Electron Energy Loss Spectroscopy Characterization of TANOS (TaN/Al₂O₃/Si₃N₄/SiO₂/Si) Stacks

Jucheol Park,^{1,*} Sung Heo,² JaeGwan Chung,² and Gyeong-Su Park²

¹Center for Materials Analysis, Research Institute for Advanced Materials, Seoul National University, 599 Gwanangno, Gwanak-gu, Seoul 151-742, Korea

²AE Group, Samsung Advanced Institute of Technology, Nongseo-Dong Mt.14-1, Giheung-gu, Yongin-si, Gyeonggi-do 446-712, Korea

Abstract: The interfacial layer between the Al₂O₃ layer and the Si₃N₄ layer formed after postdeposition annealing (PDA) of TaN/Al₂O₃/Si₃N₄/SiO₂/Si (TANOS) stacks was investigated using transmission electron microscopy (TEM), scanning transmission electron microscopy, and electron energy loss spectroscopy (EELS). From the result of the TEM analysis, it was found that the 2-nm-thick interface layer between Al₂O₃ and Si₃N₄ layers was amorphous. The high-loss EELS analysis showed that the phases of the interfacial layer weakly bound together instead of the substoichiometric silicon oxide and amorphous Al₂O₃ near the bottom interface of the crystalline Al₂O₃. The low-loss EELS analysis showed that aluminum existed in metallic state at the interface. Therefore, we speculated that SiO_xN_y could be formed by oxidation of Si₃N₄ during PDA and that metallic aluminum could be formed by the decomposition of weakly bound amorphous Al₂O₃ during electron irradiation. These complicated reactions near the interface could induce oxygen deficiency in the Al₂O₃ layer and finally degrade the retention properties of TANOS stacks.

Key words: TANOS, STEM, EELS, Al₂O₃, Si₃N₄, SiO_xN_y, interface

INTRODUCTION

Charge trap flash (CTF) memory approaches have received considerable attention because of higher scalability due to a surprisingly simple structure and because of the possibility of reliability enhancement by sharply reducing the intercell noise in sub-50-nm NAND-type floating-gate flash memory devices. One of the most promising CTF structures is TaN/Al₂O₃/Si₃N₄/SiO₂/Si (TANOS). In TANOS CTF, non-conductive silicon nitride is called a charge trap layer and it stores the data instead of floating gate in NAND devices. Aluminum oxide having a higher dielectric constant ($k = 7\text{--}10$) is called blocking oxide or the top oxide layer and it effectively blocks electron back tunneling during an erase operation (Jeon et al., 2005). TANOS CTF adopting silicon nitride and aluminum oxide has high compatibility with conventional materials used in complementary MOS memory cell manufacture. However, the major drawback of TANOS CTF is its poor retention characteristics (Tan et al., 2008; Rothschild et al., 2009). Many research groups have studied the origin of the retention degradation, but the impact of the electronic structures of silicon nitride, alumina, and/or the interface between Si₃N₄ and Al₂O₃ is still not well understood, and a detailed physical correlation between their electronic structures and the poor retention of TANOS structures is still lacking.

In this paper, the electronic structures of the alumina layer and the silicon nitride layer of TANOS stacks were investigated using transmission electron microscopy (TEM) and high-angle annular dark-field (HAADF) scanning trans-

mission electron microscopy (STEM) imaging and electron energy loss spectroscopy (EELS). We studied the low- and high-loss EELS characteristics of the interface between alumina and silicon nitride and linked them to the poor retention properties of TANOS memories.

MATERIALS AND METHODS

SiO₂ tunnel oxide was grown on *p*-type Si(100) wafers by thermal oxidation in O₂ at 850°C. Si₃N₄ as a charge-trapping layer was deposited using the low-pressure chemical vapor deposition method. High-*k* dielectric Al₂O₃ as a blocking oxide layer was deposited on top of the Si₃N₄ layer using an atomic layer deposition method. After the deposition of the Al₂O₃ layer, postdeposition annealing (PDA) was performed at 1,050°C. The TaN layer, as a high work function metal gate, was deposited by means of the chemical vapor deposition method.

STEM-EELS analysis was performed using Monochromated Titan 80-300 (FEI) with a high-resolution Gatan imaging filter (GIF Tridiem 865 ER300). The acceleration voltage of the TEM was 300 kV. The energy spread of a zero-loss peak was 0.25 eV in full-width at half-maximum. The energy dispersion was 0.05 or 0.1 eV/ch, and the entrance aperture of the HR-GIF was set at 1.0 or 2.5 mm in diameter. EELS spectra were acquired across the layers of TANOS stacks in the STEM mode. TEM specimens were prepared by the conventional method of mechanical thinning and ion milling.

Al-L edge X-ray absorption spectra were measured at room temperature at 7C1 beamline and using the Pohang Light Source. The Si(111) double-crystal monochromator was used to produce monochromatic X-ray photon energy.

Figure 1. (a) HRTEM image and (b) HAADF image of the TANOS multilayers. Crystalline Al_2O_3 , amorphous Si_3N_4 , and the formation of the interfacial layer are observed. c: EELS line scan spectra of Al-L and Si-L edges obtained along the TaN/ Al_2O_3 / Si_3N_4 / SiO_2 /Si (TANOS) multilayer. HRTEM, high-resolution transmission electron microscopy; HAADF, high-angle annular dark-field; EELS, electron energy loss spectroscopy.

RESULTS AND DISCUSSION

High-Loss EELS Analysis

The cross-sectional overview of the multilayers of the TANOS stack annealed at 1,050°C was observed by high-resolution TEM and HAADF-STEM. The 15-nm-thick Al_2O_3 layer was crystalline and the 7-nm-thick Si_3N_4 layer was amorphous (Fig. 1a). From the HAADF-STEM image (Fig. 1b), we clearly observed the ~2-nm-thick amorphous interface layer between Al_2O_3 and Si_3N_4 . The contrast of the interface layer was darker than that of Al_2O_3 and Si_3N_4 and it was similar to the contrast of SiO_2 (Fig. 1b).

To study the electronic structures of TANOS multilayers, an EELS line scan was performed in STEM mode with 1-nm spatial resolution and about 0.7 eV energy resolution. EELS spectra of the Al-L_{2,3} edge and the Si-L_{2,3} edge obtained from the line scan across the whole layers are shown in Figure 1c. Spectra 1 and 2 were typical Si-L edges of SiO_2 and Si_3N_4 , respectively. Spectra 5, 6, and 7 within the Al_2O_3 layer were typical Al-L_{2,3} edges of γ - Al_2O_3 . Spectra 3 and 4, spectra within the interface layer between Si_3N_4 and Al_2O_3 , were both Al-L_{2,3} and Si-L_{2,3} edges, which showed the different fine structures from the typical Al-L_{2,3} edge of γ - Al_2O_3 and Si-L_{2,3} of both SiO_2 and Si_3N_4 , respectively.

For deeper understanding of the electronic structures of aluminum at the interface layer between Si_3N_4 and Al_2O_3 , EELS spectra were acquired across the interface by an electron probe of 1-nm diameter in STEM mode. The positions measured were 1, 2, 3, 4, 5, 6, and 7 nm from the interface toward Al_2O_3 (Fig. 2). The peak-like features were labeled “A” to “D”. The “A” at 77 eV is a prominent peak for Al_2O_3 at the interface and the “C” at 84 eV is for Al_2O_3 farther from the interface. The “A” peak is clearly shown at the interface and slowly disappears as the distance from the interface

Figure 2. Electron energy loss spectroscopy spectra of Al-L edge in an energy range of 70–110 eV, obtained by scanning an electron probe across the interface. Position values denote displacement from the interface. The spectra reveal clear changes in the near-edge fine structure of the Al-L_{2,3} edge on moving from the amorphous interfacial layer to γ - Al_2O_3 .

increases, whereas the “C” peak is very noticeable as the probe positions approach the inside of Al_2O_3 .

The sharp features at 77–79 eV of the Al-L_{2,3} edge reflect a core-exciton absorption (Balzarotti et al., 1982; Tanaka & Adachi, 1996; Bouchet & Colliex, 2003). The energy of these excitonic peaks is highly characteristic of various alumina phases. The “A” is a prominent peak for

Figure 3. XANES spectra of as-deposited Al_2O_3 and Al_2O_3 annealed at 950 and 1,200°C. The “a” feature in the spectrum of the as-deposited sample is clearly representing amorphous Al_2O_3 .

amorphous Al_2O_3 . All striking features between 82 and 87 eV typically depend on the crystal structure, specifically the Al site environment. One major peak “C” at 84 eV corresponds to the spinel structure. For the amorphous Al_2O_3 , the peak “C” is smoother and its energy position is less clearly defined because of the destruction of the medium-range order (Bouchet & Colliex, 2003).

To confirm the electronic structures of amorphous and crystalline Al_2O_3 , X-ray absorption spectra of as-deposited Al_2O_3 (amorphous phase), and high-temperature annealed Al_2O_3 (crystalline phase), were obtained using the total electron yield method. The energy resolution was set at 0.3 eV. The peak-like features were labeled “a” to “e” (Fig. 3). The “a” at 77 eV and “c” at 79.7 eV are prominent peaks for as-deposited Al_2O_3 , and the “b” at 78 eV, “d” at 79.5 eV, and “e” at 84 eV for high-temperature annealed Al_2O_3 . These “a” to “d” features in Figure 3 correspond to the highly resolved peaks of “A” and “B” (in Fig. 2), which were observed by EELS analysis of the TANOS stack. The “a” and “d” features are prominent peaks for amorphous Al_2O_3 and the “b” and “c” for spinel $\gamma\text{-Al}_2\text{O}_3$. The “a” feature is the excitonic peak representing an amorphous Al_2O_3 . The “b” feature originated mainly from the tetrahedral Al and the “c” mainly from the octahedral Al (Kimoto et al., 2003). Generally, the “b” feature has been used to evaluate the degree of Al tetra in inverse spinel. The energy of “d” feature for amorphous Al_2O_3 was slightly higher than that for crystalline $\gamma\text{-Al}_2\text{O}_3$. The “e” feature, which originated from the medium-range order, is much higher in spinel $\gamma\text{-Al}_2\text{O}_3$ than in amorphous Al_2O_3 .

For deeper understanding of the electronic structures of silicon at the interface layer between Si_3N_4 and Al_2O_3 , the EELS spectrum of the Si-L_{2,3} edge in an energy range of 90–140 eV was acquired at the interface and compared with the spectra obtained at the Si_3N_4 and SiO_2 layers (Fig. 4).

Figure 4. Electron energy loss spectroscopy spectra of Si-L_{2,3} edge obtained at the interface between Si_3N_4 and Al_2O_3 , compared with Si_3N_4 and SiO_2 .

The peak-like features were labeled “1” to “3”. The “1” at 105.7 eV, “2” at 108.2 eV, and “3” at 115.2 eV are noticeable peaks. The spectrum of the amorphous SiO_2 layer consists of an excitonic peak at 105.7 eV, two distinctly split main peaks at 108.2 and 115.2 eV, and a broad delayed maximum at 130.5 eV (Harp et al., 1990; Batson, 1991). The first peak “1” can be identified with a Si–N bond, whereas the second peak “2” is associated with a Si–O bond because their positions in the spectrum closely coincide with measurements taken on Si_3N_4 and SiO_2 , respectively (Kimoto et al., 1997; Ziegler et al., 2004). The two main peaks “2” and “3” of SiO_2 are the likely result of final-state wave functions bound within a tetrahedron defined by strongly electronegative oxygen atoms (Harp et al., 1990; Batson, 1991). The spectrum of the interface resembled that of SiO_2 except for a slope that extended from 105.7 eV down to 99.8 eV, which exhibited a substoichiometric oxide. These results indicate that the interface layer consists of substoichiometric oxide and SiO_xN_y .

Low-Loss EELS Analysis

To investigate the low-loss characteristics of TANOS multilayers, an EELS line scan was performed in STEM mode with subnanometer spatial resolution at the energy range of 0–30 eV (Fig. 5). The plasmon energy of Si_3N_4 and Al_2O_3 was 22.9 and 23.3 eV, respectively. From the low-loss EELS spectra near the interface between the Al_2O_3 and Si_3N_4 layers, broad peaks were found at ~14.2 eV, the energy of which has been reported as the plasmon energy of aluminum (Stöckli et al., 1997; Hunt et al., 1998). This result indicated that aluminum was incorporated into the oxidized interface layer during annealing and was consistent with the results of Lisiansky et al. who showed the incorporation of Al into the SiON interfacial, as the crystalline Al_2O_3 was changed into the amorphous interfacial (Si,Al)ON layer upon annealing (Lisiansky et al., 2006). Another EELS spectrum imaging (not shown here) revealed that loosely bound nitrogen and oxygen atoms formed

Figure 5. (a) High-resolution scanning transmission electron microscopy image of the TANOS multilayers and (b) low-loss electron energy loss spectra obtained across the interface between the Si_3N_4 and Al_2O_3 layers [the red line in (a)].

nitrogen and oxygen gas and were exited at the $\text{Si}_3\text{N}_4/\text{Al}_2\text{O}_3$ interface by electron beam irradiation. From these results, we speculated that the formation of SiO_xN_y by oxidation of Si_3N_4 could occur with the oxidation of Si_3N_4 , and metallic Al could be formed by the decomposition of weakly bound Al_2O_3 during electron beam irradiation. These complicated reactions near the interface could induce oxygen deficiency in the Al_2O_3 layer and finally degrade the retention properties of TANOS (Chang et al., 2008; Park et al., 2010).

CONCLUSION

The alumina, silicon nitride, and their interfacial layer of TANOS stacks were investigated by TEM, HAADF-STEM imaging, and EELS. From the core-loss EELS analysis performed by scanning an electron probe of 1-nm diameter across the interface between Al_2O_3 and Si_3N_4 , it was found that the interfacial layer consisted of SiO_xN_y and substoichiometric oxide and that the Al_2O_3 near the interface layer was amorphous. The low-loss EELS analysis showed that aluminum also existed in metallic state at the interface. Therefore, we speculated that SiO_xN_y could be formed by oxidation of Si_3N_4 during PDA and that metallic aluminum could be formed by the decomposition of weakly bound amorphous Al_2O_3 during electron irradiation. These complicated reactions near the interface could induce oxygen deficiency in the Al_2O_3 layer and finally degrade the retention properties of TANOS.

REFERENCES

- BALZAROTTI, A., ANTONANGELI, F., GIRLANDA, R. & MARTINO, G. (1982). Core excitons in corundum. *Solid State Commun* **44**, 275–278.
- BATSON, P.E. (1991). Current trends for EELS studies in physics. *Microsc Microanal Microstruct* **2**, 395–402.
- BOUCHET, D. & COLLIEX, C. (2003). Experimental study of ELNES at grain boundaries in alumina: Intergranular radiation damage effects on Al-L₂₃ and O-K edges. *Ultramicroscopy* **96**, 139–152.
- CHANG, M., JU, Y., LEE, J., JUNG, S., CHOI, H., JO, M., JEON, S. & HWANG, H. (2008). Impact of oxygen incorporation at the $\text{Si}_3\text{N}_4/\text{Al}_2\text{O}_3$ interface on retention characteristics for nonvolatile memory applications. *Appl Phys Lett* **93**, 22101–22103.
- HARP, G.R., HAN, Z.L. & TONNER, B.P. (1990). Spatially-resolved X-ray absorption near-edge spectroscopy of silicon in thin silicon-oxide films. *Physica Scripta* **T31**, 23–27.
- HUNT, E.M., WANG, Z.L., EVANS, N.D. & HAMPIKIAN, J.M. (1998). High-spatial resolution compositionally-sensitive imaging of metallic particles using plasmon energy-loss electrons in TEM. *Micron* **29**, 191–199.
- JEON, S., HAN, J.H., LEE, J.H., CHOI, S.M., HWANG, H.S. & KIM, C.W. (2005). High work-function metal gate and high-k dielectrics for charge trap flash memory device applications. *IEEE Trans Electron Devices* **52**(12), 2654–2659.
- KIMOTO, K., MATSUI, Y., NABATAME, T., YASUDA, T., MIZOGUCHI, T., TANAKA, I. & TORIUMI, A. (2003). Coordination and interface analysis of atomic-layer-deposition Al_2O_3 on Si(001) using energy-loss near-edge structures. *Appl Phys Lett* **83**, 4306–4308.
- KIMOTO, K., SEKIGUCHI, T. & AOYAMA, T. (1997). Chemical shift mapping of Si L and K edges using spatially resolved EELS and energy-filtering TEM. *J Electron Microsc* **46**(5), 369–374.
- LISANSKY, M., HEIMAN, A., KOVLER, M., FENIGSTEIN, A., ROIZIN, Y., LEVIN, I., GLADKIKH, A., OKSMAN, M., EDREI, R., HOFFMAN, A., SHNIEDER, Y. & CLAASEN, T. (2006). $\text{SiO}_2/\text{Si}_3\text{N}_4/\text{Al}_2\text{O}_3$ stacks for scaled-down memory devices: Effects of interfaces and thermal annealing. *Appl Phys Lett* **89**, 153506–153508.
- PARK, J.K., PARK, Y., LIM, S.K., OH, J.S., JOO, M.S., HONG, K. & CHO, B.J. (2010). Improvement of memory performance by high temperature annealing of the Al_2O_3 blocking layer in a charge-trap type flash memory device. *Appl Phys Lett* **96**, 222902.
- ROTHSCHILD, A., BREUIL, L., VAN DEN BOSCH, G., RICHARD, O., CONARD, T., FRANQUET, A., CACCIATO, A., DEBUSSCHERE, I.,

- JURCZAK, M., VAN HOUTT, J., KITTL, J.A., GANGULY, U., DATE, L., BOELEN, P. & SCHREUTELKAMP, R. (2009). O₂ post deposition anneal of Al₂O₃ blocking dielectric for higher performance and reliability of TANOS Flash memory. In *Proc. ESSDERC 2009*, pp. 272–275, Athens.
- STÖCKLI, T., BONARD, J.-M., STADELMANN, P.-A. & CHÂTELAIN, A. (1997). EELS investigation of plasmon excitations in aluminum nanospheres and carbon nanotubes. *Z Phys D* **40**, 425–428.
- TAN, Y.N., WEN, H.C., PARK, C., GILMER, D.C., YOUNG, C.D., HEH, D., SIVASUBRAMANI, P., HUANG, J., MAJHI, P., KIRSCH, P.D., LEE, B.H., TSENG, H.H. & JAMMY, R. (2008). Tunnel oxide dipole engineering in TANOS flash memory for fast programming with good retention and endurance. In *International Symposium on VLSI Technology, Systems, and Applications*, pp. 54–55. Hsinchu: IEEE Electron Devices Society.
- TANAKA, I. & ADACHI, H. (1996). Calculation of core-hole excitonic features on Al *L*_{2,3}-edge X-ray-absorption spectra of α -Al₂O₃. *Phys Rev* **B54**, 4604–4608.
- ZIEGLER, A., IDROBO, J.C., CINIBULK, M.K., KISIELOWSKI, C., BROWNING, N.D. & RITCHIE, R.O. (2004). Interface structure and atomic bonding characteristics in silicon nitride ceramics. *Science* **306**, 1768–1770.