Thermal stability of plasma-nitrided aluminum oxide films on Si


Citation: Applied Physics Letters 84, 97 (2004); doi: 10.1063/1.1638629
View online: http://dx.doi.org/10.1063/1.1638629
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/84/1?ver=pdfcov
Published by the AIP Publishing

Articles you may be interested in

Influence of N\textsubscript{2}O plasma treatment on microstructure and thermal stability of WN\textsubscript{x} barriers for Cu interconnection
J. Vac. Sci. Technol. B 22, 993 (2004); 10.1116/1.1715087

Rapid thermal annealing effects on the electrical behavior of plasma oxidized silicon/silicon nitride stacks gate insulators
J. Vac. Sci. Technol. B 21, 1306 (2003); 10.1116/1.1585067

Investigation of the interlayer characteristics of Ta\textsubscript{2}O\textsubscript{5} thin films deposited on bare, N\textsubscript{2}O, and NH\textsubscript{3} plasma nitridated Si substrates
J. Appl. Phys. 91, 6428 (2002); 10.1063/1.1471926

Electrical characterization of metal–oxide–semiconductor capacitors with anodic and plasma-nitrided oxides
J. Vac. Sci. Technol. A 18, 676 (2000); 10.1116/1.582250

Effects of the surface deposition of nitrogen on the thermal oxidation of silicon in O\textsubscript{2}
Thermal stability of plasma-nitried aluminum oxide films on Si

K. P. Bastos, R. P. Pezzi, L. Miotti, G. V. Soares, C. Driemeier, and J. Morais
Instituto de Fisica-UFGRS, CP 15051 Porto Alegre 91501-970-Brazil

I. J. R. Baumvol
Centro de Ciencias Exatas e Tecnologicas-UCS, Av. Francisco G. Vargas 1130, 95070-560 Caxias do Sul-Brazil

C. Hinkle and G. Lucovsky
Department of Physics, North Carolina State University, Raleigh, North Carolina 27695-8202

(Received 8 September 2003; accepted 12 November 2003)

The effect of post-deposition rapid thermal annealing in vacuum and in dry O\textsubscript{2} on the stability of remote plasma-assisted nitried aluminum oxide films on silicon is investigated. The areal densities of Al, O, N, and Si were determined by nuclear reaction analysis and their concentration versus depth distributions by narrow nuclear reaction resonance profiling, with subnanometric depth resolution. Annealing in both vacuum and O\textsubscript{2} atmospheres produced partial loss of N from the near-surface regions of the films and its transport into near-interface regions of the Si substrate. Oxygen from the gas phase was incorporated in the AlON films in exchange for O and N previously existing therein, as well as in the near-interface regions of the Si substrate, leading to oxynitridation of the substrate. Al and Si remained essentially immobile under rapid thermal processing, confirming that the presence of nitrogen improves the thermal stability characteristics of the AlON/Si structures in comparison with non-nitried Al\textsubscript{2}O\textsubscript{3}/Si. © 2004 American Institute of Physics.

The use of metal oxide and silicate films on Si as a high-

k replacement for silicon dioxide and oxynitride gate diele-

trics in advanced very large scale integration technology pre-

sents several difficulties concerning the density of interface

states, reliability, chemical and structural (crystallization)

stability in further processing steps, oxidation of the Si sub-

strate, migration of boron and metallic species into the active

semiconductor region, transport of Si into the high-

k film, and formation of voids.\textsuperscript{1–3} Recent investigations\textsuperscript{4–9} indicated

that incorporation of nitrogen into aluminum, zirconium, and hafnium oxide and silicate films, either during or after de-

position, by plasma or thermal processing, provided substantial

improvements in the direction of overcoming the above-

mentioned difficulties, in addition to lower leakage current
density. However, since N is mainly incorporated into meta-

stable configurations in these oxide and silicate films,\textsuperscript{4,8,10}

their integration into the metal-oxide-semiconductor field-

effect transistor fabrication process flow relies on the particular

characteristics of N incorporation (concentrations and profiles) and its stability in the materials during further pro-

cessing steps. Among the relevant thermal steps, there is spe-

cial interest in Si-dopants annealing which is accomplished

by rapid thermal annealing (RTA) at temperatures as high as

1000 °C or more, as well as in annealing in oxygen contain-

ing atmospheres. Indeed, structural degradation, more spe-

ifically crystallization of the amorphous high-k film, was

observed\textsuperscript{6,7} in those regions of the high-k film from where N was lost during post-deposition thermal processing. De-

gradation of the electrical properties\textsuperscript{10,11} (lower capacitance) also resulted from N loss.

We report here on atomic scale stability studies, as in-

vestigated by determining the transport and exchange of N,

O, Al, and Si atoms during RTA of 6 or 12 nm thick alumi-

num oxide (Al\textsubscript{2}O\textsubscript{3}) films deposited on Si(001) by remote

plasma-enhanced chemical vapor deposition,\textsuperscript{4,12} followed by remote plasma-assisted nitridation (RPN)\textsuperscript{13} in 15N\textsubscript{2}. These structures (AlON/Si) were submitted to the following RTA sequences: vacuum (1 × 10\textsuperscript{-7} mbar) at 600 °C for 60 s, or vacuum at 1000 °C for 10 s, or 7 mbar of 97% 18O-enriched O\textsubscript{2} (18O\textsubscript{2}) at 1000 °C for 10 s, or vacuum at 600 °C for 60 s followed by 18O\textsubscript{2} at 1000 °C for 10 s. The aim of the present study is an atomic scale observation and understanding of the possible consequences of rapid thermal processing, like O, N, and Al migration and loss from the films, as well as incorporation of O from the gas phase into the films, and Si migration from the substrate into the AlON films and eventual incorporation therein. The results will be compared with previous results obtained in non-nitried Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{3,14,15}

The areal densities of 15N, 16O, 18O, and 27Al were de-

termined by nuclear reaction analysis in plateau regions of

the cross-section curves using the 15N(p,\alpha\gamma)12C,\textsuperscript{16} 16O(d,p)17O,\textsuperscript{16} and 18O(p,\alpha)15N reactions, respectively,\textsuperscript{16} and the resonance at 992 keV in the 27Al(p,\gamma)28Si.\textsuperscript{17} The profiles of 15N, 16O, 27Al, and 29Si were determined with subnanometric depth resolutions by nuclear resonant reaction profiling using the 15N(p,\alpha\gamma)12C,\textsuperscript{18} 18O(p,\alpha)15N,\textsuperscript{27} 27Al(p,\gamma)28Si,\textsuperscript{28} and 29Si(p,\gamma)30P reactions, near the resonances at 429, 151, 404.9, and 414 keV, respectively.\textsuperscript{16,18} The excitation curves (yield versus incident proton energy) obtained by NRP provide the depth distributions of the isotopes, since as the proton beam energy is increased deeper regions in the films are sampled.\textsuperscript{16}

The areal densities given in Table I indicate that RPN leads to incorporation of 15N into the AlON/Si films, whereas RTA leads to the partial loss of 15N from these structures. 18O\textsubscript{2}-annealing produces a larger N loss as compared to
In the initially 6 nm thick AlON films, 15 N piles-up in the near interface regions of the Si vacuum at 600 °C for 60 s followed by 18 O 2 at 1000 °C, whereas for the vacuum at 600 °C for 60 s or 18 O 2 annealing an even larger N loss. The roughly constant values near-interface regions after either vacuum or 18 O 2 annealings, reveal the oxynitridation of these samples processed in the different annealing routes. One can see that the 15 N loss takes place mostly from the near surface regions of the AlON films, the loss from the bulk regions of the films being moderate whereas the near-interface 15 N concentrations change only slightly. In all annealed samples, slightly deeper 15 N profiles reveal that the near interface regions of the Si(001) substrates are nitrided. In the initially 6 nm thick AlON films, 15 N piles-up in the near-interface regions after either vacuum or 18 O 2 annealings at 1000 °C, whereas for the vacuum at 600 °C for 60 s or vacuum at 600 °C for 60 s followed by 18 O 2 at 1000 °C for 10 s there is substantially lower pile-up. 18 O is incorporated along the whole AlION films, similar to previous investigations performed in non-nitrided Al2O3/Si.14,15 This means that the same mechanisms are in force, namely, a propagating 18 O front from the surface that interacts with the AlION network. Accumulation of 18 O in near-surface regions, from where most of the 15 N losses take place, indicates that part of the 18 O atoms are incorporated in exchange for 15 N. Incorporation of 18 O in near-interface regions of the Si(001) substrate (although much smaller than in previous studies3,14) together with the above-described 15 N incorporation in these regions, reveal the oxynitridation of the substrate. The thickness of the silicon oxynitride interlayer is not in excess to 0.5 nm.

The 27 Al excitation curves and profiles are shown in Fig. 2, indicating that there is neither redistribution nor loss of aluminum in the AlION/Si structures under thermal processing. Previous results19 indicated that N incorporation would provide a diffusion barrier, since a 1 nm thick silicon oxynitride interlayer between Al2O3 films and the Si substrate partially prevented diffusion of Al into the Si substrate. In the present work the diffusion barrier is more effective owing probably to the fact that N is incorporated into the whole film. The 28 Si excitation curves for the as-prepared samples and for the samples annealed in 18 O 2 at 1000 °C for 10 s are shown in Fig. 3. The rough superposition of the excitation curves for the as-prepared samples and for the 18 O 2-annealed curves indicates that there is essentially no migration of Si from the substrate into the AlION film (within the sensitivity of the technique). Migration of Si would lead to an increase in the gamma yield toward the resonance energy. The absence of Al

### Table I

<table>
<thead>
<tr>
<th>Sample</th>
<th>6 nm</th>
<th>12 nm</th>
<th>6 nm</th>
<th>12 nm</th>
<th>6 nm</th>
<th>12 nm</th>
<th>6 nm</th>
<th>12 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared</td>
<td>2.3</td>
<td>2.7</td>
<td>0.2</td>
<td>0.4</td>
<td>37.7</td>
<td>71.2</td>
<td>49.6</td>
<td>97.1</td>
</tr>
<tr>
<td>Vacuum 600 °C, 60 s</td>
<td>2.1</td>
<td>2.2</td>
<td>-</td>
<td>-</td>
<td>37.3</td>
<td>72.0</td>
<td>48.3</td>
<td>101.3</td>
</tr>
<tr>
<td>Vacuum 1000 °C, 10 s</td>
<td>1.7</td>
<td>1.7</td>
<td>-</td>
<td>-</td>
<td>37.9</td>
<td>72.2</td>
<td>47.7</td>
<td>96.1</td>
</tr>
<tr>
<td>18 O 2 1000 °C, 10 s</td>
<td>1.5</td>
<td>1.4</td>
<td>14.5</td>
<td>15.5</td>
<td>23.7</td>
<td>57.8</td>
<td>51.3</td>
<td>102.7</td>
</tr>
<tr>
<td>Vacuum, 600 °C, 60 s + 18 O 2</td>
<td>1.2</td>
<td>1.3</td>
<td>9.5</td>
<td>10.3</td>
<td>28.1</td>
<td>61.9</td>
<td>48.6</td>
<td>99.9</td>
</tr>
</tbody>
</table>

![Figure 1](image1.png)

**FIG. 1.** Excitation curves of the 15 N(p, γ)12 C and 14 O(p, α)12 N nuclear reactions near the resonances at 429 and 151 keV, respectively, from as-deposited AlON-Si samples (solid lines) and from samples submitted to RTA (a) and (b): initial thickness of 12 nm; (c) and (d), initial thickness of 6 nm. The corresponding profiles are shown in the insets, with 15 N and 14 O concentrations in units of 1022 cm3.

![Figure 2](image2.png)

**FIG. 2.** Excitation curves of the 27 Al(p, γ)28 Si nuclear reaction near the resonance at 404.9 keV from the same samples as in Fig. 1. The corresponding profiles are shown in the insets, with 27 Al concentrations in units of 1022 cm3. The symbols are the same as in Fig. 1.
The migration of part of the N atoms across the AlON films mostly from near-surface and bulk regions of the films, and change facts observed during RTA were association of dielectrics. The main atomic transport and exchange facts observed during migration of Si from the substrate, and ii) the oxidation of (oxynitridation in the present case) the Si substrate is much smaller in AlON than in Al₂O₃ films, resulting in a thinner intermediate silicon oxynitride layer and therefore in a smaller reduction of the overall capacitance due to series association of dielectrics. The main atomic transport and exchange facts observed during RTA were (i) the loss of N, mostly from near-surface and bulk regions of the films, and the migration of part of the N atoms across the AlON films into the near-interface layers of the Si substrate, leading to nitridation of the substrate, (ii) the incorporation of oxygen from the gas phase into the whole AlION films in exchange for previously existing O and N, and (iii) the transport of O, besides of N, into the Si substrate, leading to the formation of a SiON intermediate layer. Investigations on the chemical status of N in the AlION films of the present work before and after RTA are in progress using angle-resolved x-ray photoelectron spectroscopy.