EPDS measurement procedure

EPDS measurements were carried out at room temperature in the spectral range of 1.25<\textit{hv}<6.5 eV using an energy increment $\delta\textit{hv}$ of 0.2 or 0.3 eV (with constant wavelength resolution of 10 nm) under +2 V bias applied to the metal electrode. The exposure time per step was 1 to 3 h which guarantees removal of at least 90% of charge available for de-trapping at every $\textit{hv}$ as monitored by 0.2 or 1 MHz CV curve measurement. After analyzing an as fabricated (pristine) MOS capacitor, the latter was injected by electrons or holes by applying a 20-ms long “write” voltage pulse to the metal electrode. The pulse amplitude $V_g$ was increased in steps of 1 or 2 V to achieve different trapped charge densities. Upon charging, the capacitors were kept in darkness for 48 h to allow for completion of thermal de-trapping before exposure to light starting from the lowest photon energy of 1.25 eV. After each illumination step the charge variation in the insulating stack was monitored using CV curves. The corresponding charge density $\Delta Q_{\text{stack}}$ was calculated from the shift of the flatband point assuming uniform distribution of traps across the HfO$_2$ layer. Finally, the spectral charge density (SCD) was calculated by normalizing the density of the re-charged centers to the spectral step width $\delta\textit{hv}$. In addition, to ensure that the de-population is complete, several samples were measured using longer exposures (from 6 to 10 h). No differences between the photocharging spectra and SCD distributions as compared to the results reported in this paper were found within the accuracy limit of SCD determination of 10-15 %. The latter was evaluated on the basis of the spread of SCD values inferred from repetitive measurements.

Calculations details

Amorphous HfO$_2$ structures was obtained using the LAMMPS package [1] and a conventional melt-quench procedure [2,3] using two different force-fields: a relatively simple pair potential parametrized
in ref. 3 and a modified charge equilibration force-field COMB [4]. A cubic 96 structure was initially
equilibrated at 300K and a pressure of 1 atm. The temperature was linearly ramped to 6000K at
constant pressure, equilibrated for 500 ps at 6000K and then cooled down from to 0K in 8 ns with a
small cooling rate of 0.75 K.ps⁻¹. The Berendsen thermostat [5] was used to control the temperature
during the simulations. The supercell dimensions and atomic positions have been further optimized
using DFT and the CP2k package [6] and the non-local PBE0-TC-LRC functional with the cutoff radius set
to 2.0 Å [7]. The CP2K code uses a Gaussian basis set mixed with an auxiliary plane-wave basis set [8]. In
this work we used the double-ζ Gaussian basis set with polarization functions for hafnium and oxygen
[9]. The plane-wave cutoff was set to 6530 eV. In order to reduce the computational cost of nonlocal
functional calculations, the auxiliary density matrix method (ADMM) was employed [10]. All geometry
optimizations were performed using the Broyden–Fletcher–Goldfarb–Shanno (BFGS) optimizer to
minimize forces on atoms to within 37 pN (2.3×10⁻² eV/Å).

   (2014).
   (2010).