(Supporting Information)

Ferroelectricity of Ferroelectric $Hf_xZr_{1-x}O_2$/Antiferroelectric ZrO_2 Stack Structure Fabricated by Atomic Layer Deposition

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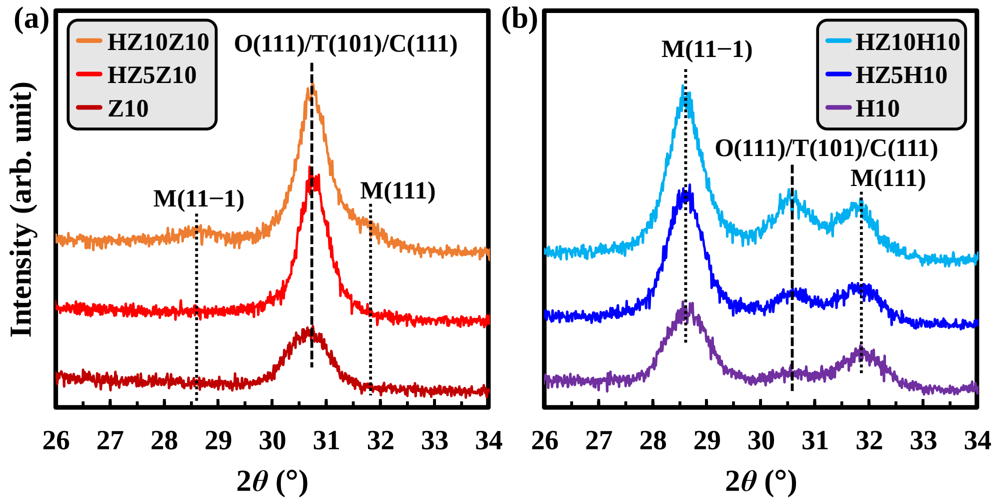

Fig. 1 (a) GI-XRD patterns of HZ/Z and HZ/H stack structures. The HZO thickness was varied from 0 to 10 nm by changing the number of ALD cycles, while the thickness of ZrO_2 and HfO_2 films were 10 nm. The PDA was performed at 600°C for 1 min in a N_2 atmosphere. The HZ/Z and HZ/H stack samples are described as: "Z#", "HZ#Z#", "H#", and "HZ#H#", where Z, H, or HZ and the attached number represent the film type and film thickness, respectively. For example, HZ5Z10 represents a stack structure consisting of a 5-nm-thick HZO film and a 10-nm-thick ZrO_2 film. The patterns of HZ/H stacks clearly showed the peaks originating from paraelectric M phase. On the other hand, the HZ/Z stacks consisted mainly of O/T/C phases.

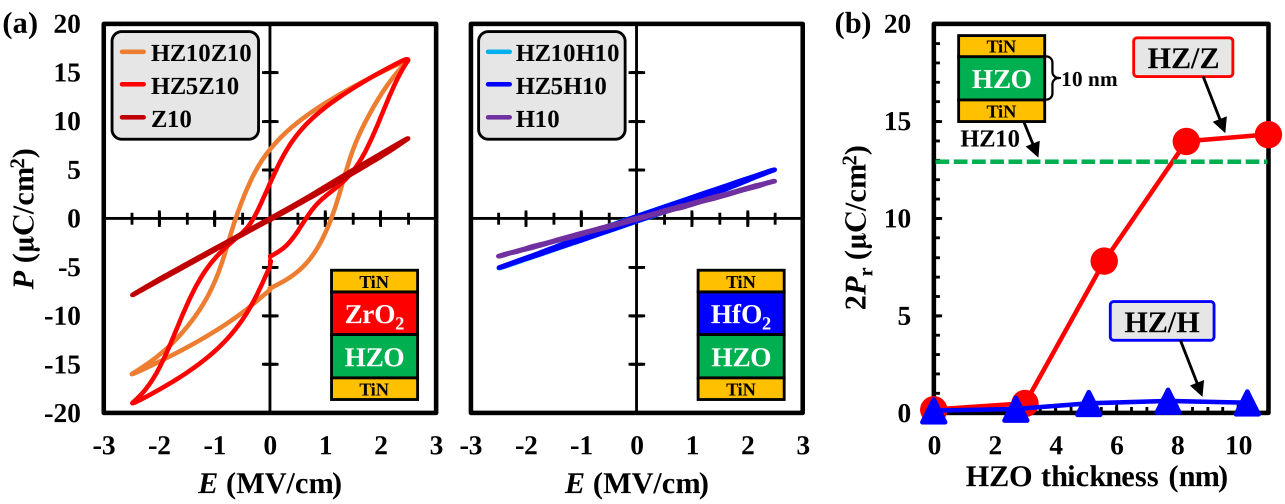

Fig. 2 (a) *P*-*E* hysteresis loops of capacitors with HZ/Z and HZ/H stack structures after wake-up cycling (10^4 cycles at 2.5 MV/cm). The HZO thickness was varied from 0 to 10 nm by changing the number of ALD cycles, while the thickness of ZrO_2 and HfO_2 films were kept at 10 nm. The HZ/H stacks showed paraelectric-like behavior regardless of the HZO thickness. On the other hand, the properties of HZ/Z stacks changed from antiferroelectricity to ferroelectricity as the HZO thickness increased. (b) $2P_r$ of capacitors with HZ/Z and HZ/H stack structures. The $2P_r$ of HZ/Z stack increased with the HZO thickness while the HZ/H stack structure kept lower $2P_r$ of < 1.0 μC/cm^2. The HZ10Z10 showed the highest $2P_r$ of 14 μC/cm^2, which was higher than that (13 μC/cm^2) of TiN/HZO (10 nm)/TiN capacitor. These results suggested that the ZrO_2 film of HZ/Z stack structure could exhibit ferroelectricity as the HZO thickness increased.