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Nanoscale (EOT= 5.6 nm) nonvolatile memory capacitors using atomic layer deposited high-k HfAlO nanocrystals

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1. Introduction

In the last decade, the nanocrystal based nonvolatile memory (NC-NVM) devices have been attracted the interest due to their potential in the semiconductor industry to overcome the limitations of the polycrystalline-silicon-oxide-[silicon-nitride]-oxide-silicon (SONOS) memory [1]. The high-κ charge trapping layers such as HfO_2, ZrO_2, Ta_2O_5, HfAlO films in a SONOS-type memory structure have been reported [2-3]. To improve the memory performance, metal nanocrystal memory devices have also been reported extensively [4-6], but it has integration problem. To overcome the integration and scaling problems, the high-κ nanocrystal memories with advantages of good scalability (<22 nm technology node), low program/erase voltage operation, high speed, highly nonvolatile, highly reproducible and uniform, etc are an alternative solution for next generation of nanoscale memory applications. The atomic layer deposited (ALD) high-κ nanocrystal has the strong potential for future nanoscale nonvolatile memory devices in our daily life, which is not reported yet. In this study, we have demonstrated the atomic layer deposited high-κ HfAlO nanocrystal memory in an n-Si/SiO_2/HfAlO (NC)/Al_2O_3/Pt structure for the first time. Furthermore, the high-κ Al_2O_3 film as a blocking oxide has been used for easy scaling of the high-κ nanocrystal memory devices.

2. Experimental

The n-type Si (100) wafers with a doping of $>1\text{x}10^{17}/\text{cm}^3$ were cleaned by the standard RCA process. After removing the native oxide from the surface of the wafers, a high quality tunneling oxide of SiO_2 was grown by RTO system at a temperature of 1000°C for 15s, which has the thickness of 3 nm. Then, the high-κ HfO_2 and Al_2O_3 films were deposited by ALD. Then, an aluminum oxide (Al_2O_3) with a thickness of 12 nm was deposited by ALD. The deposition of high-κ films can be found in detail elsewhere [2]. After deposition of all high-κ films the post deposition annealing (PDA) treatment was carried out to form the HfAlO nanocrystal and to improve the charge storage characteristics at a temperature of 900°C for 1 min in N_2 ambient. The platinum (Pt) metal gate electrode (area: $1.12\times10^{-4}\,\text{cm}^2$) was deposited by sputtering. A schematic structure of the HfAlO nanocrystal memory capacitor is shown in Fig. 1.

3. Results and discussion

Fig 2 shows the cross-sectional high-resolution transmission electron microscope (HRTEM) image of the n-Si/SiO_2/HfAlO/Al_2O_3/Pt memory structure after post deposition annealing at 900°C for 1min in N_2 ambient. The thickness of the tunneling (SiO_2) and blocking (Al_2O_3) oxides are found to be ~3 nm and ~12 nm respectively. An excellent interface between Si and SiO_2 has been observed after the PDA treatment due to the high quality tunneling oxide. It is expected that the inner side of nanocrystal is Hf-rich HfAlO and outer side is Al-rich HfAlO. The high-κ HfAlO nanocrystal embedded in the Al_2O_3 films has a small diameter of ~2 nm and expected high density of $>1\text{x}10^{12}/\text{cm}^2$. The high-κ HfAlO nanocrystals have been confirmed by x-ray photoelectron spectroscopy (XPS) measurement. Fig. 3 shows the XP spectrum of Hf*4f* signal for the as-deposited memory capacitors. The peak fitting is performed by Shirley background subtraction and Gaussian/Lorentzian functions. The peak binding energies of Hf$4f_{7/2}$ and Hf$4f_{5/2}$ electrons are found to be 16.8 eV and 18.4 eV, respectively, which is attributed to the HfO_2 film. After the annealing treatment, the peak binding energy of Hf$4f_{7/2}$ electron centered at 17.3 eV is shifted to higher binding energy, which indicates the signature of Hf-Al-O bonding, i.e. HfAlO nanocrystals [Fig. 4(a)]. For the as-deposited memory structure, the peak binding energies of Al*2p* and O*1s* electrons are found to be 74.4 eV and 531.7 eV, respectively, indicating the Al_2O_3 and HfO_2 films. [Fig. 4(b) & (c)]. After the annealing treatment, the Al*2p* and O*1s* spectra are also shifted to higher binding energies, indicating that the high-κ HfAlO nanocrystals are formed. After the PDA treatment the memory characteristics are drastically improved due to enhanced charge storage in the high-κ nanocrystals as described below. Fig 5 shows the clockwise C-V hysteresis characteristics for the as-deposited memory capacitors. A small hysteresis memory window of ΔV~0.5V is observed with a large sweeping gate voltage (V_g) of ±10 V. The hysteresis memory window is not increased with increasing the gate voltage up to 15V. It indicates that the trapping sites in the as-deposited memory capacitor are negligible. A quasi-neutral flat-band voltage (V_{FBN}) is about -0.3V, where no hysteresis memory window is observed at a sweeping gate voltage is ±2V. A negative V_{FBN} (=-0.3V) indicates the positive charges in our as-deposited memory capacitor and it can be annealed out after PDA treatment (V_{FBN}=+0.2V) as shown in Fig. 6. A large hysteresis memory window of ΔV~1.7V is observed with a small sweeping gate voltage of ±5V. It is suggesting that the memory devices can be operated below 5V also. The memory window increases with increasing the sweeping gate voltage. It means that this memory structure can be useful in future multi-level charge (MLC) storage applications. The equivalent oxide thickness (EOT) decreases (6.7 nm to 5.6 nm) after annealing treatment, due to high-κ HfAlO nanocrystal formation and it may have high dielectric constant value. It is important to note that a small EOT of our memory capacitors will be useful for below 22 nm technology node. A small leakage current density of $\sim4\text{x}10^{-7}\text{A/cm}^2$@$V_g$=-7V is observed after PDA treatment (Fig. 7). A high breakdown voltage of -17V is observed. Due to the small leakage current, the electron can be stored easily in the high-κ HfAlO nanocrystals by substrate electron injection current ($J_{electron}$) and it can be erased by hole injection current (J_{hole}) [Fig. 8]. It means that the program/erase speed can be improved due to this novel nanoscale memory structure. A significant memory window of ΔV~0.7V is observed after $1.4\text{x}10^4$ s retention time (Fig. 9). The retention can improve further by increasing the thickness of tunneling oxide in our nanoscale memory capacitors.

4. Conclusions

We have investigated the ALD high-κ HfAlO nanocrystal (small diameter of ~2nm) memory capacitor with small EOT of 5.6 nm, large memory window of 3.7V, small gate voltage operation of <5V, which can be useful in future NC-NVM devices.

Acknowledgments

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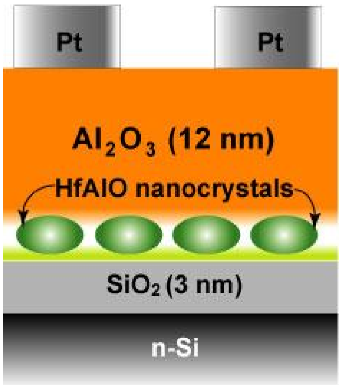


Fig. 1 Schematic memory structure of ALD HfAlO nanocrystals (diameter~2 nm) on SiO_2 (3 nm)/n-Si substrate.

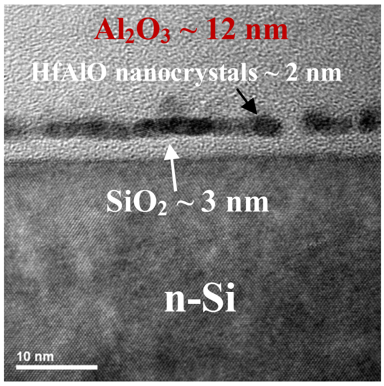


Fig. 2 Cross-sectional HRTEM image of atomic layer deposited HfAlO nanocrystals after PDA treatment. The diameter of HfAlO nanocrystal is ~ 2 nm.

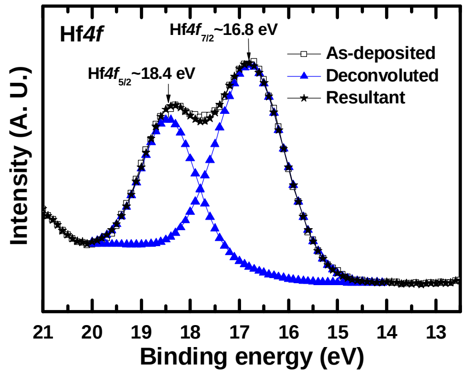


Fig. 3 XP spectra of Hf *4f* signals for as-deposited. Deconvoluted spectrum shows that the well defined $4f_{5/2}$ and $4f_{7/2}$ feature peaks that correspond to HfO_2 film.

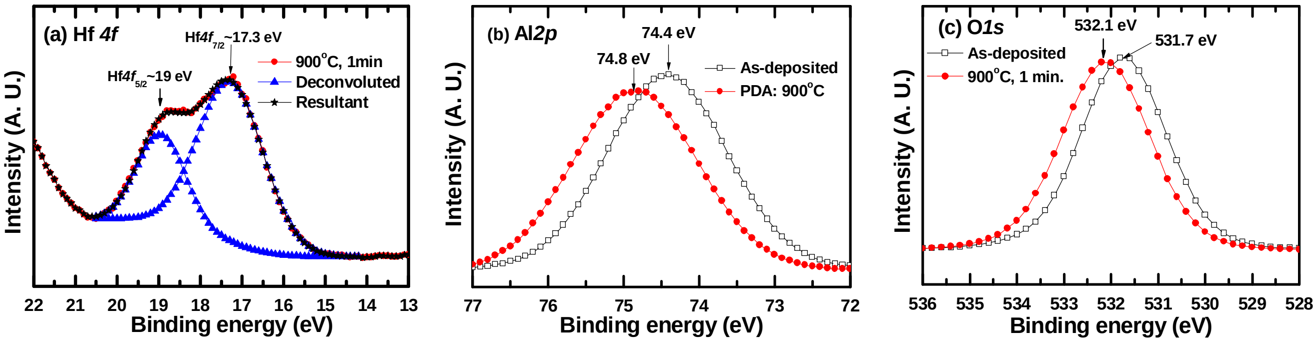


Fig.4 XP spectra of (a) Hf*4f*, (b) Al*2p* and (c) O*1s* signals. All spectra have been shifted towards the higher binding energy after PDA treatment, which confirms the formation of Hf-Al-O bonding or HfAlO nanocrystals.

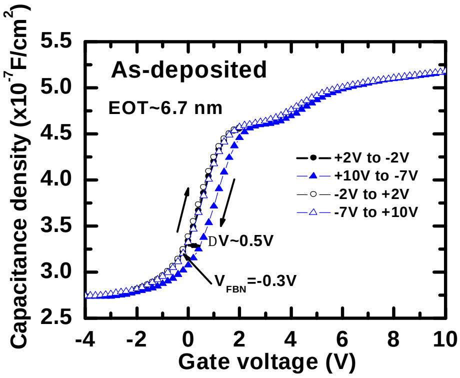


Fig. 5 The C-V (1 MHz) hysteresis shows a small memory window of ΔV~0.5V@ V_g= + 10 to -7 V for the as-deposited memory capacitors.

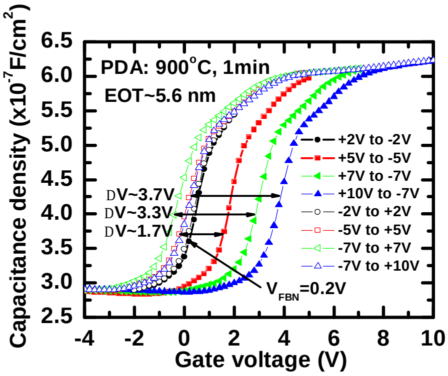


Fig.6 The C-V hysteresis shows a large memory window of ΔV~ 3.7V@ V_g= +10 V to -7V after PDA treatment.

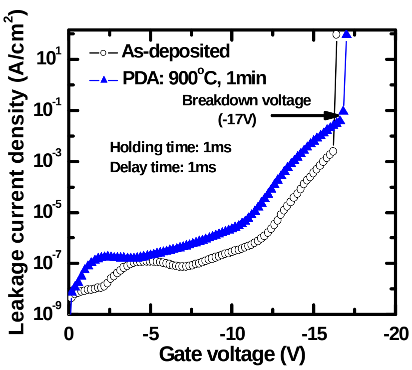
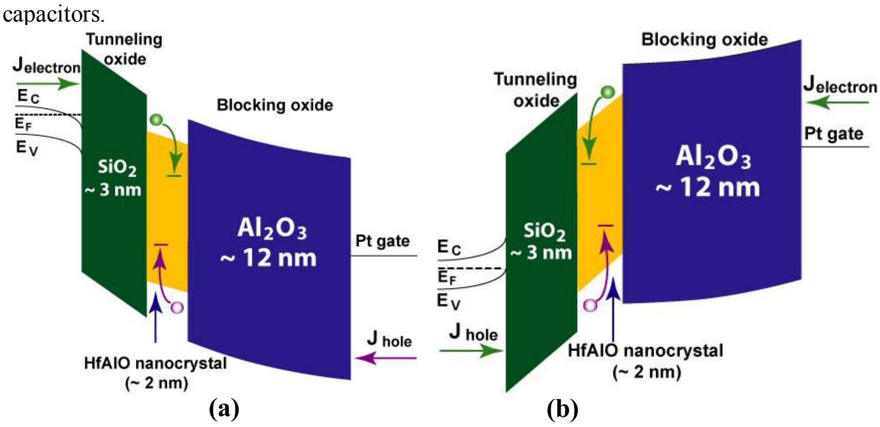


Fig. 7 Leakage current density vs gate voltage characteristics of the HfAlO nanocrystals memory capacitors.



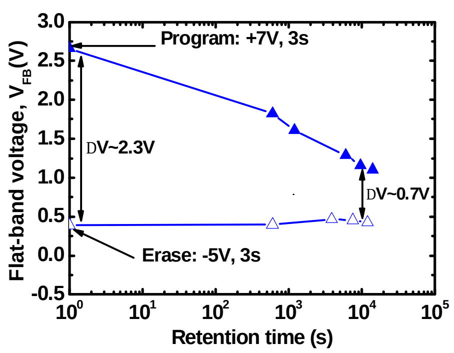


Fig. 8 Schematic energy band diagram of the high-κ HfAlO nanocrystal memory capacitors under (a) programming and (b) erasing modes.

Fig. 9 Retention characteristics of high-κ nanocrystal memory devices.