

ELECTRONIC AND VIBRATIONAL PROPERTIES OF HYDROGENATED AMORPHOUS SILICON NITRIDE

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The theoretical model calculations are used to study the electronic and vibrational properties of hydrogenated amorphous silicon nitride. The electronic densities of states of Si_3N_4 Bethe lattice, Si dangling bond (DB), SiH, SiH_2 , N DB, N-N DB, NH and NH_2 bonds are calculated. The charges are found to transfer from Si to N in the Si-N bond, Si to H in the Si-H bond and H to N in the N-H bond. Si DB, N DB and N-N DB are found to have defect states in the energy gap. These defect states can be identified by the electron spin resonance. The N site of the Si_2NH_2 complex can be positively charged and form a defect pair with the negatively charged Si DB. The vibrational densities of states of Si_3N_4 Bethe lattice, SiH, SiH_2 , NH, and NH_2 bonds are calculated. The vibrational densities of state of the SiD, SiD_2 , ND and ND_2 bonds are also calculated as an aid to identify the local modes. The Si-H bond stretching frequency higher than 2160 cm^{-1} is due to the asymmetric stretching mode of the SiH_2 bond and the N-H stretching mode of 3450 cm^{-1} is due to the asymmetric stretching mode of the NH_2 bond. The asymmetric stretching modes of the SiH_2 and NH_2 bonds seem to be more infrared sensitive than their symmetric stretching modes.

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1. Introduction

More than three decades ago, Ovshinsky, in a common paper with Cohen and Fritzsche, proposed a CFO model [1] for amorphous semiconductors. The CFO model, which described the density of states (DOS) in amorphous semiconductors, defined the valence and conduction bands and localized states for amorphous semiconductors. Since then, the electronic properties of amorphous materials become more clear and understandable. In this study, the electronic and vibrational DOS for $\alpha\text{-SiN}_x\text{:H}$ will be calculated and studied.

Silicon nitride has a wide gap and is an important dielectric material. The $\alpha\text{-SiN}_x\text{:H}$ thin films can be grown by the plasma-enhanced chemical vapor deposition (PECVD) with a mixture of $\text{NH}_3 + \text{SiH}_4$ or $\text{N}_2 + \text{SiH}_4$. The photoemission study [2] can describe the valence band spectra of $\alpha\text{-SiN}_x$ and $\alpha\text{-SiN}_x\text{:H}$. It can also describe the states induced by the local bonding structures. $\alpha\text{-SiN}_x\text{:H}$ contains defect states, which act as charge-trapping centers. The electron spin resonance (ESR) and capacitance –voltage (CV) measurements [3, 4] can be used to determine the existence of Si and N dangling bonds (DB). They can also describe the defect mechanisms involved with these two defect centers. The relaxed defect states are mostly charged instead of neutral. The negative effective correlation energy, U , model [3, 5, 6] or potential fluctuation model [7 - 9] is used to describe the existence of these charged dangling bonds. The N-N bond was considered unstable in $\alpha\text{-SiN}_x$. Yet, the N-pair defects were detected by the ESR measurements [10].

Hydrogen is incorporated as SiH and NH bonds in the PECVD $\alpha\text{-SiN}_x\text{:H}$ films. The infrared (IR) absorption spectroscopy [11 - 16] can provide microstructural information about the SiN, SiH

and NH bonds in α -SiN_x:H. The nuclear magnetic resonance (NMR) [17, 18] can be aided to identify the SiH and NH bonds. The Si-N vibrational modes are in the range of 830 ~ 890 cm⁻¹ [12]. The Si-H and N-H bond-stretching frequencies are about 2160 and 3350 cm⁻¹, respectively in α -SiN_x:H. The 1540 and 3450 cm⁻¹ modes are assigned respectively to the bond-bending and stretching mode of the NH₂ bond [12, 16]. When the α -SiN_x:H films were prepared at high NH₃/SiH₄ flow ratio, the IR detected that the Si-H bond-stretching frequency was increased to about 2190 – 2200 cm⁻¹ [14, 15].

In this study, the theoretical cluster-Bethe-lattice method [19, 20] is used to calculate the electronic and vibrational DOS of some local bonding configurations in α -SiN_x:H. The electronic DOS study can describe the electronic states induced by the local bonding structures and the vibrational study can describe the vibrational modes induced by the local bonding structures. The results from these two studies can be used to describe some phenomena found in the above experiments.

In section 2, the theoretical model calculations are briefly described. Section 3 presents the electronic DOS for some local bonding structures. The defect states induced by some local bonding structures related to the ESR signals are described. Section 4 presents the vibrational DOS for some local bonding structures. The hydrogen induced local modes are described. Section 5 provides the conclusions.

2. Theoretical methods

The cluster-Bethe lattice method [19, 20] is used in this study. The mathematical procedure is started by using the equations involving the Green's function. For the electronic problems, the equations can be written as

$$EG = 1 + HG, \quad (1)$$

where E is the energy level and H is the tight-binding Hamiltonian. The local electronic DOS at site i is related to the Green's function as

$$\rho_i(E) = -\frac{1}{\pi} \text{Im}[G_{ii}(E)]. \quad (2)$$

The effective field method is used to solve the equations for the Bethe lattice. In this way, we can have the effective fields related to each bond. The cluster-Bethe-lattice method can then be applied to different local bonding structures with the appropriate Bethe lattices attached to the surface bonds of the cluster. By attaching the appropriate Bethe lattice to each surface bond of the cluster means that the appropriate effective fields are applied to the equations for solving the Green's functions of the cluster.

The phonon problems can be studied similarly. The equations for the vibrational problems can be written as

$$\omega^2 G = 1 + DG, \quad (3)$$

where ω is the vibrational frequency and D is the dynamical matrix. A valence force field (VFF) representation of the near-neighbor interactions is used to generate the dynamical matrices. The elastic energy per atom in the VFF model is written as follows [21, 22]:

$$\begin{aligned} \Phi = & \frac{1}{2} \sum_j K_r (\Delta r_j)^2 + \frac{1}{2} \sum_{j>k} K_\theta (r_0 \Delta \theta_{jik})^2 + \sum_{j>k} K_{rr} (\Delta r_j) (\Delta r_k) \\ & + \sum_{j>k} K_{r\theta} (\Delta r_j) (r_0 \Delta \theta_{jik}), \end{aligned} \quad (4)$$

where Δr_j is the scalar change in the length of bond j about atom i , $\Delta \theta_{jik}$ is the change in the angle formed by bonds j and k about atom i , and r_0 is the equilibrium bond length. There are four force constants in Eq. (4). K_r is the two-body bond-stretching force constant for the nearest neighbor i and j . The other three are the three-body force constants for the atoms i , j , and k . K_θ ,

K_{rr} , and $K_{r\theta}$ are respectively the bond-bending, bond-stretching, and the mixed bond-stretching and bond-bending force constants. The force constant $K_{r\theta}$ is usually neglected due to its smallness. From the elastic energy, we can calculate the dynamical matrix.

The local vibrational DOS at site i can be obtained from the Green's function

$$\rho_i(\omega) = -\frac{2m\omega}{\pi} \text{Im}[\text{Tr } G_{ii}(\omega)]. \quad (5)$$

3. Electronic densities of states

The tight-binding parameters used in this study are mainly from Robertson [23]. The calculated electronic DOS for several bonding structures, including the Si_3N_4 Bethe lattice, are presented below.

3.1. Bulk Si_3N_4

Fig. 1 presents the averaged electronic DOS for the Si_3N_4 Bethe lattice and the projected DOS of the s and p states of the Si and N atoms. The lowest part of the band, from -20 to -17 eV, consists mainly of N 2s states with little Si 3s and 3p states. From -12 to -8 eV, the band consists of N 2p and Si 3s states, and from -8 to -2 eV, the band consists of N 2p and Si 3p states. The upper part of the valence band consists of N 2p states, which have non-bonding character due to the nearly planar configuration of nitrogen with its three silicon neighbors. The peak of the non-bonding p_z states is at -1.3 eV. The whole valence band is in general agreement with the experimental photoemission spectrum [2]. The lower part of the conduction band consists mainly of Si 3s states and small amounts of Si 3p and N 2s and 2p states.

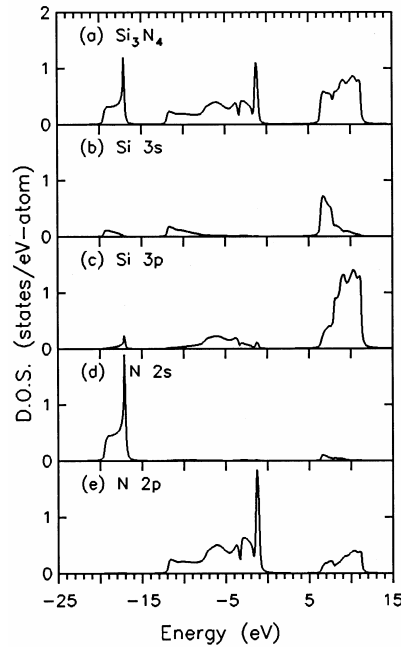


Fig. 1. (a) Averaged electronic DOS for the Si_3N_4 Bethe lattice, and the projected electronic DOS for (b) Si 3s, (c) Si 3p, (d) N 2s and (e) N 2p.

There is a charge transferred from Si to N. Each Si transfers about 1.95 e to N and each N atom receives about 1.46 e from Si. The average charge transferred from each Si to each N is about 0.49 e .

3.2. Si and N dangling bonds, and N-pair defect

Fig. 2a presents the electronic local DOS for the bonding configuration containing a Si DB. There is a non-bonding defect state at 2.7 eV in the energy gap. Fig. 2b presents the electronic local DOS for the bonding configuration containing an N DB. The N DB does not induce a defect state in the energy gap. The non-bonding N 2p states at the top of the valence band become sharper. There is a DB state at -1.8 eV, which is 0.5 eV below the peak of the non-bonding p_z states. The top of band associated with N DB is empty and has hole character.

Fig. 2c-d presents electronic local DOS for the bonding configuration containing an N-pair defect (N-N DB bond). The N-N DB bond induces two anti-bonding states, a $p\pi^*$ state at -0.6 eV and a $p\sigma^*$ at 1.6 eV in the gap. This is similar to the defect states of the Si-O-O $\cdot$ bond found in α -SiO₂ [24, 25]. The lowest s-band splits into two bands centered at -21.5 and -14.4 eV, respectively. The $p\pi^*$ could be half-filled and become ESR active [10]. A more self-consistent calculation [25, 26] is required to give a more accurate description of the defect energy levels.

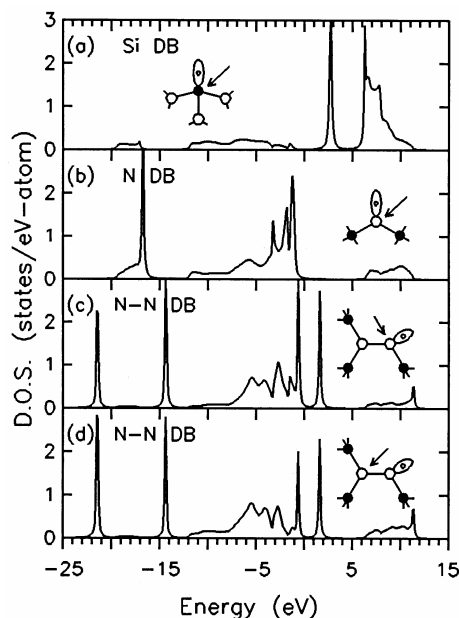


Fig. 2. Electronic DOS for (a) Si dangling bond, (b) N dangling bond. (c-d) Electronic DOS for the N-N DB: (c) N with DB and (d) N with no DB.

3.3. SiH and NH bonds

The local DOS for the bonding configurations containing N₃-SiH, N₂-SiH₂, Si₂-NH and Si-NH₂ bonding structures have been studied before [27]. The bonding states induced by the SiH and NH bonds are in the valence band and the anti-bonding states are in the conduction band. There is no electronic defect state in the energy gap induced by these bonding configurations. Fig. 3 presents the local DOS for the tetrahedral Si₂NH₂ bonding structure, of which N has four-fold coordination. There is no non-bonding p_z state of N. The peaks at -24 and -13.7 eV are from the H 1s coupled with the N 2s and 2p, respectively.

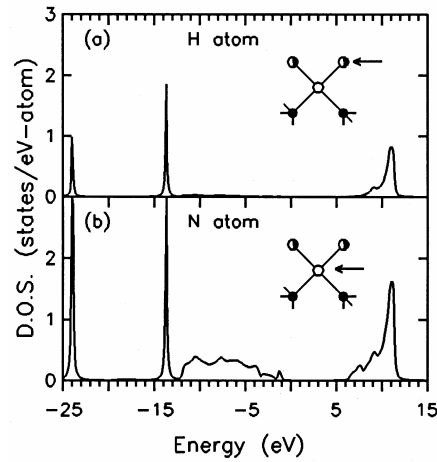


Fig. 3. Electronic DOS for the Si_2NH_2 bond: (a) H atom and (b) N atom.

3.4. Discussion

The electronic charge at each site of the local bonding structures are calculated and tabulated in Table 1. There is a charge transfer from Si to N in the Si-N bond, from Si to H in the Si-H bond and from H to N in the N-H bond. The magnitudes of electronegativity for N, H and Si are in the order of $\chi_{\text{N}} > \chi_{\text{H}} > \chi_{\text{Si}}$. The charge transfer follows the relative magnitude of the electronegativity in each bond. The calculated results in this study follow this trend. The Coulomb force between two atoms in each bond is proportional to the net charges of these two atoms. This Coulomb force can contribute bonding force between the bonding sites and hence influence the bond-stretching frequency [28].

Table 1. Calculated charges (e) at different bonding sites.

Groups	Si	N	H
Si_3N_4	2.05	6.46	
$\text{N}_3\text{-SiH}$	2.55	6.35	1.41
$\text{N}_2\text{-SiH}_2$	2.01	6.45	1.52
$\text{Si}_2\text{-NH}$	2.07	6.10	0.90
Si-NH_2	2.06	5.74	0.89
$\text{Si}_2\text{-N-H}_2$	2.07	5.20	0.90

The N DB gives a state below the top of valence band at -1.8 eV, which is the energy level of the p orbitals used in this study. The non-bonding p_z states have a peak at -1.3 eV, which is slightly higher than the neutral p orbital due to the coupling with the neighboring Si and second neighboring N. In the normal planar bonding configuration, the non-bonding p_z states have two electrons ($\uparrow\downarrow$). The DB bond state has one electron ($\uparrow$). One of two p_z electrons would fall down to the DB bond state to fill the DB state and leave the top band half empty. The neutral N DB is ESR active. In the Si-rich $a\text{-SiN}_x$, the charge can transfer from the Si DB to the N DB so that there is no ESR signal of N centers. In the N-rich $a\text{-SiN}_x$, the N DBs can be in the charge states of N_2^+ and N_2^- . The subscript denotes the coordination and the superscript denotes the charge. The negative U [3] or potential fluctuation model [7 - 9] is used to describe the existence of the charge states.

The valence electron configuration of N is s^2p^3 . The four-fold bonding structure requires four valence electrons. The extra electron can be ionized so that the four-fold coordinated N is positively charged. The undoped $a\text{-SiN}_x\text{:H}$ was slightly n type at low x , owing to slight self-doping by nitrogen

[23]. Lucovsky et al. [29] calculated the local bonding energy of the α -Si:N:H alloys and found that the ammonium $\text{Si}_2\text{N}^+\text{H}_2$ can be a stable state. The existence of the Si_2NH_2 bond can explain some part of the defect mechanisms found in α -SiN_x:H. The charged N_4 can form a defect pair, N_4^+K^- , with the Si DB [30]. K^- is equal to Si_3^- . In the as-deposited N-rich α -SiN_x:H [3], after UV illumination, there is only an ESR signal of K centers. The electron-hole pairs are generated by the UV illumination. The hole trapped at the K^- site can change the charge state to the neutral K^0 state. The K^0 center is ESR active. The trap of electron at the N_4^+ changes it to the neutral N_4^0 state. The neutral N_4^0 is ESR inactive.

4. Vibrational densities of states

The force constants used in this study are mostly from Lucovsky et al. [11, 17]. The calculated vibrational DOS for several bonding structures, including the Si_3N_4 Bethe lattice, are presented below.

4.1. Si_3N_4 Bethe lattice, Si-H and N-H bonds

Fig. 4a presents the vibrational DOS for the Si_3N_4 Bethe lattice. The high frequency region, from about 700 to 900 cm^{-1} , is due to the Si-N bond stretching motion. There are two peaks at 850 and 794 cm^{-1} in this region. The experimental data [12, 16] for the Si-N bond-stretching mode are centered in the range of 830 ~ 890 cm^{-1} and there are two peaks at 850 and 790 cm^{-1} . The calculated results in this study are in good agreement with the experimental data. The peak at 544 cm^{-1} in the middle part of the band is due to the Si breathing mode [11]. The experiment measured such a mode at 490 cm^{-1} [16]. The lower part of the band, around 290 cm^{-1} , is due to the bending motion of N, which moves perpendicular to the NSi_3 configuration.

The vibrational DOS of H sites for the $\text{N}_3\text{-SiH}$, $\text{N}_2\text{-SiH}_2$, $\text{Si}_2\text{-NH}$ and Si-NH_2 bonds are calculated and shown in Fig. 4b-e. Fig. 4b presents the vibrational DOS for the H of the $\text{N}_3\text{Si-H}$ bond. There is a Si-H bond-stretching mode at 2160 cm^{-1} . The Si-H bond-bending mode has a peak at 724 cm^{-1} . The coupling interaction between the Si-H and Si-N bonds causes the Si-N bond-stretching modes to shift to higher frequencies of 820 and 863 cm^{-1} .

Fig. 4c presents the vibrational DOS for the H of $\text{N}_2\text{Si-H}_2$ bond. The Si-H bond-stretching mode is split into a symmetrical and an asymmetrical mode at 2176 and 2190 cm^{-1} , respectively. The H-H interactions cause the Si-H bond-stretching mode to split. The bending modes are at 486, 728, 854 and 904 cm^{-1} .

Fig. 4d presents the vibrational DOS for the H of the $\text{Si}_2\text{N-H}$ bond. There is a N-H bond-stretching mode at 3350 cm^{-1} and a N-H bond-bending mode at 1180 cm^{-1} . The mode at 472 cm^{-1} is due to the coupling motion of N-H and N-Si bonds. Fig. 4e presents the vibrational DOS for the H of the Si-NH_2 bonding structure. The N-H asymmetric and symmetric stretching frequencies are at 3460 and 3412 cm^{-1} , respectively. The bending modes are at 1540, 898, 666 and 546 cm^{-1} .

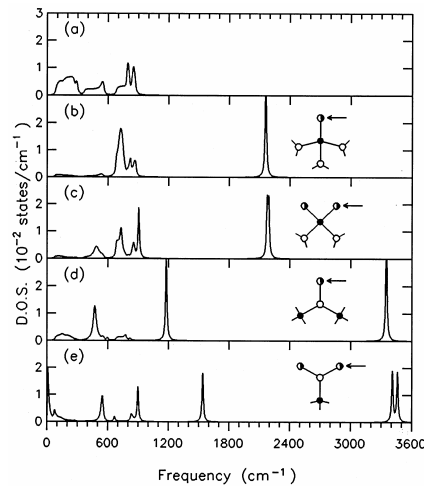


Fig. 4. (a) Averaged vibrational DOS for the Si_3N_4 Bethe lattice. (b-e) Vibrational DOS for the H atom in the clusters of (b) $\text{N}_3\text{-SiH}$, (c) $\text{N}_2\text{-SiH}_2$, (d) $\text{Si}_2\text{-NH}$ and (e) Si-NH_2 .

4.2. Si-D and N-D bonds

Fig. 5 presents the vibrational DOS for the deuterium of the N_3Si-D , N_2Si-D_2 , Si_2N-D and $SiN-D_2$ bonds. The Si-D bond induces a Si-D bond-stretching mode at 1554 cm^{-1} . The bond-bending mode splits into two modes at 560 and 580 cm^{-1} , respectively. The mode at 378 cm^{-1} is due to the coupling motion of N-D and N-Si bonds. The SiD_2 induced a symmetric and an asymmetric bond-stretching mode at 1558 and 1584 cm^{-1} , respectively. The ND bond induces a bond stretching at 2450 cm^{-1} . The bending mode splits into two modes at 966 and 650 cm^{-1} , respectively. The ND_2 bond induces an asymmetric and a symmetric bond respectively at 2548 and 2478 cm^{-1} , and three bending modes at 1142 , 660 and 424 cm^{-1} .

The calculated vibrational local modes are summarized in Table 2.

4.3. Discussion

From the above calculations, the ratio between the Si-H and Si-D bond-stretching frequencies is 1.39, which is close to the ratio between the square roots of the effective masses of the Si-H and Si-D bonds. The ratio between the N-H and N-D bond-stretching frequencies is 1.37, which is close to the ratio between the square roots of the effective masses of the N-H and N-D bonds. The results of this study are in good consistency.

The experiments found that the Si-H bond stretching frequency of $\alpha\text{-SiN}_x\text{:H}$ is normally about 2160 cm^{-1} . For the PECVD $\alpha\text{-SiN}_x\text{:H}$ films prepared at high NH_3/SiH_4 flow ratio R, the Si-H bond-stretching frequency increased to about $2190 - 2200\text{ cm}^{-1}$ [14, 15]. The increment is about $30 - 40\text{ cm}^{-1}$. By replacing hydrogen with deuterium in the similar experiments, the Si-D bond-stretching frequency was found to increase by about the same amount. From the above calculations, the difference between the Si-H bond-stretching frequency of the SiH bond and the Si-H asymmetric stretching frequency of the SiH_2 bond is 30 cm^{-1} . The difference is the same for the deuterium case. It was discussed before [31] that the $N_2\text{-SiH}_2$ bond is responsible for the Si-H bond-stretching frequency higher than 2160 cm^{-1} by $30 - 40\text{ cm}^{-1}$.

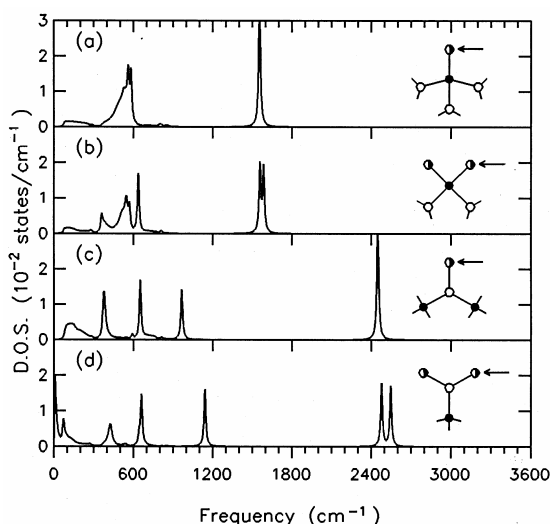


Fig. 5. Vibrational DOS for the D atom in the clusters of (a) $N_3\text{-SiD}$, (b) $N_2\text{-SiD}_2$, (c) $Si_2\text{-ND}$ and (d) $Si\text{-ND}_2$.

The calculated N-H bond-stretching frequency of the $Si_2\text{-NH}$ bond is 3350 cm^{-1} and the N-H asymmetric and symmetric stretching modes of the $Si\text{-NH}_2$ bond are at 3460 and 3412 cm^{-1} , respectively. The IR experimental data [14, 16] are 3350 cm^{-1} for the N-H bond-stretching mode of the NH bond and 3450 cm^{-1} for the N-H bond-stretching mode of the NH_2 bond. Table 3 presents the molecule vibrational modes and IR intensities of $SiNH_2(D_2)$ and $Si_2NH(D)$ calculated by the density functional theory, called B3LYP, with basis sets aug-cc-pVTZ [32]. See ref. 33 for a description of

this method. The results show that the IR intensity of the NH_2 asymmetric mode is six times higher than that of the symmetric mode. Compared with the values of the N-H bond stretching frequency of the NH bond and the symmetric and asymmetric stretching frequencies of the NH_2 bond, the experimentally measured 3450 cm^{-1} , in $\alpha\text{-SiN}_x\text{:H}$, is due to the asymmetric stretching mode of the NH_2 bond.

Table 2. Vibrational frequencies (cm^{-1}) of the local modes in $\alpha\text{-SiN}_x\text{:H}$ (D).

Group	Peaks		Groups	peaks	
	Calculated	Experiments		Calculated	Experiments
<u>$\text{N}_3\text{-SiH}$</u>	2160 724	2150 ^a , 2160 ^b 630 ~ 650 ^a	<u>$\text{N}_3\text{-SiD}$</u>	1554 580 560	1600 ^b
<u>$\text{N}_2\text{-SiH}_2$</u>	2190 2176 904 854 728 486	2170~2200 ^{a, b}	<u>$\text{N}_2\text{-SiD}_2$</u>	1584 1558 636 568 546 360	
<u>$\text{Si}_2\text{-NH}$</u>	3350 1180 472	3340 ^a , 3350 ^c 1150 ^a , 1190 ^b	<u>$\text{Si}_2\text{-ND}$</u>	2448 966 650 378	2475 ^d 970 ^d , 1000 ^b
<u>Si-NH_2</u>	3460 3412 1540 898 666 546	3450 ^{a, b} 1540 ^a , 1545 ^d	<u>Si-ND_2</u>	2548 2478 1142 660 538 424	

^a Reference 16.

^b Reference 14.

^c Reference 17.

^d Reference 12.

The charges are 2.55 e at Si and 1.41 e at H in the $\text{N}_3\text{-SiH}$, and 2.01 e at Si and 1.52 e at H in the $\text{N}_2\text{-SiH}_2$. The net charges of Si^+ and H^- are higher in the SiH_2 bond. The Si-H bond-stretching frequency is higher in the SiH_2 bond than in SiH bond. For the NH bonds, the charges are 6.1 e at N and 0.9 e at H in the $\text{Si}_2\text{-NH}$, and 5.74 e at N and 0.89 e at H in the Si-NH_2 . The net charge at the N site in the $\text{Si}_2\text{-NH}$ is larger than in the Si-NH_2 . The Coulomb force between N and H would be larger in the $\text{Si}_2\text{-NH}$ bond than in the Si-NH_2 bond. The fact that the NH bond stretching frequency is higher in NH_2 bond than in NH bond indicates that the binding energy should be the dominant factor in influencing the bond-stretching frequency of the NH_2 bond and the H-H interaction has the effect of shifting the N-H asymmetric stretching frequency higher.

5. Conclusion

Both electronic and vibrational local DOS of the $\alpha\text{-SiN}_x\text{:H}$ are calculated. In the electronic study, the Si DB can form a defect states in the middle of the bandgap. The N DB can form an empty state at the top of the valence band by transferring charge from the upper lone pair p_z state to the dangling bond state. The anti-bonding $p\pi^*$ state of the N-N DB is in the energy gap near the valence

band. The N site of the $\text{Si}_2\text{-N-H}_2$ bond can form a N_4^+K^- defect pair with Si DB.

Table 3. Vibrational frequencies (cm^{-1}) and IR strength (km mol^{-1}) of Si_2NH (D) and SiNH_2 (D_2) molecules calculated by the density function theory [32].

	N-H (D) bending		N-H (D) stretching	
	Frequency	IR strength	Frequency	IR Strength
Si_2NH	967	25.30	3517	19.70
Si_2ND	846	0.87	2578	0.73
SiNH_2	1577 (scissors)	26.60	3508 (s)	7.30
			3588 (a)	45.60
SiND_2	1184 (scissors)	0.75	2534 (s)	0.72
			2648 (a)	0.74

(s) represents symmetric stretching

(a) represents asymmetric stretching.

In the vibrational study, both of the calculated bond-stretching modes of the SiH_2 and NH_2 bonds are split. The Si-H bond-stretching frequency higher than 2160 cm^{-1} , in the region of $2190 - 2200\text{ cm}^{-1}$, is due to the asymmetric stretching mode of the SiH_2 bond. The N-H bond-stretching mode at 3450 cm^{-1} is due to the asymmetric stretching mode of the NH_2 bond. The IR intensity is high for the asymmetric stretching modes of the SiH_2 and NH_2 bonds. The experimental measured stretching modes of the SiH_2 and NH_2 bonds are ascribed to their asymmetric stretching modes. The SiH_2 and NH_2 bonds seem to have a large fraction in some heavily hydrogenated amorphous silicon nitride.

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