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Nitrogen transport during rapid thermal growth of silicon oxynitride films in N₂O

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We investigated the transport of nitrogenous species during rapid thermal growth of silicon oxynitride films on Si in N₂O, using N isotopic tracing and high resolution depth profiling techniques. The results indicate that the diffusion of nitrogenous species (most probably NO) through the growing oxynitride film to react with Si at the oxynitride/Si interface, induces the incorporation of N near this interface. This mechanism acts in parallel with a site-to-site jump mechanism (interstitialcy or vacancy) of diffusion and chemical reaction of nitrogenous species in the volume of the growing oxynitride film. The characteristic N accumulation only near the interface obtained by rapid thermal processing growth in N₂O is due to the removal of N from the near surface region of the films, here attributed to atomic exchanges O \leftrightarrow N taking place during growth. Furthermore, N \leftrightarrow N exchange was also observed. © 1996 American Institute of Physics. [S0003-6951(96)00642-0]

As metal-oxide-semiconductor (MOS) devices are scaled down to the deep submicron, a gate dielectric more reliable than SiO₂ is required. Recently, there has been interest in using nitrous oxide (N₂O) to grow thin (<10 nm) dielectric films on Si by rapid thermal processing (RTP).¹⁻⁵ The thermal growth of the oxynitride films seems to be self-limited to thicknesses between 4 and 12 nm, depending on the RTP temperature, whereas the N concentration in the films grows continuously with the RTP time.^{6,7} In the oxynitride films grown by RTP, N is located near the oxynitride/Si interface, being absent from the surface and from the bulk until a certain depth.^{2,7,8} Carr *et al.*⁸ attributed to O₂ the leading role in the growth of the oxynitride films, by means of the oxidation of Si. The reaction of NO with Si was thought to be the main cause of nitrogen incorporation into the oxynitride films. The peak N concentration in the films depends linearly on the NO concentration in the gas phase.⁹⁻¹¹ The removal of N from the near surface region of the oxynitride film grown by RTP in N₂O was demonstrated to be due to the action of O, which is produced in the vicinity of the Si wafer.⁸

Aiming to investigate the atomic transport processes taking place, we report here on the first studies of isotopic tracing of N during thermal growth of oxynitride films in N₂O using a RTP furnace. All the treatments were performed at 1050 °C, under a N₂O pressure of 30 mbar (i.e., 3 kPa). The two gases used for film growth were pure N₂O containing N and O isotopes in their natural abundances (¹⁴N₂O), and 97% ¹⁵N-enriched N₂O (¹⁵N₂O). The total amounts of the different isotopes incorporated in the oxynitride films were measured by nuclear reaction analysis (NRA).¹² The thickness of the oxynitride films can be determined based on the equivalent

thickness relationship $10^{15}(\text{O}+\text{N}) \text{ atoms/cm}^2 = 0.226 \text{ nm}$ of oxynitride film.¹² The ¹⁵N depth profiles were obtained by narrow nuclear resonance profiling (NRP), using the strong $\Gamma_R = 120 \text{ eV}$ wide isolated resonance in the cross section of the nuclear reaction $^{15}\text{N}(p, \alpha \gamma)^{12}\text{C}$ at 429 keV¹² and a tilted sample geometry ($\Psi = 65^\circ$). The measured excitation curves (i.e., yield versus incident energy) around the resonance energy E_R can be converted into concentration versus depth profiles by means of the SPACES simulation program.^{13,14} This profiling technique gives a depth resolution of approximately 1 nm near the film surface.

The excitation curves of the $^{15}\text{N}(p, \alpha \gamma)^{12}\text{C}$ nuclear reaction, and the corresponding ¹⁵N depth profiles for films grown in (i) ¹⁵N₂O, (ii) ¹⁵N₂O followed by ¹⁴N₂O, and (iii) ¹⁴N₂O followed by ¹⁵N₂O, are shown in Fig. 1. The real profiles might present less sharp edges than the rectangular ones shown here, but this fact does not change the essence of the reasonings reported here. The time of RTP in each growth step was 80 s, such that films type (ii) and type (iii) were grown during a total RTP time interval of 160 s. One can see that in sample type (i), grown in ¹⁵N₂O only, ¹⁵N is distributed with an almost constant concentration within the region between 4.5 nm from the surface and the oxynitride/Si interface. If a further oxynitridation in ¹⁴N₂O is performed on sample (i) we obtain the sample type (ii). This second treatment results in a further growth of the oxynitride film. The ¹⁵N profile is shifted deeper into the film, and the total amount of ¹⁵N decreases by 20%. In sample (iii) the ¹⁵N atoms (which have been incorporated in the film during the last treatment step) are located closer to the new interface than in sample (ii), and the total amount of ¹⁵N incorporated in the oxynitride film is smaller than in sample (ii) by 35%. In view of the symmetry of samples (ii) and (iii) with respect to the two N isotopes, we can say that the ¹⁵N profile for

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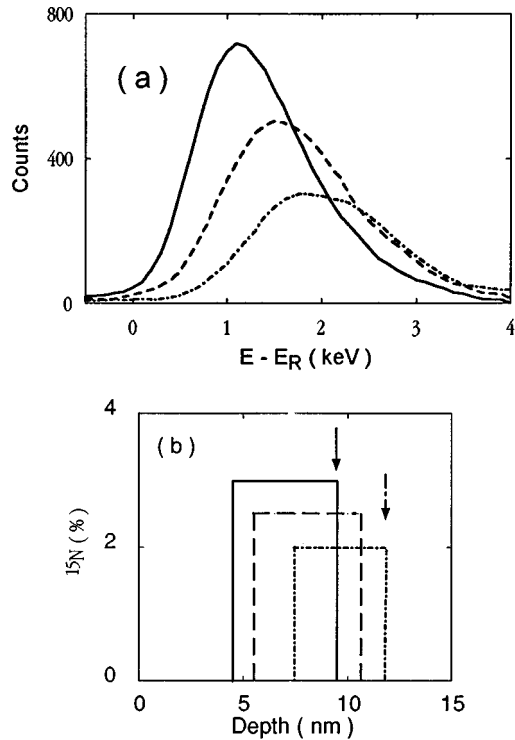


FIG. 1. (a) Excitation curves of the $^{15}\text{N}(p, \alpha \gamma)^{12}\text{C}$ nuclear reaction around the resonance energy $E_R=429$ keV, for films grown by RTP in (i) $^{15}\text{N}_2\text{O}$ (solid), (ii) $^{15}\text{N}_2\text{O}$ followed by $^{14}\text{N}_2\text{O}$ (dashed), and (iii) $^{14}\text{N}_2\text{O}$ followed by N_2O (dashed-dotted). (b) The corresponding ^{15}N depth profiles. The solid arrow indicates the position of the oxynitride/Si interface in sample (i), while the dashed arrow indicates the position of the oxynitride/Si interface in samples (ii) and (iii).

sample type (iii) corresponds to the ^{14}N profile for sample (ii).¹² So, samples (ii) and (iii) have identical nitrogen ($^{15}\text{N} + ^{14}\text{N}$) profiles, located in the region near the interface, having an appreciable mixture of ^{14}N and ^{15}N (area under the superimposed rectangles). The predominant N isotope in the gas used in the second treatment step is located closer to the interface. This last fact is an evidence that the interstitial diffusion of nitrogenous species (NO according to Ref. 10) across the growing oxynitride film with reaction at the interface is one mechanism responsible for the observed N distribution. However, the mixture of ^{14}N and ^{15}N in these profiles, the $^{14}\text{N} \leftrightarrow ^{15}\text{N}$ isotopic exchanges, the shift towards the interface of the N atoms already present in the oxynitride film, and the absence of N in the near surface region show that other mechanisms are acting in parallel, like the reaction of the diffusing nitrogenous species with the oxynitride network,¹⁵ and the replacement of earlier incorporated N by freshly arriving O and N. Indeed, in a previous work¹⁶ we have shown that during furnace reoxidation in O_2 of N_2O -grown oxynitride films, O and N atoms from the film are exchanged for O atoms from the gas. So, the removal of N from the near surface region of the oxynitride film is not only attributable to O^8 but also to O_2 . The action of O and O_2 release N which outdiffuses and desorbs. As previously reported by several authors,^{2,7,8} the removal mechanism acting in the near surface region is such that nitrogen is completely washed out, and consequently outdiffusing nitrogen atoms that could be trapped in this region are completely

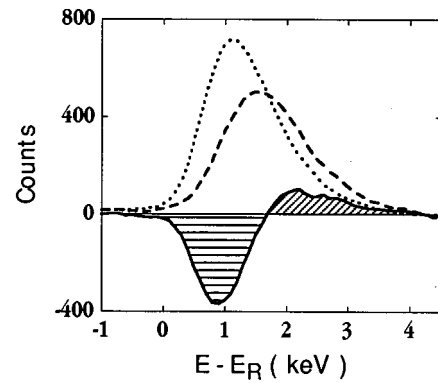


FIG. 2. Excitation curves of the $^{15}\text{N}(p, \alpha \gamma)^{12}\text{C}$ reaction for films grown by RTP in (i) $^{15}\text{N}_2\text{O}$ (dotted), (ii) $^{15}\text{N}_2\text{O}$ followed by $^{14}\text{N}_2\text{O}$ (dashed), and the difference between these two excitation curves (solid, shadowed area).

removed. This explains the fact that there is no ^{15}N observable in the region from the surface up to a depth of approximately 5.5 nm in sample (ii), as it would be expected after a second processing step in $^{14}\text{N}_2\text{O}$ of an oxynitride film grown in $^{15}\text{N}_2\text{O}$, where a loss of ^{15}N was observed. Similarly, in sample (iii) there is no ^{14}N in this near surface region, and in sample (i) there is no ^{15}N in the region from the surface up to a depth of 4.5 nm.

The migration of the N atoms already incorporated in the oxynitride film, due to longer nitridation times is shown in Figs. 2 and 3. The excitation curves of the $^{15}\text{N}(p, \alpha \gamma)^{12}\text{C}$ reaction for sample (i) and (ii), and the curve (shadowed) that results from the subtraction of these two excitation curves are given in Fig. 2. The hatched areas below and above the zero level represent, respectively, the local loss and the local gain of ^{15}N after the second growth step in $^{14}\text{N}_2\text{O}$. One can see that the effect of the second treatment step in $^{14}\text{N}_2\text{O}$ is to remove part of the ^{15}N from the region of the oxynitride film closer to the surface, and to push another part of the ^{15}N atoms towards the interface. The effect of a third treatment step in $^{14}\text{N}_2\text{O}$ is seen in Fig. 3, where we show the excitation curve of the $^{15}\text{N}(p, \alpha \gamma)^{12}\text{C}$ reaction obtained after submitting sample (i) to two additional RTP cycles in $^{14}\text{N}_2\text{O}$. After the third step the excitation curve is shifted towards higher energies as compared to that of sample (ii), which means that the ^{15}N atoms were pushed deeper into the film, and are located nearer to the new interface. One notices, however, that the area under this excitation curve is similar to that of sample (ii), so that there was no further loss of ^{15}N during the third step. This result was confirmed by NRA. The pushing of ^{15}N towards the new interface can be attributed to a site-to-site jump mechanism (interstitialcy or vacancy) of diffusion of nitrogenous species.¹⁷ Figure 3 also shows the excitation curves for sample (ii), and for an oxynitride film grown by performing two RTP steps in $^{14}\text{N}_2\text{O}$ followed by a third RTP step in $^{15}\text{N}_2\text{O}$. One can see that the area under this last excitation curve is smaller, and it remains in a lower energy interval as compared to that for the sample treated in $^{15}\text{N}_2\text{O}$ followed by two steps in $^{14}\text{N}_2\text{O}$. This means that during the third growth step, when the film thickness as well as the amount of incor-

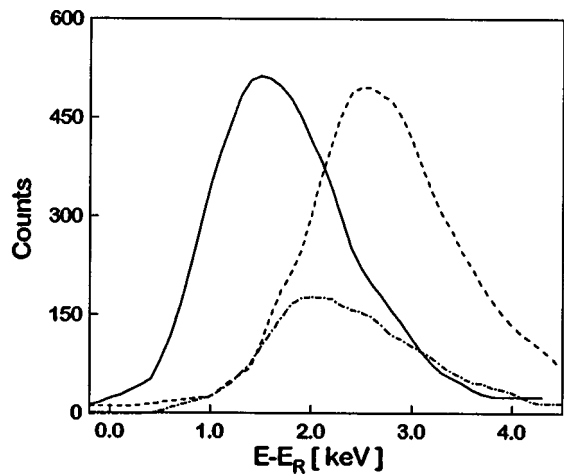


FIG. 3. Excitation curves of the $^{15}\text{N}(p, \alpha \gamma)^{12}\text{C}$ reaction, for films grown in: $^{15}\text{N}_2\text{O}$ followed by $^{14}\text{N}_2\text{O}$ (solid); $^{15}\text{N}_2\text{O}$ followed by $^{14}\text{N}_2\text{O}$, and followed by $^{14}\text{N}_2\text{O}$ (dashed); and $^{14}\text{N}_2\text{O}$ followed by $^{14}\text{N}_2\text{O}$, and followed by $^{15}\text{N}_2\text{O}$ (dashed-dotted).

porated N were larger than those after two RTP steps, the interstitial diffusion of nitrogenous species across the growing oxynitride film without interacting with it is slowed down by its diffusion barrier property, leading to a predominance of the site-to-site mechanism of diffusion. As a con-

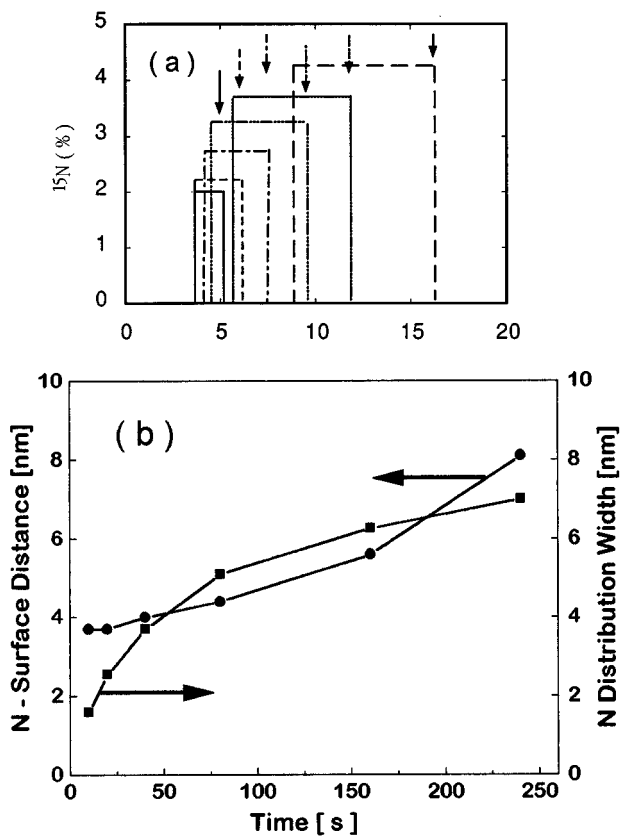


FIG. 4. (a) ^{15}N depth profiles in oxynitride films grown by RTP in $^{15}\text{N}_2\text{O}$ during: 10 s (solid), 20 s (dashed), 40 s (dashed-dotted), 80 s (dashed-three dots), 160 s (solid), 240 s (dashed). The arrows indicate the position of the oxynitride/Si interface in each sample. (b) Distance between the surface and the beginning of the N distribution, and width of the N distribution as a function of the RTP time.

sequence, N is incorporated in the regions closer to the surface.

The width of the N distribution, and the distance from the surface at which the N distribution in the film starts are given in Fig. 4 for oxynitride films grown in $^{15}\text{N}_2\text{O}$ only during RTP times between 10 and 240 s. The position of the oxynitride/Si interface is shown by arrows in each ^{15}N profile. The width of the N distribution exhibits also an increase with the processing time (i.e., with film thickness), but it is noticeable that the growth rate of this width decreases with increasing processing time. This result can be associated with the self-limited character of the film growth, on the one hand, which slows down the advance of the oxynitride/Si interface (i.e., the N front), and on the other hand to the removal of N from the near surface side.

In summary, the thermal growth of silicon oxynitride films on Si(100) in N_2O by RTP is a result of the diffusion of O_2 species, concomitantly with the diffusion of nitrogenous species (most probably NO), through the growing oxynitride film to react with Si at the oxynitride/Si interface. In parallel, site-to-site diffusion of nitrogenous species in the volume of the growing oxynitride film lead to the incorporation of N in this region. The characteristic N profile obtained by RTP growth in N_2O is due to the removal of N from the near surface region of the films. Our studies attribute this removal to the effect of atomic exchanges $\text{O} \leftrightarrow \text{N}$ produced mainly by the action of O and O_2 . Furthermore, $\text{N} \leftrightarrow \text{N}$ exchange was also observed.

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