HfO_2/Al_2O_3 high-k dielectric stacks for charge trapping non-volatile flash memories

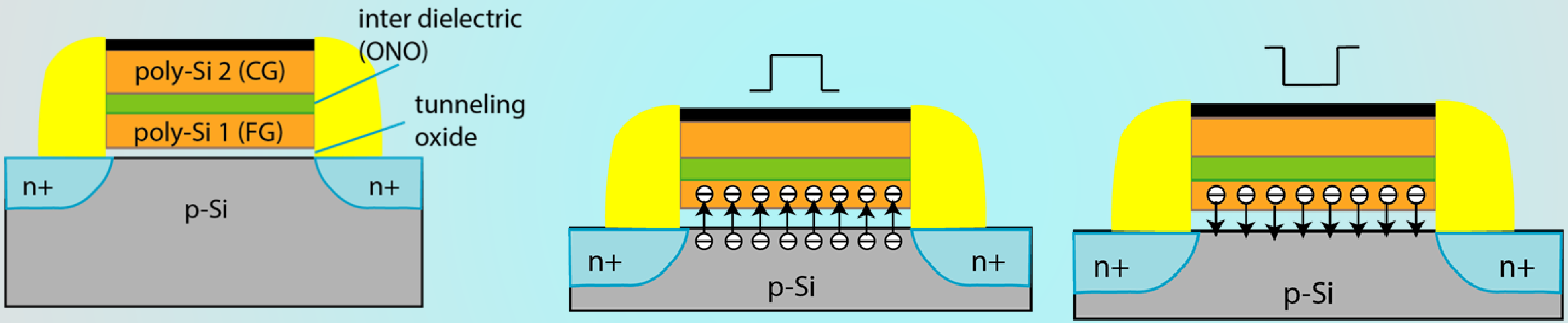
Dencho Spassov, Albena Paskaleva

Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia, Bulgaria

Flash non-volatile memories (NVM)

Flash memories are the preferred choice for data storage in portable gadgets (tablets, smart phones, etc.) because they offer a small, low-power consuming and reliable alternative to disk storage

Up-to-now the dominant flash NVM technology was the floating gate (FG) memory cell

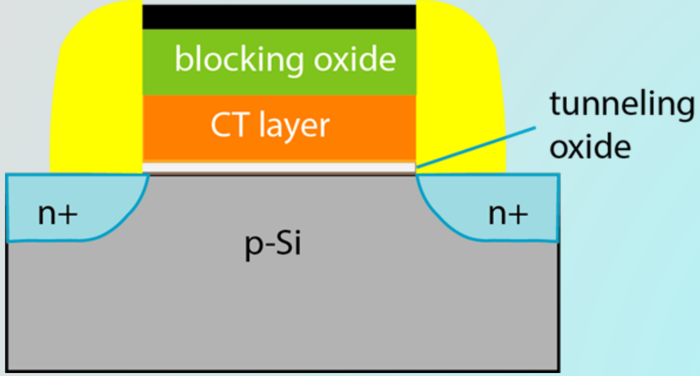


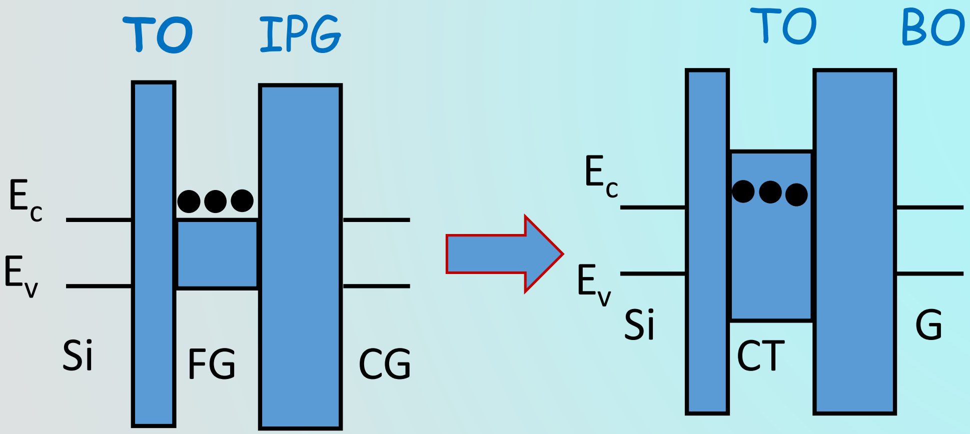
Limitations of FG technology in cell size reduction:

- the need for a relatively thick tunnel oxide to maintain acceptable reliability
- a significant decrease in the amount of electrons accumulated in FG as its thickness decreases
- maintaining a high coefficient of capacitive coupling of the control gate to the floating gate.

Advantages of charge trapping flash memories

Charge trapping cell





FG MOSFET

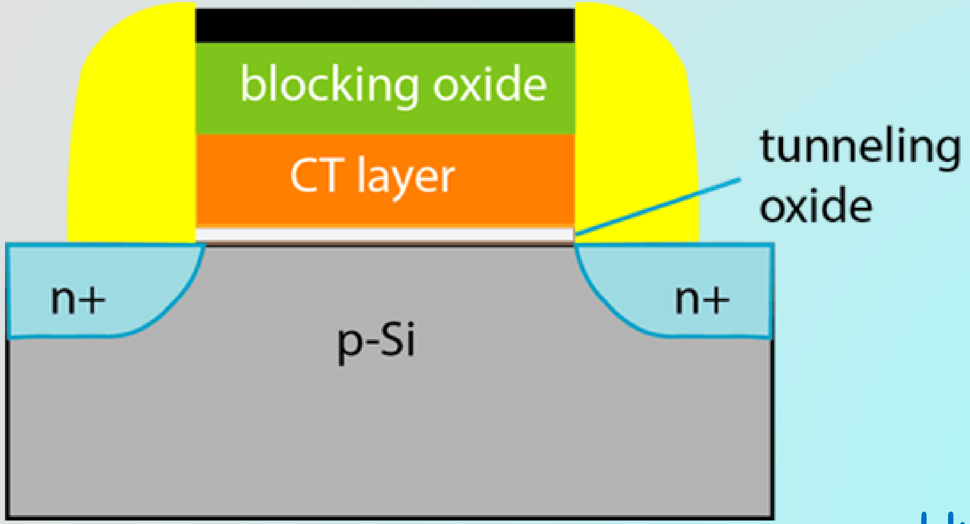
CT MOSFET

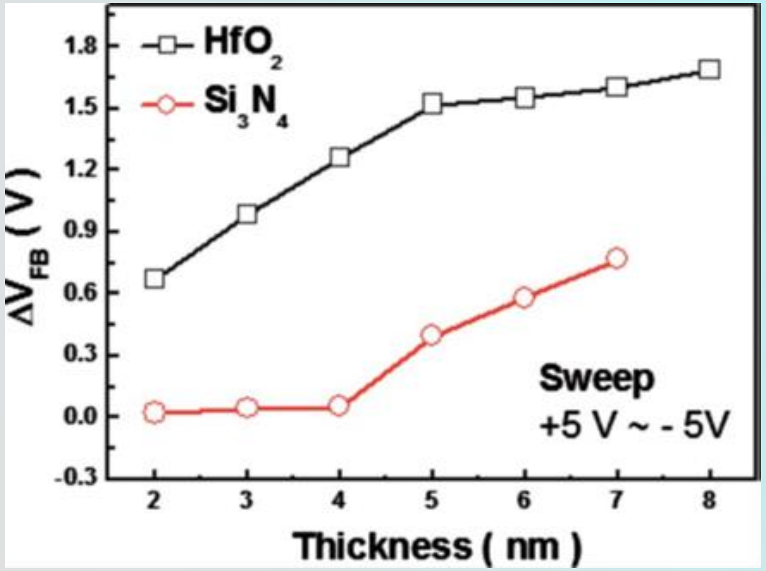
Charge trapping memory could offer solutions in a ever widening range of applications and is a very promising alternative to FG NVM.

CTM operation is similar to the floating gate cell, but the charge in CTM is stored in spatially discrete traps in the band-gap of the dielectric layer instead of the floating gate.

- Prevents the leakage of whole stored charge;
- Better operation characteristics, e.g. improved retention and endurance, lower power consumption, higher program/erase (P/E) speed
- Architecture similar to MOSFET – gate oxide is replaced by CT stack - compatible with CMOS technology;
- CT-NVM seem unavoidable in Vertical-NAND flash memory technology

Charge trapping (CT) memory stack - materials





<u>CT stack:</u>

Charge trapping layer (CTL): stores charges in traps in the band-gap of dielectric

Tunneling oxide (TO) – used to inject charges from substrate to CTL and to prevent trapped charges from back tunneling to substrate

Blocking oxide (BO) – isolates trapped charge from the gate

Up-to-now CT stack used ONO stack, i.e. Si_3N_4 as CTL and SiO_2 as TO and BO

<u>High-k dielectrics (HfO_2 – based) very promising as CTL:</u>

- high-k dielectrics are trap-rich materials;
- HfO_2 has better charge trapping ability
- HfO_2 – based dielectrics have been already adopted in CMOS technology;
- There is a large room to modify and change the density, spatial and energy location of traps by changing process parameters, applying different annealing steps, doping/mixing with other elements, etc.

Purpose of the work

To investigate HfO_2/Al_2O_3-based stacks deposited by atomic layer deposition (ALD) from the view point of their application in CT- flash memories. The charge trapping, retention and endurance characteristics of the structures are studied in dependence on:

- stack composition;
- annealing process;
- material and thickness of tunnel oxide.

Technology of charge trapping stack

- Metal electrode / blocking oxide (BO)/ high-k dielectric (CTL)/ tunnel oxide (TO) / semiconductor (p-Si) (MOHOS) structures

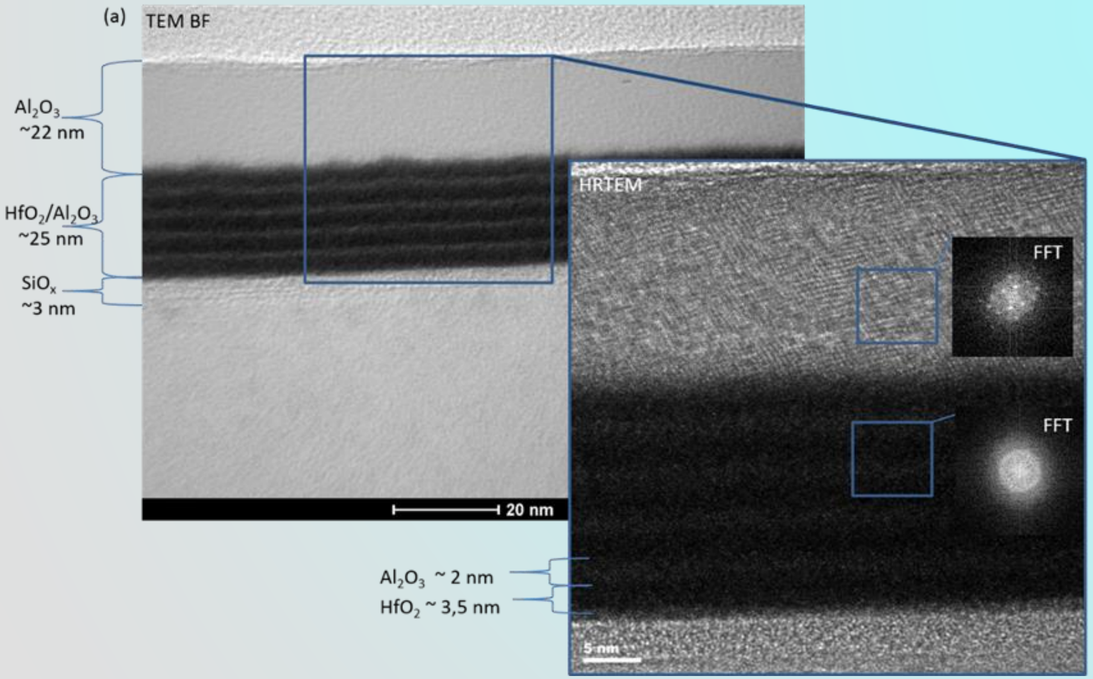
CTL - Al_2O_3/HfO_2 nanolaminated dielectric structures,

- atomic layer deposition (ALD); T_{dep} = 135° C; HfO_2 precursor- tetrakis (dimethylamido) hafnium (TDMA), and trimethylaluminum (TMA) - Al_2O_3 precursor; H_2O was used as an oxidant

Tunnel oxide - SiO_2 thermal oxidation; or Al_2O_3 – by ALD;

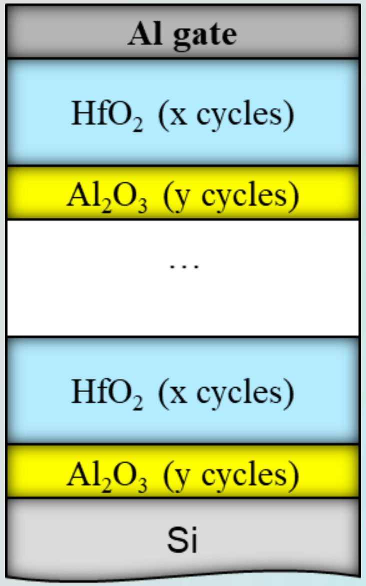
Blocking oxide - 20 nm Al_2O_3 – by ALD

- Rapid thermal annealing (RTA) in O_2, 800° C, 1 min
- Al electrodes



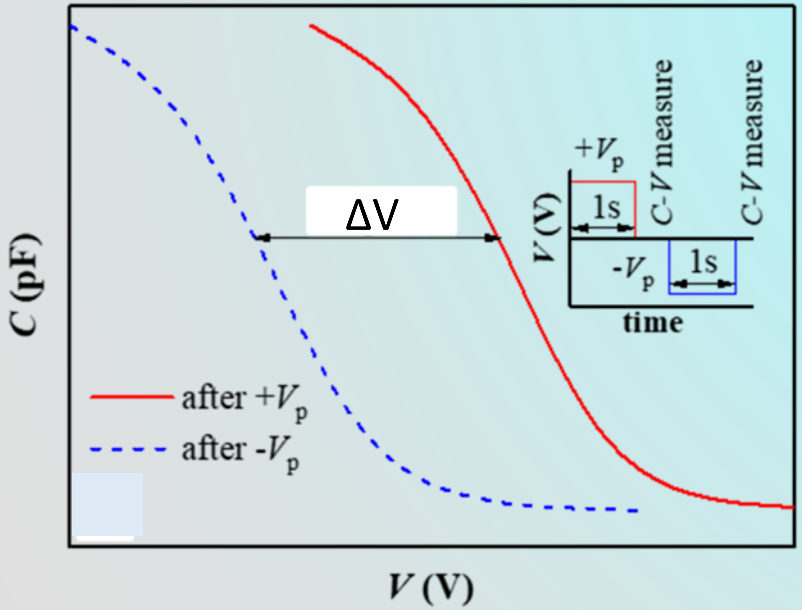
TEM cross-section:
20 nm Al_2O_3 / 5x(20:5) Al_2O_3/HfO_2 CTL / 3.5 nm SiO_2/ Si

Charge trapping layer



CTL : n x (HfO_2 (x cycles):Al_2O_3 (y cycles)):
Al_2O_3/HfO_2 nanolaminated dielectric structures
x=20÷30 (HfO_2 ALD deposition cycles); grc=0.14 nm
y=2÷30 (Al_2O_3 ALD deposition cycles); grc=0.1 nm
n=5÷10 (repetitions of bi-layer)

Without TO and BO

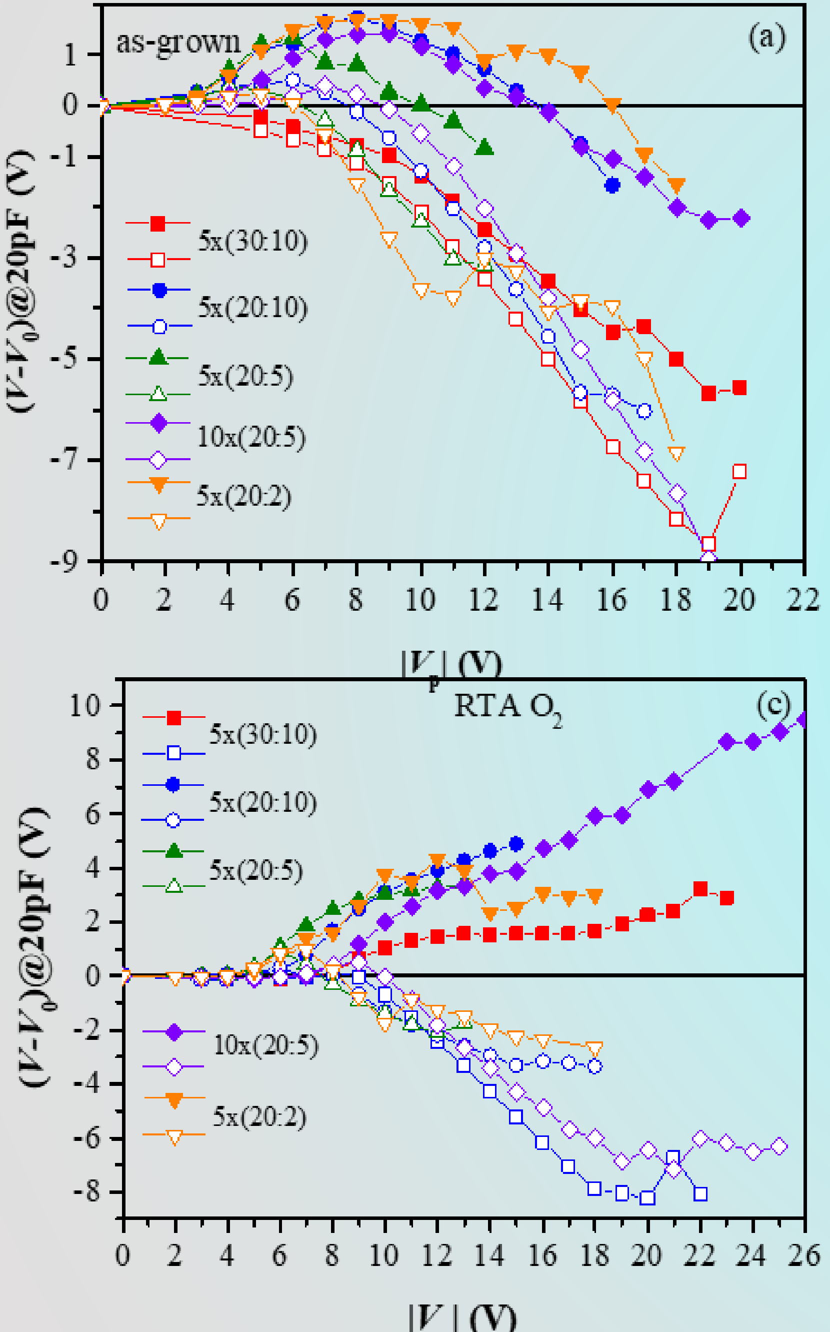


Measurement of memory window

applying square negative and positive voltage pulses of different amplitudes V_p and duration of 1 s

- memory window ΔV - the difference between the voltage shifts corresponding to the negative and positive pulses;
- Retention characteristics: monitoring the charge loss over time (change of ΔV_{fb}) after initial charging of the capacitors by applying a voltage pulse Vp;
- Endurance characteristics: monitoring of ΔV_{fb} change during the multiple P/E cycles

Memory window in dependence on CTL composition and annealing



memory window is strongly affected by: annealing ambient, total thickness and Al_2O_3 content in the films.

As-deposited stacks:

- strong h^+ trapping at - V_p; e^- trapping only at relatively low $+V_p$ – two competing processes - e^- trapping at existent traps and stress generation of positive charge; the latter outweighs e^- trapping at higher V_p; as-deposited samples are very susceptible to high field stress

- the largest h^+ trapping - for samples with the thickest HfO_2; h^+ trapping is only slightly affected by Al_2O_3 amount in the films

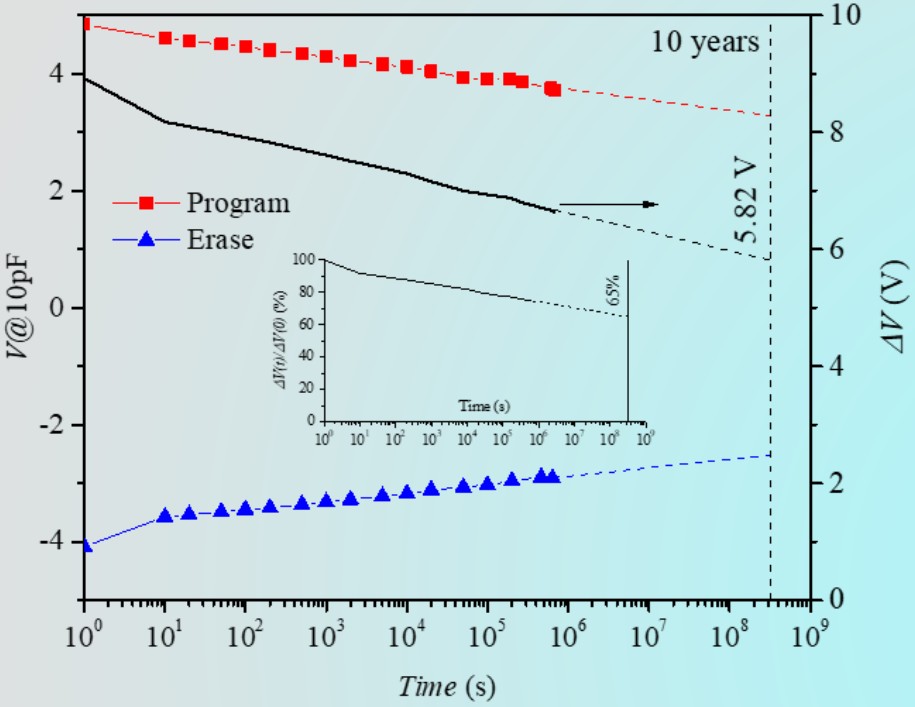
after O_2 annealing:

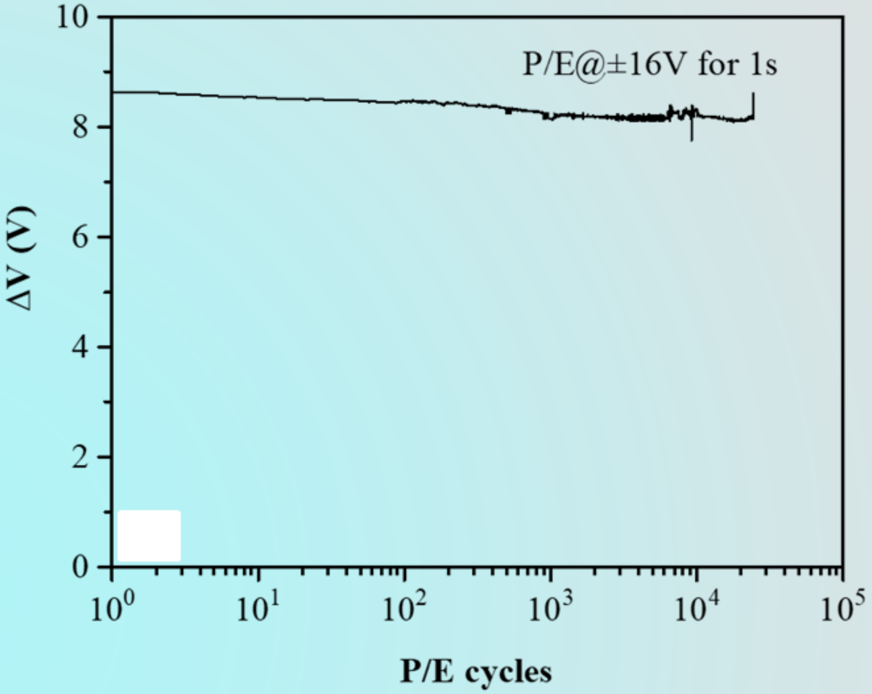
- positive charge trapping for all samples after O_2 annealing is weaker and tends to saturate

- stable e^- trapping which increases with increasing $+V_p$

- PDA in O_2 enhances the charge storage ability of the stacks and anneals defects in HfO_2 which are precursors of stress-induced positive charge.
  - O_2 annealing creates electron traps which give rise to increased memory window.
  - Negative charge traps originate form Al and the positive charge traps are rather associated to the HfO_2

Retention and endurance characteristics

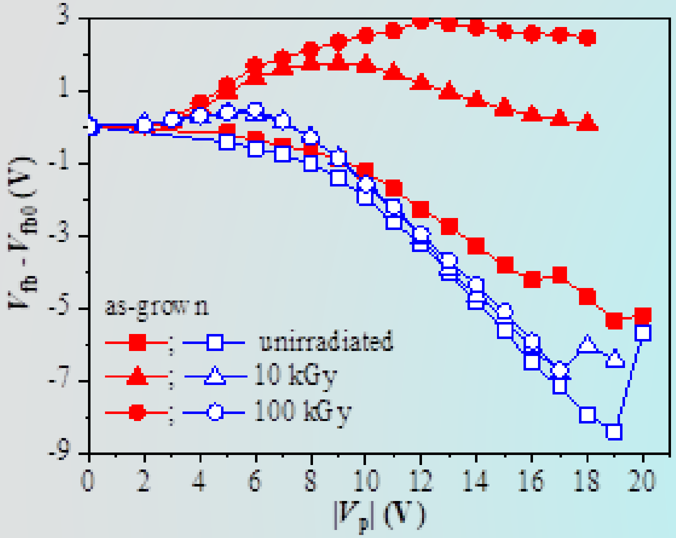


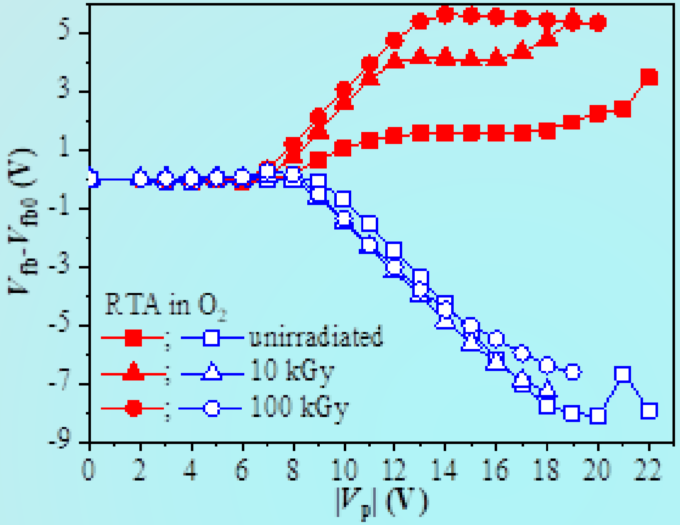


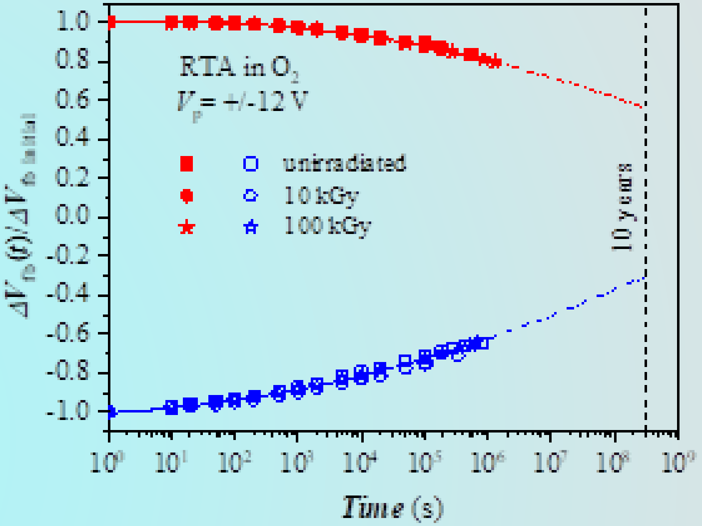
- 65% of the charge initially accumulated in the nanolaminated dielectric remains after 10 years;
- the low rate of release of the charge stored in the layer suggests the capture in deep traps.
- After $2.5x10^4$ write/erase (P/E) cycles, a ~ 6% reduction in the memory window was recorded.

Radiation hardness

HfO_2/Al_2O_3 5x(30:10); γ-radiation (^{60}Co) 10 and 100 kGy



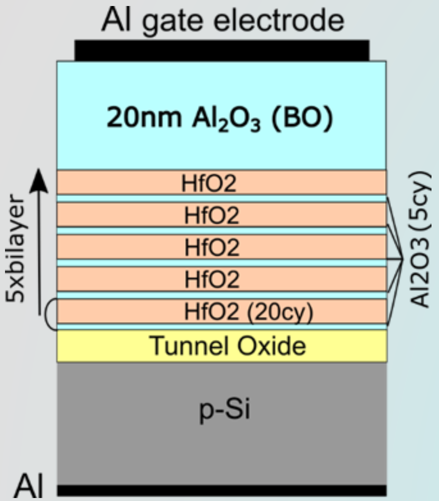


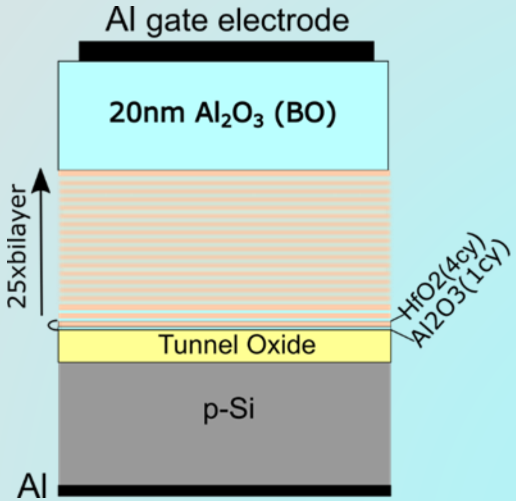


- The positive charge trapping is almost unaffected by irradiation for the as-grown and oxygen treated samples;
- γ-radiation boosts significantly electron trapping in both the O_2 annealed stacks and the stacks without PDA
- γ-radiation does not deteriorate the charge retention in oxygen treated stacks

The results clearly demonstrate that ALD Al_2O_3/HfO_2 nanolaminated stacks have good radiation tolerance to γ-rays up to very high doses of 100 kGy and can be successfully used in CTM devices working in radiation-intensive environment.

Charge trapping stack - tunneling and blocking oxides



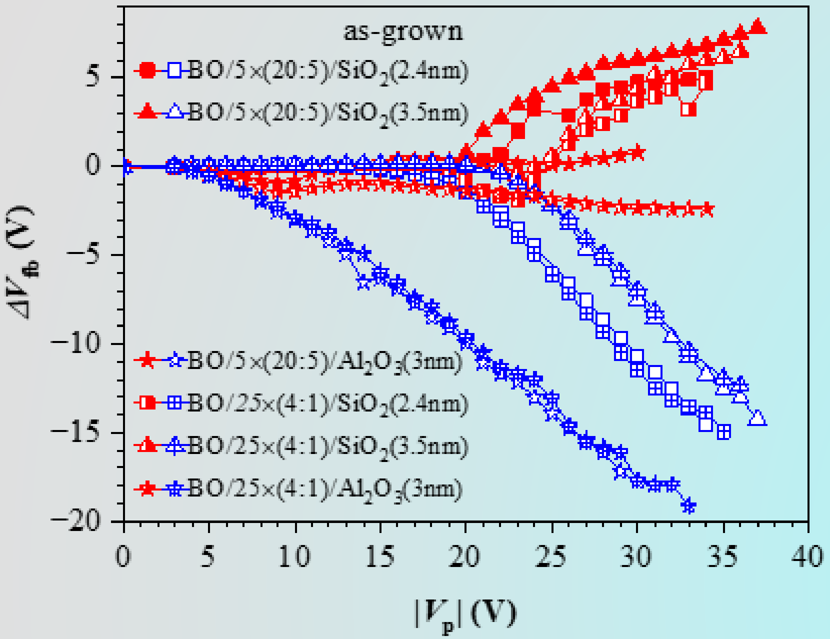


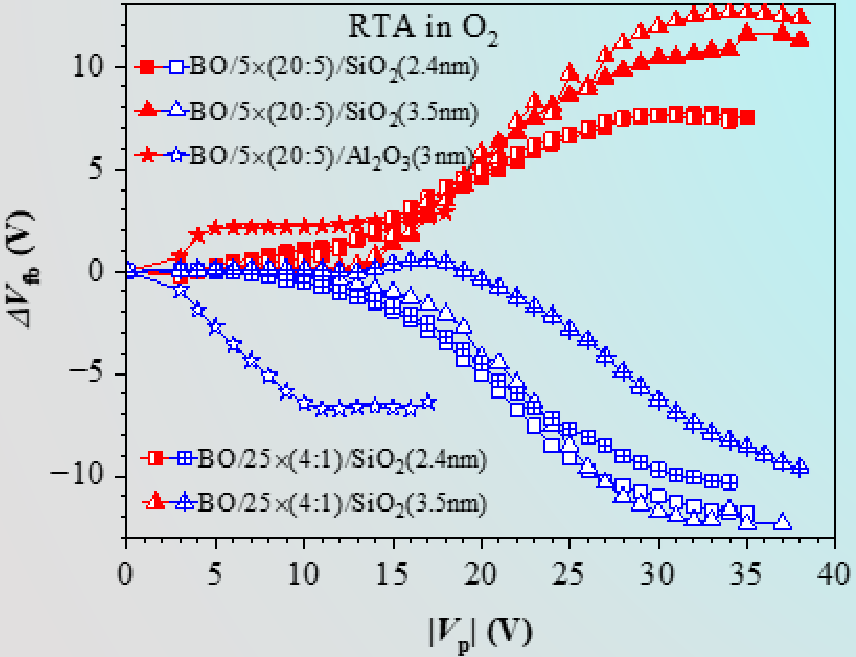
TO: SiO_2 - 2.4 or 3.5 nm
Al_2O_3 – 3 nm deposited by ALD

CTL: HfO_2 :Al_2O_3 5x(20:5) (laminated stack)
25x(4:1) (doped stack)

BO: Al_2O_3 -20 nm deposited by ALD

Memory window in dependence on tunnel oxide and annealing





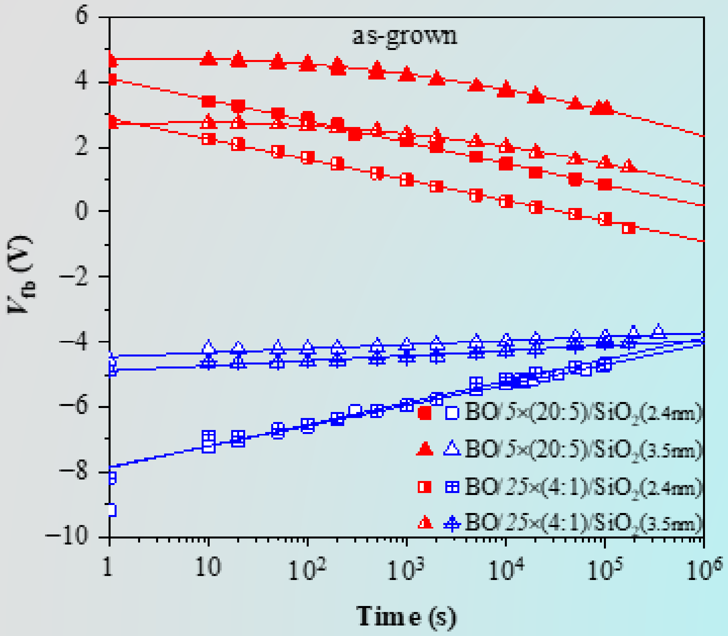
As-deposited stacks:

- significant e^- trapping; hence memory window is formed (unlike stacks without TO and BO)
- positive charge trapping depends on the tunnel oxide (and its thickness) and is weakly affected by the dielectric stack;
- the capture of electrons depends on the dielectric - it is stronger in the nanolaminated structures;
- in structures with Al_2O_3 TO, regardless of the dielectric layer, e^- trapping is very weak, which makes them unsuitable as a memory cell in CTM

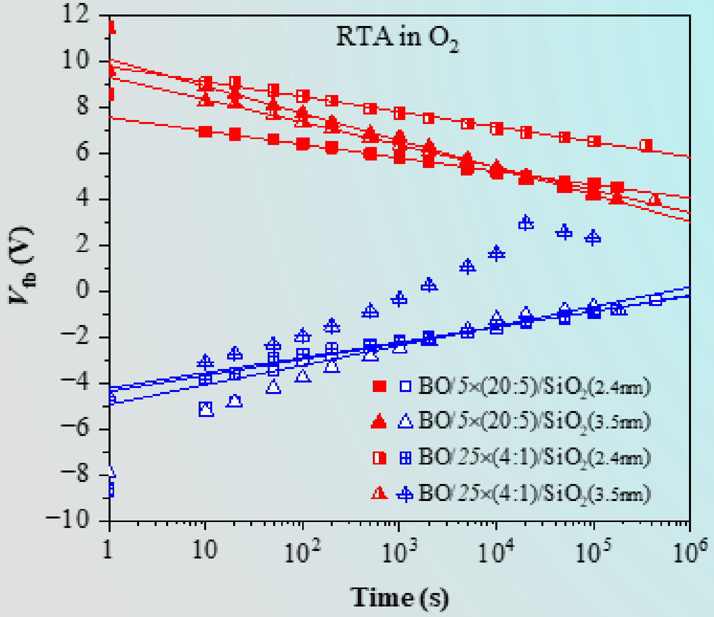
After O_2 annealing

- the trapping of electrons in all studied structures increases significantly (similar to stacks without any TO and BO
- the positive charge trapping decreases and exhibits a saturation at a higher V_p (similar to stacks without any TO and BO)
- hole trapping is stronger in nanolaminated structures;
- e^- trapping stronger in stacks with thicker SiO_2 TO.

Retention characteristics



- the h$^+$ retention depends on the TO thickness and is independent of the dielectric stack;
- the discharge of h$^+$ - linear law - trap-to-band tunneling mechanism;
- the discharge rate of h$^+$ is higher for stacks with thinner SiO$_2$;
- 3.5 nm SiO$_2$ provides a good barrier to back-tunneling of holes;
- the e$^-$ detrapping follows different laws for the samples with 2.4 and 3.5 nm SiO$_2$ – linear for 2.4nm and ln^2(t) for 3.5 nm - e$^-$ detrapping via the Poole–Frenkel mechanism ;
- electron traps in the two kinds of stacks have the same origin, but their density is higher in multilayered 5x(20:5) stacks



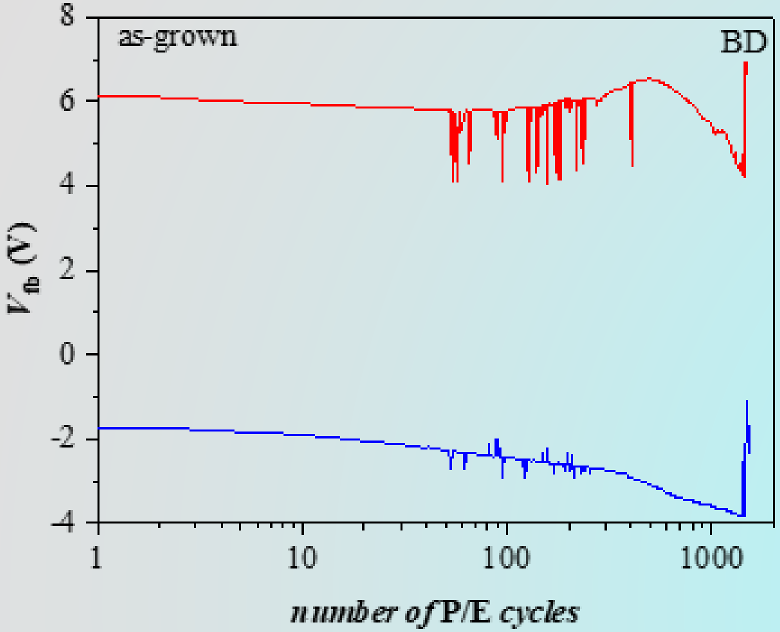
after RTA in O$_2$

significant changes in the discharge characteristics and their dependence on the parameters of the structure (thickness of TO and the type of dielectric stack)

- RTA in O$_2$ changes the density of the trapped charge, but does not alter their discharge mechanism in stacks with 2.4 nm SiO$_2$
- the e$^-$ discharge rate is higher in structures with a thicker 3.5 nm SiO$_2$ compared to stacks with thinner 2.4 nm TO and slightly depends on the dielectric stack
- The discharge rate of h$^+$ is also higher after RTA and for thicker TO

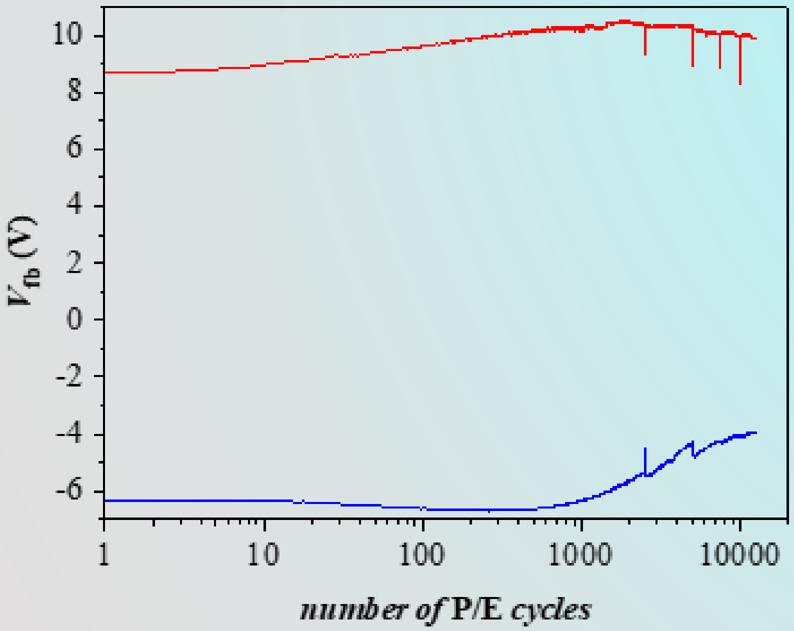
RTA in O$_2$ generates defects (due to interaction between the CTL and TO), which cause faster discharge of the stored charge.

Endurance characteristics



HfO_2/Al_2O_3 stacks with 3.5 nm SiO_2 TO; pulse voltage Vp = ±25V

Before annealing - instabilities, especially in e^- trapping, which recover
After about 600 P/E cycles - substantial degradation -
progressive accumulation of positive charge generated by the high electric field – the structures before RTA are very vulnerable to high electric field stress.



after RTA in O_2

- better endurance
- can withstand more than 10^4 P/E cycles without coming to BD

Conclusions

The charge trapping and storage in the CT-NVM structures with HfO_2/Al_2O_3-based CTL depend strongly on the stack parameters (composition of CTL; type of tunneling oxide; thickness) as well as on annealing steps:

- RTA in O_2 strongly increases e^- trapping in the stacks and improves their high electric field vulnerability;
- e^- trapping occurs in Al_2O_3 – related traps;
- h^+ traps are related to HfO_2;
- the retention of both e^- and h^+ is most strongly affected by the tunneling oxide and its thickness;
- RTA in O_2 improves endurance characteristics of the stacks (due to improved high electric field susceptibility), however it deteriorates the retention of stored charges (due to defect generation in the tunneling oxide as a result of the interfacial reaction);
- charge trapping and storage in HfO_2/Al_2O_3-based CTL are not deteriorated by γ-radiation, hence these structures are very promising for operation in radiation intensive environment.