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Effect of nano-grain on the memory characteristics of high-k HfAlO charge trapping layers for nano-scale non-volatile memory device applications

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1. Introduction

Nanocrystal floating gate memory devices have been reported extensively and it has uniformity problem [1]. Polysilicon-oxide -silicon-nitride (Si_3N_4)-oxide-silicon (SONOS) flash memory devices have been also reported, but it has poor retention and scaling issue [2]. High-κ charge trapping layers such as HfAlO or HfO_2 films in metal-oxide-high-κ-oxide-silicon (MOHOS) structure are demanded in the semiconductor industry for future nano-scale non-volatile memory (NVM) device applications [3-6]. To get a high performance flash memory devices, the HfAlO charge trapping layer with an Al_2O_3 blocking oxide in metal-Al_2O_3-high-κ-SiO_2-Si (MAHOS) structure formed by atomic layer deposition (ALD) has been proposed. In this study, the superior memory characteristics of HfAlO charge trapping layers have been investigated, for the first time, due to charge storage in the nano-grains. The term nano-grain is defined the grain which is isolated by other gains and the size is in nano-scale. The pure HfO_2 and Al_2O_3 charge trapping layers have been also studied for comparison.

2. Experimental

A p-type Si (100) wafer with a resistivity of 15-25 Ω.cm was cleaned by the RCA process. After cleaning the wafer, a high quality tunneling oxide of SiO_2 having a thickness of 3 nm was grown by RTO system at a temperature of 1000°C for 20s. Then, the high-κ HfO_2 and Al_2O_3 films were deposited by ALD using hafnium tetrachloride ($HfCl_4$) and trimethylaluminium [$Al(CH_3)_3$] precursors, respectively, at substrate temperature of 300°C. The thickness of HfAlO charge trapping layer was ~10 nm. Then, the Al_2O_3 blocking oxide with a thickness of ~10 nm was deposited *in-situ* on HfAlO charge trapping layers. For comparison, the HfO_2 charge trapping layer with a thickness of ~10 nm and the Al_2O_3 blocking oxide with a thickness of ~10 nm were grown. The Al_2O_3 charge trapping layer with a thickness of ~20 nm was deposited on SiO_2 (~3 nm-thick) treated p-Si substrate for comparison. The hysteresis memory windows were very small for as-deposited films. To get high charge trapping characteristics as well as large hysteresis memory window, the post deposition annealing (PDA) treatment at 900°C for 1 min in N_2 ambient has been performed. To study the memory characteristics, the platinum (Pt) metal as a gate electrode (area: $1.12x10^{-4}$ cm^2) was deposited by sputtering using shadow mask. The post metal annealing with a temperature of 400°C and 5 min was done using forming gas ambient. The microstructure characteristics of memory devices were carried out using FEI Tecnai F30 field emission gun TEM equipped with EDS detector for high-resolution image and compositional analysis.

3. Results and discussion

Fig 1 shows the HRTEM images of pure Al_2O_3 and HfAlO charge trapping layers at PDA treatment of 900°C for 1 min in N_2 ambient. After the PDA process, the pure HfAlO or HfO_2 film shows polycrystalline and the Al_2O_3 film shows partial crystalline. All memory structures show amorphous for as-deposited samples. After the annealing process, the thickness of tunneling oxide for pure Al_2O_3 film has been increased (~3 to ~4.3 nm) and it may be due to inter-diffusion between SiO_2 and Al_2O_3 layers [Fig. 1(a)]. The thickness of Al_2O_3 film has been decreased (~20 to ~17 nm), due to densification of high-κ films after annealing treatment. The thickness of HfAlO charge trapping layer has been decreased (~10 to ~8 nm) and the thickness of Al_2O_3 blocking oxide has been increased (~10 to ~12 nm) [Fig. 1(b)], indicating that the diffusion velocity of Al in Al_2O_3 to HfAlO direction is faster than that of Hf (and Al) in HfAlO to Al_2O_3 direction causing the interface moving toward HfAlO film. The composition ratio of Hf:Al:O measured by EDS is found to be 1.3:1.0:3.0 (Fig. 2). A large C-V hysteresis memory window of ~8.6 V@V_g=±16V with a small capacitance equivalent thickness of ~8 nm has been observed for HfAlO memory devices (Fig. 3). A maximum hysteresis memory window of HfAlO charge trapping layer is higher as compared with pure HfO_2 and Al_2O_3 charge trapping layers (Fig. 4), due to the charge storage in nano-grains. A high trapped charge density is calculated using this equation: $Q_{charge}=(+V_{FB}-V_{FBN})*C_{ox}]/(q.A)=1.2x10^{13}/cm^2$, where C_{ox} is the capacitance at accumulation region and 'A' is the gate area. The hysteresis memory windows are found to be 4.8 V, 3.9 V and 1.4 V @V_g=±10V for pure HfO_2, HfAlO and Al_2O_3 memory devices, respectively. It indicates that an operation voltage of the HfAlO or HfO_2 memory devices is smaller as compared with a pure Al_2O_3 device, due to smaller conduction band offset [$(\Delta E_c)_{HfO2}$~1.7 eV and $(\Delta E_c)_{Al2O3}$~2.8 eV)]. The HfAlO devices show similar memoy window to the pure HfO_2 layers at low gate voltage and it can be used for high-speed memory device applications. Fig. 5 shows the plan view TEM of nano-grains with diameter of 15-20 nm with an uniform size. The HfAlO nano-grains have been observed by SAED pattern (Fig. 6). Schematic band diagrams of HfAlO charge storage layers under program/erase mode are shown in Fig. 7. It indicates that the charge can be stored in the nano-grains which is similar to charge storage in the nano-crystals. The HfAlO charge trapping layer has lower backward tunneling current (similar to pure Al_2O_3 film) and it can be easily erased than that of pure HfO_2 film (Fig. 8). The HfAlO charge trapping layers can be operated up to large gate voltage of ~18V. The HfAlO memory devices have superior retention as compared with a pure HfO_2 memory device (Fig. 9). The retention characteristics of HfAlO charge trapping layers is shown in Fig. 10. An excellent retention is observed on 10 years of projection. A large memory window of ~5.7 V is observed after 10 years of retention, due to charge storage in nano-grains. The HfAlO memory device has low charge loss of ~25%. Due to large memory window and long retention of the HfAlO charge trapping layers, it can be used in future multi-level charge (MLC) storage nano-scale memory device applications.

4. Conclusions

The HfAlO charge trapping layers with an Al_2O_3 blocking oxide have large memory window with an excellent retention characteristics. The superior memory characteristics of the HfAlO charge trapping layers have been observed due to charge storage in the nano-grains and it can be used in the semiconductor market for future high-performance nano-scale flash memory device applications.

References

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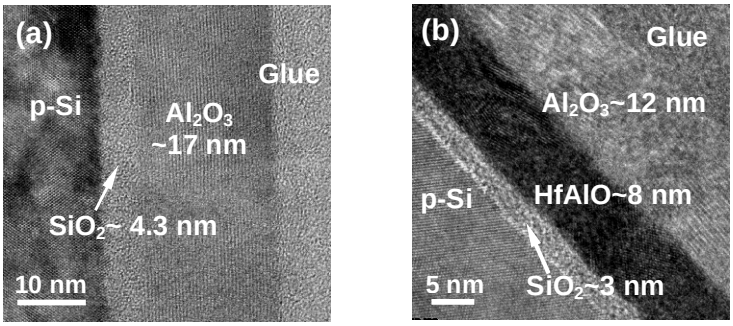

Fig. 1 Cross-sectional TEM images of (a) pure Al_2O_3 and (b) HfAlO charge trapping layers with an Al_2O_3 blocking oxide.

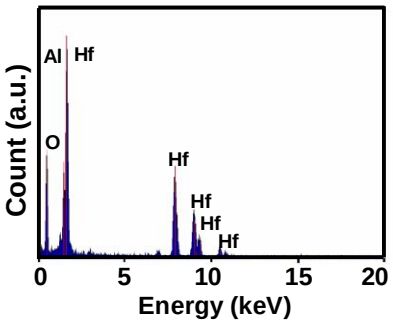

Fig. 2 EDS spectrum of the HfAlO charge trapping layers.

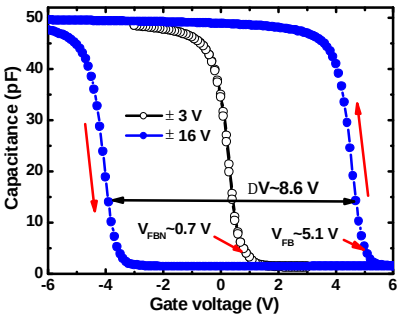

Fig. 3 A large C-V (1MHz) hysteresis memory window is observed for HfAlO charge trapping layer. The hold time was 100 ms during C-V measurement.

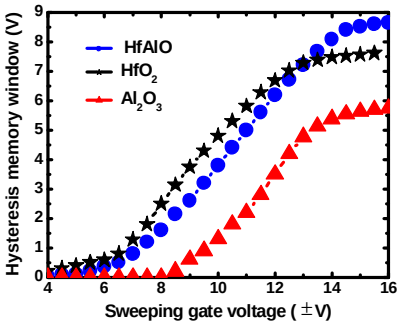

Fig. 4 Hysteresis memory window versus sweeping gate voltage for all memory devices.

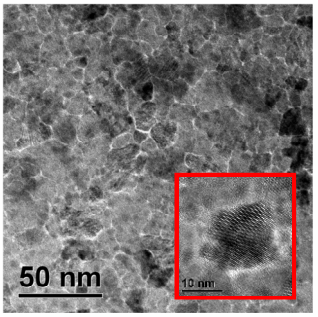

Fig. 5 Plan view TEM on HfAlO layer in p-Si/SiO_2/HfAlO/Al_2O_3 structure shows nano-grains. A single nano-grain is observed in HfAlO layer in the inset.

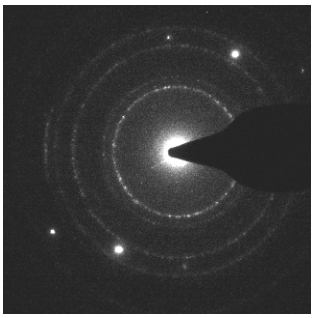

Fig. 6 Selected area electron diffraction (SAED) pattern on the HfAlO nanolayers.

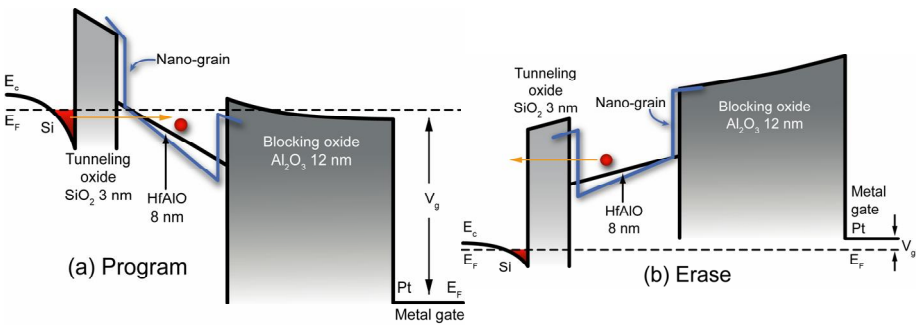

Fig. 7 Schematic energy band diagrams of p-Si/SiO_2/HfAlO nano-grain/Al_2O_3 /Pt memory structure are shown under the devices (a) program mode and (b) erase mode. The high-κ Al_2O_3 as a blocking oxide has been used to suppress the back tunneling current and to increase the program/erase speed.

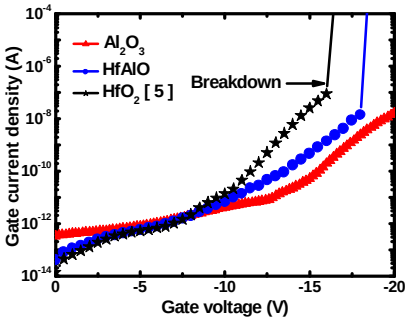

Fig. 8 The leakage current of HfAlO charge trapping layer is similar with pure Al_2O_3 charge trapping layers up to gate voltage of -18 V.

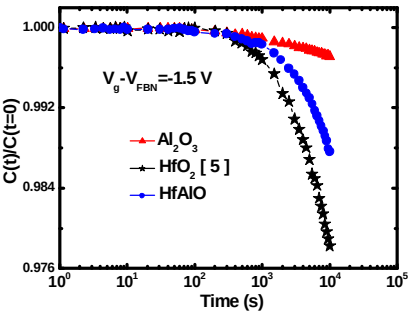

Fig. 9 Capacitance versus elapsed time (C-t) characteristics of all memory devices. All charge trapping devices were stressed with V_g-V_{FBN}=6V, 60s before C-t measurement.

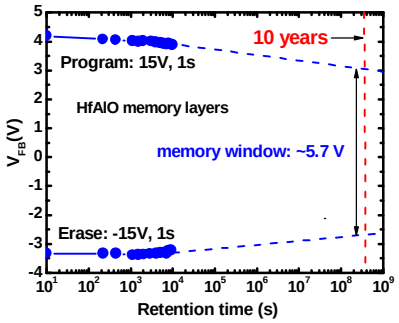

Fig. 10 Retention characteristics of HfAlO charge trapping layers. A large memory window of ~5.7 V is observed after 10 years of retention.