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Dependence of Mechanical Stresses in Silicon Nitride Films on the Mode of Plasma-Enhanced Chemical Vapor Deposition

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Abstract—Films of silicon nitride SiN_x, obtained by plasma-enhanced chemical vapor deposition from the monosilane SiH_4 and ammonia NH_3 gases, are widely used in microelectronics and micro- and nanoelectromechanical systems. Residual mechanical stresses and film composition are important characteristics for many applications. The properties of SiN_x films, particularly mechanical stresses and composition, depend largely on the conditions of production, e.g., the ratio of the reacting gas flow rates, the composition of the gas mixture, the power and frequency of the plasma generator, and the temperature and pressure during deposition. Despite the great volume of works on the subject, data regarding the dependence of the properties and composition of SiN_x films on the conditions of production remain sparse. This work considers the effect the ratio of the reacting gas flow rates has on the mechanical stresses and composition of silicon nitride films SiN_x obtained by plasma-enhanced chemical vapor deposition from gaseous mixtures of SiH_4 monosilane and NH_3 ammonia using low-frequency plasma. It is found that when the ratio of the gas flow rates of SiH_4 and NH_3 is raised from 0.016 to 0.25, the compressive mechanical stresses are reduced by 31%, the stoichiometric coefficient falls from 1.40 to 1.20, the refractive index rises from 1.91 to 2.08, the concentration of N–H bonds is reduced by a factor of 7.4, the concentration of Si–H bonds grows by a factor of 8.7, and the concentration of hydrogen atoms is reduced by a factor of 1.5. These results can be used for the controlled production of SiN_x films with such specified characteristics as residual mechanical stresses, refractive index, stoichiometric coefficient, and the concentration of hydrogen-containing bonds.

Keywords: films of PECVD silicon nitride SiN_x, mechanical stresses, IR Fourier spectroscopy, optical profilometry

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INTRODUCTION

Films of silicon nitride SiN_x, obtained by plasma-enhanced chemical vapor deposition (PECVD) from mixtures of monosilane SiH_4 and ammonia NH_3 at temperatures of 300–450°C are widely used in microelectronics, nanoelectronic devices, and micro- and nanoelectromechanical systems [1, 2]. In the production of integrated circuits, PECVD SiN_x is used as a layer of passivation for semiconductor devices, since it is a good barrier for sodium and water ions and protects metals from mechanical damage. PECVD SiN_x is also used as a subgate dielectric in the manufacturing of thin-film transistors.

An important characteristic of the PECVD SiN_x films is the magnitude of remaining mechanical stresses σ. At the same time, certain applications require films with low values of mechanical stresses [3], while others require ones with high values of mechanical stresses [4, 5]. The physical and chemical properties of SiN_x films (mechanical stresses in particular) and their composition depend strongly on the conditions of production: ratio R of the flow rates of the reacting gases (SiH_4, NH_3, and N_2), the composition of the gas mixture, the power and frequency of the generator used for plasma excitation, and the temperature and pressure during deposition.

The ratio of the flow rates of the reacting gases is one of the parameters that affect the mechanical stresses and the composition of the resulting SiN_x films. SiN_x films obtained at different values of ratio R of the reacting gas flow rates, the composition of the gas mixture, and other process parameters were studied in [6–12]. For example, the dependence of the mechanical stresses in SiN_x films on the reacting gas flow rate ratio $R = [SiH_4]/[NH_3]$ for gas mixtures of SiH_4, NH_3, and N_2 was studied in [6] at $R = 0.2–0.48$ using high frequency (HF) plasma; in [7] at $R = 1.0–2.0$ using HF and low frequency (LF) plasma; and in [8] for gas mixtures of SiH_4, NH_3, and He_2 at R = 0.4–1.33 using HF and LF plasma. The composition of SiN_x films obtained from gas mixtures of SiH_4 and NH_3 at R = 0.025–0.1 using radio frequency (RF) plasma was given in [9]. The composition of films obtained from gas mixtures of SiH_4 and N_2 at $R = [SiH_4]/[N_2] = 1:1.3$ was considered in [10], depending on the generator power and the pressure using HF plasma. The dependence of mechanical stresses and the composition of SiN_x films obtained via ECR (electron cyclotron resonance) PECVD for gas mixtures of SiH_4 and N_2 at R = 0.3–1.25 was investigated in [11]. The composition of and mechanical stresses in SiN_x films obtained from gas mixtures of SiH_4, NH_3, and N_2 for $R = [SiH_4]/[NH_3] = 1$ were considered in [12], depending on the magnitude and the ratio of the powers of LF and HF generators used for plasma excitation.

Despite the great volume of works on SiN_x films and the considerable amount of data regarding the dependence of the properties of these films on different conditions of deposition, such data are remain sparse. Data on the composition of such films in particular are qualitative in nature or incomplete, and no quantitative characteristics such as the concentration of Si–N, N–H, Si–H bonds and hydrogen in the investigated SiN_x films are given in works where the dependence of the mechanical stresses in SiN_x films obtained from gas mixtures of SiH_4 and NH_3 on the ratio of flow rates of gases were investigated.

In this work, we used IR Fourier spectroscopy and optical profilometry to study the dependence of mechanical stresses and the composition of films of PECVD SiN_x, obtained from gas mixtures of SiH_4 and NH_3 using low-frequency plasma, on the ratio of the flow rates of the reacting gases.

EXPERIMENTAL

Our SiN_x films were prepared by plasma-enhanced chemical vapor deposition (PECVD) from a gas mixture of SiH_4 and NH_3 at different reacting gas flow rate ratios $R = [SiH_4]/[NH_3]$, where R = 0.016–0.25. The temperature of deposition was 350°C, and the pressure was 1.43 Torr. To excite the plasma, we used a generator with a power of 50 W and a frequency of 110 kHz. The films were deposited on the fronts of KDB (100) silicon wafers 100 mm in diameter and 460 μm thick. The duration of deposition varied from 8 to 55 minutes, depending on the film thickness (220–1600 nm). The thickness of the deposited films was determined using a SENDURO ellipsometer (SENTECH Instruments GmbH).

The mechanical stresses in our SiN_x films were determined by the bend in a silicon wafer after depositing an SiN_x film on its front. For each silicon wafer, the profile was measured in four directions before and after deposition using a Veeco WykoNT 9300 optical profilometer. Mechanical stresses σ were then calculated from the measured surface profiles using the techniques proposed in [13–15]. The composition of the resulting SiN_x films was analyzed via IR spectroscopy. Stoichiometric parameter x was determined by measuring refractive index n [16]. We used a SENDURO ellipsometer (SENTECH Instruments GmbH) to measure refractive index n, and a Vector 22 IR Fourier spectrometer (Bruker) for IR measurements. For the silicon wafers with layers of SiN_x deposited at different values of R, the IR transmission spectra were measured in the 400–4000 cm^{-1} range of wavenumbers. After our analysis of absorption bands corresponding to Si–N, Si–H, and N–H bonds, we calculated the concentration of these bonds following the procedure described in [9, 17].

RESULTS AND DISCUSSION

The mechanical stresses in our SiN_x films were calculated using the formula [13]

$$\sigma = \frac{\delta}{r^2}\frac{E}{3(1-\nu)}\frac{T^2}{t},$$

where δ is the deviation of the profile at distance r from the center of the plate; E and ν are the Young modulus and Poisson ratio of the substrate material, respectively; and t and T are the film and substrate thickness, respectively. In our calculations for KDB (100) silicon wafers, $E/(1-\nu) = 1.81 \times 10^{11}$ Pa [14].

Figure 1 shows the surface profiles for one selected direction before and after depositing a SiN_x layer on the face of a silicon wafer. It can be seen that the deposited layer bent the plate. Such bending is typical of films with compressive (negative) mechanical stresses. The surface profiles before and after deposition are similar in appearance for the other three scanning directions. After calculating mechanical stresses σ for each profile corresponding to a certain direction, we averaged them in all four directions.

We studied the dependence of mechanical stresses σ on thickness d of the deposited SiN_x films obtained at fixed gas flow rate ratio $R = [SiH_4]/[NH_3] = 0.09$ (Fig. 2a). It can be seen that as the film thickness grew from 220 to 1600 nm, the mechanical stresses remained virtually the same at approximately $-1.25 \times 10^9 \pm 7.6 \times 10^7$ Pa.

The dependence of mechanical stresses σ on ratio $R = [SiH_4]/[NH_3]$ of the reacting gas flow rates were investigated for SiN_x films obtained at R = 0.016–0.25 (Fig. 2b). It is seen that compressive (negative) mechanical stresses σ fell as R rose. In the interval R = 0.016–0.12, the mechanical stresses diminished only slightly (from -1.25×10^9 to -1.21×10^9 Pa); then, in the range R = 0.12–0.25, they fell more strongly (from -1.21×10^9 to -8.57×10^8 Pa).

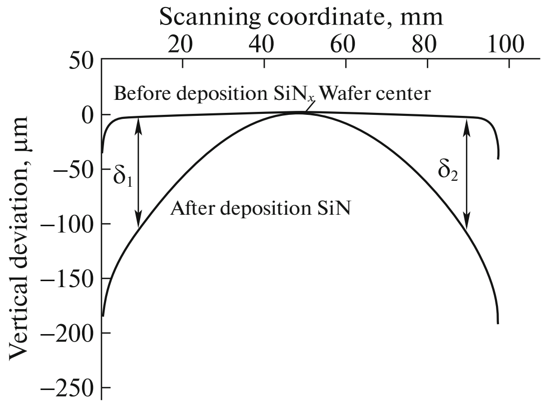

Fig. 1. Surface profile of a silicon wafer before and after the plasma–chemical deposition of SiN_x.

It should be noted that our SiN_x films were obtained with low-frequency plasma (110 kHz). As can be seen from the dependences obtained for mechanical stresses (see Fig. 2), the SiN_x films had negative (compressive) mechanical stresses, which agrees with the data given in [7, 8, 12] for SiN_x films obtained with low-frequency plasma (300–380 kHz). With high-frequency plasma (13.56 MHz), the SiN_x films had positive (tensile) mechanical stresses [6–8, 12], but adding helium to the gas mixture produced films that had negative (compressive) stresses [7]. The formation of compressive stresses was due to high-energy N_2^+ ions being formed when using low-frequency plasma. As a result of bombardment, N_2^+ ions were implanted into the film, which was compacted, and compressive stresses were generated [7, 8, 12]. The resulting dependence of mechanical stresses σ on gas flow rate ratio R (see Fig. 2b) can thus be explained as follows: The increase in ratio R corresponds to a reduction of NH_3 in the gas mixture, which lowered the concentration of N_2^+ ions in the plasma. This in turn reduced the number of N_2^+ ions implanted into the film, leading to a decrease in the compressive stresses in the film.

The obtained dependences of refractive index n and stoichiometric parameter x of the SiN_x films on gas flow rate ratio $R = 0.016$–0.25 are listed in Table 1. Stoichiometric parameter x of the SiN_x films was calculated from refractive index n, based on the dependence of n on x [16].

As can be seen from Table 1, refractive index n grew along with gas flow-rate ratio R. The silicon content in the film rose, while that of nitrogen fell. For the sample of SiN_x film deposited at $R = 0.016$, we thus have $n \approx 1.91$ and $x \approx 1.40$, which corresponds to a SiN_x film enriched with nitrogen. For the SiN_x film obtained at $R = 0.12$, we have $n \approx 1.98$, $x \approx 1.32$; i.e., the composition of the deposited film was closest to stoichiometric. At $R = 0.25$, the refractive index was $n \approx 2.08$, and $x \approx 1.20$, which corresponds to a SiN_x film enriched with silicon.

The concentration of these bonds was calculated from the IR transmission spectra for SiN_x films obtained at different values of R by analyzing the absorption bands corresponding to the Si–N, Si–H, and N–H bonds using the procedure described in [9, 17]. Figure 3 shows the IR transmission spectra for silicon wafers with deposited SiN_x films at $R = 0.016$–0.25. Characteristic absorption peaks are observed in the IR spectra or all samples of the SiN_x films. The largest peak is at ~880 cm^{-1}, corresponding to a Si–N bond; the peak at ~2180 cm^{-1} corresponds to a Si–H bond; and the peak at ~3320 cm^{-1} corresponds to a N–H bond. It is seen that as R grows, the intensity of the absorption peak for the Si–N bond remains virtually the same in the IR spectra of plasma–chemical SiN_x films, the intensity of the N–H bond peak diminishes, and that of the Si–H bond increases.

The concentration of the Si–N bond and the hydrogen-containing Si–H and N–H bonds in our

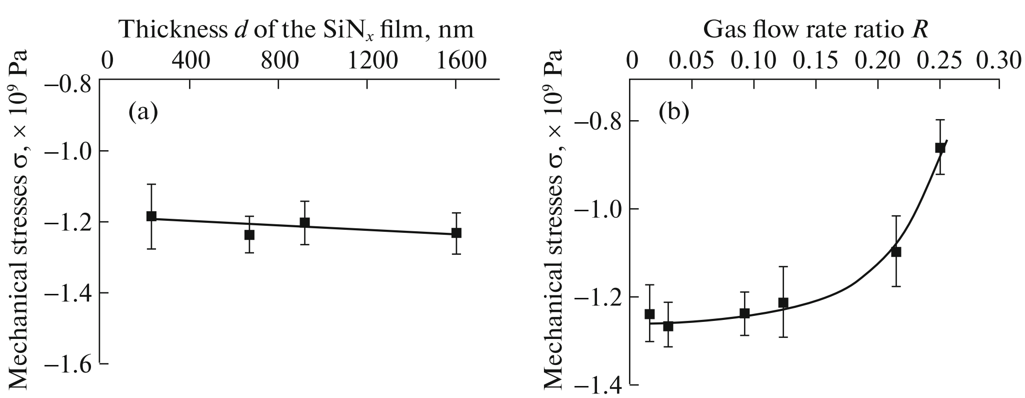

Fig. 2. Dependence of mechanical stresses σ in our PECVD SiN_x films on (a) thickness d and (b) the ratio of gas flow rates.

Table 1. Values of the obtained technological parameters of SiN_x films deposited at different gas flow rates

Gas flow rate ratio R	Mechanical stresses σ, Pa	Refractive index n	Stoichiometric parameter x	N_{Si-N}, cm^{-3}	N_{N-H}, cm^{-3}	N_{Si-H}, cm^{-3}	N_H, cm^{-3}
0.016	-1.25×10^9	1.91	1.40	9.70×10^{22}	2.36×10^{22}	1.50×10^{21}	2.51×10^{22}
0.03	-1.26×10^9	1.92	1.38	1.01×10^{23}	1.94×10^{22}	3.38×10^{21}	2.28×10^{22}
0.09	-1.23×10^9	1.96	1.35	9.87×10^{22}	1.35×10^{22}	6.01×10^{21}	1.95×10^{22}
0.12	-1.21×10^9	1.98	1.32	1.07×10^{23}	1.34×10^{22}	7.43×10^{21}	2.08×10^{22}
0.22	-1.10×10^9	2.00	1.29	1.00×10^{23}	6.57×10^{21}	1.00×10^{22}	1.66×10^{22}
0.25	-8.57×10^8	2.08	1.20	8.72×10^{22}	3.20×10^{21}	1.31×10^{22}	1.63×10^{22}

N_{Si-N}, N_{N-H}, N_{Si-H}, and N_H are the concentrations of Si–N, N–H, Si–H bonds and hydrogen, respectively.

SiN_x films was determined from the IR spectra according to the formula [9, 17]

$$N_{bond} = K_{bond}\alpha H,$$

where K_{bond} is the constant of the corresponding bond. According to [9], $K_{Si-N} = 1.82 \times 10^{16}$ cm^{-1}, $K_{N-H} = 8.2 \times 10^{16}$ cm^{-1}, and $K_{Si-H} = 5.9 \times 10^{16}$ cm^{-1}; α is the absorption coefficient, and H is the half-width of the absorption band of the corresponding bond.

The values of absorption coefficient α and the half-width H of the absorption band were determined from the corresponding absorption bands of the IR spectra according to the procedure described in [9, 17]. The calculated values of the concentration of the N_{Si-N}, N_{N-H}, and N_{Si-H} bonds, and that of hydrogen N_H for

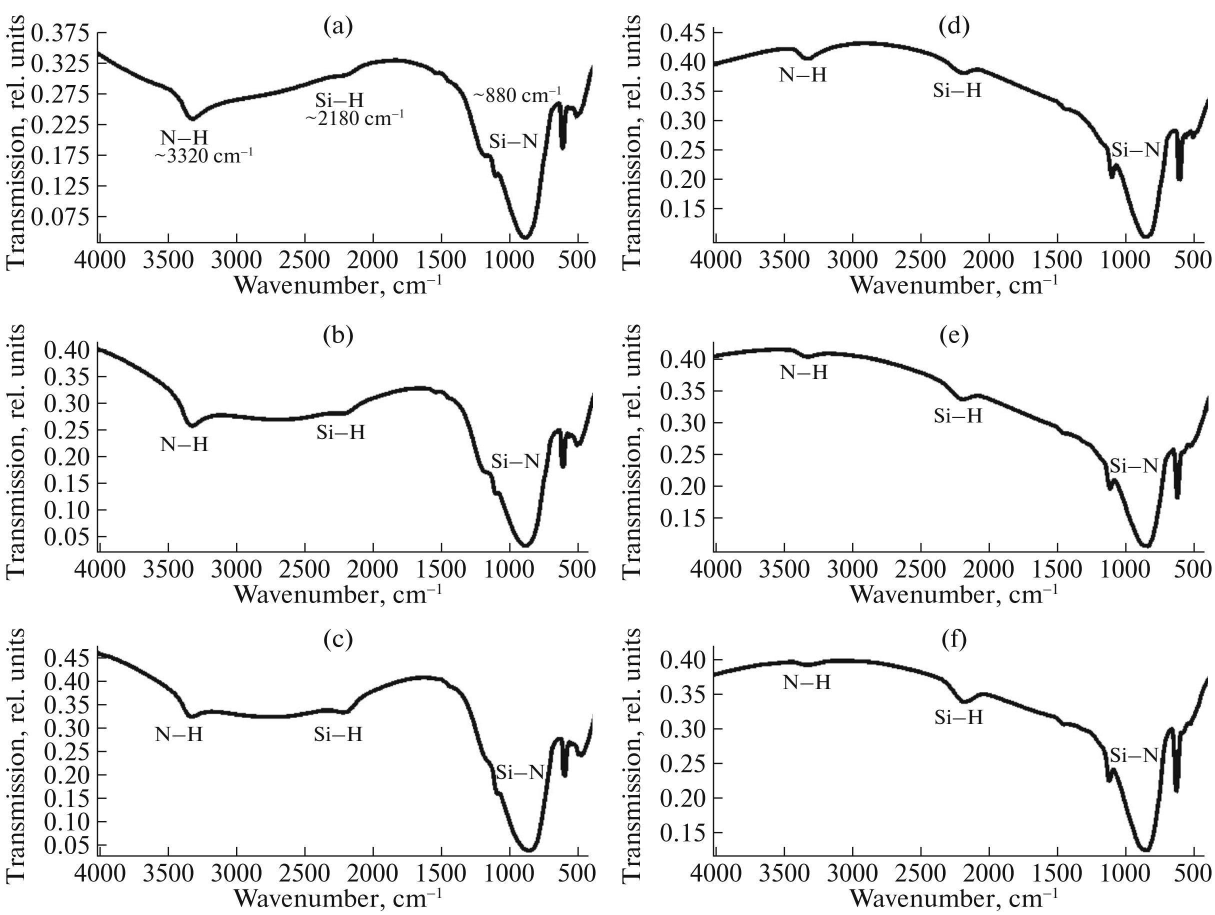

Fig. 3. IR transmission spectra for silicon wafers with deposited films of PECVD SiN_x at different gas flow rate ratios R: (a) 0.016, (b) 0.03, (c) 0.09, (d) 0.12, (e) 0.22, and (f) 0.25.

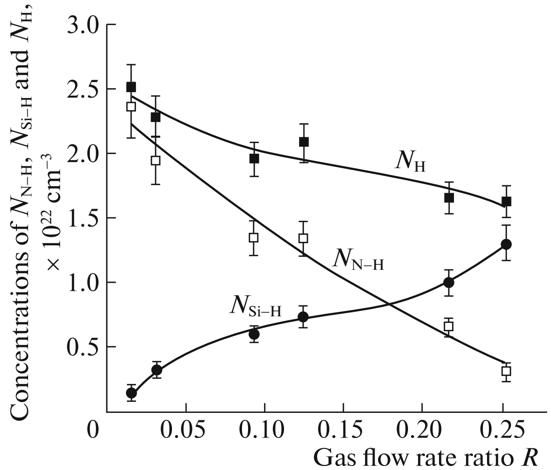

Fig. 4. Dependences of the concentrations of N–H, Si–H bonds and hydrogen on gas flow rate ratio R.

the SiN_x films obtained at different R values, are listed in Table 1 and Fig. 4. As can be seen from Table 1, the concentration of the Si–N bonds for all samples of SiN_x films with $R = 0.016–0.25$ changed slightly ($N_{Si-N} = 8.72 \times 10^{22}–10.7 \times 10^{22}$ cm^{-3}). For the SiN_x film obtained at $R = 0.016$, a pronounced peak of the N–H bond and the weak peak corresponding to the Si–H bond were observed in the IR spectrum. For this sample, $N_{N-H} = 2.36 \times 10^{22}$ cm^{-3} and $N_{Si-H} = 1.50 \times 10^{21}$ cm^{-3}. In the IR spectrum of the SiN_x film obtained at $R = 0.09$, both peaks for N–H and Si–H bonds are pronounced. Here, $N_{N-H} = 1.35 \times 10^{22}$ cm^{-3} and $N_{Si-H} = 6.01 \times 10^{21}$ cm^{-3}. For the SiN_x film at $R = 0.25$, the peak corresponding to N–H is very weak; at the same time, there is a large peak for the Si–H bond. In this case, $N_{N-H} = 3.20 \times 10^{21}$ cm^{-3} and $N_{Si-H} = 1.31 \times 10^{22}$ cm^{-3}.

CONCLUSIONS

In our PECVD SiN_x films deposited from gas mixtures of monosilane SiH_4 and ammonia NH_3 using low-frequency plasma, the concentration of N–H bonds fell from 2.36×10^{22} to 3.20×10^{21} cm^{-3} upon an increase in gas flow ratio $R = 0.016–0.25$, and the concentration of Si–H bonds rose from 1.50×10^{21} to 1.31×10^{22} cm^{-3}. Hydrogen concentration N_H fell from 2.51×10^{22} to 1.63×10^{22} cm^{-3}, and bond concentration N_{Si-N} changed slightly ($8.72 \times 10^{22}–10.7 \times 10^{22}$ cm^{-3}).

It was shown that the compressive mechanical stresses σ fell from -1.25×10^9 to -8.57×10^8 Pa, refractive index n grew from 1.91 to 2.08, and the stoichiometric coefficient x decreased from 1.40 to 1.20.

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