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Effects of the surface deposition of nitrogen on the thermal oxidation of silicon in O₂

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Nitrogen was deposited on the surface layers of Si(100) 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 O₂ at 1050 °C, and the areal densities and profiles of N and O were determined by nuclear reaction analysis and narrow nuclear resonance profiling, evidencing that: (i) the retained amounts of N just after ion beam deposition stayed in the range between 0.3 and $7 \times 10^{14} \text{ cm}^{-2}$; (ii) the oxide growth is influenced strongly by the presence of nitrogen, the thickness of the oxide films (which remained between 4 and 30 nm) decreased with the increase of the areal density of nitrogen; (iii) N is partially removed from the system as oxidation proceeds. These observations are discussed in terms of current models for the thermal growth of silicon oxide in the presence of N. © 1998 American Institute of Physics. [S0021-8979(98)06310-5]

Silicon oxynitride presents several advantages over the oxide when used in sub-10 nm films for gate and tunnel dielectrics. It provides improved resistance to dopant diffusion, increased reliability, and enhanced resistance to hot carrier degradation.¹⁻³ In particular, the thermal oxidation in O₂ of Si wafers previously implanted with N ions has been considered recently as a route to prepare silicon oxynitride films for gate dielectrics in ultralarge scale integrated (ULSI) metal-oxide semiconductor field effect transistor (MOSFET) devices.⁴⁻⁷ It has been known for a long time that the presence of rather small concentrations of N (1 at % and less) slows down the thermal oxide (oxynitride) growth in O₂.⁸ The effect of N implantation doses below and around the equivalent to 1 monolayer in reducing the rate of thermal growth of SiO₂ in dry O₂ has been reported previously.^{4,9} Trimaille *et al.*⁹ implanted $1 \times 10^{15} \text{ N cm}^{-2}$ into Si through SiO₂ films, and continued the thermal growth of the implanted film in O₂, concluding that N inhibits only the near oxide/silicon interface region where growth takes place. This effect was corroborated by several authors^{10,11} in the case of ultrathin (5 nm) oxynitride films thermally grown in N₂O, whereas the thermal reoxidation in O₂ of thicker oxynitride films (~10 nm), showed modifications on the near interface and near surface oxygen incorporations.¹² At the initial stages of thermal growth in N₂O¹³ (thicknesses between 0.5 and 3 nm), silicon oxynitrides were observed to be the main components of the film, whereas oxidation (i.e. formation of SiO₂) is the dominant process of growth above 3 nm. Sutherland *et al.*¹⁴ complemented this picture, demonstrating that 1 monolayer of N, initially existent at the oxynitride/Si in-

terface, remains essentially intact after the growth mode has switched to the production of SiO₂ (thicker films).

In spite of the wealth of well established empirical facts, there remains a considerable lack of knowledge on the growth mechanisms of silicon oxide films in the presence of N. The role of N in hampering the oxide growth was discussed by Dimitrijević *et al.*,¹⁵ which attributed the limiting step to the neutralization of the oxide growth sites at the interface by N atoms, while Ting *et al.*¹⁶ attributed the slowdown of the growth rate to the action of N as a diffusion barrier to the oxidant species—namely O₂. We report here on the thermal growth of silicon oxide films in O₂ on Si(100) substrates whose surfaces were intentionally contaminated with controlled amounts of N. We will investigate the influence of the surface concentration of N (in the range 1/30–1 monolayer) on the growth rate of silicon oxide films. The deposition of N at the Si(100) wafer surface was performed by ion implantation at the extremely low energy of 20 eV. In order to allow for highly sensitive and selective determination of the amounts of N and O in the films by nuclear reaction analysis (NRA), less abundant isotopes (¹⁵N and ¹⁸O) were used: ¹⁵N introduced by very low energy ion implantation, and ¹⁸O by performing thermal oxidations in ¹⁸O₂.

Si(100) wafers were cleaned in a 4% HF solution in ethanol (30 s) and rinsed in ethanol (30 s) just before being introduced in the vacuum of the ion implantation chamber, in order to minimize the presence of the native oxide. ¹⁵N⁺ 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, thus reducing the effective ion energy on target to zero. A battery was then used to polarize the target at -20 V, in order to slightly focus the beam. The

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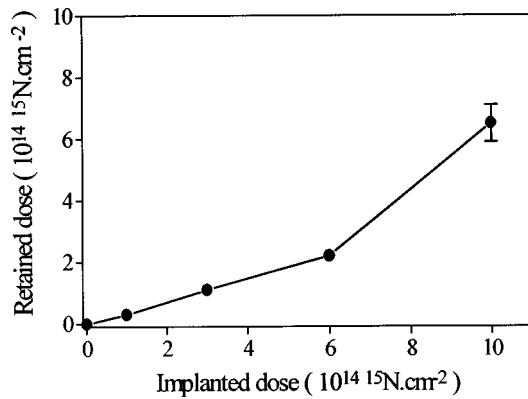


FIG. 1. The retained doses of ^{15}N on the Si(100) wafers as a function of the implanted doses.

oxidations were performed in a Joule effect heated furnace under static pressures (50 mbar) of 97% ^{18}O -enriched oxygen ($^{18}\text{O}_2$), at 1050 °C. The areal densities of ^{15}N and ^{18}O in the samples were determined with an accuracy of $\pm 5\%$, and a sensitivity to ^{15}N and ^{18}O of 10^{12} atoms cm^{-2} using, respectively, the cross section plateaus of the nuclear reactions: $^{15}\text{N}(p, \alpha \gamma) ^{12}\text{C}$ at 1000 keV and $^{18}\text{O}(p, \alpha) ^{15}\text{N}$ at 730 keV, and convenient standards.¹⁷ An estimation of the film thicknesses can be obtained using the equivalent relationship: 10^{15} O atoms $\text{cm}^{-2} \leftrightarrow 0.226$ nm of SiO_2 . The ^{15}N and ^{18}O depth distributions were obtained using the narrow and isolated resonances in the cross sections of the nuclear reactions $^{15}\text{N}(p, \alpha \gamma) ^{12}\text{C}$ at 429 keV, and $^{18}\text{O}(p, \alpha) ^{15}\text{N}$ at 151 keV.¹⁸ A tilted sample geometry ($\Psi = 65^\circ$) was used to increase the depth resolution to less than 1 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 can be converted into concentration depth distributions by means of the SPACES simulation program.¹⁹

The retained doses of ^{15}N on the Si(100) wafers, as a function of the implanted doses, are given in Fig. 1. Figure 2 shows the excitation curves of the $^{15}\text{N}(p, \alpha \gamma) ^{12}\text{C}$ nuclear reaction around the resonance at 429 keV for two different as-implanted samples. In the insets are shown the ^{15}N profiles assumed to simulate the excitation curves: erfc-like with a width of 0.7 nm, which is approximately the depth resolution of the technique near the surface and thus the minimum physically significant value. The difference in the amounts of incorporated nitrogen is evidenced by the different maximal ^{15}N concentrations in the insets [50% in Fig. 2(a) versus 15% in Fig. 2(b)].

The isotherms of ^{18}O incorporation during thermal oxidation in $^{18}\text{O}_2$ of Si(100) wafers containing different initial areal densities of ^{15}N at their surfaces, are shown in Fig. 3 (left vertical axis). The isotherms of ^{15}N evolution, as oxidation proceeds, are also shown in Fig. 3 (right vertical axis). The amount of incorporated ^{18}O for each oxidation time was seen to decrease with the increase of the ^{15}N dose, consistent with the results reported in Ref. 4. Figure 3 also shows that nitrogen is progressively lost as the oxidation time increases.

The excitation curves of the $^{18}\text{O}(p, \alpha) ^{15}\text{N}$ nuclear reaction, around the resonance at 151 keV for samples with dif-

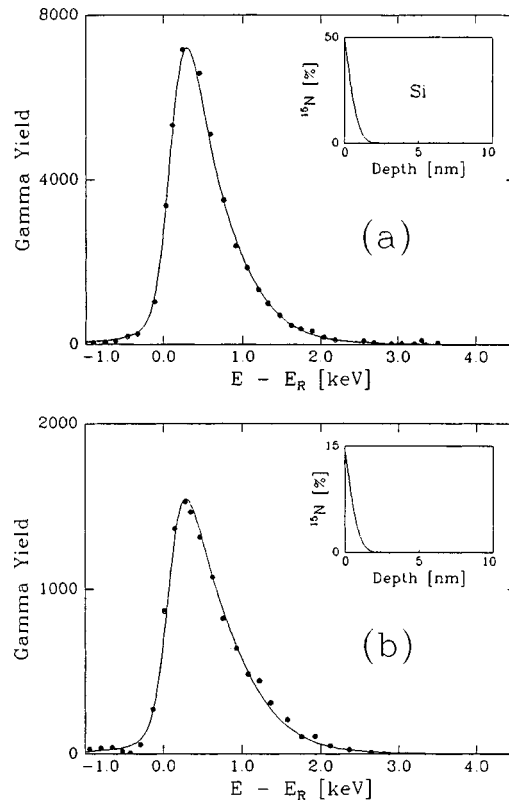


FIG. 2. Excitation curves of the $^{15}\text{N}(p, \alpha \gamma) ^{12}\text{C}$ nuclear reaction around the resonance at 429 keV for two different as-implanted samples [retained doses: (a) 6.5×10^{14} N cm^{-2} , and (b) 1.2×10^{14} N cm^{-2}]. In the insets are shown the ^{15}N profiles assumed to simulate the excitation curves.

ferent initial areal densities of ^{15}N and oxidized in $^{18}\text{O}_2$ for 15 min, are shown shown in Fig. 4(a). The arrows indicate the positions in energy ($E - E_R$) corresponding to ^{18}O atoms at the films surfaces (dashed arrow), and to ^{18}O atoms at each one of the oxide (oxynitride)/Si interfaces. The decrease of the film thickness with the increase of the ^{15}N dose is again evident. The simulation of one of these excitation curves (initial areal density of ^{15}N of 1.1×10^{14} cm^{-2}) is shown in Fig. 4(b), with the correspondent ^{18}O profile given in the inset.

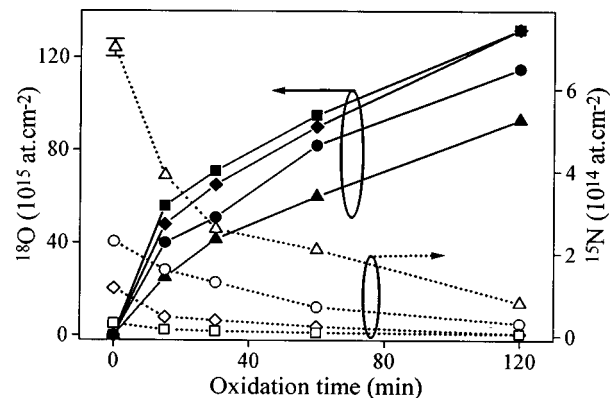


FIG. 3. The isotherms of ^{18}O incorporation during thermal oxidation in $^{18}\text{O}_2$ of Si(100) wafers containing different initial areal densities of ^{15}N at their surfaces, and the isotherms of ^{15}N evolution as oxidation proceeds.

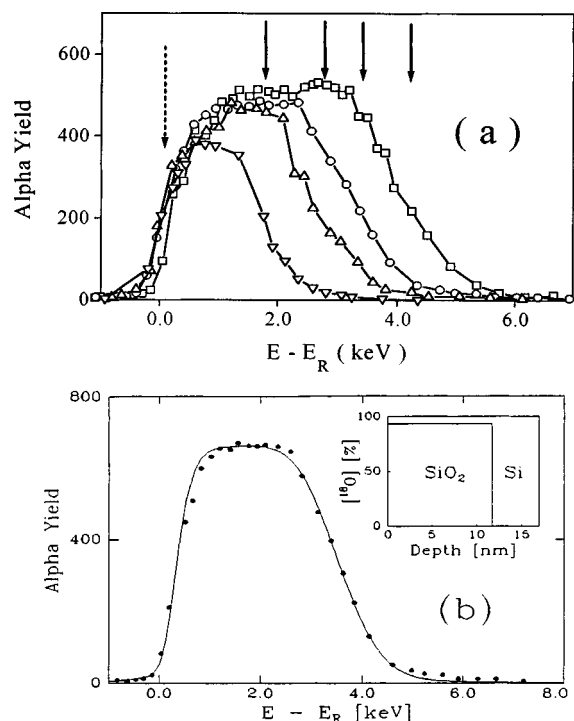


FIG. 4. (a) Excitation curves of the $^{18}\text{O}(p,\alpha)^{15}\text{N}$ nuclear reaction around the resonance at 151 keV for samples with different initial areal densities of ^{15}N and oxidized in $^{18}\text{O}_2$ for 15 min. The arrows indicate the positions in energy corresponding to ^{18}O atoms at the films surfaces (dashed arrow), and to ^{18}O atoms at each one of the oxide(oxynitride)/Si interfaces. (b) The simulation of the excitation curve for the sample corresponding to an initial areal density of ^{15}N of $1.1 \times 10^{14} \text{ cm}^{-2}$, with the correspondent ^{18}O profile given in the inset.

In summary, the thermal growth of SiO_2 films on $\text{Si}(100)$ in dry O_2 depends on the areal density of N deposited on the surface of the Si wafers prior to oxidation: the oxide thickness decreases with the increase of areal density of the deposited N. This effect remains valid for all the initial N concentrations, which go down to around 1/30 of a monolayer, as well as for all oxidation times, and consequently for all SiO_2 film thicknesses used in the present work, which varied from 4 to more than 30 nm. In contrast to a previous article,¹⁴ the N initially existent at the interface did not remain intact during oxide growth, since it was progressively lost. The loss of N during thermal reoxidation in O_2 of silicon oxynitride films was observed previously,^{12,13,15,18} which had been attributed to diffusion-reaction processes occurring in the bulk of the oxide (oxynitride) films. Preliminary results obtained in our laboratory indicate that part of the N atoms lost from the surface (interface) are found redistributed within the grown oxide (oxynitride) film, confirming the hypothesis of a diffusion-reaction driven process. However, a detailed description of the mechanisms of atomic transport responsible for the redistribution of N during oxidation has to take into account atomic exchange processes^{12,17,18} (like O–N and Si–N exchanges), and their contribution to the

modification of the nature and concentration of defects. In order to obtain this detailed description, an isotopic tracing study, not only of N but also of O and Si, is presently in progress and should be the subject of a forthcoming publication.

The two possible mechanisms described above by which N hampers the oxide growth can be equally active on the grounds of the present results: neutralization of the oxide growth sites at the interface by the N atoms that remain in the near interface region, or diffusion barrier to the oxidant species by that part of the N atoms that are redistributed in the bulk of the growing oxide (oxynitride) film. The details on the redistribution of N, as well as its effect on the mechanisms of thermal growth of the oxide film, are also being accessed by isotopic tracing of N, O, and Si and will be included in the forthcoming publication announced at the end of the previous paragraph.

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