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ADVANCED
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Supporting Information

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Forming-Free Grain Boundary Engineered Hafnium Oxide Resistive Random Access Memory Devices

Stefan Petzold, Alexander Zintler, Robert Eilhardt, Eszter Piros, Nico Kaiser, Sankaramangalam Ulhas Sharath, Tobias Vogel, Márton Major, Keith Patrick McKenna, Leopoldo Molina-Luna, and Lambert Alff**

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Forming-Free Grain Boundary Engineered Hafnium Oxide Resistive Random Access Memory Devices

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Description:
In this video, two VESTA models of cutting planes (as indicated by the dotted line in Figure 3 (a)) of monoclinic HfO2 grains are overlaid and moved laterally to each other (other degrees of freedom are not allowed in the present system). The cutting planes are the (-1-1-2) and (-121) planes for the purple (grain 1) and green (grain 2) lattice respectively. Moiré fringes are visible as the move due to the lateral shift of the lattices, also indicated by the red dotted lines.
The periodic distances of these Moiré fringes can be used to define the repeating unit cell in order to calculate the coincident site lattice for this specific grain boundary.

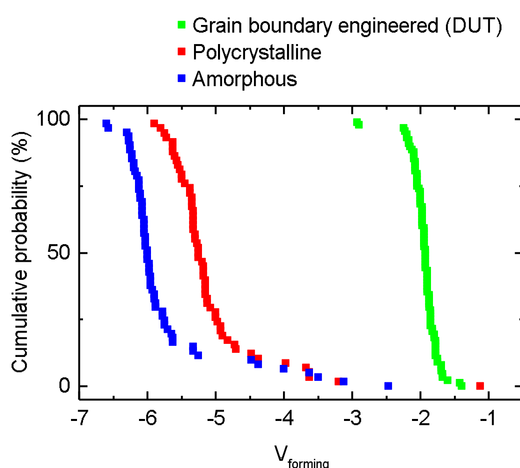

Figure S1. Cumulative distribution plots of the forming voltage for the device under test (DUT, green), a crystalline but less textured HfO_2 film (red) and an amorphous dielectric film (blue) (88, 58 and 61 devices were tested respectively). Note the more pronounced tails, higher spread and higher forming voltages of the less textured and amorphous sample.
In the growth process of the different crystallinities, only the substrate temperature was changed from 525 to 320 °C to room temperature, respectively. Note that even the polycrystalline sample is textured due to the growth by MBE, thus already showing a distribution of forming voltages comparable to the amorphous layer. The texture of the polycrystalline samples is due to the epitaxy favoring growth conditions in the MBE. While the sample grown at 320 °C (less textured) shows a variety of HfO_2 growth orientations, including the $(11\bar{1})$ orientation found in the highly textured sample. The grain boundary

engineered sample (DUT), grown at 525 °C, shows only the $(11\bar{1})$ growth orientation as described in the manuscript.

Table S1. Lattice parameters of *m*-HfO_2 predicted by density functional theory (DFT) using the PBE exchange correlation functional with comparison to experimental data.[92]

	DFT	Experiment[92]	% difference
a (Å)	5.131	5.116	+ 0.3
b (Å)	5.186	5.172	+ 0.3
c (Å)	5.311	5.295	+ 0.3
β (º)	99.70	99.18	+ 0.5
r_{Hf} (Å)	0.275, 0.043, 0.208		
r_{O1} (Å)	0.068, 0.331, 0.346		
r_{O2} (Å)	0.449, 0.758, 0.479		

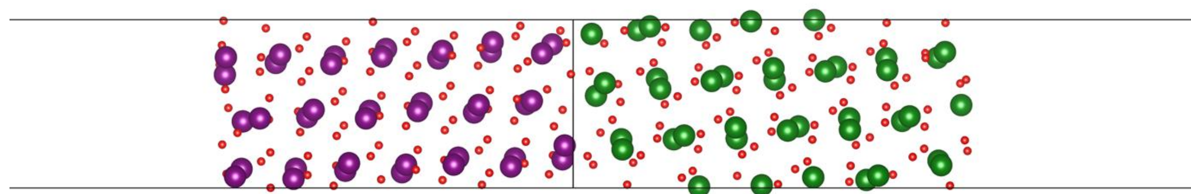

Figure S2. Supercell used to model the interface between the $(\bar{1}\bar{1}\bar{2})$ and $(\bar{1}21)$ terminated grains in *m*-HfO_2. Hf ions in grain 1 and grain 2 are represented as purple and green spheres respectively. O ions are represented by small red spheres. A vacuum gap of 10 Å is included so that the two free surfaces do not interact.

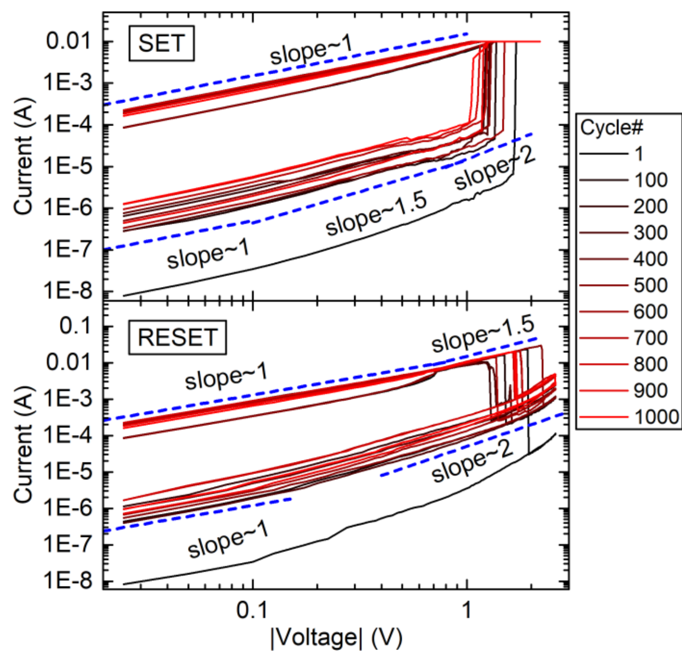

Figure S3. The conduction mechanism was analyzed for both the set and the reset process, where the I-V characteristics were found to follow Ohm's law (I~V) at low bias voltages, and Child's law ($I \sim V^2$) at higher biases, which is the signature of space charge limited conduction (SCLC) mechanism. SCLC type conduction is commonly related to charge transport through defect-related traps, e.g. oxygen vacancies.[76]