

High resolution ion scattering study of silicon oxynitridation

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High resolution medium energy ion scattering was used to characterize the nitrogen distribution in ultrathin silicon oxynitrides with sub-nm-accuracy. We show that nitrogen does not incorporate into the subsurface region of the substrate after oxidation of Si(100) in NO. Core-level photoemission experiments show two bonding configurations of nitrogen near the interface. Oxynitridation in N₂O results in a lower concentration and a broader distribution of nitrogen than in the NO case.
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Ultrathin silicon oxynitrides (SiO_xN_y) are promising dielectrics for sub-0.25 μm ULSI devices.¹⁻⁹ They exhibit several properties superior to thermal O₂ oxides (SiO₂), the most important being suppression of boron penetration, enhanced reliability, and reduced hot-electron induced degradation.¹⁰ Recent publications suggest that the performance of CMOS-based devices depends on both the concentration and distribution of the nitrogen atoms incorporated into the gate dielectric.^{5,7,9,11} Both the optimal nitrogen profile and even the best method for measuring nitrogen in ultrathin SiO_xN_y films are still under debate.

Characterizing the nitrogen distribution in ultrathin films with the required sub-nm accuracy is an analytical challenge. Two approaches have been used, secondary ion mass spectroscopy (SIMS)^{2,5,9,12} and HF etch-back methods^{3,13,14} In addition to the limited depth resolution of these methods, SIMS analysis is complicated by matrix effects, while HF etching may introduce nonuniform oxide removal (especially in the presence of nitrogen-rich regions).

Nitrogen may be incorporated into SiO₂ using either oxidation/annealing^{1-5,12-20} or deposition^{6,7,9,21} methods. Thermal oxynitridation of silicon in N₂O (Refs. 3, 4, 8, 13, 14, 17, and 19) was proposed^{1,2} to place small amounts of N (typically on the order of 5 × 10¹⁴ N/cm²) in the oxide region near the interface. Recently, oxynitridation in NO has been reported^{5,11,12,15,18} to give rise to a higher nitrogen concentration. Recent SIMS results on silicon (furnace) oxidation of a SiO₂ film in NO were interpreted in terms of a nitrogen distribution sharply peaked on the substrate (silicon) side of the interface rather than in the near-interfacial oxide.¹² In contrast, other studies¹⁸ show that nitrogen is distributed evenly throughout dielectric films grown in NO.

In this work, high-resolution (ΔE/E ~ 0.1%) medium energy ion scattering (MEIS)²² was used to accurately obtain the depth distribution profile of nitrogen in sub-5 nm oxynitrided films. The most striking result was that nitrogen is not observed in the substrate after oxynitridation, contrary to the conclusions presented in a recent SIMS study.¹² We demonstrate that a 0.3–0.5 nm accuracy (depending on the film thickness) in the nitrogen depth profiles can be achieved.

Both the depth resolution and the sensitivity to nitrogen increase in MEIS with decreasing film thickness. An additional advantage of the technique is that it provides absolute nitrogen concentrations.^{22,23}

We studied oxynitridation of Si(100) in NO, O₂/NO, and N₂O. The samples were grown in a vertical furnace at 850, 950, or 1000 °C. A proton beam with an initial energy of 97.2 keV was used as the MEIS probe. The incident ion beam was normal to the sample, and the scattering angles ranged from 100° to 140°. More details about high-resolution depth profiling by MEIS can be found elsewhere.²⁴⁻²⁶

Figure 1(a) shows a typical spectrum for a film grown in NO. The thickness was measured to be 2.2 nm by both MEIS and single wavelength ellipsometry. Two peaks are seen in

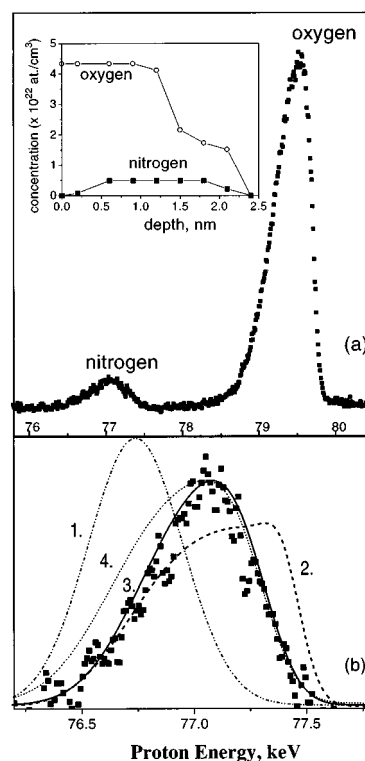


FIG. 1. (a) A MEIS spectrum for an oxynitride grown on Si(100) in a furnace at 950 °C for 60 min in NO ambient. The scattering angle is 125°. The inset shows the corresponding nitrogen and oxygen profiles (as a function of distance from the oxide surface). (b) A closeup of the spectrum in the nitrogen region along with the results of simulations for different nitrogen distributions.

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this spectrum, corresponding to nitrogen and oxygen (a third peak, originating from silicon backscattering, is not shown). The lighter mass (nitrogen) yields a peak at lower energy.^{22,23} The areas under the peaks are proportional to the total amounts of oxygen and nitrogen in the film.^{22,23} Obviously, the amount of nitrogen is much smaller than that of oxygen. The concentration of nitrogen in this sample is $(8.8 \pm 0.7) \times 10^{14}$ atoms/cm².

The shape of the nitrogen peak is determined by the depth distribution of nitrogen in the film. Because of energy loss arising from electronic excitations, protons backscattered from nitrogen atoms closer to the Si–SiO_xN_y interface have lower energy than those scattered off the atoms near the surface.^{22,24} In the same way, the sharp leading edge of the oxygen peak is formed by the protons scattered from the surface oxygen atoms, whereas the low energy tail results from scattering off oxygen atoms at the interface. The width of the oxygen peak reflects film thickness. The width of the nitrogen peak [FWHM=0.59 keV] in Fig. 1(a) is slightly smaller than the width of the oxygen peak (0.68 keV), indicating that the nitrogen distribution is narrower than the thickness of the (2.2 nm) film.

More detailed information about the nitrogen profile in the film can be obtained through spectral simulations.²⁴ These simulations include the effect of ion straggling,^{22,24} which results in energy broadening as the ion beam penetrates into the sample. Simulations for different nitrogen distributions are shown in Fig. 1(b). Curve 1 corresponds to an extreme case of all nitrogen (8.8×10^{14} N/cm²) located at the interface, and shows poor agreement with the observed spectrum. If the nitrogen atoms were located deeper, i.e., on the substrate side of the interface as claimed based on SIMS results,¹² the simulated peak would have moved further away from the observed peak towards even lower proton energies. A simulation for the other extreme case of the same amount of nitrogen uniformly distributed throughout the film (curve 2) also does not fit the data. The best fit to the data (curve 3) is obtained for the nitrogen profile shown in the inset in Fig. 1(a). This profile corresponds to a width for the nitrogen distribution of about 1.5 ± 0.3 nm and a concentration (in this region) of 7.5 at. % (also shown in the inset). The oxygen concentration is uniform in the film, except in the transition region^{26,27} near the interface (the position of the interface is defined as a point where the oxygen concentration vanishes). The width of this region in the graph is a convolution of macro- and microscopic (“peak-to-peak”) roughness¹³ and any microscopic oxygen concentration gradient in the suboxide region.²⁷ Roughness may also contribute to the width of the nitrogen distribution deduced from the simulation. Subtraction of the roughness contribution (which is on the order of 0.2–0.3 nm rms at the interface¹³) would still leave the “local” width of the nitrogen containing layer of at least 1 nm, and is inconsistent with a model of a sharp silicon nitride monolayer between SiO₂ and the Si substrate. For curve 4, we extend the nitrogen profile shown in the inset 0.3 nm into the Si substrate. The fit becomes worse, indicating again that the presence of even a small fraction of N in the first 0.3 nm of the substrate side of the interface is inconsistent with our results.

To complement the MEIS depth profiling with chemical

information about nitrogen bonding, we have used XPS (1487 eV) and SXPS ($h\nu=130\text{--}200$ eV). Our XPS analysis reveals two bonding configurations of N in the 2.2 nm film, corresponding to two features in the N 1s spectra with binding energies of 397.7 and 400 eV (calibrated to the Si 2p substrate peak at 99.2 eV), with area ratios of about 5:1 (for photoemission normal to the sample), consistent with previous studies.¹² The peak around 397.7 eV (also seen for Si₃N₄ samples^{14,28}) is usually attributed^{6,12,17,18,29,30} to nitrogen in an Si₃–N configuration. The assignment of the other feature, at higher binding energies, is less straightforward. The adsorption of NO or N₂O on surfaces at low (~ 77 K) temperatures was found^{31–35} to result in N 1s peaks in the range of 400–407 eV. Experiments²⁸ with *a*-SiN_x ($0 < x < 1.7$) showed a variation of binding energies from 397.25 to 398.39 eV, which implies that peaks above 400 eV cannot be due to variations in stoichiometry. Therefore, it is reasonable to assign (following others^{6,12,30}) the feature at 400 eV to N with at least one N–O bonded nitrogen. By comparing XPS spectra at different take-off angles (0° and 60°), we found that the higher binding energy feature (400 eV) becomes more prominent at grazing angles. This indicates that the Si₃–N configuration dominates near the interface, while the N–O bonded nitrogen is located further into the oxide. Recent XPS HF depth profiling experiments¹⁴ for oxynitridation in N₂O yield the following similar conclusions: (i) that the Si₃–N states are localized closer to the interface (within about 1.5–2 nm) whereas the Si₂–N–O configuration extends into the oxide so that the overall width of the nitrogen distribution is about 3–4 nm. Our synchrotron-based SXPS Si 2p spectra for thin (~ 2 nm) NO-grown films also imply a more silicon-nitride-like bonding of nitrogen at the interface, which is quite different from nitrogen behavior further into the oxynitride overlayer. However, MEIS and photoemission results [specifically: (i) depth distribution, (ii) low concentration of nitrogen, and (iii) multiple photoemission features] suggest that the nitrogen is not sharply concentrated right at the interface as a single continuous Si₃N₄ layer (although it may be possible to engineer a SiO₂/Si₃N₄/Si structure using other processing methods).

Near-interfacial nitrogen significantly retards the rate of the oxide growth; we see this and it has also been noted by others.^{16,21,36} This is likely the reason why oxynitridation in NO (with a high concentration of nitrogen) appears self-limiting—the thickness of the film after oxidation for 60 min at 950 °C is only 2.2 nm, as compared to 35 nm for O₂ and 10 nm for N₂O. To make a thicker NO-oxynitrided film, we first formed a 4.5 nm pre-oxide, followed by reoxynitridation in NO to a final thickness of 5.5 nm. The spectrum for this film and for the oxygen and nitrogen profiles are shown in Fig. 2. Reoxidation in NO results in nitrogen incorporation into the near-interfacial oxide with a total concentration of 1.1×10^{15} N/cm² and a width of 1.5 ± 0.5 nm.

Several groups^{5,11,12,15,18} have reported very different reaction chemistries and nitrogen profiles for oxynitridation in NO and N₂O, and for rapid thermal oxidation (RTO) versus furnace oxynitridation. A spectrum for a (5.5 nm) film grown in N₂O under conditions similar to our NO oxynitridation case is shown in Fig. 2(b). It can be clearly seen that oxynitridation in N₂O results in much smaller nitrogen con-

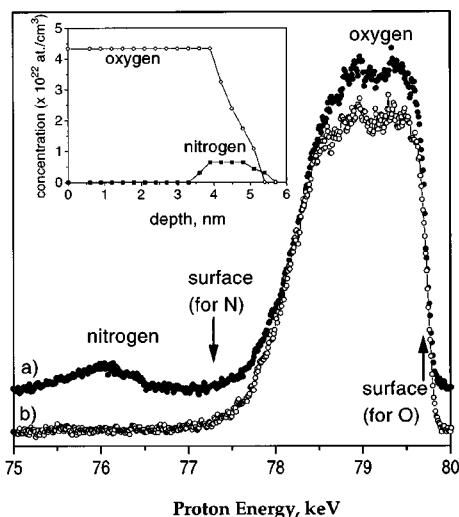


FIG. 2. MEIS spectra for (a) an O₂ (850 °C, 5.5 min/NO) (950 °C, 60 min) furnace grown oxynitride and for (b) a film grown in a furnace in N₂O at 850 °C for 110 min. The scattering angle is 125°. The oxygen and nitrogen profiles shown in the inset correspond to spectrum (a).

tent, consistent with observations by others.^{12,15,18} In addition, N₂O requires higher temperatures than NO to incorporate an equivalent amount of nitrogen.^{4,13} One can estimate from the MEIS spectrum that the total concentration of nitrogen in this film is less than 4×10^{14} N/cm² with a very broad distribution (>3 nm, at least).

For comparison, we show in Fig. 3 results of a SIMS analysis on the two samples for which MEIS data were reported in Fig. 2 as well as a third film, grown in N₂O using RTO at a slightly higher temperature. The SIMS data agree qualitatively with the MEIS data in that the total amount of nitrogen incorporated is much smaller after oxynitridation in N₂O than for oxidation in O₂ followed by NO nitridation. Also, we find that both techniques show a more pronounced nitrogen pileup near the interface for RTO than for furnace

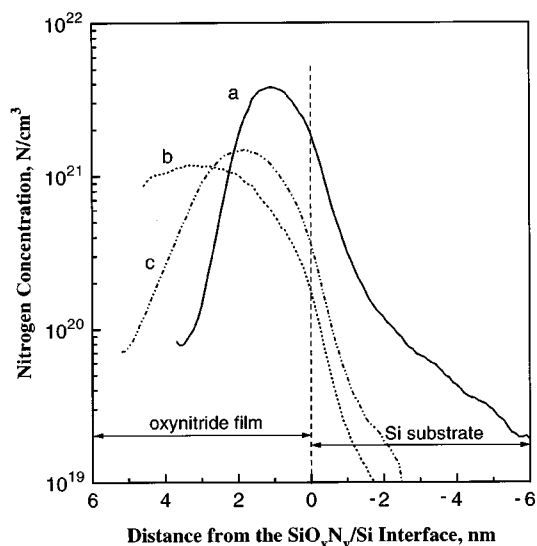


FIG. 3. Nitrogen depth profiles measured by SIMS for (a) an O₂/NO grown oxynitride [same sample as spectrum (a) in Fig. 2], (b) a film grown in a furnace in N₂O [same sample as spectrum (b) in Fig. 2]; and (c) a film grown in N₂O by RTO at 1000 °C for 2.3 min. All three samples have similar oxide thicknesses of 5.5–6 nm. The dashed vertical line shows the position of the interface.

growth in N₂O. Our SIMS data disagree with those reported by Hedge *et al.*¹² in that in all cases the nitrogen distribution is peaked in the film and not in the substrate.

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