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Evaluation of ALD grown strontium-doped HfO_2 thin films as capacitor dielectric for 40nm DRAM Device and beyond

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Introduction

As the innovative scale-down of DRAM device continues, 40nm generation becomes close at hand. To satisfy the cell capacitance of 25fF in 40nm design rule, the equivalent oxide thickness (EOT) of a dielectric material should be as low as 0.5nm. TiN/insulator/TiN(TIT) capacitor using HfO_2 has been successfully developed for 70nm generation.[1] Therefore the scale-down of DRAM device has required new high-k dielectric and electrode. When high-k dielectrics, such as Ta_2O_5 or TiO_2, were implemented as the dielectric of the TIT capacitor, it was difficult to suppress the leakage current because of low Schottky barrier height and poor interface due to interaction between TiN and the dielectrics. (Figure 1). On the other hand, Ru/Insulator/Ru (RIR) capacitor using high-k dielectrics has an advantage of EOT scaling down, but also has some problems yet to be solved, such as the contact-plug oxidation and Ru electrode agglomeration during the back-end process. Because tetragonal phase of HfO_2 is stable at high temperature, it is important to reduce the crystallization temperature to tetragonal phase. In this study, we attempted to make tetragonal HfO_2 films by atomic layer deposition using strontium doping for dielectric material of TIT capacitor. HfO_2 predominantly crystallizes in the lower k monoclinic phase, instead of forming the high k tetragonal phase in pure form.[2] Therefore, it has been reported that formation of tetragonal HfO_2 films by other material doping [3], and stabilizers with relatively low temperature has importance in essence. We have introduced Sr doped HfO_2 thin films for high-k dielectric layers. We have investigated the crystallization behavior of Sr doped HfO_2 films and electrical characteristics of TIT- Sr doped HfO_2 (Sr-HfO_2) capacitors.

Crystallization of Sr doped HfO_2 films

The purpose of Sr doping is to form stable tetragonal HfO_2 at lower temperature than pure HfO_2. The ionic radius of Sr^{2+}(1.18Å) is mush larger than that of Hf^{4+}(0.84Å), therefore it is expected to induce of the strain of HfO_2 lattice and to lower the crystallization temperature to tetragonal HfO_2 phase.

The Sr-HfO_2 films were deposited by atomic layer deposition (ALD) method. Figure 2 shows Sr and Hf precursors used in deposition of Sr-HfO_2 layer. Bis(tetramethyl-n-propylcyclopentadienyl)strontium and tetrakis (ethylmethylamino) hafnium were used as Sr and Hf precursors, respectively. The Sr atomic composition was controlled by cycle ratio of each precursor. Sr composition of Sr-HfO_2 was analyzed as inductively coupled plasma atomic emission spectroscopy (ICP-AES) and X-ray fluorescence (XRF). Sr-HfO_2 films deposited with various composition of Sr were progressed to heat treatment in N_2 atmosphere. The method of heat treatment was rapid thermal anneal (RTA) and the RTA temperature was varied from 500℃ to 600℃. The crystallization behavior of Sr-HfO_2 was analyzed as X-ray diffraction (XRD). Figure 3 shows XRD spectra of Sr-HfO_2 films with Sr composition and RTA temperature. The phase of Sr-HfO_2 films were varied as Sr composition of the film and RTA temperature. After 550℃ and 600℃ RTA, the Sr-HfO_2 films with Sr 5~8 atomic% exhibited tetragonal phase, while that with Sr 3 atomic% showed mixed phase of tetragonal and monoclinic structure. The Sr-HfO_2 films of Sr 13 atomic% was amorphous phase after 550℃ RTA, but after 600℃, the film was crystallized to tetragonal phase. Figure 4 shows high resolution transmission electron microscopy (HRTEM) image of Sr-HfO_2 film with Sr 6 atomic%. This image exhibits uniform crystalline structure without phase segregation.

Therefore, it was possible to crystallize the Sr-HfO2 films to tetragonal structure at relatively low temperature of 550℃ and the temperature could be controlled by Sr composition of ALD process

Electrical characteristics of TIT Capacitor with Sr-HfO_2 films

Table 1 shows the deposition methods for the fabrication of TIT capacitors. Top and bottom electrodes were deposited with CVD method and dielectric layers, Sr-HfO_2 with ALD method. Figure 5 shows dielectric constant of Sr-HfO_2 films with Sr atomic%. Dielectric constant of Sr-HfO_2 without RTA is about 20. The phases of as-deposed the dielectric layers were amorphous or monoclinic phase. Annealed Sr-HfO_2 films have varied from 25 to 42 and the phases of films were tetragonal or monoclinic with Sr composition. Figure 6 shows the leakage current of TIT capacitor with Sr-HfO_2 dielectric layer. Even if the dielectric layers were the same physical thickness, EOTs of TIT capacitor showed various values with Sr composition. This maybe resulted from the difference of crystal structure of the each dielectric layer with Sr composition. The specific leakage current of the TIT capacitor having EOT 8.1Å is about 1.0㎂/㎠ at +1.0V and dielectric constant of the Sr-HfO_2 film is about 40.

Conclusions

The phase and crystal structure of Sr-HfO_2 dielectric layer were varied as Sr atomic% of the film and RTA temperature After RTA550 and RTA600, the Sr-HfO_2 films with Sr 5~8 atomic% exhibited tetragonal phase, while that with Sr 3 atomic% showed mixed phase of tetragonal and monoclinic structure. The Sr-HfO_2 films of Sr 13 atomic% was amorphous phase after 550℃ RTA, but after 600℃, the film was crystallized to tetragonal phase. The dielectric constant of tetragonal Sr-HfO_2 were as high as 40 and the leakage current of TIT capacitor with the tetragonal Sr-HfO_2 to EOT 8.1Å were about 1.0㎂/㎠ at +1.0V.

References

[1] J. H. Choi. et al., IEDM2003, p661-664, 2003.
[2] S.Migita. et al., 2008 Symposiun on VLSI Technology Digest of Technical paper p152-153.
[3] D. Fischer. et al., Applied physics letters 92, 2008

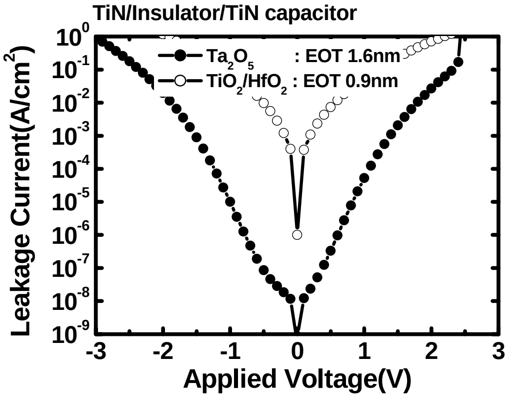


Fig. 1. Leakage current characteristics of TIT capacitor with high-k dielectric materials.

(a) (b)

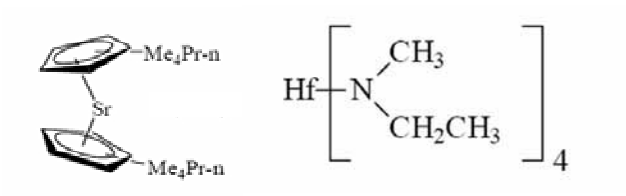
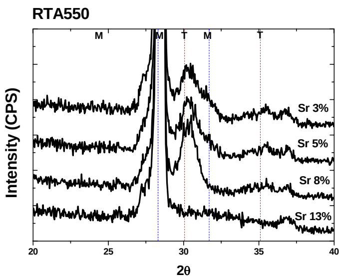


Fig. 2. The precursor Sr precursor and Hf. (a) Bis (tetrametahyl-N-propylcyclopentadiednyl)strontium (b) tetrakis(ethylmethylamino)hafnium

(a)



(b)

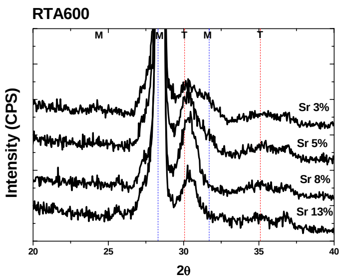


Fig. 3. XRD spectra of Sr doped HfO_2 films with Sr composition. (a) 550℃ RTA (b) 600℃ RTA

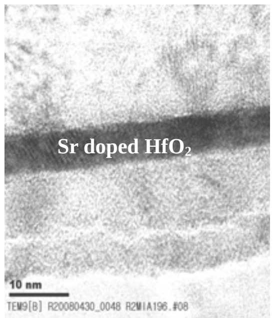


Fig. 4. TEM image of Sr-HfO_2 with Sr 6 atomic%.

Table1. Deposition methods for the fabrication of TIT capacitor.

Bottom Electrode	CVD TiN
Dielectric Deposition	ALD Sr-HfO_2
Post Treatment	RTA
Top Electrode	CVD TiN

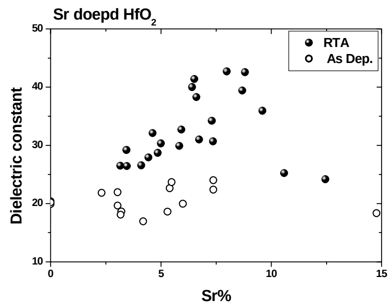


Fig. 5. Dielectric constant versus Sr composition of Sr-HfO_2 layer.

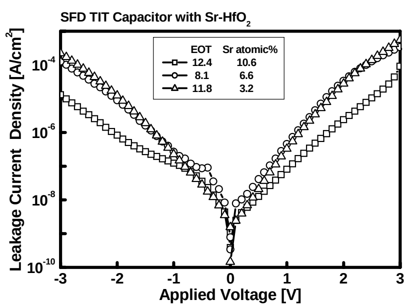


Fig. 6. Leakage current characteristics of TIT capacitor with Sr - HfO_2 dielectric layers.