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Incorporation of oxygen and nitrogen in ultrathin films of SiO$_2$ annealed in NO

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The areal densities of oxygen and nitrogen incorporated into ultrathin films of silicon dioxide during rapid thermal processing in nitric oxide, as well as the regions where these incorporations took place, were determined by combining nuclear reaction analysis and narrow nuclear resonance depth profiling with isotopic enrichment of the processing gas. Oxygen is seen to incorporate in the near-surface and near-interface regions of the oxynitride films, whereas nitrogen is incorporated only in the near-interface regions. The growth of the oxynitride film is very moderate as compared to that of a SiO$_2$ film in dry O$_2$. The thermal oxynitridation of ultrathin SiO$_2$ films takes place by two mechanisms in parallel: the major part of the NO molecules, which react with the silica, decompose in the near-surface region, the O atoms being exchanged for O atoms preexistent in this region of the SiO$_2$ films; a minor portion of the NO molecules diffuse through the silica film in interstitial sites, without reacting with it, to react at the oxynitride/Si interface. © *1998 American Institute of Physics.* [S0003-6951(98)01823-3]

Recent publications[1–4] reported on complementary metal–oxide–semiconductor (CMOS)-based devices in which the gate dielectric was made of ultrathin (between 2.5 and 8 nm) silicon oxynitride films, produced by either direct thermal growth in NO, or by thermal oxynitridation of an ultrathin SiO$_2$ film in NO. These oxynitride films exhibit several properties superior to thermal O$_2$ oxides, the most important ones being supression of boron penetration, enhanced reliability, and reduced hot-electron induced degradation. The direct thermal growth in NO is self-limited[5–7] to a maximum thickness of about 2.5 nm for temperatures below 1100 °C, most probably due to the high concentration of nitrogen in the near-interface region. For temperatures at and above 1100 °C, the oxynitride films were observed to grow at a much higher rate, up to a thickness of 80 nm.[5] On the other hand, the production of oxynitride films by thermal nitridation of SiO$_2$ films in NO provides a flexible method of tailoring continuously the film thickness in the range 2–20 nm, as well as the nitrogen concentration in the range 0.5–5.0%.[8,9] NO is believed[10–13] to be the species responsible for nitrogen incorporation into the SiO$_2$ films. In this work we report on the kinetics of oxygen and nitrogen incorporation, as well as on the depth profiles of the incorporated O and N atoms, during thermal annealing of SiO$_2$ films in NO.

The SiO$_2$ films were grown in a rapid thermal processing (RTP) furnace, at 1050 °C, in dry, ultrapure ^{16}O$_2$ (Si^{16}O$_2$ films). The thermal oxynitridations were performed in NO gas isotopically enriched (99.9%) in ^{18}O and ^{15}N (^{15}N^{18}O). The kinetics of O and N incorporation were established by determining the areal densities of ^{16}O, ^{18}O, and ^{15}N in the

samples using, respectively, the cross-sectional plateaus of the nuclear reactions: ^{16}O$(d,p_0)^{17}$O at 810 keV, ^{18}O$(p,\alpha_0)^{15}$N at 730 keV, and ^{15}N$(p,\alpha\gamma)^{12}$C at 1000 keV, and convenient standards.[14] The areal densities can be converted to film thickness based on the approximate equivalent
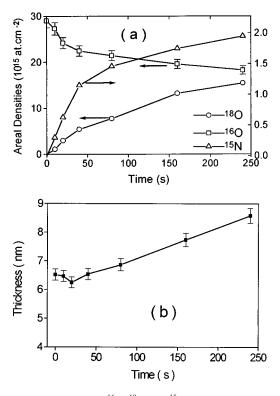

FIG. 1. (a) Areal densities of ^{16}O, ^{18}O, and ^{15}N as a function of processing time, for a 6.5 nm thick Si^{16}O$_2$ film, oxynitrided in a RTP furnace at 1050 °C, in a static pressure of 20 mbar of ^{15}N^{18}O; (b) oxynitride thickness as a function of the processing time in ^{15}N^{18}O.
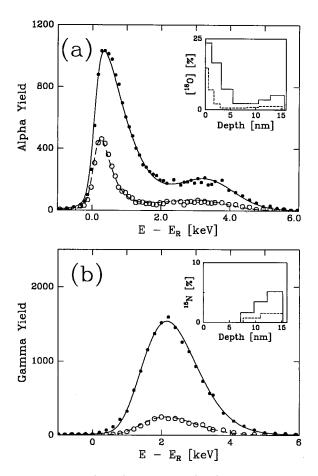
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FIG. 2. Experimental (circles) and simulated (lines) excitation curves of the nuclear reactions (a) $^{18}O(p,\alpha)^{15}N$ and (b) $^{15}N(p,\alpha\gamma)^{12}C$ around the resonance energies, and the corresponding profiles of ^{18}O and ^{15}N in the insets, for a 14 nm thick Si$^{16}O_2$ film, oxynitrided in a RTP furnace at 1050 °C, in a static pressure of 20 mbar of $^{15}N^{18}O$ during 20 s (empty circles, dashed lines) and 80 s (solid circles, solid lines).
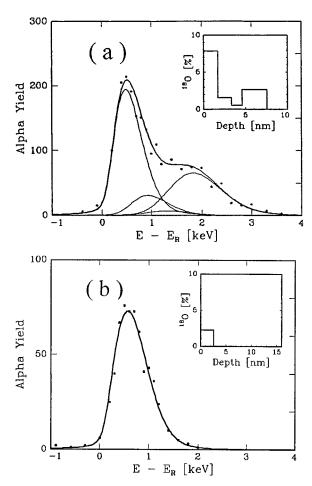

FIG. 3. Experimental (dots) and simulated (components and their sum— lines) excitation curves and the corresponding ^{18}O profiles in the insets for a 6.5 nm Si$^{16}O_2$ film oxynitrided for 10 s: (a) as-prepared and (b) after a 10 s etching in dilute HF solution.

relationship 10^{15} (O+N) atoms/cm^2=0.226 nm of oxynitride film.[14] The ^{18}O and ^{15}N depth profiles were obtained by nuclear resonance profiling (NRP), using the narrow and isolated resonances in the cross sections of the nuclear reactions $^{18}O(p,\alpha)^{15}N$ at 151 keV, and $^{15}N(p,\alpha\gamma)^{12}C$ at 429 keV, respectively, and a tilted sample geometry ($\Psi = 65°$) The measured excitation curves (i.e., α or γ yields versus incident proton energy) around the resonance energy E_R can be converted into concentration versus depth profiles by means of the SPACES simulation program.[15] This profiling method assures a depth resolution of approximately 1 nm near the film surface, and a precision in the determination of the ^{18}O and ^{15}N concentrations of approximately 5%.[16]

Figure 1(a) shows the areal densities of ^{16}O, ^{18}O, and ^{15}N in a 6.5 nm thick Si$^{16}O_2$ film, oxynitrided in a RTP furnace for different times, at 1050 °C, in a static pressure of 20 mbar of $^{15}N^{18}O$. Figure 1(b) shows the oxynitride thickness, here determined from the sum of the areal densities ($^{16}O+^{18}O+^{15}N$), as a function of processing time in $^{15}N^{18}O$. For RTP times above 40 s, there is a moderate increase of the thickness (approximately 1% of the growth rate of a thermal oxide at the same temperature and pressure). Figure 2 shows the excitation curves of the $^{18}O(p,\alpha)^{15}N$ and $^{15}N(p,\alpha\gamma)^{12}C$ nuclear reactions around the above mentioned resonance energies, and the corresponding depth distributions of ^{18}O and ^{15}N for a thicker Si$^{16}O_2$ film (14 nm), oxynitrided in a RTP

furnace at 1050 °C, in a static pressure of 20 mbar of $^{15}N^{18}O$ during 20 and 80 s. The profiles in Fig. 2 show that: (i) ^{18}O is mainly incorporated in the near-surface and near-interface regions of the Si$^{16}O_2$ films; (ii) ^{15}N is only incorporated in the near-interface region of the Si$^{16}O_2$ films; (iii) the areal densities of ^{18}O and ^{15}N incorporated in the near-interface regions are roughly the same, both having an approximately linear dependence on the RTP time in NO; (iv) there is a negligible growth of the oxynitride film thickness for these processing times; and (v) most of the ^{18}O atoms (approximately 70%) are fixed in the near-surface region.

The excitation curve and the corresponding ^{18}O profile for the 6.5 nm Si$^{16}O_2$ film oxynitrided for 10 s is shown in Fig. 3(a). The ^{18}O distribution follows essentially the same trends depicted for the thicker Si$^{16}O_2$ film of Fig. 2. Furthermore, the ^{15}N profiles (not shown here) are exactly like those in Fig. 2, leading to a ^{15}N incorporation only at the near-interface layers. These samples were etched in a dilute HF solution for 10 s, measuring the areal densities and excitation curves before and after etching. The excitation curve for the sample of Fig. 3(a), after HF etching is shown in Fig. 3(b). This procedure allowed to obtain the results shown in Table I for the samples composing the kinetics of Fig 1. One can see that as the HF etching removed between 40 and 60% of the oxynitride films, the areal densities of ^{18}O decreased by 70 to 80%, whereas the ^{15}N was roughly unchanged. So,

TABLE I. Areal densities of ^{16}O, ^{18}O, and ^{15}N for 6.5 nm thick Si $^{16}O_2$ films thermally oxynitrided by RTP in ^{15}N ^{18}O: (a) as-prepared and (b) after a 10 s etching in a diluted HF solution.

RTP Time (s)	^{16}O (10^{15} cm^{-2})	^{18}O (10^{15} cm^{-2})	^{15}N (10^{15} cm^{-2})	$^{18}O/^{16}O+^{15}N$
(a)				
10	28.7	1.1	0.4	0.04
20	24.2	2.9	0.6	0.12
40	22.4	5.4	1.1	0.23
80	21.4	8.5	1.5	0.37
160	19.6	13.2	1.7	0.62
(b)				
10	11.7	0.3	0.3	0.02
20	16.2	0.5	0.6	0.03
40	11.8	0.7	0.9	0.06
80	16.1	1.6	1.6	0.09
160	17.0	4.1	1.7	0.22

statements (ii) and (v) in the precedent paragraph remain valid for these thinner oxynitride samples.

The observed facts on the incorporation of O and N into the SiO$_2$ films can be described by two atomic transport mechanisms occurring in parallel, as in the case of the dry oxidation of silica:[17] **mechanism (i)** NO (or products of decomposition of NO) diffuses through the silica network in interstitial sites, without reacting with it, and the reaction takes place at the oxynitride/Si interface to fix N and O, eventually promoting growth; **mechanism (ii)** the fixation of ^{18}O in the near-surface region occurs by a mechanism related to a step-by-step motion of network oxygen atoms, by a simple diffusion process, induced by the presence of network defects (for example a peroxyl bridge) since no N is found in this region. In this case N is released through a non reacting gas (in the sense of nitrogen fixation) like N$_2$ or NO$_2$. There is no evidence that N is fixed in the film and then removed, as it is the case in N$_2$O anneal of oxides.[9–12,18] Mechanism (ii) leads to an exchange of oxygen atoms between the oxide network and the gas phase, explaining the loss of ^{16}O atoms observed after NO anneal. Since the majority of the ^{18}O atoms are fixed in the near-surface region, mechanism (ii) is the dominant one for ^{18}O fixation. This mechanism has been demonstrated[17,19] both theoretically and experimentally in the case of dry oxidation of Si, and in Ref. 20 we adapted the theory to the present case, making a comparison between the reaction rates and diffusion coefficients of ^{18}O in the near-surface region for the thermal annealing of Si$^{16}O_2$ films in $^{18}O_2$ (Ref. 21) and in $^{15}N^{18}O$.

In summary, the thermal oxynitridation of ultrathin SiO$_2$ films in NO by rapid thermal processing takes place by two mechanisms in parallel: the major part of the NO molecules decompose in the near-surface region, the O atoms being exchanged for O atoms preexistent in this region of the SiO$_2$ films, as a result of the migration of oxygen network atoms owing to the diffusion of network defects. The N atoms are released in the form of a nonreacting gas. Concomitantly, a minor portion of the NO molecules diffuse in interstitial sites through the silica film without reacting with it, to react at the oxynitride/Si interface. The very small growth of the film thickness which was observed takes place at the oxynitride/Si interface.

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