Supporting Information for:

Robust energy storage density and negative capacitance in antiferroelectric heterostructures grown by atomic layer epitaxy

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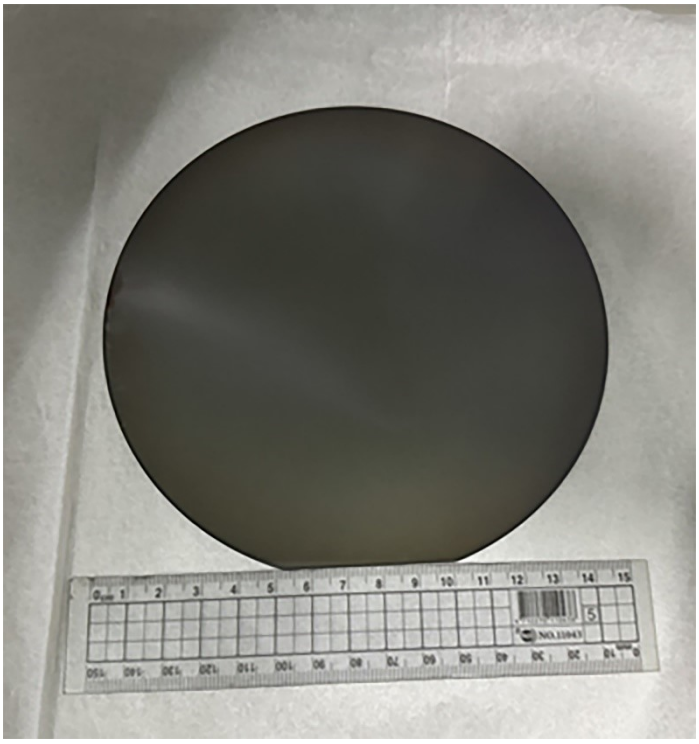

Figure S1. The epitaxial ZrO_2/TiN heterostructure was grown on a 6-inch sapphire wafer by atomic layer epitaxy, demonstrating the viability of large-area growth for the mass production of energy storage devices.

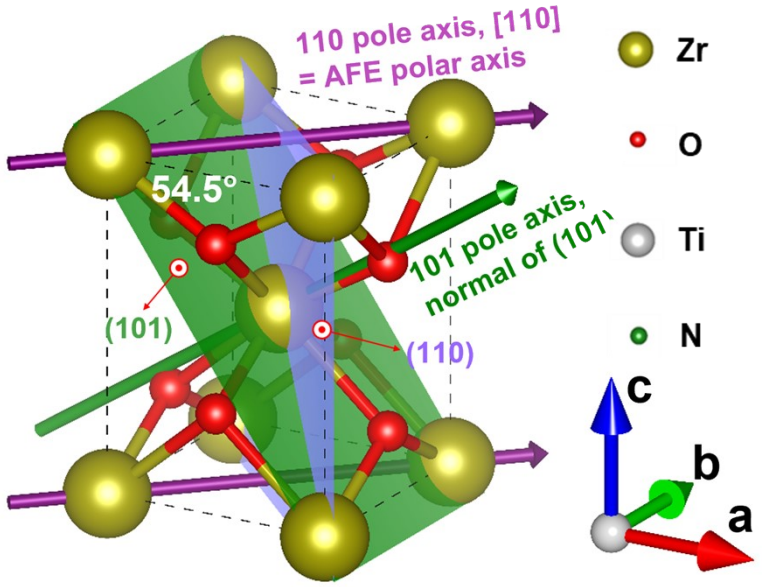

Figure S2. A unit cell of tetragonal ZrO_2. The (110) and (101) planes are depicted in purple and green, respectively, intersecting at an angle of 54.5° with each other. The pole axis is the normal of the lattice plane and is indicated by an arrow of the same color. The AFE polar axis of ZrO_2 is along the 110 pole axis, which is the [110] axis in the tetragonal lattice.

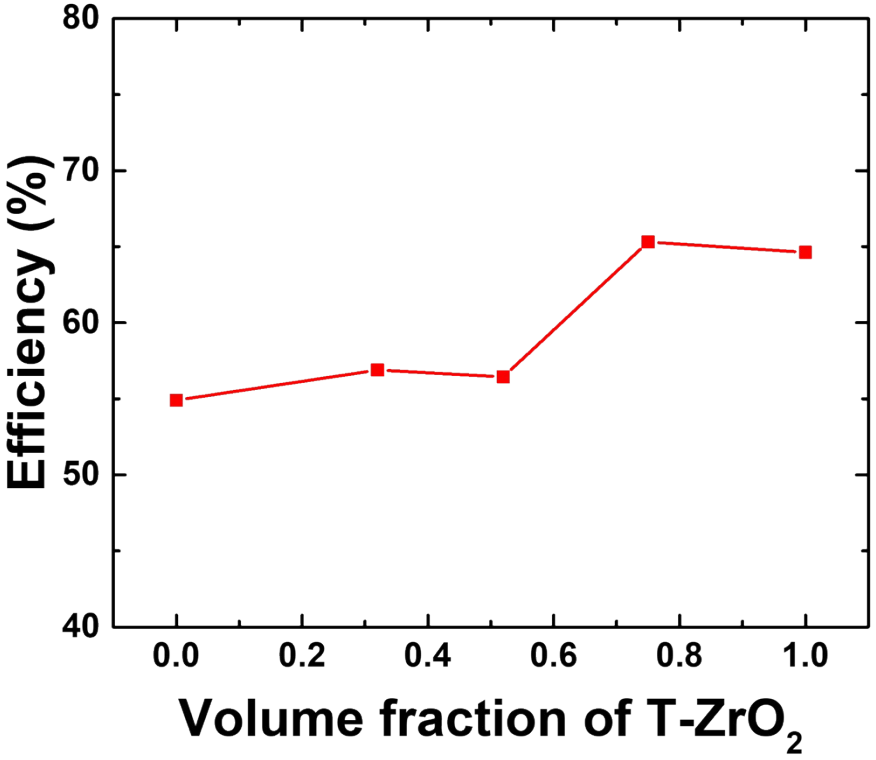

Figure S3. Dependence of energy storage efficiency on the volume fraction of T-ZrO_2, as derived from the *P-V* curves in Figure 3.

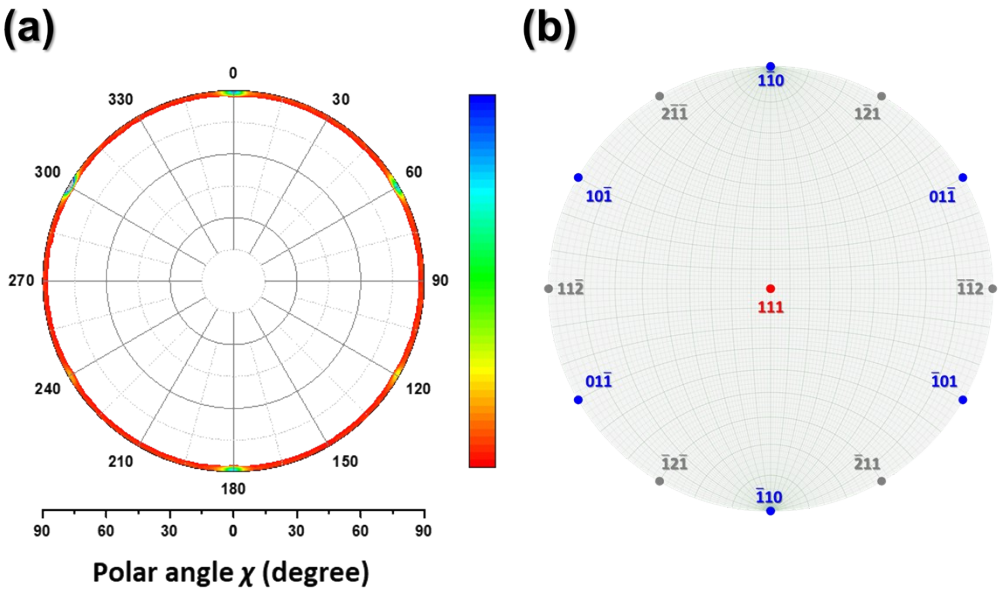

Figure S4. (a) The pole figure of the $T_{0.75}P_{0.25}$ sample at Bragg's angle of TiN(220). **(b)** The stereographic projections of TiN at the (111) pole.

Table S1. Benchmark of energy storage density in dielectric capacitors.

Material and Structure	U_{ESD} (J/cm^3)	P_{max} (μC/cm^2)	Reference
W/ZrO_2/TiN	118.6	47.7	This work
TiN/HZO/TiN	46	>30	15
Pt/TiO_2/ZrO2/TiO_2/Pt	94	>40	28
Cr/TiO_2/ZrO_2/TiO_2/Pt	114.5	>40	29
Pt/HZO/Al_2O_3/HZO/TiN	87.66	41.3	31
W/Al:HZO/W	101.4	>30	32
W/HfO_2/ZrO_2/HfO_2/W	32	~28	33
TiN/Al:HZO/TiN	53	~22	34
TiN/Al:HfO_2/TiN	35	~17	35
TiN/ZrO_2/TiN	80.2	41.3	36
Mo/ZTSO/Mo	68.59	-	37
W/HAO/W	63.7	-	38
TiN/HZO/Al_2O_3/HZO/TiN	55	~32	39
Au/HAO/ZrO_2/Pt	54.3	-	40
Pt/Al:HfO_2/Pt	63	-	41
TiN/La:HZO/TiN	50	~30	42
TiN/Si:HZO/TiN	53	-	43
TiN/HZO/TiN	55	~31	44
TiN/Si:HZO/TiN	40	~29	45
TiN/Si:HZO/TiN	61.2	~40	46
TiN/Si:HfO_2/ Si	~40	~30	47
TiN/HZO/TiN	115	~31	48