Optimizing ultrathin HfO_2-ZrO_2 structures by ALD for BEOL-compatible ferroelectric non-volatile memories

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Ferroelectric HfO_2-based materials are promising for advanced memory applications due to their CMOS compatibility, scalability, and low processing temperatures, such as 400 °C, suitable for back-end-of-line (BEOL) integration. Among these, $Hf_{0.5}Zr_{0.5}O_2$ (HZO) stands out for its strong ferroelectric properties, reaching a remanent polarization of 40 µC/cm² [1]. However, reducing the thickness of HZO to ultrathin values (<10 nm) to lower the operating voltage and meet the demands of low-power memory applications introduces critical challenges, including increased crystallization temperature, higher leakage currents, and instability that affect device endurance and reliability [2,3].

To further optimize the properties of ferroelectric films, the multilayer approach has demonstrated significant potential in addressing the challenges of ultrathin HZO films. By stacking alternating HfO_2 and ZrO_2 layers, this method can reduce leakage currents by blocking electron injection from the electrodes, thereby enhancing endurance and stability [4]. Additionally, multilayers can also provide an additional degree of control over ferroelectric performance through the careful design of the stacking sequence and layer thicknesses.

The aim of this work is to develop ultrathin ferroelectric layers by ALD for MFM (Metal Ferroelectric Metal) capacitors for non-volatile memories. Within this work, two different types of structures were investigated: HZO solid solution, made through supercycles, and HfO_2/ZrO_2 nanolaminates consisting of stacked HfO_2 and ZrO_2. To explore ferroelectric performance at reduced thicknesses, the film was scaled down to 4 nm, with the nanolaminate achieved by stacking 1 nm of HfO_2 and 0.5 nm of ZrO_2.

The experimental results demonstrate the influence of structural configuration, composition, and annealing conditions on ferroelectric performance in ultrathin HZO films. For the 10 and 6 nm HZO samples, annealed at a BEOL-compatible temperature of 400°C, ferroelectric properties were achieved, validating its potential for integration in non-volatile memories. However, reducing the thickness to 5 and 4 nm introduced challenges that required increasing the crystallization temperature to 500 °C and modifying the structure to nanolaminates with higher Hf content. The Zr composition in the multilayer structure was deliberately lowered to prevent excessive stabilization of the tetragonal phase, which is known to negatively impact ferroelectric properties in ultrathin films. Despite these adjustments, further optimization of the annealing temperature for 5 and 4 nm samples is necessary to ensure compatibility with BEOL processing, potentially through approaches such as laser or rapid thermal annealing. XRD analyses (Fig. 1) confirm the existence of a peak near $2\theta \approx 30.5°$ in the samples, indicating the presence of orthorhombic or tetragonal phases. While the HZO 1:1 at 4 nm lacked a well-defined peak due to incomplete crystallization, nanolaminates of the same thickness exhibited distinct peaks, reflecting improved crystallization.

The P-E hysteresis loops (Fig. 2) further highlight the benefits of these modifications. The 5 nm HZO, annealed at 500 °C, demonstrated superior polarization, surpassing the 6 nm sample annealed at 400 °C. In contrast, the HZO 1:1 at 4 nm displayed antiferroelectric behavior, consistent with incomplete phase stabilization. The 4 nm nanolaminates, however, achieved promising ferroelectric performance, with a remanent polarization of approximately 10 µC/cm² and low coercive voltage, favorable for low-energy applications. The Ec-Vc plot (Fig. 3) revealed a clear trend of decreasing coercive voltage with reduced thickness, further emphasizing the potential of nanolaminates to maintain ferroelectric properties at ultrathin dimensions. However, HZO films remain BEOL-compatible only down to 6 nm. Further progress requires optimizing crystallization while meeting BEOL thermal limits for advanced memory technologies.

References

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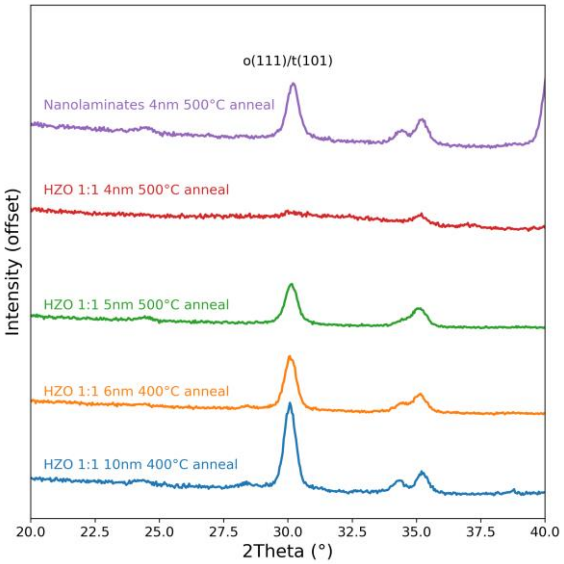

Fig. 1. In-plane XRD patterns of HZO films with varying thicknesses (10 nm, 6 nm, 5 nm, and 4 nm) and annealing conditions (400 and 500 °C), measured after the etching of the top electrode.

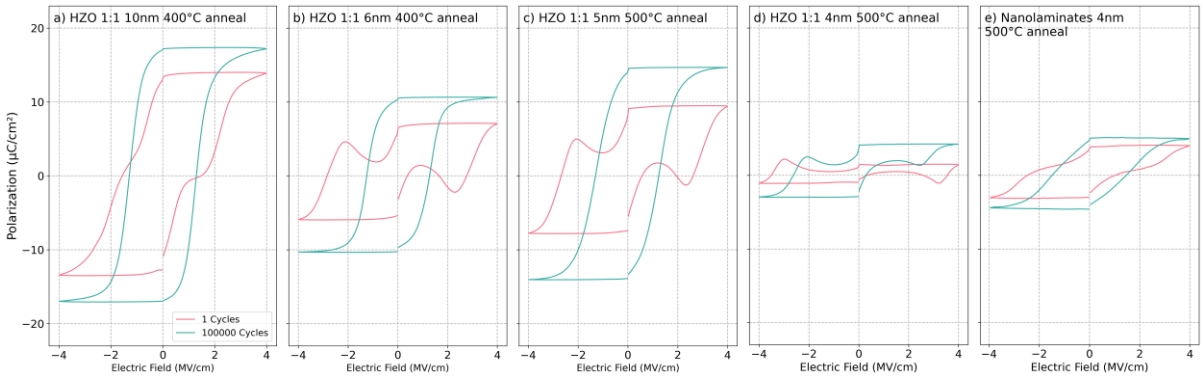

Fig. 2. P-E hysteresis loops of (a) HZO 1:1, 10 nm and (b) 6 nm, both annealed at 400 °C; (c) HZO 1:1, 5 nm, (d) 4 nm and (e) nanolaminates 4 nm, annealed at 500 °C. The nanolaminates at 4 nm show promising ferroelectric performance with a remanent polarization of approximately 10 μC/cm².

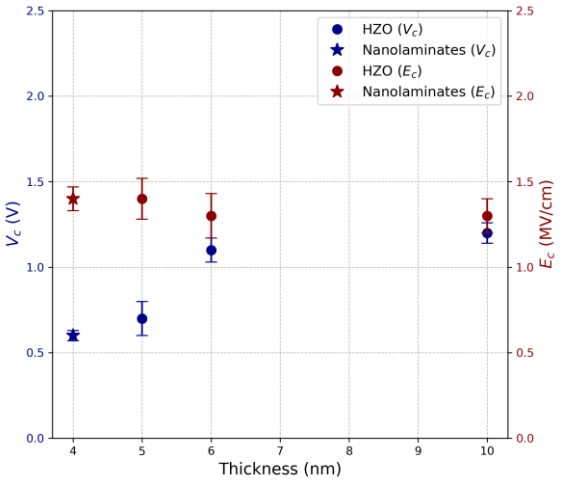

Fig. 3. Coercive voltage (Vc, blue, left axis) and coercive electric field (Ec, dark red points) as a function of film thickness after 10^5 cycles. The plotted samples include HZO 1:1 at 10 and 6 nm, both annealed at 400 °C, as well as HZO 1:1 at 5 nm and nanolaminates at 4 nm, annealed at 500 °C. Vc decreases with reduced thickness, which is favorable for low-energy applications