

Research Article

Vibrational Spectroscopy of Chemical Species in Silicon and Silicon-Rich Nitride Thin Films

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Vibrational properties of hydrogenated silicon-rich nitride ($\text{SiN}_x\text{:H}$) of various stoichiometry ($0.6 \leq x \leq 1.3$) and hydrogenated amorphous silicon (a-Si:H) films were studied using Raman spectroscopy and Fourier transform infrared spectroscopy. Furnace annealing during 5 hours in Ar ambient at 1130°C and pulse laser annealing were applied to modify the structure of films. Surprisingly, after annealing with such high-thermal budget, according to the FTIR data, the nearly stoichiometric silicon nitride film contains hydrogen in the form of Si–H bonds. From analysis of the FTIR data of the Si–N bond vibrations, one can conclude that silicon nitride is partly crystallized. According to the Raman data a-Si:H films with hydrogen concentration 15% and lower contain mainly Si–H chemical species, and films with hydrogen concentration 30–35% contain mainly Si–H₂ chemical species. Nanosecond pulse laser treatments lead to crystallization of the films and its dehydrogenation.

1. Introduction

The interest in amorphous, nano- and microcrystalline silicon films on nonrefractory inexpensive substrates and their crystallization is stimulated by demands of giant microelectronics. For example, the enlargement of sizes of flat-panel displays with active thin film transistor matrix can be described as “reverse Moor’s law.” Scientific interest in the silicon-rich nitride (SRN) films is growing due to their perspectives for application. The most important applications of SRN films are silicon-based optoelectronic devices [1], nonvolatile memory (flash-memory) devices [2], and new tandem solar cells based on silicon and silicon oxide (silicon nitride) heterostructures [3]. Silicon nanoclusters and SRN films can be applied in novel quantum-dots-based solar cells with enhanced efficiency [4].

Modern plasma-enhanced chemical vapor deposition (PECVD) technique allows the production of amorphous silicon films and SRN films with temperature of substrate lower than 100°C [5]. As reagents containing hydrogen are mainly used in PECVD, as-deposited films are hydrogenated. Hydrogen plays important role in electrical and optical properties of the films and also has influence on stability

of the films. So, it is important to develop express, nondestructive spectroscopic approaches for studies of hydrogen in amorphous hydrogenated silicon (a-Si:H) films and hydrogenated SRN films. The present paper is devoted to studies of as-deposited films as well as furnace- and pulse-laser-treated films with the use of Raman spectroscopy and Fourier Transform Infrared (FTIR) spectroscopy.

2. Experiment Details

Hydrogenated SRN films ($\text{SiN}_x\text{:H}$) of different stoichiometry were deposited on the Si (100) substrates with the use of low-frequency PECVD method. The frequency of discharge was 55 kHz, and the films were deposited from the gas mixture of ammonia (NH_3) and monosilane (SiH_4). The stoichiometry parameter x depends on the ratio of ammonia/monosilane flows. The growth technology is described elsewhere in more details [6]. All SRN films were deposited at substrate temperature 100°C, the reactor pressure during deposition was 150 Pa, the deposition time was 16 minutes, and the plasma power was 400 W. Parameters of the films are shown in Table 1.

Amorphous silicon films were deposited on glass substrates using two methods. The first method is evaporation

TABLE 1: Growth parameters, thickness, and composition of hydrogenated SRN films.

Number of samples	Flow ratio NH_3/SiH_4	Thickness, nm	Growth temperature, $^\circ\text{C}$	Stoichiometric parameter x
611	5	240	100	1.3
613	1.5	400	100	0.95
615	0.5	450	100	0.6

TABLE 2: Growth parameters, thickness, and hydrogen concentration of amorphous silicon films.

Number of samples	Thickness, nm	Growth temperature, $^\circ\text{C}$	Hydrogen concentration, atomic per cents
1	100	20	0
2	90	280	10
3	110	225	15
4	75	200	30–35

of monocrystalline silicon target by electron beam in high vacuum and deposition onto unheated substrate. The films deposited by this method do not contain hydrogen. The second method is PECVD at various temperatures using different PECVD reactors. The parameters of the films are shown in Table 2. It is known that optical gap of a-Si:H depends on hydrogen concentration [7]. According to optical gap measurements from light transmission and reflection data, the films grown at temperature 280°C contain ≈ 10 atomic % of hydrogen (optical gap ≈ 1.4 eV); the films grown at temperature 225°C contain $\approx 15\%$ of hydrogen (optical gap ≈ 1.6 eV); the films grown at temperature 200°C contain 30–35% of hydrogen (optical gap ≈ 2 eV).

Laser ellipsometry ($\lambda = 632.8$ nm) was applied to measure the thickness of the films. To study the states of hydrogen and vibration of the Si–N bonds, the FTIR spectroscopy was applied. The FTIR spectrometer FT-801, produced by scientific enterprise “SIMEX” (Novosibirsk, Russia), was used. The spectral range of the spectrometer is from 550 to 5500 cm^{-1} , and the spectral resolution can be optionally changed from 4 to 0.5 cm^{-1} . The structural properties of as-deposited and annealed films were studied using Raman spectroscopy technique. All Raman spectra were recorded in the back-scattering geometry. The 514.5 nm Ar^+ laser line was used as a light source. Triple spectrometer T64000 (Horiba Jobin Yvon) with micro-Raman setup and liquid-nitrogen-cooled CCD matrix detector was used. The spectral resolution was not worse than 1 cm^{-1} . All spectra were measured at room temperature. To avoid heating of the films, the laser beam was slightly defocused; the spot diameter was equal to about 4 – 6 μm ; the laser power reaching the sample was within 2 – 3 mW. The spectra were registered in the $Z(\text{XX})\bar{Z}$ polarization geometry. Furnace annealing of the samples in Ar ambient for 5 hours at temperature 1130°C was performed at the Institute of Electron Technology (Warsaw, Poland). The triple harmonic of YAG:Nd laser

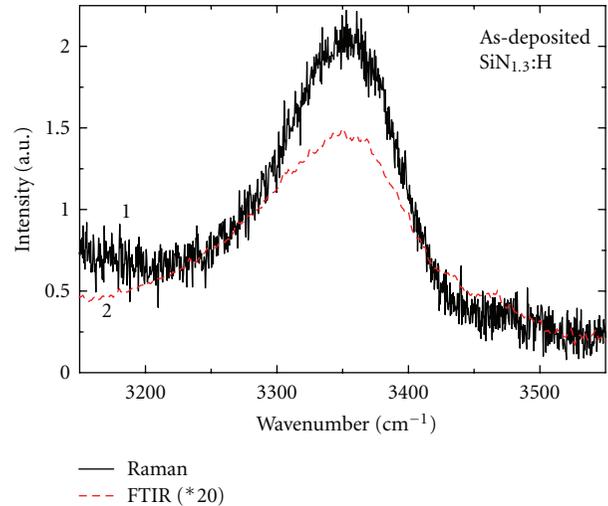


FIGURE 1: Raman and FTIR spectra of $\text{SiN}_{1.3}:\text{H}$ film in frequency range of valence vibration of N–H bonds.

($\lambda = 335$ nm, pulse duration of 10 ns) was used for laser treatments of the as-deposited films.

3. Results and Discussion

In Figure 1 one can see Raman spectroscopy and FTIR data concerning N–H valence (stretching) vibrations in sample 611 (stoichiometry is estimated as $\text{SiN}_{1.3}:\text{H}$). For convenience, the FTIR data was multiplied by 20 times. According to both Raman data and FTIR data, the position of N–H valence vibration peak is 3350 cm^{-1} . An advantage of Raman spectroscopy method is the possibility to use substrates that are not transparent in IR region. When the substrate is not transparent, only reflection setup can be used. Using multiple internal transmission, the sensitivity of IR spectroscopy can be notably improved [8]. Figure 2 shows shift of the position of N–H valence vibration peak versus NH_3 to SiH_4 ratio during deposition of $\text{SiN}_x:\text{H}$ films. With changing of stoichiometry parameter x (1.3, 0.95, and 0.6) the frequency also changes (3350 , 3342 , and 3335 cm^{-1}) accordingly. The frequency of Si–H valence vibrations changes from 2170 to 2100 cm^{-1} with decrease of stoichiometry parameter x from 1.3 to 0.6 [6]. This is because of influence of neighboring atoms on frequencies of valence modes of Si–H and N–H bonds. It should be noted that Ali with coworkers [9] have also observed the shift of the position of N–H valence vibration peak versus stoichiometry of $\text{SiN}_x:\text{H}$ films.

In Figure 3 one can see Raman spectroscopy and FTIR data concerning Si–H valence vibrations for $\text{SiN}_{1.3}:\text{H}$ film. According to the FTIR data the position of Si–H valence vibration peak is 2170 cm^{-1} , but according to the Raman spectroscopy data the position of peak is 2187 cm^{-1} . A mercury lamp was used for back lighting of LCD monitor of experimental setup, and parasitic light can reach input slit of spectrometer. So, one can see in the Raman spectra a doublet (leakage from mercury lamp). One can see also a peak

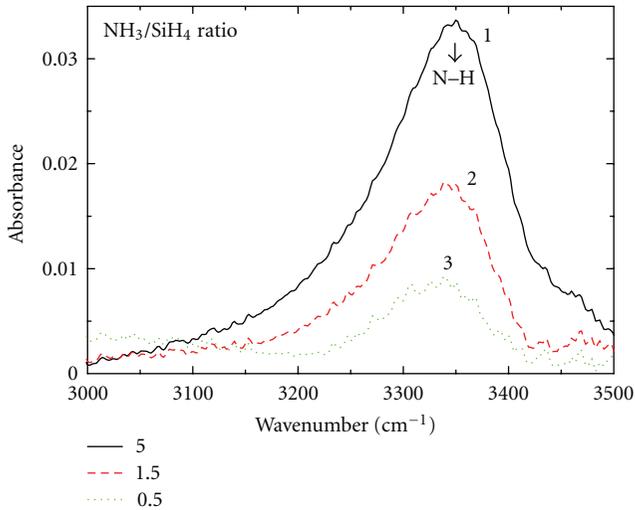


FIGURE 2: FTIR spectra of as-deposited SRN films in frequency range of valence vibration of N–H bonds.

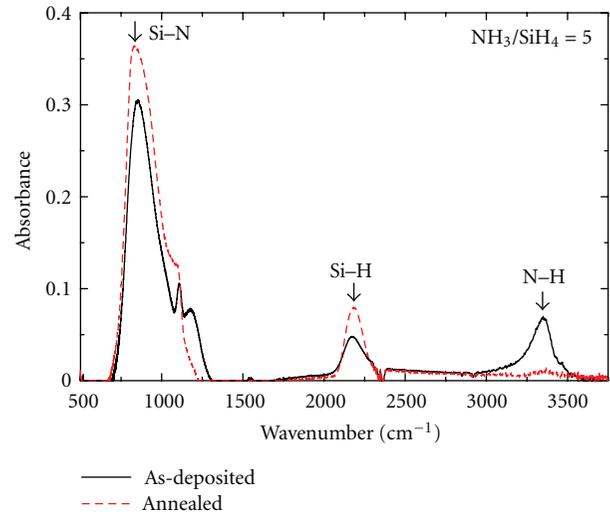


FIGURE 4: FTIR spectra of as-deposited and furnace-annealed $\text{SiN}_{1.3}\text{:H}$ film.

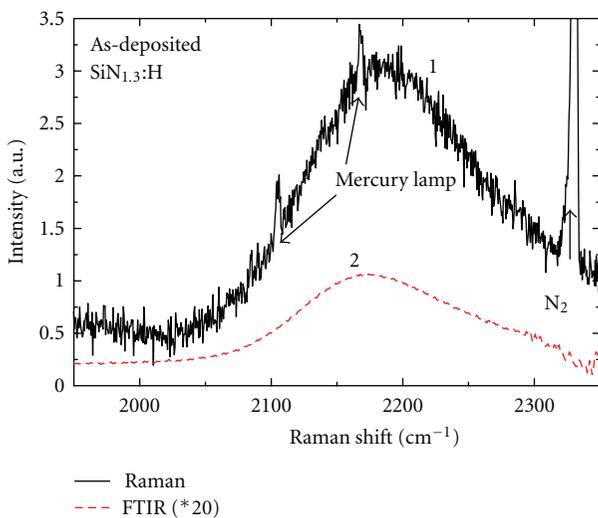


FIGURE 3: Raman and FTIR spectra of $\text{SiN}_{1.3}\text{:H}$ film in frequency range of valence vibration of Si–H bonds.

due to Raman scattering on N_2 molecules in atmosphere. Both Raman and FTIR peaks are asymmetric, so one can assume presence of Si–H and SiH_2 bonds in this film. From fitting of FTIR spectrum by two Gaussians one can assume that frequency of Si–H valence vibration is 2170 cm^{-1} and frequency of Si– H_2 valence vibration is 2260 cm^{-1} . The difference in positions of the Raman scattering and the FTIR peaks may be due to different contribution of Si–H and SiH_2 bond valence vibration in dipole moment and polarisability.

Knowing the thickness of a film and effective absorption cross-sections for Si–N, Si–H, and N–H bonds, one can calculate the concentration of chemical bonds. The effective absorption cross-section S_{eff} for valence vibration of Si–N bonds is $1.6 \cdot 10^{-19}\text{ cm}^2$ [10], and S_{eff} for valence vibration of Si–H bonds is $0.57 \cdot 10^{-19}\text{ cm}^2$ [11]. According to different

data, S_{eff} for valence vibration of N–H bonds is $0.48 \cdot 10^{-19}\text{ cm}^2$ [11] or $0.8 \cdot 10^{-19}\text{ cm}^2$ [12]. Concentration of chemical species can be calculated as $N(\text{cm}^{-3}) = A/(d(\text{cm}) \cdot S_{\text{eff}}(\text{cm}^2))$, where A is the height of absorbance peak (dimensionless parameter) and d is thickness. The results are shown in Table 3. The concentration of N–H species is calculated using S_{eff} according to Lanford [11] and Stein [12]. It should be noted that Stein and Wegener [12] have used multiple internal transmissions but Lanford and Rand [11] used normal transmission geometry. We also have used normal transmission geometry. So, the S_{eff} obtained by Lanford is more preferable for analysis of our data. From Table 3 one can see that total concentration of Si–N, Si–H, and N–H bonds decreases with decreasing of stoichiometry parameter x . This is because vibrations of Si–Si bonds do not change dipole momentum and are not active in FTIR. But they are active in Raman scattering. And Raman signal from amorphous silicon clusters was detected for sample number 615 [6]. The total concentration of Si–N bonds in stoichiometric Si_3N_4 is about $15.5 \cdot 10^{22}\text{ cm}^{-3}$ [13]. So, one can assume that annealed near stoichiometric sample number 611 (Table 3) contains not only Si–N and Si–H bonds but also some concentration of Si–Si bonds. But concentration of such bonds is not high enough to be detected by Raman spectroscopy.

The FTIR spectra of as-deposited and annealed $\text{SiN}_{1.3}\text{:H}$ films are shown in Figure 4 in range from 500 to 3900 cm^{-1} . Surprisingly, this nearly stoichiometric silicon nitride film still contains hydrogen after annealing with high-thermal budget, mainly in the form of the Si–H bonds. In this film, the peak, corresponding to absorption on stretching vibrations of the Si–H bonds, becomes even higher. The peak at 1175 cm^{-1} in spectrum of as-deposited film can be related to absorbance by bending vibrations of the N–H bonds [14]. Peculiarities at $850\text{--}900\text{ cm}^{-1}$ in spectrum of annealed film can be related to absorbance by stretching vibrations of the Si–N bonds in the α -modification of crystalline silicon

TABLE 3: Concentration of chemical species in SRN films according to FTIR data.

Number of samples	Si-N 10^{22} cm^{-3}	Si-H 10^{22} cm^{-3}	N-H (for S_{eff} according to Lanford) 10^{22} cm^{-3}	N-H (for S_{eff} according to Stein) 10^{22} cm^{-3}
611	8	3.2	5	3
611 annealed	10.5	6	bellow 0.1	bellow 0.06
613	5.58	3.64	0.9	0.54
615	3.75	2.92	0.32	0.19

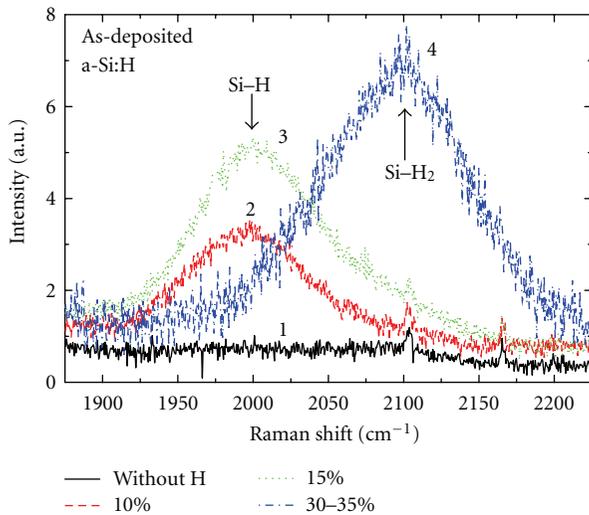


FIGURE 5: Raman spectra of a-Si:H films in frequency range of valence vibration of Si-H bonds.

nitride [15, 16]. Maybe partial crystallization of silicon nitride retards the dehydrogenization of the film. It has been detected earlier [17] that the closer is the stoichiometry parameter of the SRN films to that of stoichiometric Si_3N_4 , the higher temperature is needed for effusion of hydrogen (dehydrogenization) from these films. However, short-time annealing at temperature 850°C [17] and annealing at 800°C for 2 hours [18] lead to total dehydrogenization of the SRN films, with the stoichiometry parameter x below 1. So, as it was abovementioned, one can assume that, for the case of nearly stoichiometric silicon nitride film, furnace annealing leads to so-called hardening of silicon nitride inhibiting hydrogen outdiffusion.

Figure 5 shows Raman spectra of amorphous silicon films with different hydrogen concentrations. All films were deposited on glass substrates that are not transparent in IR region, so it was impossible to analyze them using FTIR in normal geometry. One can see peaks due to scattering on valence vibrations of Si-H bonds. In Raman spectrum of the only film deposited in vacuum (without hydrogen) this peak is absent. As one can see from Raman spectra, film deposited at temperature 200°C contains mostly Si-H₂ bonds, because the position of Si-H₂ peak is about 2100 cm^{-1} . The frequency of Si-H peak is about 2000 cm^{-1} [19]. The films deposited at temperatures higher than

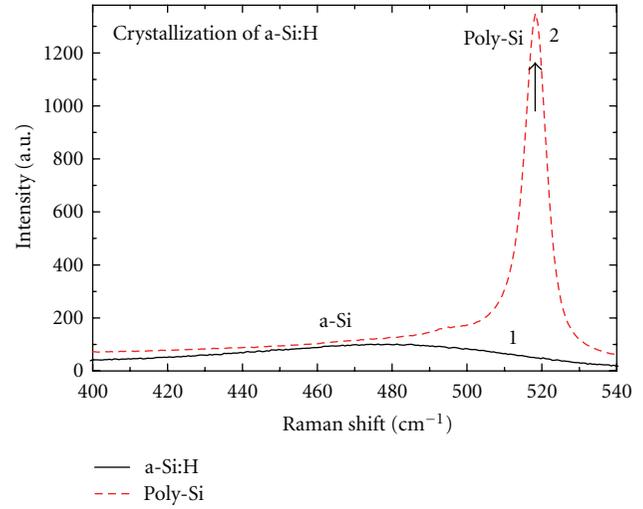


FIGURE 6: Raman spectra of as-deposited a-Si:H film and crystallized by laser pulse annealing film in frequency range of valence vibration of Si-H bonds.

200°C contain mostly Si-H bonds. It should be noted that frequencies of stretch vibrations of Si-H bonds in silicon nitride and in a-Si:H are notably different: about 2200 cm^{-1} for the first case and $2000\text{--}2100 \text{ cm}^{-1}$ for the second case. As it was shown by Hien et al. [20], the frequency of stretch vibrations of Si-H bonds in the case of neighbouring N and H atoms can reach 2122 cm^{-1} . In the case of only Si neighbouring atoms this frequency is 2012 cm^{-1} [20]. FTIR method can be used for quantitative hydrogen measurements [21], but for transmission experiments the substrate should be transparent in IR range.

Figure 6 shows the Raman spectra of as-deposited a-Si:H film and nanosecond-pulse-annealed film. The Raman spectrum of amorphous silicon contains broad peaks at approximately 480 cm^{-1} appearing as a result of effective density of transverse optical (TO) vibration modes [19]. Due to scattering on optical phonon modes localized in the nanocrystals, the Raman spectrum of nanocrystals is characterized by narrow peak at position between 500 and 520 cm^{-1} . The position and the width of the peak strongly depend on size and structure of the nanocrystals according to dispersion of the localized modes [22]. The peak width is mainly determined by size dispersion of the nanocrystals. The intensity of the “nanocrystal” peak depends on the volume of nanocrystal phase. So, one can determine the

volume part of nanocrystal phase: $V_{\text{nano-Si}}/V_{\text{full}} = I_{\text{NC}}/(I_{\text{NC}} + \sigma I_{\text{A}})$, where I_{NC} and I_{A} are integral intensities of crystalline and amorphous peaks and σ is relation between the integral Raman cross-sections of nanocrystal Si and a-Si. According to the literature data, σ can change from 0.1 for large grain polycrystalline silicon up to 1.1 for nanocrystalline Si [23]. As one can see, the used nanosecond treatment leads to almost total crystallization of as-deposited film. According to peak position, the size of nanocrystals in our case should be about 10 nm [22]. It should be noted that no Si–H peaks were detected in nanosecond-pulse-annealed film. So, the pulse annealing can be used not only for crystallization but also for dehydrogenization.

4. Conclusion

In conclusion, the FTIR method was applied for determination of concentrations of chemical species in silicon-rich nitride films containing amorphous silicon nanoclusters. It was observed that nearly stoichiometric hydrogenated silicon nitride film contains hydrogen mainly in the form of the Si–H bonds even after 5 hours of annealing at temperature 1130°C. According to Raman spectroscopy data, nanosecond pulse laser treatment leads to crystallization and dehydrogenization of a-Si:H films with initial concentration of hydrogen up to 35%.

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