Characteristics of Al_2O_3 gate dielectrics partially fluorinated by a low energy fluorine beam

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The partial fluorination of Al_2O_3 gate dielectrics was examined by exposing an oxide-nitride-aluminum oxide (ONA) stack to a low energy fluorine beam, and its effect on the properties of the ONA was investigated. Exposing ONA to about 10 eV fluorine beam resulted in a 5-nm-thick AlO_xF_y layer on the ONA by replacing some Al–O to Al–F. The electrical properties such as leakage current and memory window characteristics were improved after fluorination of the ONA, possibly due to the improved charge trapping characteristics through the formation of an AlO_xF_y layer on the Al_2O_3 without changing the blocking layer thickness. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2975183]

There is a need for more advanced materials for gate dielectrics instead of SiO_2 for the next generation of volatile and nonvolatile memory devices, such as dynamic random access memory, flash memory, etc., because the SiO_2 gate dielectric is reaching its technological and theoretical limits.[1–4] Many high-k dielectric materials have been investigated as a replacement for SiO_2 as an alternative gate dielectric. Some high-k dielectric materials, including Al_2O_3, have shown outstanding properties including a relatively high dielectric constant (8.6–10), lower leakage current at the equivalent oxide thickness, etc. However, some problems still remained to be solved, such as interface charges, capacitance frequency dispersion, etc.[1,3–5] Recently, a fluorine treatment of high-k dielectric materials by F ion implantation, F-based plasma treatments, etc., was investigated in an attempt to improve the electrical properties of high-k gate dielectric materials. It was reported that the electrical properties and oxide reliability of dielectric materials including high-k materials could be improved by fluorine incorporation.[1,3,4,6–8]

In this study, a fluorine treatment of the Al_2O_3 layer of an oxide-nitride-aluminum oxide (ONA) gate dielectric stack was carried out to improve the electrical properties, such as the charge trapping properties of silicon-oxide-nitride-oxide-silicon (SONOS)-type floating gate memory devices. In particular, a low energy F-based neutral beam was used to remove the possible charge related damage[9] during the fluorination of an Al_2O_3 layer.

An ONA structure was formed on p-type Si (100) substrates by growing a 4-nm-thick SiO_2 thin film thermally, by depositing a 7-nm-thick SiN layer on SiO_2 using low pressure chemical vapor deposition and by depositing a 15-nm-thick Al_2O_3 layer by atomic layer deposition as a blocking layer for a SONOS-type floating gate flash memory device.[6] After forming the ONA stack, postdeposition annealing was carried out by rapid thermal annealing at 1080 °C for 2 min in N_2 ambient.

The Al_2O_3 thin film was fluorinated using a low energy fluorine beam generated by the reflection of a F-based ion beam extracted from a three grid inductively coupled plasma (ICP)-type ion gun on parallel reflector plates. 300 W of 13.56 MHz rf power was applied to a 6 in. diameter ICP ion gun while 30 SCCM (SCCM denotes standard cubic centimeter per minute at STP) NF_3 was flowed to the source. An approximately 10 eV low energy fluorine beam was used. The details of the beam source are reported elsewhere.[10–12]

The Al_2O_3 thin film of the ONA stack was exposed to the fluorine beam for approximately 15 min. After the beam treatment, a metal-oxide-semiconductor (MOS) structure was formed to measure the electrical properties of the ONA stack on p-type (100) silicon wafer. The MOS structure was formed by depositing a 100-nm-thick Pt electrode (area of $50\times 50\ \mu m^2$) by dc sputtering on the top and bottom of the samples as gate electrodes followed by forming gas annealing at 400 °C for 30 min.

Figure 1 shows the depth profiles of the AlO, F, O, N, and SiN of the ONA stack measured with and without the fluorine beam treatment using secondary ion mass spectroscopy (SIMS). The figure shows that F atoms had penetrated the Al_2O_3 surface through the low energy fluorine beam treatment. The amount of F^- that penetrated the Al_2O_3 surface reached a maximum at the Al_2O_3 surface and decreased rapidly with increasing depth. The loss of O on the Al_2O_3 surface due to the fluorine beam treatment could be observed by comparing the SIMS depth profiles of O and AlO of the Al_2O_3 layer treated with the fluorine beam with the untreated sample. The depth of oxygen loss was approximately 5 nm. Therefore, some of the oxygen in Al_2O_3 appeared to have been replaced by F due to the fluorine beam treatment.

The change in the chemical binding state of Al on the Al_2O_3 surface after the fluorine beam treatment was exam-

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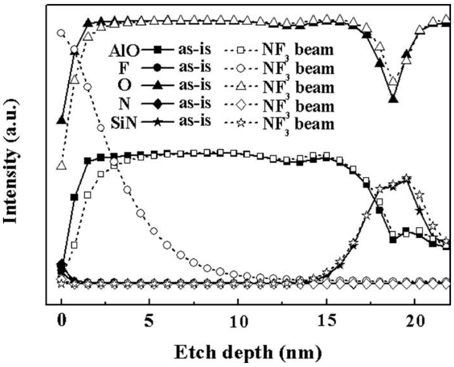

FIG. 1. SIMS depth profiles of AlO, F, O, N, and SiN in ONA stacks with/without the low energy fluorine beam treatment.

ined by a x-ray photoelectron spectroscope (XPS). Figure 2(a)–2(c) show the XPS narrow scan data of AlF_3 measured on the Al_2O_3 layer of ONA stack (a) for the untreated (as-is) sample, (b) the fluorine beam treated sample, and (c) the fluorine beam treated sample followed by sputtering for 90 s. As shown in the figure, the untreated sample showed an Al peak at 74.2 eV indicating the formation of Al–O bonds while the fluorine beam treated sample showed a peak at 76.7 eV related to Al–F bonds in addition to the peak at 74.2 eV. In addition, the peak intensity of the Al–O bonds decreased after the formation of Al–F bonds. Therefore, the Al–F bonds appeared to have formed through the replacement of Al–O bonds of the Al_2O_3 layer on the ONA stack during the beam treatment. The disappearance of the peak related to Al–F bonding after short time sputtering shows F incorporation only on the Al_2O_3 layer surface.

Figure 3 shows cross-sectional micrographs of the ONA stack observed by a transmission electron microscope (TEM) (a) for the untreated (as-is) and (b) after the fluorine beam treated sample. As shown in the figure, the untreated ONA stack consisted of 15-nm-thick Al_2O_3, 7-nm-thick SiN, and 4-nm-thick SiO_2 layers on a silicon wafer. In addition, the Al_2O_3 layer was crystallized. After the fluorine beam treatment, the total thickness of the ONA stack was similar, as shown in Fig. 3(b), indicating no etching of the Al_2O_3 layer by the low energy fluorine beam treatment. However, after the beam treatment, the Al_2O_3 layer was divided into two layers composed of a top AlO_xF_y layer and a bottom Al_2O_3 layer. The AlO_xF_y layer was amorphous and approximately 5 nm thick, which is similar to the penetration depth of F ions in ONA stack obtained by SIMS analysis in Fig. 1.

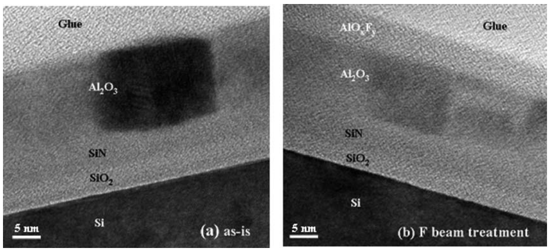

FIG. 3. Cross-sectional TEM images of the ONA stack samples. (a) untreated ONA stack and (b) the ONA stack after the fluorine beam treatment.

Figure 4 shows the capacitance-voltage (*C-V*) characteristics of the MOS devices fabricated with untreated and fluorine beam-treated ONA stack. As shown in the figure, the maximum and minimum capacitance of the untreated and beam treated samples were similar, indicating that the Al_2O_3 and AlO_xF_y layers have a similar dielectric constant. This is despite the fact that the dielectric constant of AlF_3 is approximately 6.0.[13] Therefore, the equivalent oxide thickness of the ONA stack remained similar at 14.5 nm even after the fluorine beam treatment. As shown in the *C-V* hysteresis curve obtained by sweeping ±15 V, the MOS device fabricated with the fluorine beam treated ONA stack showed wider memory window characteristics by increasing the charge trapping characteristics compared with the MOS device fabricated without the treatment. The improved charge trapping characteristics by the fluorine beam treatment are not completely understood. However, an understoichiometric AlF_3 layer can localize high density fixed charges in fluorine vacancies within the AlF_3 layer.[13,14] Therefore, the improved charge trapping characteristics obtained in this study appear to be related to the formation of a 5-nm-thick AlO_xF_y layer between the Al_2O_3 and Pt electrode through the low energy fluorine beam treatment. In addition, when current-voltage (*I-V*) characteristics of the MOS devices were compared, the

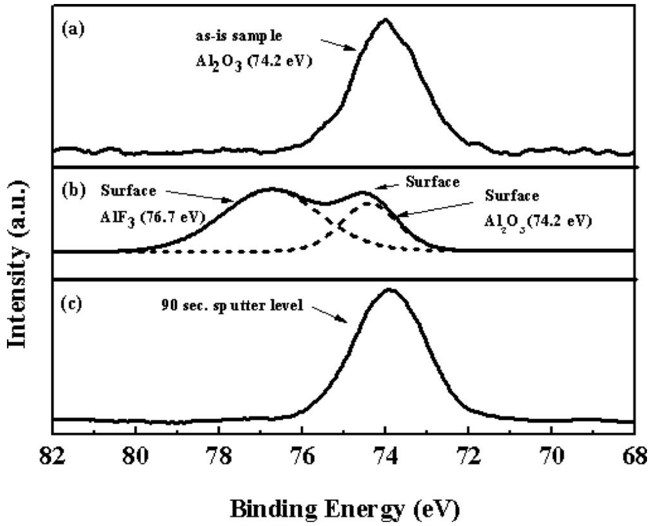

FIG. 2. Al XPS narrow scan spectra of (a) untreated ONA stack, (b) ONA stack after the fluorine beam treatment, and (c) after 90 s sputtering of (b) sample.

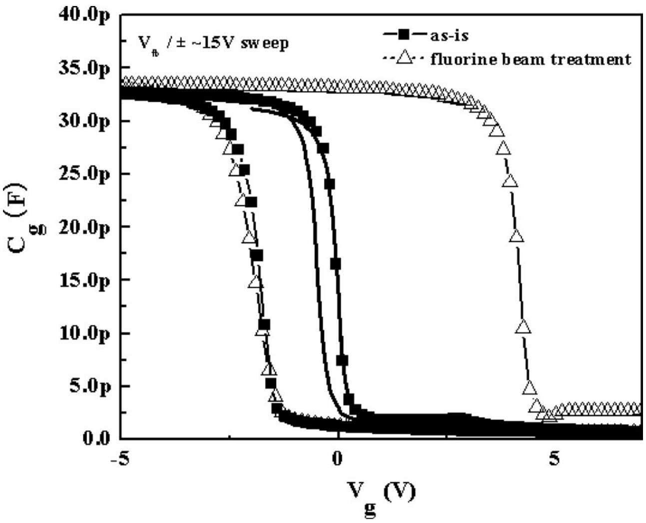

FIG. 4. *C-V* hysteresis curves of the MOS devices fabricated with the ONA stacks with/without the fluorine beam treatment.

MOS device fabricated after the beam treated ONA stack showed a slightly lower leakage current than the device fabricated with the untreated ONA stack possibly due to the passivation of the defects in the Al_2O_3 layer (not shown).

This study examined the effect of a low energy fluorine beam treatment on Al_2O_3 layer of an ONA stack on the characteristics of ONA stack for applications to SONOS devices. The surface treatment of a 15-nm-thick Al_2O_3 layer with a 10 eV fluorine beam formed a 5-nm-thick AlO_xF_y layer on the Al_2O_3 surface by replacing Al–O bonds with Al–F bonds. The total thickness of the ONA stack was similar after the beam treatment. However, the MOS device fabricated using the ONA stack treated with the beam showed wider memory window characteristics. The improved *I-V* and *C-V* characteristic obtained after the fluorine beam treatment appears to be related to defect passivation through the incorporation of fluorine in the Al_2O_3 layer and the enhanced charge trapping characteristics from the AlO_xF_y layer formed on the surface of the ONA stack.

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