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Improvement of memory performance by high temperature annealing of the Al₂O₃ blocking layer in a charge-trap type flash memory device

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The effect of postdeposition annealing (PDA) of the Al_2O_3 blocking layer in a charge-trap type memory device is investigated. Significant improvements are achieved by high temperature PDA at 1100 °C, achieving faster operation speed, good charge retention, and a wide program/erase window. Experimental evidence shows that the underlying mechanism is not the changes in the band gap of the crystallized Al_2O_3 but is due to the higher trap density in the Si_3N_4 trapping layer at a deeper energy level by the intermixing between Al_2O_3 and Si_3N_4 . The reduced trapping efficiency of the annealed Al_2O_3 also helps improve the retention property. © 2010 American Institute of Physics. [doi:10.1063/1.3442502]

Charge-trap type memory device, otherwise known as TANOS (TiN-Al₂O₃-Si₃N₄-SiO₂-Si), is one of the most promising candidates for next generation flash memory technology. This paper reports that the high-temperature post-deposition annealing (PDA) of Al₂O₃ in a TANOS device can significantly improve the memory performance of the device. It also presents experimental evidence that the dominant mechanism behind such an improvement is not a change in the band structure of Al₂O₃, as expected, but is a change in the charge trapping property of Al₂O₃ and silicon nitride.

After standard gate precleaning, a 4.5 nm thick tunnel oxide (SiO₂) was thermally grown on a p-type Si substrate, and 6 nm thick Si₃N₄ was deposited by low-pressure chemical vapor deposition to form the charge-trapping layer. For the blocking oxide, a Al₂O₃ layer with a thickness of 15 nm was deposited on the top of the nitride layer by means of atomic layer deposition (ALD) using Eureka 3000 from Jusung Engineering. The ALD temperature was fixed at 300 °C. Al(CH₃)₃ from UP Chemical Co. was used as a precursor and ozone was used as an oxidant. After the deposition of the Al₂O₃ layer, PDA was performed in the temperature range of 800-1100 °C in a N₂ ambient for 30 s. A 150-nm-thick TaN layer was deposited by reactive sputtering for the gate metal. As plasma etching of crystallized Al₂O₃ can cause plasma-induced damage to the gate stack, the gate stack etching was stopped after the metal gate etching in order to exclude the effect of plasma etch damage. Then, source/drain implantation was done through the dielectric stacks, and all of the samples underwent a rapid thermal annealing process at 900 °C for 30 s for activation of the dopant. The charge trap devices were fabricated with the gate length of 100 μ m and width of 100 μ m.

Figures 1(a) and 1(b) show a comparison of the program/erase (P/E) characteristics and charge retention properties of TANOS devices with different PDA tempera-

tures. For erase characteristic comparison, the devices were programmed to ΔV_{FB} (programmed V_{FB} —initial V_{FB}) =4 V. To reach ΔV_{FB} =4 V programmed state, programming conditions used were 160 μ s, 250 μ s, and 100 μ s at 18 V for 900 °C, 1000 °C, and 1100 °C annealed samples, respectively. Both the P/E speed and the charge retention property were greatly improved by the high-temperature PDA process, and the improvement is most apparent when the PDA temperature is 1100 °C.

To investigate the mechanism of such an improvement by the high-temperature PDA process, the leakage current performance was initially checked. The results in Fig. 2(a) do not show a reduction in the leakage current due to the high-temperature PDA compared to the low temperature PDA. Therefore, the improved P/E properties after an annealing process at a higher temperature are not likely due to reduced back tunneling current from the gate electrode.

The band structure of the high-temperature annealed Al₂O₃ was also carefully measured by high-resolution x-ray photoelectron spectroscopy (XPS).¹ The result in the inset of



FIG. 1. (Color online) Comparisons of (a) program and erase characteristics and (b) charge retention property of TANOS devices with different PDA temperatures. For more accurate comparison of retention property, the devices with the equal EOT values were selected for (b).

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FIG. 2. (Color online) (a) Comparison of the gate stack leakage currents of TANOS devices with different PDA temperatures. The inset shows the energy loss spectrum derived from the O 1*s* spectrum as measured by XPS. (b) Retention property of TANOS devices with different PDA temperatures measured at 150 and 250 °C. The inset is the flat-band voltage difference between 150 and 250 °C (ΔV_{FB} at 250 °C $-\Delta V_{FB}$ at 150 °C) as calculated from the results in (b).

Fig. 2(a) shows that there is no meaningful difference in the extracted energy band gap of the annealed Al_2O_3 (E_{G,Al_2O_3} =7.58 eV, 7.59 eV, and 7.59 eV for samples exposed to 900 °C, 1000 °C, and 1100 °C PDA, respectively). This result implies that the improvement of the P/E property and the charge retention characteristics cannot be explained simply in terms of an increase in the conduction band offset of the crystallized Al₂O₃, as claimed in a previous report on Al₂O₃ for floating gate type flash memory devices.^{2,3} The hightemperature retention analysis in Fig. 2(b) also supports the fact that there is no difference in the extracted band gap. The higher the temperature becomes, the greater the charge loss is, as shown in Fig. 2(b). If the difference of the charge loss is monitored between 150 and 250 °C, it can be considered to be the pure thermionic emission component of the charge loss.⁴ The inset of Fig. 2(b) shows the difference of the charge loss amount monitored by the flat-band voltage difference between 150 and 250 °C (ΔV_{FB} at 250 °C – ΔV_{FB} at 150 °C) calculated from the results in Fig. 2(b). Surprisingly, all of the samples (as-deposited, 1000 °C annealed, and 1100 °C annealed Al_2O_3) show an identical curve, proving that the difference of the charge loss measured at 150 and 250 °C does not depend on the Al₂O₃ PDA temperature. This is strong evidence that the memory performance improvement observed in the Al₂O₃ sample annealed at a high temperature is not due to the increased band gap caused by the crystallization of Al₂O₃.

As another possible mechanism, the trapping property of Al_2O_3 was investigated. For this test, separate samples with metal-insulator-metal (MIM: TaN-Al_2O_3-TaN) capacitor structure were prepared to study the property of the Al_2O_3 dielectric itself. Figure 3(a) shows the change in the gate voltage during a constant current stress test performed on the MIM capacitors. The amount of trapped charge in Al_2O_3 as a function of the injected charge was calculated from the gate voltage shift (not shown here).⁵ From the result, the trapping efficiency *K* was extracted.⁶ The result of the trapping efficiency is significantly reduced when the PDA temperature increases. This implies that the trap-assisted tunneling-current through the Al_Q_3 defect in a programmed



FIG. 3. (Color online) (a) Change in the gate voltage during a constant current stress test of MIM capacitors with Al_2O_3 dielectrics annealed at different temperatures. The inset is the trapping efficiency *K* as a function of the PDA temperature, as calculated from the results in (a). (b) Si depth profiles in the gate stacks after high-temperature PDA, as measured by TOF-SIMS.

state can be effectively suppressed by a high-temperature PDA process, which in turn improves the retention property.

However, the reduced trapping efficiency of Al₂O₃ alone does not by itself sufficiently explain the significant enhancement of the P/E speed and the window shown in Fig. 1(a). On the other hand, it has been reported that a deeper saturated erase flat-band voltage indicates a higher density of accessible charge traps.⁷ Moreover, the properties of the Si₃N₄ trapping layer/Al₂O₃ interface have been postulated to play a key role in the erase mechanism.⁸ Based on such considerations, it is speculated that intermixing at the interface between the Al₂O₃ blocking layer and the Si₃N₄ trapping layer may occur during high-temperature PDA, leading to the diffusion of Al into Si₃N₄, which results in yielding additional traps at a deeper trapping energy level. Figure 3(b)shows the Si depth profiles of TANOS gate stacks with different PDA temperatures, as measured by time-of-flight secondary ion mass spectrometry (TOF-SIMS). Additional Si ions diffuse out from Si₃N₄ into the Al₂O₃ blocking oxide due to the higher PDA temperature, which is evidence of intermixing between Al₂O₃ and Si₃N₄. If such intermixing occurs, the diffusion of Al ions toward the Si₃N₄ trapping layer will also take place, resulting in additional traps at a deeper trapping energy level.

The charge loss rate as a function of the PDA temperature was also investigated. Based on the slope of the plot in Fig. 4(a) and the charge loss rate, the relative trap density amount could be extracted as a function of the trap energy level, as shown in Fig. 4(b).⁹ The result in Fig. 4(b) shows that the 1100 °C PDA sample has a higher trap density at a deeper trap energy level in the Si₃N₄ trapping layer. Therefore, it can be concluded that the additional traps at the deeper trapping energy level of Si₃N₄ caused by the intermixing between Al₂O₃ and Si₃N₄ during the hightemperature PDA process is the main reason for the improved P/E properties.

function of the injected charge was calculated from the gate voltage shift (not shown here).⁵ From the result, the trapping efficiency *K* was extracted.⁶ The result of the trapping efficiency *K* in the inset of Fig. 3(a) clearly shows that the trapping efficiency is significantly reduced when the PDA temperature increases. This implies that the trap-assisted tun-This a neling, current, through the Al_2O_3 defect in a programmed sub PDA of Al_2O_3 in this result, the higher the PDA temperature of Al_2O_3 in the inset of PDA of Al_2O_3 in this result, the higher the PDA temperature of Al_2O_3 in the inset of PDA of Al_2O_3 in this result, the higher the PDA temperature of PDA of Al_2O_3 in this result, the higher the PDA temperature of PDA of Al_2O_3 in this result, the higher the PDA temperature of PDA of Al_2O_3 in this result, the higher the PDA temperature of PDA of Al_2O_3 in this result, the higher the PDA temperature of PDA of Al_2O_3 in this result, the higher the PDA temperature of PDA of Al_2O_3 in this result, the higher the PDA temperature of PDA of Al_2O_3 in the result in the resul



FIG. 4. (Color online) (a) Charge loss rate as a function of the PDA temperature. (b) Relative trap density amount as a function of the trap energy level. (c) A plot of the retention vs the saturated erase window for TANOS devices with different PDA temperatures. The saturated erase window was determined as the change in V_{FB} from the programmed V_{FB} to the V_{FB} which showed the onset of the saturation during the erasing.

becomes, the more the charge retention is improved. As analyzed in Figs. 2–4, the wide erase window and enhanced retention property upon high-temperature PDA contribute to the pre-existing intrinsic Si_3N_4 trap density plus a high trap density at a deeper trap energy level, possibly due to the diffusion of Al ions toward Si_3N_4 and the low trapping efficiency of the annealed Al_2O_3 dielectric which suppresses the trap-assisted tunneling current.

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