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Observation of incident angle dependent phonon absorption in hydrogenated amorphous silicon nitride thin films

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We have demonstrated the existence of longitudinal- and transverse-like optical modes of Si–N bond in vibrational absorption spectrum of hydrogenated amorphous silicon nitride thin films. One of the longitudinal-like optical resonances coincides with the transverse-like mode of Si–O bond, and the other closely neighbors the bending mode of N–H bond. We have also shown that the conventionally assigned asymmetric stretching mode of Si–N bond is merely a transverse-like mode of the bond. The microstructures of both longitudinal- and transverse-like modes can well be apprehended by a *p*-polarized beam at an oblique incidence light, especially at Brewster angle incidence. The spectrum distortion induced by interference fringes can be eliminated at this condition. © *1998 American Institute of Physics.* [S0003-6951(98)04452-0]

Hydrogenated amorphous silicon nitride (a-SiN$_x$:H) thin films have attracted much attention,[1,2] mainly because of their indispensable role in amorphous silicon thin-film transistor (a-Si:H TFT) structures as a superior gate insulator. Knowledge of their microstructures and the electron-phonon scattering processes is very essential for making a reliable electronic device based on such materials. In this letter, we report the observation of incident angle dependent phonon absorption in vibrational absorption spectrum of a-SiN$_x$:H by using Fourier transform infrared spectroscopy (FTIR).[3,4] We have found that the longitudinal-like optical (LO) vibrational modes associated with Si–N bonds are located in the spectrum region that overlaps with some well-known bonds such as transverse mode (TO) of Si–O and bending mode of N–H. Therefore, distinguishing those modes (bonds) is very essential in a-SiN$_x$:H film's quality assessment.

The a-SiN$_x$:H thin films studied in this work were prepared by plasma-enhanced chemical vapor deposition (PECVD) on double-side polished Si wafers. The film depositions were carried out at the process chamber pressure of 0.43 Torr, the radio frequency (rf) power of 100 W, the substrate temperature of 250 °C, and ammonia to silane flow ratio of 200/18. Following the deposition, the film's thickness was measured using Dektak surface profiler, while the film's refractive index was deduced by observing a straight and horizontal baseline at Brewster incident angle with *p*-polarized light.[5] The film's dielectric constant at low frequency (1 MHz) was derived from capacitance–voltage ($C-V$) characteristics based on the metal-insulator-semiconductor (MIS) structure. The stoichiometry and hydrogen content (H content) of the film are determined by Rutherford-backscattering spectroscopy (RBS). Hydrogen evolution (H evolution) was carried out by the thermal annealing at 600 °C under vacuum in Leybold sputtering system. The IR spectra were recorded at room temperature using Bio-Rad FTS-40 Fourier transform infrared spectrometer and analyzed with Bio-Rad Win-IR software. The aperture of probe beam and the detector gain amplification were set at 2 cm^{-1} and unity, respectively. Meanwhile, the *p*-polarized probe beam was produced by a pike ZnSe wire grid linear polarizer, which was adjusted to an appropriate incident angle by a Harrick Brewster's angle sample holder. The resultant spectrum having a spectral resolution of 8 cm^{-1} is an average of 64 scans.

It was first reported by Berreman in 1963 that the longitudinal optical mode of the thin film of cubic crystal strongly absorbs *p*-polarized light at oblique incidence.[6] Since then many similar observations of the TO-LO pairs in amorphous materials have been reported.[7–9] According to Berreman's theory, a thin film with cubic or cubic-like structure has two normal modes of polarized lattice vibrations. One of the vibrations is parallel to the film surface with its frequency of ω_t, while the other is normal to the film surface with its frequency of ω_1. The former produces no electric field and occurs when the dielectric constant is very large. On the other hand, the latter produces an electric field normal to the surface due to the surface polarization and occurs when the dielectric constant is minimized. If an electric field parallel to the film surface with its frequency near ω_t is incident upon the film, lattice vibrations parallel to the surface will have a large amplitude due to a resonance phenomenon, since internal and external components of electric field parallel to the film surface must match. Likewise, an electric field normal to the film surface with its frequency near ω_1 will result in a large amplitude lattice vibrations normal to the surface, since the internal and external components of electric displacement normal to the surface must match.

When a *p*-polarized light beam strikes film with an oblique incidence, as illustrated in Fig. 1, the p vector can be treated as the sum of vectors normal ($p_\perp$) and parallel ($p_\parallel$) to the film surface. Apparently, $p_\perp$ is responsible for LO mode resonance while $p_\parallel$ attributes to TO mode resonance. The intensities of the LO and TO resonances are proportional to the magnitudes of $p_\perp$ and $p_\parallel$ vectors, respectively. As indicated in Fig. 1, at normal incidence, $p_\perp$ vector vanishes and no LO-like modes can be observed in the vibrational

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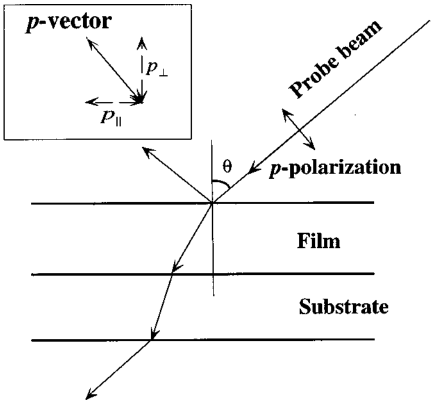

FIG. 1. Illustration of *p*-polarized light beam incidence on thin film at an oblique angle.

absorption spectrum. With the increase of light incident angle θ, $p_\perp$ increases and $p_\parallel$ decreases. Consequently, an increase of LO-like and a decrease of TO-like peak densities should be observed in vibrational absorption spectrum.

Figure 2 compares the vibrational absorption spectra of a-SiN$_x$:H collected at various incident angles with *p*-polarized beam. When the beam incident angle increases from 0° to 75°, the peak of so-called asymmetric stretching mode of Si–N bond[10,11] located at 880 cm^{-1} shrinks. In contrast, the shoulder of that peak evolves into another peak at 1040 cm^{-1}, which is the wave number conventionally assigned to Si–O (TO) bond.[12,13] In addition, the peak assigned to bending mode of N–H [N–H(b)] bond located at 1180 cm^{-1} is significantly intensified,[11,14] and its location is slightly shifted to 1215 cm^{-1}. Meanwhile the densities of the peaks assigned to stretching mode of N–H [N–H(s)] and Si–H [Si–H(s)] bonds, and bending mode of N–H$_2$ [N–H$_2(b)$] bond remain relatively constant with increasing incident angle, although the peak shapes are distorted by interference fringes.[15] The observation suggests that the bond associated with these decreasing and increasing absorption peaks contains longitudinal-like components of infrared-active vibrations which are sensitive to long-range electric forces. Thus, these decreasing and increasing peaks can be labeled as TO- and LO-like modes in a-SiN$_x$:H, respectively. The observed variation of the optical densities with *p*-polarized light at oblique incidence clearly indicates that the conventionally assigned asymmetric stretching mode of Si–N bond located at 880 cm^{-1} is, in fact, only a TO-like resonance of that mode. In addition, the association of LO-like peaks with this TO-like resonance is suggested by the fact that Si–N (TO like) mode is the only peak decreasing with the increasing incident angle, since LO- and TO-like modes are normally paired to each other in the absorption spectrum. Theoretically, frequency of LO phonons, ω_l, is related to that of TO phonons, ω_t, by the Lyddane–Sachs–Teller relation:[6,16]

$$\frac{\omega_l^2}{\omega_t^2}=\frac{\epsilon_0}{\epsilon_\infty}, \tag{1}$$

where ϵ_0 and ϵ_∞ are the dielectric constants at low and high frequency, respectively.

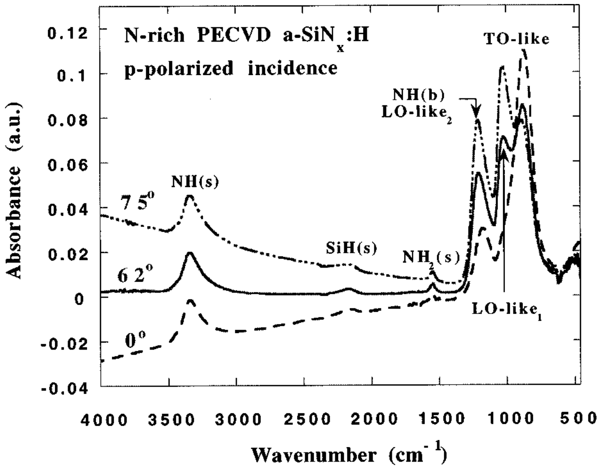

FIG. 2. Vibrational absorption spectra of N-rich PECVD a-SiN$_x$:H thin film collected with *p*-polarized light beam incidents at 0°, 62° (Brewster angle), and 75°, respectively. The thickness and refractive index of the film are 1500 Å and 1.88, correspondingly. The scripts of *s* and *b*, in the parentheses stand for stretching, bending modes, respectively, while LO-like stands for longitudinal-like mode and TO-like represents transverse-like optical modes of Si–N bond.

According to Eq. (1), the frequencies of LO modes should be always greater than those of TO modes, since $\epsilon_0 > \epsilon_\infty$, which is consistent with current observation. In particular, frequencies of both LO-like modes are greater than that of TO-like mode, but smaller than or equal to those of all other absorption modes of different bonds. This fact implies that the LO-like modes are only pairing with TO-like mode of Si–N bond and are irrelevant to other bonds. The frequency relation between 1215 and 800 cm^{-1} absorptions can even be related numerically by using measured values of ϵ_∞ (3.53) and ϵ_0 (6.8) in Eq. (1) $(1215/880\approx\sqrt{6.80/3.53})$. These LO-like modes may be tentatively labeled as LO-like$_1$ and LO-like$_2$ modes as indicated in Figs. 2, 3, and 4. Note that in order to present and compare vibrational absorption spectra free of the distortion induced by interference fringes, all spectra illustrated hereafter were collected at Brewster angle with only *p*-polarized beam incidence unless otherwise indicated.[15]

To further confirm the conclusion drawn above, a-SiN$_x$:H film was thermally annealed at 600 °C for 20 min. The comparison of the spectra before and after thermal annealing is shown in Fig. 3. It is well established that upon thermal annealing, hydrogen evolves out from the film and leaves behind the Si- and N-dangling bonds. These Si- and N-dangling bonds passivate each other to form a new Si–N bond. This will result in an enhanced density of Si–N bond and reduced densities of all hydrogen related bonds in the absorption spectrum.[17,18] In Fig. 3, the peak amplitudes of both TO- and LO-like$_1$ modes have increased after thermal annealing indicating their association with Si–N bond. On the other hand, the optical densities of all other modes have been reduced with the exception of the peak located at 1215 cm^{-1} (LO-like$_2$). If this peak only represented hydrogen related bond [N–H(b)] as assigned conventionally, its amplitude would be reduced upon thermal annealing. But instead, its amplitude is enhanced after H evolution indicating that the density reduction of N–H (b) mode is overcome by the density enhancement of another bond. In a-SiN$_x$:H films, the only enhanced density after H evolution is that of Si–N bond as indicated in a previous study.[17] Therefore, it is le-

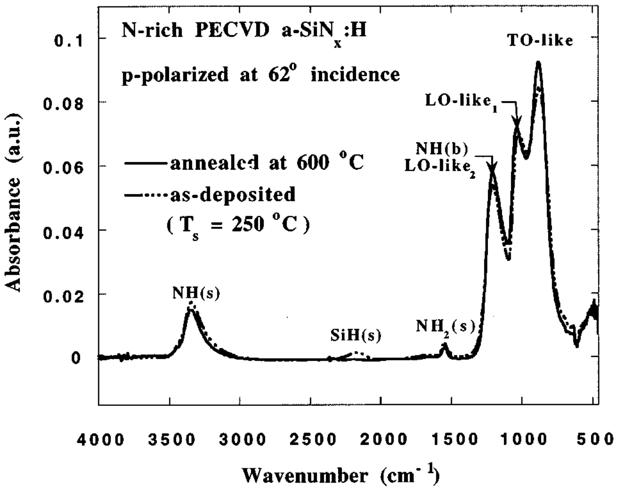

FIG. 3. Vibrational absorption spectrum comparison between as-deposited and after thermal annealing (at 600 °C for 20 min) a-SiN$_x$:H thin films. Spectra were collected at Brewster angle with p-polarized beam. The thickness and refractive index of the film are 1500 Å and 1.88, respectively.

gitimate to conclude that one of the LO-like modes, which is pairing with the TO mode of Si–N, contributes to the optical density of 1215 cm^{-1} absorption. Moreover, comparison between the absorption spectra of films with a similar stoichiometry and thickness but different H contents shows a very similar trend (not shown), which is also consistent with the suggested TO-LO identification.

The absorption spectra of the films with very similar thicknesses and H contents but different stoichiometries are given in Fig. 4. The film with atomic composition closer to stoichiometry exhibits larger TO-like and LO-like$_1$ peak densities, since it contains a larger Si–N bond density than other films. Meanwhile, the density of 1215/1240 cm^{-1} absorption is proportional to nitrogen content (N content) of the film, which is the direct result of the proportionality between the N content and N–H (b) density in the film. However, comparison of this peak among the spectra with different atomic ratios shows that the density difference for x of 1.73 and 1.22 is very small, while this difference is significantly large between x of 1.73 and 1.00 as well as between x of 1.22 and 1.00. According to the suggested relation between TO- and LO-like modes, the 1215/1240 absorption density should be proportional to the densities of N–H (b) (N content) and Si–N. When the film's composition changes from N- to Si-rich, density of N–H (b) decreases monotonically; while Si–N density increases first, reaches maximum at stoichiometry, and starts to decline beyond the stoichiometry. Namely, the densities of N–H (b) and LO-like$_2$ modes have an opposite trend within N-rich to stoichiometry range, and have the same trend within Si-rich to stoichiometry range. This relation is reflected by the variation of LO-like$_2$ absorption as a function of film's atomic ratio in Fig. 4.

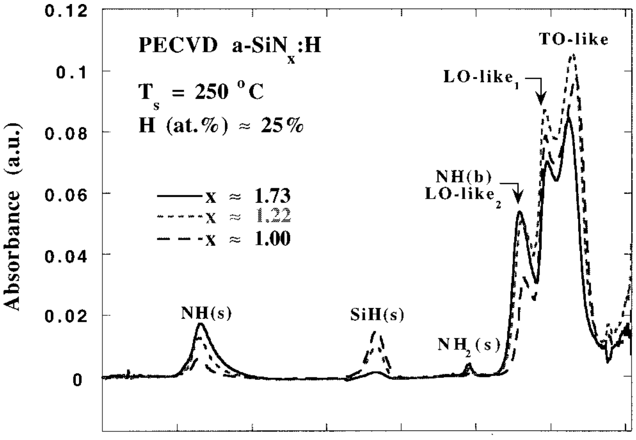

FIG. 4. Vibrational absorption spectrum comparison among films with the same thickness but different stoichiometries. The stoichiometry is represented by atomic ratio x=N/Si. Spectra were collected at Brewster angle with p-polarized beam. The thickness of the film is 1500 Å. The refractive indices of films with x of 1.00, 1.22, and 1.73 are 2.00, 1.95, and 1.88, respectively.

In conclusion, we have observed the longitudinal-like modes in the vibrational absorption spectrum of a-SiN$_x$:H thin films, and suggested their association with the transverse mode counterpart. The LO-like$_1$ and LO-like$_2$ modes are located at about 1040 and 1215 cm^{-1}, respectively, while TO-like mode is located at 880 cm^{-1} in the FTIR spectrum of a-SiN$_x$:H film. It should be noted that the LO-like$_1$ overlaps with TO-like mode of Si–O (1040 cm^{-1}), and the LO-like$_2$ shares the same frequency range with the bending mode of N–H bonds (1180 cm^{-1}). Furthermore, the conventionally assigned asymmetric stretching mode of Si–N bond is merely a transverse-like optical mode of the bond.

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