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Thermal stability of plasma-nitrided aluminum oxide films on Si

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The effect of post-deposition rapid thermal annealing in vacuum and in dry O_2 on the stability of remote plasma-assisted nitrided 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_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-nitrided Al_2O_3/Si. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1638629]

The use of metal oxide and silicate films on Si as a high-*k* replacement for silicon dioxide and oxynitride gate dielectrics in advanced very large scale integration technology presents several difficulties concerning the density of interface states, reliability, chemical and structural (crystallization) stability in further processing steps, oxidation of the Si substrate, migration of boron and metallic species into the active semiconductor region, transport of Si into the high-*k* film, and formation of voids.[1–3] Recent investigations[4–9] indicated that incorporation of nitrogen into aluminum, zirconium, and hafnium oxide and silicate films, either during or after deposition, 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 metastable configurations in these oxide and silicate films,[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 processing steps. Among the relevant thermal steps, there is special 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 containing atmospheres. Indeed, structural degradation, more specifically crystallization of the amorphous high-*k* film, was observed[6,7] in those regions of the high-*k* film from where N was lost during post-deposition thermal processing. Degradation of the electrical properties[10,11] (lower capacitance) also resulted from N loss.

We report here on atomic scale stability studies, as investigated by determining the transport and exchange of N, O, Al, and Si atoms during RTA of 6 or 12 nm thick aluminum oxide (Al_2O_3) films deposited on Si(001) by remote plasma-enhanced chemical vapor deposition,[4,12] followed by remote plasma-assisted nitridation (RPN)[13] in $^{15}N_2$. These structures (AlON/Si) were submitted to the following RTA sequences: vacuum (1×10^{-7} mbar) at 600 °C for 60 s, or vacuum at 1000 °C for 10 s, or 7 mbar of 97% ^{18}O-enriched O_2 ($^{18}O_2$) at 1000 °C for 10 s, or vacuum at 600 °C for 60 s followed by $^{18}O_2$ 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-nitrided Al_2O_3.[3,14,15]

The areal densities of ^{15}N, ^{16}O, ^{18}O, and ^{27}Al were determined by nuclear reaction analysis in plateau regions of the cross-section curves using the $^{15}N(p,\alpha\gamma)^{12}C$, $^{16}O(d,p)^{17}O$, and $^{18}O(p,\alpha)^{15}N$ reactions, respectively,[16] and the resonance at 992 keV in the $^{27}Al(p,\gamma)^{28}Si$.[17] The profiles of ^{15}N, ^{18}O, ^{27}Al, and ^{29}Si were determined with subnanometric depth resolutions by nuclear narrow resonant reaction profiling using the $^{15}N(p,\alpha\gamma)^{12}C$, $^{18}O(p,\alpha)^{15}N$, $^{27}Al(p,\gamma)^{28}Si$, and $^{29}Si(p,\gamma)^{30}P$ reactions, near the resonances at 429, 151, 404.9, and 414 keV, respectively.[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.[16]

The areal densities given in Table I indicate that RPN leads to incorporation of ^{15}N into the AlON/Si films, whereas RTA leads to the partial loss of ^{15}N from these structures. $^{18}O_2$-annealing produces a larger N loss as compared to

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TABLE I. Areal densities (in units of 10^{15} cm^{-2}) of ^{15}N, ^{18}O, ^{16}O, and ^{27}Al in the AlON films on Si(001) as determined by nuclear reaction analysis. Typical errors are 5% for ^{15}N and ^{18}O and 10% for ^{16}O and ^{27}Al.

Sample	^{15}N		^{18}O		^{16}O		^{27}Al	
	6 nm	12 nm	6 nm	12 nm	6 nm	12 nm	6 nm	12 nm
As-prepared	2.3	2.7	0.2	0.4	37.7	71.2	49.6	97.1
Vacuum 600 °C, 60 s	2.1	2.2	-	-	37.3	72.0	48.3	101.3
Vacuum 1000 °C, 10 s	1.7	1.7	-	-	37.9	72.2	47.7	96.1
$^{18}O_2$ 1000 °C, 10 s	1.5	1.4	14.5	15.5	23.7	57.8	51.3	102.7
Vacuum, 600 °C, 60 s+ $^{18}O_2$, 1000 °C, 10 s	1.2	1.3	9.5	10.3	28.1	61.9	48.6	99.9

vacuum-annealing and the (vacuum+ $^{18}O_2$)-annealing sequence an even larger N loss. The roughly constant values (within experimental errors) of the (^{18}O+ ^{16}O) areal densities indicate that ^{18}O from the gas phase is incorporated during $^{18}O_2$ or (vacuum+ $^{18}O_2$)-annealing in replacement for ^{16}O previously existing in the AlON/Si structures. A small fraction of the ^{18}O atoms may be incorporated in exchange for ^{15}N atoms as discussed below. Finally, Table I shows that the ^{27}Al areal densities remain constant within experimental errors for all annealing routes.

Figure 1 shows the ^{15}N and ^{18}O excitation curves and profiles for the as-deposited and nitrided samples and for 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 AlON films, similar to previous investigations performed in non-nitrided Al_2O_3/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 AlON 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 studies[3,14]) 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 AlON/Si structures under thermal processing. Previous results[19] indicated that N incorporation would provide a diffusion barrier, since a 1 nm thick silicon oxynitride interlayer between Al_2O_3 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 ^{29}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 and for the $^{18}O_2$-annealed curves indicates that there is essentially no migration of Si from the substrate into the AlON 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

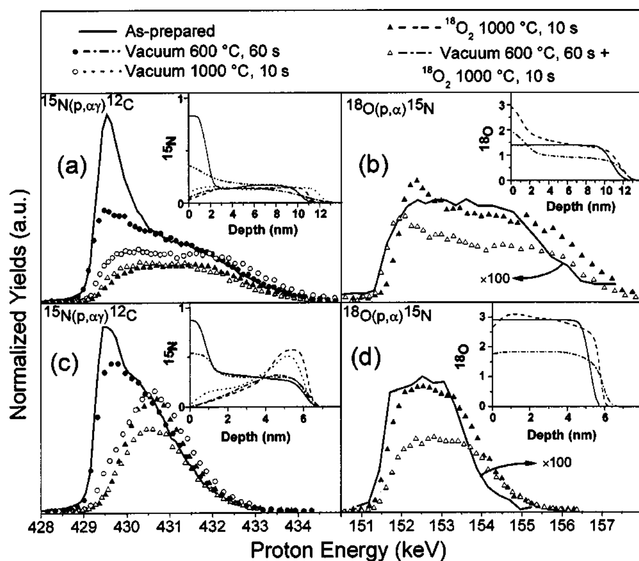

FIG. 1. Excitation curves of the $^{15}N(p,\alpha\gamma)^{12}C$ and $^{18}O(p,\alpha)^{15}N$ nuclear reactions near the resonances at 429 and 151 keV, respectively, from as-deposited $AlO^{15}N$ samples (solid lines) and from samples submitted to RTA (a) and (b): initial thickness of 12 nm; (c) and (d), initial thickness of 6 nm. The corresponding profiles are shown in the insets, with ^{15}N and ^{18}O concentrations in units of 10^{22} cm^{-3}.

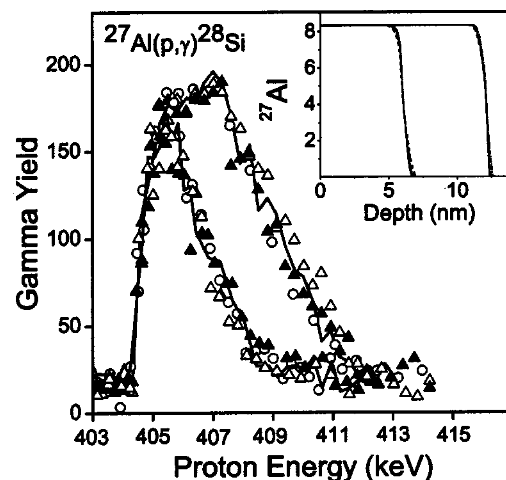

FIG. 2. Excitation curves of the $^{27}Al(p,\gamma)^{28}Si$ nuclear reaction near the resonance at 404.9 keV from the same samples as in Fig. 1. The corresponding profiles are shown in the insets, with ^{27}Al concentrations in units of 10^{22} cm^{-3}. The symbols are the same as in Fig. 1.

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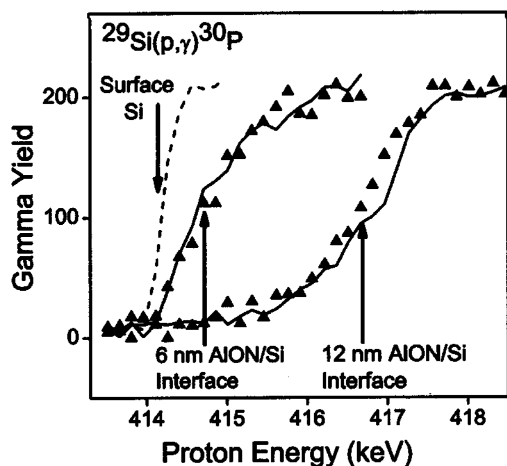

FIG. 3. Excitation curves of the $^{29}Si(p,\gamma)^{30}P$ nuclear reaction near the resonance at 414 keV. Solid lines: as-deposited and plasma-nitrided 6 and 12 nm AlON films on Si; solid triangles: RTA in $^{18}O_2$ at 1000 °C for 10 s. An excitation curve from a HF-cleaned Si wafer is also shown (dashed line). The arrows indicate the energy positions of ^{29}Si at the Si surface and at the AlON/Si interfaces.

and Si transport during annealing here observed is in strong contrast with previous observations in non-nitrided Al_2O_3 films on Si.[14,20]

In summary, remote plasma-assisted nitridation of 6 and 12 nm aluminum oxide films deposited on Si(001) led to heavy nitridation of the near-surface regions of the films and rather light nitridation of the bulk and near-interface regions. The incorporation of nitrogen has rendered the AlON films far more stable against thermal processing, either in vacuum or in O_2 atmospheres, than the non-nitride Al_2O_3 films studied previously, justifying the reported improvements on reliability and electrical characteristics. The most important features of the improved stability were (i) there is no loss of Al from the films, (ii) there is also no change of composition (and consequently of dielectric constant) of the films owing to migration of Si from the substrate, and (iii) the oxidation (oxynitridation in the present case) of the Si substrate is much smaller in AlON than in Al_2O_3 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 AlON 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 AlON films of the present work before and after RTA are in progress using angle-resolved x-ray photoelectron spectroscopy.

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