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HAX-PES Study of SiN Film for Charge Storage Layer in High Performance SONOS Type Flash Memory Cell

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1. Introduction

Hard X-ray photoelectron spectroscopy (HAX-PES) is a research field that receives an increasing interest due to the possibility of studying bulk properties of materials and deeply buried interfaces [1]. In this study, SiN films were investigated by HAX-PES. We prepared various SiN films for charge storage layer in high performance silicon-oxide-nitride-oxide-silicon (SONOS) type flash memory cell by microwave plasma-enhanced chemical vapor deposition (CVD). We considered the mechanism of charge trapping in the SiN film by comparing the result of electrical properties and HAX-PES. Detailed depth profiles of chemical states in the SiN films were also obtained by HAX-PES.

2. Experimental procedure

Table 1 shows the process conditions for SiN deposition. There are three kinds of SiN films deposited on 4 nm SiO_2/Si substrates at 450 ^oC by microwave plasma-enhanced CVD. The SiN film thicknesses were approximately 8 nm. H concentrations in SiN films obtained by secondary ion mass spectroscopy were 1.64E+20 cm^{-3} for SiN #1 and 9.63E+21 cm^{-3} for SiN #3, respectively. O_2 gas flow was implemented in the deposition process for the SiN #2. Moreover, thick SiN films of approximately 20 nm were also prepared for evaluating the depth profiles of chemical states in detail.

HAX-PES measurements were performed using hemispherical electron energy analyzer SCIENTA R-4000 at BL46XU in SPring-8 (#2008B2073). Incident photon energy is approximately 7940 eV, and then ejected photoelectrons have large escaping depth due to high kinetic energy. For example in this study, Si 1s, Si 2p, N 1s, and O 1s have kinetic energies between 6100 to 7790 eV, the inelastic mean free path of which was approximately 17 nm [1]. Total energy resolution of the measurement was estimated to be 235 meV by measuring Fermi edge of gold. We obtained chemical information corresponding several depths by changing photoelectron's take-off angle (TOA) from sample to analyzer as shown in Fig. 1. HAX-PES measurements were performed after native oxide removal by diluted HF treatment. X-ray reflectometry measurements were also performed with 12.4 KeV X-rays at BL46XU in SPring-8 to obtain film densities.

Electrical characteristics of SONOS type memory cells with the films shown in Table 1 were compared with the chemical states of the SiN films.

3. Results and discussion

Electrical properties

Figure 2 shows flat band voltage shifts as a function of program operation time. The program voltage was 25 [V]. Figure 3 shows retentions as a function of program voltage after annealing at 300 ^oC for 1 hr. As shown in Figs. 2 and 3, the memory cells with the H-less SiN #1 and #2 have higher charge storage properties than that with the conventional SiN #3. Moreover, O_2 flow in the deposition process was effective for the increase of the flat band shift as shown in Fig. 2.

Chemical states in H-less and conventional SiN films

Si 1s photoelectron spectra were compared between the SiN films #1 and #3 in Fig. 4. Peaks of the kinetic energies of approximately 6100, 6096, and 6094 eV correspond to Si-Si bond in Si substrate, Si-N bond in SiN film, and Si-O bond in SiO_2 layer, respectively. Moreover, one faint peak was observed between 6096 and 6100 only in the spectrum from the H-less SiN #1 (as indicated by the arrow in Fig. 4(a)).

N 1s photoelectron spectra from the H-less and conventional SiN films are shown in Fig. 5. As shown in this figure, it was clarified that the kinetic energy of N 1s photoelectron from the H-less SiN #1 had lower energy and that the full width at half maximum was larger than that from the conventional SiN #3. This implies that O with high electronegativity was in the vicinity of N in the SiN film [2]. As shown in Fig. 6, N 1s binding energies (BEs) and densities of the SiN #1 and #3 clearly indicates that the higher BE of N 1s in the SiN #1 was not caused by the density. Therefore, the peak between 6096 and 6100 eV as indicated in Fig. 4 may be caused by the intermediate states originated in Si-O bonds in SiN. As results, The H-less SiN #1 should have large amount of the intermediate state originated in Si-O bonds which may be caused by O diffusion.

On the other hand, for the conventional SiN #3, an amount of the intermediate state was reduced as shown in Fig. 4. This indicates that H blocked forming the Si-O bonding. Therefore, we consider that the H-less SiN film with many charge trapping sites improved the electrical properties of SONOS type flash memory cell as shown in Figs. 2 and 3 [3].

Chemical state depth profiles

Figure 7(a) shows the N 1s photoelectron spectra as a function of TOA for the hydrogen-less SiN with O_2 flow. In Fig. 7(b), each profile was obtained by subtraction of the

data with the 1st smaller TOA from the original data as follows: the profile of 55° in Fig. 7(b) was subtraction of the observed data at 30° from those at 55°. Figure 8 shows the depth profiles of N 1s BEs for the SiN films with and without O_2 flow, extracted from the processed data similar to Fig. 7(b). It was clearly seen that the chemical state depth profiles depended on the deposition conditions, as shown in Fig. 8. The difference of depth profiles in the SiN films with and without O_2 flow was observed especially at TOA of 80° which means the deep region close to SiN/SiO_2 interface. For the SiN film with O_2 flow, BE energy at TOA of 80° showed higher than at 15°, 30°, and 55°. This may indicate that there are more Si-O bonds at the SiN/SiO_2 interface than at the interlayer owing to the O_2 flow in the deposition process. As results, the write operation properties of memory cell were improved for the SiN #2 with O_2 flow as shown in Fig. 2.

4. Conclusions

Various SiN films were studied by HAX-PES. The results from HAX-PES and electrical properties were compared to clarify the charge trapping mechanism. As results, H-less SiN has large amount of intermediate state originated in Si-O bonds. On the other hand, for the conventional SiN, an amount of intermediate state was reduced. This indicates that H blocked forming the Si-O bonding. Therefore, we assume that the H-less SiN film with many charge trapping sites improved the electrical properties of SONOS type flash memory cell.

Chemical state depth profiles for the SiN films with and without O_2 flow were evaluated by changing photoelectron's TOA from sample to analyzer. For the SiN films with O_2 flow, N 1s BE energy at TOA of 80° showed higher than at 15°, 30°, and 55°. This may indicate that there are more Si-O bonds at the SiN/SiO_2 interface than at the interlayer owing to the O_2 flow in the deposition process. As results, the write operation properties of memory cell were improved for the SiN with O_2 flow.

References

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Table 1 Sample conditions

Sample #	Hydrogen	Note
1	Less	
2	Less	O_2 flow
3	Much	

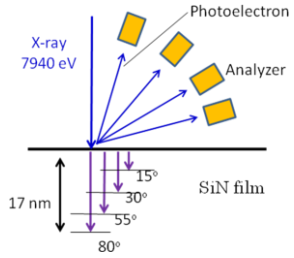

Fig. 1 Schematic image of measurement to obtain chemical depth profiles by changing TOA.

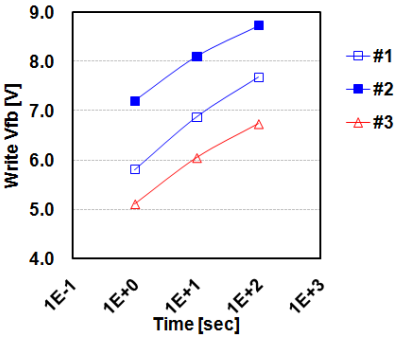

Fig. 2 Flat band voltage shifts as a function of program operation time for SONOS type memory cells with SiN #1 - 3.

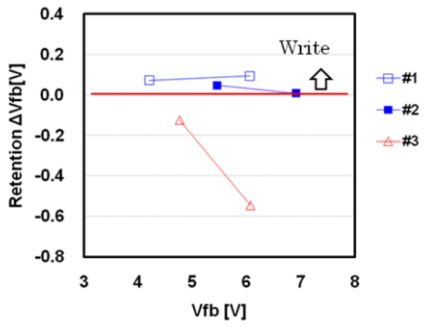

Fig. 3 Retentions as a function of program voltage after annealing at 300 °C for 1 hr for SONOS type memory cells with SiN #1 - 3.

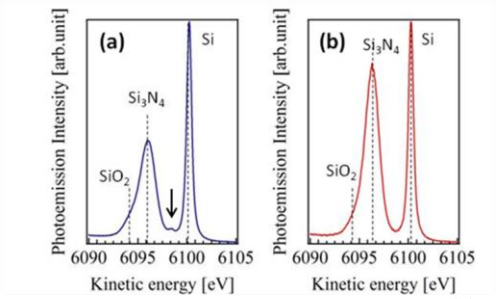

Fig. 4 Si 1s photoelectron spectra from (a) SiN #1 (b) #3.

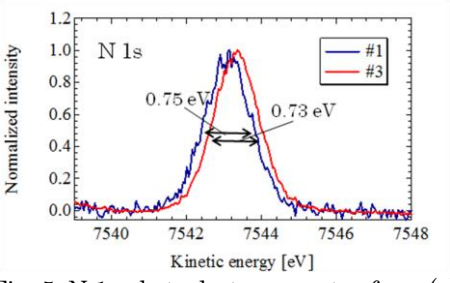

Fig. 5. N 1s photoelectron spectra from (a) SiN #1 and (b) #3.

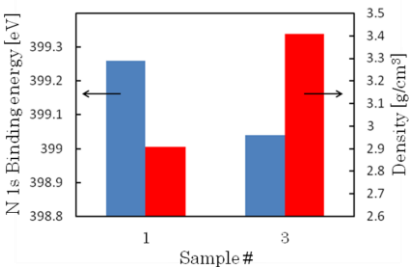

Fig. 6. N 1s BE energies and densities of SiN #1 and #3.

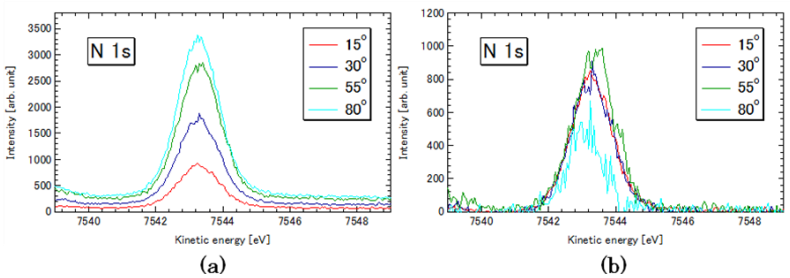

Fig. 7 (a) N 1s photoelectron spectra as a function of take-off angle for hydrogen-less SiN with O_2 flow, (b) subtraction of data with 1st smaller TOA from original data.

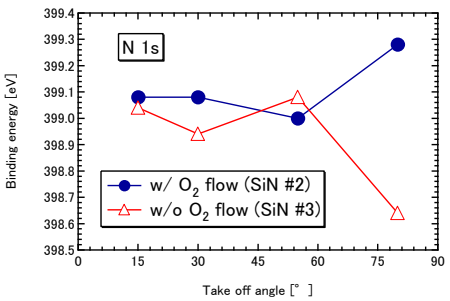

Fig. 8 Depth profiles of N 1s BE energies for SiN with and without O_2 flow.