(Supplemental Document)

Enhancement of Ferroelectric Phase Formation of HfO_2/ZrO_2 Nanolaminate Films by Tuning HfO_2 and ZrO_2 Thicknesses Using Atomic Layer Deposition

Takashi Onaya et al.

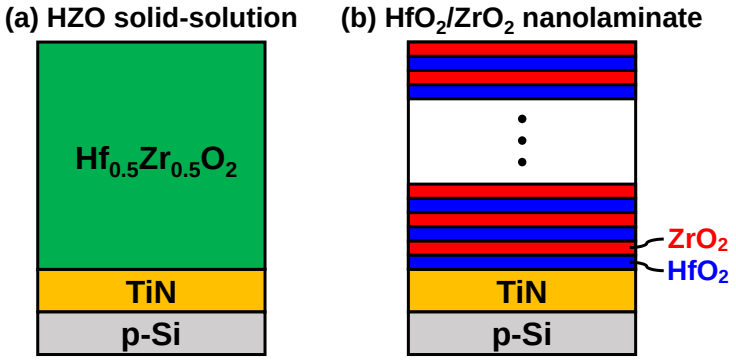

Fig. 1 Schematic illustrations of (a) $Hf_xZr_{1-x}O_2$ (HZO) solid-solution and (b) HfO_2/ZrO_2 nanolaminate films with the thickness of 10 nm fabricated on TiN/p-Si substrates. A 10-nm-thick HZO solid-solution film was deposited by atomic layer deposition (ALD) at 300°C using a $Hf/Zr[N(C_2H_5)CH_3]_4$ cocktail precursor and H_2O. A 10-nm-thick HfO_2/ZrO_2 nanolaminate film was deposited by alternately depositing HfO_2 and ZrO_2 layers using ALD at 300°C. HfO_2 and ZrO_2 layers were deposited using $Hf[N(C_2H_5)CH_3]_4$ and $Zr[N(C_2H_5)CH_3]_4$ precursors, respectively, and H_2O as an oxidant. The ALD growth rates of HfO_2 and ZrO_2 were almost the same of ~0.08 nm/cycle. The Hf:Zr ratios in HZO solid-solution and HfO_2/ZrO_2 nanolaminate films were 1:1. For HfO_2/ZrO_2 nanolaminate films, the ALD cycle ratio was varied from HfO_2/ZrO_2=1/1 to 60/60 so that each HfO_2 and ZrO_2 thickness would be varied from 0.08 to 5 nm while keeping the same thickness of HfO_2 and ZrO_2 layers.

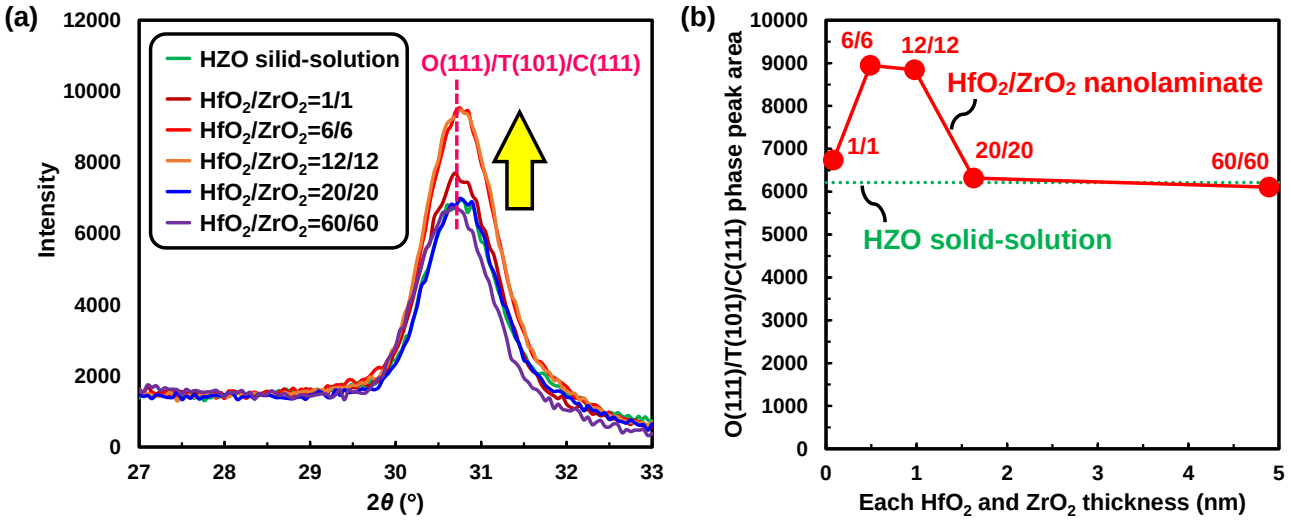

Fig. 2 (a) Grazing-incidence X-ray diffraction (GIXRD) spectra and (b) peak areas of orthorhombic (O) (111), tetragonal (T) (101), and cubic (C) (111) phases for HZO solid-solution and HfO_2/ZrO_2 nanolaminate films after the post-deposition annealing at 600°C. The HfO_2/ZrO_2=1/1 and HZO solid-solution films exhibited similar O/T/C peak area, because Hf and Zr atoms could be uniformly mixed in the HfO_2/ZrO_2=1/1 film. On the other hand, the O/T/C peak areas of the HfO_2/ZrO_2=6/6 and 12/12 films were ~1.4 times larger than that of the HZO solid-solution film, where each HfO_2 and ZrO_2 thickness was 0.5−1 nm (1−2 monolayers). Therefore, the ZrO_2 layers in HfO_2/ZrO_2 nanolaminate films should play a role to provide nuclei efficiently to enhance the formation of O/T/C phases in the HfO_2/ZrO_2=6/6 and 12/12 films.