Structural differences between deuterated and hydrogenated silicon nitride/oxynitride

An Shih, Shin-Hung Yeh, and Si-Chen Lee^{a)}

Department of Electrical Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

T. R. Yang

Department of Physics, National Normal University, Taipei, Taiwan, Republic of China

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Hydrogenated and deuterated silicon nitride ($a\text{-SiN}_x\text{:H}$ and $a\text{-SiN}_x\text{:D}$) and silicon oxynitride ($a\text{-SiO}_x\text{N}_y\text{:H}$ and $a\text{-SiO}_x\text{N}_y\text{:D}$) films are prepared by plasma-enhanced chemical vapor deposition. Their transmission and photoluminescence spectra were measured. Both the photoluminescence and transmission spectra show that the deuterated films have higher energy gaps than those of the hydrogenated films in the same growth condition. The infrared absorption spectra of these samples are identified and compared in detail. From the infrared spectra, the interaction between N–D bond rocking vibration and Si–N bond stretching vibration is observed, which pushes N–D bond rocking vibration to a higher energy. It is also observed that the refractive index of deuterated film is lower than the hydrogenated film in the same growth condition due to its lower density. © 2001 American Institute of Physics. [DOI: 10.1063/1.1364645]

I. INTRODUCTION

Recently, the hot electron degradation in silicon metal oxide semiconductor field effect transistor (MOSFET) has been found to be greatly reduced by passivating the silicon–silicon dioxide interface using deuterium instead of hydrogen¹ and several articles^{2–5} also demonstrate that the incorporation of deuterium instead of hydrogen in amorphous silicon tends to slow the decay of its photoconductivity under illumination and improves the reliability of thin film transistor.⁶ It encourages us to study the effect when deuterium atoms are incorporated into the insulator such as silicon nitride and silicon oxynitride. Silicon nitride and silicon oxide are the most popular insulators in the microelectronic device technology. They are widely used for many applications, such as surface passivation, interlayer insulator, diffusion mask, and gate insulator. Plasma-enhanced chemical vapor deposition (PECVD) is usually used to deposit silicon nitride. However, when N_2O gas is used in PECVD to prepare silicon dioxide, the grown films contain nitrogen atoms and become silicon oxynitride films. Hydrogenated and deuterated silicon nitride ($a\text{-SiN}_x\text{:H}$ and $a\text{-SiN}_x\text{:D}$) and silicon oxynitride ($a\text{-SiO}_x\text{N}_y\text{:H}$ and $a\text{-SiO}_x\text{N}_y\text{:D}$) films were prepared by PECVD. Their Fourier transform infrared (FTIR) spectra, photoluminescence (PL) spectra, transmission spectra, growth rates, and refractive indexes were measured and studied in detail in this article.

II. EXPERIMENT

Hydrogenated and deuterated silicon nitride ($a\text{-SiN}_x\text{:H}$ and $a\text{-SiN}_x\text{:D}$) and silicon oxynitride ($a\text{-SiO}_x\text{N}_y\text{:H}$ and $a\text{-SiO}_x\text{N}_y\text{:D}$) films were deposited on high-resistivity ($30\ \Omega\text{cm}$) two-sided polished (100) crystalline silicon by

PECVD. The reason for using two-sided polished substrates is because unpolished substrates tend to strongly scatter the IR light in the wavelength range $2\text{--}10\ \mu\text{m}$. The deposition parameters were as follows: rf power density is $0.26\ \text{W}/\text{cm}^2$, the substrate temperature $250\ ^\circ\text{C}$, the electrode space $3\ \text{cm}$, and chamber pressure $0.45\ \text{Torr}$. The gas flow rates and growth rates of eight samples are listed in Table I. The gas phase composition X_g is defined as $\text{ND}_3/(\text{SiD}_4+\text{ND}_3)$ or $\text{NH}_3/(\text{SiH}_4+\text{NH}_3)$ in the silicon nitride materials and as $\text{N}_2\text{O}/(\text{SiD}_4+\text{N}_2\text{O})$ or $\text{N}_2\text{O}/(\text{SiH}_4+\text{N}_2\text{O})$ in the silicon oxynitride materials. To identify the IR absorption peaks of hydrogenated and deuterated silicon nitride and silicon oxynitride films, these samples were prepared in high dilution and low dilution conditions, respectively. In order to identify which radical group gave rise to the observed peak, the samples were annealed at the temperature from 300 to $800\ ^\circ\text{C}$ for $10\ \text{min}$ in each step. The refractive index and growth rate were measured by ellipsometry which utilized a He–Ne laser ($\lambda=632.8\ \text{nm}$) as the light source. Because the thickness of the samples might alter the escaping rates of hydrogen and deuterium atoms, the thicknesses of silicon nitride samples with $X_g=0.95$ are kept the same, $100\ \text{nm}$ thick; the silicon nitride samples with $X_g=0.5$ and silicon oxynitride samples with $X_g=0.6$ are kept the same, $200\ \text{nm}$ thick; and the silicon oxynitride samples with $X_g=0.15$ are kept the same, $80\ \text{nm}$ thick. The SIMS data were used to determine the concentration of hydrogen atoms, measured by Cameca $5f$ in ultrahigh vacuum. The hydrogen standard sample was purchased from Charles Evans Standard, which was prepared by ion implanting known quantity of hydrogen atoms into the $c\text{-Si}$ substrate. The FTIR spectra were measured by Bruker IFS 120 HR IR spectrometer. The resolution of the infrared spectra was $0.48\ \text{cm}^{-1}$. Since the IR spectra of Si–D stretching mode was mixed with the absorption of water vapor in air, the infrared spectra of all samples were measured at room

^{a)}Electronic mail: scllee@cc.ee.ntu.edu.tw

TABLE I. Gas flow rates, growth rates, and refractive indexes of hydrogenated and deuterated silicon nitride ($a\text{-SiN}_x\text{:H}$ and $a\text{-SiN}_x\text{:D}$) and silicon oxynitride ($a\text{-SiO}_x\text{N}_y\text{:H}$ and $a\text{-SiO}_x\text{N}_y\text{:D}$) films.

Sample No.	Material	Xg	Gas flow rate (sccm)	Growth rate (nm/min)	Refractive index
1	$a\text{-SiN}_x\text{:D}$	0.95	$\text{SiD}_4\text{:ND}_3 = 1:19$	9.6	1.714
2	$a\text{-SiN}_x\text{:H}$	0.95	$\text{SiH}_4\text{:NH}_3 = 1:19$	12.8	1.8
3	$a\text{-SiN}_x\text{:D}$	0.5	$\text{SiD}_4\text{:ND}_3 = 2:2$	23.3	2.28
4	$a\text{-SiN}_x\text{:H}$	0.5	$\text{SiH}_4\text{:NH}_3 = 2:2$	19.4	2.74
5	$a\text{-SiO}_x\text{N}_y\text{:D}$	0.6	$\text{SiD}_4\text{:N}_2\text{O:D}_2 = 2:3:5$	32.4	1.564
6	$a\text{-SiO}_x\text{N}_y\text{:H}$	0.6	$\text{SiH}_4\text{:N}_2\text{O:H}_2 = 2:3:5$	28.6	1.828
7	$a\text{-SiO}_x\text{N}_y\text{:D}$	0.15	$\text{SiD}_4\text{:N}_2\text{O:D}_2 = 2:0.35:5$	10.2	3.02
8	$a\text{-SiO}_x\text{N}_y\text{:H}$	0.15	$\text{SiH}_4\text{:N}_2\text{O:H}_2 = 2:0.35:5$	9.5	3.31

temperature in high vacuum. To obtain higher resolution, the spectra were measured and averaged for 1024 times. The PL spectra were measured via excitation by an argon laser at a wavelength of 457.9 nm or He–Cd laser at a wavelength of 325 nm.

III. RESULTS AND DISCUSSION

The growth rates and refractive indexes measured at 632.8 nm of silicon nitride and oxynitride are listed in Table I. Apparently, the refractive index of deuterated material is lower than that of hydrogenated material in the same growth condition. The growth rate of $a\text{-SiO}_x\text{N}_y\text{:D}$ is faster than that of $a\text{-SiO}_x\text{N}_y\text{:H}$. This phenomenon still exists in silicon nitride when Xg equals 0.5 (low dilution condition), such as samples 3 and 4. The low dilution growth condition would suggest that a higher effective dilution is obtained for SiD_4 than for SiH_4 , which leads to a higher electron temperature and thus a higher dissociation rate and a higher growth rate. The similar phenomenon is observed in amorphous silicon films⁷ but when Xg equals 0.95 (high dilution condition), to the contrary, the growth rate of hydrogenated silicon nitride becomes faster than that of deuterated silicon nitride, which means replacing SiH_4 with SiD_4 will increase the growth rate, but using ND_3 instead of NH_3 will slow down the growth rate.

A. Optical absorption spectra

Figures 1(a) and 1(b) display the absorption spectra, i.e., $(\alpha h\nu)^{1/2}$ vs $h\nu$, for the silicon nitride samples with Xg = 0.95 and 0.5, respectively. By extrapolating the linear part of the figure to the horizontal axis, the optical gap (E_{gopt}) of the films can be extracted according to the empirical formula derived by Tauc;⁸

$$(\alpha h\nu)^{1/2} = B(h\nu - E_{\text{gopt}}). \quad (1)$$

The optical gaps of deuterated and hydrogenated silicon nitride films with Xg = 0.95 are 5.13 and 4.98 eV, respectively. The optical gaps of deuterated and hydrogenated silicon nitride films with Xg = 0.5 are 2.44 and 2.23 eV, respectively. It is obvious that the deuterated silicon nitride has a higher optical gap than that of the hydrogenated one in the same growth condition. The silicon oxynitride films also exhibit the similar characteristics as show in Figs. 1(c) and 1(d). The optical gaps of deuterated and hydrogenated silicon oxyni-

tride films with Xg = 0.6 are 3.18 and 2.68 eV, respectively, and with Xg = 0.15 are 2.09 and 2.01 eV, respectively.

B. PL spectra

The PL spectra of $a\text{-SiN}_x\text{:D}$ and $a\text{-SiN}_x\text{:H}$ films with Xg = 0.5 are shown in Fig. 2. The PL spectra were measured at 15 K via He–Cd laser with 325 nm as the excitation source. Obviously, the PL peak of $a\text{-SiN}_x\text{:D}$ film is at higher energy than that of the $a\text{-SiN}_x\text{:H}$ film in the same growth condition. Both are 0.3 to 0.5 eV lower than their respective optical gap. Therefore, the PL band originates from recombination of carriers trapped in the band tails. The wider optical gap of $a\text{-SiN}_x\text{:D}$ makes its PL peak higher than that of $a\text{-SiN}_x\text{:H}$. Several peaks are observed in PL spectra of $a\text{-SiN}_x\text{:D}$ and $a\text{-SiN}_x\text{:H}$ films, which means that inhomogeneity and thus the different quantum confinement effect exists in these films.⁹ The PL spectra of $a\text{-SiO}_x\text{N}_y\text{:D}$ and $a\text{-SiO}_x\text{N}_y\text{:H}$ films with Xg = 0.6 are shown in Fig. 3. The PL spectra were measured at 15 K using 325 nm He–Cd laser as the excitation source. The PL peak of $a\text{-SiO}_x\text{N}_y\text{:D}$ (2.2 eV) is at a higher energy than the peak of $a\text{-SiO}_x\text{N}_y\text{:H}$ (2.08 eV) because of its higher optical energy gap as well. Figure 4 displays the PL spectra of $a\text{-SiO}_x\text{N}_y\text{:D}$ and $a\text{-SiO}_x\text{N}_y\text{:H}$ films with Xg = 0.15. The PL spectra were measured at 10 K using 457.9 nm Ar^+ laser as the excitation source. Because the photoluminescence efficiency of these two samples are poorer than those of the other samples, the Ar^+ laser is used to replace the He–Cd laser as the pumping source to get the better spectra. The PL peak of $a\text{-SiO}_x\text{N}_y\text{:D}$ (1.7 eV) is at higher energy than that of $a\text{-SiO}_x\text{N}_y\text{:H}$ (1.65 eV) because of its higher optical energy gap. Because the optical gaps of $a\text{-SiN}_x\text{:D}$ and $a\text{-SiN}_x\text{:H}$ films with Xg = 0.95 are too high to get the PL spectra via the He–Cd laser as pumping source, the PL spectra of these two samples are not shown in this article.

C. IR spectra

Figure 5 shows the IR spectra of deuterated and hydrogenated silicon nitride with Xg = 0.95 and 0.5, respectively. For $a\text{-SiN}_x\text{:H}$ film with Xg = 0.95, the N–H stretching mode vibration is at 3342 cm^{-1} .¹⁰ The small peak in 3445 cm^{-1} is the N–H₂ stretching mode vibration. For $a\text{-SiN}_x\text{:D}$ film with Xg = 0.95, the N–D stretching mode vibration is at 2470 cm^{-1} ¹¹⁰ and the N–D₂ stretching mode vibration is 2562

FIG. 1. $(\alpha h\nu)^{1/2}$ vs photon energy plot of (a) $a\text{-SiN}_x\text{:D}$ and $a\text{-SiN}_x\text{:H}$ with $X_g=0.95$, (b) $a\text{-SiN}_x\text{:D}$ and $a\text{-SiN}_x\text{:H}$ with $X_g=0.5$, (c) $\text{SiO}_x\text{N}_y\text{:D}$, and $a\text{-SiO}_x\text{N}_y\text{:H}$ with $X_g=0.6$, (d) $\text{SiO}_x\text{N}_y\text{:D}$, and $a\text{-SiO}_x\text{N}_y\text{:H}$ with $X_g=0.15$. The solid lines represent the spectra of the deuterated materials and the dashed lines represent the hydrogenated materials.

cm^{-1} . The ratio of N–H stretching mode vibration frequency to N–D stretching mode vibration frequency is 1.35, approximately inversely proportional to the square root of the ratio of their reduced mass. The ratio of N–H₂ bending mode frequency to N–D₂ bending mode frequency is also approximately equal to 1.35. In the $a\text{-Si:H}$ films, the stretching mode for Si–H monohydride located in a small void (one silicon vacancy) is at 2000 cm^{-1} , whereas for SiH monohy-

dride and SiH₂ dihydride located in a large void, the peak shifts to $2070\text{--}2090\text{ cm}^{-1}$. In $a\text{-SiN}_x\text{:H}$ film, the existence of nitrogen atoms back bonded to SiH_n radicals shifts the 2080 cm^{-1} peak to the higher frequency because of the greater electronegativity of nitrogen atom as compared to silicon atom.^{11,12} Therefore, in the hydrogenated silicon nitride sample with $X_g=0.95$, the small peak at 2150 cm^{-1} is the Si–H stretching mode vibration with nitrogen atoms back

FIG. 2. 15 K PL spectra of $a\text{-SiN}_x\text{:D}$ and $a\text{-SiN}_x\text{:H}$ with $X_g=0.5$.

FIG. 3. 15 K PL spectra of $a\text{-SiO}_x\text{N}_y\text{:D}$ and $a\text{-SiO}_x\text{N}_y\text{:H}$ with $X_g=0.6$.

FIG. 4. 10 K PL spectra of $a\text{-SiO}_x\text{N}_y\text{:D}$ and $a\text{-SiO}_x\text{N}_y\text{:H}$ with $X_g=0.15$.

bonded to Si–H. The Si–D stretching mode vibration of deuterated silicon nitride sample with $X_g=0.95$ is too small to be identified clearly. The concentration of N–H bonds can be calculated by the experimentally measured FTIR spectral areas according to the relation:¹³

$$N_{\text{N-H}} = \frac{cn\omega_i}{2\pi^2} \frac{\mu}{e_s^{*2}} \int \frac{\alpha(\omega)}{\omega} d\omega, \quad (3)$$

$$= A_{\text{N-H}}^s \times \int \frac{\alpha(\omega)}{\omega} d\omega, \quad (4)$$

where c is the light velocity, n the refractive index, μ the reduced mass of N and H, ω_i the peak absorption frequency, e_s^* the effective charge of the N–H bond, and α the absorp-

FIG. 5. IR spectra of $a\text{-SiN}_x\text{:D}$ and $a\text{-SiN}_x\text{:H}$ films with $X_g=0.95$ and 0.5.TABLE II. Optical gaps, concentration of N–D(H) bonds and concentration of Si–D(H) bonds of deuterated and hydrogenated silicon nitride ($a\text{-SiN}_x\text{:H}$ and $a\text{-SiN}_x\text{:D}$) and silicon oxynitride ($a\text{-SiO}_x\text{N}_y\text{:H}$ and $a\text{-SiO}_x\text{N}_y\text{:D}$) films.

Sample No.	Material	X_g	Optical gap (eV)	N–D/N–H (cm^{-3})	Si–D/Si–H (cm^{-3})
1	$a\text{-SiN}_x\text{:D}$	0.95	5.13	4.7×10^{22}	
2	$a\text{-SiN}_x\text{:H}$	0.95	4.98	2.4×10^{22}	8.4×10^{20}
3	$a\text{-SiN}_x\text{:D}$	0.5	2.44	6.5×10^{21}	2.1×10^{22}
4	$a\text{-SiN}_x\text{:H}$	0.5	2.23	2.5×10^{21}	1.9×10^{22}
5	$a\text{-SiO}_x\text{N}_y\text{:D}$	0.6	3.18		5.7×10^{21}
6	$a\text{-SiO}_x\text{N}_y\text{:H}$	0.6	2.68		1.1×10^{22}
7	$a\text{-SiO}_x\text{N}_y\text{:D}$	0.15	2.09		1.4×10^{22}
8	$a\text{-SiO}_x\text{N}_y\text{:H}$	0.15	2.01		1.2×10^{22}

tion coefficient. This relationship can also be applied to measure the N–D, Si–H, and Si–D concentration. $A_{\text{N-H}}^s$ is the proportionality constant relating the integrated stretching mode absorption to the concentrations of N–H bonds. Similarly, $A_{\text{N-D}}^s$ is the proportionality constant of N–D bonds to integrated N–D absorption spectra. The hydrogen concentration of $a\text{-SiN}_x\text{:H}$ with $X_g=0.95$ was measured by SIMS to be $2.4 \times 10^{22} \text{ cm}^{-3}$ which equals the sum of N–H bonds plus Si–H bonds. $A_{\text{Si-H}}^s$ and $A_{\text{Si-D}}^s$ are 6.9×10^{19} and 1×10^{20} , respectively.⁷ Then the averaged values for $A_{\text{N-H}}^s$ can be determined by Eq. (4), which is equal to 2.6×10^{20} . From Eq. (3), since the $\omega_i\mu$ value of N–D stretching mode is $\sqrt{2}$ times larger, where other parameters are the same as these values of a N–H stretching mode vibration, $A_{\text{N-D}}^s$ should be $\sqrt{2}$ times larger than $A_{\text{N-H}}^s$, which is 3.7×10^{20} then the concentrations of N–D, N–H, Si–D, and Si–H bonds could be obtained by Eq. (4), which are listed in Table II. The Si–D stretching mode IR peak of $a\text{-SiN}_x\text{:D}$ with $X_g=0.95$ is too small to integrate accurately; therefore, the concentration of Si–D bonds of this sample cannot be obtained.

In Fig. 5, the peaks of $a\text{-SiN}_x\text{:H}$ film with $X_g=0.95$ at 1544, 1170, and 870 cm^{-1} are N–H₂ bending mode, N–H rocking mode, and Si–N stretching mode vibration, respectively.^{10,11} The peak of $a\text{-SiN}_x\text{:D}$ film with $X_g=0.95$ at 1165 cm^{-1} is N–D₂ bending mode vibration. The position of N–D rocking mode vibration could be obtained by dividing the frequency of N–H rocking mode vibration by $\sqrt{2}$, which is equal to 829 cm^{-1} but this position is close to the position of Si–N stretching mode vibration, therefore the interaction between N–D rocking mode and Si–N stretching mode vibration is expected. As shown in Fig. 5, two peaks could be the candidates for the N–D rocking mode vibration. One peak is at 987 cm^{-1} and the other is the shoulder at approximately 860 cm^{-1} . However, because the peak at 987 cm^{-1} decreases with the rise of the annealing temperature as shown in Fig. 6(a), it should be the N–D rocking mode vibration and the shoulder at 860 cm^{-1} should be the Si–N stretching mode vibration. The ratio of N–H to N–D stretching mode vibration frequency is 1.35, whereas the ratio of N–H to N–D rocking mode vibration is only 1.19. The reason is that the interaction between the N–D rocking mode and Si–N stretching mode vibrations pushes N–D rocking mode to a higher energy.

In Fig. 6(a), when $a\text{-SiN}_x\text{:D}$ and $a\text{-SiN}_x\text{:H}$ films with

FIG. 6. IR spectra of (a) $a\text{-SiN}_x\text{:D}$ film with $X_g=0.95$ annealed at the temperature from 300 to 800 °C for 10 min in each step. (b) The variation of integrated IR peak intensities of $a\text{-SiN}_x\text{:D}$ (●) and $a\text{-SiN}_x\text{:H}$ (▲) as a function of different annealing temperatures.

$X_g=0.95$ were annealed to over 600 °C, a new peak at 1070 cm^{-1} emerges, which should be the transverse optical phonon band of SiN_x network.¹⁴ In Fig. 6(a), a small band at 1128 cm^{-1} emerges from the shoulder when $a\text{-SiN}_x\text{:D}$ film with $X_g=0.95$ is annealed, which is assigned to be the LO mode of the Si-N stretching mode vibration.^{15,16} The Si-H stretching mode vibration of $a\text{-SiN}_x\text{:H}$ film with $X_g=0.5$ is

at 2133 cm^{-1} which is slightly lower than the $a\text{-SiN}_x\text{:H}$ film with $X_g=0.95$ (2150 cm^{-1}) resulting from the decrease of the nitrogen ratio. The peak at 1565 cm^{-1} in $a\text{-SiN}_x\text{:D}$ film with $X_g=0.5$ is the Si-D stretching mode bonded to nitrogen atoms; the shoulder at 1523 cm^{-1} is assigned to be Si-D or Si-D₂ located in a large void in the silicon nitride environment.⁷ In $a\text{-SiN}_x\text{:H}$ film with $X_g=0.5$, the peak at 660 cm^{-1} is the Si-H wagging mode vibration back bonded to nitrogen atoms. A peak of $a\text{-SiN}_x\text{:D}$ film with $X_g=0.5$ is at 603 cm^{-1} , which is attributed to the mixture of the N₃Si-D and N₂Si-D bending mode vibrations. The small peak at 704 cm^{-1} should be the Si-D₂ bending mode vibration in the N₂Si-D₂ configuration. In the $a\text{-SiN}_x\text{:D}$ film with $X_g=0.5$, the weak peak at 527 cm^{-1} is related to the Si-D rocking mode vibration in the plane defined by the D-Si-N unit. In $a\text{-SiN}_x\text{:H}$ film with $X_g=0.5$, the small peak at 590 cm^{-1} might attribute to the carbon impurity in the substrate.¹⁷

A measure of the amount of microvoid is given by the ratio, $R = I_{3445} / (I_{3342} + I_{3445})$. This is calculated to be 1.9% for the $a\text{-SiN}_x\text{:H}$ films with $X_g=0.95$. By analogy, the microvoid fraction of the $a\text{-SiN}_x\text{:D}$ films with $X_g=0.95$, obtained from the modes at 2470 and 2562 cm^{-1} , is 3.2%. This means that there are more microvoids in the $a\text{-SiN}_x\text{:D}$ film. Therefore, the refractive index of the $a\text{-SiN}_x\text{:D}$ film is smaller than that of the $a\text{-SiN}_x\text{:H}$ film. Figure 6(b) shows the normalized integrated IR intensity of the N-D stretching mode vibration in $a\text{-SiN}_x\text{:D}$ film with $X_g=0.95$ and N-H stretching mode vibration in $a\text{-SiN}_x\text{:H}$ film with $X_g=0.95$ versus the annealing temperature. The integrated intensity is normalized to original intensity prior to the thermal annealing. Although the growth rate of $a\text{-SiN}_x\text{:D}$ film with $X_g=0.95$ is lower than that of $a\text{-SiN}_x\text{:H}$ film with $X_g=0.95$, the disappearance rate of N-D bonds is more rapid than that of N-H bonds. It also suggests that the $a\text{-SiN}_x\text{:H}$ film is denser than $a\text{-SiN}_x\text{:D}$ film in the same growth condition although the growth rate of the $a\text{-SiN}_x\text{:D}$ film is slower, which is consistent with the difference in the refractive indexes.

Figures 7(a) and 7(b) display the IR spectra of silicon oxynitride films. In Fig. 7(a), the SiH_n bond stretching band in $a\text{-SiO}_x\text{N}_y\text{:H}$ film with $X_g=0.6$, between 2300 and 2000 cm^{-1} , shows three distinct peaks at 2245, 2195, and 2145 cm^{-1} .¹⁸ The main peak of this vibration in the $a\text{-SiO}_x\text{N}_y\text{:H}$ film with $X_g=0.15$ is 2095 cm^{-1} , which corresponds to the Si-H_n in a large void in the oxygen environment. In the $a\text{-SiO}_x\text{N}_y\text{:H}$ film with $X_g=0.6$, the fractions of peaks at 2245 and 2195 cm^{-1} increase because the ratio of N₂O increases. The Si-H groups can be written as $\text{HSiSi}_{3-n}\text{O}_n$, with $n=0-3$, and the proposed frequencies are $2095 + 50n$ cm^{-1} . The greater electronegativity of oxygen compared to nitrogen draws charge away from the Si atom of Si-H bond and causes the Si-H stretching frequency to 2245 cm^{-1} . In Fig. 7(b), for $a\text{-SiO}_x\text{N}_y\text{:D}$ film with $X_g=0.15$, a small peak at 1528 cm^{-1} would be the Si-D or Si-D₂ in large void in the oxygen environment. With the similar concept as hydrogenated silicon oxynitride, as shown in Figs. 7(a) and 7(b), the Si-D groups can be written as $\text{DSiSi}_{3-n}\text{O}_n$, with $n=0-3$, and the proposed frequencies are $1528 + 34n$ cm^{-1} .

FIG. 7. IR spectra of $a\text{-SiO}_x\text{N}_y\text{:D}$ and $a\text{-SiO}_x\text{N}_y\text{:H}$ with (a) $X_g=0.6$, (b) $X_g=0.15$. The upper curve is the IR spectra of $a\text{-SiO}_x\text{N}_y\text{:D}$ and the lower curve is the IR spectra of $a\text{-SiO}_x\text{N}_y\text{:H}$.

The concentrations of Si-D and Si-H bonds of the $a\text{-SiO}_x\text{N}_y\text{:D}$ and $\text{SiO}_x\text{N}_y\text{:H}$ film with $X_g=0.6$ are listed in Table II, calculated by Eq. (4). The Si-D stretching mode of $a\text{-SiO}_x\text{N}_y\text{:D}$ film with $X_g=0.6$ was almost at 1630 cm^{-1} , in the configuration of $\text{O}_3\text{Si-D}$, and the concentration of Si-D is smaller than that of Si-H. Therefore, the fraction of oxygen atoms of $a\text{-SiO}_x\text{N}_y\text{:D}$ film with $X_g=0.6$ should be larger than that of $a\text{-SiO}_x\text{N}_y\text{:H}$ film with $X_g=0.6$, and thus the band gap of $a\text{-SiO}_x\text{N}_y\text{:D}$ film with $X_g=0.6$ is larger

than $a\text{-SiO}_x\text{N}_y\text{:H}$ film with $X_g=0.6$, which is consistent with the PL and transmission spectra. The stretching mode of Si-O-Si bond of $a\text{-SiO}_x\text{N}_y\text{:D}$ and $\text{SiO}_x\text{N}_y\text{:H}$ films with $X_g=0.6$ and 0.15 are at 1036 , 1041 , 1031 , and 1016 cm^{-1} , respectively. In the $a\text{-SiO}_x\text{N}_y\text{:D}$ and $\text{SiO}_x\text{N}_y\text{:H}$ film with $X_g=0.15$, a small band at 1128 cm^{-1} which is small and like a shoulder in $a\text{-SiO}_x\text{N}_y\text{:D}$ and $\text{SiO}_x\text{N}_y\text{:H}$ films with $X_g=0.6$ is assigned to be the LO mode of the Si-N stretching mode vibration rather than the LO mode of the Si-O-Si stretching mode vibration. This peak is the stretching mode of Si-N and the weak band at 774 cm^{-1} is suggested to be the Si-N stretching mode in $\text{DSi}_2\text{-Si-N}$ configuration, which is comparatively lower than the Si-N stretching mode in $\text{H-Si}_2\text{-Si-N}$ configuration by 6 cm^{-1} due to the difference in the mass.¹⁴ The peak at 798 cm^{-1} is the Si-O-Si bending mode vibration.¹⁷ In Fig. 7(a), the shoulders of $a\text{-SiO}_x\text{N}_y\text{:H}$ film with $X_g=0.6$ at 978 and 938 cm^{-1} are the Si-H bending and wagging mode vibration in the configuration of $\text{H}_2\text{-Si-O}_2$.¹⁴ In the hydrogenated silicon oxynitride films with $X_g=0.6$ and 0.15 , the small peak at 704 cm^{-1} is the rocking mode of the $\text{O}_2\text{Si-H}_2$ configuration.¹⁸ By multiplying the shoulders of the deuterated silicon oxynitride films with $X_g=0.6$ and 0.15 at 700 , 673 , and 490 cm^{-1} by $\sqrt{2}$, they correspond to 989 , 951 , and 693 cm^{-1} , which are close to the Si-H bending, wagging, and rocking mode vibration in the configuration of $\text{H}_2\text{-Si-O}_2$, respectively. Therefore, the peaks at 700 , 673 , and 490 cm^{-1} are the Si-D bending, wagging, and rocking mode vibration in the configuration of $\text{D}_2\text{-Si-O}_2$, respectively. In the hydrogenated silicon oxynitride films with $X_g=0.6$ and 0.15 , the peak at 855 cm^{-1} is assigned to be the Si-H bending modes with HSi-O_3 and the HSi-O_2 configurations.^{19,20} Since the two vibration frequencies are very close, the two modes may overlap. Corresponding to these two peaks, the 634 cm^{-1} bands of the deuterated silicon oxynitride films with $X_g=0.6$ and 0.15 are proposed to be the Si-D bending modes vibration with DSi-O_3 and the DSi-O_2 configurations. In $a\text{-SiO}_x\text{N}_y\text{:H}$ with $X_g=0.15$, the Si-H rocking mode vibrations at 796 and 645 cm^{-1} occur when the Si-H group has one nearest O-atom neighbor, that is, the HSi-OSi_2 configuration.¹³ The 796 cm^{-1} band is related to the Si-H rocking mode vibration in the plane defined by the H-Si-O unit. This vibration couples with the Si-O-Si bending mode vibration.²⁰ The 645 cm^{-1} band is associated with Si-H rocking mode vibration perpendicular to the plane defined by the H-Si-O unit.²¹ The 430 cm^{-1} band of $a\text{-SiO}_x\text{N}_y\text{:H}$ with $X_g=0.6$ is the rocking mode vibration of Si-O-Si. This peak of $a\text{-SiO}_x\text{N}_y\text{:D}$ with $X_g=0.6$ is at 440 cm^{-1} , which is a little higher than $a\text{-SiN}_x\text{:H}$ with $X_g=0.5$. When the IR spectra of the silicon oxynitride films with $X_g=0.15$ in Fig. 7(b) are compared, the peak of $a\text{-SiO}_x\text{N}_y\text{:D}$ with $X_g=0.15$ at 440 cm^{-1} protrudes from the Si-O-Si rocking mode band. This is the Si-D rocking mode vibration when the Si-D group has one nearest O-atom neighbor, i.e., the DSi-OSi_2 configuration. The 532 cm^{-1} band is related to the Si-D rocking mode vibration in the plane defined by the D-Si-O unit. The 440 cm^{-1} band is associated with Si-D rocking mode vibration perpendicular to the plane defined by

the D–Si–O unit, which couples with Si–O–Si rocking mode vibration.

IV. CONCLUSION

Hydrogenated and deuterated silicon nitride ($a\text{-SiN}_x\text{:H}$ and $a\text{-SiN}_x\text{:D}$) and silicon oxynitride ($a\text{-SiO}_x\text{N}_y\text{:H}$ and $a\text{-SiO}_x\text{N}_y\text{:D}$) films were studied in detail. The IR spectra of $a\text{-SiN}_x\text{:H}$, $a\text{-SiN}_x\text{:D}$, $a\text{-SiO}_x\text{N}_y\text{:H}$, and $a\text{-SiO}_x\text{N}_y\text{:D}$ are identified and compared. On one hand, the refractive indexes of the deuterated materials are lower than those of the hydrogenated materials in the same growth condition, and on the other hand, the optical gaps and PL peaks of the deuterated materials are higher than those of the hydrogenated materials. Besides, it is observed that the $a\text{-SiN}_x\text{:H}$ film is denser than $a\text{-SiN}_x\text{:D}$ film, and the growth rate of $a\text{-SiO}_x\text{N}_y\text{:D}$ is higher than $a\text{-SiO}_x\text{N}_y\text{:H}$ in the same growth condition. From the IR spectra, the interaction between the N–D bond rocking vibration and Si–N bond stretching vibration is observed. This interaction pushes the N–D bond rocking vibration to a higher energy.

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