

J-1-6

## Properties of $\text{Al}_2\text{O}_3/\text{Nb}_2\text{O}_5$ and $\text{Ta}_2\text{O}_5/\text{Nb}_2\text{O}_5$ Stacked and Mixed Films for Gigabit DRAM Capacitor

Masaki Yamato,<sup>1)</sup> Masami Tanioku,<sup>2)</sup> Hikaru Hara,<sup>1)</sup> and Takamaro Kikkawa<sup>1)</sup><sup>1)</sup> Research Institute for Nanodevice and Bio Systems, Hiroshima University,  
1-4-2 Kagamiyama, Higashi-Hiroshima, 739-8527<sup>2)</sup> Elpida Memory, Inc.,

7-10 Yoshikawakogyodanchi Higashi-Hiroshima, 739-0198

E-mail: yamato-ma@hiroshima-u.ac.jp, kikkawat@hiroshima-u.ac.jp

### 1. Introduction

The requirements for Gigabit DRAM are the leakage current less than 0.1 fA/cell and the capacitor dielectric film physical thickness of approximately 8 nm. Therefore, equivalent oxide thickness (EOT) must be less than 0.7 nm and the leakage current density must be less than  $10^{-8}$  A/cm<sup>2</sup> at 1 V. In order to satisfy the requirements, both wide band gap and high dielectric constant materials must be investigated. In this study, the stacked films shown in Fig. 1, having  $\text{Al}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$  whose thicknesses are less than 10 nm have been investigated as candidates for wider bandgap and higher dielectric constant materials.

### 2. Experimental

After RCA cleaning, Si (100) substrate was cleaned in 0.5 % HF solution. 50 nm thick  $\text{SiO}_2$  was grown by wet oxidation at 1000°C. A 140 nm thick Pt bottom electrode was deposited on  $\text{SiO}_2$  using DC magnetron sputtering at the sputtering power and gas pressure of 50 W and 1 Pa, respectively.  $\text{Al}_2\text{O}_3$  and  $\text{Nb}_2\text{O}_5$  thin films were deposited by RF magnetron sputtering with the sputtering power of 50 W and gas pressure of 2.5 Pa ( $\text{Ar} / \text{O}_2 = 35 / 35$  sccm) at 450°C.  $\text{Ta}_2\text{O}_5/\text{Nb}_2\text{O}_5$  mixed and stacked films were deposited by RF magnetron sputtering with the power of 50 W and gas pressure of 0.5 Pa ( $\text{Ar} / \text{O}_2 = 10 / 10$  sccm) at 300°C. A Pt top electrode was deposited on  $\text{Nb}_2\text{O}_5/\text{Al}_2\text{O}_3$  thin films with a screen mask having  $\phi 1.6$  mm. Sample structure is shown in Fig. 1(a). The films were annealed in a furnace at 600°C in  $\text{O}_2$  ambient for 5 min.

### 3. Results and Discussion

Figure 2 shows loss energy spectra of  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$  films. The bandgap was determined by the difference between core level peak of the O1s and the threshold of the energy loss spectra [1]. The band gaps of  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$  were determined as 4.25 eV, 4.70 eV and 6.80 eV, respectively. Figure 5 shows valence band spectra of Pt,  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$ . The valence band offset from Fermi level of Pt was calculated by differentiating threshold energies of photoelectron intensities between  $\text{Nb}_2\text{O}_5$  and Pt,  $\text{Ta}_2\text{O}_5$  and Pt, and  $\text{Al}_2\text{O}_3$  and Pt, respectively. The valence band offset of  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$  were 2.60 eV, 2.90 eV and 3.10 eV, respectively. The conduction band offset was calculated from the difference between the band gap and the valence band offset. The conduction band offset of  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$  were calculated as 1.65 eV, 1.80 eV and 3.70 eV, respectively. Figure 4 shows the leakage current density of  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$ . The  $\text{Ta}_2\text{O}_5$  and the  $\text{Al}_2\text{O}_3$  films which have wider band gap suppressed leakage current than  $\text{Nb}_2\text{O}_5$  film. Figure 5 shows the influence of the thickness on the dielectric constant and the EOT. All films were crystallized, and oriented  $\text{Nb}_2\text{O}_5$  (001) and (002). The dielectric constant decreased as the  $\text{Nb}_2\text{O}_5$  thickness decreased below 20 nm. The EOT was approximated as a straight-line and intercepted at about 0.4 nm of EOT. Therefore,  $\text{Nb}_2\text{O}_5$  film has an interface layer whose dielectric constant was lower than the crystalline layer. Then, the EOT of  $\text{Nb}_2\text{O}_5$  film was calculated by the following equation.

$$EOT = \frac{3.9 \times d}{k_c} - \frac{3.9 \times d_A}{k_A} + \frac{3.9 \times d_A}{k_A} \quad (1)$$

Where,  $d$  is the thickness of  $\text{Nb}_2\text{O}_5$  film,  $k_c$  is the dielectric constant of crystalline layer,  $k_A$  is the dielectric constant of interface layer,  $d_A$  is thickness of the interface layer. By using the slope of the fitted line, the dielectric constant of the crystalline  $\text{Nb}_2\text{O}_5$  layer was found to be 158. Figure 6 shows XRD spectra of  $\text{Nb}_2\text{O}_5/\text{Pt}$  and  $\text{Nb}_2\text{O}_5/\text{Sr}_5\text{Nb}_9\text{O}_{25}/\text{Pt}$  films.  $\text{Nb}_2\text{O}_5/\text{Sr}_5\text{Nb}_9\text{O}_{25}/\text{Pt}$  film did not show  $\text{Nb}_2\text{O}_5$  diffraction peak. This is because the mismatch of the lattice constants between  $\text{Nb}_2\text{O}_5$  and  $\text{Sr}_5\text{Nb}_9\text{O}_{25}$  occurred and the resulting dielectric constant became as low as 51.  $d_A$  was calculated by use of equation (1) and  $k_A = 51$  as well as y-intercept of the fitted line in Fig.7. The calculated value of  $d_A$  was 4.9 nm. Figure 7 shows  $\text{Nb}_2\text{O}_5$  thickness versus the XRD intensity peak of  $\text{Nb}_2\text{O}_5(001)$  annealed at 600°C and 800°C. The thickness of the interface layer can be obtained by the intercept of x-axis. The thicknesses of NbO interface layers annealed at 600°C and 800°C were 4.60 nm and 4.52 nm, respectively. The thicknesses of the interface layers are in good agreement with the electrical properties, and they showed no dependence on anneal temperatures. Figures 8 and 9 show the influences of  $\text{Al}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$  thicknesses on the dielectric constant and the EOT, respectively. The dielectric constant stayed constant as approximately 8.5 and 23, respectively. The fitted lines of EOT did not have the intercept, so that  $\text{Al}_2\text{O}_3$  and  $\text{Ta}_2\text{O}_5$  films were found to be homogeneous. In order to achieve thinner EOT and lower leakage current, mixed and stacked films are investigated. At first,  $\text{Al}_2\text{O}_3/\text{Nb}_2\text{O}_5$  stacked films were investigated. The structure of stacked film was  $\text{Pt}/\text{Al}_2\text{O}_3/\text{Nb}_2\text{O}_5/\text{Pt}/\text{SiO}_2$  as shown in Fig.1(b). Figures 10 and 11 show the EOT and the leakage current density at 1V, respectively.  $\text{Nb}_2\text{O}_5$  thicknesses were fixed at 6 nm and 10 nm, while  $\text{Al}_2\text{O}_3$  thickness was varied. The EOT decreased and the leakage current density at 1V increased with decreasing the  $\text{Al}_2\text{O}_3$  thickness. The minimum EOT of 1.30 nm was obtained with suppressing leakage current at  $6 \times 10^{-8}$  A/cm<sup>2</sup> at 1V. Figures 12 and 13 show the loss energy spectra of O1s and the leakage current at 1V for TaNbO mixed films. The band gap of TaNbO mixed film increased with increasing Ta content so that the leakage current decreased. The EOT and the leakage current density at 1V for TaNbO mixed films and  $\text{Ta}_2\text{O}_5/\text{Nb}_2\text{O}_5$  stacked films were investigated as shown in Figs.14 and 15. Film structures are shown in Figs.1(c), (d) and (e). The minimum EOT of 0.66 nm was obtained with suppressing leakage current at  $2.6 \times 10^{-8}$  A/cm<sup>2</sup> at 1V by using  $\text{Nb}_2\text{O}_5/\text{Ta}_2\text{O}_5/\text{Nb}_2\text{O}_5$  stacked structure whose Ta content was 25 %.

### 4. Conclusion

By using  $\text{Nb}_2\text{O}_5/\text{Ta}_2\text{O}_5/\text{Nb}_2\text{O}_5$  stacked structure whose Ta content was 25 %, minimum EOT of 0.66 nm was obtained with suppressing leakage current at  $2.6 \times 10^{-8}$  A/cm<sup>2</sup> at 1V. For  $\text{Al}_2\text{O}_3/\text{Nb}_2\text{O}_5$  stacked films, the EOT could not be reduced less than 1 nm when the  $\text{Al}_2\text{O}_3$  thickness was 2 nm. This is attributed to the fact that  $\text{Nb}_2\text{O}_5$  has an interface layer between  $\text{Nb}_2\text{O}_5$  and Pt, whose thickness and dielectric constant were 4.6-4.9 nm and 51, respectively.

### Reference

[1] S. Miyazaki, J. Vac. Sci. Technol. B **19**, 2212 (2001)

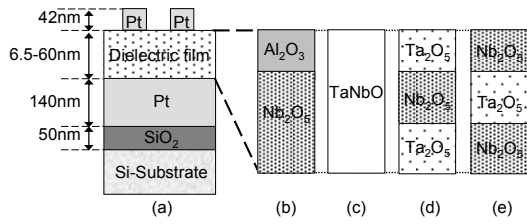


Fig. 1. Cross-sectional structures of MIM capacitors (a). (b)  $\text{Al}_2\text{O}_3/\text{Nb}_2\text{O}_5$ . (c)  $\text{Ta}_x\text{Nb}_{1-x}\text{O}_z$ . (d)  $\text{Ta}_2\text{O}_5/\text{Nb}_2\text{O}_5/\text{Ta}_2\text{O}_5$ . (e)  $\text{Nb}_2\text{O}_5/\text{Ta}_2\text{O}_5/\text{Nb}_2\text{O}_5$ .

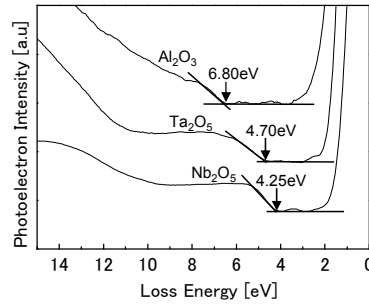


Fig. 2. Loss energy spectra of O1s of  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$ .

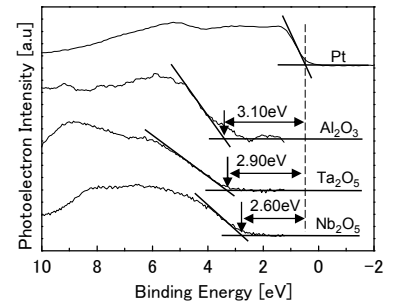


Fig. 3. Valence band spectra of  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$ .

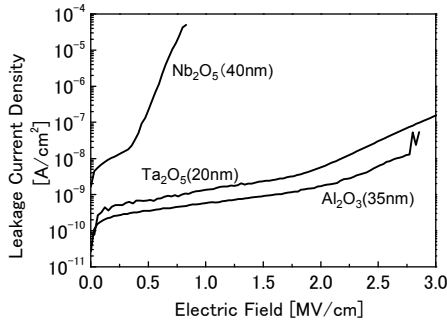


Fig. 4. Leakage current density of  $\text{Nb}_2\text{O}_5$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{Al}_2\text{O}_3$  versus electric field.

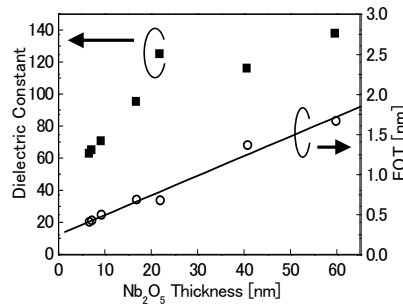


Fig. 5. Dielectric constant and EOT versus  $\text{Nb}_2\text{O}_5$  thickness.

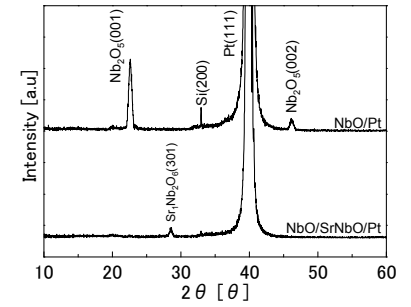


Fig. 6. X-ray diffraction spectra of  $\text{Nb}_2\text{O}_5/\text{Pt}$  and  $\text{Nb}_2\text{O}_5/\text{SrNbO}_{2.5}/\text{Pt}$  structures.

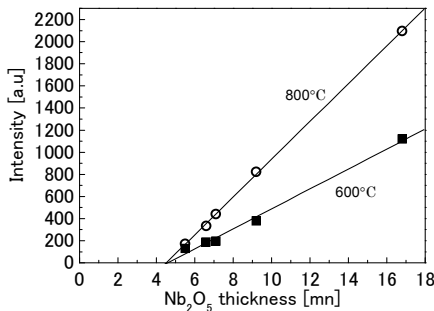


Fig. 7. Intensity of x-ray diffraction spectra of  $\text{Nb}_2\text{O}_5$  (001) versus  $\text{Nb}_2\text{O}_5$  thickness.

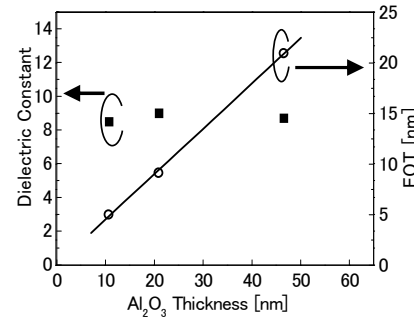


Fig. 8. Dielectric constant and EOT versus  $\text{Al}_2\text{O}_3$  thickness.

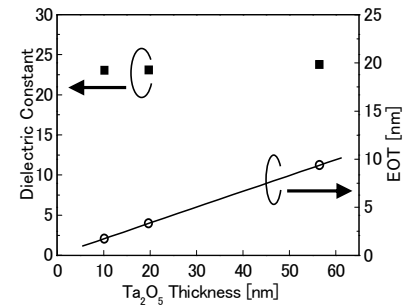


Fig. 9. Dielectric constant and EOT versus  $\text{Ta}_2\text{O}_5$  thickness.

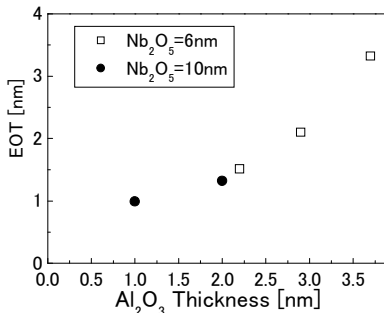


Fig. 10. EOT versus  $\text{Al}_2\text{O}_3$  thickness for  $\text{Al}_2\text{O}_3/\text{Nb}_2\text{O}_5$  stacked films.

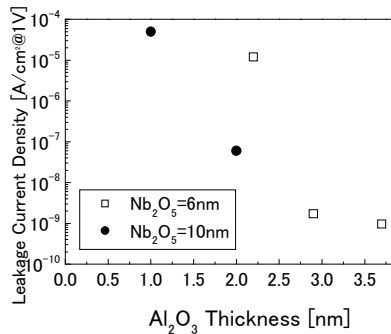


Fig. 11. Leakage current density at 1V versus  $\text{Al}_2\text{O}_3$  thickness for  $\text{Al}_2\text{O}_3/\text{Nb}_2\text{O}_5$  stacked films.

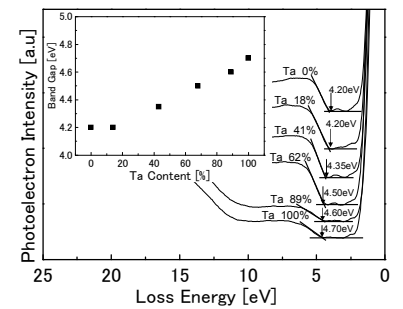


Fig. 12. Loss energy spectra for  $\text{Ta}_x\text{Nb}_{1-x}\text{O}_z$  mixed film.

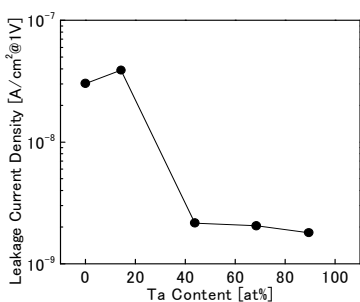


Fig. 13. Leakage current density at 1V versus Ta content for  $\text{Ta}_x\text{Nb}_{1-x}\text{O}_z$  mixed film.

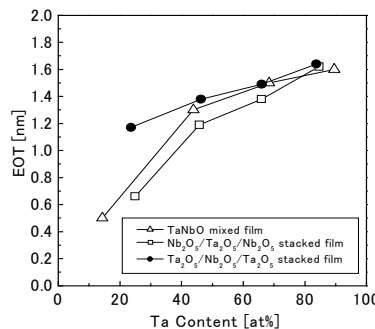


Fig. 14. EOT versus Ta content for  $\text{Ta}_2\text{O}_5/\text{Nb}_2\text{O}_5$  stacked and mixed films.

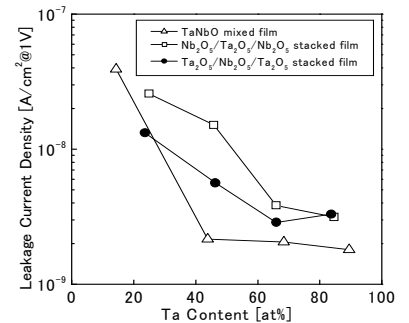


Fig. 15. Leakage current density versus Ta content for  $\text{Ta}_2\text{O}_5/\text{Nb}_2\text{O}_5$  stacked and mixed films.