Estimation of Charge Trap Positions in Silicon Nitride Films Using Voltage-applied Hard X-ray Photoelectron Spectroscopy

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1. Introduction

Silicon nitride (Si_3N_4, hereafter referred to as SiN) films are used as charge trapped layers in three-dimentional NAND flash memory [1]. Previous studies have used electrical measurements to estimate the charge centroid and trap level of charges [2,3], but there are no studies that provide a physical evaluation of the distribution of charges trapped in SiN. In this study, in-situ voltage-applied angle-resolved hard X-ray photoelectron spectroscopy (AR-HAXPES) measurements were performed on devices with a metal-nitride-oxide-semiconductor (MNOS) structure, and the positions of charge traps were estimated by determining the potential distribution from the photoelectron spectrum shape.

2. Experimental Procedure

The experiment was performed on a SiN film of approximatly 5 nm deposited by chemical vaper deposition on a 5 nm-SiO_2/p-Si substrate. The raw materials are Dichlorosilane (DCS) or Hexachlorodisilane (HCDS). The sample preparation conditions are shown in Table 1. Different top electrodes were then deposited for C–V and HAXPES measurements. Electrical measurements were performed in a MNOS capacitor structure with Al electrodes deposited on both sides of the sample using a resistance heating evaporation method. The top electrodes for the HAXPES measurement samples were approximatly 10 nm Ni films deposited by resistance heating evaporation method. Voltage-applied AR-HAXPES measurements were performed at BL09XU of SPring-8 [4]. The Ni electrode was grounded, and a voltage was applied to the back contact of the p-Si(100) substrate. In the figure and text, the polarity of the applied voltage is indicated by the potential of the Ni electrode relative to p-Si(100) substrate. The N 1*s*, O 1*s*, Ni 2*p* and Si 1*s* photoelectron spectra were measured at a photoelectron take-off angle (TOA) range from 10° to 70°. The excitation X-ray energy of 7935 eV.

3. Results and Discussion

The C–V measurement results shown in Fig. 1 are for SiN samples produced from HCDS as the raw material. The flat-band voltage (V_{FB}) has shifted in the positive direction, indicating that electron trapping has occurred throughout the sample. The initial V_{FB} value is shifted more negatively than the value estimated from the work function difference between Al and p-Si(100), suggesting that hole may be present within the film as an initial charge. The HAXPES measurement results in Fig. 2 show that the Si 1*s* photoelectron spectra from SiN and SiO_2 shift before and after -7 V application. Figure 3 shows the V_{FB} calculated from the full width at half maximum (FWHM) of the SiO_2 peak. HAXPES measurements were performed while applying voltage, and the FWHM was determined using linear extrapolation. The result of determining the V_{FB} based on the intersection point was approximately -0.5 V. When comparing the V_{FB} obtained from C–V measurements with that obtained from HAXPES measurements, this V_{FB} is a reasonable value when considering the work function difference between Al and Ni. Figure 4 shows the chemical shift between p-Si(100) and SiN. Before voltage application, TOA dependence suggests that the surface region of the sample exhibits smaller chemical shifts compared to the interior, indicating that electrons may be confined within the SiN layer. Figure 5 shows the change in the binding energy of Si 1*s* photoelectrons from SiO_2 and SiN before and after voltage application. The shift of the SiN peak towards the high binding-energy side suggested either hole trapping or electron release. Considering the TOA dependence of the shift, it can be assumed that the charge is uniformly distributed within the SiN film. On the other hand, the SiO_2 peak is shifted in the opposite direction to the SiN peak, suggesting the possibility of counter charges occurring at the SiN/SiO_2 interface. From the perspective of charge centroid, electrical characteristics are greatly affected by charges existing at the SiN/SiO_2 interface rather than charges in the SiN film near the top electrode. Therefore, assuming that hole traps are uniformly distributed in the SiN film, the charge centroid becomes closer to the electrode, and the effect on the electrical characteristics becomes relatively small. This does not contradict the fact that electron traps are observed in the C–V measurement results.

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4. Conclusions

In the C–V measurement, a positive V_{FB} shift was observed, confirming the presence of electron traps within the insulating film. HAXPES results indicate that holes are uniformly trapped in SiN films and that electron traps exist at the SiN/SiO_2 interface. Considering the charge centroid, this is consistent with the C–V measurement results.

Acknowledgements

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References

[1] H. Tanaka et al., in *2007 IEEE Symposium on VLSI Technology* pp. 14. [2] R. Kawashima et al., Jpn. J. Appl. Phys. **62**, SG1035 (2023). [3] H. Seki et al., Jpn. J. Appl. Phys. **58**, SBBK02 (2019). [4] A. Yasui et al., J. Synchrotron Radiat. **30**, 1013 (2023).

Table I The sample preparation conditions.

Materials	Temp. (°C)	Thickness (nm)
Dichlorosilane (DCS)	640	5
Hexachlorodisilane (HCDS)	700	5

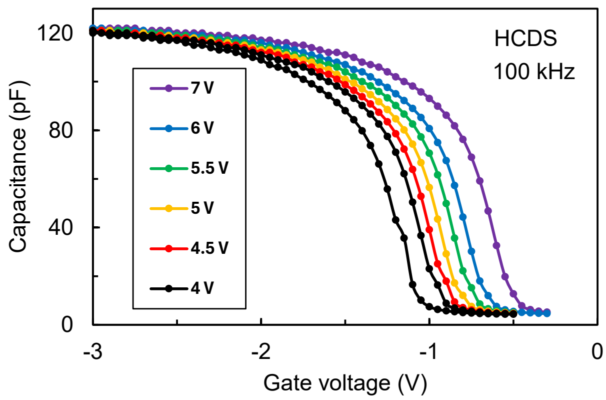

Fig. 1 The C–V measurement results of samples using HCDS.

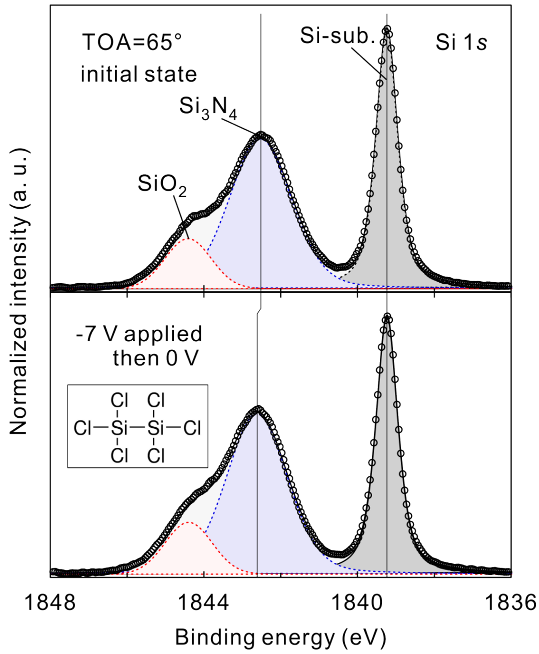

Fig. 2 Measurement results of Si 1*s* photoelectron spectroscopy spectra of samples using HCDS materials.

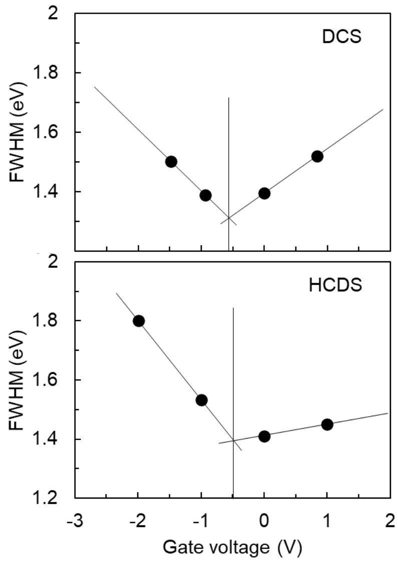

Fig. 3 Estimation of the flat band voltage from the voltage dependence of the FWHM of the SiO_2 peak.

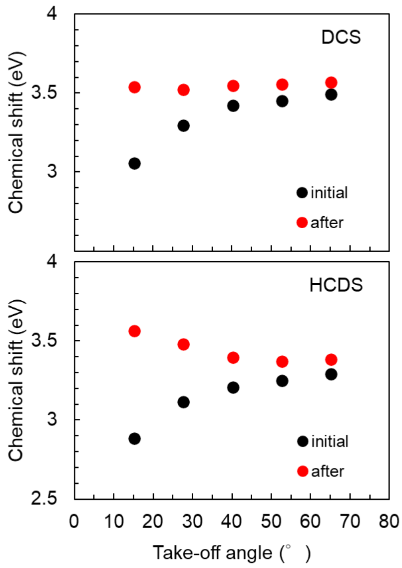

Fig. 4 Chemical shift between SiN peak and p-Si(100) substrate peak before and after voltage application.

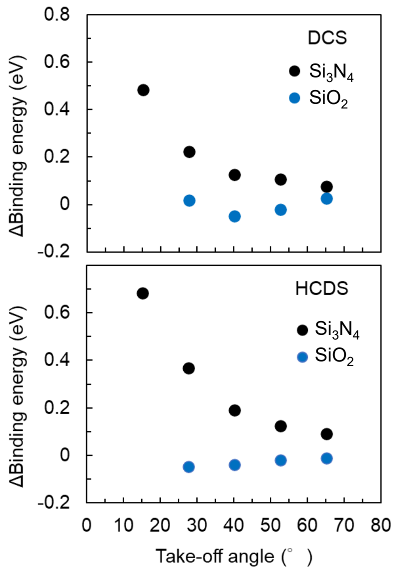

Fig. 5 Changes in the binding energy of SiN peaks and SiO_2 peaks before and after voltage application.

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