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

I. J. R. Baumvol, J.-J. Ganem, L. G. Gosset, I. Trimaille, and S. Rigo

Citation: Applied Physics Letters 72, 2999 (1998); doi: 10.1063/1.121520
View online: http://dx.doi.org/10.1063/1.121520
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/72/23?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in
Characteristics of ultrathin SiO$_2$ films using dry rapid thermal oxidation and Pt catalyzed wet oxidation
J. Vac. Sci. Technol. A 21, 1004 (2003); 10.1116/1.1582455

Integrity of hafnium silicate/silicon dioxide ultrathin films on Si
Appl. Phys. Lett. 81, 2995 (2002); 10.1063/1.1515112

Stability of zirconium silicate films on Si under vacuum and O$_2$ annealing

Ultrathin silicon oxynitride film formation by plasma immersion nitrogen implantation
Appl. Phys. Lett. 74, 806 (1999); 10.1063/1.123374

On the behavior of deuterium in ultrathin SiO$_2$ films upon thermal annealing
Appl. Phys. Lett. 72, 450 (1998); 10.1063/1.120801
Incorporation of oxygen and nitrogen in ultrathin films of SiO₂ annealed in NO

I. J. R. Baumvol a)
Instituto de Física, UFRGS, Porto Alegre, RS, 91509-900 Brazil

J.-J. Ganem, L. G. Gosset, I. Trimaille, and S. Rigo
Groupe de Physique des Solides, UMR 77-88—CNRS, Universités Paris 6 et Paris 7, 2, Place Jussieu, 75251 Paris, Cedex 05, France

(Received 24 November 1997; accepted for publication 3 April 1998)

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 SiO₂ film in dry O₂. The thermal oxynitridation of ultrathin SiO₂ 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 SiO₂ 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.

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 SiO₂ film in NO. These oxynitride films exhibit several properties superior to thermal O₂ oxides, the most important ones being suppression 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 SiO₂ 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 to be the species responsible for nitrogen incorporation into the SiO₂ 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 SiO₂ films in NO.

The SiO₂ films were grown in a rapid thermal processing (RTP) furnace, at 1050 °C, in dry, ultrapure ₁₆O₂ (Si₁₆O₂ films). The thermal oxynitridations were performed in NO gas isotopically enriched (99.9%) in ₁₈O and ₁₅N (₁₅N₁₈O). The kinetics of O and N incorporation were established by determining the areal densities of ₁₆O, ₁₈O, and ₁₅N in the samples using, respectively, the cross-sectional plateaus of the nuclear reactions: ₁₆O(d,p)₁₇O at 810 keV, ₁₈O(p,α)₁₅N at 730 keV, and ₁₅N(p,αγ)₁₂C at 1000 keV, and convenient standards 1₄. The areal densities can be converted to film thickness based on the approximate equivalent

---

a) Electronic mail: israel@if.ufrgs.br

FIG. 1. (a) Areal densities of ₁₆O, ₁₈O, and ₁₅N as a function of processing time, for a 6.5 nm thick Si₁₆O₂ film, oxynitrided in a RTP furnace at 1050 °C, in a static pressure of 20 mbar of ₁₅N₁₈O; (b) oxynitride thickness as a function of the processing time in ₁₅N₁₈O.
ergies, and the corresponding depth distributions of $^{18}$O and $^{15}$N in nuclear reactions around the above mentioned 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).

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 oxide at the same temperature and pressure.

For RTP times above 40 s, there is a moderate increase of the oxide at the same temperature and pressure. The excitation curve and the corresponding $^{18}$O profile in Fig. 2 shows 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 in 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,
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.


---

**TABLE I.** Areal densities of $^{18}$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.

<table>
<thead>
<tr>
<th>RTP Time (s)</th>
<th>$^{18}$O ($\times 10^{15}$ cm$^{-2}$)</th>
<th>$^{18}$O ($\times 10^{15}$ cm$^{-2}$)</th>
<th>$^{15}$N ($\times 10^{15}$ cm$^{-2}$)</th>
<th>$^{18}$O$^{18}$O$^{15}$N</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.1</td>
<td>1.0</td>
<td>0.4</td>
<td>0.04</td>
</tr>
<tr>
<td>20</td>
<td>2.8</td>
<td>2.9</td>
<td>0.8</td>
<td>0.20</td>
</tr>
<tr>
<td>40</td>
<td>5.4</td>
<td>5.4</td>
<td>1.7</td>
<td>0.23</td>
</tr>
<tr>
<td>80</td>
<td>8.5</td>
<td>8.5</td>
<td>1.7</td>
<td>0.37</td>
</tr>
<tr>
<td>160</td>
<td>13.2</td>
<td>13.2</td>
<td>1.7</td>
<td>0.62</td>
</tr>
<tr>
<td>(b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.02</td>
</tr>
<tr>
<td>20</td>
<td>0.8</td>
<td>0.8</td>
<td>0.6</td>
<td>0.06</td>
</tr>
<tr>
<td>40</td>
<td>1.6</td>
<td>1.6</td>
<td>0.9</td>
<td>0.06</td>
</tr>
<tr>
<td>80</td>
<td>1.6</td>
<td>1.6</td>
<td>1.6</td>
<td>0.09</td>
</tr>
<tr>
<td>160</td>
<td>4.1</td>
<td>4.1</td>
<td>1.7</td>
<td>0.22</td>
</tr>
</tbody>
</table>