100 °C, a SiN absorption band at 790 cm^{-1} has been observed, and an increase in T_d higher than 300 °C changed the absorption into a broad line centered around 840 cm^{-1}.[15] The peak wave number of this broad line increased from around 840 to 900 cm^{-1} as x increased.[16,19] The broad line for PECVD films, however, was able to be decomposed into two components at around 750- and 840-cm^{-1} bands for values of x lower than 0.2,[19] and those at around 840- and 960-cm^{-1} band for high x.[16,19]

The band above 750–800 cm^{-1}, which is observable for low x, will be assigned to isolated SiN bonds dispersed into a Si network, having only Si nearest and next-nearest neighbors.[15,19] The assignment of the 840- and 960-cm^{-1} bands is rather complex. Lucovsky *et al.*[15] suggested that the 840-cm^{-1} band arises from an N site in which there is at least one H atom as a second neighbor. On the other hand, Della Sala *et al.*[16] assumed that the 840- and 960-cm^{-1} bands are due to Si_3-SiN and N_3-SiN bonds, respectively. Furthermore, the present authors have recently proposed a model different from the above assignment: one in which the 840- and 960-cm^{-1} bands arise from Si-N(Si_2) and Si-NH-Si bonds, respectively.[10] This model and an origin of the 750–800 cm^{-1} band will be examined in more detail in this paper.

In PECVD a-SiN_x:H films, SiH stretching absorption at 2000–2200 cm^{-1} is observed, and its peak shifts toward a higher wave number with increasing x. In previous papers,[10,18] we have shown that the profiles of the SiH absorption can be decomposed into two components at around 2000 and 2100–2200 cm^{-1}. The 2000-cm^{-1} band is assigned to isolated SiH bonds without N atoms as nearest neighbors, and the intensity monotonically decreased with x. By contrast, the 2100–2200-cm^{-1} band increased with increasing x up to $x = 0.5$, and this indicates the increased formation of N-SiH bonds.[10,18] Above $x = 0.5$ this band decreased, accompanying a rapid increase in the density of NH bonds.[10] The dependence of this SiH and NH absorption as a function of x has been successfully interpreted in terms of a modified random-bonding (MRB) model including H atoms.[10]

The peak shifts of the SiN and SiH absorption are understood as indicating a change in the SiN and SiH bond length, which can be connected with additional charge on their respective atoms. Lucovsky[13] evaluated the elec-

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tronegativity sum (ENS), which reflects a change in the additional charge of the constituent atomic species bonded to SiH. As a result, it has been found that the SiH peak wave number is proportional to the ENS values. In this model, however, it is impossible to determine the conditions of the charge neutrality for given bonding systems. Furthermore, for the absorption from SiH and SiH_2 groups, the SiH and SiH_2 peaks as functions of the ENS values must be represented by their respective formulas, determined independent of each other. Furthermore, Yin and Smith[21] recently proposed a free-energy model (FEM) for interpreting the bonding properties in a-$Si_xN_yH_z$ and other Si-related alloys. This model will be a useful technique for analyzing formation of bonds such as Si-Si, Si-N, Si-H, and N-H as functions of y/x, if the H concentration is fixed. However, in the present films, the ratio of the density of H atoms to that of Si atoms, where the H atoms form Si-H and N-H bonds, increases from 8% to more than 100% as the N content x (in SiN_x) increased (this work and Ref. 10).

Moreover, incorporation of H atoms into films should be influenced by the presence of internal (intrinsic) stress in the films, which is related to the local bonding geometry.[22] This is because the stress will be relaxed by incorporation of H atoms which can only be singly coordinated.[22,23] In the above-mentioned MRB model, H atoms were imported into the films corresponding to a change in the local bonding geometry predicted by the random bonding model (RBM),[10] in contrast to the FEM.[21] Recently, we have shown that shifts of the Si 2p, N 1s, and O 1s core-level spectra with increasing x for a-SiN_x:H and a-SiO_x:H films can be interpreted in terms of a charge-transfer model (CTM) combined with the RBM,[7] in which the effective partial charge on the constituent atoms was estimated as a function of x, using Sanderson's electronegativity.[24] This charge transfer will cause shifts of the SiH and SiN absorption peaks.

In the present work, we investigate the dependence of the SiH and SiN absorption as a function of x for PECVD a-SiN_x:H films. For various bonding configurations based on the MRB model, the partial charge on Si, N, and H atoms in each configuration is estimated on the basis of the CTM. From a change in the SiH and SiN bond lengths determined using the values of these partial charges, the peak shifts of the SiH and SiN absorption are examined as functions of x. In Sec. II, we present a method for calculating SiH and SiN bond lengths and their absorption peaks. In Sec. III, we describe the experimental details of the sample deposition and a method of determining the density of SiH and SiN bonds from their absorption intensities. In Sec. IV, a change in the vibrational absorption of a-SiN_x:H films is investigated as a function of x. These experimental results are correlated with the calculated ones. In Sec. V, we summarize these results.

II. CHARGE-TRANSFER MODEL

A. Partial charge and bond length

Using Sanderson's model,[24] estimates of the SiH and SiN bond lengths (d_{SiH} and d_{SiN}), respectively, are approximated by summing the radii r_M (M = Si, N, or H) of Si and H or Si and N atoms as $d_{SiH}=r_{Si}+r_H$ or $d_{SiN}=r_{Si}+r_N$. Also, the values of r_M could be linearly related to partial charge δ_M on their respective atoms as follows:[24]

$$r_M=r_M(0)-B_M\delta_M \ . \tag{1}$$

Here, $r_M(0)$ is nonpolar covalent radius [$r_{Si}(0)=1.17$ Å, $r_N(0)=0.74$ Å, and $r_H(0)=0.32$ Å], and B_M is the empirical factor having a positive value. Accordingly, the value of d_{AB} in A-B bonds is given by

$$d_{AB}=d_{AB}(0)-B_A\delta_A-B_B\delta_B \ , \tag{2}$$

where, $d_{AB}(0)$ is the A-B bond length under the nonpolar conditions.

For an a-SiN_x:H film, if its bonding structure can be decomposed into some bonding units (minimum clusters) $Si_kN_mH_n$ holding charge-neutrality conditions within each bonding unit, the partial charge δ_M on the constituent M (Si, N, or H) atom can be estimated by[24]

$$\delta_M=(S_{BU}-S_M)/(2.08S_M^{1/2}) \ , \tag{3}$$

where

$$S_{BU}=(S_{Si}^kS_N^mS_H^n)^{1/(k+m+n)} \ . \tag{4}$$

Here, S_{Si}, S_N, and S_H, respectively, are the electronegativity of S, N, and H atoms as defined by Sanderson:[24] $S_{Si}=2.84$, $S_N=4.49$, and $S_H=3.55$. The value of S_{BU} is the effective electronegativity of the corresponding bonding unit. In Eq. (3), it is also assumed that the Si, N, and H atoms in each bonding unit occupy equivalent bonding sites, respectively. Therefore, the charge neutrality implies $k\delta_{Si}+m\delta_N+n\delta_H=0$. In a previous paper,[7] a more detailed examination of Eq. (3) and the validity of the RBM as a convenient way of decomposing the bonding structure into some bonding units have been demonstrated.

B. Absorption peaks

The peak wave number of absorption from an A-B bond can be determined from the values of its force constant and reduced mass, and the former force constant depends on the bonding geometry such as the bond length and bond angle. Lucovsky *et al.*[15] have calculated the peak wave number of SiN-related absorption, with the use of the inferred force constants for various bonds in cluster of intermediate size.[25] On the other hand, in the cases of both SiH and CH stretching absorption, it has been found that the scaling law between the wave number ν_{MH} (M = Si or C) and interatomic distance d_{MH} of M-H bonds is of the general form[26,27]

$$\nu_{MH}(d_{MH})^3=\text{const} \ . \tag{5}$$

For the SiH absorption, by applying the rule of Eq. (5) to the absorption observed for various Si substituents,[13,27] the constant ($=C_{SiH}$) has been estimated to be approximately 7074, using cm^{-1} and Å as units of ν_{SiH} and d_{SiH}, respectively. The relationship of Eq. (5) indicates that the force constants determining the stretching absorption peaks for SiH and CH groups are mainly controlled by their respective values of the bond length. Thus, if the wave number of the stretching absorption is determined by the bond length, it can be estimated from the values of the bond length in Eq. (2) through the relationship predicted by Eq. (5).

III. EXPERIMENT

A. Sample preparation

The samples were deposited on a single-crystal Si substrate by rf glow-discharge decomposition of a SiH_4-NH_3 mixture in a fused quartz reactor, employing inductive coupling of rf power, and inserted into an electric furnace set at 300 °C. The details of the deposition system have been described elsewhere.[28] The gas volume ratios $[NH_3]/[SiH_4]$ were varied from 0 to 30 under a fixed total flow rate of 10 cubic centimeter per minute at STP (SCCM) and a fixed pressure of 0.3 Torr. The supplied rf power was maintained at 10 W. These samples in the present work were the same as those in previous letters.[10,29] The N content x in SiN_x was determined from the intensities of Si $K\alpha$ and N $K\alpha$ signals using electron probe microanalysis (EPMA) in comparison with those from standards of boron nitride and single-crystal Si, using a well-known correction technique. The x values were also estimated from the N 1s and Si 2p core-level spectra in x-ray-induced photoelectron spectroscopy (XPS). The infrared vibrational spectra, using a Fourier-transform spectrometer (Nicolet 5DX), were measured at normal incidence. In these measurements, the typically 1.3-μm-thick films were used, and their thinnest and thickest values were approximately 1 and 2 μm, respectively. The refractive index n_r of the films was estimated from the multiple reflections in nonabsorbing regions around 800 nm of the optical absorption spectra. Figure 1(a) shows the n_r values as a function of the x values determined by EPMA. The values of n_r rapidly decrease from 3.6 to 2.2 as x increases over the range of x lower than 0.7, and then gradually decrease up to $n_r = 1.8$.

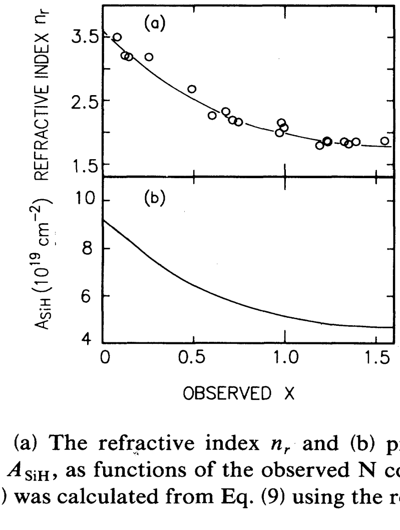

FIG. 1. (a) The refractive index n_r and (b) proportionality coefficient A_{SiH}, as functions of the observed N content x. The curve in (b) was calculated from Eq. (9) using the results in (a).

B. Absorption intensity

The density [SiH] of SiH bonds was estimated from the intensity I_{SiH} of SiH stretching absorption at 2000–2200 cm^{-1}, using the following relationship:

$$[SiH] = A_{SiH} I_{SiH} \ . \tag{6}$$

Here, A_{SiH} is the proportionality coefficient. The estimates of I_{SiH} were done using a method suggested by Brodsky, Cardona, and Cuomo (BCC).[30] However, Langford *et al.*[31] and Maley[32] have recently shown that estimation by the BCC method causes significant errors in the I_{SiH} values, which arise from effects of coherent multiple reflections in multilayer samples. The magnitude of the errors depends on the product ωd frequency ω of the vibrational mode and film thickness d, and its error (overestimate) becomes remarkable if the value of ωd is below a critical value $(\omega d)_c$ which can be determined as a function of the refractive index n_r.[32] Furthermore, the degree of this overestimate at the values of d close to zero increases with increasing n_r values, from less 10% for $n_r = 2$ to 70% for $n_r = 3.5$. Accordingly, as shown in Fig. 1(a), the effects of this optical interference will yield a significant error for films having x lower than 0.7, if their d values are thinner than a critical d_c value. For ωd greater than $(\omega d)_c$, the error in I_{SiH} is usually less than 10%, although the overestimate and underestimate change periodically as a function of ωd. As shown in Fig. 1(a), the values of n_r change from 3.6 for $x = 0$ to 1.8 for $x = 1.5$. The values of $(\omega d)_c$ have been shown to be approximately 0.11 for $n_r = 2.5$ and 0.06 for $n_r = 3.5$.[32] Accordingly, for the 2000–2200-cm^{-1} bands, the error in I_{SiH} will be less than 10% as the d values are greater than approximately 0.3 μm for $x = 0$ $(n_r = 3.6)$ and 0.6 μm for $x = 0.5$ $(n_r = 2.5)$. As stated above, the film thickness of the present films is sufficiently larger than these critical d values. Therefore, in the present work, we will ignore the above-described effects of coherent multiple reflections for all films used.

Another problem in the evaluation of the SiH density is the uncertainty of the value of A_{SiH} in Eq. (6). Although a constant A_{SiH} value of 1.4×10^{20} cm^{-2} (Ref. 33) is usually used for both 2000- and 2100-cm^{-1} bands in a-Si:H films, Amato *et al.*[34] and Langford *et al.*[31] have recently shown that the A_{SiH} value for the 2000-cm^{-1} band (isolated monohydride) is different from that for the 2100-cm^{-1} band (dihydride and clustered monohydride); $A_{SiH}(2000 \text{ cm}^{-1}) = 7.3\text{–}9.0 \times 10^{19}$ cm^{-2} and $A_{SiH}(2100 \text{ cm}^{-1}) = 2.1\text{–}2.2 \times 10^{20}$ cm^{-2}. In the case of the present films, a-Si:H films exhibited a single-Gaussian shape centered at 2000 cm^{-1}, and the absorption for a-SiN_x:H films was able to be decomposed into two Gaussian components at around 2000 and 2100–2200 cm^{-1}, as presented in Sec. IV A. For the latter 2100–2200-cm^{-1} band, the intensity increased with increasing value of x lower than 0.5, keeping a fixed peak wave number of 2100 cm^{-1}.[10,18] If the density of H_2-Si(Si_2) (dihydride) bonds increases with x, H_2-Si(SiN) bonds will also be formed in the films, whose absorption occurs at 2140 cm^{-1}.[13] For films having x values below 0.5, however, such absorption has not been found through a simulation analysis.[18] Furthermore, the density of SiH bonds as a function of x was able to be interpreted in terms of the MRB model, which describes the probability for generating individual H-Si($Si_{3-n}N_n$) bonds (this work and Ref. 10). Therefore, the presence of dihydride will be ignored for the absorption analyses in the present work.

For a-SiN_x:H, a-SiO_x:H, and a-SiC_x:H films, although the value of A_{SiH} will not be varied over the narrow range of the x values,[35] the assumption of a constant A_{SiH} value over the wide x range may not be valid, as suggested for the SiH and CH absorption in a-SiC_x:H films.[36] The value of A_{SiH} can be related to the effective charge e^* of the Si-H dipole and the n_r value as

$$A_{SiH}=cn_r\mu\omega/(2\pi^2e^{*2}) , \tag{7}$$

where c is the speed of light and μ the reduced mass.[30,37] If the values of e^* are known, the values of A_{SiH} can be determined. The e^* values may be estimated from the partial charge on Si and H atoms, as described in Sec. II A as

$$e^*=f_c[(\delta_{Si}-\delta_H)/2] , \tag{8}$$

where f_c is the coordination number;[7] $f_c=4$ for Si. Using Eq. (3), the value of δ_{Si}-δ_H is found to be 0.196 ± 0.005, roughly independent of the number of N atoms bonded to a Si atom. This is because an additional positive charge on a Si atom increases and the negative charge on a H atom decreases as a N atom is bonded to the Si atom in SiH bonds. These results will also be presented in Sec. IV A (Table II). As a result, the value of $e^*=0.39\pm0.01$ (in units of the electron charge) can be obtained from Eq. (8). For comparison, we will also examine the e^* value of a SiH_2 bonding unit in a-Si:H. When we turn our attention to one H atom in a SiH_2 unit, the SiH dipole may be formed between the H atom and the residual SiH element. If the effective charge on the SiH element is given by the sum of the respective charges on the Si and H atoms, the e^* value for SiH_2 units is estimated from Eq. (8) to be 0.260. These e^* values are in excellent agreement with those (0.39–0.44 and 0.26 for the 2000- and 2100-cm^{-1} bands, respectively) estimated from their respective A_{SiH} values for a-Si:H films, as stated above.[31,34]

In Eq. (7), when a constant ω value of 2000 cm^{-1} is assumed, then we obtain

$$A_{SiH}=2.58\times10^{19}n_r \ (cm^{-2}) . \tag{9}$$

The values of A_{SiH} as a function of x, estimated using the results shown in Fig. 1(a), are shown in Fig.1(b). Thus, the A_{SiH} value decreases with x from 9.2×10^{19} cm^{-2} for $x=0$ to 4.7×10^{19} cm^{-2} for $x=1.5$ through a decrease in the n_r value. The former A_{SiH} value is in good agreement with that for the 2000-cm^{-1} band suggested by Langford *et al.*[31] On the other hand, Wieder, Cardona, and Guarnieri[36] have assumed that changes of A_{SiH} and A_{CH} values with x for the SiH and CH absorption in a-SiC_x:H films is caused by changes in their respective e^* values. Although the applicability of Eq. (9) should be confirmed by measurements independent of vibrational absorption, we believe that the e^* value of the SiH dipole for a-SiN_x:H films does not appreciably change as a function of x, as predicted from the CTM model. Indeed, the magnitude of charge transferred from Si to N or O atoms in a-SiN_x and a-SiO_x films has been consistent with the shifts of the Si 2p and N 1s lines in the XPS spectra, and also agree well with the experimentally determined value of the transferred charge in crystalline SiO_2.[7] Furthermore, in the case of a-SiN_x:H films, as a result of resonant nuclear-reaction measurements, the A_{SiH} value has been reported to be roughly constant over the range of x from 0.8 to 1.4.[38] For this range of x, the variation of n_r is around 25%, as shown in Fig. 1(a). In the present work, therefore, the density [SiH] was evaluated by using the A_{SiH} values shown in Fig. 1(b).

In contrast, the proportionality coefficient A_{SiN} for SiN asymmetric stretching absorption at around 840–960 cm^{-1} is most likely to be independent of x over the range of x lower than 1.0,[19] although the n_r values changes with x. For this band, it is obvious that the effects of the above-mentioned multiple reflections[32] are also negligible. Figure 2 shows the intensity I_{SiN} of the SiN absorption as a function of the x values which were determined by EPMA and XPS measurements. In this figure, the results for the present films are shown together with those for films deposited under other deposition conditions. Thus a clearly linear relationship between the I_{SiN} and x values can be found for x below 1.0. From the slope of this line, the value of $A_{SiN}=6.3\times10^{18}$ cm^{-2} is obtained. The deviation of I_{SiN} values from the line for x greater than 1.0 may indicate an increase in the A_{SiN} value. The density of NH bonds was evaluated from the intensity of NH absorption at around 3350 cm^{-1}, using a constant A_{NH} value of 2.8×10^{20} cm^{-2},[38] because NH bonds rapidly increased for x above 0.5.

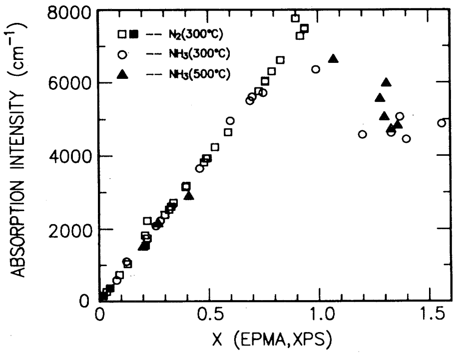

FIG. 2. Integrated intensity I_{SiN} of the SiN asymmetric stretching absorption at around 840–960 cm^{-1} as a function of the values of x determined by EPMA (open symbols) and XPS (closed symbols) for films shown in Fig. 1, along with those deposited under other various deposition conditions. From the linear relationship over the range of x below 1.0, a constant value of $A_{SiN}=6.3\times10^{18}$ cm^{-2} is obtained.

IV. RESULTS AND DISCUSSION

A. SiH absorption

Figure 3 shows the absorption profiles in the 1800–2500-cm^{-1} range as a function of x, and the result of a simulation analysis. The simulation analysis indicates that the profiles can be decomposed into two Gaussian components at around 2000 and 2100–2200 cm^{-1}, except for the occurrence of a relatively weaker signal at 2250–2280 cm^{-1} for films having x greater than 1.0 [Fig. 3(c)]. In this fitting procedure, a component at around 2000 cm^{-1}, whose width ranges from 75 to 85 cm^{-1}, was first determined as a part of the profile, and then the 2100–2200-cm^{-1} component was simulated. The width for the latter component ranged from 105 to 140 cm^{-1}, exhibiting a maximum value at around $x=0.7$. Although the choices of the peak wave number and its width were rather arbitrary, the integrated intensity of each band was able to be determined within an error of 10%. In Fig. 4(a), the density ratios [SiH]/[Si] for the 2000- and 2100–2200-cm^{-1} bands are shown, and Fig. 4(b) shows the [SiH]/[Si] ratio for the sum of both SiH bands and the [NH]/[Si] ratio as a function of the observed x. The density of SiH bonds is reduced to less than half, as compared with the results in a previous letter,[10] which have been estimated using a constant A_{SiH} value of 1.4×10^{20} cm^{-2}.[33]

On the basis of the MRB model, it has been shown that the bonding structure of a-SiH_x:H films an be represented as a statistically controlled mixture of five bonding units without H atoms [$\mathrm{Si(Si_{4-n}N_n)}$; a SiN_x group], occurring at a probability $f_n(x')$ ($n=0,\ldots,4$) for generating each bonding unit for a given x', and some bonding units with H atoms [a $\mathrm{SiN}_x\mathrm{(H)}$ group]. Here n in $f_n(x')$ means the number of N atoms bonded to a Si atom, and the parameter x' is the atomic ratio [N]/[Si] expected in the case of absence of H atoms. In the MRB model, it has been assumed that the SiH bonds are introduced by replacing one Si nearest neighbor at the Si site in $\mathrm{Si(Si_{4-n}N_n)}$ by a H atom, and the Si-NH-Si bonds are formed instead of $\mathrm{N(Si_3)}$ bonds to relax the stress as x increased.[10,22] Then, the identification of bonding units composing a-SiN_x:H films can be done by fitting the calculated [SiH]/[Si] and [NH]/[Si] ratios to the observed ones shown in Fig. 4. Here the calculated values, including $A_p(n)$ values as the fitting parameters, are obtained as a function of x' by averaging statistically the number of SiH or NH bonds in each bonding unit occurring at $f_n(x')$ for a given value of n. The $A_p(n)$ value is the occupying probability in the film of a bonding unit with H

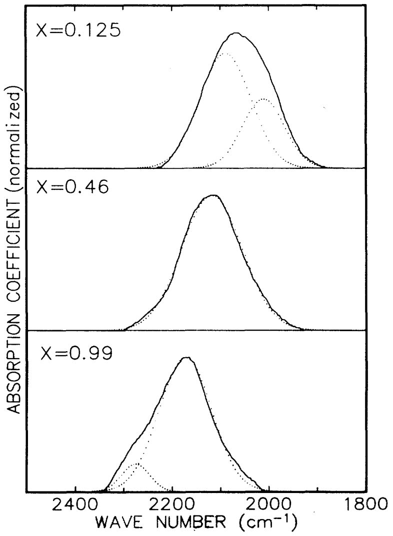

FIG. 3. Vibrational spectra in the 1800–2500-cm^{-1} range for a-SiN_x:H films with x values of 0.125, 0.46, and 0.99. The broken lines are the result of a simulation analysis.

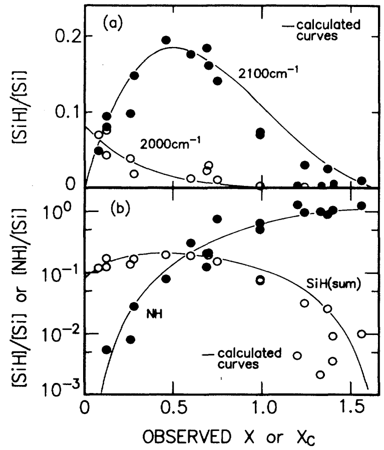

FIG. 4. (a) Ratios [SiH]/[Si] of the density of SiH bonds to that of Si atoms for the 2000- (open circles) and 2100-cm^{-1} (closed circles) bands; and (b) the ratio [SiH]/[Si] (open circles) for the sum of both bands in (a) and the ratio [NH]/[Si] (closed circles), as a function of the observed x. The solid curves as a function of x_c are calculated by the MRB model including SiH and NH bonds.

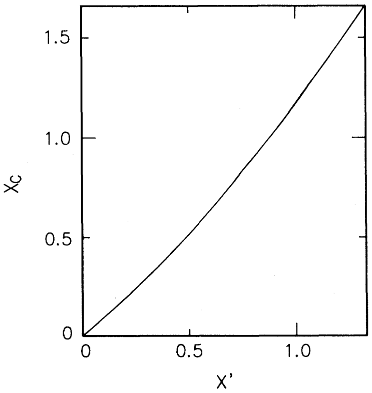

FIG. 5. Nitrogen content x_c estimated on the basis of the MRB model including NH bonds as a function of x' in the probability $f_n(x')$.

Table I. Modified random-bonding model for a-SiN$_x$:H. $f_n(x')$ is a generation probability, in which p is 0.75. The bonding unit denotes a minimum cluster originating in the basic bond. $A_p(n)$ is the occupying probability in the film of the bonding units with hydrogen (Ref. 10).

		SiN$_x$		SiN$_x$(H)		
n	$f_n(x')$	Basic bond	Bonding unit	Basic bond	Bonding unit	$A_p(n)$
0	$(1\text{-}px')^4$	Si(Si$_4$)	Si	H-Si(Si$_3$)	SiH	0.08
1	$4(px')(1-px')^3$	Si(Si$_3$N)	Si$_3$N	H-Si(Si$_2$N)	(SiH)$_3$N	0.28
2	$6(px')^2(1-px')^2$	Si(Si$_2$N$_2$)	Si$_3$N$_2$	H-Si(SiN$_2$)	(SiH)$_3$N$_2$	0.25
3	$4(px')^3(1-px')$	Si(SiN$_3$)	SiN	HN-Si(SiN$_2$)	Si$_6$N$_4$(NH)$_3$	1.0
4	$(px')^4$	Si(N$_4$)	Si$_3$N$_4$	(HN)$_2$-Si(N$_2$)	Si$_3$N$_2$(NH)$_3$	1.0

atoms. In the case of Si nitride films including NH bonds, we must pay attention to the point that the ratio [N]/[Si] ($=x_c$) expected to be actually observed is different from the value of x' used as a parameter in $f_n(x')$. The expected ratio x_c can also be estimated as a function of x' using the $f_n(x')$ and $A_p(n)$ values. The values of x_c as a function of x' for the present a-SiN$_x$:H films are shown in Fig. 5. Thus results predicted as a function of x' on the basis of the MRB model should be converted into those as a function of x_c, in order to compare the predicted results with the observed ones. The details of these calculation methods have been described in a previous paper,[10] and a method for calculating the x_c values will also be represented in Sec. IV B.

The calculated results as a function of x_c are shown by the solid curves in Fig. 4. The observed [SiH]/[Si] and [NH]/[Si] ratios are in excellent agreement with their respective calculated curves. In this fitting procedure, we were able to determine the $A_p(n)$ values within an error of ± 0.02, and their values are shown in Table I. In the present work, although the A_{SiH} value decreased with x, a variety of bonding units predicted to be included in the films were the same as those obtained by assuming a constant A_{SiH} value in a previous paper,[10] except for the decreased A_p (0, 1, and 2) values. Figure 6 shows the schematic representation of the predicted local-bonding geometry. The 2000-cm^{-1} band in Fig. 3 is assigned to the bonding configuration without N atoms of (b)-0 in Fig. 6, and the 2100–2200-cm^{-1} band arises from the configurations of (b)-1 and (b)-2.[10] The basic bonds corresponding to each geometry in the SiN$_x$ and SiN$_x$(H) groups shown in Fig. 6, the bonding unit (minimum cluster) originating in the basic bond, and the function $f_n(x')$ are summarized in Table I.

If these bonding units hold charge-neutrality conditions, the partial charge on Si, N, and H atoms in each bonding unit can be calculated using Eq. (3). However, in the case of the bonding units with NH bonds, a N atom in N(Si$_3$) and in Si-NH-Si bonds should be distinguished in the calculation procedure of the partial charge. Since a NH molecule in the latter bond will act as an atomlike element in the charge-transfer process between NH and Si, the partial charge on a NH element was estimated by using the effective electronegativity of the NH element obtained from Eq. (4), and then the value of the charge was divided between the N and H atom in NH bonds, proportionally to their respective electronegativities. These results are shown in Table II. In this table, the values of $\delta_{\text{N}A}(n)$ and $\delta_{\text{N}B}(n)$ denote the partial charge on a N atom in N(Si$_3$) and Si-NH-Si bonds, respectively. Figure 7 shows the effective peak wave number $\nu_{\text{SiH}}(x)$ obtained as the center of gravity of the SiH stretching absorption, as a function of x. Here, a weak signal at 2250–2280 cm^{-1}, observed at high x as seen in Fig. 3(c), was excepted from components to be averaged. The $\nu_{\text{SiH}}(x)$ values rapidly increases from 2000 to 2180 cm^{-1} with increasing x up to 1.0, and then saturates. If the relationship of Eq. (5) is also retained for a-SiN$_x$:H films, the increase in $\nu_{\text{SiH}}(x)$ indicates a decrease in d_{SiH} with increasing x. This has been well known as a result of an increase in the number of N atoms on the three back bonds of the SiH bond, because nitrogen has a larger electronegativity value than Si.

When we adopt the bonding configurations predicted for the present a-SiN$_x$:H films as shown in Fig. 6 and Table I, the wave number of 2000 cm^{-1} for $x=0$ and the

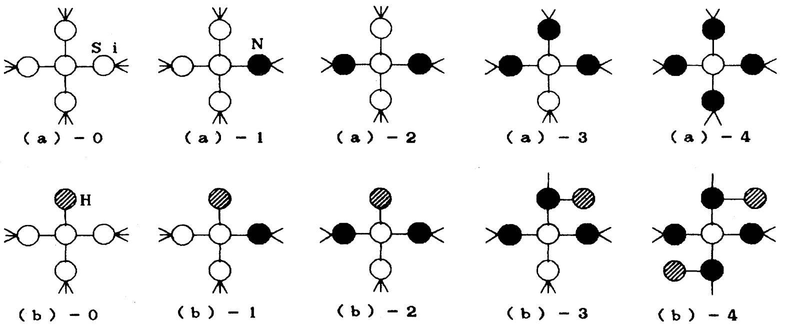

FIG. 6. A schematic representation of the local bonding geometry near a Si-N bond. (a) The five bonding units without hydrogen (a SiN$_x$ group), and (b) the corresponding five bonding units including SiH and NH bonds [a SiN$_x$(H) group].

TABLE II. Partial charge $\delta_{\mathrm{Si}}(n)$, $\delta_{\mathrm{N}}(n)$, and $\delta_{\mathrm{H}}(n)$ on Si, N, and H atoms, respectively, in each bonding unit with or without hydrogen for a-SiN$_x$:H shown in Table I. The results for a SiH$_2$ bonding unit are also shown for comparison. The values of $\delta_{\mathrm{NA}}(n)$ and $\delta_{\mathrm{NB}}(n)$ denote the partial charge on a N atom in N(Si$_3$) and Si-NH-Si bonds, respectively.

	SiN$_x$			SiN$_x$(H)				
n	Bonding unit	$\delta_{\mathrm{Si}}(n)$	$\delta_{\mathrm{N}}(n)$	Bonding unit	$\delta_{\mathrm{Si}}(n)$	$\delta_{\mathrm{NA}}(n)$	$\delta_{\mathrm{NB}}(n)$	$\delta_{\mathrm{H}}(n)$
0	Si	0		SiH	0.096			−0.096
1	Si_3N	0.099	−0.296	$(SiH)_3N$	0.142	−0.262		−0.055
2	Si_3N_2	0.163	−0.245	$(SiH)_3N_2$	0.178	−0.233		−0.022
3	SiN	0.209	−0.209	$Si_6N_4(NH)_3$	0.199	−0.216	−0.061	−0.048
4	Si_3N_4	0.243	−0.182	$Si_3N_2(NH)_3$	0.222	−0.198	−0.050	−0.040
				SiH_2	0.130			−0.065

final value of 2180 cm^{-1} for large x, respectively, are expected to be due to H-Si(Si$_3$) and H-Si(SiN$_2$) bonds. By using the values of these wave numbers and the $\delta_{\mathrm{Si}}(n)$ and $\delta_{\mathrm{H}}(n)$ values for $n=0$ and 2 in the SiN$_x$(H) group shown in Table II, the values of B_{Si} and B_{H} in Eq. (2) can be determined from Eq. (5). As a result, values of 0.111 for B_{Si} and 0.463 for B_{H} were found. The values of $d_{\mathrm{SiH}}(n)$ and $\nu_{\mathrm{SiH}}(n)$ for a given value of n in H-Si(Si$_{3-n}$N$_n$) units, estimated from Eqs. (2) and (5) using these B_{Si} and B_{H} values, are summarized in Table III.

The observed peak wave number $\nu_{\mathrm{SiH}}(x)$ shown in Fig. 7 can be correlated with the statistical average of $\nu_{\mathrm{SiH}}(n)$ over n from 0 to 2, as given by

$$\nu_{\mathrm{SiH}}(x')=\sum_{n=0}^{2}\nu_{\mathrm{SiH}}(n)A_p(n)f_n(x')\Bigg/\sum_{n=0}^{2}A_p(n)f_n(x') \;. \tag{10}$$

The values of parameters $A_p(n)$ in Eq. (10) are presented in Table I. The calculated result of Eq. (10) is shown by the solid curve in Fig. 7. Here, the values of x' were converted into x_c as stated above (see Fig. 5). An excellent agreement between the calculated curve and the experimental results is found. Furthermore, in order to judge the applicability of Eqs. (2) and (5), we estimated the values of d_{SiH} and ν_{SiH} for other SiH-related bonding units, such as H-Si(N$_3$) and H$_2$-Si(Si$_2$) bonds whose respective bonding units are (SiH)N and SiH$_2$. Although the presence of these bonds is ignored in the present films, the calculated ν_{SiH} values will make it possible to compare with the results reported by other research groups.[13,18,39–41] The results are also shown in Table III for comparison.

The typical value of a maximum peak wave number for high x which has been reported for a SiH vibration was approximately 2200 cm^{-1},[13,18,40,41] and the 2200-cm^{-1} band has been assigned to the H-Si(N$_3$) bond.[13,41] However, by using the CTM, and SiH absorption from this bond was predicted to occur at 2248 cm^{-1}, as shown in Table III. Also, the predicted 2248-cm^{-1} band is found to correspond well with a weak satellite signal at 2250–2280 cm^{-1}, as shown in Fig. 3(c). Furthermore, in the case of a-SiN$_x$:H films fabricated by a microwave glow-discharge technique, five separated lines due to SiH bonds have been observed, and the 2220–2230-cm^{-1} band which is a component with the highest peak wave number in the spectra was assigned to H-Si(N$_3$).[39] From these results, the SiH absorption due to H-Si(N$_3$) bonds is predicted to occur at 2230–2250 cm^{-1} higher than the value (2200 cm^{-1}) suggested by Lucovsky.[13] On the basis of this prediction, it is suggested that H-Si(N$_3$) bonds are unstable and NH bonds will be formed instead of SiH bonds as x increases, as shown in Table I and Fig. 6. Such instability of H-Si(N$_3$) bonds and formation of NH bonds may be due to the increased intrinsic tensile stress in films with increasing x.[22] So we believe that the absorption at around 2200 cm^{-1} in previous reports will arise mainly from H-Si(SiN$_2$) bonds. In fact, for PECVD a-SiN$_x$:H films having x from 0.8 to 1.4, Lanford and Rand[38] observed SiH absorption at 2160 cm^{-1}, which is close to a maximum value (2180 cm^{-1}) found in the present films (see Fig. 7), and this band has been assigned to H-Si(SiN$_2$).[13]

For H$_2$-Si(Si$_2$) dihydrogen bonds, the experimentally determined wave number was 2089 cm^{-1}.[13] As shown in Table III, this value is also comparable to the calculated one. Furthermore, on the basis of the CTM, we note that spacing of the SiH absorption line arising from each of four H-Si(Si$_{3-n}$N$_n$) bonding units decreases with increasing n values, as shown in Table III. On the other hand, by using the ENS model proposed by Lucovsky[13] (see

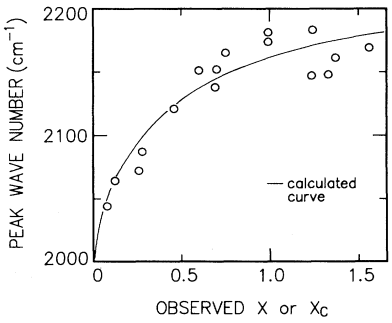

FIG. 7. The effective peak wave number ν_{SiH} obtained as the center of gravity of the SiH stretching absorption as a function of the observed N content x. The solid curve as a function of x_c are calculated on the basis of the CTM combined with the MRB model including H atoms.

Table III. Calculated interatomic distances $d_{\mathrm{SiH}}(n)$ and $d_{\mathrm{SiN}}(n)$ (Å as a unit) of SiH and SiN bonds, and the peak wave numbers $\nu_{\mathrm{SiH}}(n)$ and $\nu_{\mathrm{SiN}}(n)$ (cm^{-1} as a unit) of the SiH and SiN stretching absorption, respectively, for each bonding unit shown in Table I. The results for some other bonding units are also shown for comparison. The subscripts SiNA and SiNB denote a SiN bond in $N(Si_3)$ and Si-NH-Si bonds, respectively. In the estimation of d_{SiH} and d_{SiN} using Eq. (2), $d_{\mathrm{SiH}}(0)$ of 1.490 Å and $d_{\mathrm{SiN}}(0)$ of 1.736 Å, and B_{Si} of 0.111, B_{N} of 0.228, and B_{H} of 0.463, were used. Also, as the constants in Eqs. (5) and (14), C_{SiH} of 7074 and C_{SiN} of 4770 were used. The symbol * means the data used as the standards for determining the values of the unknown parameters in Eqs. (2), (5), and (14).

	SiN_x			$SiN_x(H)$						
n	Bonding unit	$d_{\mathrm{SiN}}(n)$	$\nu_{\mathrm{SiN}}(n)$	Bonding unit	$d_{\mathrm{SiH}}(n)$	$d_{\mathrm{SiNA}}(n)$	$d_{\mathrm{SiNB}}(n)$	$\nu_{\mathrm{SiH}}(n)$	$\nu_{\mathrm{SiNA}}(n)$	$\nu_{\mathrm{SiNB}}(n)$
0	Si			SiH	1.524			2000*		
1	Si_3N	1.792	829	$(SiH)_3N$	1.500	1.780		2098	846	
2	Si_3N_2	1.773	855	$(SiH)_3N_2$	1.481	1.769		2180*	862	
3	SiN	1.760	875	$Si_6N_4(NH)_3$		1.763	1.728		871	925
4	Si_3N_4	1.750*	890*	$Si_3N_2(NH)_3$		1.756	1.722		881	933
				SiH_2	1.506			2073		
				(SiH)N	1.465	1.761		2248	874	
				Isolated SiN		1.821			790*	
				$Si(NH)_2$			1.726			928

Sec. I), the above four SiH-absorption lines are suggested to be equally spaced. An effect arising from such charge transfer between constituent atoms can be observed directly as shifts in the Si 2p core-level spectra. As described in Sec. I, we have recently shown that spacing of the Si 2p lines in $Si(Si_{4-n}N_n)$, estimated on the basis of the CTM, also decreases as the n value increases, and that the observed shifts of the Si 2p spectra as a function of x can be well explained using the predicted spacing values.[7] Thus the CTM combined with the MRB model is seen to provide a convenient way of numerical analyses of the shifts in stretching absorption and core-level spectra for various compounds, if their bonding structures are determined by the RBM.

B. SiN absorption

Figure 8 shows the absorption profiles in the 400–1500-cm^{-1} range and the result of a simulation analysis for the same samples as those in Fig. 3. The profiles were composed of Gaussian components at around 450, 630, 790, 840, 960, and 1200 cm^{-1}. As indicated by Lucovsky *et al.*,[15] the 450-, 630-, and 1200-cm^{-1} bands are assigned to a SiN symmetric stretching mode, a SiH wagging mode, and a NH bending mode, respectively. Also, the absorption in the 790–960-cm^{-1} range will be related to a SiN asymmetric stretching mode.[10,15,19] In the present fitting procedure for the 790–960-cm^{-1} band shown in Fig. 8, a component at around 830–845 cm^{-1}, whose width ranges from 140 to 155 cm^{-1}, exhibiting a maximum value at around $x=0.7$, was first determined as a part of the profile, and then the remainder was allocated for the 790- or 960-cm^{-1} component. As stated in Sec. IV A, although the obscurity in determining the peak wave number and its width cannot be avoided, the intensity (area) of each component can be determined more exactly.

Figure 9 shows the integrated absorption intensity for the 840- and 960-cm^{-1} bands as a function of x. The intensity for the 960-cm^{-1} band rapidly increases with x after the absorption begins at around $x=0.4$. Since the increase in this 960-cm^{-1} band corresponded well with that in the density of NH bonds, we have assumed that the 840- and 960-cm^{-1} bands arise from $N(Si_3)$ and Si-NH-Si bonds, respectively.[10] Then the intensity for the 840- and 960-cm^{-1} bands can be calculated by using ten bonding units shown in Table I. As a parameter used in this calculation, the [SiN]/[Si] ratio of the number of SiN bonds, forming $N(Si_3)$ and Si-NH-Si bonds, to the number of Si atoms, is obtained from the composition of each bonding unit in Table I. The [SiN]/[Si] ratios [$x_n(N)$ and $x_n(NH)$] responsible for $N(Si_3)$ and Si-NH-Si bonds, respectively, are shown in Table IV.

By using the values of these [SiN]/[Si] ratios and $A_p(n)$ in Table I, the statistically averaged [SiN]/[Si] ra-

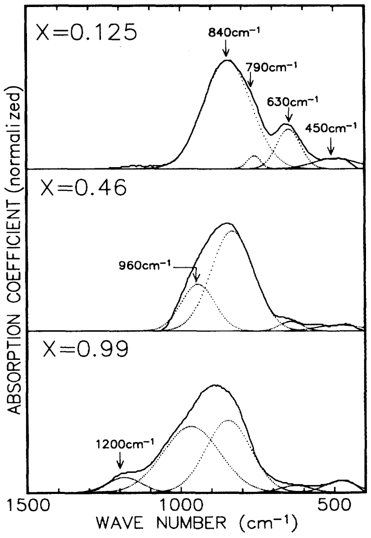

FIG. 8. Vibrational spectra in the 400–1500-cm^{-1} range for a-SiN_x:H films with the x values of 0.125, 0.46, and 0.99. The broken lines are the result of a simulation analysis.

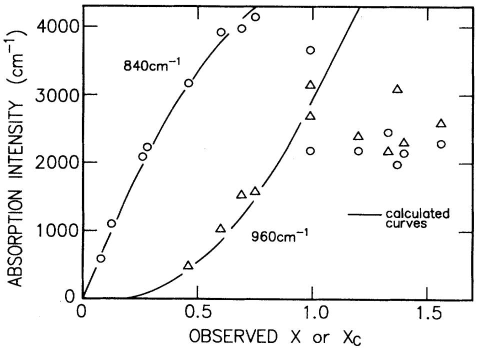

FIG. 9. Integrated absorption intensity of the 840- (circles) and 960-cm^{-1} (triangles) bands obtained from the SiN asymmetric stretching mode, as a function of the observed N content x. The solid curve as a function of x_c are calculated on the basis of the MRB model including SiH and NH bonds.

tios related to the 840- and 960-cm^{-1} bands, [SiN]/[Si](840) and [SiN]/[Si] (960), can be estimated as a function of x', as

$$[\mathrm{SiN}]/[\mathrm{Si}](840) = \sum_{n=1}^{4} \{[1-A_p(n)]x_n(N)+A_p(n)x_n^*(N)\}f_n(x') \,, \tag{11}$$

$$[\mathrm{SiN}]/[\mathrm{Si}](960)= \sum_{n=3}^{4} A_p(n)x_n(\mathrm{NH})f_n(x') \,. \tag{12}$$

It is obvious that the sum of the [SiN]/[Si](840) and [SiN[/[Si](960) ratios is equal to the values of $x_c(x')$ shown in Fig. 5, as

$$x_c(x')=[\mathrm{SiN}]/[\mathrm{Si}](840)+[\mathrm{SiN}[/[\mathrm{Si}](960) \,. \tag{13}$$

The ratios in Eqs. (11) and (12) can be converted into the statistically averaged intensity of the 840- and 960-cm^{-1} bands, by using the oscillator strength of 6.3×10^{18} cm^{-2} for both 840- and 960-cm^{-1} bands (see Fig. 2). The results obtained as a function of x_c are shown by the solid curves in Fig. 9. As seen in this figure, up to around $x=0.9$ the observed values for both bands agree well with the corresponding calculated curves, but fall off at x above 0.9. This may be caused by a change in the A_{SiN} value as stated in Sec. III B. Thus the results for x up to 0.9 support a model in which the 960-cm^{-1} band arises from Si-NH-Si bonds. Also, on the basis of this model, the peak wave number of the SiN absorption arising from Si-NH-Si bonds must be higher than that from N(Si$_3$) bonds.

TABLE IV. [SiN]/[Si] ratios $x_n(N)$ and $x_n^*(\mathrm{N})$ for SiN bonds forming a N(Si$_3$) structure, and the ratio $x_n(\mathrm{NH})$ for SiN bonds forming a Si-NH-Si structure, in each bonding unit.

	SiN$_x$		SiN$_x$(H)		
n	Bonding unit	x_n(N)	Bonding unit	$x_n^*(N)$	x_n(NH)
1	Si$_3$N	$\frac{1}{3}$	(SiH)$_3$N	$\frac{1}{3}$	0
2	Si$_3$N$_2$	$\frac{2}{3}$	(SiH)$_3$N$_2$	$\frac{2}{3}$	0
3	SiN	$\frac{3}{3}$	Si$_6$N$_4$(NH)$_3$	$\frac{2}{3}$	$\frac{1}{2}$
4	Si$_3$N$_4$	$\frac{4}{3}$	Si$_3$N$_2$(NH)$_3$	$\frac{2}{3}$	1

A stretching vibrational mode means the vibration in interatomic distance. Therefore, in the SiN stretching absorption, its force constant may be controlled mainly by the bond length, as is the case for the SiH stretching vibration, although the bond angle will affect the force constant as described in Sec. II B. This prediction is also supported by Tsu, Lucovsky, and Mantini.[9] In this case, the peak wave number ν_{SiN} might be linked to the bond length d_{SiN} in the same way as that in Eq. (5), as

$$\nu_{\mathrm{SiN}}(d_{\mathrm{SiN}})^3=C_{\mathrm{SiN}} \,. \tag{14}$$

By using this relationship, the values of ν_{SiN} can be calculated through Eq. (2), and the validity of Eq. (14) will be judged by comparing the calculated ν_{SiN} and d_{SiN} values with the experimentally obtained ones.

In the estimation of d_{SiH} described in Sec. IV A, the value of $d_{\mathrm{SiH}}(0)$ in Eq. (2) was determined using the nonpolar covalent radii of Si and H atoms as found by Sanderson.[24] For the covalent radius of N, however, rather different values of 0.74 (Ref. 24) and 0.65 Å (Ref. 38) have been reported, although that of Si was almost the same value of 1.15–1.17 Å. Thus the value of $d_{\mathrm{SiN}}(0)$ cannot be determined uniquely from previously reported results. Furthermore, when the morphology of SiN bonds is contrasted with that of SiH bonds, the freedom in bonding of N atoms with the coordination number of 3 will be less than that of H atoms, which can only be singly coordinated. This suggests that the nonpolar covalent radius of a N atom may depend on constituent species of the bonding network. Accordingly, as unknown parameters in calculating the ν_{SiN} values, the values of $d_{\mathrm{SiN}}(0)$ and B_{N} in Eq. (2) and C_{SiN} in Eq. (14) must be determined. The value of B_{Si} has been determined to be 0.111, as shown in Sec. IV A.

As the standards for determining these unknown parameters, we selected the observed values of ν_{SiN} and d_{SiH} as follows: d_{SiN} of 1.75 Å (Refs. 42 and 43) and ν_{SiN} of 890 cm^{-1} (Refs. 11, 14, and 15) for Si$_3$N$_4$, and ν_{SiN} of 790 cm^{-1} for an isolated SiN bond.[15,19] As described in Sec. I, the 790-cm^{-1} band is observable in a low range of x for both PECVD and ion-implanted SiN$_x$ films,[12,17,15,19] and will be due to a N atom having only Si nearest and next-nearest neighbors.[15,19] Therefore, such bonding units as shown in Table I cannot be determined for the 790-cm^{-1} band. However, since the additional partial charge on a Si atom in the NSi$_3$ bond would be rather small because of an induction effect, we put the partial charge on the Si and N atom at approximately $\delta_{\mathrm{Si}}=0$ and $\delta_{\mathrm{N}}=-0.374$, which were estimated using a relation suggested from Eq. (3). From these results, the values of $d_{\mathrm{SiN}}(0)=1.736$ Å, $B_{\mathrm{N}}=0.228$, and $C_{\mathrm{SiN}}=4770$ were found.

The values of d_{SiN} and ν_{SiN} for various bonding units, estimated from Eqs. (2) and (14), are shown in Table III. As seen in this table, when the ν_{SiN} values for the Si$_3$N$_n$ and (SiH)$_3$N$_n$ bonding units having a given value of n are compared, it is found that the peak shifts due to formation of a SiH bond are rather small: 829 and 846 cm^{-1}

for $n=1$, 855 and 862 cm^{-1} for $n=2$, and 875 and 874 cm^{-1} for $n=3$. This is because the electronegativity value of hydrogen is closer to that of silicon than nitrogen. Furthermore, the values of 829 and 846 cm^{-1} for $n=1$ agree well with the typical value (840 cm^{-1}) observed for films having a relatively low x value.[14–16,19] On the other hand, Lucovsky *et al.*[15] have suggested that the 790-cm^{-1} band due to a N site having only Si neighbors shifts to 840 cm^{-1} as the N atom has at least one H atom as a second neighbor.

In the case of the bonding units including NH bonds, it is found that the values of d_{SiN} and ν_{SiN} for a SiN bond with Si-NH-Si structure are roughly fixed at 1.725 ± 0.003 Å and 929 ± 4 cm^{-1}, respectively for three different bonding units, as shown in Table III. The estimate of this ν_{SiN}, which is considerably higher than those with $\mathrm{N(Si_3)}$ structure, is consistent with the prediction induced from the results of a simulation analysis for the SiN absorption intensity shown in Fig. 9. Furthermore, we note that the value of $d_{\mathrm{SiN}}=1.725$ Å agrees well with the experimentally determined value (1.725 Å) for silazane, $\mathrm{(H_3Si)_2}$-NH.[44]

As stated earlier in this section, the peak wave number determined by a simulation analysis may include a rather large error. Therefore, in Fig. 10 the effective peak wave number $\nu_{\mathrm{SiN}}(x)$, obtained as the center of gravity of the SiN absorption, is shown. The values of $\nu_{\mathrm{SiN}}(x)$ increase with increasing x, and saturate at around 910 cm^{-1} for x greater than 1.0. The values of this $\nu_{\mathrm{SiN}}(x)$ can also be calculated by using the values of $\nu_{\mathrm{SiN}}(n)$ in Table III, $A_p(n)$ in Table I, and [SiN]/[Si] ratios in Table IV, as

$$\nu_{\mathrm{SiN}}(x')=y(x')/x_c(x') \ , \tag{15}$$

where

$$y(x')=\sum_{n=1}^{4}[1-A_p(n)]x_n(N)\nu_{\mathrm{SiN}}(n)f_n(x') + \sum_{n=1}^{4}A_p(n)[x_n^*(N)\nu_{\mathrm{SiN}A}(n) + x_n(\mathrm{NH})\nu_{\mathrm{SiN}B}(n)]f_n(x') \ . \tag{16}$$

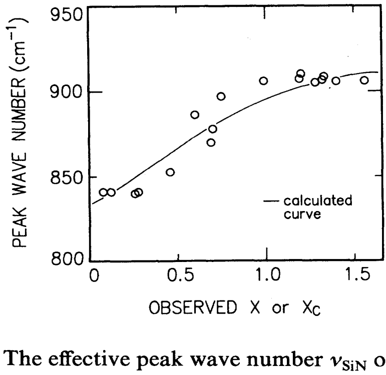

FIG. 10. The effective peak wave number ν_{SiN} obtained as the center of gravity of the SiN stretching absorption as a function of the observed N content x. The solid curve as a function of x_c is calculated on the basis of the CTM combined with the MRB model including SiH and NH bonds.

Here, $x_c(x')$ is given by Eq. (13). The calculated $\nu_{\mathrm{SiN}}(x_c)$ values are shown by the solid curve in Fig. 10. Although the data points are rather scattered against the predicted curve, the increase in the observed $\nu_{\mathrm{SiN}}(x)$ values with increasing x is found to be well characterized by the solid curve. Thus the dependence of the peak wave number and intensity of the SiN absorption as a function of x can be interpreted in terms of the CTM combined with the MRB model.

V. SUMMARY

For PECVD a-SiN_x:H films deposited at 300 °C using $\mathrm{SiH_4}$-$\mathrm{NH_3}$ mixtures, the dependence of SiH and SiN stretching absorption as a function of the N content x was investigated. By the use of a model based on the MRB model reported in a previous paper,[10] the bonding structure of a-SiN_x:H films were decomposed into five bonding units without H atoms, $\mathrm{Si_3N}_n$ ($n=0$–4), and a corresponding five with H atoms, $\mathrm{(SiH)_3N}_n$ ($n=0$–2), $\mathrm{Si_6N_4(NH)_3}$, and $\mathrm{Si_3N_2(NH)_3}$. Using Sanderson's model,[24] the partial charge on Si, N, and H atoms in these bonding units was estimated, and then the interatomic distance between Si and H or N atoms was estimated from the values of their partial charge. Furthermore, the oscillator strength of the SiH absorption as a function of x was examined by the use of the CTM model.

The SiH and SiN peak wave numbers, $\nu_{\mathrm{Si}M}$ ($M=$H or N), were able to be linked to the bond length $d_{\mathrm{Si}M}$ by the relation $\nu_{\mathrm{Si}M}(d_{\mathrm{Si}M})^3=\mathrm{const}$. This relation means that a change in the bond length is more important as a factor determining the force constant in the vibration. For SiH absorption, the constant in the above relation is approximately 7074 using cm^{-1} and Å as units of $\nu_{\mathrm{Si}M}$ and $d_{\mathrm{Si}M}$, respectively.[13,27] Also, the constant for SiN absorption was estimated to be approximately 4770 by referring to some observed data points. By using this relation, along with the calculated values of the bond length, the values of $\nu_{\mathrm{Si}M}$ for various bonding units were estimated.

The dependence of the observed peak wave number as a function of x, obtained as the center of gravity of SiH and SiN absorption, respectively, agreed well with the statistically averaged ν_{SiH} and ν_{SiN} values for various bonding units based on the MRB model. As a result of the analysis of this SiH absorption, it was suggested that the absorption at around 2180 cm^{-1}, which has generally been observed for films having near-stoichiometric composition, is due to H-$\mathrm{Si(SiN_2)}$ bonds. Furthermore, the absorption from the H-$\mathrm{Si(N_3)}$ bond was predicted to occur at around 2230–2250 cm^{-1}. For the SiN absorption, the calculated values of ν_{SiN} due to a SiN bond with Si-NH-Si structure were found to be considerably higher than those with a $\mathrm{N(Si_3)}$ structure, in agreement with the point predicted as the result of a simulation analysis based on the MRB model for the SiN absorption profiles. Furthermore, it was found that the peak shifts of the SiN absorption due to incorporation of hydrogen, such as a change from $\mathrm{Si(Si_{4-n}N_n)}$ to H-$\mathrm{Si(Si_{3-n}N_n)}$ structure, are considerably smaller than the shift range predicted by

Lucovsky *et al.*[15] Thus shifts in the bond length and the absorption peak for SiH and SiN bonds due to a compositional change of a-SiN$_x$:H films can be interpreted in terms of a simple model obtained by combining the CTM with the MRB model.

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