

1 Ultrathin ferroic HfO₂-ZrO₂ superlattice gate stack for advanced transistors

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38

39 With the scaling of lateral dimensions in advanced transistors, an increased gate capacitance
40 is desirable both to retain the control of the gate electrode over the channel and to reduce
41 the operating voltage¹. This led to the adoption of high- κ dielectric HfO₂ in the gate stack in
42 2008², which remains as the material of choice to date. Here, we report HfO₂-ZrO₂
43 superlattice heterostructures as a gate stack, stabilized with mixed ferroelectric-
44 antiferroelectric order, directly integrated onto Si transistors, and scaled down to ~ 20 Å,
45 the same gate oxide thickness required for high performance transistors. The overall EOT
46 (equivalent oxide thickness) in metal-oxide-semiconductor capacitors is equivalent to ~ 6.5
47 Å effective SiO₂ thickness. Such a low effective oxide thickness and the resulting large
48 capacitance cannot be achieved in conventional HfO₂-based high- κ dielectric gate stacks
49 without scavenging the interfacial SiO₂, which has adverse effects on the electron transport
50 and gate leakage current³. Accordingly, our gate stacks, which do not require such
51 scavenging, provide substantially lower leakage current and no mobility degradation. This
52 work demonstrates that ultrathin ferroic HfO₂-ZrO₂ multilayers, stabilized with competing
53 ferroelectric-antiferroelectric order in the 2 nm thickness regime, provide a new path
54 towards advanced gate oxide stacks in electronic devices beyond the conventional HfO₂-
55 based high- κ dielectrics.
56

57 With the two-dimensional scaling of silicon field-effect transistors reaching fundamental limits¹,
58 new functional improvements to transistors⁴, as well as novel computing paradigms and vertical
59 device integration at the architecture-level⁵, are currently under intense investigation^{1,4,6}. Gate
60 oxides play a critical role in this endeavor as a common performance booster for all devices,
61 including silicon², new high-performance channel materials^{7,8}, and even materials suitable for
62 three-dimensional integrated transistors^{9,10}. Indeed, the gate oxide transition from SiO₂ to high- κ
63 dielectric (DE) is considered a paradigm shift in computing technology. In this context,
64 ferroelectric oxides offer new functionalities¹¹ considered promising for energy-efficient
65 electronics^{4,9}. The advent of atomic layer deposition (ALD) grown ferroelectric doped-HfO₂¹²
66 has overcome much of the material compatibility issues that plague traditional perovskite-based
67 ferroelectric materials². In addition, ferroic order persists down to a thickness of 1 nm in this
68 system¹³⁻¹⁵, fostering integration into the most aggressively-scaled devices in which the state-of-
69 the-art high- κ oxide thickness is less than 2 nm.

70
71 In an advanced silicon transistor, the gate oxide is a combination of two distinct layers. The first
72 is an interfacial SiO₂ formed with a self-limiting process, resulting in \sim 8.0-8.5 Å thickness¹⁶.
73 The next is the high- κ (HK) dielectric HfO₂ layer that is typically \sim 2 nm in thickness. Higher
74 capacitance of this series combination is desirable to suppress short channel effects. The
75 capacitance is conventionally represented by equivalent oxide thickness (EOT), $EOT = t_{SiO_2} +$
76 $t_{HK}/(\epsilon_{HK}/\epsilon_{SiO_2})$, where lower EOT represents higher capacitance. Therefore, the EOT minimum
77 value is limited by the interfacial SiO₂ thickness. Typically, with HfO₂ as the high- κ layer, the
78 EOT is approximately 9.5 Å. To go below this value^{17,18}, the semiconductor industry has
79 implemented sophisticated scavenging techniques^{16,18,19} to reduce the SiO₂ thickness after the
80 full gate stack has been deposited. Although this technique is effective in scaling EOT, the
81 thinner SiO₂ results in undesirable leakage²⁰, mobility degradation^{2,16} and reliability issues.

82
83 In this work, we present an ultrathin HfO₂-ZrO₂ superlattice gate stack that exploits mixed
84 ferroelectric-antiferroelectric (FE-AFE) order (Fig. 1a,b), stabilized down to 2 nm thickness –
85 the same high- κ oxide thickness used in advanced transistors. When integrated on silicon, the
86 gate stack shows an overall EOT of 6.5 Å, even though both transmission electron microscopy
87 (TEM) and electrical characterization reveal an 8.0-8.5 Å interfacial SiO₂ thickness, as is
88 typically expected from a chemically grown interfacial layer without scavenging. No scavenging
89 of the interfacial SiO₂ results in substantially lower leakage current for the same EOT compared
90 to benchmarks established by major semiconductor industries³. In addition, no mobility
91 degradation is observed as EOT is scaled with these HfO₂-ZrO₂ ferroic gate stacks. Therefore,
92 ultrathin HfO₂-ZrO₂ gate stacks exploiting ferroic order offer a promising pathway toward
93 advanced energy-efficient transistors.

94 95 **Ultrathin FE-AFE HfO₂-ZrO₂ superlattices**

96
97 Thin films of HfO₂-ZrO₂ are grown using ALD in which the nanolaminate periodicity is dictated
98 by the sequence of Hf:Zr (4:12) ALD cycles before the Hf-Zr superstructure is repeated various
99 times (Fig. 1c, Methods). After top metal deposition, the entire gate stack undergoes a low-
100 temperature post-metal anneal (200 C, 60s, N₂) which does not interfere with the HfO₂-ZrO₂
101 multilayer structure: various characterization techniques – synchrotron x-ray reflectivity (XRR),
102 layer-resolved electron energy loss spectroscopy (EELS) and angle-resolved X-ray photoelectric

103 spectroscopy (XPS) – confirm the expected Hf 4 Å - Zr 12 Å periodicity (Extended Data Fig. 1).
104 The underlying mixed ferroic order in these HfO₂-ZrO₂ heterostructures is structurally
105 established by high-resolution transmission electron microscopy (TEM) (Fig. 1d, Extended Data
106 Fig. 2e,f) and in-plane grazing incidence diffraction (Fig. 1e, Extended Data Fig. 2a). Both
107 techniques indicate the presence of the tetragonal (P4₂/nmc, *T*-) and orthorhombic (Pca2₁, *O*-)
108 phase, which correspond to antiferroelectric and ferroelectric order in fluorite-structure films,
109 respectively. Furthermore, local TEM imaging indicates the ferroelectric (orthorhombic) and
110 antiferroelectric (tetragonal) phases are laterally intertwined (Fig. 1d, Extended Data Fig. 2e,f).
111 Synchrotron X-ray spectroscopy and optical spectroscopy further confirm the presence of
112 inversion symmetry breaking in the 2 nm HfO₂-ZrO₂-HfO₂ (HZH) multilayer (Extended Data
113 Fig. 2c,d).

114
115 We note here that the original Kittel view of an "antipolar" crystal structure²¹ does not apply to
116 the nonpolar tetragonal lattice attributed to fluorite-structure antiferroelectricity. Instead, the
117 field-induced tetragonal-to-orthorhombic (nonpolar-to-polar) phase interconversion as the origin
118 of antiferroelectricity has been examined in both ZrO₂^{22,23} and HfO₂^{22,24}. Therefore, at low
119 electric fields, the mixed ferroelectric-antiferroelectric behavior is analogous to a ferroelectric-
120 dielectric (polar-nonpolar) heterostructure, which can impart depolarization fields on the
121 ferroelectric layer²⁵. The laterally-intertwined nonpolar-polar phases present in the ultrathin
122 HfO₂-ZrO₂-HfO₂ heterostructure are conducive to flattening the ferroelectric energy landscape
123 through the aforementioned depolarization fields²⁶⁻²⁸ (Fig. 1a). Furthermore, heterogeneous
124 elastic energies in structurally inhomogeneous systems have been shown to destabilize long-
125 range polarization, suppress polarization, and thereby flatten energy landscapes²⁸.

126
127 Additionally, the polarization in the ultrathin HfO₂-ZrO₂-HfO₂ multilayer exhibit an in-plane
128 component. 2D reciprocal space maps indicate a strong out-of-plane (111) texture (Extended
129 Data Fig. 2b), which is consistent with TEM images demonstrating vertically-stacked planes of
130 111- interplanar lattice spacing (Extended Data Fig. 2f). Therefore, considering the polarization
131 is directed along a principal lattice direction for the Pca2₁ orthorhombic structure, the highly-
132 oriented out-of-plane (111) texture indicates an in-plane projected polarization. The in-plane
133 polarization introduces additional depolarization field due to the electrostatic coupling with the
134 nonpolar antiferroelectric phases in the lateral direction. Notably, exploiting inhomogeneity to
135 induce depolarization fields and enhance susceptibility has been demonstrated for perovskites
136 exhibiting heterogeneous polar-nonpolar regions²⁸. Following the same underlying mechanisms,
137 our work demonstrates that it is possible to stabilize a mixed nonpolar-polar phase competition in
138 2-nm-thick binary oxide films and enhance its permittivity. We also note that flattening of the
139 energy landscape via depolarization fields is the same underlying principle of the negative
140 capacitance (NC) effect^{11,29}, in which depolarization fields stabilize the ferroelectric locally at a
141 higher energy state compared to the ground state of an isolated, homogeneous ferroelectric,
142 leading to negative curvature energy landscapes^{30,31}.

143
144 To confirm the higher susceptibility in the mixed AFE-FE system directly, we have performed
145 capacitance-voltage (*C*-*V*) hysteresis loops in metal-insulator-metal (MIM) capacitor structures
146 on thicker films with the same superlattice periodicity (Fig. 2a). Besides features indicative of
147 mixed FE-AFE order, the total capacitance for the superlattice is larger than both conventional
148 AFE ZrO₂ and FE Zr:HfO₂ of the same thickness (Fig. 2a), demonstrating enhanced

149 susceptibility. To quantify the permittivity, capacitance measurements were performed across the
150 superlattice thickness series. These measurements yield an extracted permittivity of ~ 52 (Fig.
151 2b, Methods), which is larger than both FE orthorhombic Zr:HfO₂ and AFE tetragonal ZrO₂
152 values³².

153
154 To further understand the ferroic evolution in these HfO₂-ZrO₂ superlattices, we performed low
155 temperature measurements where enhanced FE phase stabilization is expected. Indeed,
156 temperature-dependent *C-V* loops for thicker HfO₂-ZrO₂ multilayers demonstrate an evolution
157 from mixed-ferroic to FE-like hysteresis upon cooling slightly below room temperature (~ 240
158 K, Fig. 2c), consistent with temperature-dependent X-ray spectroscopy indicating transition from
159 mixed tetragonal-orthorhombic phase to predominately orthorhombic structure at similar
160 temperatures (Extended Data Fig. 3c). The capacitance decrease upon cooling as the system
161 moves away from the highly-susceptible mixed ferroic phase is consistent with previous work on
162 NC in FE-DE systems²⁹ which establishes the energy landscape link between enhanced
163 capacitance and susceptibility near phase transitions. Notably, the intertwined FE-AFE phases
164 within the superlattice and resulting enhancement in susceptibility from the competition of FE
165 and AFE phases is analogous to negative stiffness composites of ferroelastics within a metal
166 matrix^{33,34}, i.e., the mechanical analog to NC.

167 168 **Ultrathin FE-AFE HfO₂-ZrO₂ MOS capacitors**

169
170 Next, the superlattices were grown on Si substrates in metal-oxide-semiconductor (MOS)
171 capacitor structures. A self-limiting chemical oxide SiO₂ was grown first, resulting in ~ 8.0 - 8.5 Å
172 thickness³, following the standard practice in advanced Si devices (Methods). Subsequently, a
173 20-cycle thick multilayer was grown with ALD following the same stacking as before i.e.
174 Hf:Zr:Hf 4:12:4. Accumulation *C-V* curves of the superlattice stack results in significantly larger
175 capacitance in comparison to other conventional stacks – DE HfO₂, AFE ZrO₂, FE Zr:HfO₂ – of
176 the same 20 Å thickness (Fig. 2d). Furthermore, the Hf:Zr:Hf 4:12:4 trilayer demonstrates
177 enhanced capacitance compared to a bilayer (Hf:Zr 8:12) and solid solution (Hf:Zr [2:3]₄) of the
178 same thickness and Hf:Zr composition (Fig. 2e).

179
180 Notably, the composition in our films is close to where several previous reports have postulated a
181 possible morphotropic phase boundary (MPB) in thicker HfO₂-ZrO₂ solid solution films³⁵. Note
182 MPB systems follows strict symmetry requirements³⁶, which have not been established for the
183 HfO₂-ZrO₂ system. In our ultrathin HfO₂-ZrO₂-HfO₂ multilayers, the negative free energy
184 curvature of the polar FE O-phase compensates the positive curvature of the nonpolar AFE T-
185 phase (Fig. 1a), leading to a flattened energy landscape. Similarly, energy landscape flattening is
186 postulated as the thermodynamic origin of enhanced piezoelectric response in the canonical
187 perovskite ferroelectrics³⁶, in which multiple crystal symmetries are nearly degenerate across a
188 composition phase boundary (MPB). However, a critical distinction is that here, the overall
189 energy landscape flattening, and corresponding increase in capacitance, is determined by the
190 stacking of the atomic-scale HfO₂-ZrO₂ layers, and not the volume fraction of the constituent
191 elements³⁷: solid solution of the same Hf:Zr composition does not provide the same high
192 capacitance (Fig. 2e). Furthermore, compared to HfO₂-ZrO₂ solid solutions across a range of
193 typically-reported Zr-rich "MPB"-like compositions³⁵, the HfO₂-ZrO₂-HfO₂ multilayer
194 demonstrates larger capacitance (Extended Data Fig. 4). This indicates the enhanced capacitance

195 in HfO₂-ZrO₂-HfO₂ films is not simply driven by doping^{32,38}, but can instead be tuned by the
196 configuration of the multilayer structure (Extended Data Fig. 4, 5). In the ultrathin regime,
197 surface energies become a more dominant consideration for determining polymorphic phase
198 stability²²; accordingly, the importance of stacking is amplified.

199
200 To quantify the observed capacitance, we have performed EOT simulations of MOS capacitors
201 using the industry standard Synopsys simulation platform (Methods). The Hf:Zr:Hf 4:12:4
202 trilayer stacks vary between 6.5-7.0 Å EOT (Fig. 2f), consistent over many measured capacitors.
203 Notably, this EOT is smaller than the expected thickness of the interfacial SiO₂ layer (8.0-8.5 Å),
204 as mentioned. To investigate further, high-resolution TEM of the gate stacks (Extended Data Fig.
205 6) illustrates the SiO₂ thickness is indeed ~ 8.5 Å. To supplement this physical characterization,
206 we next implemented electrical characterization of the interfacial layer via inverse capacitance vs
207 thickness analysis of conventional dielectric HfO₂ and Al₂O₃ thickness series grown on the same
208 SiO₂ (Methods, Extended Data Fig. 6). All thermal processing is kept the same as the HfO₂-ZrO₂
209 superlattice gate stack. The extracted HfO₂ and Al₂O₃ permittivity – 19 and 9, respectively – is
210 consistent with the typical dielectric phases of these two materials. Therefore, one can reliably
211 extract the SiO₂ layer thickness, yielding 8 Å (Extended Data Fig. 6), consistent with the HR-
212 TEM results and values established by the semiconductor industry³.

213
214 Moreover, the consistent interlayer thickness extracted from both material systems indicates that
215 neither Hf nor Al encroaches into the interfacial SiO₂, which would reduce its thickness and/or
216 increase its permittivity. This is expected considering the gate oxides are processed at much
217 lower temperature than that needed for silicate formation³⁹ and works reporting an increased
218 SiO₂ interlayer permittivity⁴⁰. Furthermore, XRR, EELS and XPS data indicate that for both the
219 undoped control HfO₂ gate stack and the superlattice gate stack, the HfO₂ layer sits right on top
220 of SiO₂, leading to the same interface in both cases (Extended Data Fig. 1). Therefore,
221 considering the interfacial layer thickness as 8 Å, the HfO₂-ZrO₂-HfO₂ multilayer gate stack
222 demonstrates an overall EOT ~ 1.5 Å lower than the constituent SiO₂ thickness. We note for
223 simplicity, we have used an EOT to quantify the capacitance of the superlattice stack; however,
224 for a rigorous description, one should solve for the non-linearities that are expected to emerge
225 from the ferroic nature of the gate-oxide⁴¹.

226
227 To supplement the *C-V* evidence of capacitance enhancement, pulsed current-voltage (*I-V*)
228 measurements of MOS capacitors integrating the ~ 2 nm HfO₂-ZrO₂-HfO₂ gate stack – which
229 can quantify the amount of charge as a function of voltage²⁶ (Methods, Extended Data Fig. 7) –
230 demonstrate larger stored charge than if just interfacial SiO₂ was sitting on top of Si. This
231 provides further electrical evidence of charge enhancement in the ultrathin mixed ferroic gate
232 stack (Extended Data Fig. 7e). Furthermore, from these measurements, the extracted
233 polarization- electric field relationship for just the HfO₂-ZrO₂-HfO₂ multilayer (Extended Data
234 Fig. 7f) exhibits a regime of negative slope, which mathematically corresponds to negative
235 capacitance stabilization²⁶.

236 237 **Ultrathin FE-AFE HfO₂-ZrO₂ Device Results**

238
239 The practical implication of this capacitance enhancement can be clearly seen in Fig. 3b, which
240 shows leakage current vs. EOT behavior. The leakage current is measured at $V_G - V_{fb} = -1$ V,

241 where V_{fb} is the flatband voltage of the semiconductor. All other data points on this plot are taken
242 from reported industrial gate stacks³. The leakage current for the Hf:Zr:Hf 4:12:4 stack is
243 substantially lower at the same EOT. Note that below 9 Å, the other gate stacks need
244 sophisticated scavenging techniques to reduce the thickness of the interfacial SiO₂³. On the other
245 hand, the ferroic gate stack can achieve ~ 6.5 Å without any scavenging, resulting in the lower
246 leakage current (Fig. 3b).

247
248 Furthermore, the scavenging of the interfacial SiO₂ leads to a loss of mobility of ~20 cm²/V-s per
249 every Å of scavenged SiO₂ due to an increase in remote phonon scattering^{3,16}. To examine how
250 the mobility evolves with EOT, we compared transistors implementing the lower-EOT HfO₂-
251 ZrO₂-HfO₂ gate stack compared to higher-EOT conventional HfO₂ gate stack, both of the same
252 physical thickness (Methods). Notably, the mobility remains essentially the same for both stacks,
253 demonstrating there is no fundamental change in electron transport due to the mixed-ferroic
254 multilayer gate stack compared to the standard high-κ dielectric gate stack (Extended Data Fig.
255 8d). Furthermore, this work demonstrates no penalty in mobility below 9 Å EOT, the point
256 where conventional high-κ gate stacks display mobility degradation due to scavenging necessary
257 for lowering EOT (Fig. 3c, Extended Data Fig. 8d). Indeed, raw mobility extracted from long-
258 channel transistors integrating the 2 nm HfO₂-ZrO₂-HfO₂ (HZH) mixed-ferroic heterostructure
259 gate stack exceed that of industry-reported long-channel transistors integrating standard 2 nm
260 HfO₂ high-κ dielectric gate stacks⁴² at the same EOT (Fig. 3c).

261
262 To examine how the capacitance enhancement in the 2 nm HfO₂-ZrO₂-HfO₂ gate stack behaves
263 at high frequency, radio frequency (RF) measurements were performed on the same long channel
264 ($L_G = 1 \mu\text{m}$) devices (Methods, Extended Data Fig. 9) to extract device parameters up to ~800
265 MHz for our devices (close to the cut-off frequency). Of particular interest is the
266 transconductance (g_m), which is proportional to the product of capacitance and electron velocity
267 (mobility). From Y -parameter measurements one can find AC transconductance as $Re(Y_{21}) =$
268 $g_m + af^2$, where f is the frequency (Methods). This yields an AC transconductance as a function of
269 applied gate voltage (V_G). Plotting this dependence together with DC transconductance ($\partial I_D / \partial V_G$
270 from DC I_D - V_G) (Fig. 3h) illustrates DC and AC transconductance are similar, with AC
271 transconductance roughly 15% larger at the peak value. This slightly larger AC transconductance
272 may result from the fact that certain interface traps, which affect the DC behavior, cannot
273 respond at frequencies larger than 100 MHz, leading to better gate control. More importantly,
274 these RF results show that the observed capacitance enhancement is not limited to the low
275 frequency regime^{43,44}.

276
277 Next, shorter channel ($L_G = 90 \text{ nm}$) devices, fabricated on a silicon-on-insulator (SOI) transistor
278 with 18 nm SOI thickness, were examined. The transfer and output characteristic of a typical
279 transistor are shown in Fig. 3e,f. Note that the threshold voltage of this device is 0.55 V, which
280 is consistent with the work function of W used as the gate metal. Because of this, the transistors
281 have been driven up to 1.6 V gate voltage so that an overdrive voltage ($V_{ov} = V_G - V_T$) of ~1 V
282 can be applied. It is found that at a drain voltage (V_D) and V_{ov} of 1 V, the drain current exceeds 1
283 mA/ μm . Additionally, the measured extrinsic transconductance of ~1.1 mS/ μm (Fig. 3g)
284 corresponds to an intrinsic transconductance of ~1.75 mS/ μm (Methods, Extended Data Fig. 10).
285 The transconductance is substantially larger than conventional 90 nm transistors. In addition, it is
286 larger than control devices with HfO₂ gate stack of the same physical thickness, demonstrating

287 the dual benefits of the HfO₂-ZrO₂-HfO₂ mixed-ferroic gate stack: low EOT without adversely
288 affecting the electron transport.

289
290 Finally, to probe the interface quality, especially trap-induced effects⁴⁵ relevant for MOSFET
291 reliability – a very crucial aspect for commercial application – we performed positive bias
292 temperature instability (PBTI) measurements on nFET transistors (Extended Data Fig. 8e-h). The
293 results demonstrate very similar behavior for both the HfO₂-ZrO₂-HfO₂ and control HfO₂ stacks
294 of the same physical thickness, and similar to those reported in literature for high- κ HfO₂
295 stacks⁴⁶. This is not unexpected; reliability characteristics are predominantly determined by the
296 interfacial oxide and its high- κ interface⁴⁶; here, both stacks have the same un-scavenged SiO₂
297 interlayer (Extended Data Fig. 1). Furthermore, stress measurements on capacitors demonstrate
298 negligible V_{fb} shift and non-existent capacitance degradation with increased stress time
299 (Extended Data Fig. 8i,j).

300 301 **Discussion**

302
303 Capacitance enhancement via negative capacitance (NC) has been demonstrated for ferroelectric-
304 dielectric superlattices in many single-crystalline perovskite-structure systems^{30,31,47,48}. This
305 work demonstrates that the same enhancement is possible in HfO₂-ZrO₂ fluorite-structure
306 superlattices on Si, which exhibit mixed ferroelectric-antiferroelectric (polar-nonpolar) order in
307 films as thin as just ~ 2 nm. The ability to go down to such thickness and still stabilize
308 competing ferroic order, conducive for NC mediated capacitance enhancement, is very important
309 for advanced electronic devices as dimensional scaling requires ultrathin gate stacks.
310 Furthermore, this work establishes the critical role of atomic-layer stacking – as opposed to
311 conventional doping techniques^{32,38} – in controlling the ferroic phase space and permittivity of
312 fluorite-structure oxides down to ultrathin limits, leveraging its unique size effects¹³⁻¹⁵ and rich
313 antiferroelectric-ferroelectric polymorphs^{22,23}. When this mixed phase HfO₂-ZrO₂ multilayer is
314 integrated on Si, the gate stack exhibits a capacitance enhancement, lowering the EOT below a
315 threshold which traditionally required careful scavenging of interfacial SiO₂, which would
316 otherwise degrade mobility³. Additionally, this EOT is achieved at over an order of magnitude
317 lower leakage current. Therefore, harnessing atomic-scale layering in ultrathin HfO₂-ZrO₂ ferroic
318 gate oxides presents a promising materials design platform for future Si transistors beyond the
319 conventional high- κ dielectrics which have spurred semiconductor industry scaling over the past
320 two decades.

- 321 1. Theis, T. N. & Wong, H.-S. P. The End of Moore's Law: A New Beginning for
322 Information Technology. *Computing in Science & Engineering* **19**, 41–50 (2017).
- 323 2. Schlom, D. G., Guha, S. & Datta, S. Gate Oxides Beyond SiO₂. *MRS Bulletin* **33**, 1017–
324 1025(2008).
- 325 3. Ando, T. Ultimate Scaling of High- κ Gate Dielectrics: Higher- κ or Interfacial Layer
326 Scavenging? *Materials* **5**, 478–500 (2012).
- 327 4. Salahuddin, S., Ni, K. & Datta, S. The era of hyper-scaling in electronics. *Nature*
328 *Electronics* **1**, 442–450 (2018).
- 329 5. Shulaker, M. M. *et al.* Three-dimensional integration of nanotechnologies for computing
330 and data storage on a single chip. *Nature* **547**, 74–78 (2017).
- 331 6. Wong, H.-S. & Salahuddin, S. Memory leads the way to better computing. *Nature*
332 *Nanotechnology* **10**, 191–194 (2015).
- 333 7. Del Alamo, J. A. Nanometre-scale electronics with III–V compound semiconductors.
334 *Nature* **479**, 317–323 (2011).
- 335 8. Butler, S. Z. *et al.* Progress, challenges, and opportunities in two-dimensional materials
336 beyond graphene. *ACS Nano* **7**, 2898–2926 (2013).
- 337 9. Khan, A. I., Keshavarzi, A. & Datta, S. The future of ferroelectric field-effect transistor
338 technology. *Nature Electronics* **3**, 588–597 (2020).
- 339 10. Dutta, S. *et al.* Monolithic 3D Integration of High Endurance Multi-Bit Ferroelectric FET
340 for Accelerating Compute-In-Memory. In *2020 IEEE International Electron Devices*
341 *Meeting (IEDM)*, 36.4.1–36.4.4 (IEEE, 2020).
- 342 11. Salahuddin, S. & Datta, S. Use of Negative Capacitance to Provide Voltage Amplification
343 for Low Power Nanoscale Devices. *Nano Letters* **8**, 405–410 (2008).
- 344 12. Böscke, T. S., Müller, J., Bräuhäus, D., Schröder, U. & Böttger, U. Ferroelectricity in
345 hafnium oxide thin films. *Applied Physics Letters* **99**, 102903 (2011).
- 346 13. Cheema, S. S. *et al.* Enhanced ferroelectricity in ultrathin films grown directly on
347 silicon. *Nature* **580**, 478–482 (2020).
- 348 14. Lee, H.-J. *et al.* Scale-free ferroelectricity induced by flat phonon bands in HfO₂. *Science*
349 **369**, 1343–1347 (2020).
- 350 15. Noheda, B. & Iniguez, J. A key piece of the ferroelectric hafnia puzzle. *Science* **369**, 1300–
351 1301 (2020).
- 352 16. Ando, T. *et al.* Understanding mobility mechanisms in extremely scaled HfO₂ (EOT 0.42
353 nm) using remote interfacial layer scavenging technique and V_t -tuning dipoles with gate-
354 first process. In *2009 IEEE International Electron Devices Meeting (IEDM)*, 1–4 (IEEE,
355 2009).
- 356 17. Wong, H. & Iwai, H. On the scaling of subnanometer EOT gate dielectrics for ultimate
357 nano CMOS technology. *Microelectronic Engineering* **138**, 57–76 (2015).
- 358 18. Narasimha, S. *et al.* 22nm High-performance SOI technology featuring dual-embedded
359 stressors, Epi-Plate High-K deep-trench embedded DRAM and self-aligned Via 15LM
360 BEOL. In *2012 International Electron Devices Meeting*, 3.3.1–3.3.4 (IEEE, 2012).
- 361 19. Huang, J. Gate first high-k/metal gate stacks with zero SiO_x interface achieving

- 362 EOT=0.59nm for 16nm application. In *2009 Symposium on VLSI Technology*, 34–35
363 (2009).
- 364 20. Yeo, Y.-C., King, T.-J. & Hu, C. Direct tunneling leakage current and scalability of
365 alternative gate dielectrics. *Applied Physics Letters* **81**, 2091–2093 (2002).
- 366 21. Kittel, C. Theory of Antiferroelectric Crystals. *Physical Review* **82**, 729–732 (1951).
- 367 22. Materlik, R., Künneth, C. & Kersch, A. The origin of ferroelectricity in $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$: A
368 computational investigation and a surface energy model. *Journal of Applied Physics* **117**,
369 134109 (2015).
- 370 23. Reyes-Lillo, S. E., Garrity, K. F. & Rabe, K. M. Antiferroelectricity in thin-film ZrO_2 from
371 first principles. *Physical Review B* **90**, 140103 (2014).
- 372 24. Qi, Y. & Rabe, K. M. Phase competition in HfO_2 with applied electric field from first
373 principles. *Physical Review B* **102**, 214108 (2020).
- 374 25. Lomenzo, P. D., Richter, C., Mikolajick, T. & Schroeder, U. Depolarization as Driving
375 Force in Antiferroelectric Hafnia and Ferroelectric Wake-Up. *ACS Applied Electronic*
376 *Materials* **2**, 1583–1595 (2020).
- 377 26. Hoffmann, M. *et al.* Unveiling the double-well energy landscape in a ferroelectric
378 layer. *Nature* **565**, 464–467 (2019).
- 379 27. Íñiguez, J., Zubko, P., Luk'yanchuk, I. & Cano, A. Ferroelectric negative capacitance.
380 *Nature Reviews Materials* **4**, 243–256 (2019).
- 381 28. Li, F., Zhang, S., Damjanovic, D., Chen, L.-Q. & Shrout, T. R. Local Structural
382 Heterogeneity and Electromechanical Responses of Ferroelectrics: Learning from Relaxor
383 Ferroelectrics. *Advanced Functional Materials* **28**, 1801504 (2018).
- 384 29. Khan, A. *et al.* Experimental evidence of ferroelectric negative capacitance in nanoscale
385 heterostructures. *Applied Physics Letters* **99**, 113501 (2011).
- 386 30. Yadav, A. K. *et al.* Spatially resolved steady-state negative capacitance. *Nature* **565**, 468–
387 471 (2019).
- 388 31. Das, S. *et al.* Local negative permittivity and topological phase transition in polar
389 skyrmions. *Nature Materials* **20**, 194–201 (2021).
- 390 32. Müller, J. *et al.* Ferroelectricity in Simple Binary ZrO_2 and HfO_2 . *Nano Letters* **12**, 4318–
391 4323 (2012).
- 392 33. Lakes, R. S., Lee, T., Bersie, A. & Wang, Y. C. Extreme damping in composite materials
393 with negative-stiffness inclusions. *Nature* **410**, 565–567 (2001).
- 394 34. Jaglinski, T., Kochmann, D., Stone, D. & Lakes, R. S. Composite Materials with
395 Viscoelastic Stiffness Greater Than Diamond. *Science* **315**, 620–622 (2007).
- 396 35. Ni, K. *et al.* Equivalent Oxide Thickness (EOT) Scaling With Hafnium Zirconium Oxide
397 High- κ Dielectric Near Morphotropic Phase Boundary. In *2019 IEEE International*
398 *Electron Devices Meeting (IEDM)*, 7.4.1–7.4.4 (IEEE, 2019).
- 399 36. Budimir, M., Damjanovic, D. & Setter, N. Piezoelectric response and free-energy
400 instability in the perovskite crystals BaTiO_3 , PbTiO_3 , and $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$. *Physical Review B*
401 **73**, 174106 (2006).
- 402 37. Noheda, B. *et al.* A monoclinic ferroelectric phase in the $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ solid

- 403 solution. *Applied Physics Letters* **74**, 2059–2061 (1999).
- 404 38. Schroeder, U. *et al.* Recent progress for obtaining the ferroelectric phase in hafnium
405 oxide based films: impact of oxygen and zirconium. *Japanese Journal of Applied Physics*
406 **58**, SL0801 (2019).
- 407 39. Schlom, D. G. & Haeni, J. H. A Thermodynamic Approach to Selecting Alternative Gate
408 Dielectrics. *MRS Bulletin* **27**, 198–204 (2002).
- 409 40. Bersuker, G. *et al.* The effect of interfacial layer properties on the performance of Hf-based
410 gate stack devices. *Journal of Applied Physics* **100**, 094108 (2006).
- 411 41. Liao, Y.-H. *et al.* Electric Field-Induced Permittivity Enhancement in Negative-
412 Capacitance FET. *IEEE Transactions on Electron Devices* 1–6 (2021).
- 413 42. Ragnarsson, L.-Å. *et al.* Ultrathin EOT high- κ /metal gate devices for future technologies:
414 Challenges, achievements and perspectives. *Microelectronic Engineering* **88**, 1317–1322
415 (2011).
- 416 43. Chatterjee, K., Rosner, A. J. & Salahuddin, S. Intrinsic speed limit of negative capacitance
417 transistors. *IEEE Electron Device Letters* **38**, 1328–1330 (2017).
- 418 44. Kwon, D. *et al.* Response Speed of Negative Capacitance FinFETs. *2018 IEEE Symposium*
419 *on VLSI Technology* 49–50 (2018).
- 420 45. Pae, S. *et al.* Reliability characterization of 32nm high-K and Metal-Gate logic transistor
421 technology. In *2010 IEEE International Reliability Physics Symposium*, II, 287–292 (IEEE,
422 2010).
- 423 46. Mukhopadhyay, S. *et al.* Trap Generation in IL and HK layers during BTI/TDDDB stress in
424 scaled HKMG N and P MOSFETs and implications on t_{inv} -scaling. In *2014 IEEE*
425 *International Reliability Physics Symposium*, GD.3.1–GD.3.11 (IEEE, 2014).
- 426 47. Gao, W. *et al.* Room-Temperature Negative Capacitance in a Ferroelectric–Dielectric
427 Superlattice Heterostructure. *Nano Letters* **14**, 5814–5819 (2014).
- 428 48. Zubko, P. *et al.* Negative capacitance in multidomain ferroelectric superlattices. *Nature*
429 **534**, 524–528 (2016).
- 430 49. Wong, J. C. & Salahuddin, S. Negative Capacitance Transistors. *Proceedings of the*
431 *IEEE* **107**, 49–62 (2019).
- 432
- 433

434 **Acknowledgements** This research was supported in part by the Berkeley Center for Negative
435 Capacitance Transistors (BCNCT), the DARPA Technologies for Mixed-mode Ultra Scaled Integrated
436 Circuits (T-MUSIC) program, the University of California Multicampus Research Programs and
437 Initiatives (UC MRPI) project and the U.S. Department of Energy, Office of Science, Office of Basic
438 Energy Sciences, Materials Sciences and Engineering Division under Contract No. DE-AC02-05-
439 CH11231 (Microelectronics Co-Design program) for the development of materials for low-power
440 microelectronics. This research used resources of the Advanced Photon Source, a U.S. Department of
441 Energy (DOE) Office of Science User Facility at Argonne National Laboratory and is based on research
442 supported by the U.S. DOE Office of Science-Basic Energy Sciences, under Contract No. DE-AC02-
443 06CH11357. VAS and JWF were supported by the US Department of Energy, Office of Science, Basic
444 Energy Sciences, under Award Number DE-SC-0012375. Use of the Stanford Synchrotron Radiation
445 Light source, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy,
446 Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. This
447 research used resources of the Advanced Light Source, which is a DOE Office of Science User Facility
448 under contract no. DE-AC02-05CH11231. Electron microscopy of was performed at the Molecular
449 Foundry, LBNL, supported by the Office of Science, Office of Basic Energy Sciences, US Department of
450 Energy (DE-AC02-05CH11231). Device fabrication was performed at the Marvell Nanofabrication
451 Laboratory at U.C. Berkeley. This material is based upon work supported by the Secretary of Defense for
452 Research and Engineering under Air Force Contract No. FA8702-15-D-0001. Any opinions, findings,
453 conclusions or recommendations expressed in this material are those of the author(s) and do not
454 necessarily reflect the views of the Secretary of Defense for Research and Engineering.

455
456 **Author contributions** S.S.C. and S.S. designed the research. S.S.C. performed design, synthesis, and
457 optimization of the superlattice oxide heterostructure and its ferroic characterization. N.S. and C.-H.H.
458 performed capacitor fabrication. C.-H.H. helped optimize annealing treatments. N.S. and S.S.C.
459 performed capacitor measurements and analysis. L.-C.W. fabricated the transistors and performed DC
460 characterization. D.W.K. and J.B. developed the initial processes for transistor fabrication. Y.-H.L.
461 performed simulations including EOT estimation, series resistance determination and mobility and
462 transconductance analysis. M.S.J., J.G. and W.L. contributed to RF electrical measurements and analysis.
463 N.S. performed MOSCAP stress measurements. W.C. and N.S. performed MOSFET reliability
464 measurements under the guidance of S.D., S.M, and S.S. M.M., R.R., C.S., D.P., G.P., M.C., B.T.
465 contributed to capacitor fabrication and characterization at MIT LL. S.-L.H. performed TEM. S.S.C. and
466 S.-L.H. performed TEM analysis. Y.R. performed second harmonic generation. S.K.V. performed X-ray
467 photoelectron spectroscopy. S.S.C. and C.-H.H. performed synchrotron soft X-ray spectroscopy at ALS.
468 S.S.C., V.A.S., J.W.F. performed synchrotron X-ray spectroscopy at APS. S.S.C., C.-H.H., V.A.S., Z.Z.
469 performed synchrotron in-plane diffraction at APS. S.S.C. and N.S. performed synchrotron X-ray
470 reflectivity and 2D diffraction at SSRL. S.S.C. and S.S. co- wrote the original manuscript; S.S.C., N.S.
471 and S.S. revised the manuscript. S.S. supervised the research. All authors contributed to discussions and
472 manuscript preparations.

473
474 **Competing interests** The authors declare that they have no competing financial interests.

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478 **Fig. 1. Atomic-scale design of negative capacitance in ultrathin HfO₂-ZrO₂.** (a) Energy
479 landscape flattening. A ferroelectric (FE) double-well energy landscape is flattened by the
480 depolarization field energies (Dep) originating from electrostatic and elastic inhomogeneities
481 present in the laterally-arranged polar-nonpolar (orthorhombic ferroelectric - tetragonal
482 antiferroelectric) thin film system. The energy landscape flattening increases the overall system's
483 permittivity, as susceptibility is proportional to the inverse landscape curvature; such flattening is
484 analogous to negative capacitance stabilization^{29,30,49}. (b) Engineering ferroic phase competition
485 in the HfO₂-ZrO₂ fluorite-structure system. Beyond the conventionally-studied tuning parameters
486 – composition, electric field, temperature^{32,38} – here we introduce dimensional confinement via
487 superlattice layering to tailor ferroic phase competition at the atomic-scale. (c) Schematic of the
488 HfO₂-ZrO₂ fluorite-structure multilayer on Si; the heterostructures maintain distinct layers (i.e.
489 not solid solution alloys) based on EELS, XRR, and depth-resolved XPS (Extended Data Fig. 1).
490 The role of the layering on the underlying ferroic order and capacitance is studied by electrical
491 measurements as a function of HfO₂-ZrO₂ stacking structure and annealing temperature
492 (Extended Data Fig. 4 and 5, respectively). (d) HR-TEM image of the atomic-scale HfO₂-ZrO₂-
493 HfO₂ trilayer (top) and extracted *d*-lattice spacings (bottom) corresponding to the fluorite-
494 structure AFE tetragonal (P4₂/nmc, red) and FE orthorhombic (Pca2₁, blue) phases, respectively.
495 The layer delineations are approximate, as the HfO₂-ZrO₂ and SiO₂ interlayer thicknesses are
496 more rigorously determined by XRR and TEM analysis (Extended Data Fig. 1 and 6,
497 respectively). Note imaging the crystallinity of the HfO₂-ZrO₂ layers requires mistilt with respect
498 to the Si lattice (Methods). (e) Synchrotron IP-GiD demonstrating the presence of both the AFE
499 *T*-phase (101)_t and FE *O*-phase (111)_o reflections whose *d*-lattice spacings are consistent with
500 those extracted from TEM. Detailed indexing for structural identification is provided by wide-
501 angle synchrotron diffraction (Extended Data Fig. 2a).

502 **Fig. 2. Enhanced capacitance in ultrathin HfO₂-ZrO₂ mixed-ferroic heterostructures. (a)**
503 **MIM *C-V* hysteresis loops for a mixed FE-AFE HfO₂-ZrO₂ multilayer demonstrating higher**
504 **capacitance compared against its AFE (ZrO₂) and FE (Zr:HfO₂) counterparts of the same**
505 **thickness. (b) Inverse capacitance versus thickness for MIM HfO₂-ZrO₂ multilayers up to 5**
506 **superlattice repeats (10 nm); the extracted permittivity of 52 is large for HfO₂-based oxides. (c)**
507 **MIM *C-V* hysteresis loops for HfO₂-ZrO₂ multilayers of the same periodicity demonstrating an**
508 **evolution from mixed-ferroic to FE-like hysteresis upon cooling slightly below room**
509 **temperature. The proximity to the temperature-dependent phase transition (Extended Data Fig. 3)**
510 **suggests the HfO₂-ZrO₂ heterostructures lies near its maximum electric susceptibility position,**
511 **ideal for negative capacitance stabilization^{30,49}. (d) MOS accumulation *C-V* of HfO₂-ZrO₂-HfO₂**
512 **trilayer compared to AFE ZrO₂, FE Zr:HfO₂, and DE HfO₂, all of the same thickness (20 Å),**
513 **indicating mixed-ferroic behavior is optimal for enhancing capacitance. (e) Accumulation *C-V* of**
514 **the HfO₂-ZrO₂-HfO₂ (HZH) trilayer compared to bilayer and solid solutions films of the same**
515 **thickness (ALD cycles) and composition (Hf:Zr cycles), demonstrating the capacitance**
516 **enhancement is not simply driven by Hf:Zr composition^{32,38}, but rather the atomic-scale stacking**
517 **(Extended Data Fig. 4, 5). Inset: Schematic multilayer versus solid solution (Hf and Zr cations**
518 **vertically-separated versus intermixed). (f) Accumulation *C-V* for a 2 nm HZH grown on sub-nm**
519 **SiO₂ fit EOT simulations. Inset: Gate leakage of the same stack. 2 nm HZH on SiO₂**
520 **demonstrates lower EOT than the thickness of SiO₂ interlayer alone, carefully extracted via**
521 **physical (8.5 Å) and electrical (8.0 Å) methodologies (Extended Data Fig. 6), providing evidence**
522 **of capacitance enhancement via NC. Furthermore, these 2 nm ferroic gate stacks demonstrate**
523 **amplified charge from pulsed *I-V* measurements relative to the SiO₂ interlayer (Extended Data**
524 **Fig. 7), marking the thinnest demonstration of charge and/or capacitance enhancement (Extended**
525 **Data Fig. 7).**

526 **Fig. 3. Device performance benefits utilizing ultrathin mixed-ferroic HfO₂-ZrO₂ gate**
527 **stacks.**

528 **(a)** EOT scaling pathways: conventional interlayer scavenging implementing standard high- κ
529 dielectric HfO₂ reduces the EOT by thinning the SiO₂ interlayer (red), leading to leakage and
530 mobility degradation³; integrating a ferroic NC oxide exhibiting a capacitance enhancement
531 effect on SiO₂ (blue) lowers the EOT without reducing the SiO₂ interlayer thickness. **(b)**
532 Leakage-EOT scaling of the HfO₂-ZrO₂-HfO₂ (HZH) multilayer gate stacks (blue) benchmarked
533 against reported HKMG literature³, including interlayer-scavenged 2 nm HfO₂ (red), high- κ
534 doped HfO₂ (gray), and SiO₂/poly-Si (black). The leakage is the lowest reported for a 6.5 Å EOT
535 MOS capacitor on silicon³, and similar as the standard higher-EOT 2 nm HfO₂ high- κ dielectric
536 (black), due to maintaining the same SiO₂ thickness. **(c)** Raw mobility versus EOT for long-
537 channel transistors integrating the 2 nm HZH (blue) versus industry-reported long-channel
538 transistors integrating standard 2 nm HfO₂ (red)⁴², reported at 10¹³/cm² charge density. The raw
539 mobility for HZH sits above the industry-reported trend line⁴² due to scaling EOT without
540 requiring scavenging. Mobility results are also benchmarked against other industrial HKMG
541 reports³ (Extended Data Fig. 8d). **(d)** Schematic transistor device layout which integrates the 2
542 nm HZH gate stack. **(e, f, g)** DC I - V transfer characteristics (I_d - V_{gs} , e), DC output characteristics
543 (I_d - V_{ds} , f), and DC transconductance (g_m - V_{gs} , g) for short-channel ($L_G = 90$ nm) SOI transistors.
544 Notably, the maximum on-current and g_m at $V_{DS} = 1$ V exceeds 1 mA/ μ m and 1 mS/ μ m,
545 respectively. **(h)** Transconductance versus gate voltage for long-channel bulk transistors ($L_G = 1$
546 μ m) via DC (derivative of I_d - V_{gs}) and RF ($Re[Y_{21}]$) measurements at $V_{DS} = 1$ V. Inset: De-
547 embedded $Re[Y_{21}]$ (open circles) as a function of squared frequency at different DC bias points
548 extrapolated to the zero-frequency limit (dotted lines) to extract the RF g_m (Extended Data Fig.
549 9).

550 **Methods**

551

552 **Gate stack**

553

554 **Gate oxide** Thin films of HfO₂-ZrO₂ were grown by atomic layer deposition (ALD) in a Fiji
555 Ultratech/Cambridge Nanotech tool (U.C. Berkeley) at 270°C in which tetrakis
556 (ethylmethylamino) hafnium and tetrakis (ethylmethylamino) zirconium precursors are heated to
557 75°C and water vapor is used as the oxidant. For metal-ferroelectric-insulator-semiconductor
558 (MFIS) capacitor structures, sub-nm chemically-grown SiO₂ on lightly-doped Si (10¹⁵ cm⁻³) was
559 prepared by the standard clean (SC-1) solution (5:1:1 H₂O:H₂O₂:NH₄OH at 80°C for 10 minutes)
560 after the Si wafer was cleaned in Piranha (120°C for 10 minutes) to remove organics and HF
561 (50:1 H₂O:HF at room temperature for 30 s) to remove any native oxide. Subsequently, HfO₂-
562 ZrO₂-HfO₂ multilayers are deposited at 270°C by ALD. After ALD deposition, post-deposition
563 annealing (PDA) was performed at 175°C (20 min, forming gas N₂/H₂ background) to help cure
564 the SiO₂-oxide interface. For confirmation and reproducibility, HfO₂-ZrO₂-HfO₂ multilayers of
565 the same ALD cycling were also deposited at MIT Lincoln Laboratory (MIT LL); after ALD
566 deposition, PDA was performed at 250°C (1 min, N₂ background).

567

568 **Gate metal** For UC Berkeley capacitors, the first layer of the gate metal, TiN, is deposited by
569 ALD (250°C, 20 cycles, 15 Å) in N₂ and H₂ plasma. Subsequently, W is deposited by sputtering
570 (room temperature, 60 nm). For MIT LL capacitors, the gate metal, TiN, is deposited by PVD
571 (room temperature).

572

573 **Annealing** The entire gate stack undergoes a low-temperature post-metal anneal (200°C, 1 min,
574 N₂) to cure interface defects. This low temperature does not interfere with the HfO₂-ZrO₂-HfO₂
575 multilayer structure, as confirmed by various characterization techniques (Extended Data Fig. 1),
576 and maintains the mixed ferroic behavior, as high-temperature annealing would induce purely
577 ferroelectric behavior (Extended Data Fig. 5). X-ray diffraction and TEM confirm the presence
578 of crystalline ultrathin films despite the low deposition temperature, afforded by the low
579 crystallization temperature of ZrO₂⁵⁰. In fact, non-post-annealed ALD-grown ZrO₂ has
580 previously demonstrated crystallization into the ferroelectric orthorhombic phase on Si⁵¹.

581

582 **Device fabrication**

583

584 **MOS and MIM capacitors, Bare Structures** For MOS capacitor structures, after gate stack
585 deposition, top electrodes are defined by photolithography and dry etching. For bare structures
586 (structural studies), the top metal is removed by chemical etching to expose the gate oxide
587 surface. For metal-insulator-metal (MIM) capacitors, W is deposited by sputtering (room
588 temperature, 30 nm) on a lightly-doped Si substrate as the bottom metal electrode. After ferroic
589 film deposition by ALD, 60 nm of W is deposited by sputtering. The top electrodes are then
590 again defined by photolithography and dry etching.

591

592 **Bulk transistors** The n-type bulk transistors were fabricated by a non-self-aligned gate-last
593 process on bulk silicon wafers (10¹⁷ cm⁻³) with local oxidation of silicon (LOCOS) as device
594 isolation technique. First, a 10 nm of SiO₂ thermal oxide and a 30 nm of low-pressure chemical
595 vapor deposition (LPCVD) Si₃N₄ were grown on the Si substrates. After the active region was

596 defined by photolithography and $\text{Si}_3\text{N}_4/\text{SiO}_2$ etching, dry oxidation was performed to form the
597 LOCOS isolation. Next, the source/drain regions were defined by photolithography and ion
598 implantation with an ion dose of 3×10^{15} ions/cm². The dopants were then activated by a rapid
599 thermal anneal (RTA) at 900°C for 7 min in N_2 ambient. The gate stacks with the sub-nm
600 chemically-grown SiO_2 , 2 nm $\text{HfO}_2\text{-ZrO}_2\text{-HfO}_2$ heterostructure, and 100 nm of sputtered W gate
601 were then deposited. After the gate fingers (from 500 nm to 50 μm) were patterned by
602 photolithography and etched by inductively-coupled plasma (ICP) metal etching, the 400 nm
603 thick interlayer dielectric (ILD) SiO_2 was deposited using plasma-enhanced CVD (PECVD).
604 Last, after the contact hole opening, the Ti/TiN contact metal was deposited by sputtering,
605 defined by photolithography, and then etched by ICP metal etching.

607 **Short-channel SOI Transistors** The n-type short-channel transistors were fabricated by a non-
608 self-aligned gate-last process on SOI substrates with a gate length (L_G) down to 90 nm. First, the
609 device layer was thinned down to 20 nm and the active regions were defined by
610 photolithography with expose regions etched slightly into the buried oxide. The hydrogen
611 silsequioxane (HSQ) negative resist were written by e-beam lithography as a hard mask for the
612 ion implantation with a dose of 5×10^{15} ions/cm². The dopant activation was conducted in an
613 RTA at 900°C for 15 seconds in N_2 ambient. The gate stacks with the sub-nm chemically-grown
614 SiO_2 , 2 nm $\text{HfO}_2\text{-ZrO}_2\text{-HfO}_2$ heterostructure, 1.5 nm of PEALD TiN, and 100 nm of sputtered W
615 were sequentially deposited. The gate region (250 nm) was then patterned by photolithography.
616 Like the back-end process for the bulk transistors, 400 nm of ILD and sputtered Ti/TiN contact
617 metal were deposited and defined by photolithography and ICP etching.

619 **Microscopy**

621 **Transmission electron microscopy** Electron microscopy was performed at the National Center
622 for Electron Microscopy (NCEM) facility of the Molecular Foundry at Lawrence Berkeley
623 National Laboratory (LBNL). The high-resolution bright field TEM images of $\text{HfO}_2\text{-ZrO}_2\text{-HfO}_2$
624 thin films were performed by FEI ThemIS 60-300 microscope with image aberration corrector
625 operated at 300 kV (Fig. 1d, Extended Data Fig. 2e,f). To prepare cross-sectional TEM samples
626 of $\text{HfO}_2\text{-ZrO}_2\text{-HfO}_2$ thin films, mechanical polishing was employed by using an Allied High
627 Tech Multiprep at a 0.5° wedge to thin down the total thickness of samples down to 10 μm .
628 Later, Ar ion milling of the Gatan Precision Ion Milling System was utilized to make an
629 electron-transparent sample, starting from 4 keV down to 200 eV as final cleaning energy. For
630 high-resolution imaging, in order to capture the crystallinity of the $\text{HfO}_2\text{-ZrO}_2\text{-HfO}_2$ layers, the
631 zone axis alignment required varying degrees of mistilt with respect to the Si lattice, explaining
632 the slightly obscured Si atomic columns (Fig. 1d, Extended Data Fig. 2e,f).

634 The local interplanar d -spacing in the ultrathin $\text{HfO}_2\text{-ZrO}_2\text{-HfO}_2$ films (Extended Data Fig. 2e,f)
635 was measured by DigitalMicrograph software using its line profile plus integration width
636 analysis. For the 2 nm $\text{HfO}_2\text{-ZrO}_2\text{-HfO}_2$ multilayer film, the extracted interplanar lattice spacings
637 were averaged over multiple lattice periodicities and confirmed across various local regions of
638 the film (Extended Data Fig. 2e,f). The SiO_2 interlayer thickness from low-magnification wide
639 field-of-view (FoV) imaging was determined by the same method (Extended Data Fig. 6a). In
640 particular, the intensity line scan from the wide FoV image (Extended Data Fig. 6a) is obtained
641 from averaging across the entire FoV specified by the teal-colored box (~150 nm). Next, the

642 inflection points of the intensity peak were used as the criteria to set the boundaries of the SiO₂
643 interlayer (Extended Data Fig. 6a). This methodology was also utilized to determine the
644 boundaries of the HfO₂-ZrO₂-HfO₂ layers from the EELS spectrum (Extended Data Fig. 1c).
645 Regarding the wide FoV cross-sectional TEM (Extended Data Fig. 6a), both the low atomic
646 weight and lack of crystallinity of the SiO₂ layer contribute to its weak scattering (bright color),
647 which aids in the visual delineation of the layer boundaries and the thickness extraction from the
648 corresponding averaged intensity line scan.

649
650 **Optical microscopy** Second harmonic generation (SHG) measurements (Extended Data Fig. 2d)
651 were performed with a Ti:sapphire femtosecond laser (Tsunami, Spectra Physics, $\lambda \sim 800$ nm,
652 frequency ~ 80 MHz). The linearly polarized femtosecond laser beam was focused through 50X
653 objective lens ($NA \sim 0.42$) which results in a focal spot size of 2 μm . The generated SHG signal
654 was collected through the same objective lens and separated from the fundamental beam by the
655 harmonic separator. After passing through the optical bandpass filter, the SHG signals were
656 registered to the photon multiplier tube (PMT) without a polarizer. The fundamental beam was
657 mechanically chopped, and the signal collected by the PMT was filtered by a lock-in amplifier to
658 reduce the background noise. For SHG spatial mapping, a two-axis piezo stage was utilized and
659 the coordinate was synchronized with the PMT signal. The SHG intensity was obtained by
660 averaging the mapping signals across a 100 $\mu\text{m} \times 100 \mu\text{m}$ sample area.

661
662 **X-ray characterization**

663
664 **X-ray reflectivity** Synchrotron X-ray reflectivity (XRR) – performed at Sector 33-BM-C
665 beamline of the Advanced Photon Source, Argonne National Laboratory and at Beamline 2- 1 of
666 the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory –
667 confirmed the thickness of HfO₂-ZrO₂-HfO₂ heterostructures (Extended Data Fig. 1b). The
668 overall thickness of the HfO₂-ZrO₂-HfO₂ heterostructures is consistent with the growth rate (~ 1
669 $\text{\AA}/\text{cycle}$) of ALD-grown Zr:HfO₂ as demonstrated in our previous work¹³. Furthermore, the
670 presence of irregularly spaced fringes in the thicker HfO₂-ZrO₂-HfO₂ heterostructures suggests
671 the presence of well-separated HfO₂-ZrO₂-HfO₂ layers, i.e. not a solid solution. This is
672 confirmed by XRR fitting (Extended Data Fig. 1b) performed with the python package GenX⁵²
673 which considers factors such as density, roughness, and thickness.

674
675 **In-plane grazing incidence diffraction** Synchrotron in-plane grazing-incidence diffraction
676 (GID) (Fig. 1e, Extended Data Fig. 2a) was performed at Sector 33-ID-D beamline of the
677 Advanced Photon Source, Argonne National Laboratory. A Pilatus-II 100K Area Detector
678 mounted on the del-arm was used to collect diffraction signal with a grazing incidence geometry.
679 The region-of-interest on the detector was set such that the ring-like signal was fully integrated.
680 In-plane GID was collected by sweeping the in-plane angle ν ($8-50^\circ$) with a fixed out-of-plane
681 grazing angle δ ($\delta = 0.9^\circ$); the corrected Bragg angle (2θ) over which the data is plotted and
682 indexed is determined from the relationship $\cos(2\theta) = \cos(\nu) \cdot \cos(\delta)$ set by the geometry of the
683 diffractometer. The X-ray source was fixed at 16 keV ($\lambda = 0.775 \text{\AA}$). In-plane diffraction yields
684 more diffraction peaks with better defined width, likely due to the preferred orientation and disc-
685 shape domains in the film. Therefore, in-plane GID enables clear indexing to the ferroelectric
686 orthorhombic (Pca2₁) and antiferroelectric tetragonal (P4₂/nmc) fluorite structure in the ultrathin
687 HfO₂-ZrO₂-HfO₂ films, as the presence of many reflections from the in-plane GID spectra (Fig.

688 1e, Extended Data Fig. 2a) allow for clear distinction from other nonpolar fluorite-structure
689 polymorphs. Such diffraction spectra would be otherwise prohibited in typical out-of-plane
690 geometry due to the lack of vertical diffraction planes and the large linewidth inherent to
691 ultrathin films.

692
693 **Two-dimensional diffraction** Two-dimensional reciprocal space maps (Extended Data Fig. 2b)
694 were measured at Beamline 11-3 of the Stanford Synchrotron Radiation Lightsource, SLAC
695 National Accelerator Laboratory. Rayonix MX225 CCD area detector collected diffraction flux
696 in grazing incidence ($<0.20^\circ$) geometry; the X-ray source (50 microns vertical x 150 microns
697 horizontal beam size) was fixed at 12.7 keV. The sample-detector work distance was set to 80
698 mm to enable detection of a wide region of reciprocal space (Q -range 0.2 to 5 \AA^{-1}) at the expense
699 of reciprocal space resolution, set by the pixel size. The two-dimensional diffraction scans – in
700 which a wide portion of the entire reciprocal space was collected simultaneously, rather than at
701 discrete regions in Q_x - Q_y space – were averaged over data collection time and for repeated scans.
702 These measurement features, in tandem with the high X-ray flux afforded by the synchrotron
703 source, enabled sufficient diffraction signal detection and contrast in films just two nanometers
704 in thickness. Data analysis was performed Nika, an Igor Pro package for correction, calibration,
705 and reduction of two-dimensional areal maps into one-dimensional data⁵³. Two-dimensional
706 reciprocal space maps on bare HfO_2 - ZrO_2 - HfO_2 heterostructures confirm the presence of
707 crystalline ultrathin films despite the low deposition temperature, afforded by the low
708 crystallization temperature of ZrO_2 on Si ⁵⁰.

709
710 **Ferroic phase identification from diffraction** For fluorite-structure thin films, the main phases
711 to consider are the dielectric monoclinic ($\text{P}2_1/\text{c}$), antiferroelectric tetragonal ($\text{P}4_2/\text{nmc}$), and
712 ferroelectric orthorhombic ($\text{Pca}2_1$) phases. Various diffraction reflections from the wide-angle
713 IP-GiD spectra enable indexing to the orthorhombic $\text{Pca}2_1$ phase. Lattice parameters (a , b , c) –
714 determined via Bragg's law from the d_{200} family of reflections – are self-consistently checked
715 against the (111) lattice spacing ($\frac{1}{d_{111}^2} = \frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2}$) as well as other higher-order reflections
716 present in the in-plane diffraction spectra (Extended Data Fig. 2a). For example, the lattice
717 parameters extracted from the {200} reflections were $a = 5.36 \text{ \AA}$, $b = 5.23 \text{ \AA}$, $c = 5.47 \text{ \AA}$. This
718 corresponds to a d_{211} lattice spacing of 2.209 \AA , which agrees well with the lattice spacing (2.205
719 \AA) obtained from Bragg's law based on the reflection position.

720
721 The monoclinic phase was ruled out due to a lack of two {111} peaks in the diffraction spectra
722 and the $(111)_o$ and $(101)_t$ reflections being significantly offset from its expected peak position in
723 the monoclinic phase. With regards to the indexing of tetragonal $(101)_t$ peak (Extended Data Fig.
724 2a), it is always reported that the tetragonal $(101)_t$ reflection has a smaller d -spacing⁵⁴ in thicker
725 HfO_2 -based films⁵⁵, and is therefore expected to be present at a higher angle compared to the
726 orthorhombic $(111)_o$ reflection, which is the case in the indexed diffraction spectra (Extended
727 Data Fig. 2a) based on the self-consistent indexing methodology outlined above provides.

728
729 In terms of extracting the phase fraction of the tetragonal and orthorhombic phases, while
730 Rietveld refinement has been applied to grazing incidence x-ray diffraction of thick (10 nm)
731 Zr:HfO_2 ⁵⁶ to determine the orthorhombic phase fraction, that methodology cannot be applied in
732 the ultrathin regime, as the films are highly oriented, as opposed to fully polycrystalline
733 (Extended Data Fig. 2b), which is a requirement to apply Rietveld refinement.

734

735 Regarding strain effects: strain-induced ferroelectricity in antiferroelectrics is a key
736 consideration; strain-induced ferroelectricity has been predicted in ZrO_2 ²³, which is indeed what
737 we observe in certain lateral regions of our film. From the cross-sectional TEM (Fig. 1d,
738 Extended Data Fig. 2e,f), the presence of both the FE orthorhombic Pca_21 phase grains and AFE
739 $\text{P4}_2/\text{nmc}$ tetragonal phase grains can be locally identified to persist throughout the entire HfO_2 -
740 ZrO_2 - HfO_2 thickness. Considering the 2 nm HfO_2 - ZrO_2 - HfO_2 heterostructure has distinct layers
741 (evidenced by XRR, EELS, and XPS characterization in Extended Data Fig. 1), that means the
742 middle ZrO_2 layer has local regions where it is stabilized in the FE orthorhombic phase, and
743 other local regions where it is stabilized in the AFE tetragonal phase.

744

745 Regarding structural indicators of such strain effects, again we look to the measured d_{111} (O -
746 phase) and d_{101} (T -phase) lattice spacings for the ~ 2 nm HfO_2 - ZrO_2 - HfO_2 (HZH) film –
747 structural markers for distortion and strain in this fluorite-structure system¹³. Note that truly
748 stress-free values cannot be obtained as bulk ferroelectricity is not stabilized in this material
749 system, so we compare against DFT values²² for HfO_2 , ZrO_2 , and Zr:HfO_2 (HZO)²², which
750 closely match experimental values for thicker HfO_2 - ZrO_2 ferroic films⁵⁷.

751

752 In particular, the ferroelectric O -phase d_{111} -spacing for HfO_2 - ZrO_2 - HfO_2 (3.09 Å) is larger than
753 typical values for thick ferroelectric HZO films (2.95 Å)²², demonstrating that the individual
754 HfO_2 and ZrO_2 layers in the HZH multilayer are in fact strained i.e. increased rhombic distortion.
755 This is consistent with the ultrathin-enhanced lattice distortions trend observed in previous ALD-
756 grown highly-oriented orthorhombic ferroelectric HZO films¹³ as well as epitaxial orthorhombic
757 ferroelectric HZO films⁵⁸. On the other hand, we observe that the d -spacing for the tetragonal
758 (101) reflection (2.95 Å) is nearly the same as is expected for prototypical antiferroelectric T -
759 phase ZrO_2 (2.94 Å)²². This is expected: when the tetragonal phase is strained, it transitions to
760 the lower symmetry orthorhombic phase as opposed to remaining in the tetragonal phase, as it
761 does not have the same tolerance of the FE O -phase to maintain its symmetry when strained.
762 Consequently, the larger d -spacing is always attributed to the FE O -phase⁵⁷, as confirmed by
763 self-consistent indexing to higher-order reflections (Extended Data Fig. 2a). These diffraction-
764 based d -spacings are confirmed by cross-sectional TEM (Extended Data Fig. 2e,f). Furthermore,
765 the presence of the ZrO_2 layer developing ferroelectricity is supported by the presence of orbital
766 polarization at the Zr L -edge from synchrotron X-ray linear dichroism (Extended Data Fig. 2c).

767

768 **X-ray absorption spectroscopy** Hard and soft synchrotron X-ray spectroscopy (Extended Data
769 Fig. 2c) was measured at beamline 4-ID-D of the Advanced Photon Source, Argonne National
770 Laboratory and Beamline 4.0.2. of the Advanced Light Source, Lawrence Berkeley National
771 Laboratory, respectively. Spectroscopy measurements were taken at the oxygen K -edge (520-550
772 eV), zirconium $M_{3,2}$ -edge (325-355 eV), hafnium M_3 -edge (2090-2150 eV), and zirconium $L_{3,2}$ -
773 edge (2200-2350 eV). X-rays were incident at 20° off grazing. XAS (XLD) was obtained from
774 the average (difference) of horizontal and vertical linearly polarized X-rays. To eliminate
775 systematic artifacts in the signal that drift with time, spectra measured at ALS were captured
776 with the order of polarization rotation reversed (e.g., horizontal, vertical, vertical, and horizontal)
777 in successive scans, in which an elliptically polarizing undulator tuned the polarization and
778 photon energy of the synchrotron X-ray source⁵⁹. Spectra measured at ALS were recorded under
779 total electron yield (TEY) mode⁵⁹ from room temperature down to 100 K. Spectra measured at

780 APS were recorded under various modes: total electron yield (TEY), fluorescence yield (FY),
781 and reflectivity (REF).

782

783 **Ferroic phase identification from spectroscopy** X-ray spectroscopy provides various
784 signatures to distinguish the competing ferroelectric orthorhombic ($Pca2_1$) and antiferroelectric
785 tetragonal ($P4_2/nmc$) phase. Simulated XAS spectra at the oxygen K -edge (Extended Data Fig.
786 3d) for ZrO_2 in the various fluorite-structure polymorphs (orthorhombic $Pca2_1$ and tetragonal
787 $P4_2/nmc$) were computed through the Materials Project⁶⁰ open-source database for XAS
788 spectrum⁶¹. The T -phase ($P4_2/nmc$) nonpolar distortion (D_{4h} , 4-fold prismatic symmetry) from
789 regular tetrahedral (T_d , full tetrahedral symmetry) fluorite-structure symmetry does not split the
790 degenerate e -bands ($d_{x^2-y^2}$, $d_{3z^2-r^2}$), as confirmed by experiment⁶² and the aforementioned
791 XAS simulations¹³. Meanwhile, the O -phase ($Pca2_1$) polar rhombic pyramidal distortion (C_{2v} , 2-
792 fold pyramidal symmetry) does split the e -manifold based on crystal field symmetry, providing a
793 spectroscopic means to distinguish the T - and O -phases. The additional spectroscopic feature
794 present between the main e - and t_2 - absorption features due to orthorhombic symmetry-lowering
795 distortion is illustrated by its crystal field diagram (Extended Data Fig. 3b). This provides a
796 spectroscopic fingerprint for phase identification beyond diffraction which can often be
797 ambiguous due to the nearly identical T - and O -phase lattice parameters. For the 2 nm HfO_2 -
798 ZrO_2 - HfO_2 trilayer, the experimental O K -edge XAS spectra demonstrates tetrahedral and
799 rhombic splitting features closely matching the polar O -phase ($Pca2_1$) emerge slightly below
800 room temperature, indicative of the mixed tetragonal-orthorhombic to orthorhombic phase
801 transition upon cooling. This temperature-dependent tetragonal-orthorhombic structural
802 evolution is expected for fluorite-structure thin films⁶³ and is consistent with temperature-
803 dependent capacitance measurements (Extended Data Fig. 3f). Further XAS phase identification
804 details are provided in previous work on ultrathin $Zr:HfO_2$ films¹³.

805

806 **X-ray photoelectron spectroscopy** Angle-resolved photoelectron spectroscopy (ARPES) was
807 performed using a Phi Versaprobe III at the Stanford Nano Shared Facilities (Extended Data Fig.
808 1d). A monochromated aluminum source was used to give a photon energy of 1486.6 eV. Data
809 was fit and analyzed using CasaXPS. Angle-dependent XPS at various incident grazing angles
810 enabled depth-resolved composition analysis to help confirm the HfO_2 - ZrO_2 - HfO_2 multilayer
811 structure.

812

813 **Dielectric measurements**

814

815 **Metal-oxide-semiconductor (MOS) capacitance** Capacitance-voltage (C - V) measurements
816 were performed using a commercial Semiconductor Device Analyzer (Agilent B1500) with a
817 multi-frequency capacitance measuring unit (MFCMU). 19 micron W tips (d.c.P-HTR 154-001,
818 FormFactor) made electrical contact within a commercial probe station (Cascade Microtech);
819 voltage was applied to the W top electrode and the lightly-doped Si bottom electrode was
820 grounded. To eliminate contributions from series and parasitic resistances, frequency-dependent
821 C - V measurements were performed. In particular, C - V data was analyzed at two frequencies
822 (100-500 kHz regime) to allow for the extraction of accurate frequency-independent C - V via a
823 three-element circuit model consisting of the capacitor and the parasitic series and parallel
824 resistors⁶⁴. The frequency-independent capacitance is given by

$$C = \frac{f_1^2 C_1 (1 + D_1^2) - f_2^2 C_2 (1 + D_2^2)}{f_1^2 - f_2^2}$$

825 where C_i and D_i refer to the measured capacitance in parallel mode (C_p - R_p) and dissipation
 826 values at frequency f_i . The dissipation factor is given by $D = -\cot \theta$, where θ is the phase. In
 827 order to maximize the accuracy of this method, it is important the dissipation factors are small
 828 ($\ll 1$) at the frequencies chosen; therefore, high frequencies were selected.

829
 830 **Permittivity extraction** The permittivity of Al_2O_3 and HfO_2 dielectric layers was extracted from
 831 thickness-dependent MOS C - V measurements on lightly-doped p-substrates (Extended Data Fig.
 832 6). In the accumulation region of the MOS C - V measurements, the MOS capacitor can be
 833 modeled as three capacitors (Al_2O_3 or HfO_2 dielectric layer, SiO_2 interlayer, and Si space charge
 834 layer) in series using the following equation

$$\frac{1}{C} = \frac{1}{\epsilon_0 \epsilon_{HK}} t_{HK} + \frac{1}{\epsilon_0 \epsilon_{SiO_2}} \left[t_{SiO_2}^{phys} + \frac{t_{CL} \epsilon_{SiO_2}}{\epsilon_{Si}} \right]$$

835 where t_{HK} is the thickness of the high- κ (Al_2O_3 or HfO_2) layer, t_{phys} is the physical SiO_2
 836 thickness, and t_{CL} is the charge layer thickness in silicon. The physical SiO_2 thickness is constant
 837 across all the thickness series (Al_2O_3 and HfO_2 single layers). Additionally, the capacitance
 838 values were extracted at various values of fixed charge ($Q = 0$ to $-3 \mu\text{C}/\text{cm}^2$) which ensures that
 839 the charge- layer thickness is constant across all thicknesses and in the accumulation region.
 840 Therefore, the inverse capacitance at a fixed charge as a function of film thickness should result
 841 in a line and the permittivity can be extracted from the slope. This yielded extracted
 842 permittivities of 9 and 19 for the Al_2O_3 and HfO_2 thickness series, respectively, as expected for
 843 these systems. Note that for the HfO_2 thickness series, thicknesses of 6 nm and higher were used
 844 to ensure HfO_2 stabilizes in the dielectric monoclinic phase ($\kappa \sim 18$)²². Similarly, the permittivity
 845 of the HfO_2 - ZrO_2 - HfO_2 heterostructures was extracted from thickness-dependent MIM C - V
 846 measurements (Fig. 2b). The inverse capacitance is a linear function of the film thickness, and
 847 the permittivity can be extracted from the slope.

848
 849 **Electrical interlayer thickness extraction** The thickness of the SiO_2 interlayer was determined
 850 not only by TEM (Extended Data Fig. 6a), but also electrically via C - V measurements of both
 851 dielectric HfO_2 and Al_2O_3 thickness series on SiO_2 -buffered Si (Extended Data Fig. 6f). The
 852 inverse capacitance at a fixed charge as a function of dielectric thickness should result in a line
 853 and the capacitance-equivalent thickness (CET) of the SiO_2 interlayer and Si charge layer can be
 854 extracted from the y-intercept. By extracting the CET at different charge values, the Q - V relation
 855 of the SiO_2 interlayer and Si charge layer can be calculated through the following equation

$$V - V_{fb} = \int_0^Q \frac{t_{SiO_2}^{phys} + \frac{t_{CL} \epsilon_{SiO_2}}{\epsilon_{Si}}}{\epsilon_0 \epsilon_{SiO_2}} dQ$$

856 where V_{fb} is the flatband voltage (Extended Data Fig. 6b,d). To confirm this methodology,
 857 another method for determining the Q - V relation of the SiO_2 interlayer and Si charge layer was
 858 extracted from the Q - V relations of both the dielectric HfO_2 and Al_2O_3 thickness series. At a
 859 fixed charge, the corresponding voltage values of each thickness were fit to a line and the y-
 860 intercept corresponds to the voltage value for the SiO_2 interlayer and Si charge layer Q - V relation
 861 (Extended Data Fig. 6c,e). As expected, both methods lead to the same extracted Q - V relation
 862 (Extended Data Fig. 6c,e), corresponding to 8 Å EOT (Extended Data Fig. 6f) – close to the SiO_2
 863 physical thickness of 8.5 Å obtained via TEM (Extended Data Fig. 6a) – based on simulated

864 TCAD Q - V relations of different SiO_2 thicknesses on lightly-doped Si.

865

866 **Hysteretic C - V measurements** Capacitance-voltage (C - V) measurements on MIM capacitors
867 were performed using a commercial Semiconductor Device Analyzer (Agilent B1500) with a
868 multi-frequency capacitance measuring unit. 19 micron W tips (d.c.P-HTR 154-001,
869 FormFactor) made electrical contact within a commercial probe station (Cascade Microtech);
870 voltage was applied to the W top electrode and the W bottom electrode was grounded.

871

872 **Electrical characterization**

873

874 **Benchmarking to HKMG literature** In Fig. 3b, the leakage-equivalent oxide thickness (J_G -
875 EOT) scaling of the negative capacitance multilayer gate stack benchmarked against reported
876 HKMG literature includes references taken from interlayer-scavenged 2 nm HfO_2 ^{16,19,65} (red),
877 high- κ doped HfO_2 ¹⁹(gray), and $\text{SiO}_2/\text{poly-Si}^3$ (black). In Fig. 3c, the raw mobility of long-
878 channel transistors integrating the negative capacitance multilayer gate stack (blue) is
879 benchmarked against industry-reported long-channel transistors integrating standard 2 nm HfO_2
880 high- κ dielectric gate stacks (red) of various EOT⁴². In Extended Data Fig. 8d, the normalized
881 mobility versus EOT scaling of the negative capacitance multilayer gate stack benchmarked
882 against reported HKMG literature includes references taken from interlayer-scavenged 2 nm
883 HfO_2 ^{16,19,42} (red) and hybrid silicate-scavenged interlayer¹⁶ (magenta). In the Extended Data Fig.
884 8d inset, the SiO_2 interlayer thickness versus EOT scaling scatter plot considers the 7.0 Å EOT
885 HfO_2 - ZrO_2 - HfO_2 trilayer to HKMG references which employ interlayer scavenging to reduce
886 EOT^{16,19,65,66}.

887

888 **Transistor transfer and output characteristics** Transistor I_d - V_g and I_d - V_d characterization of
889 short-channel and long-channel transistors were performed using a commercial Semiconductor
890 Device Analyzer (Agilent B1500). 19 micron W tips (d.c.P-HTR 154-001, FormFactor) made
891 electrical contact within a commercial probe station (Cascade Microtech); voltage was applied to
892 the gate and drain contacts, while the source and Si substrate were grounded.

893

894 **Mobility extraction** The low-field transistor mobility for SOI transistors integrating ~ 2 nm
895 HfO_2 - ZrO_2 - HfO_2 ferroic multilayers and standard high- κ HfO_2 gate stacks of the same physical
896 thickness (Fig. 3c, Extended Data Fig. 8c) is calculated based on the channel resistance (R_{ch}) and
897 inversion sheet charge density (Q_{inv}), which are extracted respectively from transfer
898 characteristics (I_d - V_{gs} , Extended Data Fig. 8b) and from the intrinsic gate capacitance-voltage
899 (C_{gg} vs V_{gs} - V_{fb} , Extended Data Fig. 8a) measurements. Given the device aspect ratio of channel
900 length (L) and channel width (W), we have

$$R_{ch}(V_{gs}) = \frac{L}{W} \times \frac{1}{\mu_{eff}(V_{gs})Q_{inv}(V_{gs})}$$

901 Firstly, the channel resistance is extracted at 50 mV drain-to-source bias (V_{ds}) by subtracting the
902 parasitic resistance (R_p) from the measured drain-to-source resistance (R_{ds}).

$$R_{ds}(V_{gs}) = \frac{V_{ds}}{I_D(V_{gs})} = R_{ch}(V_{gs}) + R_p$$

903 where R_p is ascribed to the resistance of the source and the drain contacts and the n+ extension
904 regions that are extrinsic to the channel region. When the overdrive voltage ($V_{ov} = V_{gs} - V_T$,
905 where V_T is the threshold voltage) is sufficiently large, R_{ch} is known to be inversely proportional

906 to V_{ov} . Therefore, R_p can be extracted using a linear extrapolation of the $R_{ds} - 1/V_{ov}$ relationship,
 907 which is derived from the $I_d - V_{gs}$ (Extended Data Fig. 8b) from which V_T can be characterized
 908 with the max- g_m method. Secondly, the C_{gg} vs $V_{gs} - V_{fb}$ (Extended Data Fig. 8a) is integrated and
 909 normalized to the channel area to estimate the inversion charge.

$$Q_{inv}(V_{gs}) \approx \int_{-\infty}^{V_{gs}} \frac{C_{gg}(v_{gs})}{A} dv_{gs}$$

910 Finally, we combine the above characterizations to obtain the effective mobility (Fig. 3c,
 911 Extended Data Fig. 8c).

912
 913 **Transconductance extraction from DC measurements** The measured transconductance ($g_m =$
 914 $\partial I_d / \partial V_{gs}$) and the output conductance ($g_{ds} = \partial I_d / \partial V_{ds}$) are affected by the series resistance on the
 915 source (R_s) and the drain sides (R_d), as they reduce the voltage drops on the channel region,

$$\begin{aligned} V_{gs,i} &= V_{gs} - I_d R_s \\ V_{ds,i} &= V_{ds} - I_d (R_s + R_d) \end{aligned}$$

916
 917 where $V_{gs,i}$ and $V_{ds,i}$ are the gate-to-source and the drain-to-source voltages intrinsic to the
 921 channel, respectively. $R_s \approx R_d \approx R_p/2$ because the transistor is symmetric. R_p can be extracted
 922 from the $R_{ds} - 1/V_{ov}$ relationships as discussed in the "Mobility Extraction" Methods section.
 923 Besides, devices with different gate length (L_G) series are fabricated on Silicon-On-Insulator
 924 (SOI) wafers, which enables another extraction method with $R_{sd} - L_G$ relations. At low V_d and a
 925 given V_{ov} , Q_{inv} and μ_{eff} are unchanged across different L_G if short-channel effects are not
 926 significant, making R_{ch} proportional to the channel length. Such condition is confirmed by the
 927 consistency of V_T across measured L_G (Extended Data Fig. 10a). Therefore, the L_G offset as well
 928 as the R_p can be found at the intersection of the linear relations of the $R_{sd} - L_G$ with different V_{ov}
 929 (Extended Data Fig. 10c). The two R_p extraction methods yield consistent results.

930
 931 The following equation is solved to extract the intrinsic $g_{m,i} = \partial I_d / \partial V_{gs,i}$ and $g_{ds,i} = \partial I_d / \partial V_{ds,i}$
 932 without the degradation due to R_s and R_d .

$$\begin{pmatrix} 1 - g_m R_s & -g_m (R_s + R_d) \\ -g_{ds} R_s & 1 - g_{ds} (R_s + R_d) \end{pmatrix} \begin{pmatrix} g_{mi} \\ g_{ds,i} \end{pmatrix} = \begin{pmatrix} g_m \\ g_{ds} \end{pmatrix}$$

934
 935 where g_m and g_{ds} are measured, and $R_s \approx R_d \approx R_p/2$ from the above discussed characterizations.
 936 Using this methodology, the intrinsic $g_{m,i}$ and intrinsic $g_{ds,i}$ are extracted (Fig. 3g, Extended Data
 937 Fig. 10d,e).

938
 939 **Transconductance extraction from RF measurements** Scattering-parameters (S -parameters)
 940 for $L_G = 1 \mu\text{m}$ bulk transistors (henceforth referred to as the device under test, DUT) at various
 941 DC biases as well as open and short structures (Extended Data Fig. 9a) are measured using a
 942 Keysight E8361C Network Analyzer in conjunction with a Keysight 4155C Semiconductor
 943 Parameter Analyzer. The devices were measured using low contact resistance Infinity Series
 944 probes. To calibrate the measurement setup, a line-reflect-reflect-match (LRRM) calibration was
 945 performed with a Cascade Microtech Impedance Standard. Following calibration, S -parameters
 946 were measured for each of the DUT, open, and short structures. These measured S -parameters
 947 were converted to admittance parameters (Y -parameters), Y_{DUT} , Y_{open} , and Y_{short} . To remove the

948 effects of parasitic shunt parasitic pad capacitance and series pad resistance and inductance of the
 949 DUT, the following de-embedding process was followed. First, to decouple the effect of shunt
 950 parasitic capacitances, the Y -parameters of the open structure (Y_{open}) are subtracted from the Y -
 951 parameters of the DUT and short structure, and then are converted to impedance parameters (Z -
 952 parameters):

$$953 \quad Z_1 = (Y_{DUT} - Y_{open})^{-1}$$

$$954 \quad Z_2 = (Y_{short} - Y_{open})^{-1}$$

956 Next, to decouple the effect of series pad resistance and inductance of DUT, Z_2 is subtracted
 957 from Z_1 and the resulting difference is converted back to admittance parameters, Y_{corr} :

$$958 \quad Y_{corr} = (Z_1 - Z_2)^{-1}$$

961 Y_{corr} represents the de-embedded admittance parameters of the DUT. This de-embedding
 962 procedure is schematically represented in Extended Data Fig. 9a.

964 To extract the transconductance (g_m) from the de-embedded admittance parameters, a small-
 965 signal model of the transistor was assumed (Extended Data Fig. 9b). Under this small-signal
 966 model, the Y -parameters can be written in terms of model parameters and frequency (assuming
 967 $R_s = R_d = 0$, $C_{gg} = C_{gs} + C_{gd}$, and $4\pi^2 C_{gg}^2 R_g^2 f^2 \ll 1$)

$$968 \quad Y_{11} = 4\pi^2 C_{gg}^2 R_g f^2 + j2\pi f C_{gg}$$

$$969 \quad Y_{12} = -4\pi^2 C_{gd} C_{gg} R_g f^2 - j2\pi f C_{gd}$$

$$970 \quad Y_{21} = g_m - 4\pi^2 C_{gd} C_{gg} R_g f^2 + j2\pi f (C_{gd} + g_m R_g C_{gg})$$

$$971 \quad Y_{22} = g_{ds} + 4\pi^2 C_{gd} R_g (C_{gd} + C_{gg} g_m R_g) f^2 + j2\pi f (C_{ds} + C_{gd} + C_{gd} g_m R_g).$$

974 The transconductance (g_m) can therefore be extracted at a fixed DC bias via the following
 975 relation (Fig. 3h, Extended Data Fig. 9c).

$$976 \quad g_m = \text{Re}(Y_{21})|_{f^2=0}$$

977 **Reliability** Positive bias temperature instability (PBTi) measurements were performed on bulk
 978 nMOSFET devices integrating the ~ 2 nm mixed-ferroic $\text{HfO}_2\text{-ZrO}_2\text{-HfO}_2$ (HZH) and
 979 conventional high- κ dielectric HfO_2 gate stacks at 85°C at electric fields up to 9 MV/cm
 980 (Extended Data Fig. 8f,g). A measure-stress-measure (MSM) voltage scheme (Extended Data
 981 Fig. 8e) was used to apply the PBTi bias, where the drain current was measured with a
 982 minimized delay time (600 μs) at $V_{ds} = 50$ mV to minimize the recovery effect⁶⁷. The measured
 983 drain current was then converted to a ΔV_T shift by comparing it to the drain current measured on
 984 the virgin device. Additionally, the time exponent, n , was extracted by noting that⁶⁷ $\Delta V_T = A t^n$.
 985 The extracted time exponent, n , was found to similar to those reported in literature for high- κ
 986 HfO_2 stacks⁶⁷, which is expected considering the reliability characteristics are predominantly
 987 determined by the interfacial (IL) oxide and IL-high- κ interface⁴⁶; both stacks with different
 988 EOT have HfO_2 sitting on the same SiO_2 IL (Extended Data Fig. 1). Furthermore, the DC
 989 lifetime⁶⁷ – the stress time needed to induce a 50 mV ΔV_T shift – was extracted as a function of
 990 electric field from the PBTi measurements for the HZH and HfO_2 gate stacks. Both HZH and
 991 HfO_2 show comparable rates of degradation as a function of field (Extended Data Fig. 8h), which
 992 is expected for the aforementioned reasons related to the consistent SiO_2 IL.

993

994 Additionally, the extracted time exponent for HZH ($n = 0.14$, Extended Data Fig. 8f) is closer to
995 the ideal value⁶⁷ of $n = 0.16$ compared to HfO₂ ($n = 0.10$, Extended Data Fig. 8g), indicating that
996 there are initially a smaller number of interface traps for HZH. When field stress is applied, trap
997 generation accelerates until the number of traps reaches a certain threshold beyond which it
998 eventually saturates. As a result, the relative degradation is larger for HZH at smaller fields,
999 although the absolute degradation is always slightly smaller than HfO₂. This can also be seen
1000 directly from the extracted DC lifetimes (Extended Data Fig. 8h) as the DC lifetime is slightly
1001 better for HZH at intermediate field stresses before it becomes similar to HfO₂ at high field
1002 stresses. We again note that extracted n values are similar to what has been reported in literature
1003 for HfO₂ based high- κ metal gate stacks⁶⁷.

1004

1005 Stress measurements were also performed on lightly-doped p-type MOS capacitors with the ~ 2
1006 nm mixed-ferroic HfO₂-ZrO₂-HfO₂ and conventional high- κ dielectric HfO₂ gate stacks at room
1007 temperature (Extended Data Fig. 8i,j) at $V_g - V_{fb} = -1$ V. The stresses were applied again with a
1008 MSM voltage scheme, where the accumulation C - V was measured in between bias application at
1009 500 kHz. The stress-induced effect was found to be minimal (Extended Data Fig. 8i,j) and no
1010 EOT degradation was observed after 10^3 s of stress at $V_g - V_{fb} = -1$ V (Extended Data Fig. 8i,j).

1011

1012 **Charge boost measurements** Pulsed charge-voltage measurements (Extended Data Fig. 7)
1013 were conducted on p-Si/SiO₂/HfO₂-ZrO₂-HfO₂ (2 nm)/TiN/W capacitor structures to extract the
1014 energy landscape of the ferroic HfO₂-ZrO₂-HfO₂ heterostructure, following the measurement
1015 scheme detailed in previous works^{26,68-70}. The capacitor structures were connected to an Agilent
1016 81150A Pulse Function Arbitrary Noise Generator and the current and voltage was measured
1017 through an InfiniiVision DSOX3024A oscilloscope with 50 Ω and 1 M Ω input impedances,
1018 respectively. Short voltage pulses (500 ns) with increasing amplitudes were applied to the
1019 capacitor (Extended Data Fig. 7c). From the integration of the measured discharging current, a
1020 charge vs voltage relationship was extracted (Extended Data Fig. 7d). The voltage was calculated
1021 by $\max(V - IR)$, where V is the applied voltage pulse, I is the measured current, and R is a
1022 combination of the oscilloscope resistance (50 Ω) and parasitic resistances associated with the
1023 setup and lightly-doped substrate (220 Ω). Fast voltage pulses were applied in order to minimize
1024 charge injection into the ferroelectric-dielectric interface, which could mask the observation of
1025 the negative capacitance regime^{26,69}. Additionally, short voltage pulses help prevent electrical
1026 breakdown of the SiO₂ layer. The Q - V relation of the series capacitance of the SiO₂ interlayer
1027 and Si charge layer was determined via thickness-dependent C - V measurements of Al₂O₃ and
1028 HfO₂ (Extended Data Fig. 6, Methods, Electrical interlayer thickness extraction), which
1029 corresponded to 8 Å SiO₂ on lightly-doped Si. The charge boost was calculated by integrating
1030 the difference between the Q - V relations of the 2 nm HfO₂-ZrO₂-HfO₂ heterostructure and the
1031 series combination of the SiO₂ interlayer and the Si charge layer (Extended Data Fig. 7e).

1032

1033 In order to determine the polarization-electric field (P - E_F) relation of just the 2 nm HfO₂-ZrO₂-
1034 HfO₂ heterostructure (Extended Data Fig. 7f), the electric field across the ferroic HfO₂-ZrO₂-
1035 HfO₂ heterostructure was calculated by subtracting the voltage across the series capacitance of
1036 the SiO₂ interlayer and Si charge layer (V_D) at a fixed charge value,

$$E_F = \frac{1}{t}(V - V_D)$$

1037 where t is the thickness of the $\text{HfO}_2\text{-ZrO}_2\text{-HfO}_2$ heterostructure.

1038

1039 **Modeling**

1040

1041 **Energy landscape considerations** One can write the total free energy (F) of the system as:

1042

$$F = \int_V [f_{bulk} + f_{elas} + f_{elec} + f_{grad}] dV$$

1043 where V is the volume, f_{bulk} is the bulk free energy (Landau), f_{elas} is the elastic energy density, f_{elec}
1044 is the electrostatic energy density, and f_{grad} is the gradient energy density.

1045

1046 For the laterally-arranged mixed FE-AFE phase present in our material, all of the above terms
1047 are important, especially the gradient terms, which are by default present due to the mixed polar-
1048 nonpolar (FE-AFE) phase distribution. Additionally, heterogeneous elastic energies in
1049 structurally inhomogeneous systems – like our mixed orthorhombic-tetragonal (FE-AFE) system
1050 – have been shown to destabilize long-range polarization, leading to suppressed polarization and
1051 a flattened energy landscape^{28,71}. Furthermore, considering the polarization in our films has an
1052 in-plane component (as described in the Main Text), this leads to an additional depolarization
1053 field on the ferroelectric grains, similar to a ferroelectric-dielectric heterostructure (albeit in the
1054 in-plane direction). At low electric fields, the mixed ferroelectric-antiferroelectric behavior is
1055 analogous to a ferroelectric-dielectric (polar-nonpolar) heterostructure – due to the nonpolar
1056 parent structure of fluorite-structure antiferroelectricity – which has been shown to impart
1057 depolarization fields on the ferroelectric layer^{25,72}. The laterally-intertwined nonpolar-polar
1058 phases present in the ultrathin $\text{HfO}_2\text{-ZrO}_2\text{-HfO}_2$ heterostructure are conducive to flattening the
1059 ferroelectric energy landscape through the aforementioned depolarization fields^{26–28} (Fig. 1a).

1060

1061 Overall, the above contributions all lead to a suppression of the bulk polarization via
1062 depolarization fields. As it has been shown^{26–28}, the depolarization field essentially flattens the
1063 bulk energy landscape for the ferroelectric – ($E_d \propto -P$ hence $\vec{E} \cdot \vec{P} > 0$) – and leads to a
1064 permittivity enhancement ($\epsilon \propto [\partial^2 F / \partial D^2]^{-1}$). Depolarization field induced flattening of the energy
1065 landscape is also the underlying physics of the negative capacitance effect^{26,27,29,30,49}.

1066

1067 **Technology computer-aided design simulations** The measured C - V curves are calibrated to
1068 Sentaurus Technology computer-aided design simulations (TCAD) device simulator which
1069 solves the electrostatics, electron and hole transports, and the quantum confinement effect self-
1070 consistently⁷³. MOS capacitors with 10^{15} cm^{-3} p-type substrate doping and planar SOI
1071 MOSFETs are simulated with finite-element methods. The equivalent oxide thickness (EOT) and
1072 the metal work function (ϕ_m) are the only two parameters that are fit to the MOS capacitor
1073 measurement results, yet the slope of the accumulation capacitance can be successfully captured
1074 by the model (Fig. 2f, Extended Data Fig. 6). Similarly, the intrinsic C_{gg} vs $V_{gs} - V_{fb}$ extracted
1075 from SOI transistors can be successfully model by the TCAD model with appropriate EOT and
1076 ϕ_m (Extended Data Fig. 8a).

1077

1078 **Atomic-scale $\text{HfO}_2\text{-ZrO}_2\text{-HfO}_2$ mixed-ferroic heterostructure**

1079

1080 **Thickness limits and atomic-scale heterostructures** Recent perspectives on HfO_2 -based

1081 ferroelectricity for device applications^{9,74-77} posed the technological challenges stemming from
1082 thickness limit concerns of HfO₂-based ferroelectricity, and thereby, negative capacitance. The
1083 use of short-period superlattices i.e. nanolaminates is common in the high- κ field to enhance per-
1084 mittivity⁷⁸⁻⁸²; in particular, rutile-structure TiO₂ is often paired with fluorite-structure HfO₂
1085 and/or ZrO₂ in DRAM capacitors⁸³. Recently, fluorite-structure nanolaminates were employed to
1086 tune the ferroelectric behavior of HfO₂-ZrO₂-HfO₂ films⁸⁴⁻⁸⁶. However, all of these works have
1087 studied nanolaminates with thick periodicity, going as thin as 10 ALD cycles (\sim 1.1 nm) per
1088 superlattice sub-layer⁸⁴. In this work, we scale down to a much thinner thickness limit while still
1089 maintaining physical separation of the individual layers (Extended Data Fig. 1). The reasoning
1090 behind using a short-period superlattice structure to scale down the ferroic behavior of HfO₂-
1091 ZrO₂-HfO₂ rather than simply thinning down a solid solution stems from the notorious thickness-
1092 dependent ferroelectric behavior in Zr:HfO₂ at fixed composition^{38,57,63}. Here, the use of
1093 nanolaminated structures can help provide thickness-independent scaling of ferroic order, as has
1094 been previously demonstrated to overcome the upper thickness limit of HfO₂-based
1095 ferroelectricity⁸⁶. The persistence of high capacitance for these 2 nm films is notable considering
1096 other high- κ dielectric systems suffer from significant permittivity degradation in the thin film
1097 (sub-10 nm) regime, particularly TiO₂- and SrTiO₃-based oxides^{83,87}. Sustaining the mixed
1098 ferroic order underlying negative capacitance to the 2 nm regime is extremely relevant for
1099 advanced technology nodes⁸⁸ which budget only \sim 2 nm for the oxide layer.

1100
1101 **Iso-structural polycrystalline multilayer** Previous attempts to heterostructure ferroelectric
1102 Zr:HfO₂ with dielectric Al₂O₃^{26,69,70} failed to demonstrate capacitance enhancement, which was
1103 attributed to the fixed charges at the ferroelectric-dielectric interface. These charges can screen
1104 the ferroelectric polarization, pushing the stable point of the energy well to one the minimum
1105 points, and thereby preventing stabilization of negative capacitance regime via depolarization
1106 fields from the dielectric. Here, the use of iso-structural HfO₂-ZrO₂-HfO₂ to serve as both the
1107 nonpolar (antiferroelectric) and polar (ferroelectric) layers and leveraging the high (low) onset
1108 crystallization temperature of HfO₂ (ZrO₂) on Si⁵⁰, enables interfaces with diminished defects,
1109 allowing for the polar layer to experience the depolarization fields and stabilize in the
1110 "forbidden" NC regime. Regarding the polycrystalline nature of the ultrathin multilayers, it has
1111 been experimentally⁴⁸ and theoretically⁸⁹ established that negative capacitance can be stabilized
1112 in the presence of ferroelectric domains, as recently reviewed⁷⁶.

1113

1114

1115

1116 **Methods References**

- 1117 50. Hsain, H. A., Lee, Y., Parsons, G. & Jones, J. L. Compositional dependence of
1118 crystallization temperatures and phase evolution in hafnia-zirconia ($\text{Hf}_x\text{Zr}_{1-x}\text{O}_2$) thin
1119 films. *Applied Physics Letters* **116**, 192901 (2020).
- 1120 51. Lin, B.-T., Lu, Y.-W., Shieh, J. & Chen, M.-J. Induction of ferroelectricity in nanoscale
1121 ZrO_2 thin films on Pt electrode without post-annealing. *Journal of the European Ceramic*
1122 *Society* **37**, 1135–1139 (2017).
- 1123 52. Björck, M. & Andersson, G. GenX : an extensible X-ray reflectivity refinement program
1124 utilizing differential evolution. *Journal of Applied Crystallography* **40**, 1174–1178 (2007).
- 1125 53. Ilavsky, J. Nika : software for two-dimensional data reduction. *Journal of Applied Crystal-*
1126 *lography* **45**, 324–328 (2012).
- 1127 54. Park, M. H., Shimizu, T., Funakubo, H. & Schroeder, U. Structural Origin of Temperature-
1128 Dependent Ferroelectricity. In *Ferroelectricity in Doped Hafnium Oxide: Materials,*
1129 *Properties and Devices*, 193–216 (Elsevier, 2019).
- 1130 55. Mehmood, F., Mikolajick, T. & Schroeder, U. Lanthanum doping induced structural
1131 changes and their implications on ferroelectric properties of $\text{Hf}_{1-x}\text{Zr}_x\text{O}_2$ thin film. *Applied*
1132 *Physics Letters* **117**, 092902 (2020).
- 1133 56. Mukundan, V. et al. Quantifying non-centrosymmetric orthorhombic phase fraction in 10
1134 nm ferroelectric $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ films. *Applied Physics Letters* **117**, 262905 (2020).
- 1135 57. Park, M. H. et al. Ferroelectricity and Antiferroelectricity of Doped Thin HfO_2 -Based
1136 Films. *Advanced Materials* **27**, 1811–1831 (2015).
- 1137 58. Lyu, J., Fina, I., Solanas, R., Fontcuberta, J. & Sánchez, F. Growth Window of
1138 Ferroelectric Epitaxial $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ Thin Films. *ACS Applied Electronic Materials* **1**, 220–
1139 228 (2019).
- 1140 59. Young, A. T. et al. Variable linear polarization from an x-ray undulator. *Journal of*
1141 *Synchrotron Radiation* **9**, 270–4 (2002).
- 1142 60. Jain, A. et al. The materials project: A materials genome approach to accelerating materials
1143 innovation. *APL Materials* **1**, 011002 (2013).
- 1144 61. Mathew, K. et al. High-throughput computational X-ray absorption spectroscopy. *Scientific*
1145 *Data* **5**, 180151 (2018).
- 1146 62. Cho, D.-Y., Jung, H.-S. & Hwang, C. S. Structural properties and electronic structure of
1147 $\text{HfO}_2\text{-ZrO}_2$ composite films. *Physical Review B* **82**, 094104 (2010).
- 1148 63. Park, M. H. & Hwang, C. S. Fluorite-structure antiferroelectrics. *Reports on Progress in*
1149 *Physics* **82**, 124502 (2019).
- 1150 64. Yang, K. & Hu, C. MOS capacitance measurements for high-leakage thin dielectrics. *IEEE*
1151 *Transactions on Electron Devices* **46**, 1500–1501 (1999).

- 1152 65. Changhwan Choi *et al.* Fabrication of TaN-gated ultra-thin mosfets (eot >1.0nm) with
1153 HfO₂ using a novel oxygen scavenging process for sub 65nm application. In *2005*
1154 *Symposium on VLSI Technology*, 226–227 (IEEE, 2005).
- 1155 66. Takahashi, M. *et al.* Gate-First Processed FUSI/HfO₂/HfSiO_x/Si MOSFETs with EOT=0.5
1156 nm - Interfacial Layer Formation by Cycle-by-Cycle Deposition and Annealing. In *2007*
1157 *IEEE International Electron Devices Meeting (IEDM)*, 523–526 (IEEE, 2007).
- 1158 67. Mahapatra, S. (ed.) *Fundamentals of Bias Temperature Instability in MOS Transistors*, vol.
1159 *52 of Springer Series in Advanced Microelectronics* (Springer India, New Delhi, 2016).
- 1160 68. Kim, Y. J. *et al.* Time-Dependent Negative Capacitance Effects in Al₂O₃/BaTiO₃
1161 Bilayers. *Nano Letters* **16**, 4375–4381 (2016).
- 1162 69. Hoffmann, M. *et al.* Demonstration of High-speed Hysteresis-free Negative Capacitance
1163 in Ferroelectric Hf_{0.5}Zr_{0.5}O₂. *2018 IEEE International Electron Devices Meeting (IEDM)*
1164 31.6.1–31.6.4 (2018).
- 1165 70. Kim, K. D. *et al.* Transient Negative Capacitance Effect in Atomic-Layer-
1166 Deposited Al₂O₃/Hf_{0.3}Zr_{0.7}O₂ Bilayer Thin Film. *Advanced Functional Materials* **29**,
1167 1808228 (2019).
- 1168 71. Chen, L. Q. Phase-field method of phase transitions/domain structures in ferroelectric
1169 thinfilms: A review. *Journal of the American Ceramic Society* **91**, 1835–1844 (2008).
- 1170 72. Lomenzo, P. D. *et al.* A Gibbs energy view of double hysteresis in ZrO₂ and Si-doped
1171 HfO₂. *Applied Physics Letters* **117**, 142904 (2020).
- 1172 73. Synopsys. *Sentaurus Device User Guide, Version O-2018.06* (2018).
- 1173 74. Park, J. Y. *et al.* A perspective on semiconductor devices based on fluorite-structured ferro-
1174 electrics from the materials–device integration perspective. *Journal of Applied Physics* **128**,
1175 240904 (2020).
- 1176 75. Hoffmann, M., Slesazek, S., Schroeder, U. & Mikolajick, T. What’s next for negative
1177 capacitance electronics? *Nature Electronics* **3**, 504–506 (2020).
- 1178 76. Hoffmann, M., Slesazek, S. & Mikolajick, T. Progress and future prospects of negative
1179 capacitance electronics: A materials perspective. *APL Materials* **9**, 020902 (2021).
- 1180 77. Mikolajick, T. *et al.* Next generation ferroelectric materials for semiconductor process
1181 integration and their applications. *Journal of Applied Physics* **129**, 100901 (2021).
- 1182 78. Li, Y.-L. *et al.* Electrical and Reliability Characteristics of FinFETs With High-k Gate
1183 Stack and Plasma Treatments. *IEEE Transactions on Electron Devices* **68**, 4–9 (2021).
- 1184 79. Padmanabhan, R., Mohan, S., Morozumi, Y., Kaushal, S. & Bhat, N. Performance and
1185 Reliability of TiO₂/ZrO₂/TiO₂ (TZT) and AlO-Doped TZT MIM Capacitors. *IEEE*
1186 *Transactions on Electron Devices* **63**, 3928–3935 (2016).
- 1187 80. Shin, Y. *et al.* Crystallized HfLaO embedded tetragonal ZrO₂ for dynamic random access

- 1188 memory capacitor dielectrics. *Applied Physics Letters* **98**, 173505 (2011).
- 1189 81. Mise, N. *et al.* Scalability of TiN/HfAlO/TiN MIM DRAM capacitor to 0.7-nm-EOT and
1190 beyond. In *2009 IEEE International Electron Devices Meeting (IEDM)*, 1–4 (IEEE, 2009).
- 1191 82. Kil, D.-S. *et al.* Development of New TiN/ZrO₂/Al₂O₃/ZrO₂/TiN Capacitors Extendable to
1192 45nm Generation DRAMs Replacing HfO₂ Based Dielectrics. In *2006 Symposium on VLSI*
1193 *Technology*, 38–39 (IEEE, 2006).
- 1194 83. Kim, S. K. & Popovici, M. Future of dynamic random-access memory as main memory.
1195 *MRS Bulletin* **43**, 334–339 (2018).
- 1196 84. Park, M. H. *et al.* A comprehensive study on the mechanism of ferroelectric phase formation
1197 in hafnia-zirconia nanolaminates and superlattices. *Applied Physics Reviews* **6**, 041403
1198 (2019).
- 1199 85. Weeks, S. L., Pal, A., Narasimhan, V. K., Littau, K. A. & Chiang, T. Engineering of Fer-
1200 roelectric HfO₂-ZrO₂ Nanolaminates. *ACS Applied Materials & Interfaces* **9**, 13440–13447
1201 (2017).
- 1202 86. Riedel, S., Polakowski, P. & Müller, J. A thermally robust and thickness independent ferro-
1203 electric phase in laminated hafnium zirconium oxide. *AIP Advances* **6**, 095123 (2016).
- 1204 87. Osada, M. & Sasaki, T. The rise of 2D dielectrics/ferroelectrics. *APL Materials* **7**, 120902
1205 (2019).
- 1206 88. IRDS Executive Summary. In *The International Roadmap for Devices and Systems:*
1207 *2020* (IEEE, 2020). URL <http://irds.ieee.org>.
- 1208 89. Park, H. W., Roh, J., Lee, Y. B. & Hwang, C. S. Modeling of Negative Capacitance in
1209 Ferroelectric Thin Films. *Advanced Materials* **31**, 1805266 (2019).
- 1210 90. Park, M. H. *et al.* Morphotropic Phase Boundary of Hf_{1-x}Zr_xO₂ Thin Films for Dynamic
1211 Random Access Memories. *ACS Applied Materials & Interfaces* **10**, 42666–42673 (2018).
- 1212 91. Das, D. & Jeon, S. High- κ Hf_xZr_{1-x}O₂ Ferroelectric Insulator by Utilizing High Pressure
1213 Anneal. *IEEE Transactions on Electron Devices* **67**, 2489–2494 (2020).
- 1214 92. Kim, S. *et al.* Method to Achieve the Morphotropic Phase Boundary in Hf_xZr_{1-x}O₂ by
1215 ElectricField Cycling for DRAM Cell Capacitor Applications. *IEEE Electron Device Letters*
1216 **42**, 517–520 (2021).
- 1217 93. Kashir, A. & Hwang, H. Ferroelectric and Dielectric Properties of Hf_{0.5}Zr_{0.5}O₂ Thin Film
1218 Near Morphotropic Phase Boundary. *physica status solidi (a)* **218**, 2000819 (2021).
- 1219 94. Appleby, D. J. R. *et al.* Experimental Observation of Negative Capacitance in
1220 Ferroelectrics at Room Temperature. *Nano Letters* **14**, 3864–3868 (2014).
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- 1222

1223 **Data availability** The experimental data contained in the manuscript are available for download
1224 at <https://doi.org/10.5281/zenodo.5797030>.
1225

1226 **Extended Data Fig. 1. Atomic-scale multilayer structure.** (a) Schematic of the HfO₂-ZrO₂
1227 multilayer structure on SiO₂-buffered Si. (b) Synchrotron x-ray reflectivity (XRR) of thicker
1228 HfO₂-ZrO₂ heterostructures (left) repeated with the same periodicity as the thinner trilayer
1229 structure; XRR fitting (right) demonstrates the presence of well-separated HfO₂-ZrO₂ layers, i.e.
1230 not a solid- solution, for three different multilayer repeats of fixed periodicity, all approximately
1231 following the expected 4 Å - 12 Å - 4 Å HfO₂-ZrO₂-HfO₂ structure. (c) Layer-resolved electron
1232 energy loss spectroscopy (EELS) of the 2 nm HfO₂-ZrO₂-HfO₂ trilayer, demonstrating clear
1233 separation of HfO₂ and ZrO₂ layers. The exact layer thicknesses are extracted from XRR, which
1234 spans a wider sample footprint, rather than the local EELS measurement in which the apparent
1235 width increase can be due to beam spreading and local thickness variation. (d) Angle-resolved
1236 X-ray photoelectric spectroscopy (XPS) of the 2 nm HfO₂-ZrO₂-HfO₂ trilayer (left) and the
1237 extracted atomic composition (right). The presence of increasing Zr-content as the grazing angle
1238 increases is expected from the multilayer structure in which Zr-content increases after the surface
1239 Hf-rich layer. Therefore XRR, EELS, and XPS data all indicate the presence of a multilayer
1240 structure in which the HfO₂ layer is directly on the SiO₂ layer.

1241 **Extended Data Fig. 2. Ferroic phase insights from structural characterization.** (a) (left) In-
1242 plane synchrotron grazing-incidence diffraction (IP-GiD) of a bare 2 nm HfO₂-ZrO₂-HfO₂
1243 trilayer indexed to the tetragonal P4₂/nmc and orthorhombic Pca2₁ phases and (right) zoom-in of
1244 the spectrum about the orthorhombic (111)_o and tetragonal (101)_t reflections, confirming the co-
1245 existing structural polymorphs in the 2 nm film. These two peaks were differentiated via self-
1246 consistent indexing of the entire spectrum, in which interplanar lattice spacings – determined
1247 from the {200}_o family of reflections – closely match the *d*-spacings for all other reflections –
1248 (111)_o, (120)_o, (211)_o, (202)_o – determined by Bragg’s law (Methods). (b) Two-dimensional
1249 reciprocal space map of the bare 2 nm HfO₂-ZrO₂-HfO₂ trilayer, indexed by integrating the
1250 diffraction spectrum. The lack of fully polycrystalline rings illustrates that the 2 nm HfO₂-ZrO₂-
1251 HfO₂ trilayer is highly-oriented, consistent with TEM imaging. (c) Synchrotron spectroscopy
1252 (XAS) of the bare 2 nm HfO₂-ZrO₂-HfO₂ trilayer at the (left) Hf M₃- and (center) Zr L_{3,2}-edges:
1253 (right) the presence of linear dichroism (orbital polarization) provides further evidence of
1254 symmetry-breaking in these oriented thin films. (d) Second harmonic generation (SHG) mapped
1255 across the bare 2 nm HfO₂-ZrO₂-HfO₂ trilayer; the presence of SHG intensity confirms broken
1256 inversion symmetry in these ultrathin ferroic films. (e, f) Additional cross-sectional TEM
1257 providing complementary evidence of the (e) tetragonal P4₂/nmc and (f) orthorhombic Pca2₁
1258 phases, in which the extracted (101)_t lattice spacing (~ 2.95 Å) and (111)_o lattice spacing (~ 3.08
1259 Å) extracted from IP-GiD are consistent with the average lattice spacings extracted from the
1260 periodicity of the TEM-imaged planes. The white scale bars in all the TEM images represent 1
1261 nm.

1262 **Extended Data Fig. 3. Ferroic phase insights: proximity to temperature-dependent phase**
1263 **transition.** (a) Schematic of temperature-dependent antiferroelectric-ferroelectric phase
1264 evolution in fluorite-structure oxides. At lower temperatures, the higher symmetry tetragonal
1265 phase is expected to transition to the lower symmetry orthorhombic phase. (b) Schematic crystal
1266 field splitting diagram for fluorite-structure polymorphs; symmetry-induced *e*-splitting provides
1267 a spectroscopic signature for the polar *O*-phase (Methods). (c) Temperature-dependent XAS at
1268 the oxygen *K*-edge for a 2 nm HfO₂-ZrO₂-HfO₂ bare film demonstrating clearer spectroscopic
1269 signatures of the ferroelectric *O*-phase emerge slightly below room temperature. (d) Simulated
1270 oxygen *K*-edge XAS spectra (Materials Project) for the respective *O*- and *T*-phases. XAS
1271 provides spectroscopic signatures to distinguish between the *O*- and *T*-phases (difficult to resolve
1272 from GI-XRD). (e) Prototypical *C-V* behavior for mixed antiferroelectric-ferroelectric (shoulder-
1273 like features in addition to the characteristic butterfly-like shape) and ferroelectric films (just
1274 butterfly-like) in MIM capacitor structures. (f) Temperature-dependent *C-V* for thicker HfO₂-
1275 ZrO₂ multilayers of the same periodicity (in MIM capacitor structure) demonstrating an
1276 evolution from mixed-ferroic to ferroelectric-like hysteresis upon cooling slightly below room
1277 temperature. Thinner HfO₂-ZrO₂ multilayers films suffer from leakage-limitations, preventing
1278 such hysteretic *C-V* measurements. The thicker HfO₂-ZrO₂ multilayers of the same periodicity –
1279 annealed at the same low-temperature condition to maintain the multilayer structure –
1280 demonstrate a similar mixed ferroic to ferroelectric phase transition slightly below room
1281 temperature as the thinner 2 nm multilayer (c).

1282 **Extended Data Fig. 4. Solid solutions versus superlattice structure: Role of ALD period and**
1283 **Zr-content. (a)** Schematic of HfO₂-ZrO₂ multilayer and Zr-rich Hf:ZrO₂ solid solution films.
1284 With shorter ALD periods, the mixed FE-AFE multilayer structure transitions towards a Hf:ZrO₂
1285 solid-solution with AFE-like behavior. In the solid-solution state, the loss of the mixed ferroic
1286 order yields diminished capacitance due to the lack of mixed-ferroic-induced capacitance
1287 enhancement (Fig. 1a). **(b)** MOS accumulation *C-V* of the HfO₂-ZrO₂-HfO₂ trilayer (60% Zr)
1288 compared to solid solutions films of the same thickness (2 nm) and composition (60% Zr), as
1289 well as solid solutions films of the same thickness and higher Zr-composition (67%-100% Zr).
1290 **(c)** MIM *C-V* hysteresis loops of the HfO₂-ZrO₂ superlattice (60% Zr) compared to solid
1291 solutions films of the same thickness (6 nm) and composition (60% Zr), as well as solid solutions
1292 films of the same thickness and higher Zr-composition (67%-100% Zr). Hf:ZrO₂ solid solution
1293 films with higher Zr-content (60%-75%) is around the range attributed to the "MPB" in thicker
1294 Hf:ZrO₂ alloys^{35,55,90-93}. These results indicate the capacitance enhancement in multilayer films is
1295 not simply driven by Zr-content^{32,38,57,63}, but instead the atomic-scale stacking, as the solid
1296 solution films with sub-atomic superlattice period do not demonstrate the same mixed ferroic
1297 behavior and enhanced capacitance as the superlattices.

1298 **Extended Data Fig. 5. Solid solutions versus superlattice structure: Role of annealing**
1299 **temperature.** (a) Schematic of HfO₂-ZrO₂ multilayer and Hf:ZrO₂ solid solution films. Under a
1300 high-temperature anneal, the multilayer structure transitions towards a Hf:ZrO₂ solid-solution-
1301 like structure demonstrating more FE-like behavior. The solid solution state yields diminished
1302 capacitance due to the lack of both the higher-permittivity AFE phase and the mixed-ferroic-
1303 induced capacitance enhancement (Fig. 1a). (b) Comparison of MOS capacitor accumulation C-
1304 V characteristics in HfO₂-ZrO₂ multilayers, where the superstructure was repeated (left) 1,
1305 (center) 2, or (right) 3 times, under both low- and high-temperature anneals. (c) Comparison of
1306 mixed-ferroic behavior in low-temperature treated MIM HfO₂-ZrO₂ multilayers versus FE
1307 behavior in the same multilayers annealed at high temperatures, where the superstructure was
1308 repeated (left) 3, (center) 4, or (right) 5 times. In all instances, the high-temperature anneal (>
1309 500°C) results in diminished accumulation capacitance compared to the low-temperature
1310 anneals, as the multilayered mixed-ferroic films presumably transition to more FE-like solid-
1311 solution alloys.

1312 **Extended Data Fig. 6. SiO₂ interlayer thickness.** (a) Wide field-of-view (FoV) cross-sectional
1313 TEM images of the HfO₂-ZrO₂ multilayer structure and its corresponding intensity line scan
1314 (bottom right) averaged across the entire top cross-sectional image FoV (~ 150 nm, teal-colored
1315 box). Note the vertical teal-colored lines in the intensity line scan correspond to the inner teal-
1316 colored box in the wide-FoV image, which delineate the SiO₂ interlayer boundaries. The bottom
1317 cross-sectional TEM image highlights the thin SiO₂ interlayer (white region) without
1318 obfuscation by the teal-colored box. A physical SiO₂ thickness of 8.6 Å is extracted from
1319 analysis of the averaged intensity line scan of the wide FoV TEM (Methods). (b), (d) *C-V*
1320 measurements of HfO₂ (b) and Al₂O₃ (d) thickness series in MOS capacitor structures (left),
1321 extracted inverse capacitance versus thickness at different charge values (center), and extracted
1322 *Q-V* relation Si charge layer and SiO₂ interlayer (SiL) (right), which fits to TCAD simulations
1323 for 8.0 Å SiO₂. The SiL *Q-V* relation was found by integrating the extracted capacitance
1324 equivalent thickness of SiL versus charge (right, inset). This electrical interlayer thickness (8.0
1325 Å) is slightly less than the physical thickness determined by TEM (8.6 Å). As a sanity check, the
1326 extracted permittivity from this methodology for HfO₂ and Al₂O₃ corresponds to 19 and 9,
1327 respectively, as is expected (Methods, Permittivity Extraction). (c), (e) *Q-V* curves for HfO₂ (c)
1328 and Al₂O₃ (e) thickness series obtained from integrating MOS *C-V* measurements (left),
1329 extracted voltage vs thickness at various charge values (center), and extracted *Q-V* relation of
1330 SiL (right). The SiL *Q-V* relation is consistent with the *Q-V* relation extracted from the *C-V* data
1331 (inset). (f) Consistency in the SiL *Q-V* relation extracted from the *C-V* data from both the HfO₂
1332 and Al₂O₃ thickness series, which both fit to 8.0 Å SiO₂ interlayer thickness.

1333 **Extended Data Fig. 7. Capacitance and charge enhancement.** (a) MOS schematic of the 20 Å
1334 HfO₂-ZrO₂-HfO₂ (HZH) mixed ferroic trilayer sample on lightly-doped Si (10¹⁵ cm⁻³)
1335 considered for the following *C-V* and pulsed *I-V* measurements. (b) Accumulation *C-V* curves
1336 for 2 nm HZH grown on sub-nm SiO₂ fit to equivalent oxide thickness (EOT) simulations
1337 (Methods). Inset: Externally verified MOS accumulation *C-V* of the same trilayer stack
1338 (Methods), demonstrating 6.5 Å EOT. The 2 nm trilayer on top of SiO₂ demonstrates lower EOT
1339 than the thickness of SiO₂ interlayer alone, carefully extracted via physical (8.5 Å) and electrical
1340 (8.0 Å) methodologies (Extended Data Fig. 6), providing evidence of capacitance enhancement.
1341 (c) The applied voltage pulse (top), measured current response (center), and integrated charge
1342 (bottom) as a function of time for 2 nm HZH in MOS capacitors. (d) The maximum charge Q_{max} ,
1343 the residual charge Q_{res} , and their difference, Q_{rev} , derived from the charge vs time curve for each
1344 of the voltage pulses (Methods). (e) The reversible charge of the MOS layer (top) compared
1345 against the extracted charge of the Si charge layer plus SiO₂ interlayer (SiL) derived electrically
1346 (Extended Data Fig. 6f). The charge boost (bottom) present in the total MOS structure (SiL plus
1347 HZH capacitors) compared to just the SiL is a signature of negative capacitance (NC)^{26,69}. (f)
1348 The polarization-electric field ($P-E_F$) relationship for just the 2 nm HZH layer, extracted from
1349 the charge-voltage relationship in (e). Note the presence of a negative slope regime in the
1350 extracted $P-E_F$ relation corresponds to NC stabilization^{26,69}. (g) Scatter plot of reported
1351 ferroelectric-dielectric systems demonstrating capacitance or charge enhancement at the
1352 capacitor-level, via *C-V* or pulsed *I-V* measurements, respectively. The plot considers fluorite-
1353 structure bilayers^{26,69} (red), perovskite-structure bilayers^{29,94} (blue, BL), and perovskite-structure
1354 superlattices^{30,31,47,48} (blue, SL). This work marks the thinnest demonstration of NC.

1355 **Extended Data Fig. 8. Mobility and Reliability** (a) Intrinsic C_{gg} vs $V_{gs}-V_{fb}$ for ~ 20 Å HfO₂-
1356 ZrO₂-HfO₂ (HZH) and HfO₂ gate stacks, which fit to 7.5 Å and 9.5 Å, respectively, extracted
1357 from SOI transistors. (b) I_d vs $V_{gs} - V_T$ at $V_d= 50$ mV for transistors implementing HZH and
1358 HfO₂ gate stacks. (c) EOT and mobility (at $5 \times 10^{12}/\text{cm}^2$) for HZH and HfO₂, demonstrating no
1359 mobility degradation. (d) Normalized mobility versus EOT for transistors integrating the 2 nm
1360 HZH mixed-ferroic gate stack (blue) versus a 2 nm HfO₂ standard high- κ dielectric gate stack
1361 (black) of higher EOT, demonstrating no mobility degradation. These results are also
1362 benchmarked against reported HKMG literature³ implementing interlayer-scavenged 2 nm HfO₂
1363 (red). Inset: SiO₂ interlayer thickness versus EOT for 6.5 Å EOT HZH stack against notable
1364 HKMG literature employ interlayer scavenging³. This scatter plot highlights the underlying
1365 reason for the improved leakage-EOT and mobility-EOT behavior in the ultrathin HZH gate
1366 stacks: achieving low EOT without reducing the SiO₂ interlayer thickness. (e) Measure-Stress-
1367 Measure scheme used in PBTI reliability measurements. (f, g) ΔV_T vs stress time for long-
1368 channel bulk transistors integrating HZH (f) and HfO₂ (g) at varying stress conditions (up to 9
1369 MV/cm), measured at 85°C. The extracted time exponent, n , is similar to reported high- κ HfO₂
1370 stacks⁶⁷, which is expected considering the similar interfacial (IL) oxide and IL-high- κ
1371 interface⁴⁶; both stacks with different EOT have HfO₂ sitting on the same SiO₂ IL (Extended
1372 Data Fig. 1). (h) DC lifetime (stress time needed to induce a 50 mV ΔV_T shift) vs electric field
1373 for HZH and HfO₂, demonstrating similar rates of degradation. (i, j) Evolution of MOSCAP
1374 accumulation $C-V$ curves as a function of stress time at a stress of $V_{fb} - 1$ V for HZH (i) and HfO₂
1375 (j).
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1378 **Extended Data Fig. 9. RF device characterization.** (a) De-embedding procedure for extracting
1379 corrected admittance parameters (Y_{corr}) by decoupling parasitic shunt capacitance and series
1380 resistance and inductance by measuring scattering parameters for the device under test (DUT) as
1381 well as open and short structures. More details can be found in the Methods. (b) Small-signal
1382 model for transistor used to extract transconductance (g_m) and total gate capacitance ($C_{gg} = C_{gs} +$
1383 C_{gd}). (c) De-embedded $(2\pi f)^{-1}Re(Y_{21})$ points extrapolated to the zero frequency limit (dotted
1384 lines) to extract the RF g_m . All data shown were extracted from bulk transistors ($L_G = 1 \mu\text{m}$)
1385 integrating the 2 nm HfO₂-ZrO₂-HfO₂ ferroic gate stack.
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1387 **Extended Data Fig. 10. Transconductance extraction.** (a) Threshold voltage extraction by
1388 linear extrapolation for various channel lengths. All channel lengths give nearly constant V_T (\sim
1389 0.42 V), satisfying the assumption for the line resistance method. (b) Source/drain series
1390 resistance extracted using the I/V_{ov} method (Methods). By performing a linear interpolation of
1391 the total resistance for $V_{ov} = 0.5-0.6$ V, the extracted series resistance is $\sim 500 \Omega\text{-}\mu\text{m}$. (c)
1392 Source/drain series resistance extracted using the line resistance method (Methods). The trend is
1393 considered down to $L_G = 90$ nm, which intersects at $\sim 500-600 \Omega\text{-}\mu\text{m}$ – consistent with the I/V_{ov}
1394 method– with an L_G offset of ~ 50 nm. (d, e) Measured (left) and extracted (right)
1395 transconductance (d) and output conductance (e) versus V_g for $V_{ds} = 0.9-1.1$ V, assuming $R_s = R_d$
1396 = $250 \Omega\text{-}\mu\text{m}$ for $L_G = 90$ nm. The de-embedding of intrinsic $g_{m,i}$ and $g_{ds,i}$ from extrinsic g_m and
1397 g_{ds} is described in the Methods. All data shown were measured on SOI short-channel transistors
1398 integrating the 2 nm HfO₂-ZrO₂-HfO₂ ferroic gate stack.





