Interface properties of SiO$_x$N$_y$ layer on Si prepared by atmospheric-pressure plasma oxidation-nitridation

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Abstract

SiO$_x$N$_y$ films with a low nitrogen concentration (< 4%) have been prepared on Si substrates at 400°C by atmospheric-pressure plasma oxidation-nitridation process using O$_2$ and N$_2$ as gaseous precursors diluted in He. Interface properties of SiO$_x$N$_y$ films have been investigated by analyzing high-frequency and quasistatic capacitance-voltage characteristics of metal-oxide-semiconductor capacitors. It is found that addition of N into the oxide increases both interface state density ($D_{it}$) and positive fixed charge density ($Q_f$). After forming gas anneal, $D_{it}$ decreases largely with decreasing N$_2$/O$_2$ flow ratio from 1 to 0.01 while the change of $Q_f$ is insignificant. These results suggest that low N$_2$/O$_2$ flow ratio is a key parameter to achieve a low $D_{it}$ and relatively high $Q_f$, which is effective for field effect passivation of n-type Si surfaces.

Keywords: SiO$_x$N$_y$ film, Interface properties, Interface state density, Atmospheric-pressure plasma, Plasma oxidation-nitridation

Background

Silicon oxynitride (SiO$_x$N$_y$) is a very useful material for applications in microelectronic and optoelectronic devices due to the possibility of tailoring the film composition and property according to the O/N ratio. Recently, considerable attention has been focused on SiO$_x$N$_y$ for anti-reflection coatings and surface passivation films for thin crystalline Si solar cells [1-3]. It has been reported that SiO$_x$N$_y$ films with high positive fixed charge density ($Q_f$) in the range of 10$^{12}$ cm$^{-2}$ is effective for field-effect passivation of n-type Si surfaces [2].

So far, several methods have been applied to grow SiO$_x$N$_y$ films. For example, high-temperature (>900°C) processes such as the direct thermal oxynitridation of Si in NO or N$_2$O ambient [4,5] and the annealing of SiO$_2$ in nitrogen-containing ambient [6,7] have been widely used. However, the high-temperature processes suffer a large thermal budget and a redistribution problem of dopant atoms. Plasma-enhanced chemical vapor deposition (PECVD) process is a low-temperature alternative below 400°C [8-10]. However, the PECVD method needs toxic precursor gases, and it is also noted that the interfacial properties prepared by this method are usually inferior to those of thermal oxides [11], because the deposition method does not consume the substrate Si unlike thermal oxidation. Moreover, in the films prepared by low-temperature PECVD, the concentration of hydrogen atoms in the form of Si-OH and Si-H bonds is high, which are responsible for poor dielectric properties [12]. Nitridation of silicon oxide in low-pressure nitrogen plasma has also been investigated to fabricate SiO$_x$N$_y$ at low temperatures [13,14]. In the case of low-pressure nitrogen plasma, the ion bombardment of the film surface is a serious problem to develop highly reliable ultra-large-scale integrated circuits [15]. Recently, we have studied the plasma oxidation of Si wafers to grow SiO$_2$ films using atmospheric-pressure (AP) plasma generated by a 150-MHz very-high-frequency (VHF) electric field and demonstrated that high-quality SiO$_2$ films can be obtained using He/O$_2$ or Ar/O$_2$ plasma at 400°C [16,17]. We have also reported that the AP VHF plasma oxidation process at 400°C is capable of producing material quality of SiO$_2$ films comparable to those of...
high-temperature (>1,000°C) thermal oxides. The SiO₂/Si structure with low interface state density (D_it) around the midgap of 1.4 × 10^{10} cm⁻² eV⁻¹ and moderately high Q_f of 5.3 × 10^{11} cm⁻² has been demonstrated [18]. Therefore, addition of N into the SiO₂ film by AP plasma oxidation-nitridation using O₂ and N₂ precursor gas mixture is an alternative approach for obtaining SiOₓNᵧ films at a low temperature of 400°C.

The purpose of this work is to present a method for preparing SiOₓNᵧ films by AP VHF plasma oxidation-nitridation with a detailed analysis of interface properties of SiOₓNᵧ layer by capacitance-voltage (C-V) measurements on metal-SiOₓNᵧ-Si capacitors.

**Methods**

The details of the AP VHF plasma apparatus have been reported previously [18]. A schematic illustration of an electrode for AP VHF plasma oxidation-nitridation is shown in Figure 1. In the gap between the substrate and parallel-plate electrode, stable plasma is generated at atmospheric pressure with 150-MHz VHF power using a gas mixture of 1% O₂/He. N₂ gas was simultaneously introduced into the AP VHF plasma with gas flow rates of 1, 10, and 100 sccm. The N₂/O₂ gas flow ratios were 0.01, 0.1, and 1. The temperature of the Si wafer was fixed at 400°C by monitoring by a thermocouple embedded in the substrate heating stage. The detailed experimental conditions are shown in Table 1.

The substrates used in the present experiments were n-type (001) CZ-Si wafers (4-in. diameter) with a resistivity of 1 to 10 Ω cm. They were cleaned by a room-temperature chemical cleaning method [19] and were finished by a diluted HF treatment. After AP plasma oxidation-nitridation, some of the samples were subjected to a forming gas anneal (FGA) in 10% H₂/He for 30 min at 400°C. In order to investigate Q_f and D_it of the SiOₓNᵧ film, Al/SiOₓNᵧ/Si metal-oxide-semiconductor (MOS) capacitors were fabricated with 0.5-mm-diameter Al pads by vacuum deposition. A back contacting electrode at the rear Si surface was also made by Al deposition.

The thickness of the SiOₓNᵧ layer was determined by ellipsometry (Rudolph Auto EL III) with a wavelength of 632.8 nm. The chemical bonding in the material was investigated by Fourier transform infrared absorption (FTIR) spectrometry (Shimadzu FTIR–8600PC) in the wave number range of 400 to 4,000 cm⁻¹. X-ray photoelectron spectroscopy (XPS; ULVAC-PHI Quantum 2000) was used to investigate the depth profile of atomic composition and bonding of atoms in SiOₓNᵧ films. High-frequency (HF) and quasistatic (QS) C-V measurements were performed using a 1-MHz C meter/CV plotter (HP 4280A) and quasistatic CV meter (Keithley 595), respectively.

**Results and discussion**

Thicknesses of films prepared at 400°C for 9 min under N₂/O₂ flow ratios of 0.01, 0.1, and 1 were 20.8, 19.5, and 18.9 nm, respectively. (The film thickness was a mean value for measurements of eight different sites on the sample.) Since the difference in the film thickness is

| Condition                           | Value      |
|-------------------------------------|------------|
| Pressure (Torr)                     | 760        |
| O₂ concentration (%)                | 1          |
| He flow rate (slm)                  | 10         |
| O₂ flow rate (sccm)                 | 100        |
| N₂ flow rate (sccm)                 | 1, 10, and 100 |
| VHF (MHz)                           | 150        |
| VHF power (W)                       | 1,000 to 1,500 |
| Plasma gap (mm)                     | 0.8 to 1   |
| Substrate temperature (°C)          | 400        |
| Oxidation-nitridation time (min)    | 9 to 25    |

**Table 1 Oxidation-nitridation conditions for Si wafer**

**Figure 1** Schematic illustration of the AP VHF plasma oxidation-nitridation apparatus used in this study. The electrode is made of stainless steel plate coated with Al₂O₃, and its diameter is 50 mm.

**Figure 2** IR spectra of films prepared by AP VHF plasma oxidation-nitridation under different N₂/O₂ flow ratios.
small (<±5%), its effect on the interface state properties may be negligible. Figure 2 shows FTIR spectra of the films prepared at 400°C for 9 min under different N₂/O₂ flow ratios. The dotted lines in Figure 2 indicate the stretching and bending vibration modes of Si-O-Si bonds at the wave numbers of 1,075 and 810 cm⁻¹, respectively. Almost no apparent peak for Si-N stretching mode at 835 cm⁻¹ is observed [1], which may be related with the larger dissociation energy of N₂ than that of O₂ molecules.

In Figure 2, the strongest peak in IR spectra corresponds to Si-O-Si stretching mode, indicating that the film consists predominantly of SiO₂. The dielectric constant of the film was calculated using the maximum accumulation capacitance obtained by $C$-$V$ curves. The result showed that the dielectric constant was fairly uniform over the sample area with a variation of about 2% and that the average dielectric constants of the films were 4.26 and 4.01 for N₂/O₂ flow ratios of 0.01 and 1, respectively. Since the dielectric constants of SiO₂ and Si₃N₄ are 3.9 and 7.5, respectively, nitrogen atoms are considered to be incorporated in the SiO₂ structure.

XPS spectra in the Si 2$p$ region for the SiOₓNᵧ layer formed at 400°C for 9 min with a N₂/O₂ gas flow ratio of 0.1 are shown in Figure 3. The Si 2$p$ peak observed at 99.7 eV is from the Si substrate and the one at 103.5 eV from Si-O-Si bonding. On the as-grown sample, as shown in Figure 3a, after five times of surface layer sputtering by 10-keV Ar ions (duration of one sputtering is 10 s), Si-O-Si bonding peak is strong, but a small peak from the Si substrate is also seen. By the sixth and seventh sputtering, the Si-O-Si peak decreases and the bulk Si peak increases. It is noteworthy that Si-N bonding at 102.4 eV is also detected. Since the Si-N peak becomes clear before the Si-O-Si peak vanishes, Si-N bonding is supposed to be located at the SiO₂/Si interface region.

In the annealed sample, as shown in Figure 3b, the decrease of the Si-O-Si peak after the sixth sputtering is not significant as compared to that in the as-grown sample and the Si-O-Si peak still remains after the seventh sputtering. The Si-N peak becomes well observable after the seventh sputtering in the annealed sample instead of the sixth sputtering for the as-grown case. However, the tendency of decreasing Si-O-Si peak and increasing...
bulk Si peak with increasing sputtering time is the same for both as-grown and annealed samples. These results can be understood by considering the increase in SiO\textsubscript{2} thickness by the annealing and the presence of Si-N bonding at the SiO\textsubscript{2}/Si interface region. The thickness increase in the annealed SiO\textsubscript{2} sample is considered to be due to the density relaxation of SiO\textsubscript{2} by the thermal annealing [20,21].

Figure 4 shows depth profiles of Si, O, and N atom concentrations in SiO\textsubscript{x}N\textsubscript{y} films measured by XPS as a function of sputtering time, which reveals that incorporated N atoms (approximately 4%) locate at the film/substrate interface for all the samples. These results are similar to those by the high-temperature process, such as the direct thermal oxynitridation of Si in N\textsubscript{2}O ambient at 1,000°C [5]. According to the thermodynamics of Si-N-O system, nitrogen in bulk SiO\textsubscript{2} is not thermodynamically stable but may be stable at the interface [22]; therefore, it has been assumed that nitrogen incorporated into the film during oxynitridation (especially in high-temperature N\textsubscript{2}O or NO process) reacts only with Si-Si bonds at or near the interface, not with Si-O bonds in the bulk of the SiO\textsubscript{2} overlayer. Similarly, we suppose that since the dissociation of nitrogen molecules is not significant in the present case, nitrogen migrates to the Si/SiO\textsubscript{2} interface during AP plasma oxidation-nitridation.

Finally, the interface electrical quality of SiO\textsubscript{x}N\textsubscript{y} layers prepared by AP VHF plasma oxidation-nitridation process has been investigated. Figure 5 shows typical HF C-V curves of the MOS capacitors utilizing SiO\textsubscript{x}N\textsubscript{y} layers formed by various N\textsubscript{2}/O\textsubscript{2} flow ratios. The HF C-V curve shifts to a negative gate bias direction with increasing N\textsubscript{2}/O\textsubscript{2} flow ratios, which shows an increase in

![Figure 6 HF and QS C-V curves for Al/SiO\textsubscript{x}N\textsubscript{y}/Si MOS capacitors (before annealing) utilizing SiO\textsubscript{x}N\textsubscript{y} layers. The layers were prepared under N\textsubscript{2}/O\textsubscript{2} gas flow ratios of 0.01, 0.1, and 1.](image)

![Figure 7 HF and QS C-V curves for Al/SiO\textsubscript{x}N\textsubscript{y}/Si MOS capacitors (after annealing) utilizing SiO\textsubscript{x}N\textsubscript{y} layers. The layers were prepared under N\textsubscript{2}/O\textsubscript{2} gas flow ratios of 0.01, 0.1, and 1.](image)
positive $Q_{f}$ with incorporation of more N atoms into the SiO$_2$ film (Figure 4). The values of $Q_{f}$ have been estimated by flat-band voltage shift to be 5.1 x $10^{11}$, 8.1 x $10^{11}$, and 8.4 x $10^{11}$ cm$^{-2}$ for N$_2$/O$_2$ flow ratios of 0.01, 0.1, and 1, respectively.

The HF (blue) and QS (cyan) C-V curves for Al/SiO$_2$/N$_x$/Si MOS capacitors before and after FGA are shown in Figures 6 and 7, respectively. The annealed Al/SiO$_2$/N$_x$/Si MOS capacitors show better interface properties compared with those without FGA. $D_{it}$ after FGA were 6.1 x $10^{11}$, 1.2 x $10^{12}$, and 2.3 x $10^{12}$ cm$^{-2}$ eV$^{-1}$ for N$_2$/O$_2$ flow ratios of 0.01, 0.1, and 1, respectively. It is well known that an introduction of a small amount of nitrogen into the SiO$_2$ gate oxide leads to an enhanced defect density in the case of N pileup at the Si/SiO$_2$ interface [23]. From our XPS results, when the N$_2$/O$_2$ gas flow ratio increases, the more N atoms pileup at the Si/SiO$_2$ interface during AP plasma oxidation-nitridation; therefore, $D_{it}$ increases largely with increasing N$_2$/O$_2$ flow ratio from 0.01 to 1. The corresponding values of $Q_{f}$ were 1.2 x $10^{12}$, 1.4 x $10^{12}$, and 1.5 x $10^{12}$ cm$^{-2}$, respectively. It is noted that $D_{it}$ decreases largely with decreasing N$_2$/O$_2$ flow ratio from 1 to 0.01, while the decrease of $Q_{f}$ is insignificant. These results suggest that a significantly low N$_2$/O$_2$ flow ratio is a key parameter to achieve a small $D_{it}$ and relatively large $Q_{f}$ which is effective for field-effect passivation of n-type Si surfaces.

Conclusions
SiO$_2$/N$_x$ films with a low nitrogen concentration (approximately 4%) have been prepared on n-type (001) Si wafers at 400°C for 9 min by oxidation-nitridation process in AP plasma using O$_2$ and N$_2$ diluted in He gas. Interface properties of SiO$_2$/N$_x$ films have been investigated by C-V measurements, and it is found that addition of N into the oxide increases both the values of $D_{it}$ and $Q_{f}$. After FGA, $D_{it}$ at midgap decreases from 2.3 x $10^{12}$ to 6.1 x $10^{11}$ cm$^{-2}$ eV$^{-1}$ with decreasing N$_2$/O$_2$ flow ratio from 1 to 0.01, while the decrease of $Q_{f}$ is insignificant from 1.5 x $10^{12}$ to 1.2 x $10^{12}$ cm$^{-2}$. These results suggest that a low N$_2$/O$_2$ flow ratio is a key parameter to achieve a low $D_{it}$ and relatively high $Q_{f}$ which is useful to realize an effective field-effect passivation of n-type Si surfaces.

Competing interests
The authors declare that they have no competing interests.

Authors’ contributions
ZZ helped in the oxidation-nitridation experiments and sample characterization, and wrote the manuscript. YS and YK performed the atmospheric-pressure plasma oxidation-nitridation of Si wafers and XPS, FTIR, and C-V measurements. TY, HO, and HK helped in designing the work. KY discussed the results and proofread the manuscript. All authors read and approved the final manuscript.

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