

Properties of "Stoichiometric" Silicon Oxynitride Films

LeNian HE, Takao INOKUMA and Seiichi HASEGAWA

Department of Electronics, Faculty of Technology, Kanazawa University, Kanazawa 920, Japan

The properties of plasma-deposited amorphous SiO_xN_y films are investigated as a function of x (and y). A relationship of $2x + 2.8y = 4$ was found, suggesting that the densities of homobonds and of Si-H, O-H and O-N bonds are sufficiently smaller than those of Si-O or Si-N bonds. No split of the stretching absorption peaks arising from Si-O and Si-N bonds suggests that the film is a homogeneous alloy. The properties of the dangling bonds are discussed.

1. Introduction

Stoichiometric silicon nitride ($\text{SiN}_{1.3}$) films, prepared by plasma-enhanced chemical vapor deposition (PECVD) methods, are used in a variety of electronic devices, as a passivation layer and as a gate insulator in thin-film transistors. However, high densities of both positively and negatively charged defects are included in these films, acting as charge-trap centers. Further, $\text{SiN}_{1.3}$ films exhibit a high tensile stress which would lead to occurrence of cracks in the films on some substrate, notably after post-deposition heat-treatments. On the other hand, it has been reported that silicon dioxide (SiO_2) films exhibit lower stress and the Si dangling bond in these films is unstable in its negatively charged states.¹⁾ Further, the value of the dielectric constant is considerably lower than that of nitride films. When an insulator film is used as passivation or isolation layers, a lower value of the dielectric constant is required. However, we notice that the power for obstructing the passage of contaminants in the oxide film is weaker than that in nitride films.

Silicon oxynitride (SiO_xN_y) films would show an intermediate property between those of Si oxide and nitride films. Further, under proper deposition conditions, PECVD SiO_xN_y films with very low concentration of Si-Si bonds are expected to be obtained, giving good insulating and structural properties. Such films can be tailored to suit diverse applications in the field of microelectronics. For these reasons the examination of the properties of PECVD SiO_xN_y films prepared as a function of the composition, x and/or y , is of great interest. In the present work, we investigate the structural and dielectric properties, and the characteristics of the native defects (dangling bond) for PECVD SiO_xN_y films deposited as a function of x (and y).

2. Experiment

The samples were deposited by rf glow-discharge decomposition of a $\text{SiH}_4\text{-NH}_3\text{-O}_2$ mixture. Two different series of deposition conditions were used. One samples were deposited by varying the O_2 flow rate from 0 to 1.6 sccm under fixed conditions of the SiH_4 and NH_3 flow rates in which near-stoichiometric nitride films can be grown as the O_2 flow rate is zero (Series A), and the other were deposited by varying the NH_3 flow rate from 8.1 to 0 sccm under fixed SiH_4 and O_2 flow rate conditions in which stoichiometric oxide films can be grown as the NH_3 flow rate is zero (Series B). The rf power was maintained at 10 W and the pressure at 0.17 Torr. The deposition temperature was fixed at 300°C. Approximately 1- μm -thick films were deposited simultaneously on Corning 7059 glass substrates for electron spin reso-

nance (ESR) measurement, on fused quartz for optical absorption measurement and on single-crystal Si (c-Si) for infrared (IR) measurement.

The O content, x , and the N content, y , in SiO_xN_y films were determined by electron probe microanalysis (EPMA), using quartz (SiO_2), boron nitride (BN) and c-Si as standards. The values of x and y were also estimated from O 1s, N 1s and Si 2p core-level spectra in x-ray-induced photoelectron spectroscopy (XPS), using 500-Å-thick films deposited on a c-Si substrate. The ESR spectra were measured using JEX-RE1X (JEOL) spectrometer operated at an X band frequency. The IR vibrational spectra, using a Fourier-transform spectrometer (Nicolet 5DX), were measured at a normal light incidence. The refractive index n_r was estimated from the multiple reflections in nonabsorbing regions around 700 nm of the optical absorption spectra. The stress was estimated from changes in curvature of the substrate/film system.²⁾

3. Results and discussion

Figure 1 shows the O content x and N content y in SiO_xN_y films as a function of (a) O_2 flow rate (Series A) and (b) NH_3 flow rate (Series B). The values of x and y vary continuously from 0 to 2 and 1.5 to 0, respectively.

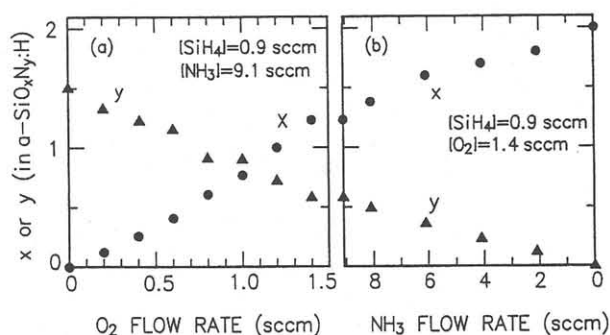


Fig. 1. Variation in the content x and y in SiO_xN_y as a function of (a) O_2 flow rate and (b) NH_3 flow rate. The values of x and y were determined by EPMA or XPS. As seen in Figs 1(a) and 1(b), near-stoichiometric Si nitride or stoichiometric oxide films can be grown as the O_2 or NH_3 flow rate is zero, respectively.

Figure 2 shows the dependence of x on y in SiO_xN_y . The values of x was found to be proportional to y . The straight line in Fig. 2 is the result of a least-squares fit on the experimental data. From the straight line, a relationship of $2x + 2.8y = 4$ was found. If each Si

atom is bonded to either O or N atoms, the relationship between x and y would be expected as $2x + 3y = 4$, because the coordination numbers of an O, N and Si are 2, 3 and 4, respectively. The reduction from 3.0 to 2.8 of the coefficient for y in the linear function of Fig. 2 would be due to the incorporation of N-H bonds in the films as shown at a later stage, because an effective coordination number of N-H molecules is 2. As a result, the relationship in Fig. 2 indicates that the densities of homobonds such as Si-Si, O-O and N-N bonds, and of Si-H, O-H and O-N bonds are sufficiently smaller than that of Si-O or Si-N bonds. Consequently, for the present films, if the value of x is known, the value of y can be distinctly determined.

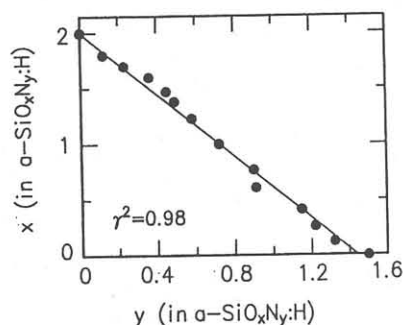


Fig. 2. Dependence of the content, x on y . These data were obtained from Fig. 1. The solid line in this figure is the result of a least-squares fit on the experimental data.

In order to examine the bonding properties of SiO_xN_y films, IR absorption measurements have been carried out. The dominant absorption spectra occur over the range of $840\text{--}1080\text{ cm}^{-1}$ (Si-N and Si-O stretching modes). In addition, weaker absorptions are observed at $3300\text{--}3400\text{ cm}^{-1}$ (N-H stretching mode), 1150 cm^{-1} (N-H bending mode), 800 cm^{-1} (Si-O bending mode associated with the $\text{Si}(\text{O}_4)$ configuration) and 470 cm^{-1} (Si-O rocking mode or Si atom breathing mode in Si_3N_4). O-H and Si-H stretching absorptions, which should occur at around 3650 and 2200 cm^{-1} , respectively, were not observed. Therefore, the concentrations of O-H and Si-H bonds for all films used would be smaller than $\sim 10^{20}\text{ cm}^{-3}$, as estimated from their detection limit in the spectrometer.

It has been known that the Si-O and Si-N stretching absorptions occur at around 1070 cm^{-1} in SiO_2 and at around 890 cm^{-1} in $\text{SiN}_{1.3}$. On the other hand, with respect to the vibrational spectra over the range of $840\text{--}1080\text{ cm}^{-1}$ for the present SiO_xN_y films, splits corresponding to the 890-- and 1070 cm^{-1} peaks were not observed. Figure 3 shows (a) peak frequency and (b) the half width at half maximum (HWHM) of the main absorption band at around 1000 cm^{-1} , as a function of x . Since the N-H bending absorption at 1150 cm^{-1} overlaps with the Si-O and/or Si-N absorption bands on the higher frequency side, the values of HWHM were determined from that for the main peak band on the lower frequency side. As shown in Fig. 3(a), the peak frequency monotonically shifts from 890 to 1070 cm^{-1} with

increasing x . Furthermore, the value of HWHM has a maximum value at around $x = 1.0$ (or $y = 0.72$). These results suggest that O and N atom nearest-neighbors at a Si site are randomly bonded to the Si atom; that is, the structure of the present films can not be described by bonding geometry including phase separation of SiO_2 and Si_3N_4 portions.

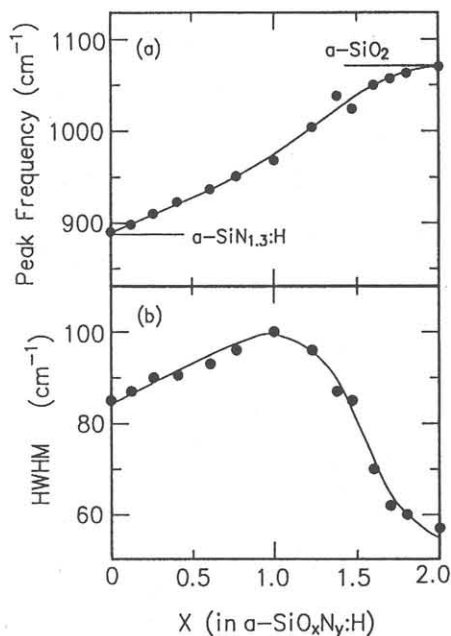


Fig. 3. (a) Peak frequency and (b) half width at half maximum (HWHM) of vibrational spectra around 1000 cm^{-1} , as a function of x in SiO_xN_y .

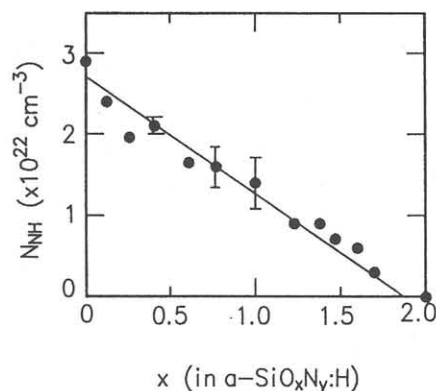


Fig. 4. Density of N-H bonds as a function of x in SiO_xN_y .

The density of N-H bonds was estimated from the intensity, I_{NH} , of the N-H stretching absorptions around 3350 cm^{-1} , as $N_{\text{NH}} = A_{\text{NH}}I_{\text{NH}}$. Here, the A_{NH} value of $2.8 \times 10^{20}\text{ cm}^{-2}$ was used.³⁾ Figure 4 shows the density of N-H bonds as a function of x . A linear reduction of N-H bonds with increasing the O content is found. This results would be because the effective coordination number of an N-H molecule is same as that of O atom. Moreover, the peak frequency of N-H stretching absorption was observed to be shifted from 3300 to 3400 cm^{-1} with increasing x .

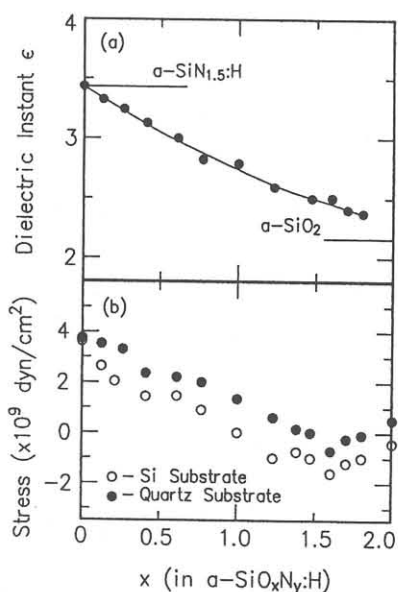


Fig. 5. (a) Dielectric constant ϵ and (b) stress for SiO_xN_y films deposited on c-Si and fused quartz substrates, as a function of x .

Figure 5 shows (a) the dielectric constant ϵ ($\epsilon = n_r^2$) and (b) the stress value observed for SiO_xN_y films deposited on c-Si and fused quartz substrates, as a function of x . The value of ϵ monotonically decreases with x from 3.42 for nitride to 2.25 for dioxide film. A decrease in the stress with x may arise from a reduction in the average coordination number over all the constituent atoms in SiO_xN_y , due to replacement of threefold coordinated N atoms by twofold coordinated O atoms.

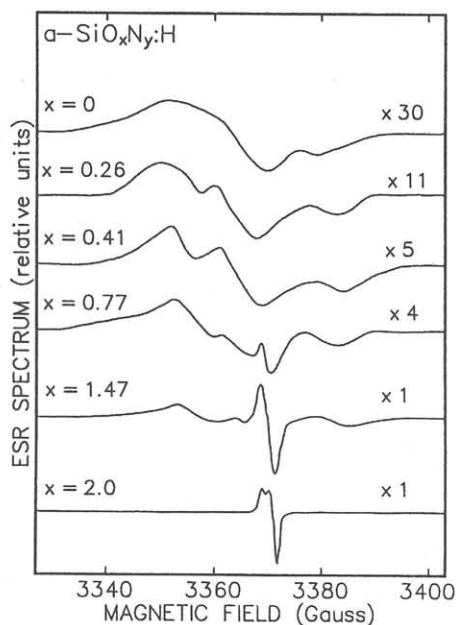


Fig. 6. Profiles of the ESR spectra as a function of x in SiO_xN_y .

Figure 6 shows the ESR spectra of films with different values of x . For Si nitride films ($x = 0$), a component forming the ESR spectrum can be attributed to either

Si or N dangling bonds. ESR signals similar to the spectrum for $x = 0$ in Fig. 6 were also observed for LPCVD and PECVD Si_3N_4 films by Nguyen *et al.*⁴⁾ As seen in Fig. 6, the structure (or splitting) of the spectra is found to become clear with increasing the O content, and then the spectra show the characteristics of the E' center as x approaches 2.0. The origin of E' centers is essentially Si dangling bonds with three O atom neighbors. On the other hand, for $x = 0.26$ or 0.41 the spectrum appears to consist of at least three lines. Further, the profiles of these spectra are found to agree well with the spectra arising from N dangling bonds observed after the sequence of annealing and UV illumination for N-rich films,⁵⁾ with the exception that the line spacing of the spectral components shown in Fig. 6 is considerably narrower than that observed by Warren *et al.*⁵⁾

In addition, spectral structure with narrower line spacing similar to that for $x = 1.47$ in Fig. 6 has also been observed for evaporated $\text{SiO}_{1.82}\text{N}_{0.16}$ films without any operation after deposition.⁶⁾ Hence it is suggested that the structure of the spectra shown in Fig. 6 would be connected with the hyperfine interaction of an unpaired electron on nitrogen nuclei with spin $I = 1$. Thus, these results suggest that the creation of N dangling bonds would be enhanced by incorporating O atoms in the nitride films. Further, the magnitude of the hyperfine constant for N dangling bonds in as-deposited SiO_xN_y films may be smaller than that for N dangling bonds created after the anneal/UV sequence. Although the mechanism for the creation of N dangling bonds is not clear, the binding energy (4.82 eV) of Si-O bonds larger than that (3.45 eV) of Si-N bonds may dominate its creation.

5. Conclusions

The properties of PECVD amorphous SiO_xN_y films are investigated as a function of x (and y). A relationship $2x + 2.8y = 4$ was found, suggesting that the densities of homobonds such as Si-Si, O-O and N-N bonds, and of Si-H, O-H and O-N bonds are sufficiently smaller than that of Si-O or Si-N bonds. No split of the stretching absorption peaks arising from Si-O and Si-N bonds suggests that the film is a homogeneous alloy. The density of N-H bonds, dielectric constant and stress monotonically decreased with increasing x . The origins of ESR signals for SiO_xN_y films are discussed. As a result, the creation of N dangling bonds may be enhanced by incorporating O atoms in the nitride films.

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