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Isotopic substitution of N, O, and Si in the thermal oxidation of nitrogen-deposited silicon

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Nitrogen was deposited on the surface of Si(100) wafers by ion implantation at a very low energy (approximately 20 eV), at fluences between 1 and $10 \times 10^{14} \text{ cm}^{-2}$. The samples were thermally oxidized in dry O_2 at temperatures between 800 and 1050 °C. Atomic transport of the chemical species involved in the process was investigated by isotopic tracing of N, O, and Si, using depth profiling with nanometric resolution. The obtained results indicate that: (i) the nitrogen atoms deposited on the Si surface are redistributed during thermal oxidation in O_2 within the silicon oxide (oxynitride) film, with maxima at the near-surface and near-interface regions; (ii) during growth, O is fixed not only in the near-interface and near-surface regions like in the thermal growth of SiO_2 films on Si, but also in the bulk of the growing oxide (oxynitride) film; and (iii) Si is immobile during the thermal oxidation process. The observed modifications in the mechanisms of thermal growth of SiO_2 (SiO_xN_y) films on Si due to the presence of N are discussed. © 1999 American Institute of Physics. [S0003-6951(99)01113-4]

In a recent publication¹ we reported on the thermal oxidation in dry O_2 of Si(100) wafers whose surfaces were previously covered with around 1/30–1 ML of N atoms by N^+ implantation at 20 eV. This kind of processing has recently been considered as a convenient route to prepare silicon oxynitride ultrathin films for gate dielectrics in ultra-large-scale integration (ULSI) metal–oxide–semiconductor field-effect transistor (MOSFET) devices.^{2–5} The presence of N atoms at the surface of Si at these concentrations significantly decreased the growth rate of the silicon oxide film,¹ whereas the N atoms were partially removed from the system as thermal oxidation proceeded. Several questions arose from this previous work: (i) What is the depth distribution of the remaining N atoms? (ii) Which are the mobile species and which are the atomic transport mechanisms taking place during the thermal growth of the silicon oxide (oxynitride) film? (iii) What is the mechanism by which N reduces the thermal growth rate? This last question, in particular, has been the subject of many debates in the literature in the context of the thermal growth of silicon oxynitride films in N_2O and NO .^{6–11} The limiting step was attributed either to neutralization of the reaction sites at the interface by N atoms,¹² or to the action of N as a diffusion barrier to the oxidant species, namely, O_2 .¹³

In order to clarify these aspects, we performed isotopic tracing of N, O, and Si during the thermal oxidation of the system described at the beginning of the previous paragraph. The use of narrow nuclear resonance profiling allowed highly sensitive and selective, as well as highly depth-resolved profiling of these species. Si(100) wafers were cleaned in a 4% HF solution in ethanol (30 s) and rinsed in

ethanol (30 s) in order to minimize the presence of native oxide, and immediately introduced into the ion implantation chamber, which was then pumped down to 10^{-8} mbar. $^{15}\text{N}^+$ ions were extracted from the ion source at an energy of 30 keV and mass analyzed by a 90° magnet. The samples were polarized at +30 keV, so reducing to zero the effective ion energy on target. A battery was then used to polarize the target at –20 V, in order to slightly focus the beam. The implantation fluences were between 1 and $10 \times 10^{14} \text{ cm}^{-2}$, and the corresponding retained doses were given in Ref. 1. Some of the samples had an ultrathin layer (approximately 3 nm) of ^{29}Si epitaxially deposited on the surface of the Si(100) wafers prior to ^{15}N implantation, to allow for isotopic tracing of Si. This epitaxial deposition of ^{29}Si was also accomplished by very low-energy (20 eV) implantation: the implanted fluence was $1.2 \times 10^{16} \text{ }^{29}\text{Si cm}^{-2}$, and the wafers were kept at 600 °C during implantation. After implantation, the wafers were submitted to a further annealing at 750 °C for 30 min, under ultra-high-vacuum conditions, in order to epitaxially recrystallize the deposited ^{29}Si layer.¹⁴ The oxidations were performed in a Joule-effect heated furnace under static pressures (50 mbar) of either electronic grade pure oxygen ($^{16}\text{O}_2$), or 97% ^{18}O -enriched oxygen ($^{18}\text{O}_2$). The ^{15}N , ^{18}O , and ^{29}Si depth distributions were obtained using the narrow and isolated resonances in the cross-section curves of the nuclear reactions $^{15}\text{N}(p, \alpha \gamma)^{12}\text{C}$ at 429 keV ($\Gamma_R = 120$ eV), $^{18}\text{O}(p, \alpha)^{15}\text{N}$ at 151 keV ($\Gamma_R = 100$ eV), and $^{29}\text{Si}(p, \gamma)^{30}\text{P}$ at 414 keV ($\Gamma_R = 100$ eV).^{14,15} A tilted sample geometry ($\Psi = 65^\circ$) was used to increase the depth resolution to about 0.7 nm near the film surface. The measured excitation curves (i.e., α -particle or γ -ray yields versus incident proton energy) around the resonance energies (E_R) were converted into concentration depth distributions by means of the SPACES simulation program.¹⁶

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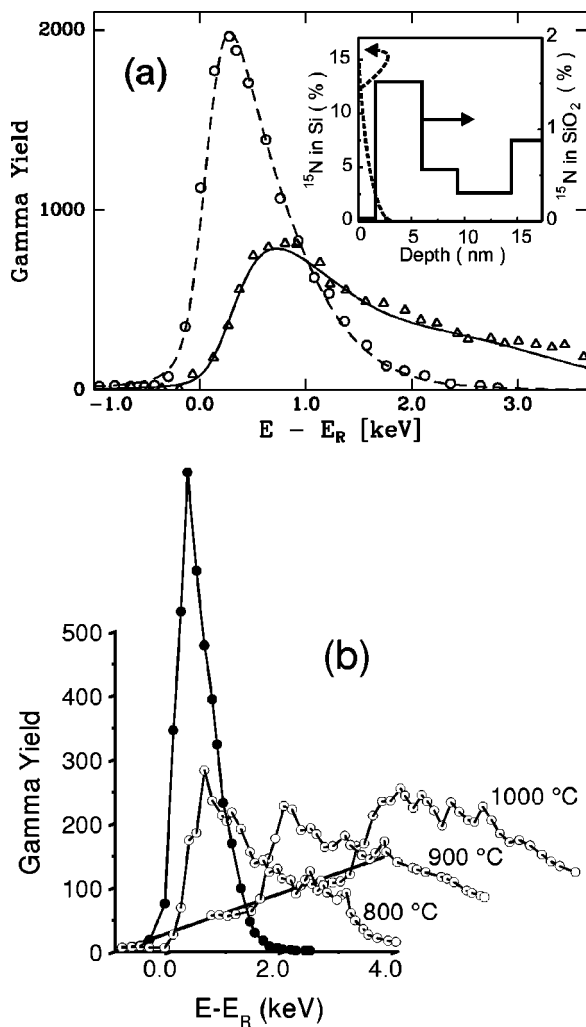


FIG. 1. (a) Excitation curves of the nuclear reaction $^{15}\text{N}(p, \alpha)^{12}\text{C}$ around the resonance at 429 keV, and the corresponding ^{15}N depth profiles (in the inset) for $2 \times 10^{14} \text{ cm}^{-2}$ ^{15}N -deposited Si(100), before (circles, dashed line) and after (triangles, solid line) oxidation in dry O_2 for 30 min at 1050 °C; (b) excitation curves around 429 keV of $0.3 \times 10^{14} \text{ cm}^{-2}$ ^{15}N -deposited samples, before (solid circles) and after (hollow circles) oxidation in dry O_2 at the indicated temperatures for 15 min.

In Fig. 1(a) are shown the excitation curves of the nuclear reaction $^{15}\text{N}(p, \alpha)^{12}\text{C}$ around 429 keV, and the corresponding ^{15}N depth profiles, before and after oxidation in dry O_2 for 30 min at 1050 °C. The ^{15}N areal density before oxidation was $2 \times 10^{14} \text{ cm}^{-2}$. The nitrogen atoms deposited on the Si(100) surface are redistributed after thermal oxidation within the grown oxide (oxynitride) film, with maxima in the near-surface and near-interface regions. This behavior is confirmed in Fig. 1(b) by the excitation curves for a sample containing, before oxidation, $0.3 \times 10^{14} \text{ cm}^{-2}$ (solid circles), and oxidized in dry O_2 at 800, 900, and 1000 °C for 15 min (hollow circles). The ^{15}N losses during oxidation are evidenced by the reduction in the areas of the corresponding excitation curves.

Sequential oxidations in $^{16}\text{O}_2$ (30 min) followed by $^{18}\text{O}_2$ (30 min), at 1000 °C were performed on samples with different doses of deposited ^{15}N , in order to investigate the incorporation of ^{18}O in the different regions of the oxide (oxynitride) film during the second oxidation step, as well as its dependence on the ^{15}N -implanted dose. The excitation curves of the $^{18}\text{O}(p, \alpha)^{15}\text{N}$ nuclear reaction around 151 keV

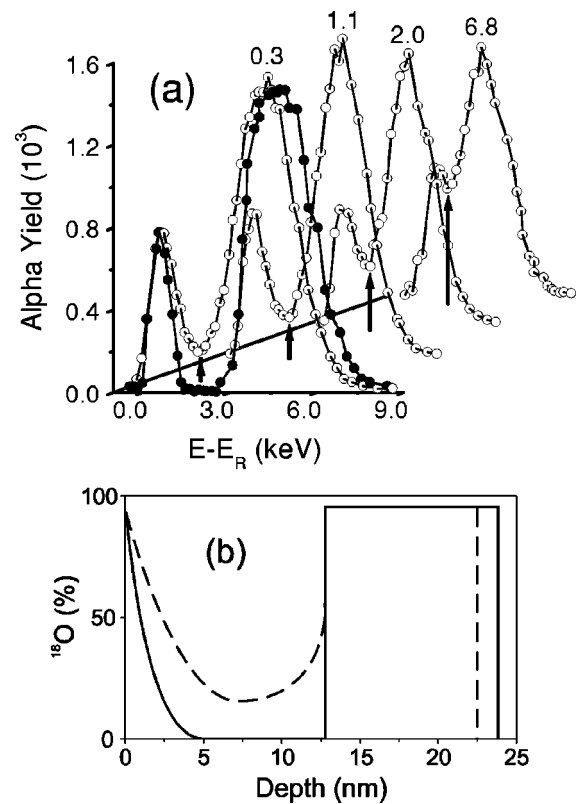


FIG. 2. (a) Excitation curves of the $^{18}\text{O}(p, \alpha)^{15}\text{N}$ nuclear reaction around the resonance at 151 keV for the unimplanted (solid circles) and ^{15}N -deposited (hollow circles) Si(100) samples, after sequential oxidations in $^{16}\text{O}_2$ (30 min) followed by $^{18}\text{O}_2$ (30 min) at 1000 °C. The retained doses of ^{15}N in each sample, before oxidation, are given in units of 10^{14} cm^{-2} . (b) ^{18}O depth profiles for the unimplanted (solid line) and $0.3 \times 10^{14} \text{ cm}^{-2}$ ^{15}N -deposited (dashed line) samples.

for the unimplanted (solid circles) and implanted (hollow circles) samples, are shown in Fig. 2(a). ^{18}O depth profiles for the unimplanted and one of the implanted ($1 \times 10^{14} \text{ cm}^{-2}$ ^{15}N retained before oxidation) samples are shown in Fig. 2(b). The unimplanted sample displays: (i) ^{18}O incorporated in the near-interface region, according to the Deal and Grove^{17,18} model whereby the thermal growth of the SiO_2 films in dry O_2 is due to the diffusion of molecular oxygen (O_2) through the growing oxide, without reacting with it, to react with Si at the SiO_2/Si interface, promoting growth; (ii) ^{18}O incorporated in the near-surface region, due to ^{16}O - ^{18}O exchange driven by defect networks at the surface of the Si^{16}O_2 film grown in the first oxidation step,¹⁸ and (iii) no ^{18}O incorporated in the bulk of the SiO_2 film. The samples with nitrogen deposited at their surfaces prior to thermal oxidation also presented ^{18}O in the near-surface and near-interface regions after oxidation. However, differently from the unimplanted sample, ^{18}O was also found incorporated in the bulk of the oxide (oxynitride) films, in concentrations that increase with the ^{15}N dose, as shown by the arrows in Fig. 2(a). This indicates that another mechanism of growth is also taking place in parallel: oxygen atoms are being fixed in the bulk of the growing oxide, either in defect networks created by the migration of nitrogen, or by reacting with the nitrogenous species present in this region. So, in the presence of even very small concentrations of nitrogen at the silicon wafer surface, the Deal and Grove assumption of O_2

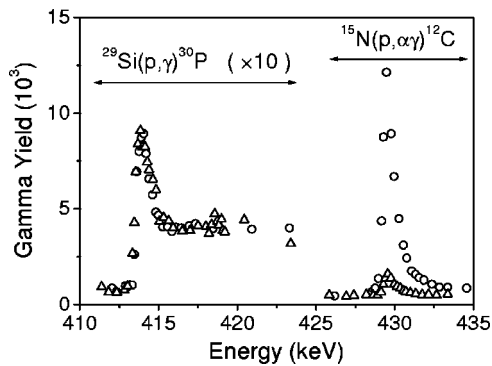


FIG. 3. Excitation curves obtained before (circles) and after (triangles) thermal oxidation at 1050 °C during 60 min. The incident proton energy was scanned between 410 and 435 keV, in order to access the resonances in the nuclear reactions $^{29}\text{Si}(p,\gamma)^{30}\text{P}$ at 414 keV and $^{15}\text{N}(p,\alpha\gamma)^{12}\text{C}$ at 429 keV.

diffusing through the growing oxide without reacting with it is no longer valid.

^{15}N was also deposited on Si(100) samples containing a 3 nm thick, epitaxial ^{29}Si -enriched layer at the surface. Samples containing 2×10^{14} ^{15}N cm^{-2} were oxidized in O_2 at 1000 °C for 60 min. Figure 3 shows the excitation curve obtained before thermal oxidation (circles) by scanning the incident proton energy between 410 and 435 keV, in order to access both resonances in the nuclear reactions $^{29}\text{Si}(p,\gamma)^{30}\text{P}$ at 414 keV and $^{15}\text{N}(p,\alpha\gamma)^{12}\text{C}$ at 429 keV. One notices that the ^{29}Si signal does not reach the background level at the higher-energy side of the excitation curve, due to the contribution of the ^{29}Si atoms in the Si substrate (the natural isotopic abundance of ^{29}Si is 4.7%). The excitation curve obtained for the same proton energy range after thermal oxidation (triangles) is also shown in Fig. 3. If Si were a mobile species during oxidation, one should expect a modification in the ^{29}Si signal in the excitation curve, the nature of this modification bearing information on the mechanism of Si migration.¹⁴ However, inspection of Fig. 3 evidences that the ^{29}Si regions of the excitation curves before and after thermal oxidation are identical, indicating that ^{29}Si is found near the surface of the grown oxide (oxynitride) after oxidation and is, therefore, immobile during the process. The ^{15}N signal shows a decrease in the amplitude, as well as a broadening, consistent with the results of Fig. 1. One should stress here that the circles refer to excitation curves for ^{29}Si and ^{15}N in Si, whereas the triangles refer to excitation curves for these isotopes in SiO_2 .

In summary, during thermal oxidation in dry O_2 the N atoms deposited on the surface of the Si(100) wafers are partly lost by desorption, and partly redistributed within the growing oxide (oxynitride) film, occupying mainly the near-surface and near-interface regions, and having a minor concentration in the bulk. The N atoms at the interface may inhibit growth by blocking reaction sites. The growth mechanism of the oxide (oxynitride) film suffers a further modification, as part of the main mobile species (i.e., oxygen) is fixed in the bulk of the growing film. So, the N atoms in this region seem to be also inhibiting growth by acting as an additional diffusion barrier to the mobile species. Finally, Si is found to be immobile during thermal oxidation, as it is known to be in the absence of N.

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