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Dry oxidation mechanisms of thin dielectric films formed under N₂O using isotopic tracing methods

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We investigated the mechanisms of thermal reoxidation in dry O₂ of silicon oxynitride films prepared by processing Si(100) wafers in a rapid thermal furnace in a pure nitrous oxide (N₂O) ambient, using isotopic tracing of oxygen and nitrogen. Standard nuclear reaction analyses for the measurement of the total amounts of the different isotopes, and very narrow resonant nuclear reactions for high resolution (1 nm) depth profiling of these elements were used. The silicon oxynitride films grown in pure ¹⁵N₂¹⁶O were 8-nm thick, with a small amount of nitrogen localized near the interfacial region. Under reoxidation in dry ¹⁸O₂, the thickness of the dielectric film increased while a pronounced isotopic exchange took place between the ¹⁸O from the gas and the ¹⁶O from the film, as well as a significant loss of ¹⁵N. This is in contrast with the reoxidation in dry O₂ of pure SiO₂ films, where the oxygen exchange is rather small as compared to that observed in the present case. © 1996 American Institute of Physics. [S0003-6951(96)03717-8]

The developments in very large-scale integration (VLSI) devices require reliable gate insulator materials with thicknesses compatible with the scaling rules, namely 10 nm and less. Various methods have been used to produce these dielectric films, the most promising ones being the thermal growth of a silicon oxynitride film on silicon in a nitrous oxide (N₂O) environment.^{1,2} Although atomic transport processes are fundamental for the understanding of the growth mechanisms, so far only a few studies have considered this aspect.³⁻⁵ In this letter we report on the atomic transport mechanisms during thermal reoxidation⁶ of oxynitride films previously grown on Si (001) under N₂O, using isotopic tracing experiments of nitrogen and oxygen.

Pure N₂O (>99.998 %) enriched in ¹⁵N (99% labelled gas) was used for the oxynitridation of the silicon, and dry 99 % ¹⁸O enriched oxygen gas (¹⁸O₂) was used for thermal reoxidation. The treatment temperature was fixed at 1090 °C for both oxynitridation and reoxidation. Oxynitridation under ¹⁵N₂O was performed in a rapid thermal furnace at a pressure of 10³ Pa during 180 s treatment time, and reoxidations were performed under 10⁴ Pa of dry ¹⁸O₂ for times of 20 min, 40 min and 120 min in a classical resistance heated furnace. The thicknesses of the oxynitride films after the thermal treatments were 8.2 nm before reoxidation and 15.8 nm, 20.5 nm and 31.8 nm after reoxidation times of 20 min, 40 min and 120 min, respectively. A 15 nm-thick control oxide was also grown at 1050°C by subsequent oxidations in 10⁴ Pa of dry ¹⁶O₂ gas for 450 s and in dry ¹⁸O₂ for 150 s.

The total amounts of nitrogen ¹⁵N, ¹⁶O, and ¹⁸O were determined through nuclear reactions analyses (NRA) using the cross section plateaus of the reactions ¹⁵N(p,αγ)¹²C at 1000 keV, ¹⁶O(d,p₀)¹⁷O at 810 keV and ¹⁸O(p,α₀)¹⁵N at 730 keV.⁷ The total amount of the different isotopes were determined by comparison with standards having uncertainties less than 2%. The thicknesses of the films can be given in

SiO₂ equivalent: 10¹⁵ oxygen atoms.cm⁻² corresponds to 0.226 nm, assuming a density of the silicon oxide of 2.21 g/cm³. For atomic depth profiling (¹⁵N and ¹⁸O), we used nuclear narrow resonant reaction analysis and the SPACES simulation program.^{8,9} In the present work we used the narrow resonance (Γ = 100 eV) at 152 keV of the ¹⁸O(p,α)¹⁵N nuclear reaction for the ¹⁸O depth profiling,⁹ and the narrow resonance (Γ = 120 eV) at 429 keV of the ¹⁵N(p,αγ)¹²C nuclear reaction for the ¹⁵N depth profiling.⁷ In both cases the samples were tilted at 65° with the respect to normal incidence in order to increase the depth resolution to 1 nm near the surface.

Figure 1 presents the excitation curves of the nuclear reaction ¹⁸O(p,α₀)¹⁵N near the narrow resonance (Γ = 100 eV) at E_p = 152 keV, for the control oxide (Fig. 1 top) and for the oxynitride (Fig. 1 bottom) films. In the insets, the local concentrations of ¹⁸O, namely ¹⁸O/¹⁸O+¹⁶O, as a function of depth (¹⁸O depth profile) corresponding to the simulation of the experimental data are shown.^{8,9} The double location of the ¹⁸O in Fig. 1 (top) (near the surface and at the interface) is consistent with : (i) The oxidizing species are dissolved into interstitial positions and diffuse into the silica network without reacting with the bulk; they react with Si at the SiO₂/Si interface to form the new oxide. This is in agreement with the Deal and Grove theory;⁵ (ii) An exchange mechanism takes place between the oxygen from the gas and the oxygen from the silica network due to local defects present near the surface of the SiO₂ film.^{10,11} This phenomenon is independent of the first mechanism described in (i). The mechanism (i) is responsible for a pure Si¹⁸O₂ film localized at the oxide/silicon interface with a sharp transition between Si¹⁶O₂ and Si¹⁸O₂. The mechanism (ii) leads to a fixation of ¹⁸O near the external surface and the ¹⁸O depth profile which correspond to it is erfc-like.^{10,11}

In Fig. 1 (bottom) the shape of the profile is different, being the concentration of ¹⁸O atoms different from zero in

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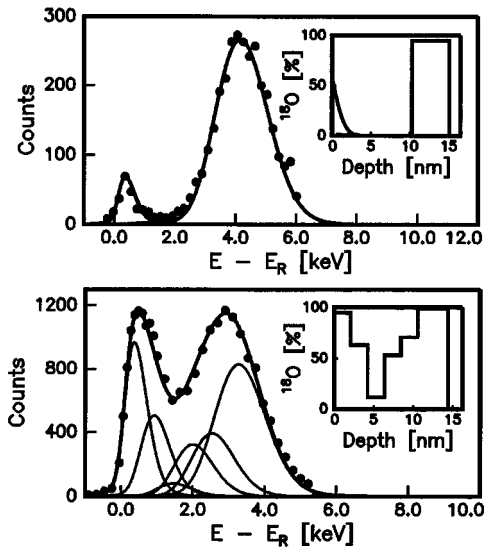


FIG. 1. Excitation curves of the nuclear reaction $^{18}\text{O}(p,\alpha)^{15}\text{N}$ near the resonance at 152 keV from (top) the control oxide grown at 1050°C in 10^4 Pa of dry $^{16}\text{O}_2$ for 450 s subsequently reoxidized in $^{18}\text{O}_2$ in the same conditions but for 150 s, and (bottom) a sample oxynitrided in 10^3 Pa of N_2O at 1090°C for 180 s and subsequently reoxidized in 10^4 Pa of dry $^{18}\text{O}_2$ during 20 min at 1090°C. The related local concentration depth profiles of ^{18}O , namely $[^{18}\text{O}] = \frac{^{18}\text{O}}{^{18}\text{O} + ^{16}\text{O}}$, extracted from the experimental data are shown in the insets.

the bulk of the film. The NRA show that the reoxidation of the oxynitride in $^{18}\text{O}_2$ is accompanied by an important exchange phenomenon between the ^{18}O atoms from the gas and the ^{16}O atoms from the oxynitride network. This exchange is much more effective compared to that observed in the case of dry reoxidation of pure SiO_2 .^{10,11} Approximately 29% of the oxygen atoms are exchanged during the first 20 min of reoxidation; as the reoxidation time increases, this phenomenon is enhanced to reach approximately 67% for 120 min of reoxidation time. Furthermore, the amount of ^{16}O lost by exchange is proportional to the square root of the reoxidation time, which indicates that this phenomenon is probably governed by a diffusion process. Figure 2 displays the evolution of the ^{18}O depth profile with reoxidation time. As the film grows, the ^{18}O surface peak becomes wider due to the dif-

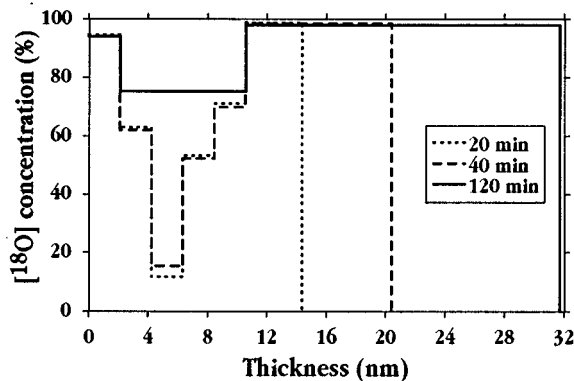


FIG. 2. Concentration depth profiles of ^{18}O in films grown in 10^3 Pa of $^{15}\text{N}_2\text{O}$ at 1090°C for 180 s and subsequently reoxidized in 10^4 Pa of dry $^{18}\text{O}_2$ at 1090°C for 20 min, 40 min, and 120 min.

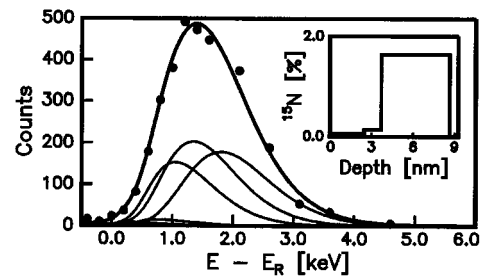


FIG. 3. Excitation curve of the nuclear reaction $^{15}\text{N}(p,\alpha)^{12}\text{C}$ near the resonance at 429 keV ($\Gamma=100$ eV) from a silicon oxynitride obtained by thermal annealing under 10^3 Pa of pure $^{15}\text{N}_2^{16}\text{O}$ at 1090°C for 180 s. The related local concentration depth profile of ^{15}N , namely $[^{15}\text{N}] = \text{N}/(\text{N}+\text{O})$ extracted from the experimental data is shown in the inset.

fusing defects in the oxynitride film. Oxygen vacancy or interstitial defects could explain those profiles. But an annealing at high temperature in vacuum or in non-reactive atmosphere, did not show any modification in the ^{18}O or nitrogen depth profiles.¹² This indicates that the defect responsible for the exchange phenomenon is more likely interstitialcy. Otherwise, the presence of ^{18}O at the oxynitride/Si interface, with a local concentration equal to the labelling of the gas (99%), indicates that an oxidation within the framework of the Deal and Grove model still occurs in parallel with the exchange phenomenon. However, the sharp transition between the ^{16}O -rich region and the ^{18}O -rich region existing in the case of the oxide is not observable after reoxidation in $^{18}\text{O}_2$ of the oxynitride, a fact that can be attributed to the significant overall diffusion of defects into the bulk of the oxynitride, leading to a $^{16}\text{O}/^{18}\text{O}$ mixture in the film.

The nitrogen distribution after the thermal treatment in $^{15}\text{N}_2^{16}\text{O}$ is shown in Fig. 3. The nitrogen is fixed near the oxynitride/Si interface and less than 0.1% of nitrogen ($\text{N}/(\text{N}+\text{O})$) has been detected near the surface region, in agreement with previous observations.¹³⁻¹⁵ As the reoxidation in $^{18}\text{O}_2$ proceeds, the distribution of nitrogen becomes wider, a loss of nitrogen is observed and the position of the maximum concentration of ^{15}N shifts towards the surface as shown in Fig. 4. The broadening of the peak, and the loss of nitrogen

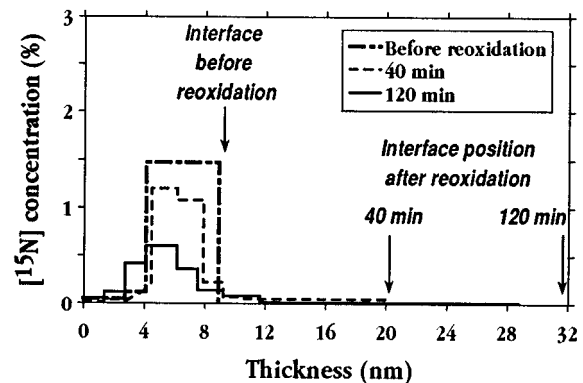


FIG. 4. Concentration depth profiles of ^{15}N in a film grown in 10^3 Pa of $^{15}\text{N}_2\text{O}$ at 1090°C for 180 s, and in samples subsequently reoxidized in 10^4 Pa of dry $^{18}\text{O}_2$ at 1090°C for 40 min and 120 min. The arrows indicate the position of the oxynitride/Si interface for the different samples.

are also proportional to the square root of the reoxidation time, most probably due to defect diffusion in the film. For the same reasons developed for the ^{18}O diffusion, the migration of nitrogen atoms is also probably due to interstitial defects. However the shift of the distribution towards the surface cannot be explained by a simple diffusion of N atoms. Let us consider the samples reoxidized for 40 min and 120 min; in the first one, the new position of the oxynitride/Si interface is far enough from the nitrogen atoms to allow us to neglect its effect on the N diffusion during the additional 80 min of reoxidation necessary to form the second sample. If the outside surface would be permeable, then after a certain diffusion time, mathematically the position of the maximum concentration of nitrogen should move deeper into the film. On the contrary, if we assume now that the surface is like a reflecting wall, the maximum concentration should shift towards the surface. But after 120 min of reoxidation, the experimentally observed shift of N towards the sample surface is too large to be correlated to the broadening of the nitrogen distribution; in this case one cannot explain the transport mechanisms by a standard diffusion process. To account for this phenomenon, we must consider a drift of the nitrogen in the direction of the sample surface during thermal reoxidation. The origin of this drift is not clearly identified, but should be due to a concentration gradient of defects.

By simulating the evolution of the nitrogen and oxygen profiles with the reoxidation time, we have extracted the effective diffusion coefficients for nitrogen D_N , as well as its drift velocity, V_d^N , and the effective diffusion coefficient for oxygen, D_O . For both species, we made the hypothesis that they diffuse in a semi-infinite medium. We found $10^{-18} \text{ cm}^2\text{s}^{-1} < D_N < 2 \times 10^{-18} \text{ cm}^2\text{s}^{-1}$, $10^{-17} \text{ cm}^2\text{s}^{-1} < D_O < 3 \times 10^{-17} \text{ cm}^2\text{s}^{-1}$, and $V_d^N 1 \times 10^{-2} \text{ nm min}^{-1}$. These diffusion coefficients show that the oxygen atoms diffuse faster than the nitrogen atoms. But the magnitudes of D_N and D_O are too close to conclude that the defect responsible for the migration of nitrogen is different from that responsible for the diffusion of oxygen. In a recent study, based on electron paramagnetic resonance (EPR) measurements on oxynitrides, the authors established that the nature of nitrogen and oxygen defects are different.¹⁶

In summary, we have studied the mechanisms of thermal reoxidation of silicon oxynitride films using isotopic tracing

experiments with ^{18}O and ^{15}N as tracers. ^{15}N depth profile revealing that after the thermal treatment under nitrous oxide the nitrogen is localized near the oxynitride/Si interface in a rather small concentration ($\text{N}/\text{N}+\text{O} \approx 2\%$). During reoxidation, we observed that the oxygen atoms react at the interface to form new silicon oxide layers, near the surface, and in the bulk of the oxynitride film a significant exchange phenomenon takes place between the oxygen from the gas and the oxygen in the film. The nitrogen atoms diffuse in the film and drift to the sample surface. A significant loss of nitrogen is also found. Most probably, the defects responsible for the migration of nitrogen and oxygen atoms are interstitialcies. No evidence has been found for equivalent defects linked with nitrogen and oxygen. To explain the nitrogen behavior during reoxidation, we propose the existence of a concentration gradient of defects which favours the migration of nitrogen atoms towards the surface.

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