# ALD GeAsSeTe ovonic threshold switch for 3D stackable crosspoint memory

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# outline

# introduction

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In the heart of the Silicon Valley from 2004 Intermolecular develops workflows that physically & electrically characterize thin films and film stack for the material innovation in memory, logic, ferroelectrics and quantum computing fields. From Sep ’19 we are proud to be part of Merck KGaA, Darmstadt, Germany. During last years we are pioneering

# ALD chalcogenides

# where is the memory industry with 3D crosspoint technology?

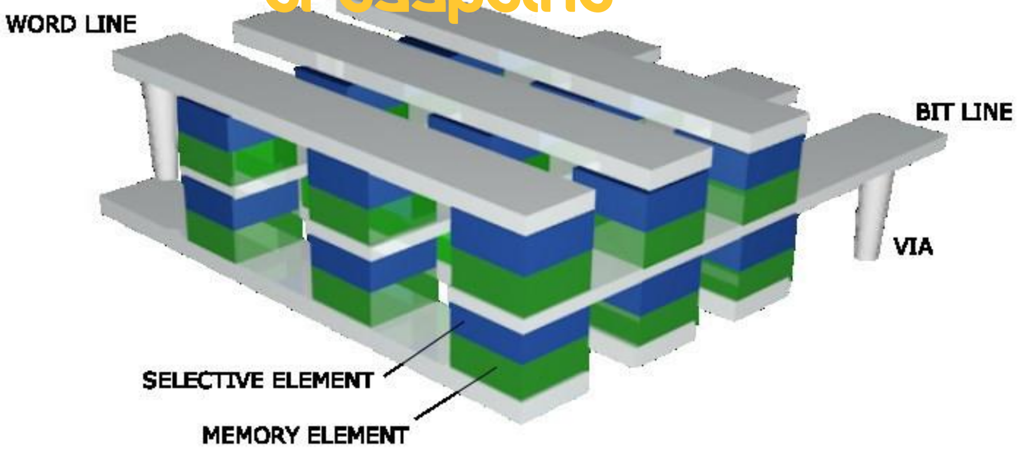

In 2017 Intel released the first product of Optane™ series


Micron announced in 2019 first product

Semiconductor industry is spending huge amount of resources in R&D to fill the gap between DRAM and NAND and in the next years we will have more companies in this market

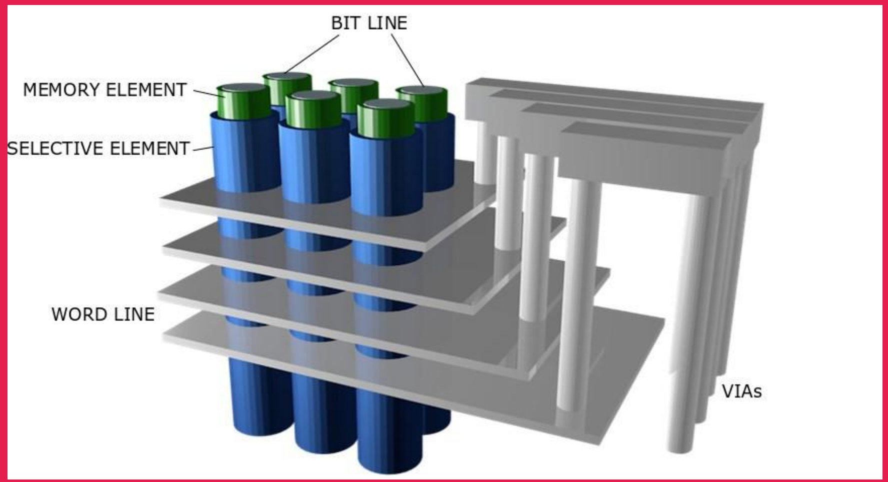
# Why do we need ALD chalcogenides?

## PVD 3D crosspoint crosspoint



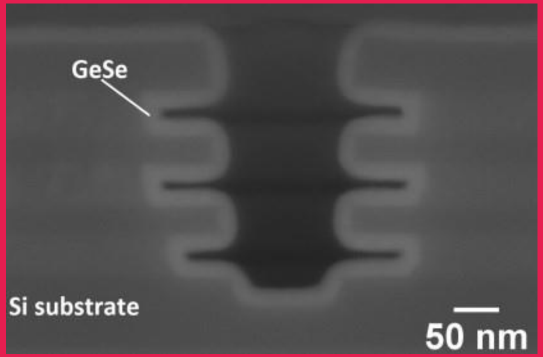

PVD process limits film conformality and homogeneity on a large scale precluding the integration of tens of decks in a 3D crosspoint architecture

## ALD vertical 3D

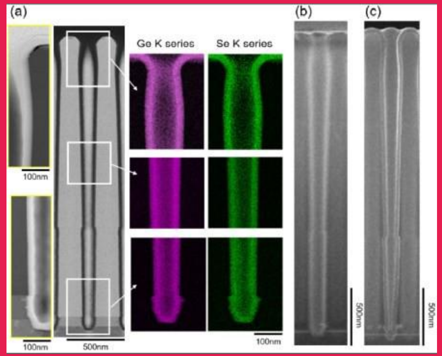



ALD process allows for future 3D vertical integration with higher density and reduced cost paving the way for expansion of 3D crosspoint market

# ALD chalcogenides OTS state of art

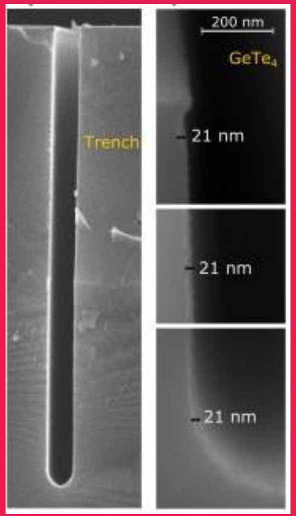



CVD GeSe, IMEC-ASM, ALD 2019 Conference

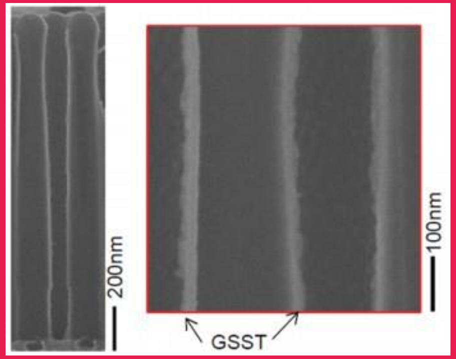



ALD $Ge_xSe_{1-x}$, Seoul University, ACS Appl. Mat. Interfaces Apr.2020

- In recent years, several research institutes and universities have tried to developed ALD OTS films, but electrical performances in terms of leakage and endurance similar to PVD OTS haven't been demonstrated yet
- **Intermolecular, <u>for the first time</u>, has developed a quaternary ALD OTS GeAsSeTe film with electrical performances similar or better compared with PVD OTS references in literature**




ALD $GeTe_4$ Intermolecular ACS Nano, Sept. 2019




ALD GeSbSeTe, Seoul University, J. Mater. Chem. C, Sept. 2019

# physical characterization of GeAsSeTe ALD film

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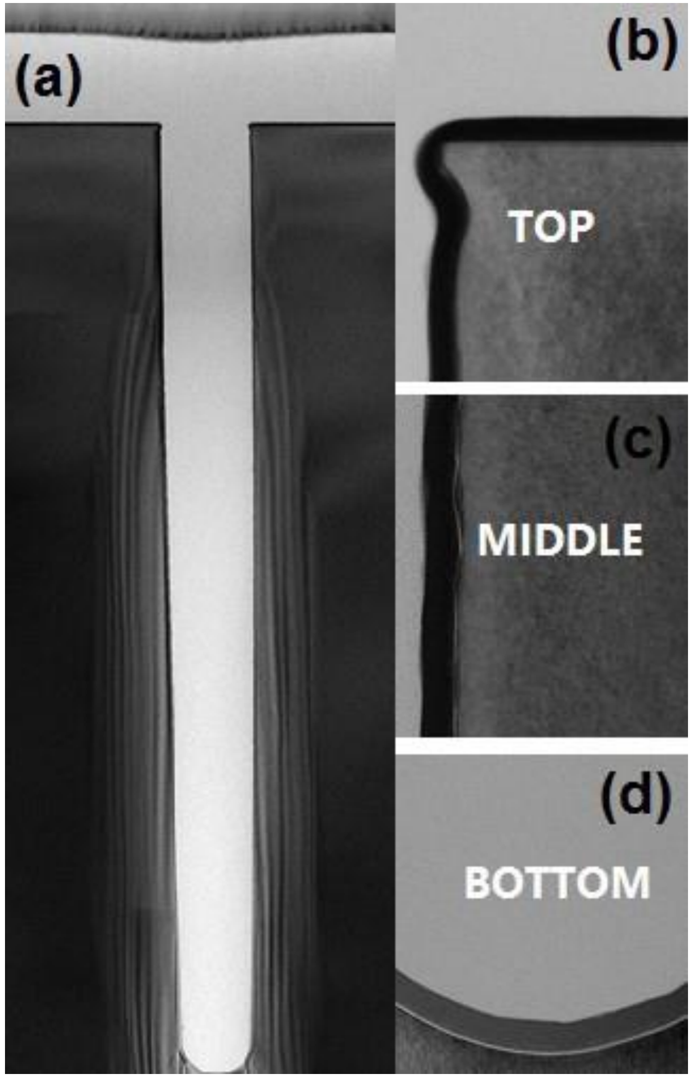
# Conformality and uniformity of ALD GeAsSeTe film

## TEM image of silicon trench structure with high aspect ratio (20:1)

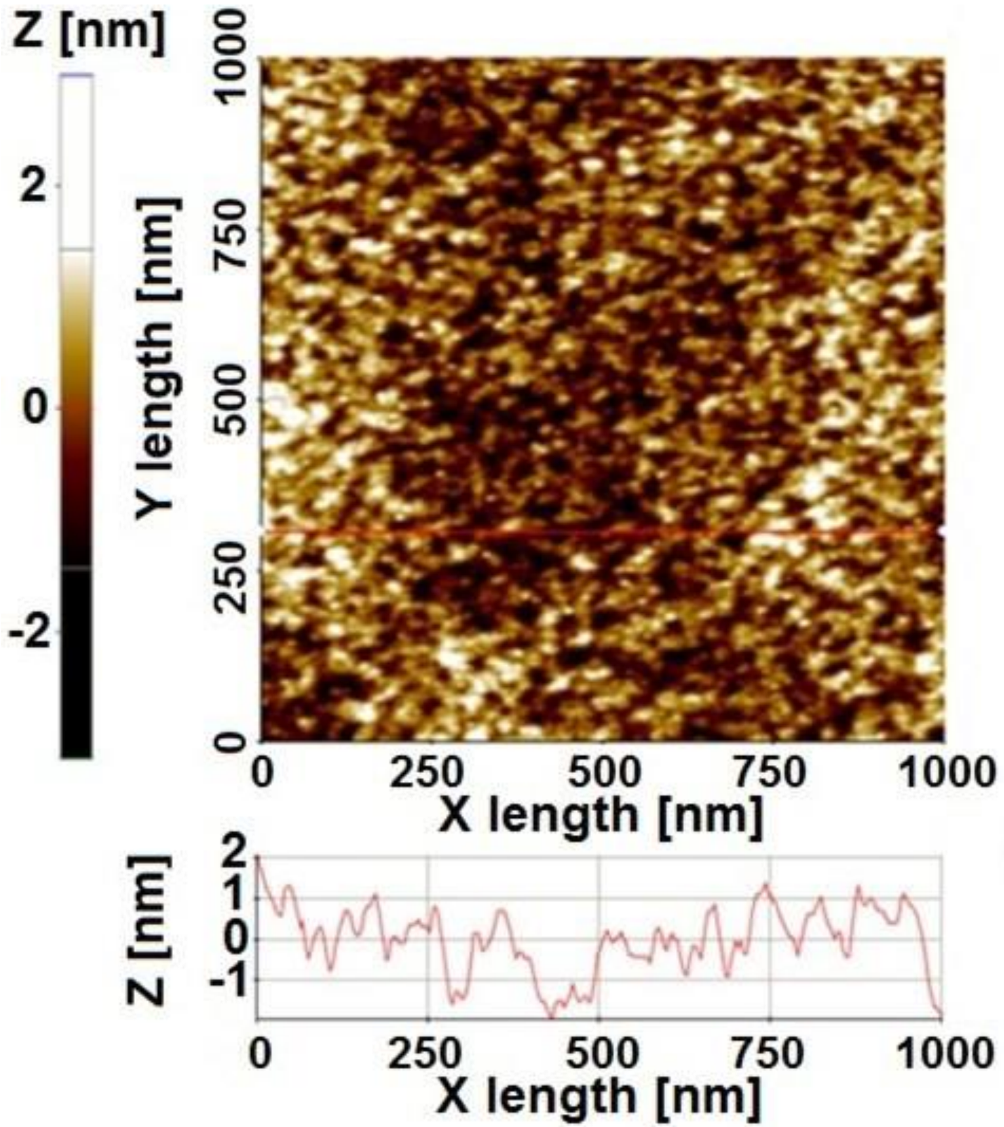
- TEM image demonstrates conformal coverage of a silicon trench (aspect ratio 20:1) with 10 nm thick GeAsSeTe film. By increasing the magnification of the TEM image we can clearly see that same chalcogenide film exhibits the same thickness along all the trench depth
- The composition analysis using previously calibrated X-ray fluorescence (XRF) defined the stoichiometry of the film as $Ge_{23}As_{38}Se_{15}Te_{24}$
- The introduction of Se in the composition increases the $E_G$ of the material increasing consequently its resistivity and the high content of As allows for higher thermal stability preventing the crystallization of the film at high temperatures



# Surface morphology of ALD $Ge_{23}As_{38}Se_{15}Te_{24}$ film

## **Atomic Force Microscopy study**

- The surface morphology was characterized by atomic force microscopy (AFM) to estimate the roughness and the quality of the ALD film used for the integration of the OTS device
- The surface profile along X-axis shows that the root mean square (RMS) of the roughness is well below 1 nm, confirming the high quality of our ALD film.





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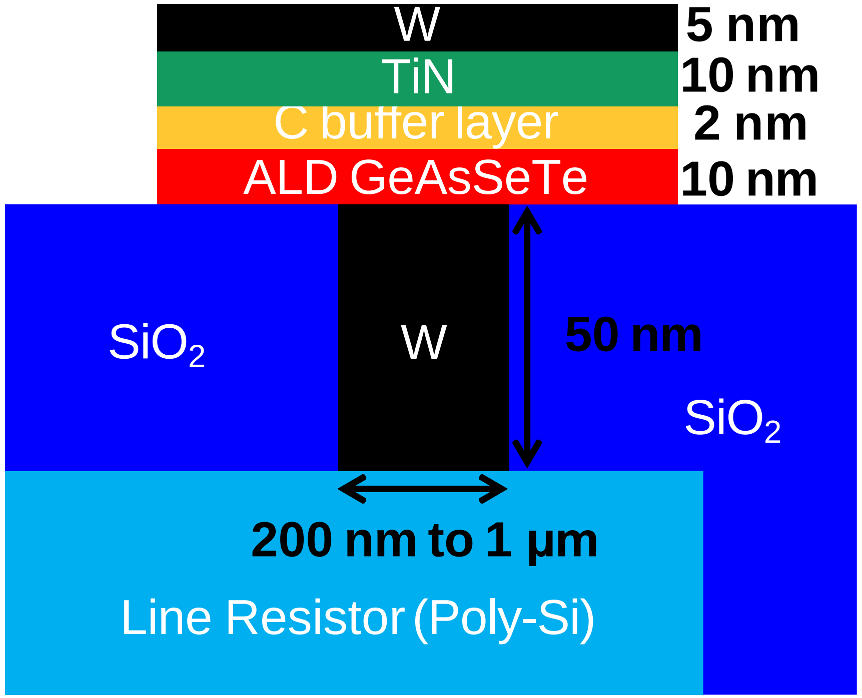
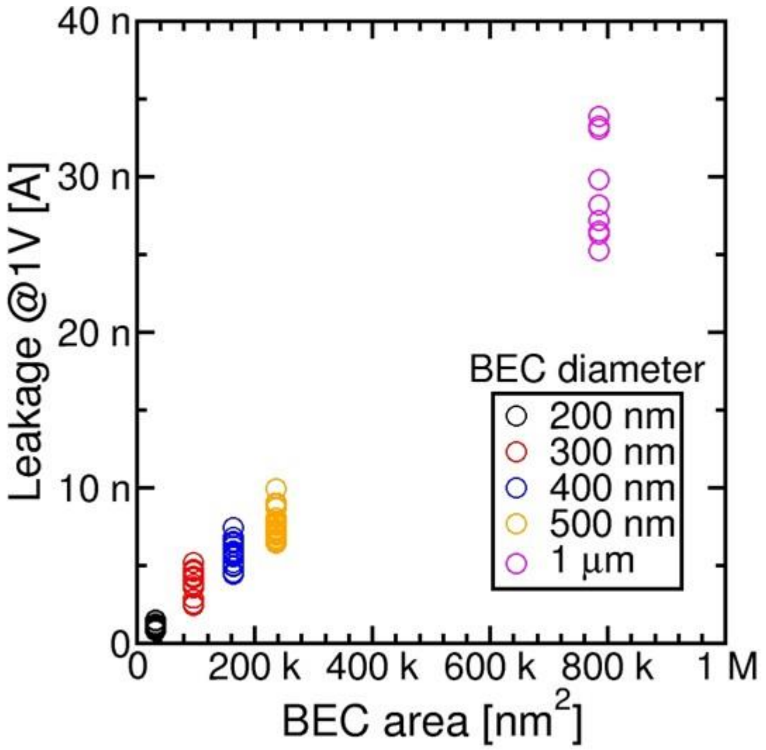
# Device integration and OTS device performance

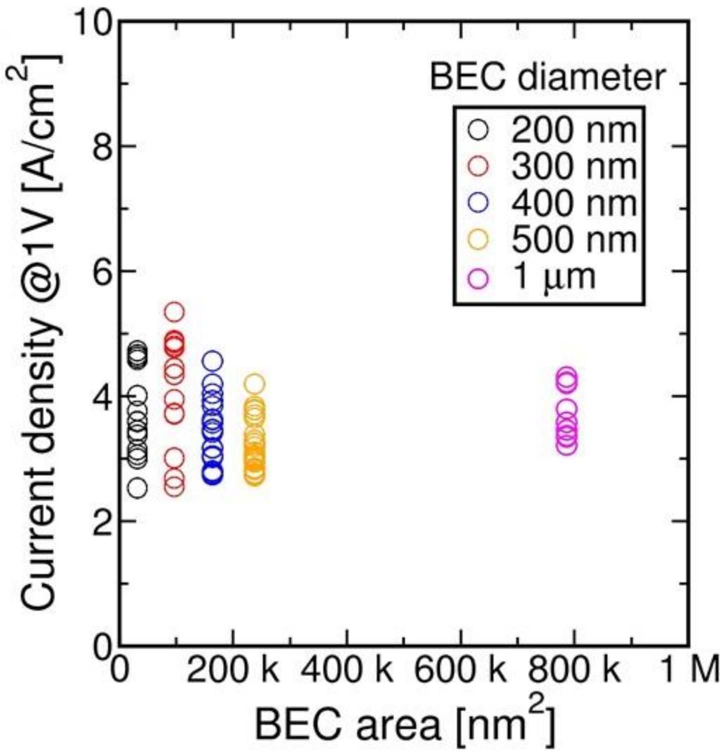
# OTS device integration
## ALD $Ge_{23}As_{38}Se_{15}Te_{24}$ integration on test vehicle

1. Preclean of substrate
2. Deposition of ALD film and PVD TEC stack
3. Photolithographic patterning of TEC
4. Etching and photoresist stripping



# OTS device performance
## Leakage scaling of as-deposited material



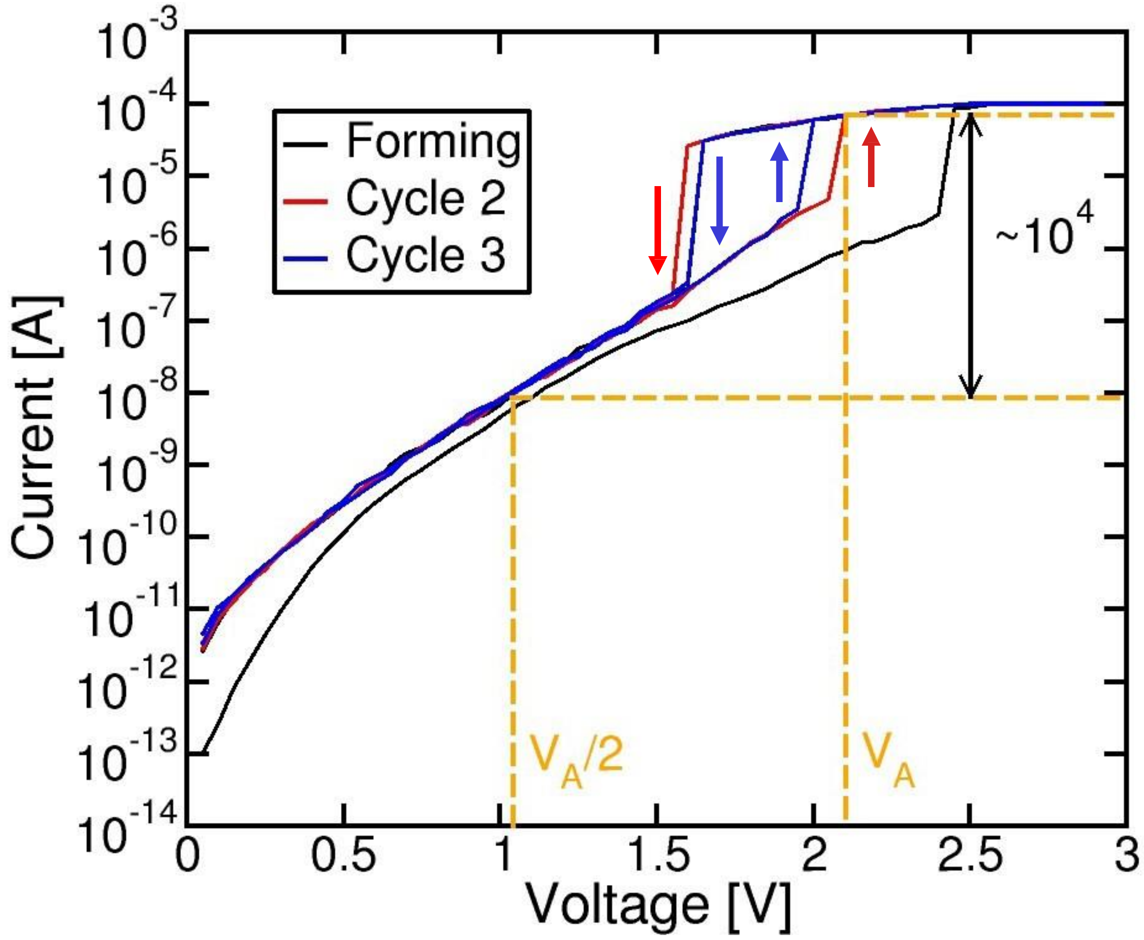




**The current measured on 80 devices scales with plug area since the as-deposited material demonstrates bulk conduction. The BEC area-normalized current density confirms the expected scaling**

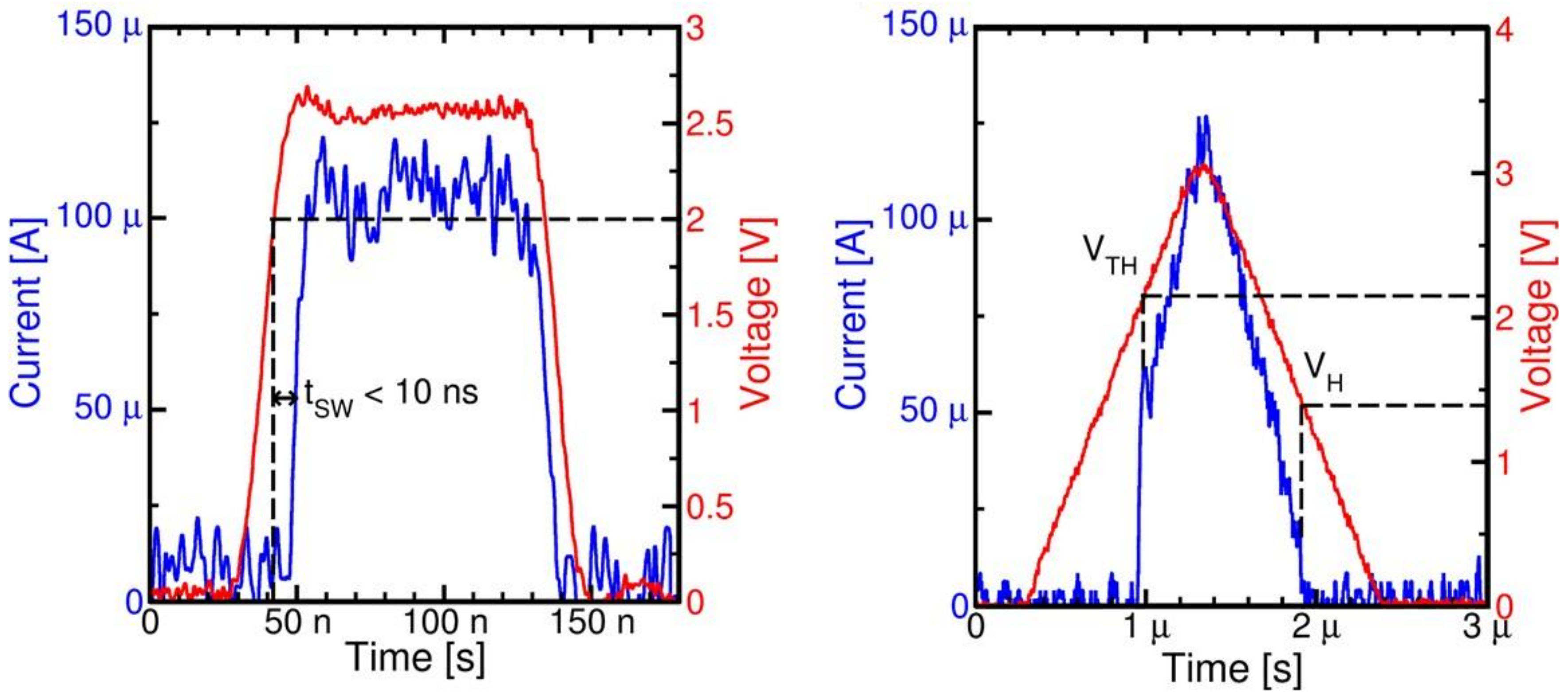
# OTS device performance

## DC-IV characteristics of ALD $Ge_{23}As_{38}Se_{15}Te_{24}$ OTS

- Demonstrated good switching in DC regime at 100 μA of ALD $Ge_{23}As_{38}Se_{15}Te_{24}$ device (200 nm BEL diameter)
- The first cycle (forming operation) shows lower subthreshold leakage and higher Vth as expected. The device shows repeatable IV characteristics after forming and good stability under field stress during long DC operation
- Using the typical V/2 scheme of a crosspoint array, we can estimate the selectivity of the OTS choosing $V_A$ = 2.1V as reading voltage in the ON state and consequently $V_A/2$ in the OFF state reaching almost 4 orders of magnitude of current window



# Switching time and $V_{TH}$ and $V_H$ detection in pulsed regime

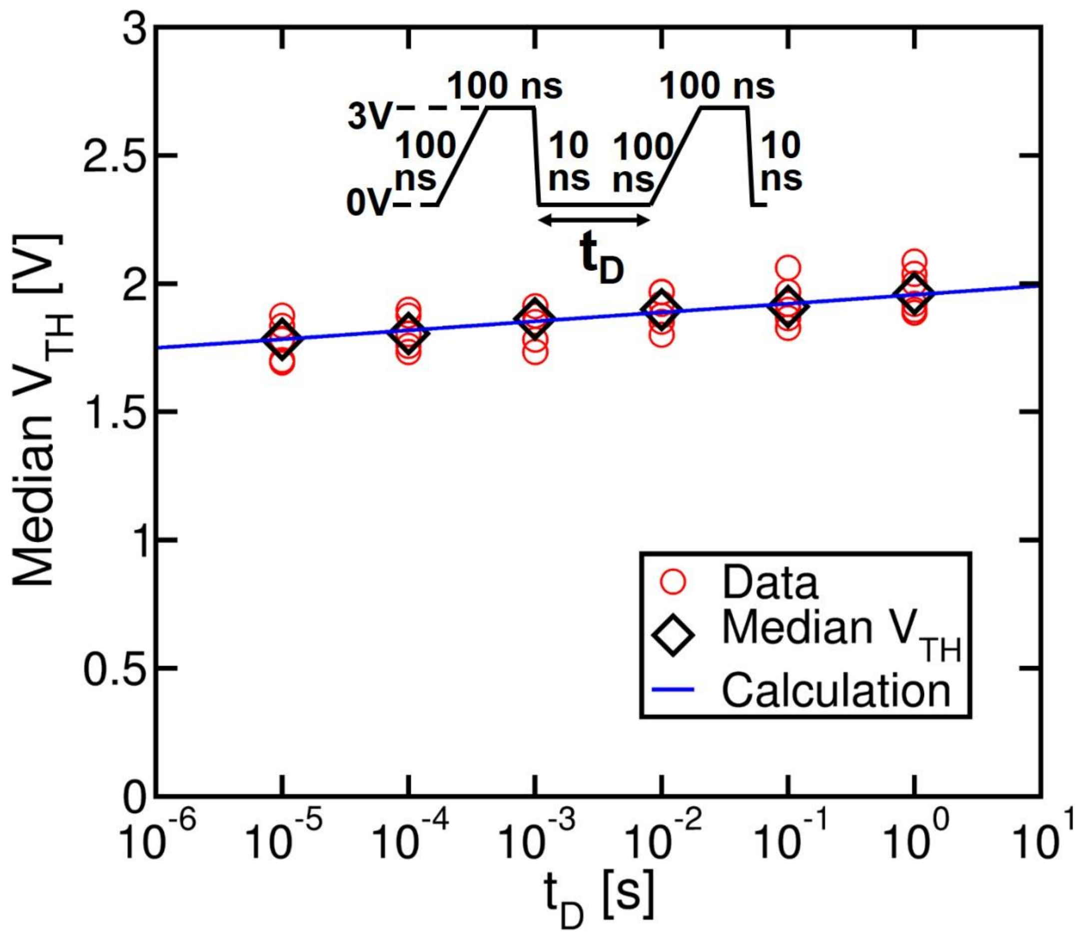



**Detected switching time faster than 10 ns applying trapezoidal pulse higher than $V_{TH}$ (width = 100 ns, rise/fall time ≈ 10 ns). Through triangular pulse (rise/fall time = 1 µs) clearly detected OTS switching with $V_{TH}$ ≈ 2.1 V and the switching off at $V_H$ ≈ 1.4 V.**

# OTS device performance

## $V_{TH}$ drift study on ALD $Ge_{23}As_{38}Se_{15}Te_{24}$ OTS

- As widely studied in the past, chalcogenide glasses tends to change electrical properties over time due to structural relaxation (SR), generally interpreted by thermally activated annihilation of disorder-induced defects
- Inset shows the scheme adopted for $V_{TH}$ drift measurement and corresponding results obtained from 6 devices with 200 nm BEL diameter.
- To reduce impact of the variability, we measured 10 times $V_{TH}$ at each delay time ($t_D$) after first switching in order to finally extract the median value for each device.
- Demonstrated $V_{TH}$ drift lower than 40 mV/dec

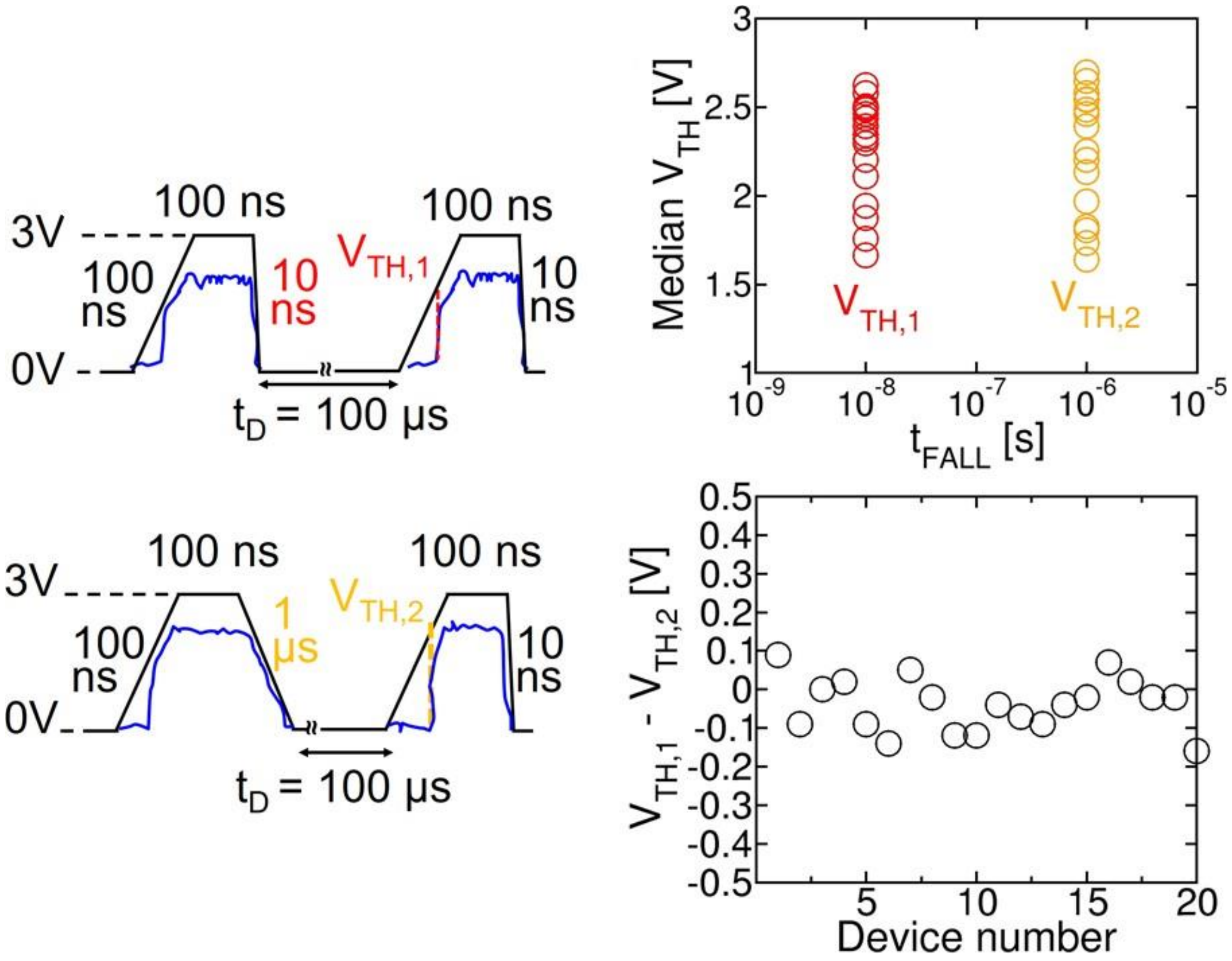


# OTS device performance

## $V_{TH}$ stability with different $t_{FALL}$

- To verify the potential use of the device in the 1S1R structure with PCM, we measured $V_{TH}$ after different fall time ($t_{FALL}$) in order to simulate slow quenching time typical of crystallization operation in PCM device and fixed $t_D$ = 100 μs was used to avoid $V_{TH}$ variability due to drift component.

- Test on 20 devices (200 nm BEL diameter) clearly display that the difference between $V_{TH,1}$ ($t_{FALL}$ = 10 ns) and $V_{TH,2}$ ($t_{FALL}$ = 1 μs) is lower than 0.1V suggesting that the OTS film developed is not prone to crystallization with slow quenching time.



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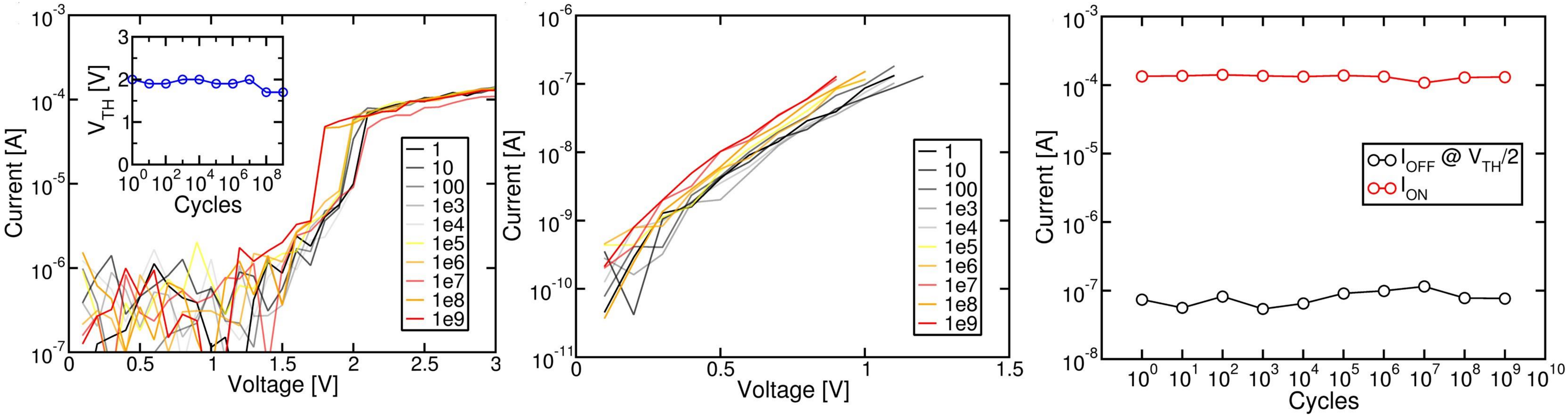
# OTS device performance
## Cycling Endurance of $10^9$ cycles




**Pulsed I-V curves as a function of cycles using 100 ns trapezoidal pulse shows very stable $V_{TH} \approx 2$ V during endurance with slight decrease only after $10^8$ cycles and stable subthreshold conduction. Current in the ON state @3V and in the OFF state @$V_{TH}/2$ shows stable selectivity higher than 3 orders of magnitude for at least $10^9$ cycles.**

# Modeling of GeAsSeTe ALD OTS subthreshold conduction

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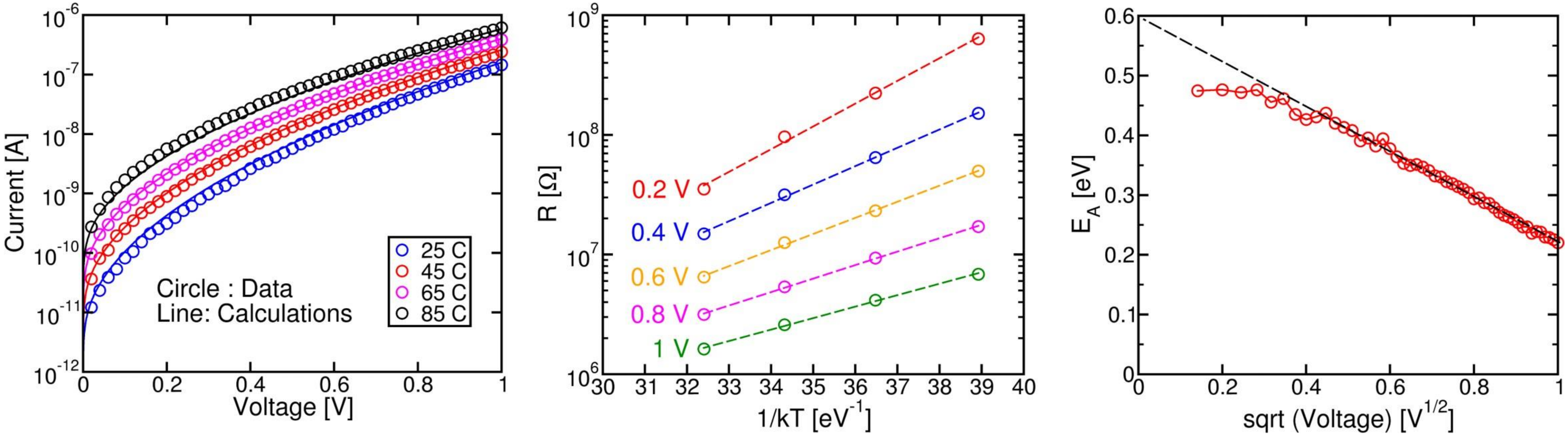
# Modeling of $Ge_{23}As_{38}Se_{15}Te_{24}$ OTS
## **IV characteristics at different T**




**Adopting the Poole-Frenkel (PF) conduction mechanism we were able to nicely reconstruct the IV curves at different T and PF barrier lowering with the following equation:**

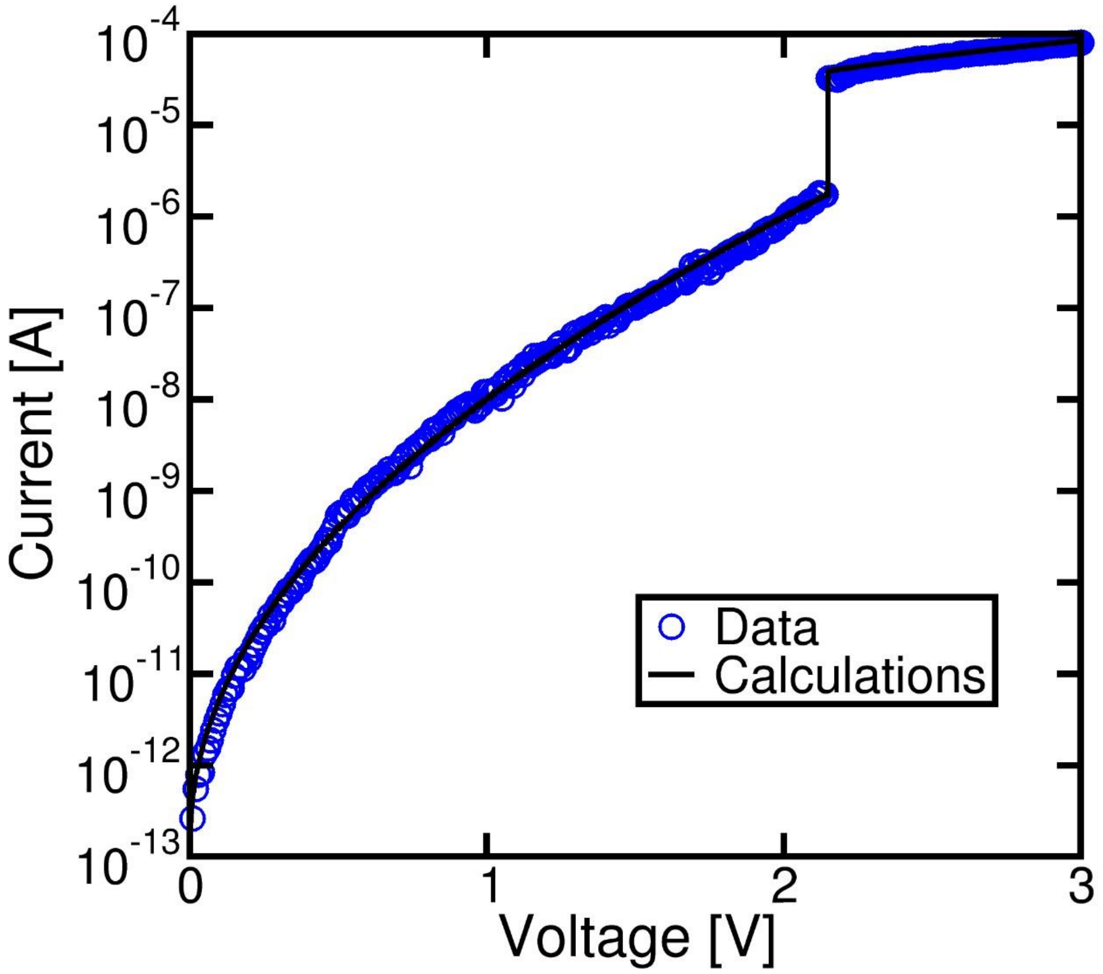
$$I = 2qNTA\ \frac{\Delta z}{\tau_0}\ exp^{\frac{-EA}{kT}}\ \sinh\left(\frac{q}{kT}\sqrt{\frac{qV}{\pi\varepsilon_r t_{OTS}}}\right)$$

$N_T = 3*10^{18}\ cm^{-3}$, $\Delta z = 11$ nm, $\tau_0 = 10^{-13}$ s, $E_A = 0.47$ eV, $\varepsilon_r = 7$, $t_{OTS} = 10$ nm


**Y. H. Shih et al., IEDM Tech. Dig., pp. 753-756, 2009.**
**D.Ielmini et al., J. Appl. Phys., vol.102, 054517, 2007.**

# Modeling of $Ge_{23}As_{38}Se_{15}Te_{24}$ OTS
## **Full DC-IV characteristic modeling**

- In order to verify the robustness of the model, we calculated full DC-IV characteristic adopting the same parameters and equation previously used
- Calculated IV is in good agreement with experimental data and the model could be used for future development of ALD OTS devices through fine tuning of film thickness and composition



# conclusions

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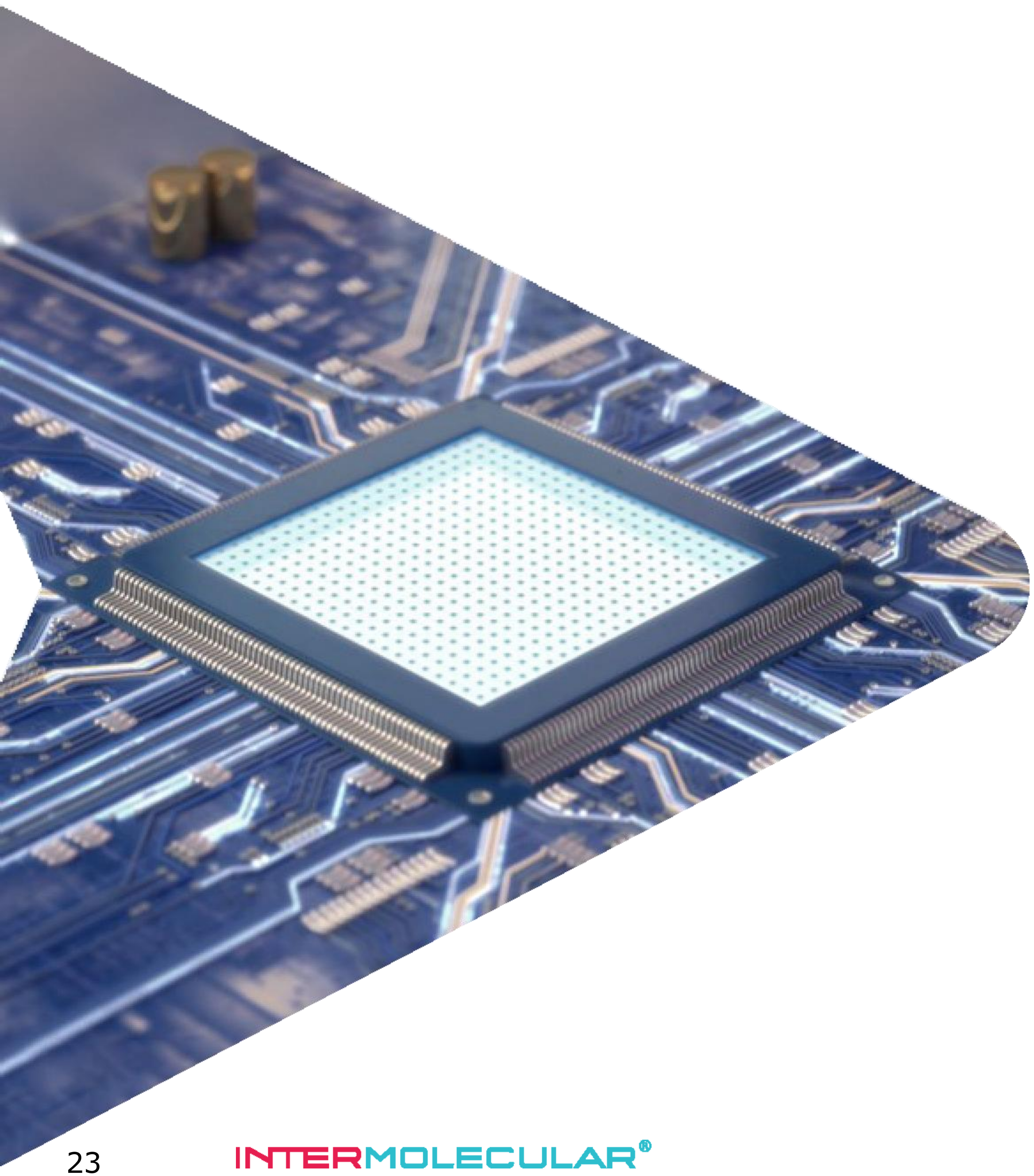

## Conclusions

- Integrated **for the first time** ALD quaternary GeAsSeTe OTS device
- Demonstrated high selectivity (**> $10^4$**), excellent endurance (**> $10^9$ cycles**), low $V_{TH}$ drift (**< 40 mV/dec**), fast switching (**< 10 ns**)
- Successfully proposed model for GeAsSeTe OTS subthreshold conduction for potential optimization of ALD film stoichiometry and thickness
- Future development of ALD chalcogenide films can definitely pave the way for the use of ALD chalcogenide-based selectors as leading technology for multiple stacks integration of crosspoint memory arrays

# thanks for the attention

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