Pulsed CVD/ALD of Amorphous GeSe for Application as OTS Selector

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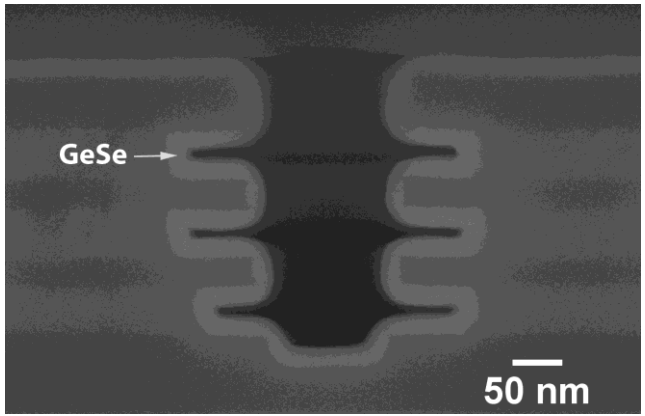
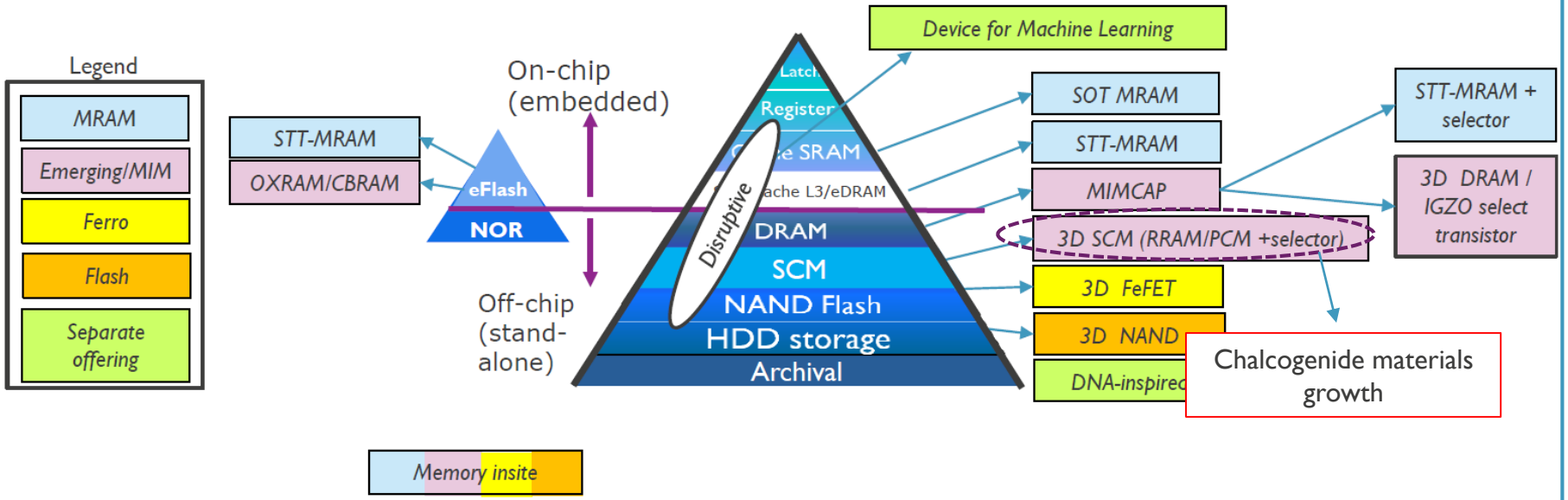


MEMORY AT IMEC: SUMMARY

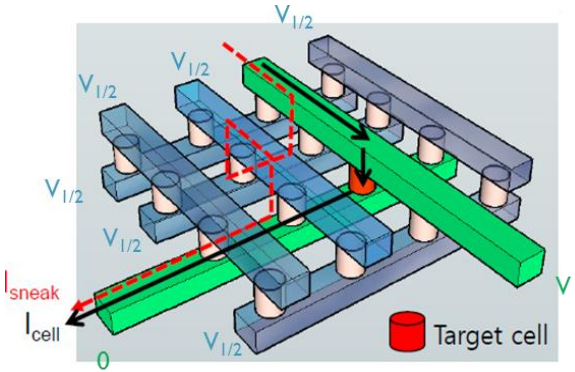


SELECTOR DEVICE

CROSSBAR MEMORY AND SELECTOR DEVICES

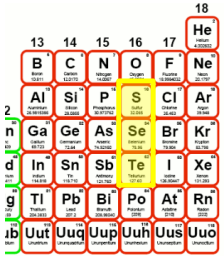
- Dense **memory** arrays – cross bar memory
- 2 – terminal memory devices → current sneak path problem

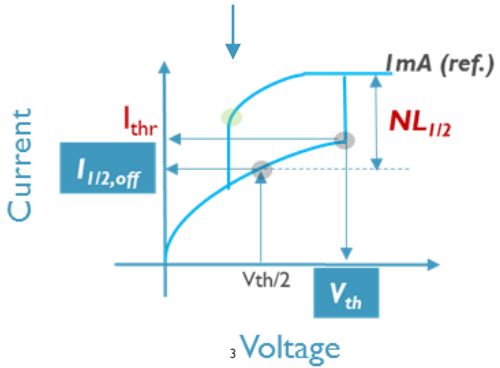
Current sneakpath problem



- Need for a **selector device** to select a specific memory cell
  - Threshold switch
    - Non conductive for $V<V_{th}$, conductive for $V>V_{th}$
    - **Amorphous Ge Chalcogenides** showing **Ovonic Threshold Switching** (OTS)

Materials containing S, **Se**, or Te





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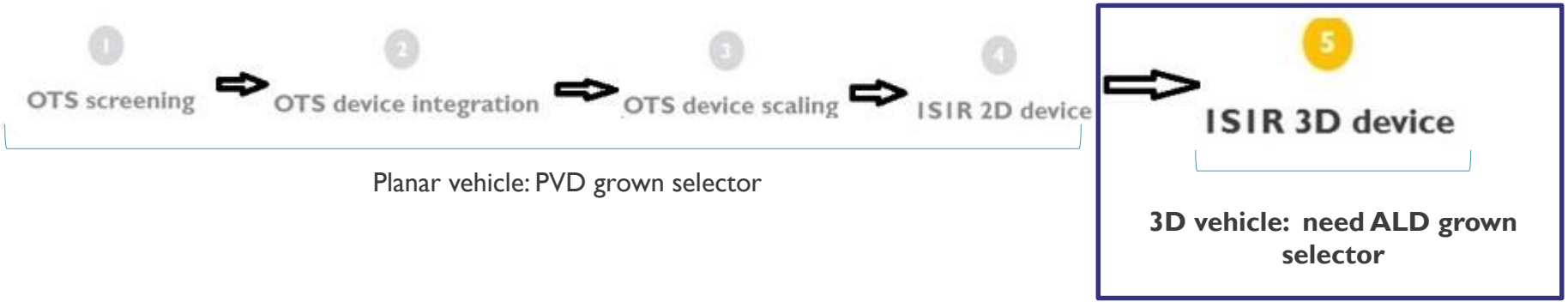
MOTIVATION TO GROW ALD GeSe



1. 3D conformality for selector
2. Amorphous phase, thermally stable throughout full processing cycle (up to 400 °C)
3. Uniform films (300 mm wafer), thickness (10-20 nm), and composition control

ALD OF GeTe BY UNI OF HELSINKI

$$MCl_x + x(Et_3Si)_2Te \longrightarrow MTe_x + xEt_3SiCl$$ ***Formation of alkylsilylchloride drives the reaction***

$$^{1}GeCl_2.stabilizer + ((C_2H_5)_3Si)_2Te \xrightarrow{90\ ^\circ C} GeTe + 2(C_2H_5)_3Si\ Cl + C_4H_8O_2$$

What we are trying at IMEC

Te ⟶ **Se**

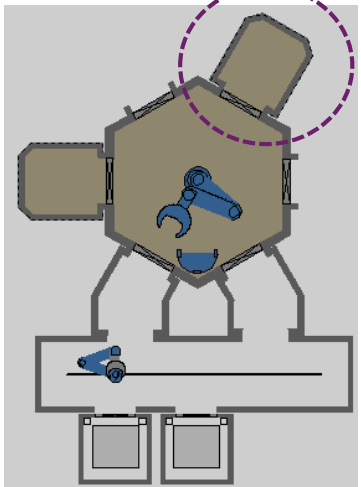
[1]ASMM and Univ. of Helsinki, V. Pore et al., JACS Comm 131, 3478, 2009

Experimental

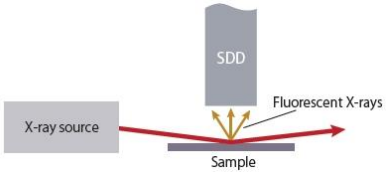
Ge precursors	Se precursors
Stabilized germanium dichloride. ($GeCl_2$.stabilizer)	Bis(trimethylsilyl)selenide $((CH_3)_3Si)_2Se$ $(TMS)_2Se$
	Bis(triethylsilyl)selenide $((C_2H_5)_3Si)_2Se$ $(TES)_2Se$

ASM POLYGON 2 Pulsar platform

ALD chalcogenides



1. Film growth in ASM Pulsar 300 mm cross flow reactor (various reactor conditions)
2. Total reflection X-ray fluorescence (TXRF) to study precursor chemisorption
   - Trace element analysis
   - Quantitative
   - Whole wafer (300 mm) analysis



3. Material characterization: SEM, TEM, ERD, EDX, XRR, Temp programmed XRD...

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OUTLINE

- Ge and Se precursor chemisorption studies by TXRF
- GPC trends with processing conditions
- GeSe properties

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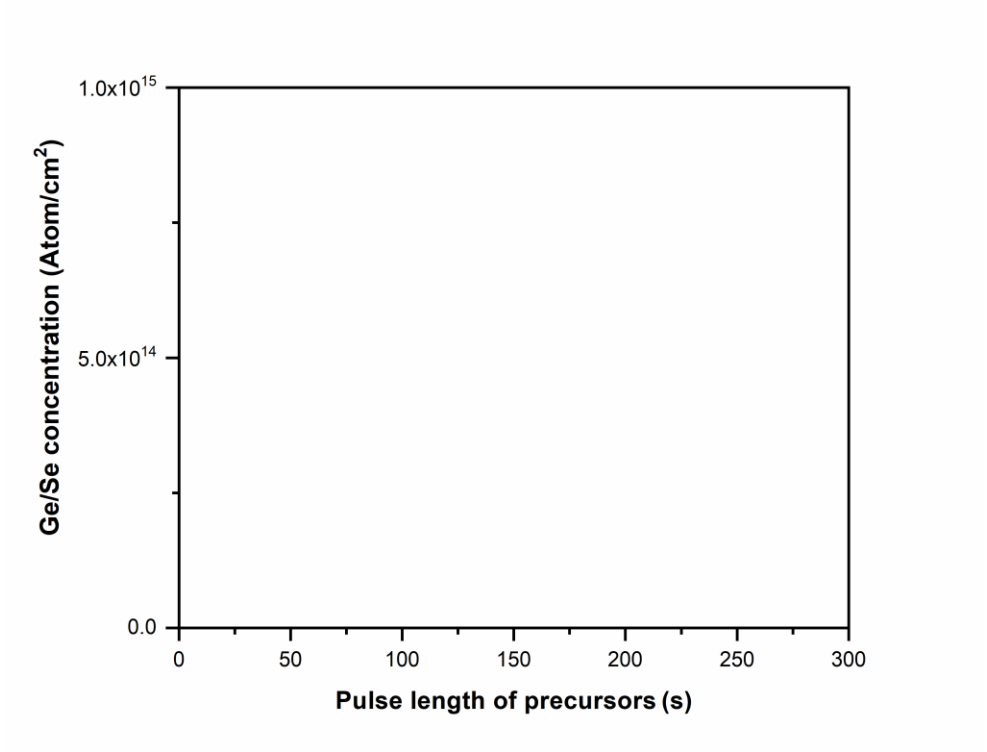
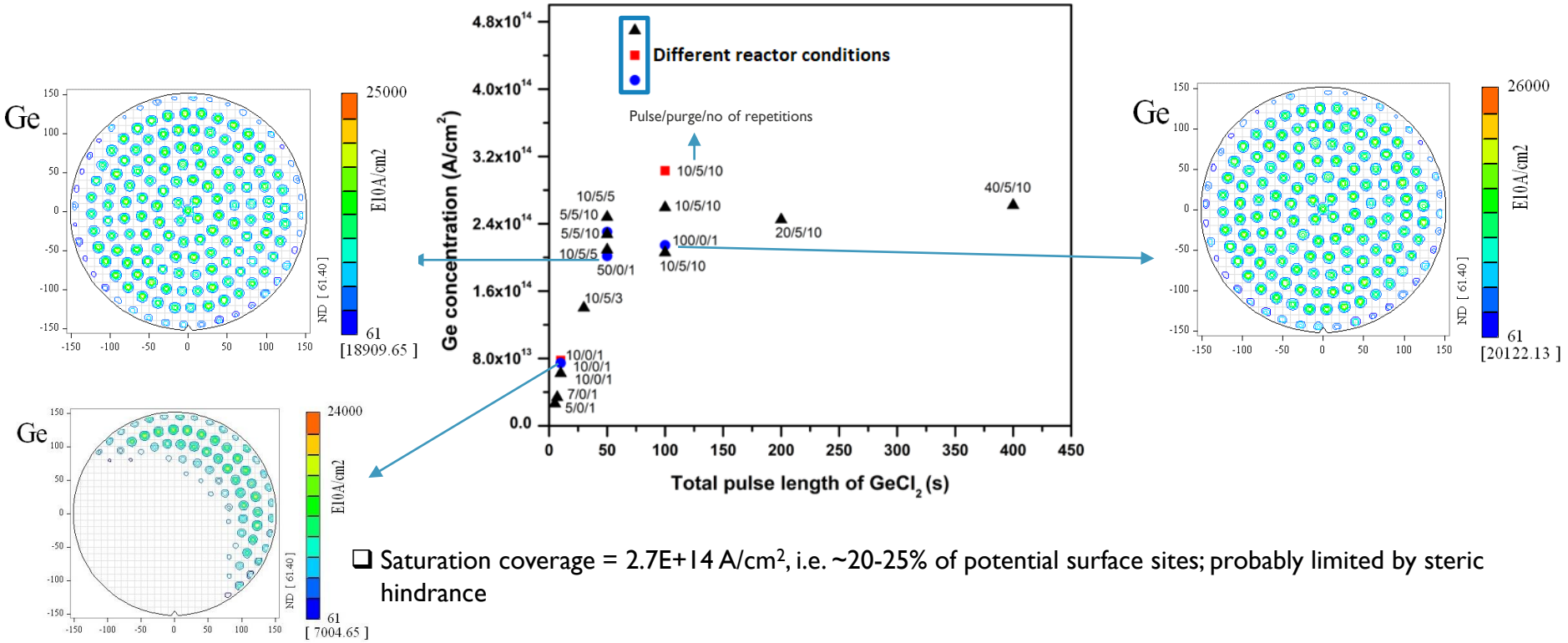
TXRF measurements: Precursor Chemisorption Studies



Stabilized $GeCl_2$ Chemisorption

$GeCl_2$ chemisorption on SiO_x is slow, limited by precursor supply/slower injection

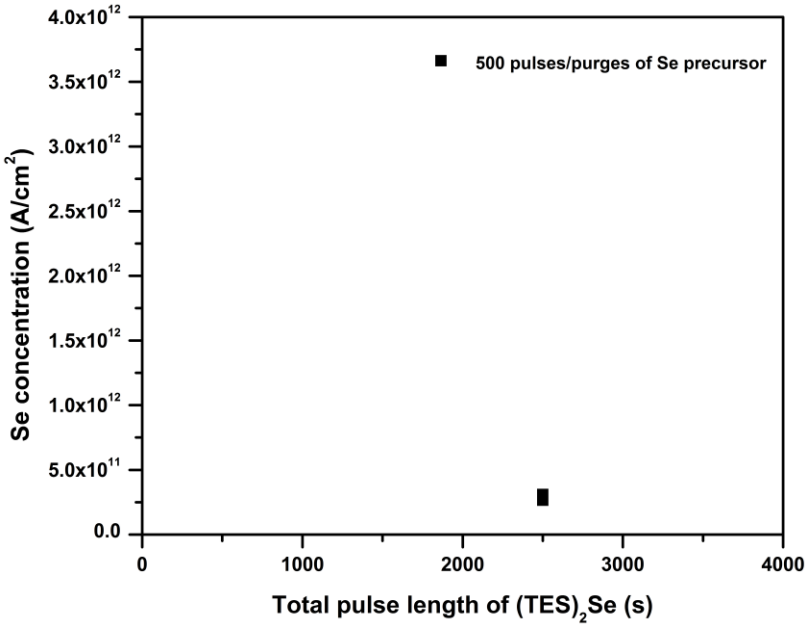
~50 sec needed for Ge saturation on 300 mm wafer



- Saturation coverage = 2.7E+14 A/cm², i.e. ~20-25% of potential surface sites; probably limited by steric hindrance

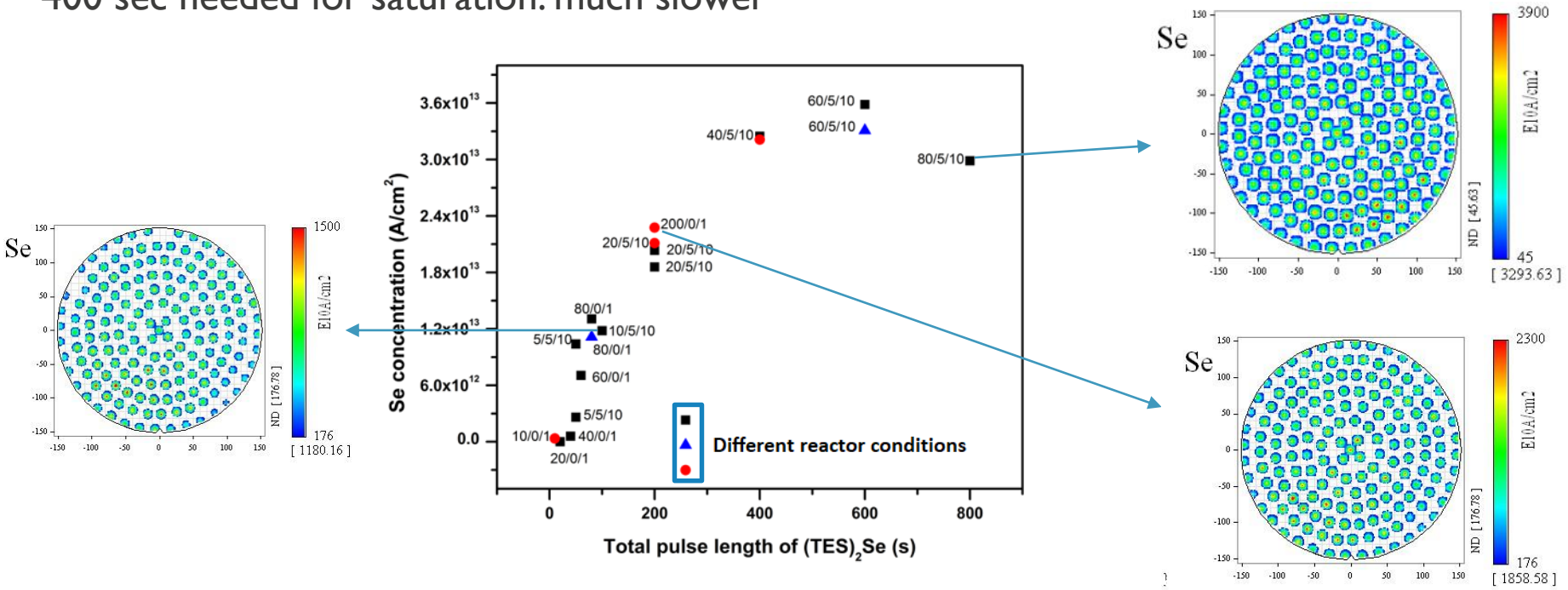
Se precursor chemisorption

Se doesn't chemisorb on SiO_X



Se chemisorbs on $GeCl_X$: Cl sites needed for precursor ligands exchange reaction

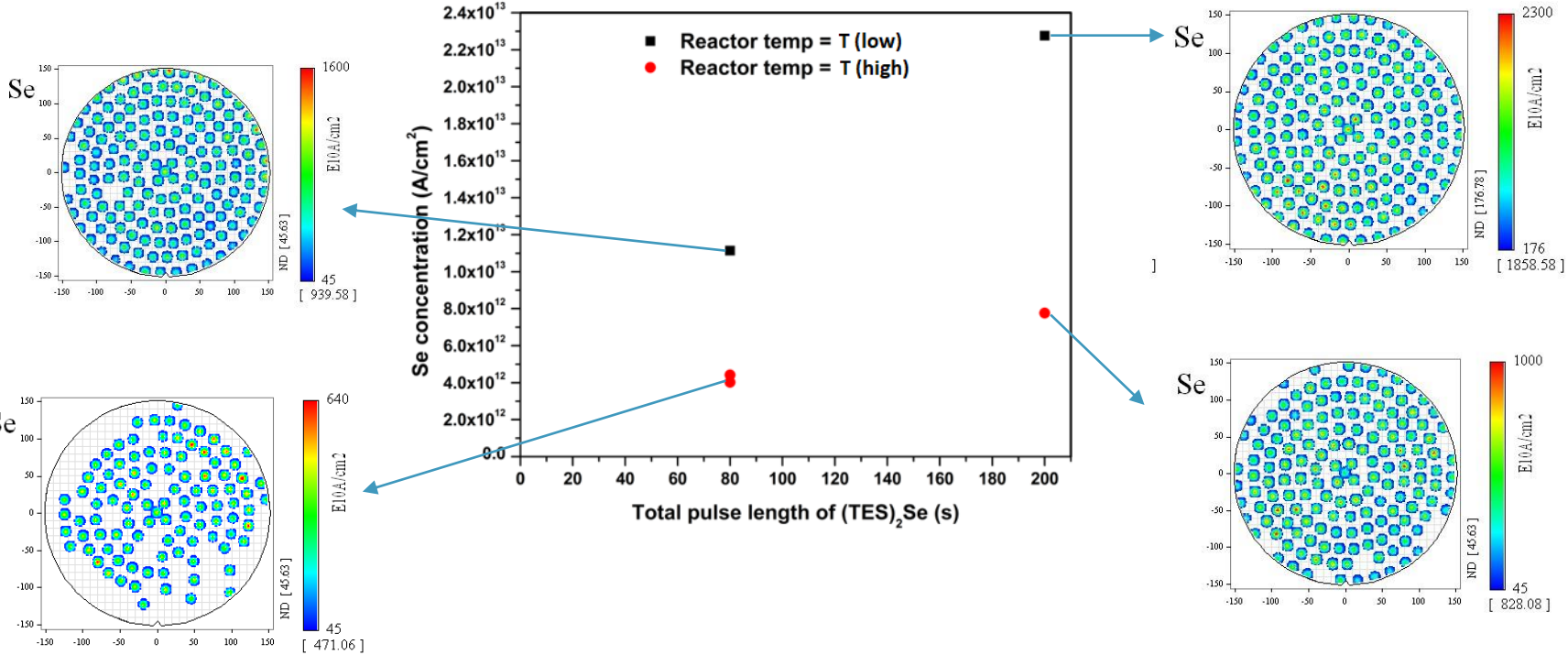
~400 sec needed for saturation: much slower



- Saturation coverage is ~3.5E+13A/cm2 (only ~15% of Ge sites)

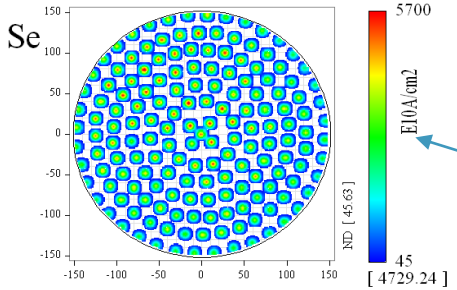
Se CONCENTRATION AT DIFFERENT REACTOR TEMPERATURES

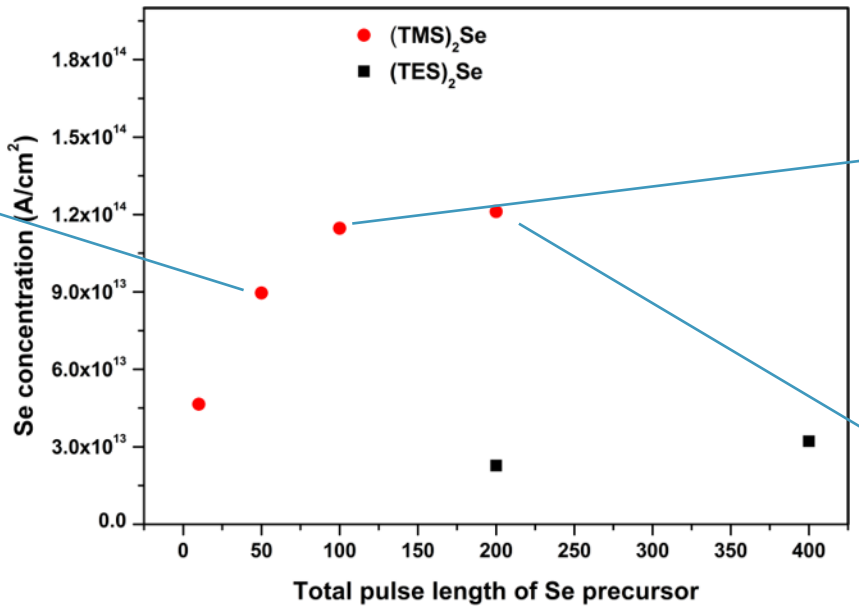
Se CONC DECREASE AT HIGHER REACTOR TEMPERATURE

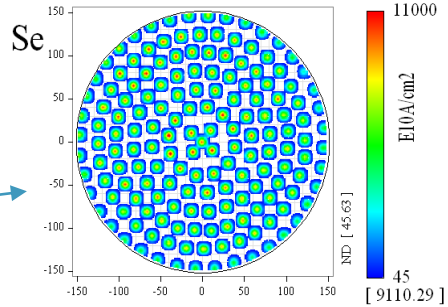


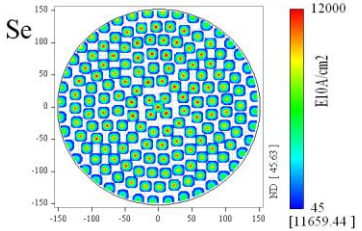
Se chemisorption becomes faster with $(TMS)_2Se$ on $GeCl_X/Si$

~100 sec needed for saturation vs 400 sec for previous precursor









- Saturation coverage with $(TMS)_2Se$ is ~1.1E+14/cm2 (~75 % of Ge sites are covered)

OUTLINE

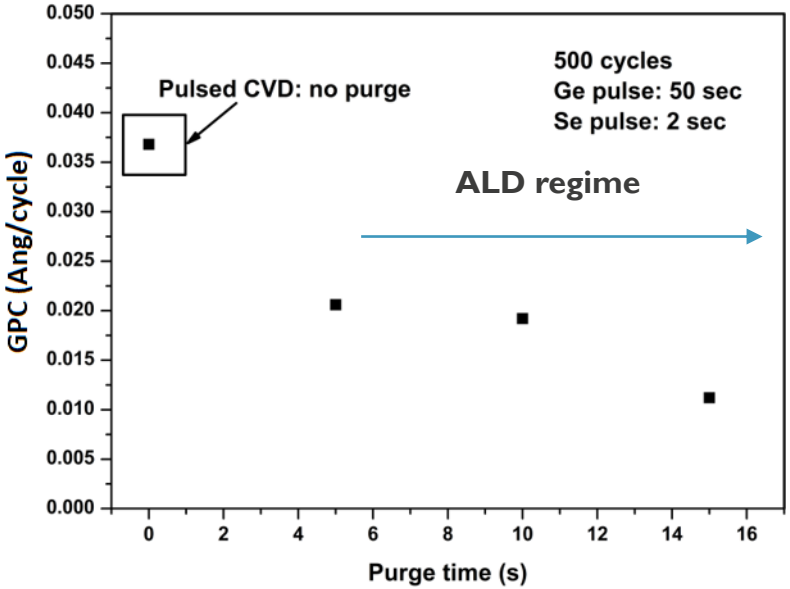
- Ge and Se precursor chemisorption studies by TXRF
- GPC trends with processing conditions
- GeSe properties

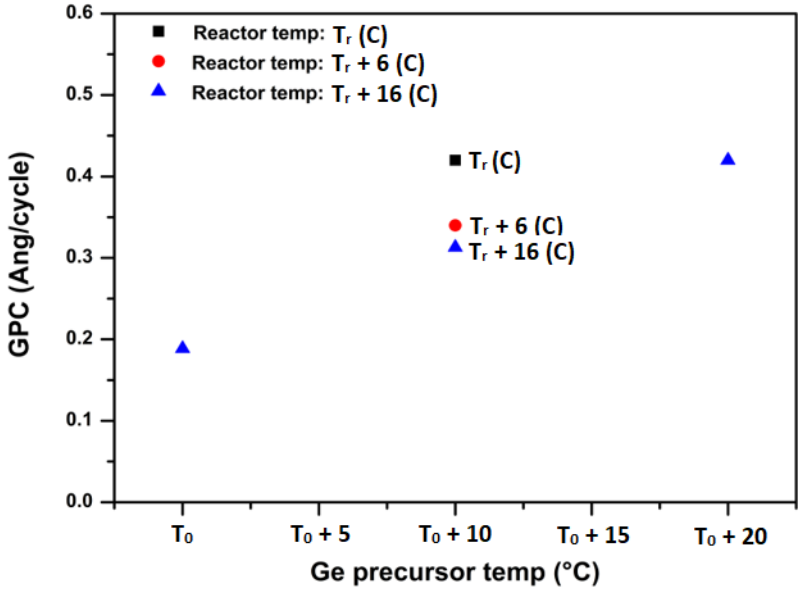
Limited by Ge precursor delivery
Slow kinetics
Processing conditions
Best precursor combination

OUTLINE

- Ge and Se precursor chemisorption studies by TXRF
- **GPC trends with processing conditions**
- GeSe properties

GPC is higher in (1) pulsed CVD regime, (2) with higher $GeCl_2$ delivery, and (3) low reactor temp

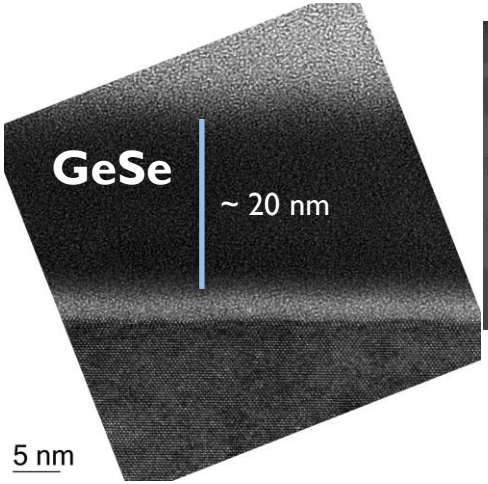


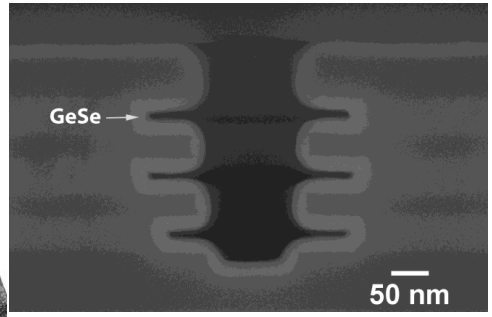


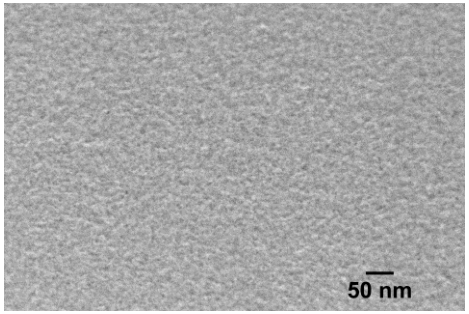
OUTLINE

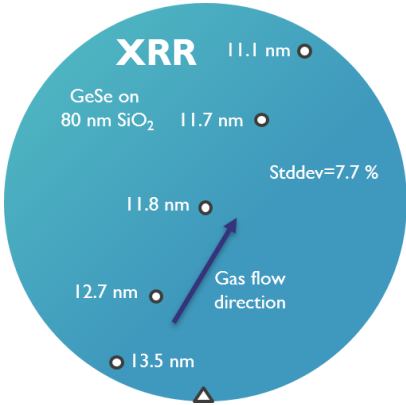
- Ge and Se precursor chemisorption studies by TXRF
- GPC trends with processing conditions
- **GeSe properties**

GeSe is conformal, amorphous, uniform, smooth and near stoichiometric.





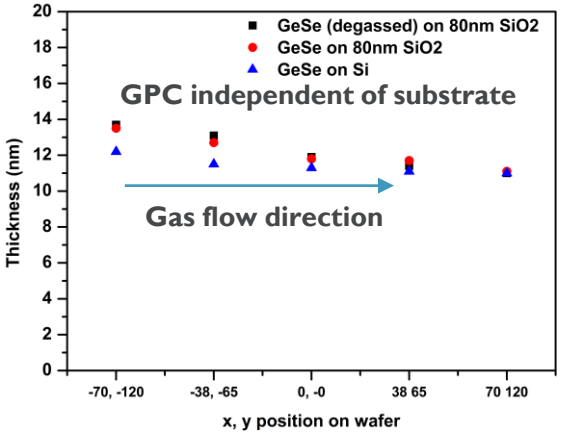




EDX analysis	
Element	at.%
Chlorine	4.1
Germanium	49.20
Selenium	46.71

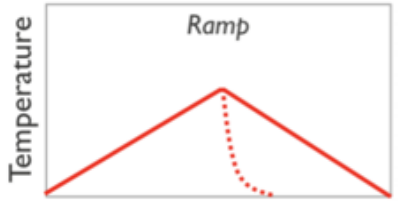
$Ge_{51}Se_{49}$ if normalized to 100 atom% GeSe
C, O ignored (stemming from specimen storage at air)

ERD depth analysis	
Element	at.%
Hydrogen	~5
Carbon	~5

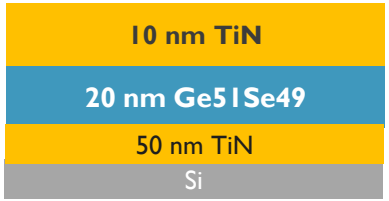


Thermal Stability Data by In-situ Temperature Programmed XRD

GeSe on TiN and SiO_2 substrates: Crystallization peaks at ~365-370 °C



Pulsed CVD Ge51Se49
This work



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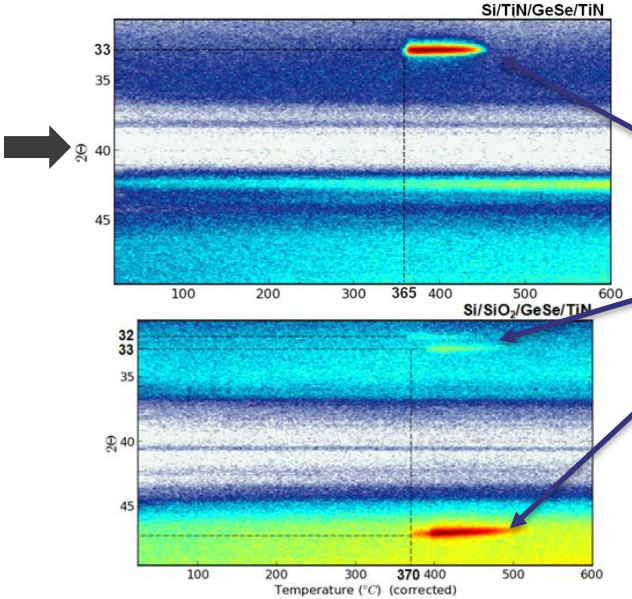

Orthorhombic GeSe phase
2Θ (33°)=(040)
2Θ (47°)=(002)

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SUMMARY AND CONCLUSION

1. TXRF studies: Ge chemisorption limited by Ge precursor delivery, overall slow kinetics
2. Key parameters to obtain higher GeSe GPC
   - Pulsed CVD regime
   - Higher delivery of $GeCl_2$ precursor
   - Lower reactor temperature
3. GeSe is conformal and amorphous.

OUTLOOK

- Benchmarking PVD GeSe vs ALD GeSe
- Optimization of GeSe process
  - Controlling the impurities in GeSe

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