Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Stable chemical enhancement of passivating stacks grown by atomic layer deposition on silicon

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Contents

S1. Si/HfO_2/Al_2O_3 on *p*-type silicon 2
S2. Si/Al_2O_3/HfO_2 with 10 nm HfO_2 3
S3. Re-annealing Si/HfO_2/Al_2O_3 4
S4. Re-annealing Si/HfO_2 5
S5. Re-annealing Si/HfO_2 with 10 nm HfO_2 6
S6. Corona charging of Si/HfO_2/Al_2O_3 7
S7. Impact of rinsing Si/HfO_2/Al_2O_3 in DI water following HF dip 8
S8. Si/Al_2O_3 and Si/HfO_2 controls 9
S9. Etch rate of Al_2O_3 10
S10. XPS spectra of Si/Al_2O_3/HfO_2 immersed in HF 11
S11. XPS spectra of Si/Al_2O_3/HfO_2 with 10 nm HfO_2 immersed in HF 12
S12. Si/HfO_2/Al_2O_3 with 10 nm HfO_2 13
S13. Si/HfO_2/Al_2O_3 – H_2O dip control 14
S14. Other chemical treatments 15

S1. Si/HfO_2/Al_2O_3 on *p*-type silicon

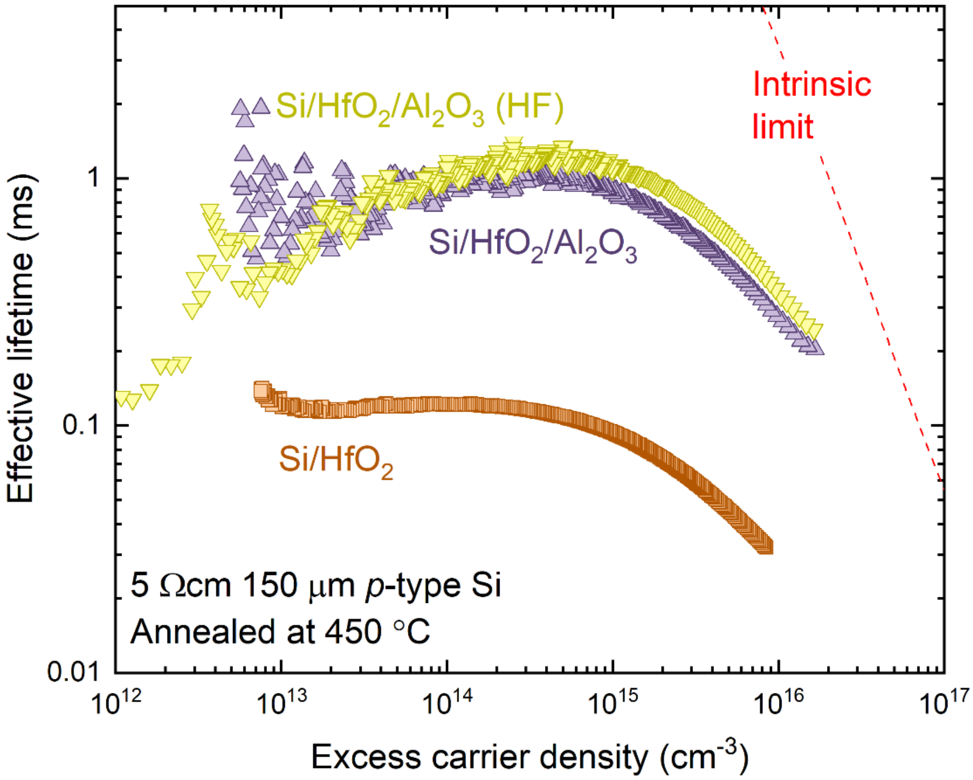

Figure S1: Effective lifetime curves for Si/HfO_2 (orange squares), Si/HfO_2/Al_2O_3 as-annealed (purple triangles) following a HF dip (yellow triangles). In each case, the HfO_2 layer was 1 nm (10 cycles), and the Al_2O_3 layer was 30 nm (250 cycles). All samples were annealed at 450 °C. Also shown is the intrinsic effective lifetime limit for 5 Ωcm 150 μm p-type c-Si.[1] *Effective lifetime curves are the average of five measurements. Measurements made under long flash conditions are assumed to be accurate to 11%, and those made under short-flash conditions are assumed accurate to 8%.*[2]

Ultra-thin HfO_2 passivates *p*-type Si less well than for *n*-type, with an average SRV (extracted at Δn = $1\text{x}10^{15}$ cm^{-3}) of 101 cms^{-1} for HfO_2 annealed at 450 °C. This passivation quality corresponds to an average single-side $J_{0,s}$ of 393.62 $fAcm^{-2}$ Depositing 30 nm Al_2O_3 reduces the average SRV ($J_{0,s}$) to just 6.8 cms^{-1} (25.02 $fAcm^{-2}$), a near 14-fold improvement (although less competitive than *n*-type Si/HfO_2/Al_2O_3). The lesser initial passivation quality for *p*-type Si/HfO_2 (relative to *n*-type Si/HfO_2) is not unexpected, as similar observations have been reported previously.[3] Nevertheless, we demonstrate that this reduced passivation can be overcome with an Al_2O_3 capping layer. 5 s immersion in 1% HF causes a further improvement in passivation, reducing average SRV ($J_{0,s}$) to 5.77 cms^{-1} (19.35 $fAcm^{-2}$).

S2. Si/Al_2O_3/HfO_2 with 10 nm HfO_2

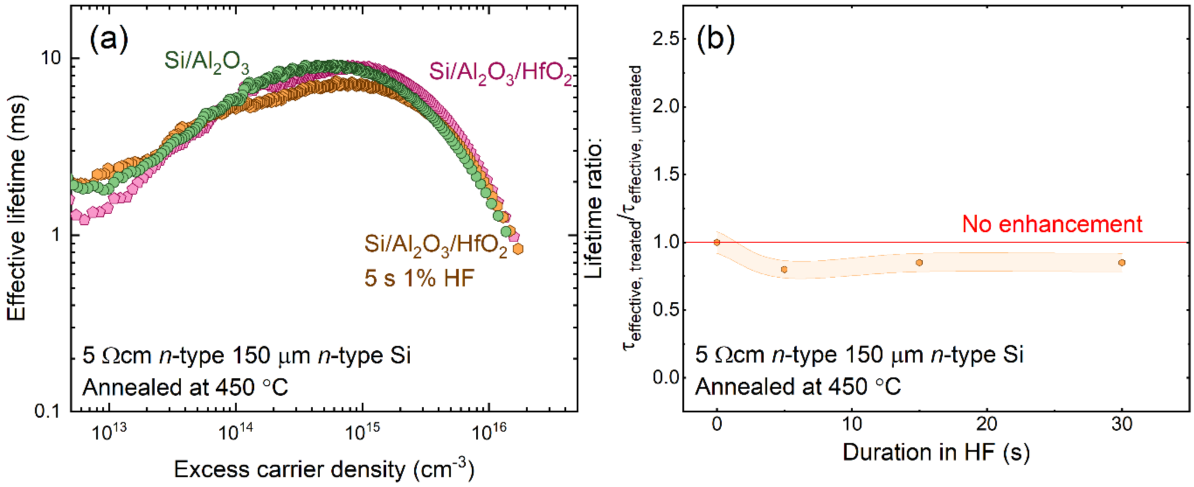

Figure S2: (a) Effective lifetime measurements for Si/Al_2O_3 (green circles) and Si/Al_2O_3/HfO_2 with 10 nm HfO_2 and 30 nm Al_2O_3 as annealed (pink pentagons) and after 5 s immersion in 1% HF (orange hexagons) (b) Effective lifetime enhancements (determined as $\tau_{effective,\ as\text{-}annealed}/\tau_{effective,\ HF\ dip}$, with $\tau_{effective}$ extracted at $\Delta n = 1 \times 10^{15}$ cm^{-3}) as a function of duration in 1% HF. All effective lifetime data are the average of 5 measurements, and have an uncertainty of 8%.[2]

S3. Re-annealing $Si/HfO_2/Al_2O_3$

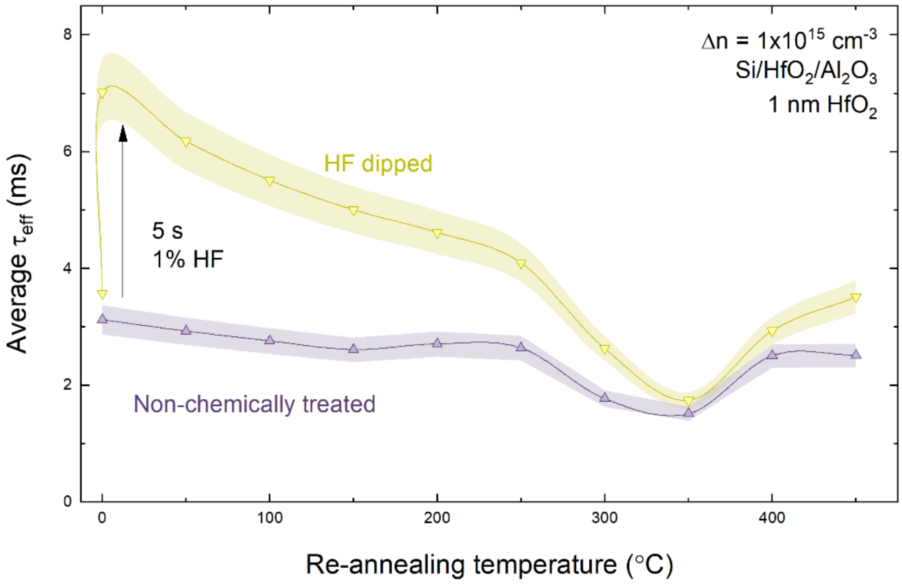

Figure S3: (a) Average effective lifetime for $Si/HfO_2/Al_2O_3$ with 1 nm HfO_2 extracted at an excess carrier density of 1×10^{15} cm^{-3}. Purple triangles correspond to non-chemically treated stacks, and yellow triangles correspond to HF dipped stacks. Effective lifetime was measured following re-annealing at temperatures between 50-450 °C for 30 min. Effective lifetime values are the average of five measurements and reported SRV corresponds to the average of two parallel samples. Error bars correspond to relative uncertainty of the effective lifetime measurements made under these conditions. Connections between the data points were added to serve as guide to the eye.

S4. Re-annealing Si/HfO₂

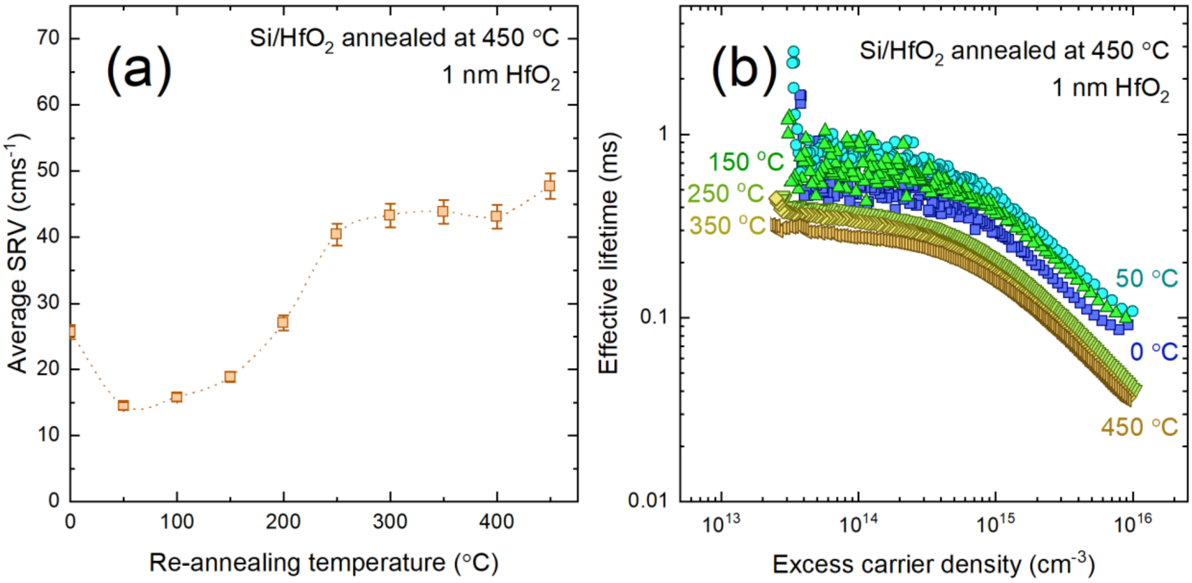

Figure S4: (a) Average SRVs for Si/HfO$_2$ with 1 nm HfO$_2$ extracted at an excess carrier density of 1×10^{15} cm^{-3}. Effective lifetime (from which SRV is extracted) was measured following re-annealing at temperatures between 50-450 °C for 30 min. Effective lifetime values are the average of five measurements and reported SRV corresponds to the average of two parallel samples. Error bars correspond to relative uncertainty of SRV. Connections between the data points were added to serve as guide to the eye. (b) Selected representative effective lifetime curves for one of the parallel Si/HfO$_2$ samples, after re-annealing at temperatures between 50-450 °C for 30 min

S5. Re-annealing Si/HfO$_2$ with 10 nm HfO$_2$

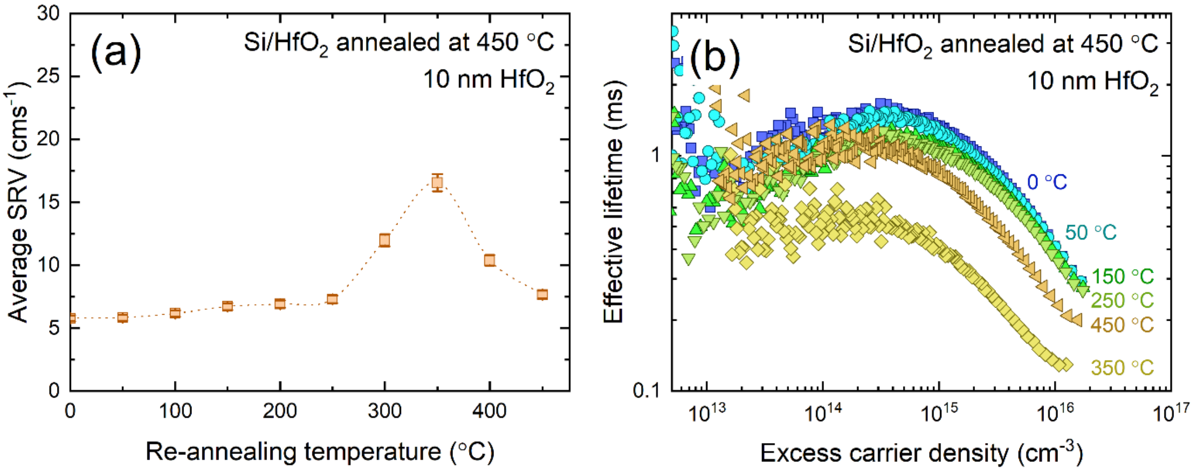

Figure S5: (a) Average SRVs for Si/HfO$_2$ with 10 nm HfO$_2$ extracted at an excess carrier density of 1×10^{15} cm^{-3}. Effective lifetime (from which SRV is extracted) was measured following re-annealing at temperatures between 50-450 °C for 30 min. Effective lifetime values are the average of five measurements and reported SRV corresponds to the average of two parallel samples. Error bars correspond to relative uncertainty of SRV. Connections between the data points were added to serve as guide to the eye. (b) Selected representative effective lifetime curves for one of the parallel Si/HfO$_2$ samples, after re-annealing at temperatures between 50-450 °C for 30 min

S6. Corona charging of Si/HfO_2/Al_2O_3

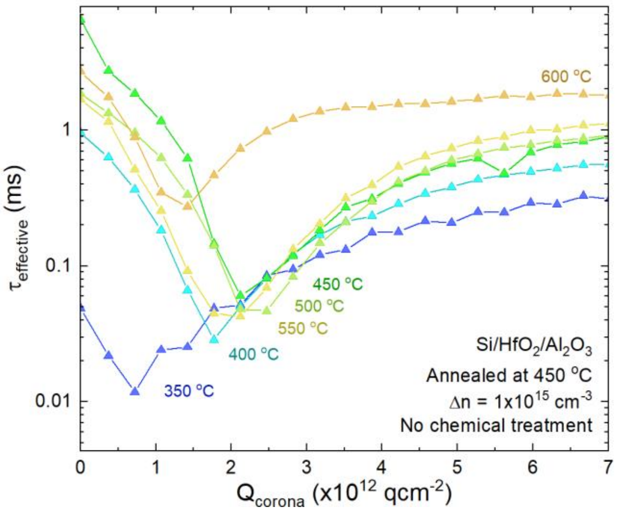

Figure S6: Effective lifetime as a function of Q_{corona} *for non-chemically treated Si/*HfO_2*/*Al_2O_3 *stacks with 1 nm* HfO_2 *and 30 nm* Al_2O_3 *activated at temperatures between 350-600 °C.*

S7. Impact of rinsing Si/HfO_2/Al_2O_3 in DI water following HF dip

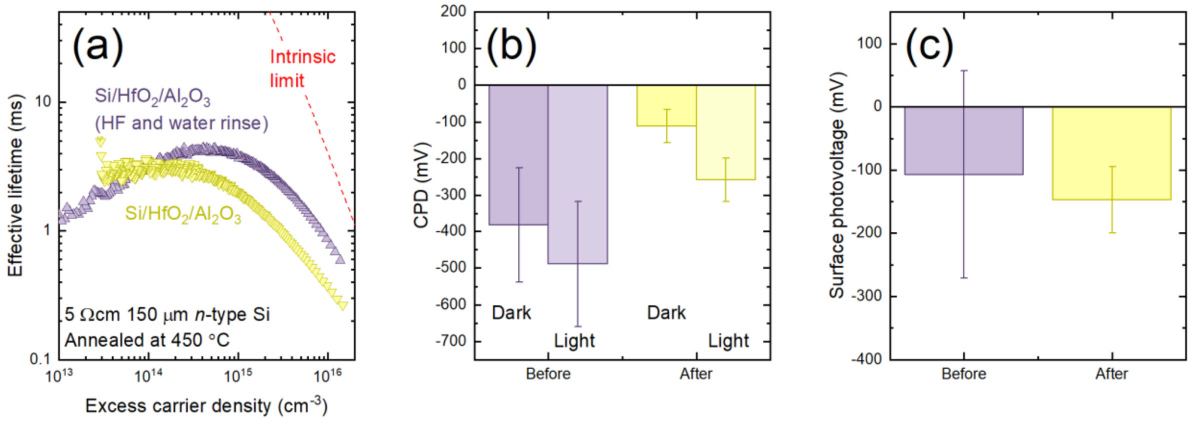

Figure S7: (a) Effective lifetime curves for Si/HfO_2/Al_2O_3 stacks with 1 nm HfO_2 and 30 nm Al_2O_3 activated at 450 °C as-annealed (purple triangles), and after a HF dip with a final water rinse (yellow triangles). Also shown is the intrinsic lifetime limit for 5 Ωcm 150 µm n-type Si.[1] Effective lifetime curves are the average of five measurements. Measurements made under short-flash conditions are assumed accurate to 8%.[2] KP analysis of sample before and after HF dip and rinse, from which (b) CPD under dark conditions and illumination, and (c) SPV for both as-annealed stacks (purple) and stacks following a HF dip and rinse (yellow). For each sample, at least five locations are measured in duplicate, and the reported SPV for each point determined is the mean SPV calculated for each darkness-illumination measurement cycle. The error bars are the mean standard deviation of these measurements.

S8. Si/Al_2O_3 and Si/HfO_2 controls

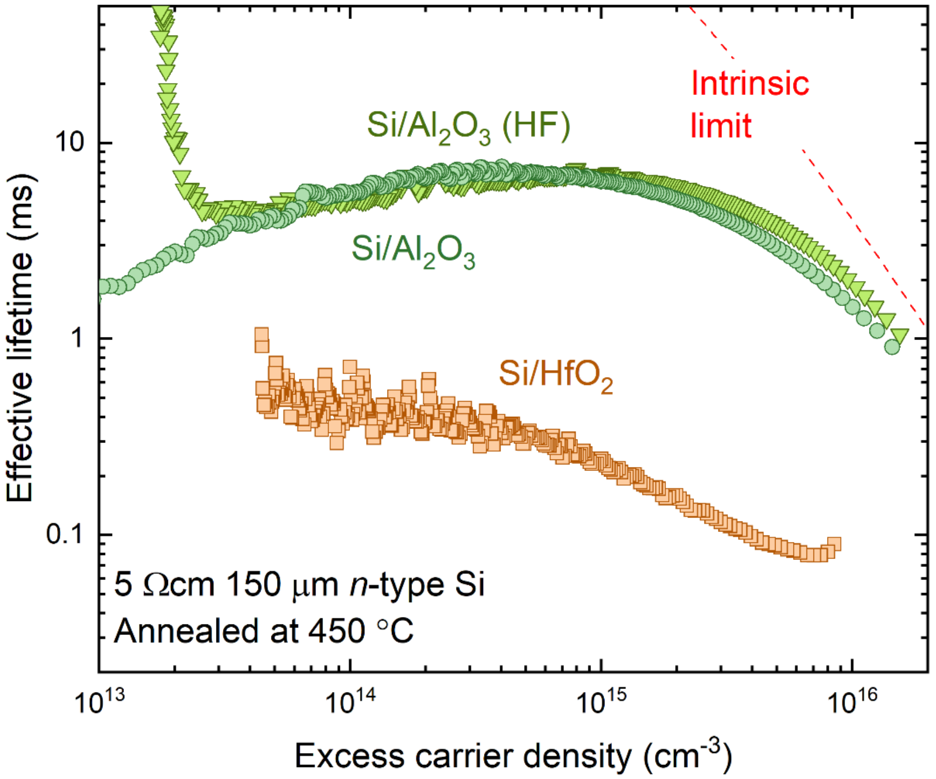

Figure S8: Effective lifetime curves for (a) Si/Al_2O_3 (30 nm, green) and (b) Si/HfO_2 (1 nm, orange) as-annealed (circles and squares, respectively) and after a HF dip (triangles). A lifetime curve could not be obtained for Si/HfO_2 following a HF dip as the passivation was removed. Both samples were annealed at 450 °C. Also shown is the intrinsic effective lifetime limit for 5 Ωcm 150 µm n-type c-Si.[1] *Effective lifetime curves are the average of five measurements. Measurements made under long flash conditions are assumed to be accurate to 11%, and those made under short-flash conditions are assumed accurate to 8%.*[2]

S9. Etch rate of Al_2O_3

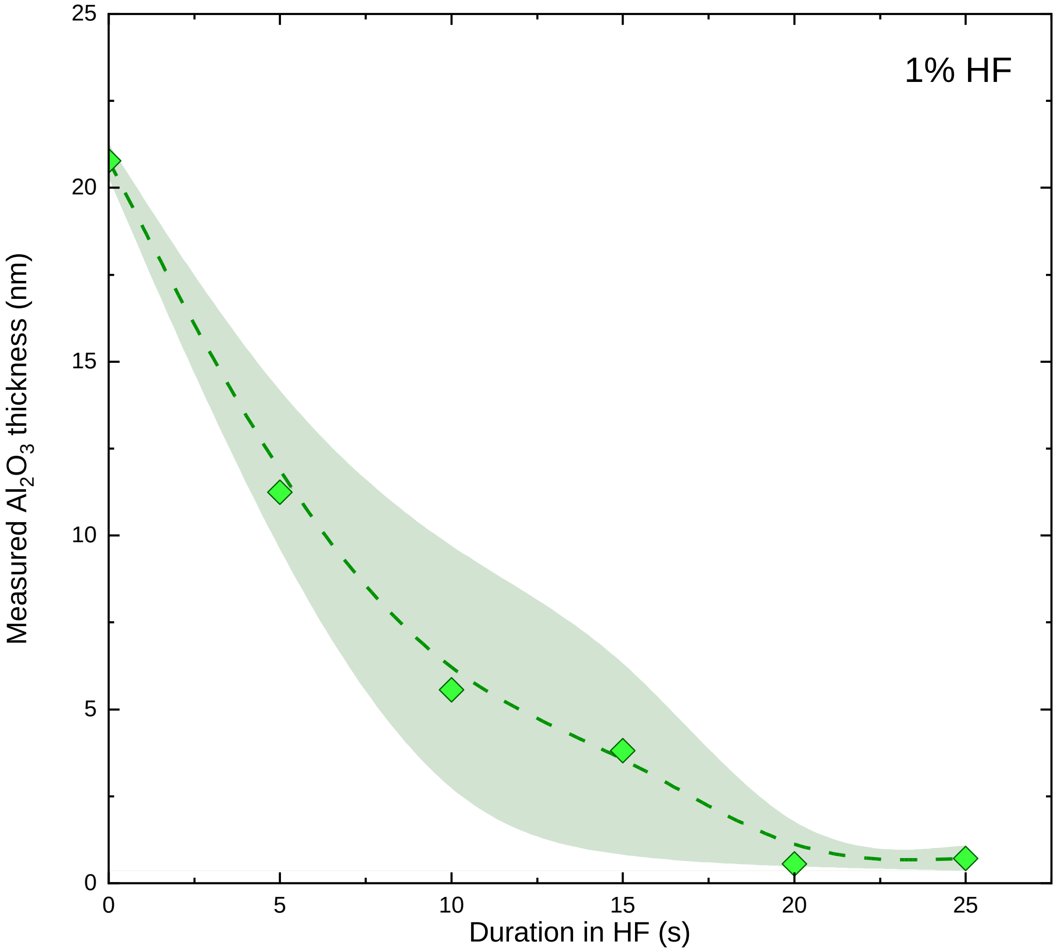

Figure S9: Calibrated etch rate of Al_2O_3 on silicon in 1% HF determined by spectral reflectance. Each point is the average thickness measured at three locations across each sample. The dashed green line is a guide to the eye and the shaded region is the standard deviation of the three measurements. Etching was performed at room temperature.

S10. XPS spectra of $Si/Al_2O_3/HfO_2$ immersed in HF

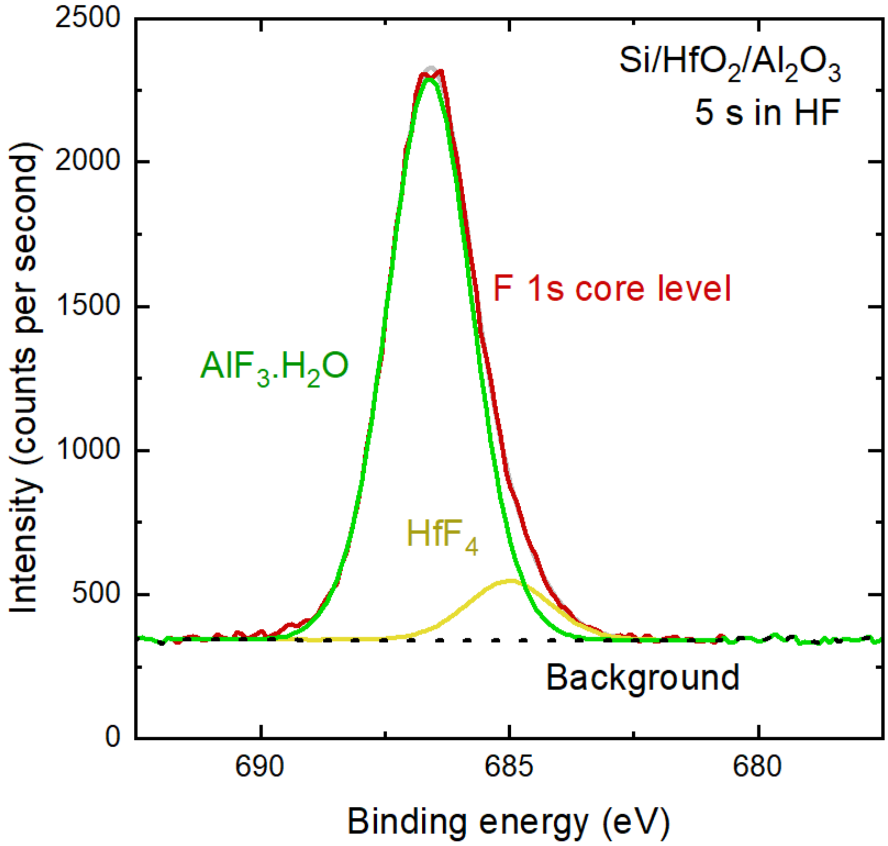

Figure S10: Deconvoluted F 1s core level measured from $Si/HfO_2/Al_2O_3$ with 1 nm HfO_2 and 30 nm Al_2O_3 following 5 s in 1 % HF, with HfF_4 and $AlF_3.H_2O$ contributions identified

S11. XPS spectra of Si/Al_2O_3/HfO_2 with 10 nm HfO_2 immersed in HF

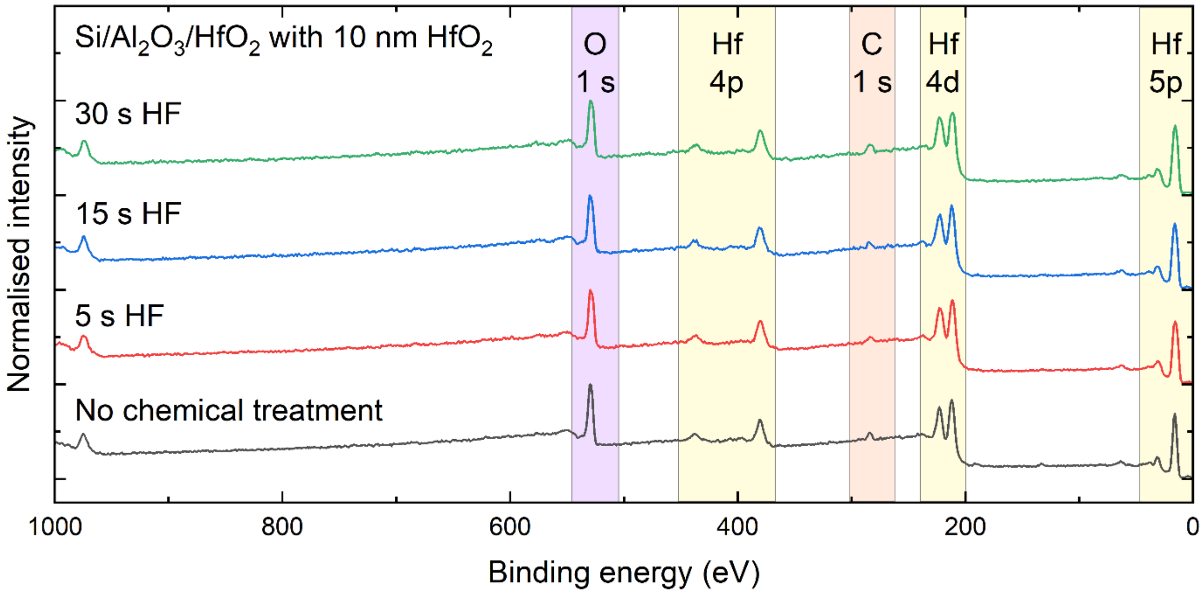

Figure S11: XPS survey scans for Si/Al_2O_3/HfO_2 stacks with 10 nm HfO_2 and 30 nm Al_2O_3 as annealed, and following 5, 15 and 30 s treatment with 1% HF. Core level peaks in the spectra are labelled.

S12. Si/HfO_2/Al_2O_3 with 10 nm HfO_2

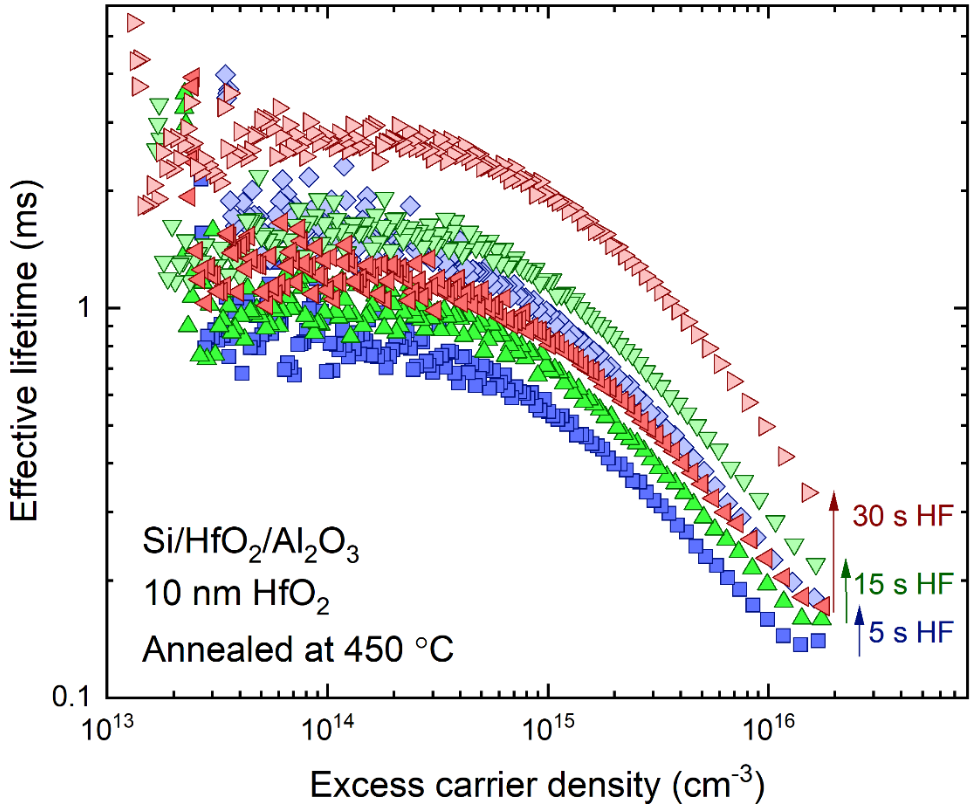

Figure S12: Effective lifetime measurements for Si/HfO_2/Al_2O_3 with 10 nm HfO_2 before (dark shades) and after (light shades) 5 s (squares/diamonds), 15 s (up/down pointing triangles) and 30 s (left/right pointing triangles). Effective lifetime curves are the average of 5 measurements, and have an uncertainty of 8%.[2]

S13. Si/HfO_2/Al_2O_3 – H_2O dip control

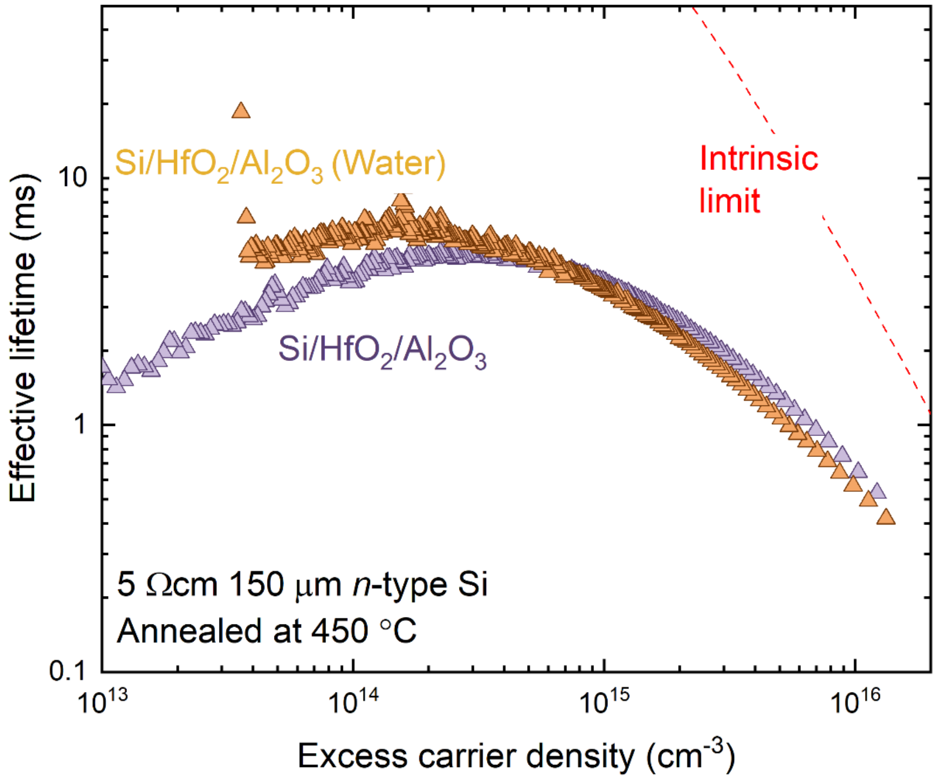

Figure S13: Effective lifetime curves for Si/HfO_2/Al_2O_3 with 1 nm HfO_2 and 30 nm Al_2O_3 as-annealed (yellow triangles) and after immersion in DI water (orange triangles) . The sample was annealed at 450 °C after deposition. Also shown is the intrinsic effective lifetime limit for 5 Ωcm 150 µm n-type c-Si.[1] Effective lifetime curves are the average of five measurements. Measurements made under short-flash conditions are assumed accurate to 8%.[2]

S14. Other chemical treatments

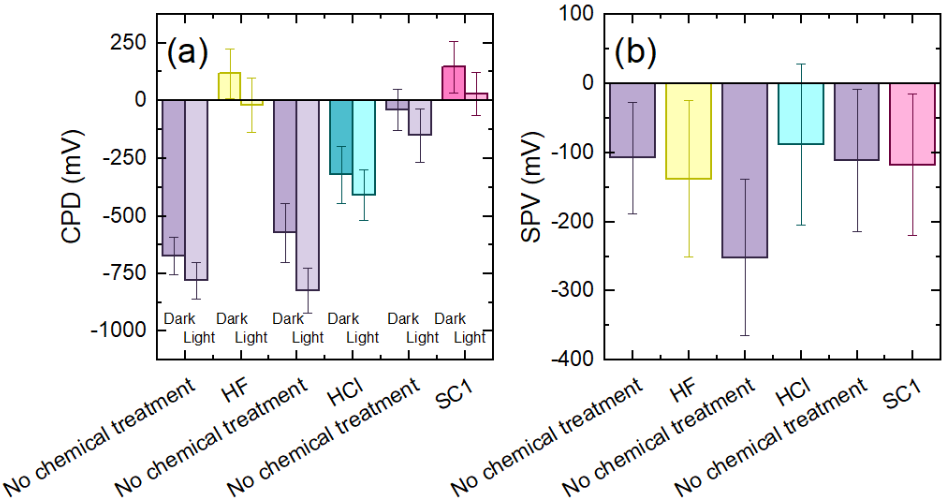

Figure S14: (a) CPD measured under dark and light conditions for as-annealed Si/HfO_2/Al_2O_3 (purple), and following immersion in HF (yellow), HCl (blue) and SC1 (pink). The HfO_2 layer was 1 nm thick and the Al_2O_3 layer was 30 nm thick. Darker shades correspond to measurements made under dark conditions, and lighter shades correspond to those made under illumination. (b) SPV for as-annealed Si/HfO_2/Al_2O_3 (purple), and following immersion in HF (yellow), HCl (blue) and SC1 (pink). For each sample, at least five locations are measured in duplicate, and the reported SPV at each point is the mean calculated for each darkness-illumination cycle. Error bars are the mean standard deviation of these measurements.

As with HF treatment, immersion in HCl and SC1 also causes a significant change in CPD that is not matched by a comparable change in SPV, as shown in Figure S14 (a) and (b). According to Henning *et al.,* the consistent direction of the shift following treatment with each solution suggests that the resulting surface dipoles have the same sign/direction.[4] There is a slight shift in average SPV following HCl treatment but given the considerable variation in these values we do not necessarily consider this indicative of a different mechanism. The variability of SPV measurements is well-reported, due to the influence of both material properties and surface defects.[5, 6] As a shift in CPD without a corresponding shift in SPV is a common feature with all three solutions, the improved passivation achieved in all cases is perhaps linked to the presence of surface dipoles.[7]

References

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