

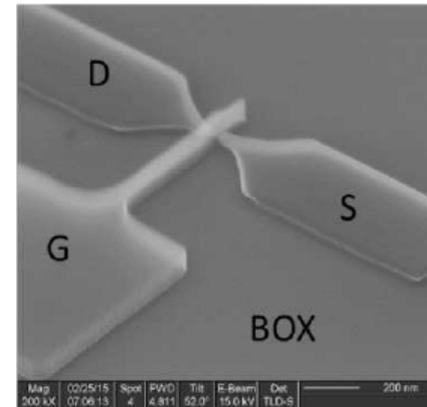
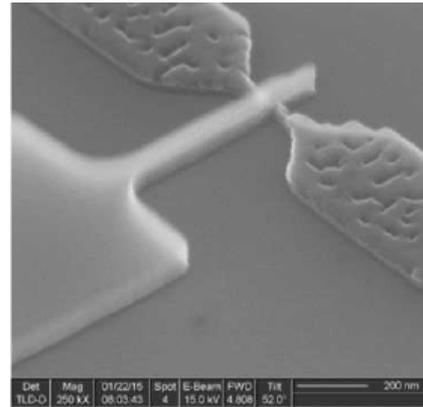


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STUDY AND DEVELOPMENT OF ADVANCED SURFACE PREPARATIONS FOR THE INTEGRATION OF NEW MATERIALS IN MICRO/NANOELECTRONICS



WET and Siconi™ cleaning sequences for SiGe pMOS channel

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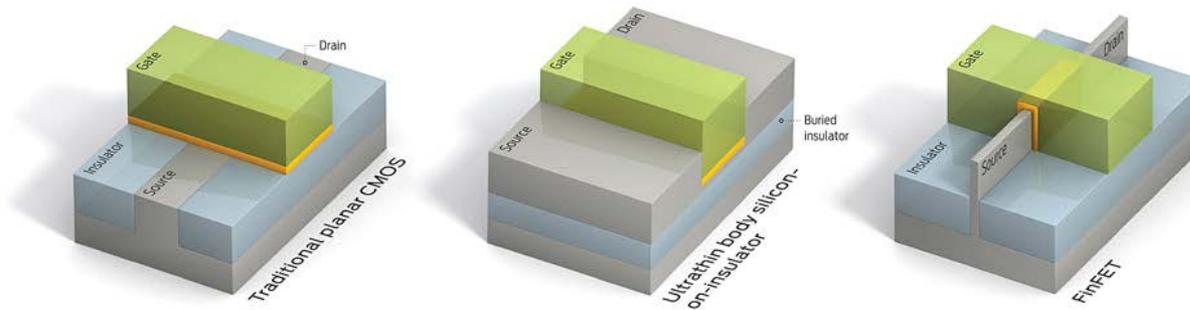
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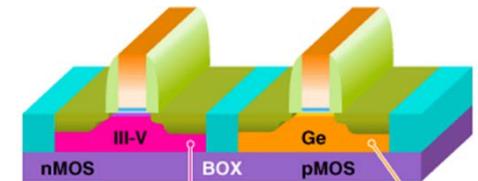
Source : Integration of Low Temperature SiGe:B Raised Sources and Drains in p-type FDSOI Field Effect Transistors. ECS Transactions, 75 (8) 51-58 (2016). The Electrochemical Society



- **3D architectures** and critical **transistor dimensions** of new devices involve major challenges in terms of surfaces and **lower thermal budget** treatments.

- Integration of new materials  improve performances:

- **SiGe** or **Ge** for pMOS transistor (hole mobility).
- **III/V alloys materials** (InGaAS, InAs, AsGa) for nMOS transistor (electron mobility) and photonic applications (direct gap).

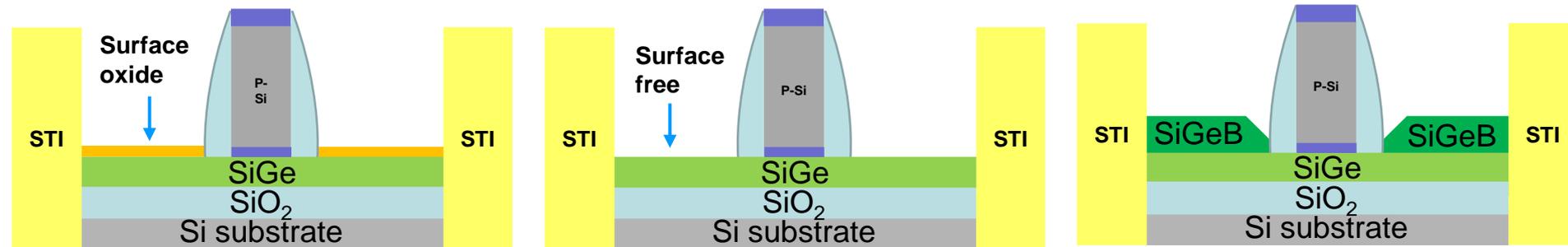


| Material | Si | InGaAs | Ge |
|---|-------|--------|-------|
| Electron mobility (cm ² /Vs) | 1,600 | 10,000 | 3,900 |
| Hole mobility (cm ² /Vs) | 430 | 250 | 1,900 |

Existing channel material

- New materials present very reactive surfaces in ambient air  WET and in situ surface treatment combination

➤ SiGe source/drain epitaxial re-growth :



Surface preparation **WET-DRY**
(Epi-Ready)

Epitaxy Growth

- **Remove surface oxide**
- **Low Contamination C, O, N, Cl, F**
(Epi-killer)
- **Low Roughness, defectivity,**
substrate consumption

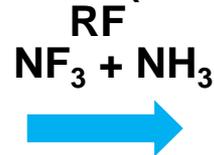
Substrate use :

Strained SiGe 40% layers epitaxially grown on Si bulk or SOI (wafer 300 mm)

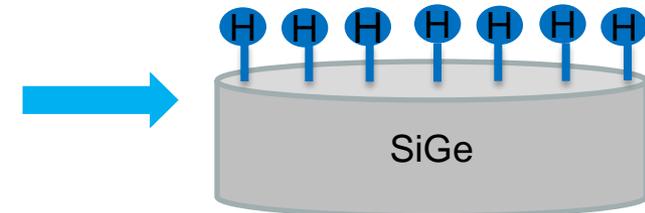


Siconi principle :

1-Etch Process (remote plasma)

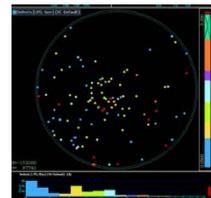
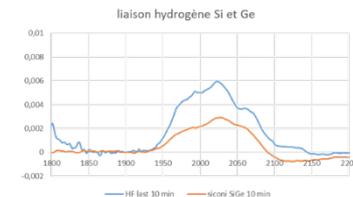
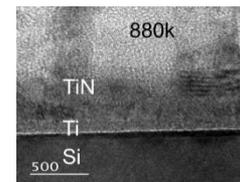


2- Anneal Process (>100 °C)



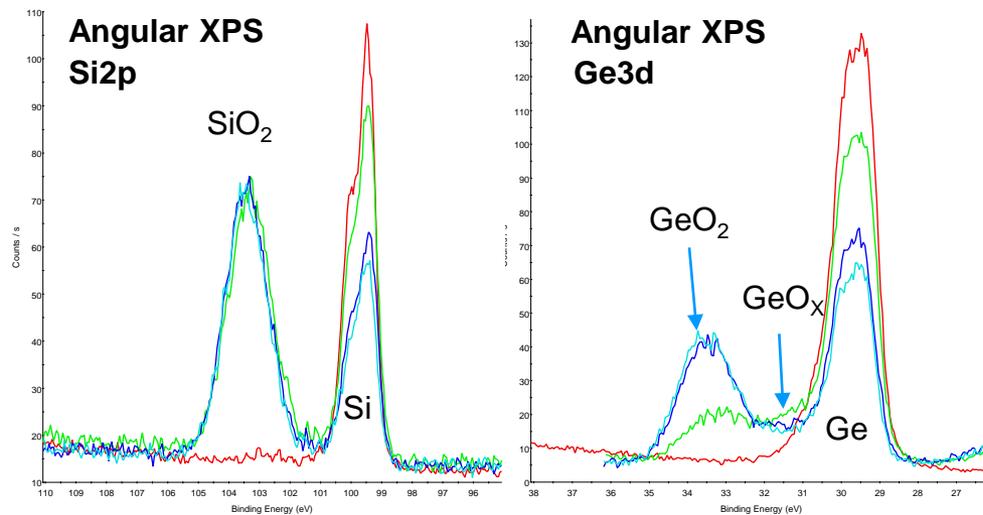
Characterization :

XPS grazing angle thermo theta 300, AFM, ellipsometry, FTIR-ATR and FTIR MIR



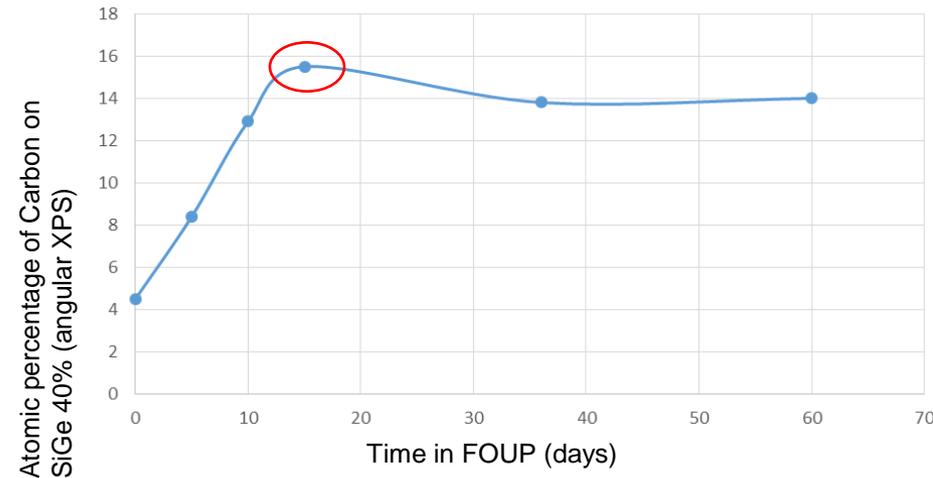
Grazing XPS angular characterization :

- SiGe 40% 4 minutes air exposure
- SiGe 40% 5 days air exposure
- SiGe 40% 10 days air exposure
- SiGe 40% 15 days air exposure



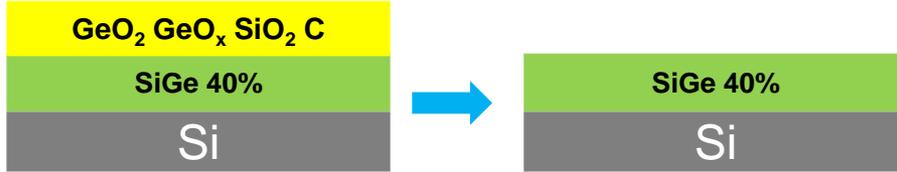
- Growth of a **mixed oxide** SiO₂, GeO_x and GeO₂ on clean room atmosphere

Evolution of Carbon contamination on a clean SiGe in clean room atmosphere

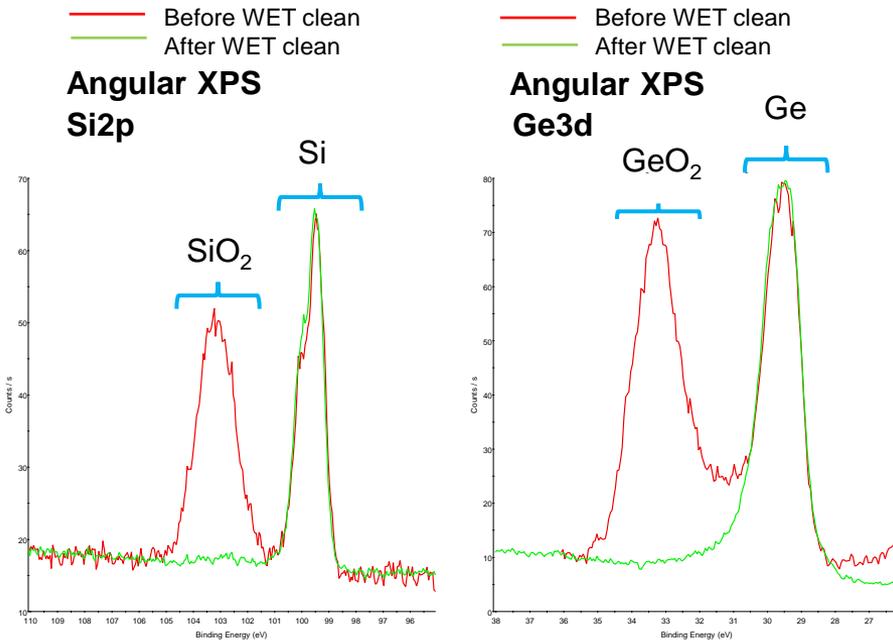


- **Carbon contamination increase** on surface substrate
- Maximum Carbon contamination **after 15 days**

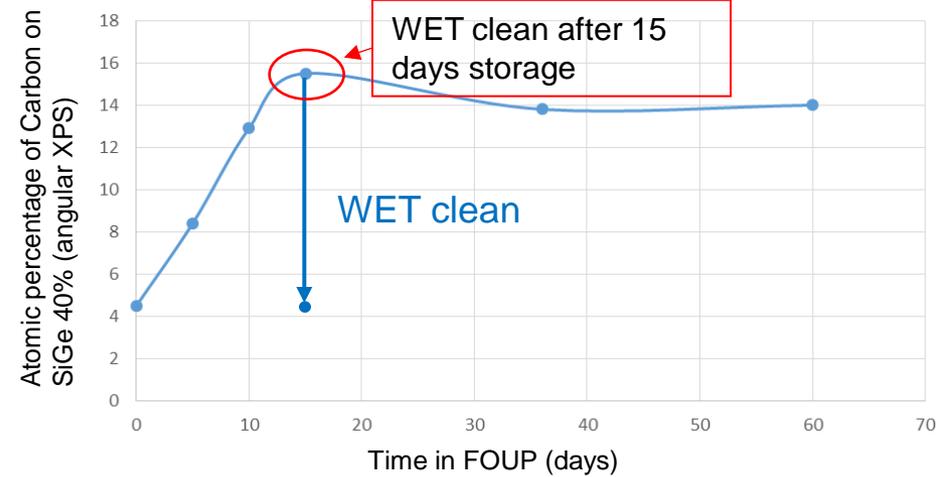
15 days aged sample will be used for cleaning efficiency Characterization



WET clean



Evolution of Carbon contamination on a clean SiGe in clean room atmosphere



Angular XPS Quantification SiGe 40% Before and after WET clean

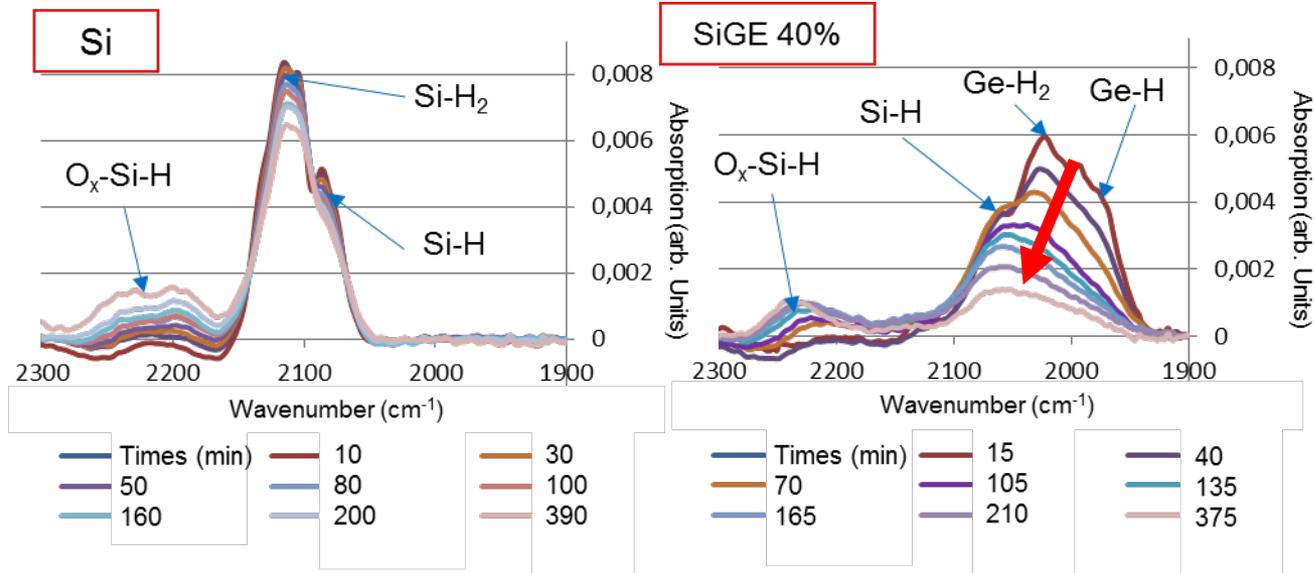
| | Native oxide | WET clean |
|---------------------------|--------------|-----------|
| Air exposure | | 4 minutes |
| C % (C1s) | 15,5 | 5 |
| GeO _x % (Ge3d) | 1,26 | N.D. |
| GeO ₂ % (Ge3d) | 5,41 | 0 |
| SiO ₂ % (Si2p) | 14,83 | 0 |

- Roughness ≈ 0,2 nm
- SiGe consumption ≈ 5 Å
- WET cleaning : efficiency toward oxide and C contamination removal





Evolution of IV-H bond in atmosphere after WET clean (FTIR-MIR)



- IV-H bonds decrease after the WET clean in benefit of Si-O bonds
- **SiGe 40% Hydrogen passivation:**
 - half of the Si-H and Ge-H loss after 2 hours for SiGe40%
- Air break can't be managed

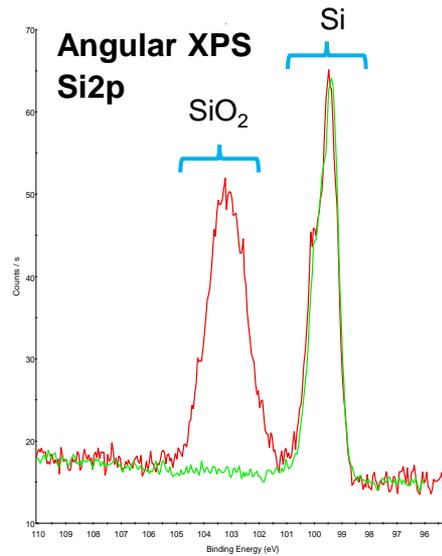
Very fast surface evolution → **"in situ" clean mandatory**



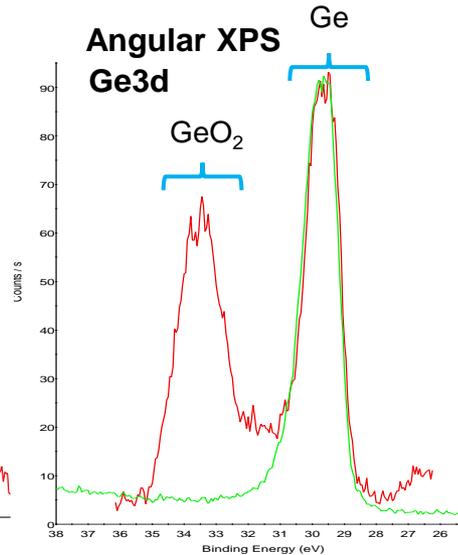


Siconi and HF comparison :

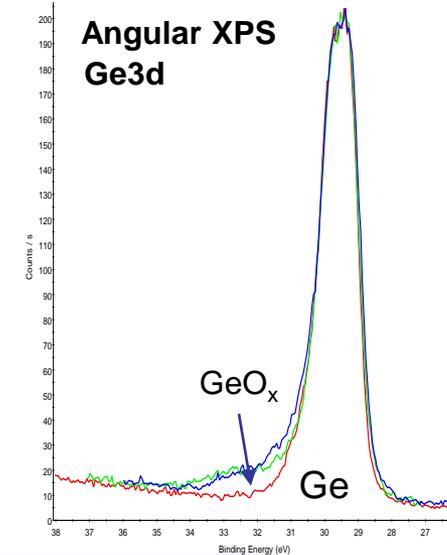
— Before Siconi
— After Siconi



— Before Siconi
— After Siconi



— WET clean 4 minutes air exposure
— Siconi clean no air break
— Siconi clean 4 minutes air exposure



- Roughness ≈ 0,2 nm
- SiGe consumption ≈ 5 Å
- Siconi clean : SiO₂ and GeO₂ removal efficient
Less efficient on GeO_x than HF



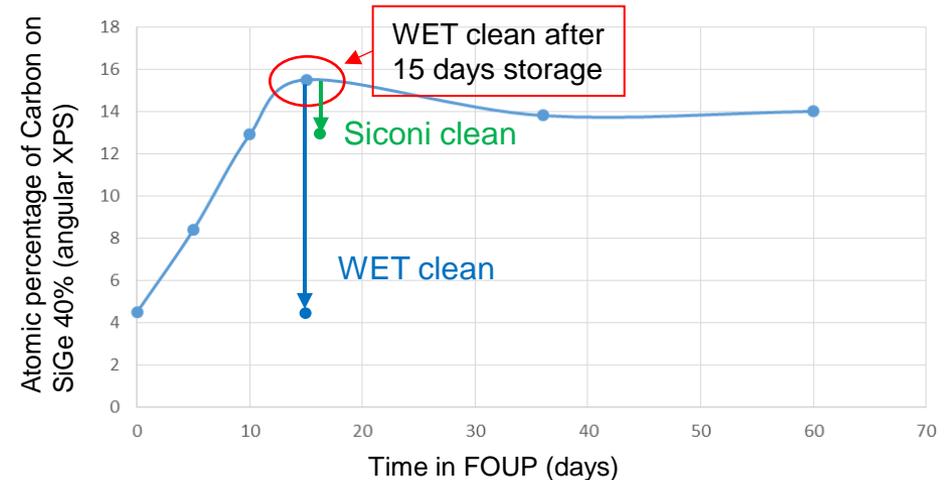


Carbon contamination efficiency:

Angular XPS Quantification SiGe
40% Before and after Siconi clean

| | Native oxide | Siconi |
|------------------|--------------|-----------|
| Air exposure | | 4 minutes |
| C % (C1s) | 15,5 | 12,6 |
| GeO_x % (Ge3d) | 1,26 | N.D. |
| GeO_2 % (Ge3d) | 5,41 | 0 |
| SiO_2 % (Si2p) | 14,83 | 0 |

Evolution of Carbon contamination on a
clean SiGe in clean room atmosphere



Siconi doesn't work on Carbon contamination



➤ **WET clean (HF removal oxide):**

- **Efficiency on GeO_2 , SiO_2 , GeO_x and C contamination removal** 
- **air break incompatible reactive surface** 

➤ **Siconi treatment :**

- **Process in-situ: no Q-time** 
- **Efficiency on GeO_2 and SiO_2** 
- **Poor efficiency on GeO_x** 
- **Inefficient Carbon contamination** 



Alternative cleaning strategy mandatory



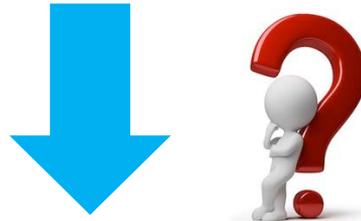
Aged sample



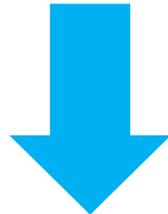
Goal : No oxide and carbon to be epi ready surface



Aged sample



- No GeO₂, GeO_x
- No Carbon contamination



No air break → siconi



Goal : No oxide and carbon to be epi ready surface



Aged sample



Which wet chemistry can manage the surface composition?



- No GeO₂, GeO_x
- No Carbon contamination



No air break → siconi



Goal : No oxide and carbon to be epi ready surface

Angular XPS
Quantification
SiGe 40%

| | HF-HOT SPM | HF-O ₃ | HF- HOT SC1 | HF-COLD SC1 |
|---------------------------|------------|-------------------|-------------|-------------|
| SiO ₂ % (Si2p) | 21,4 | 18,5 | 21,5 | 18 |
| GeO ₂ % (Ge3d) | 2,1 | 1,8 | N.D. | N.D. |
| C% (C1s) | 1,6 | 3,5 | 1,6 | N.D. |
| Oxide Thickness nm | 1,96 | 1,45 | 1,8 | 1,3 |



HF



SC1
based



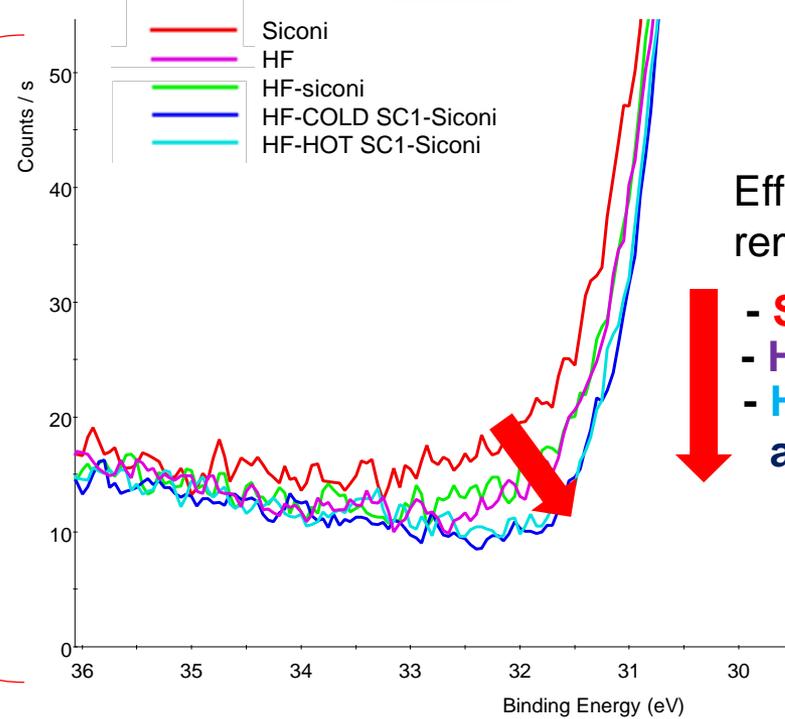
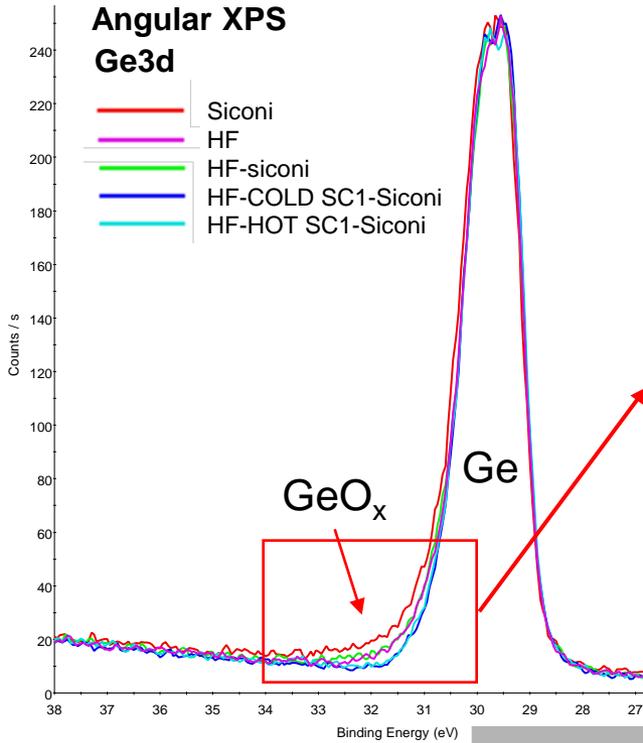
- Roughness <0,2nm
- GeO₂ dissolution with HOT SC1 and COLD SC1 (SiO₂ oxide growth)
- Low carbon contamination



HOT SC1 and Cold SC1 chemical oxide pre-siconi



Angular XPS Ge3d



Efficiency on GeO_x removal :

- **Siconi only**
- **HF and HF-Siconi**
- **HF-COLD SC1-siconi and HF-Hot SC1-Siconi**

Angular XPS
Quantification
SiGe 40%

| | Siconi | HF | HF-Siconi | HF-COLD SC1-Siconi | HF-HOT SC1-Siconi |
|-----------|--------|------|-----------|--------------------|-------------------|
| O % (O1s) | 10.41 | 8,54 | 6.78 | N.D. | N.D. |
| C % (C1s) | 10.87 | 3.26 | 4.23 | N.D. | N.D. |

Efficiency on Oxygen and Carbon removal

- HF-COLD SC1-Siconi
- HF-HOT SC1-Siconi

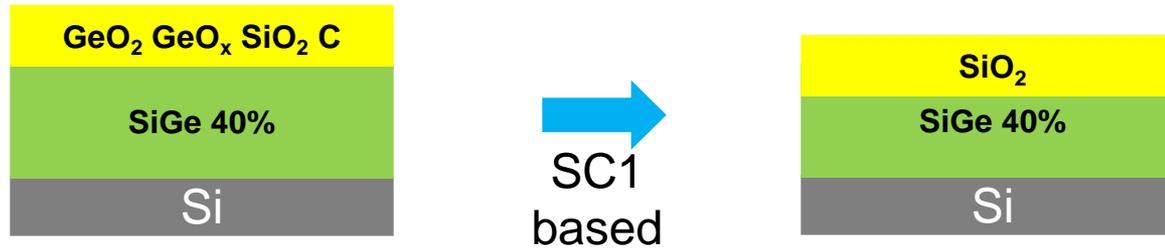


Best Epi ready surface



HF mandatory ???

SC1 clean only direct on aged sample



HF remove the native oxide before the SC1

WET oxide clean without the native oxide removal

Angular XPS
Quantification
SiGe 40%

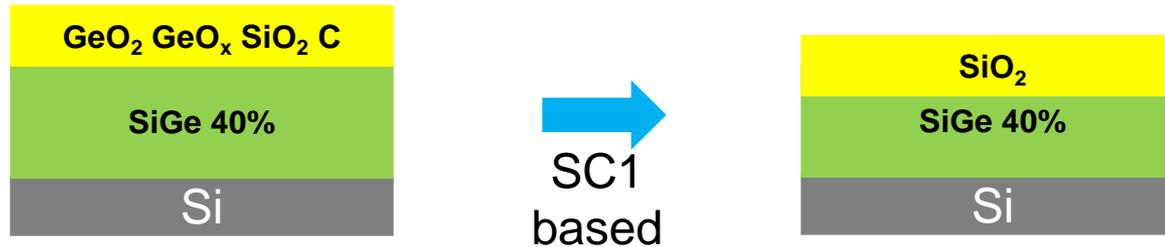
| | NATIVE OXIDE | HF- HOT SC1 | HF-COLD SC1 | HOT SC1 | COLD SC1 |
|---------------------------|--------------|-------------|-------------|---------|----------|
| SiO ₂ % (Si2p) | 14,8 | 21,5 | 18 | 22,3 | 21,4 |
| GeO ₂ % (Ge3d) | 5,4 | N.D. | N.D. | N.D. | 1,3 |
| C % (C1s) | 15,5 | 1,6 | N.D. | N.D. | 9,1 |



Cold SC1 not efficient enough on :

- GeO₂ Dissolution
- Carbon contamination

SC1 clean only direct on aged sample



HF remove the native oxide before the SC1

WET oxide clean without the native oxide removal

Angular XPS
Quantification
SiGe 40%

| | NATIVE OXIDE | HF- HOT SC1 | HF-COLD SC1 | HOT SC1 | COLD SC1 | COLD SC1 (Times treatment longer) |
|---------------------------|--------------|-------------|-------------|---------|----------|--------------------------------------|
| SiO ₂ % (Si2p) | 14,8 | 21,5 | 18 | 22,3 | 21,4 | 17 |
| GeO ₂ % (Ge3d) | 5,4 | N.D. | N.D. | N.D. | 1,3 | N.D. |
| C % (C1s) | 15,5 | 1,6 | N.D. | N.D. | 9,1 | 5,6 |



- SC1 based mixture alone can manage germanium oxide and carbon
- HF STEP can be removed if consumption fine tuning is mandatory

SC1 + Siconi on aged sample



Angular XPS
Quantification
SiGe 40%

| | HF | Siconi | HF- HOT SC1- Siconi | HF-COLD SC1- Siconi | COLD SC1- Siconi | HOT SC1- Siconi |
|-----------|---|---|---|---|---|---|
| O % (O1s) | 8.2 | 10,4 | N.D. | N.D. | N.D. | N.D. |
| C % (C1S) | 3.2 | 10,8 | N.D. | N.D. | 4.2 | 4.4 |
| |  |  |  |  |  |  |

➤ SC1 based mixture + siconi permit very good epi ready surface

conclusion

- **Siconi** and **HF** remove **GeO₂** and **SiO₂** 
- Inefficiency of **Siconi** / **Carbon** contamination 
- lower efficient of Siconi on **GeO_x** 
- **SC1 based mixture** WET cleanings :
 - can **manage germanium oxide** and **carbon** (Siconi –ready) 
 - **HF STEP** can be removed if **consumption fine tuning is mandatory**
- **SC1 based mixture + Siconi** :
 - permit very good **epi ready surface** 

Perspectives :

- Epitaxy growth of Si on SiGe with WET-Siconi clean
 - Contamination quantification (SIMS)
 - Morphological quality (DRX, AFM...)

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