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Nitrogen-bonding environments in glow-discharge—deposited *a*-Si:H films

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We have studied the local bonding of nitrogen atoms in glow-discharge—deposited films of *a*-Si:H by using ir absorption spectroscopy. We find two different bonding environments for N, which are identified through different frequencies for the Si-N asymmetric bond-stretching vibration, 840 cm^{-1} for the high-T_s films, and 790 cm^{-1} for the low-T_s films. In films deposited on substrates held at temperatures in excess of 300 °C, the N is incorporated in a planar site with three silicon nearest neighbors, and one hydrogen second-nearest neighbor. In films produced on substrates held below 200 °C, the N atom is also in a threefold-coordinated planar site, but with all of the nearest and second-nearest atoms being Si atoms.

I. INTRODUCTION

In a recent paper,[1] we presented a study of the local bonding environments of oxygen in *a*-Si:(H,O) films produced by the glow-discharge decomposition of SiH_4, H_2, and O_2. For films containing hydrogen concentrations to approximately 25 at. % and oxygen concentrations up to about 15 at. %, the oxygen and hyrdogen atoms are bonded to a common silicon site with the Si—H bond in the same plane as the Si—O—Si group (see Fig. 9 of Ref. 1). The geometry of this bonding site, which may either have a *cis* or a *trans* character, has been determined from an analysis of ir absorption data on *a*-Si:H, *a*-Si:O, and *a*-Si:(H,O) films using chemically adjusted valence forces in calculations of the local-mode, alloy-atom vibrations.[2,3] This paper extends the study of alloy-atom bonding environments to ternary alloys of silicon, hydrogen, and nitrogen, hereafter designated as *a*-Si:(H,N). These films have been produced by the glow-discharge decomposition of SiH_4 and N_2. In contrast to the results we have reported for *a*-Si:(H,O) alloys, we find two qualitatively different nitrogen-bonding environments in *a*-Si:(H,N) films with comparable concentrations of nitrogen and hydrogen. For films produced at substrates held at temperatures (T_s) in excess of 300 °C, and with hydrogen concentrations of approximately 15 at. %, and nitrogen concentrations up to 10 at. %, we find a site that is the analog of the oxygen-bonding site. The nitrogen atom is in a planar configuration with three silicon neighbors and there is a single hydrogen atom bonded to one of the three silicon neighbors. This site is characterized by three ir absorptions, a Si-N in-plane stretching vibration at 840 cm^{-1}, a shifted Si-H stretching vibration at 2060 cm^{-1},[4] and a disorder-induced in-plane silicon breathing mode at 495 cm^{-1}. Qualitatively similar spectra have recently been reported by Watanabe, Katoh, and Yasui,[5] who find a Si-N vibration at 840 cm^{-1}, and a Si-H vibration at 2100 cm^{-1}. They studied films produced in an rf glow discharge using a mixture of SiH_4, H_2, and N_2, but restricted their depositions to a single substrate temperature of 250 °C. The film for which they displayed the ir data, contained a significantly higher nitrogen concentration, 25 at. %, and a smaller hydrogen concentration. Both of these factors explain the higher frequency of the Si-H stretching vibration; i.e., the calculations presented in Ref. 4, as well as the relative nitrogen and hydrogen concentrations, suggest that the Si—H group had two nitrogen neighbors, rather than one as in our films with smaller nitrogen to hydrogen ratios. Our studies have also included a range of substrate temperatures, $T_s = 50$—400 °C, and a wider range of relative nitrogen and hydrogen concentrations, and have thereby enabled us to identify the third feature at 495 cm^{-1} in the high-T_s films ($T_s \geq 300$ °C), as well as a second type of nitrogen center in the low-T_s films ($T_s \leq 100$ °C). The second Si—N bonding geometry is characterized by a single ir absorption at 790 cm^{-1}.

II. SAMPLE PREPARATION AND ir MEASUREMENTS

Thin films of *a*-Si:(H,N) were prepared by the glow-discharge decomposition of a mixture of SiH_4 and N_2. The N_2 concentration in the gas mixture was varied between 5 and 60 vol %. The input rf power was maintained at 10 W, and the pressure at 0.5 Torr. The substrate temperature was varied between 50 and 400 °C. The higher-T_s films ($T_s \geq 300$ °C) have hydrogen incorporated in the monohydride- (SiH) bonding geometry, while the lower-T_s films (50—150 °C) yield hydrogen in polysilane or $(SiH_2)_n$ configurations.[6-8] Films were grown on high-resistivity (> 10 Ω cm) crystalline-silicon substrates. The film thickness, nominally 1—3 μm, was determined by an interferometric technique. The nitrogen composition was determined by both x-ray photoelectron spectroscopy (XPS) and electron-microprobe analysis using a stoichiometric film of Si_3N_4 for a calibration standard, and the hydrogen concentration was determined by the integrated absorption in the Si—H stretching band (2000—2100 cm^{-1}).[6,9] Infrared absorption spectra in the the range 400—4000 cm^{-1} were obtained using a Perkin-Elmer model 580B double-beam ratio-recording spectrophotometer.[1] Spectral resolution was approximately 3 cm^{-1} and the transmission data are accurate to ±0.5%.

Figure 1 shows the ir spectra for three films produced with $T_s = 400$ °C: (a) for pure SiH_4, (b) for 20 vol % N_2 and 80 vol % SiH_4, and (c) for 40 vol % N_2 and 60 vol % SiH_4. Also shown in the figure is an inset (d), indicating

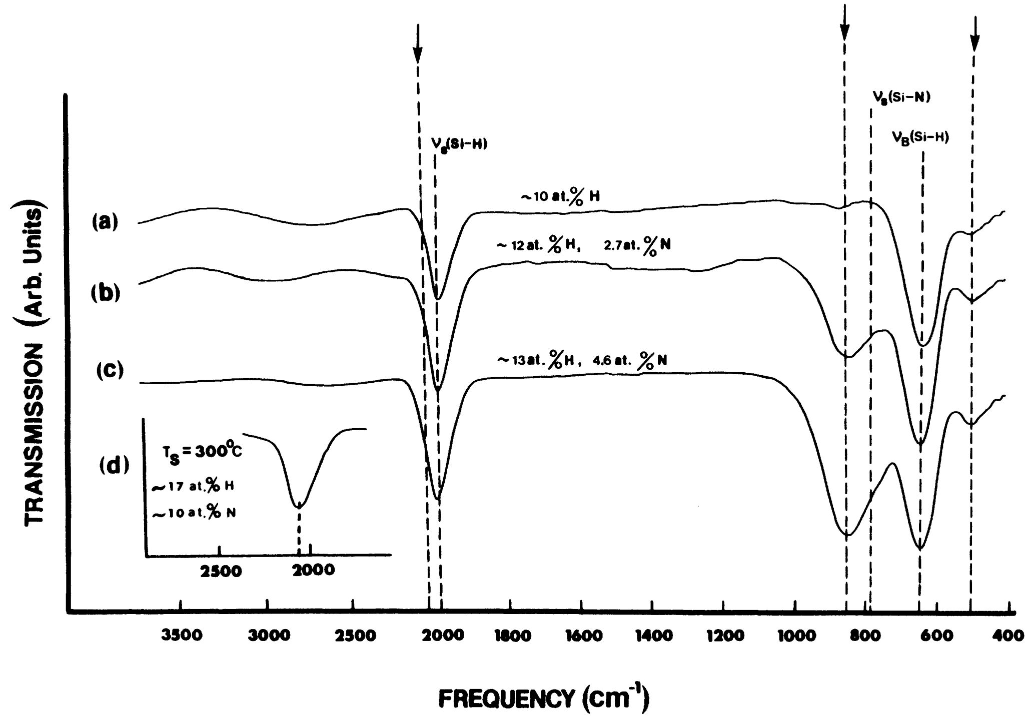

FIG. 1. Infrared absorption spectra of films prepared at $T_s = 400\,^\circ\mathrm{C}$ with different N_2 concentrations in the gas mixture. (a) 0 vol % N_2, (b) 20 vol % N_2, and (c) 40 vol % N_2. Inset (d) is the absorption in the bond-stretching regime for a film with $T_s = 300\,^\circ\mathrm{C}$ and grown from a gas mixture containing 50 vol % N_2. Bonded-N concentration is approximately 10 at. %. Arrows indicate the N-related features. Also indicated on the figure are the frequencies of the Si—H vibrations in *a*-Si:H. ν_s is the stretching vibration and ν_B is the bonding vibration. ν_s (Si—N) is the asymmetric Si—N stretching vibration in *a*-Si:N. The figure also includes the bonded N and H concentrations.

the ir absorption in the bond-stretching regime for a film produced at a slightly lower substrate temperature, $T_s = 300\,^\circ\mathrm{C}$, but with a higher N_2-gas fraction. This absorption establishes the position of the shifted Si—N band at 2060 cm^{-1}. The reference spectrum in 1(a) shows the characteristic monohydride vibrations: the Si—H bond-stretching vibration at 2000 cm^{-1}, and the Si—H bond-bending (or wagging) vibration at 630 cm^{-1}.[1,6,7] Consider-

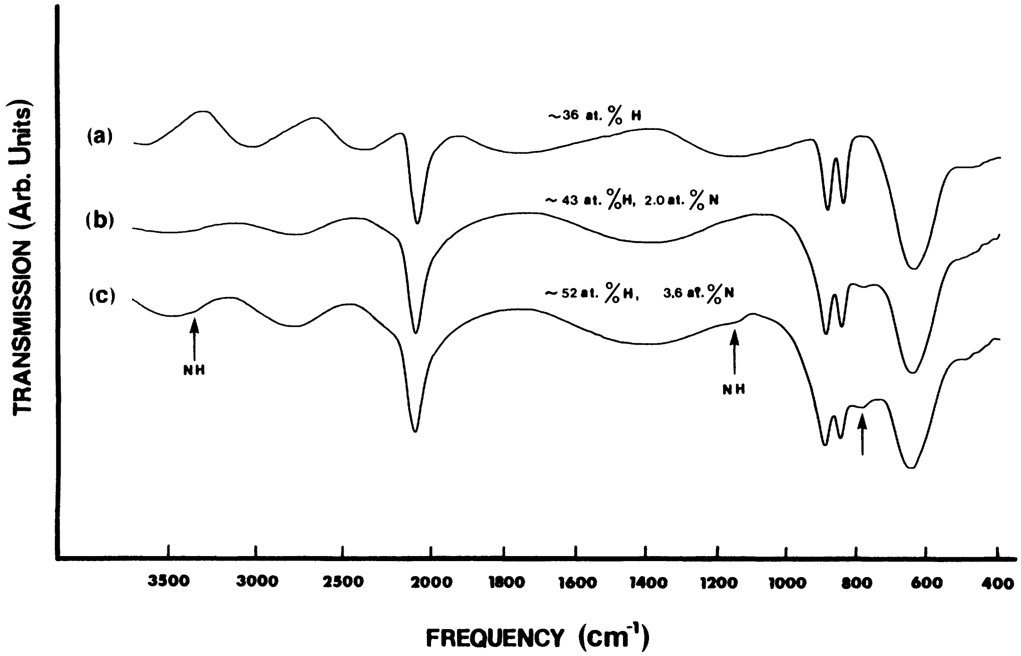

FIG. 2. Infrared absorption spectra of films prepared at $T_s = 100\,^\circ\mathrm{C}$ with different N_2 concentrations in the gas mixture: (a) 0 vol % N_2, (b) 20 vol % N_2, and (c) 40 vol % N_2. Arrows indicate the N-related features. The figure also includes the bonded N and H concentrations.

ably weaker features in the vicinity of 1000 cm^{-1} are attributed to oxygen contamination,[1] and at about 875 cm^{-1} to SiH_2 formation.[6–8] The film also displays characteristic interference fringes, as well as another weak feature near 490 cm^{-1}. The films grown with N_2 gas added to SiH_4 show systematic changes in the ir absorption that are linked to the presence of bonded nitrogen: (1) A broad absorption band centered at 840 cm^{-1}, (2) a broadening at the high-wave-number side of the 2000-cm^{-1} Si—H stretching vibration, with the eventual development of a satellite peak at about 2060 cm^{-1}, and (3) an increase in the relative strength of the absorption at 495 cm^{-1}. The amounts of bonded hydrogen and nitrogen are shown in the diagram. For these films (deposited at $T_s = 400\,^\circ C$) we have shown that the increased absorption at 2060 and 495 cm^{-1} scale with the absorption at 840 cm^{-1}. The integrated ir absorption, as well as the absorption constant at 840 cm^{-1}, scales linearly with the amount of bonded N in the film. The "concave" shape of the absorption band tail of the 840-cm^{-1} vibration at about 950—1000 cm^{-1} in Figs. 1(b) and 1(c) indicates very little oxygen incorporation in the films grown with N_2 gas in the chamber. The growth morphology of the $T_s = 400\,^\circ C$ films has been studied by a scanning electron microscope (SEM) and has been found to be homogeneous; i.e., there is no evidence for a columnar structure.[10] In contrast the films produced with $T_s = 100\,^\circ C$ show a distinctly columnar growth morphology, and, as expected, the ir absorption shown in Fig. 2 is dominated by sharp features at 2100, 890, and 845 cm^{-1} known to be associated with polysilane, $(SiH_2)_n$, incorporation.[7] Figure 2 also contains spectra for three films: (a) pure SiH_4, (b) 20 vol% N_2, and (c) 40 vol% N_2. A comparison of the features in the three spectra indicates that the obvious nitrogen-induced feature is a band centered at approximately 790 cm^{-1}. This band grows linearly with the fraction of N_2 in the SiH_4,N_2 mixture. The larger amplitude interference fringes [with respect to those in Figs. 1(a)—1(c)] result from a decrease in the effective dielectric constant of the film brought on by the increase in the hydrogen concentration. A careful examination of the spectra in Fig. 2, in particular the spectrum in Fig. 2(c), indicates the presence of NH bonding groups. Very weak absorption at ~ 3350 cm^{-1} is due to an N—H stretching vibration, and at 1150 cm^{-1} to a bending vibration. Note that *a*-Si:(H,O) films do not display any measurable absorption due to OH groups.[1–3] Finally, Fig. 3 shows spectra for three films, 0, 20, and 40 vol% N_2, grown with $T_s = 250\,^\circ C$. The film grown without N_2 gas shows both monohydride and dihydride incorporation, as evidenced by the character of the stretching band at 2000—2100 cm^{-1} and the doublet absorption at 890 and 845 cm^{-1}. The spectra in Figs. 3(b) and 3(c) indicate a behavior in the region of Si—N stretching frequencies that is intermediate to that shown in Figs. 1(b) and 1(c) and Figs 2(b) and 2(c). The film grown with 20 vol% N_2 shows a distinct feature near 790 cm^{-1}, with evidence for additional absorption at higher wave number near 840 cm^{-1}. The film grown with 40 vol% N_2 shows increased absorption near 840 cm^{-1} as well as a growth in the absorption at 495 cm^{-1}.

III. STRUCTURAL INTERPRETATION

Structural studies of crystalline Si_3N_4 and the molecule $(SiH_3)_3N$ indicate that the local bonding geometry of N atoms is in a planar configuration with three Si neighbors.[11] Studies of *a*-Si_3N_4 by Raman spectroscopy indicate that this planar geometry persists in the amorphous phase as well.[12] Figure 4 includes a schematic representation of the local bonding geometry at (a) a N-atom site in an *a*-Si host, and (b) a bonding site similar to (a), but including

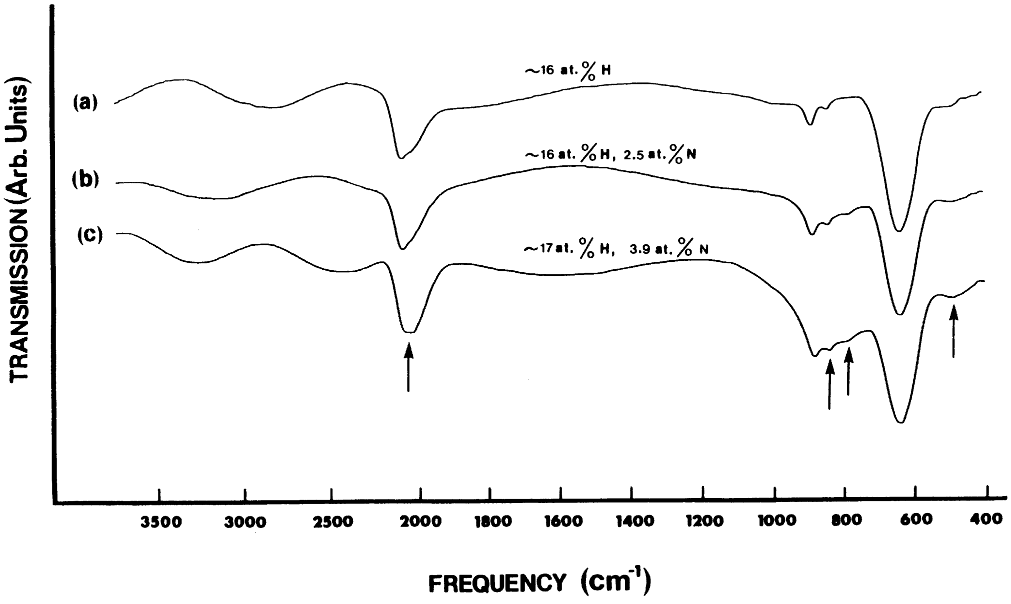

FIG. 3. Infrared absorption spectra of films prepared at $T_s = 250\,^\circ C$ with different N_2 concentrations in the gas mixture: (a) 0 vol% N_2, (b) 20 vol% N_2, and (c) 40 vol% N_2. Arrows indicate the N related features. The figure also includes the bonded N and H concentrations.

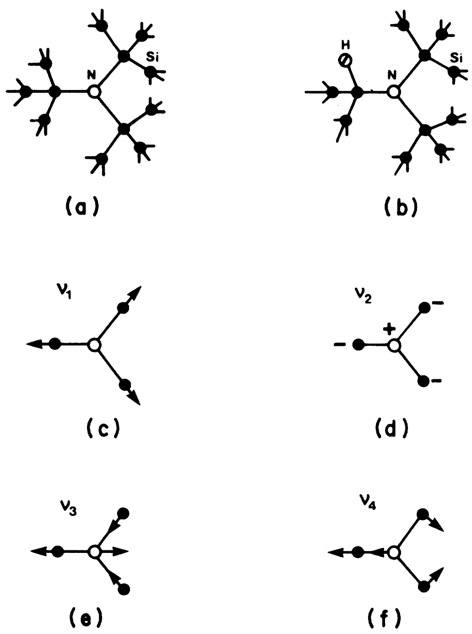

FIG. 4. Schematic representation of planar bonding of N atoms at (a) a site with only Si-nearest and next-nearest neighbors (b) a site with one H-atom next-nearest neighbor, and (c)—(f) skeletal vibrations of the Si_3N group. Arrows indicate the directions of the in-plane displacements for ν_1, ν_3, and ν_4, while the plus and minus sign indicate the directions of the out-of-plane motions for the ν_2 vibration.

one H second neighbor as in a-Si:(H,N) alloys and the local vibrations of the so-called "skeletal Si_3N group," (c)—(f).[13] ν_1 with A_1' symmetry, is a symmetric breathing mode of the three Si atoms; it is Raman active and polarized. ν_2 with A_2'' symmetry, is an out-of-plane mode with both Si- and N-atom displacements; it is ir active. ν_3 and ν_4 are doubly degenerate E' modes with both ir and depolarized Raman activity. ν_3 is an asymmetric in-plane bond-stretching vibration and ν_4 is an in-plane bending mode. The assignment of the skeletal features for the $(SiH_3)_3$ N molecule,[14] as well as studies of the vibrational properties of a-Si_3N_4 films[15,16] gives the following results: ν_1 has a frequency of approximately 450—500 cm^{-1}, ν_2 is very weakly ir active with a frequency of about 300 cm^{-1}, ν_3 is strongly ir active with a frequency between 800 and 950 cm^{-1}, and ν_4 has not been observed but is expected to be ir active with a frequency of less than 200 cm^{-1}.

We now assign the N-induced or modified absorptions in a-Si:(H,N) alloys based on what has been stated above, and on the analysis previously developed for a-Si:(H,O).[1–3] Consider first the films deposited on the low-temperature ($T_s = 100\,^\circ C$) substrate. The band at 790 cm^{-1} is assigned to an in-plane Si—N stretching vibration with Si and N atom displacements similar to those shown for ν_3 in Fig. 4. Additional support for this assignment derives from studies of N-ion implantation in which unannealed N-ion-implanted films display a broad absorption with its maximum between 750 and 800 cm^{-1}.[17] The assignment of this featue in the glow-discharge—deposited films is in accord with the diphasic character of the $T_s = 100\,^\circ C$ material. The material in the columns is assumed to be a-Si with isolated N-atom bonding sites [see Fig. 4(a)] and the connective material is $(SiH_2)_n$ with little or no N-atom "defects." This low-temperature material is qualitatively similar to alloys of a-Si:(H,O) grown on low-T_s substrates[1] ($T_s = 50$ and $100\,^\circ C$), but with one important difference. The O atoms in the columnar phase always have H second neighbors, while the N atoms in the columnar phase do not have H second neighbors. Our measurement did not extend to low frequencies where one might observe the two other expected ir-active modes, ν_2 the out-of-plane vibration, and ν_4 the in-plane bending mode. The vibrations are in the frequency band of the a-Si host network and therefore are difficult to observe unless they are particularly strong in ir intensity.

The high-T_s films (400 °C) show three N-related absorptions at 495, 840, and 2060 cm^{-1}. We interpret the band at 840 cm^{-1} as the in-plane Si—N stretching mode. Its frequency is shifted from 790 cm^{-1} at the isolated N site (all Si nearest and next-nearest neighbors) to 840 cm^{-1} for the N site in which there is at least one H atom as a second neighbor [see Fig. 4(b)]. The increase in frequency for a H second neighbor parallels the shift of the Si—O asymmetric stretching vibration from 940 cm^{-1} in a-Si:O binary alloys to 980 cm^{-1} in a-Si:(H,O) ternary alloys.[1] For the oxygen case, calculations of the vibrational properties indicate that the frequency shift is due to force-constant changes that are determined by the near-neighbor chemistry, as opposed to a purely dynamical effect associated with changes in atomic displacements, which are driven by different second-neighbor masses and coordinations.[2,3] We interpret the 495 cm^{-1} feature as the breathing mode of the three Si atoms that are bonded to the N atom. Normally this mode is ir inactive. In our model

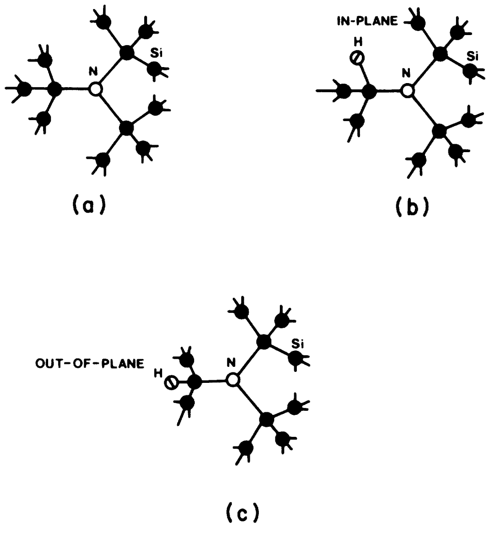

FIG. 5. (a) Intermediate-size (13-atom) cluster for calculation of vibrational properties of an isolated N site. The N atom and its three immediate Si neighbors are in a plane. The remaining nine Si atoms are in a tetrahedral arrangement with respect to the Si—N bonds. (b) and (c) are environments in which one of the second-neighbor Si atoms is replaced by a single H atom. (b) shows this H atom in the plane of the Si_3N group and (c) shows the H atom in a bonding position out the Si_3N plane.

the ir activity derives from a loss of symmetry that is brought about by the presence of a H atom bonded to one of the three Si atoms in question. Note, that if all three Si atoms had H neighbors or if none of these Si atoms had H neighbors, then the local symmetry of the site would be the same as that of the skeletal Si_3N configuration and no ir activity would be allowed. Infrared absorption is observed at approximately 500 cm^{-1} in a large number of alloy systems including *a*-Si:(H,O) (Ref. 1) and *a*-Si:F.[18] In each instance it is due to the motion of the Si atoms that are bonded to the alloy atom. The degree of ir activity then depends on the local geometry, and the amount of charge transfer in and between the Si and the alloy atom.[18] For the $T_s = 100\,^{\circ}C$ films the Si atoms bonded to the N atom have only Si neighbors and no appreciable ir absorption is found at 495 cm^{-1}. Finally, the absorption at 2060 cm^{-1} is assigned to a Si—H stretching vibration wherein one of the atoms backbonded to the Si atom is a N atom.[4] The frequency of the Si—H stretching vibration is shifted from 2000 to 2060 cm^{-1} due to the decrease in the Si—H bond length that is induced by the N neighbor.[4] Therefore, all the features in the high-T_s film are explained by a structural model in which at least one of the three Si atoms that is bonded to the N atom has a H neighbor as well.

We have calculated the vibrational properties of the N sites in *a*-Si:H alloys and have confirmed the assignments given above. We have used the technique described in Ref. 2, namely we have calculated the properties of the local-mode vibrations through the use of cluster of intermediate size. This cluster contains the alloy-atom bonding configuration of interest and a sufficient number of tetrahedrally bonded Si atoms to ensure that there is no motion of the Si atoms at the boundary of the cluster for those vibrations involving significant displacements of the alloy atoms. This means that the alloy-atom motions do not depend on the boundary conditions imposed on the Si atoms terminating the cluster. Figure 5 indicates the configurations we have used: (a) is an isolated nitrogen atom at the center of a configuration of Si atoms, and (b) and (c) are similar clusters containing a single hydrogen atom bonded to one of the three Si atoms that are the nearest neighbors of the central N atom. Figure 5(b) has the H atom in the plane of the Si_3N skeletal group and Fig. 5(c) has the H atom in an out-of-plane position. We have restricted our analysis to local-mode vibrations where the freqencies of vibration are in excess of about 480 cm^{-1}, the highest vibrational frequency of the *a*-Si host. The force constants for this calculation are included in Table I, which also gives the vibrational frequencies calculated for the local modes.

Figure 6 includes the displacements of the local modes. For the isolated N site [Fig. 5(a)], we find two local-mode vibrations; a breathing mode of the three Si atoms, Fig. 6(a), and a Si—N asymmetric stretching mode, Fig. 6(b). These vibrations correspond to two of the skeletal vibrations shown in Fig. 4. For the local atomic configurations in which the N atom has a second-neighbor H atom, as in Figs. 5(b) and 5(c), we find five local-mode vibrations. Two of these are simply the bond-stretching and bond-

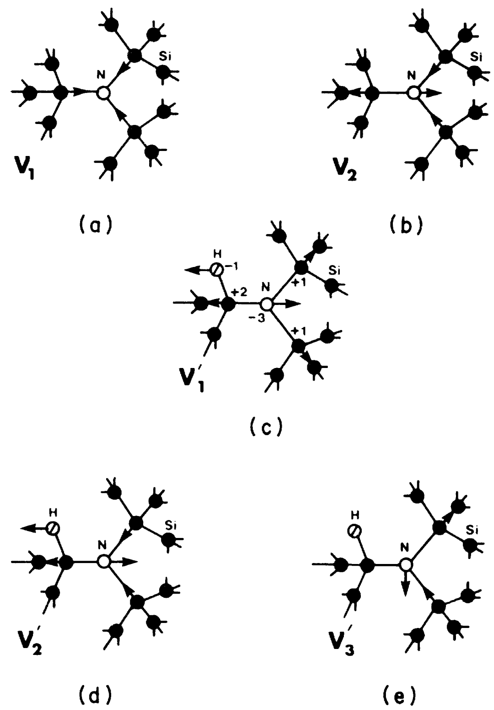

FIG. 6. Schematic representation of displacement reactors for the local modes involving N-atom motion. (a) and (b) are for the isolated center shown in Fig. 5(a). (a) ν_1 is the Si breathing mode and (b) ν_2 is the asymmetric Si—N bond-stretching mode. (c)—(e) are the displacement reactors for the H-associated center. (c) ν_1' is the Si-breathing mode modified by the presence of a H second neighbor. The formal changes on the Si, H, and N atoms coupled with the displacements serve to identify the origin of the ir activity. (d) and (e) are the displacements for the asymmetric Si—N stretching vibrations. ν_2' involves H-atom motion, while ν_3' does not.

TABLE I. Force constants and calculated frequencies for *a*-Si:(H,N). na denotes not applicable.

(a) Force constants (10^5 dyn/cm)

	Isolated N site	N site with H neighbor
K_r(Si—N)	2.27	2.64
K_r(Si—H)	na	2.43
K_r(Si—Si)	1.52	1.52
K'_{rr}(Si—N—Si)	0.042	0.027
K'_{rr}(H—Si—N)	na	0.012
K'_{rr}(H—Si—Si)	na	0.012
K'_{rr}(Si—Si—Si)	0.012	0.012
K_θ(Si—N—Si)	0.092	0.092
K_θ(H—Si—N)	na	0.180
K_θ(H—Si—Si)	na	0.180
K_θ(Si—Si—Si)	0.092	0.092

(b) Calculated frequencies (cm^{-1})

Isolated N site		N site with H neighbor		
			In plane	Out of plane
ν_1	493	ν_1'	492	493
ν_2	790	ν_2'	854	841
		ν_3'	843	836

bending vibrations of the Si—H bond; the stretching vibration is at 2060 cm^{-1} and the bending vibration is at 630 cm^{-1}. These vibrations are insensitive to the orientation of the Si—H bond relative to the planar Si_3N group. Figures 6(c)—6(e) illustrate the other three vibrations which involve displacements of N atom. The frequencies of these vibrations differ by small amounts, ~ 10 cm^{-1}, for the in- and out-of-plane H atom configurations, Figs. 5(b) and 5(c), respectively. We show the displacement vectors for the in-plane configuration and note that the displacement vectors for the out-of-plane configuration are qualitatively similar.

Figure 6(c) illustrates the displacement vectors for the Si breathing mode. The introduction of a second-neighbor H atom reduces the symmetry of the alloy-atom site and the vibration now involves both N-atom and H-atom motion as well as Si-atom motion. The vibration we show is for the in-plane configuration. To illustrate the induced ir activity of this mode we have included in the diagram formal charges on the Si, N, and H atoms. We assign charges of -3 to N, -1 to H, and charges of either $+1$ or $+2$ to the Si atoms where the magnitude of the charge on the Si atom reflects the total number of H and N neighbors. The two Si atoms bonded to only N and Si atoms are assigned a charge of $+1$, while the Si atom with both N and H nearest neighbors is assigned a charge of $+2$. The vibration can then be viewed as a stretching mode involving two multiatom groups: an Si—H group on the left, and an $N—Si_2$ group on the right. With the use of the formal charges discussed above, the Si—H group has a net positive charge and the $N—Si_2$ group a net negative charge, hence the H-atom-induced ir activity.

The asymmetric Si—N bond-stretching mode is normally doubly degenerate; however, the inclusion of a near-neighbor H atom removes the degeneracy. Figures 6(d) and 6(e) illustrate the two different Si—N vibrations. One of these modes, ν_2' in Fig. 6(d) includes appreciable H-atom motion and its frequency is about 10 cm^{-1} higher than the frequency of the vibration shown in Fig. 6(e) which does not involve any appreciable H-atom motion. The frequency difference between ν_2' and ν_3' is smaller for the out-of-plane H-bonding geometry and the H-atom displacements are smaller. We have rotated the Si—H bond through a variety of different orientations relative to the Si_3N plane and find that the three vibrations described above do not change in any fundamental way. Moreover, the differences we have identified above between ν_2' and ν_3' are too small to be resolved in an amorphous material. Therefore, we are not able to find a spectroscopic signature that discriminates between different orientations of the Si—H bond relative to the Si_3N plane. This is in contrast to the situation for the *a*-Si:(H,O) films, where there is an ir absorption at 780 cm^{-1} that is unique to a particular orientation of the Si—H bond relative to the plane of the Si—O—Si configuration. This 780 cm^{-1} feature couples Si—H and Si—O—Si motions for only one of two possible configurations in which the Si—H bond is in the same plane of the Si—O—Si group (see Fig. 9 of Ref. 1).

We have also estimated the relative strengths of the ir absorption bands at 840 and 495 cm^{-1}. This is done by assigning formal changes to the atoms, as we have indicated above, and then calculating the ir moment by using the atomic displacements we have obtained through the vibrational calculations. If we assume that the actual effective charges are proportional to the formal charges, then the ratio of the square of the moments should be proportional to the ratio of the strengths of the ir absorption bands. Proceeding in this way, we calculate a value of 290 for the ratio of the strengths, $I(840\ \mathrm{cm}^{-1})/I(495\ \mathrm{cm}^{-1})$. Using the ir data in Figs. 1(a)—1(c), we estimate a ratio of absorption strengths of 230 ± 50. Therefore, there is qualitative agreement between the calculation and the data. This agreement adds further strength to our assignment of the 495 cm^{-1} mode as a disorder-induced Si breathing mode, wherein the "disorder" is the presence of the H atom.

TABLE II. Comparison of Si—N and Si—O stretching frequencies.

Material	Vibrational frequency (cm^{-1}) Si—N	 Si—O
Stoichiometric compounds	875 (Si_3N_4)	1080 (SiO_2)
Ion-implanted material	790[a]	940[b]
a-Si:(H,*X*) alloys (*X*=N,O)		
(i) Low-T_S films	790	980
(ii) High-T_s films	840	980

[a] Reference 17.

[b] Reference 1.

The calculations we have undertaken therefore confirm the assignments described above. Table II summarizes the results reported in this paper, and includes additional data and comparisons with Si—O vibrations in films containing oxygen. These comparisons emphasize a qualtiatively similar behavior for N- and O-atom incorporation in hydrogenated *a*-Si. In particular, the Si—N and Si—O asymmetric stretching vibrations are lower at isolated alloy atom sites in *a*-Si:N and *a*-Si:O alloys than in the respective stoichiometric compounds *a*-Si_3N_4 and *a*-SiO_2: 790 and 875 cm^{-1} for the respective Si—N vibrations, and 940 and 1080 cm^{-1} for the respective Si—O vibrations. For Si—N and Si—O bonding sites in *a*-Si:(H,N) and *a*-Si:(H,O) alloys deposited on high-temperature substrates (300—400 °C), the vibrational frequencies of the asymmetric stretching modes are at intermediate frequencies, respectively, 840 and 980 cm^{-1}. The incorporation of N and O is qualitatively different in films deposited on low-temperature substrates. For the low-temperatue N-alloy film, the frequency of 790 cm^{-1} is assigned to an isolated Si—N site with no hydrogen second neighbors, whereas for the low-temperature O-alloy film, there is evidence in the form of 780-cm^{-1} absorption for O sites with second-neighbor H atoms.

Note added in proof. We have recently studied the ir spectra of films of *a*-Si:(D,N) produced by the glow-discharge decomposition of SiD_4 and N_2. For films produced on substrates held at 400 °C, the interpretation of the ir spectra supports the conclusions presented in this paper for *a*-Si:(H,N) films grown with the same T_s. For low-T_s films (<150 °C), the D for H-substitution shifts the polysilane scissors-wagging doublet from 890 cm^{-1} (845 cm^{-1}) to 650 cm^{-1} (635 cm^{-1}), revealing an additional Si-N feature at 875 cm^{-1}, and leading to a reinterpretation of the data for the low-T_s *a*-Si:(H,N) film. The Si-N absorption band in the *a*-Si:(H,N) films at 790 cm^{-1} is accompanied by absorption due to H-N groups at 3350 and 1150 cm^{-1}; in a parallel manner absorption at 705 cm^{-1} in *a*-Si:(D,N) films is accompanied by D-N vibrations at 2445 and 980 cm^{-1}. For the low-T_s *a*-Si:(H,N) films (1) the triad of vibrations discussed above, 3350, 1150, and 790 cm^{-1}, is assigned to a local bonding arrangement involving a terminal H-N group attached to the Si-host network (the 790-cm^{-1} feature is one of two Si-N vibrations at this site), and (2) a vibration at 875 cm^{-1} (in part obscured by the polysilane scissors-wagging doublet) is assigned to regions in which the incorporation of N atoms results in a local bonding geometry that is like that of *a*-$\mathrm{Si_3N_4}$. Thus the low-T_s films are viewed as being inhomogeneous with one phase having a polysilane component, and the second being an *a*-Si:N alloy in which the N atoms are clustered in regions with a stoichiometry corresponding to $\mathrm{Si_3N_4}$. Prior to the studies of the deuterated films, we had assumed the second phase to contain isolated, rather than clustered N-atom sites. For further details, please refer to a paper by G. Lucovsky, S. S. Chao, J. Yang, J. Tyler, and W. Czubatyj to appear in [J. Vac. Sci. Technol. A (in press)].

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