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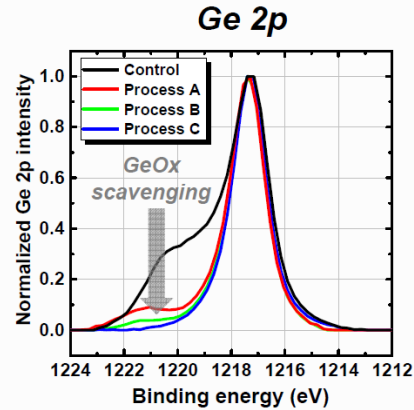
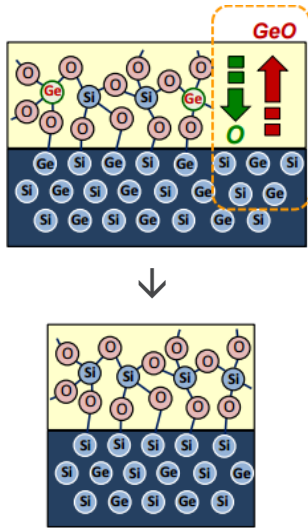
SELECTIVE Ge REMOVAL FROM SiGe SURFACES FOR Si-CAP-FREE
SiGe PASSIVATION

KURT WOSTYN,, HIROAKI ARIMURA, ANDRIY HIKAVYY, DIRK RONDAS, ADRIAN
VAISMAN CHASIN, THIERRY CONARD, LARS-ÅKE RAGNARSSON, NAOTO HORIGUCHI

Si-CAP-FREE SiGe PASSIVATION

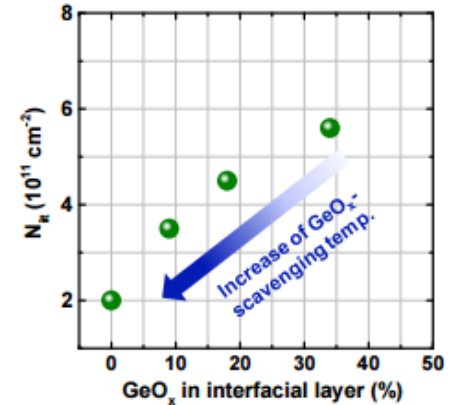
SiGe FIN OR GAA PASSIVATION IN RMG

Ge-free oxide IL **and** interface enables SiGe passivation
= similar to Si cap without depositing Si-cap.



Process A, B and C:

- Removes GeO
- Variable efficiency in GeO_x removal



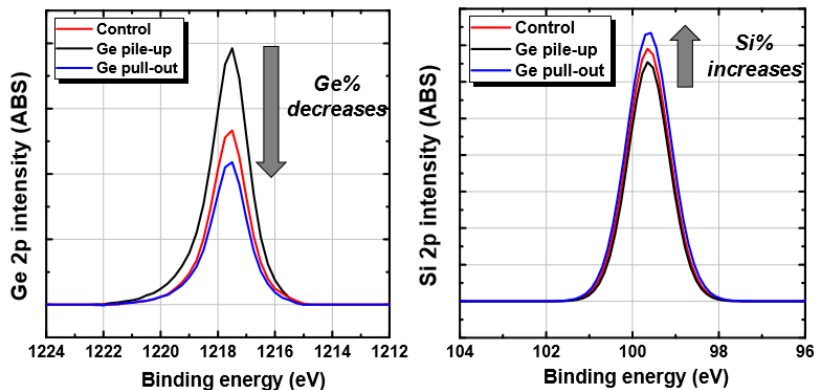
GeO_x scavenging
reduces D_{IT}

[Lee et al. VLSI 2016 and Siddiqui
et al. MRS Spring 2016]

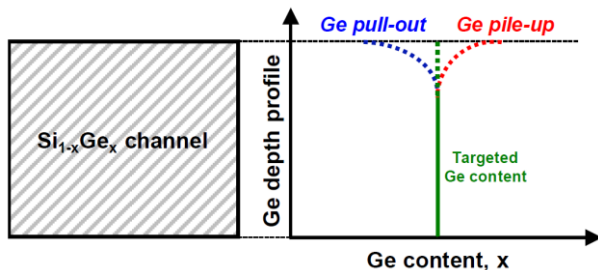
Si-CAP-FREE SiGe PASSIVATION

IMPACT OF SURFACE PREPARATION PRIOR TO IL GROWTH

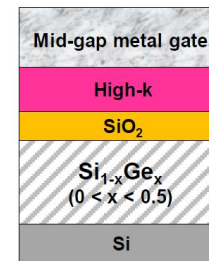
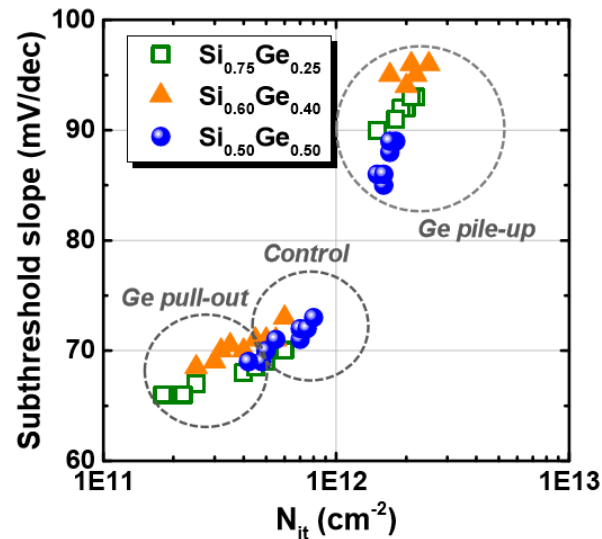
Ge conc at SiGe surface



- Ge poor surface == Ge pull-out
- Ge rich surface == Ge pile-up



Electrical impact



(b)

Ge poor surface, i.e. Ge pull-out, results in best electrical performance. Unfortunately, no process information was shared.

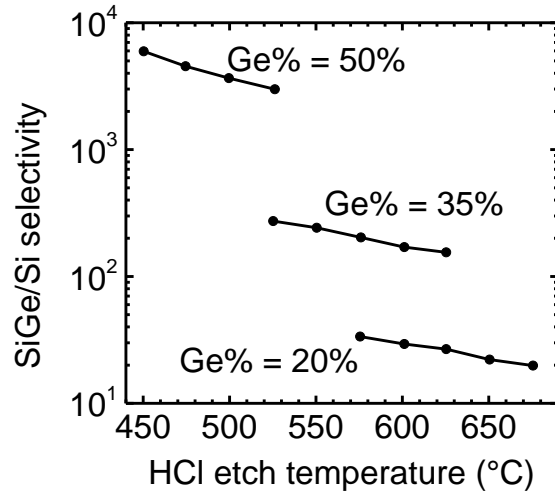
OUTLINE

- INTRODUCTION
- Ge PULL-OUT – SELECTIVE REMOVAL OF Ge FROM SIGE SURFACE
- IMPACT GE PULL-OUT ON Si-CAP-FREE SiGe PASSIVATION
- CONCLUSION

SELECTIVE Ge REMOVAL FROM SiGe SURFACE

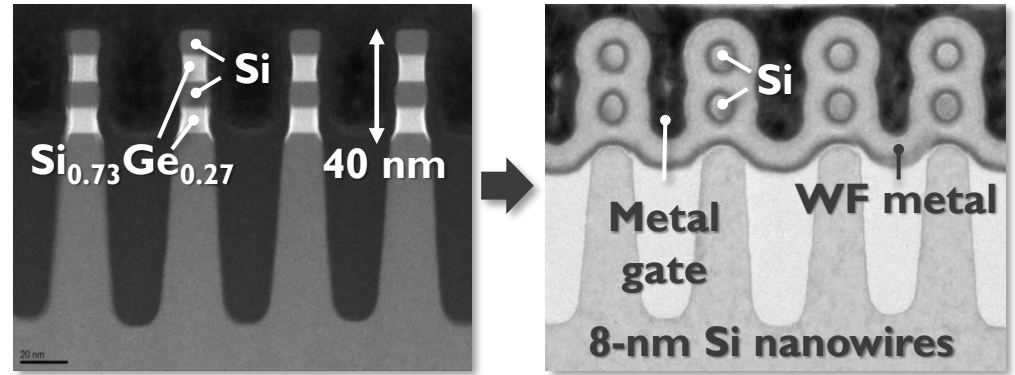
INSPIRED BY Si GAA SELECTIVE ETCH

HCl (G) SELECTIVE ETCH



[Destefanis et al., Semicond. Sci. Technol. 23, (2008) 105019]

Si GAA BY HCl (G)

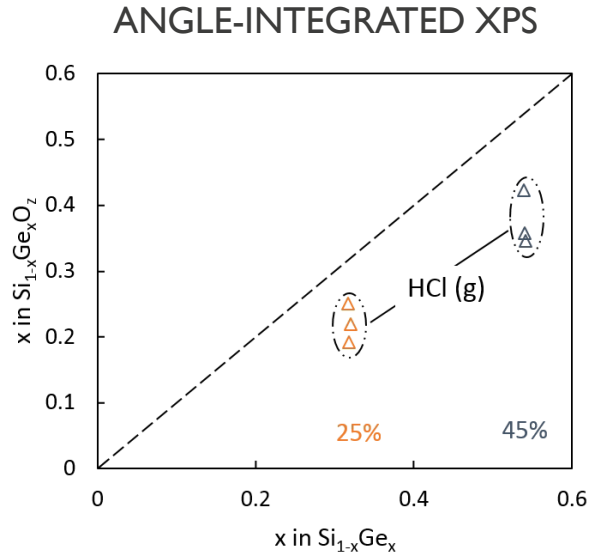
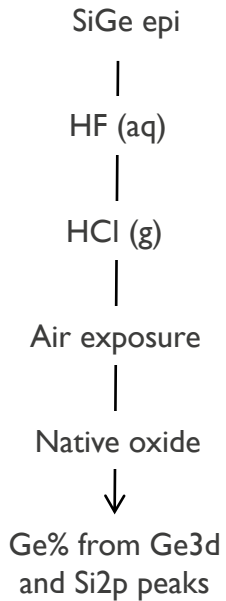


[H. Mertens et al. VLSI Tech. Dig. (2016) p. 158]

- SiGe vs Si selective etch in HCl (g) enables Si GAA
 - Selectivity attributed to enhanced GeCl_2 desorption compared to SiCl_2 in HCl (g) ambient.
- Possible to use HCl (g) for surface preparation?

Ge PULL OUT – SELECTIVE Ge REMOVAL

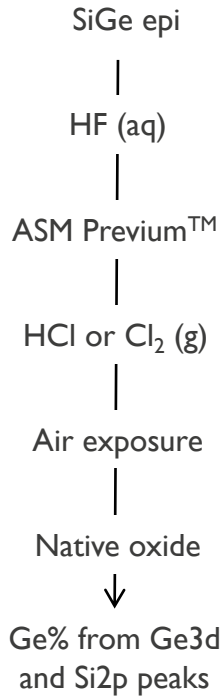
NATIVE OXIDE COMPOSITION AFTER SURFACE TREATMENT



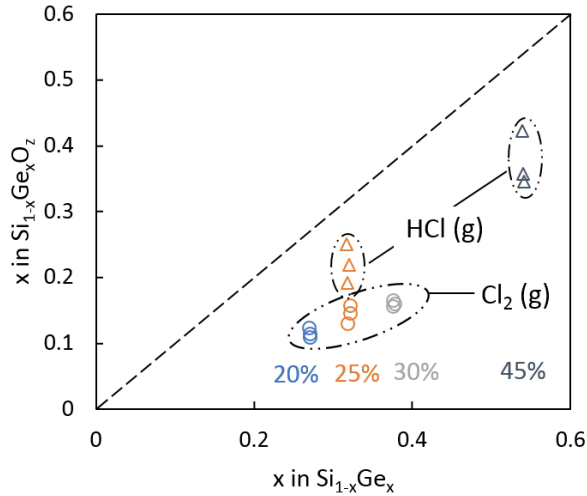
- SiGe surface becomes Ge poor in HCl (g) ambient.

Ge PULL OUT – SELECTIVE Ge REMOVAL

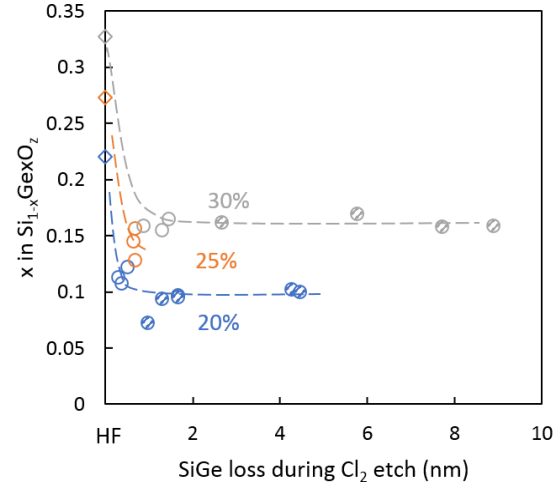
NATIVE OXIDE COMPOSITION AFTER SURFACE TREATMENT



ANGLE-INTEGRATED XPS



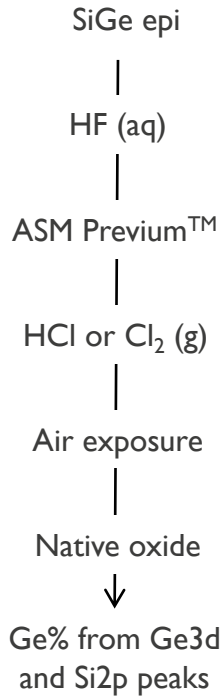
IMPACT OF Cl₂ (g) TREATMENT TIME



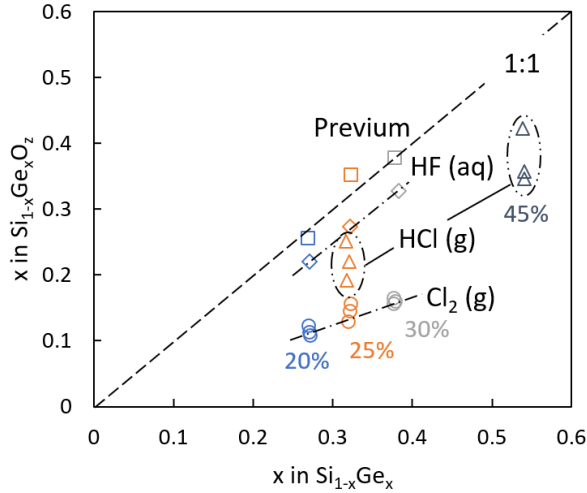
- SiGe surface becomes Ge poor in HCl (g) and Cl₂ (g) ambient.
- Tuning process conditions allows for SiGe loss reduction while maintaining selective Ge removal → surface treatment.

Ge PULL OUT – SELECTIVE Ge REMOVAL

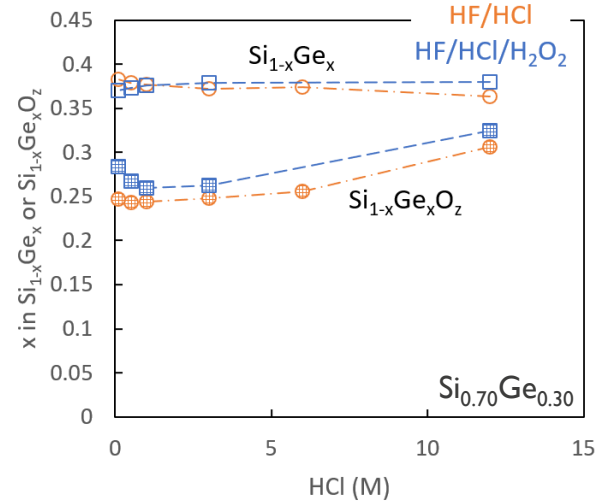
NATIVE OXIDE COMPOSITION AFTER SURFACE TREATMENT



ANGLE-INTEGRATED XPS



AQUEOUS HF SOLUTIONS



- SiGe surface becomes Ge poor in HCl (g) and Cl₂ (g) ambient.
- Tuning process conditions allows for SiGe loss reduction while maintaining selective Ge removal → surface treatment.
- Ge pull-out also observed in aqueous HF solutions. Ge pull-out efficiency depends on [HCl] and [H₂O₂], however never as efficient as Cl₂ (g).

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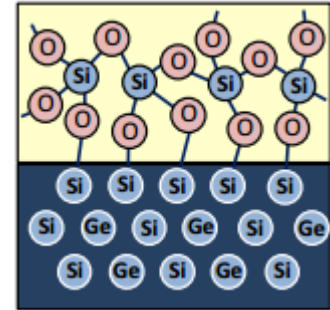
SiGe PASSIVATION – HOW TO? CHALLENGES.

Ge-OXIDE-FREE INTERLAYER

- Avoid Ge-oxide formation
 - Si cap – reference passivation method
 - Thermal interlayer – pure SiO_2 formed by Ge condensation
 - Ge pull-out prior to IL formation
- Ge-oxide scavenging
 - High solubility of GeO_2 in aqueous solutions
 - Scavenging prior to high-k deposition
 - Scavenging during post-metallization anneal (PMA)

} Imec POR

Ideal SiGe passivation



[Lee et al. VLSI 2016]

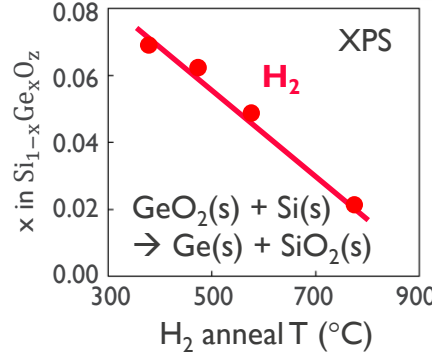
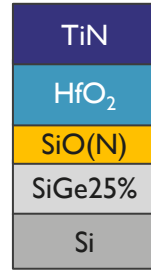
- Oxide and interface composition:
- Pure SiO_2
 - Interface contains only Si – O bonds
 - No Ge gradient below interface

GeO SCAVENGING

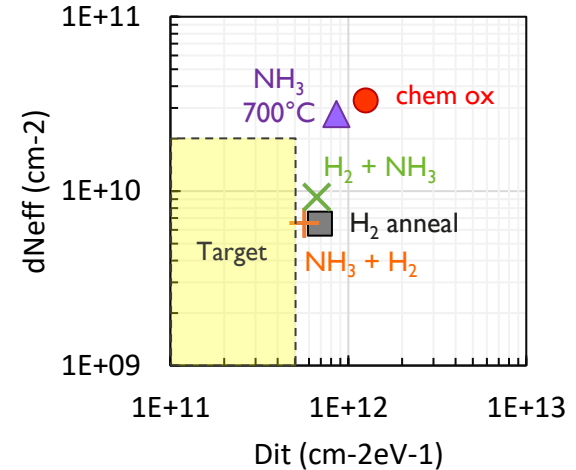
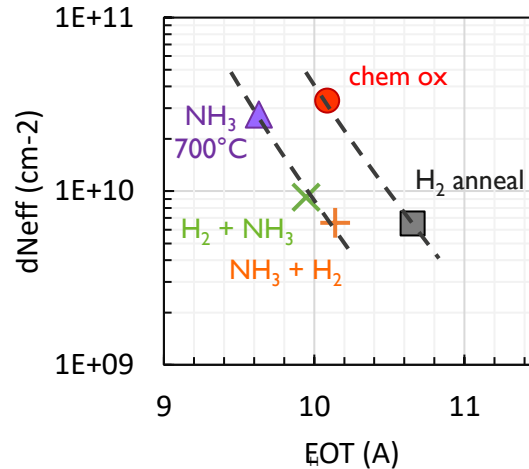
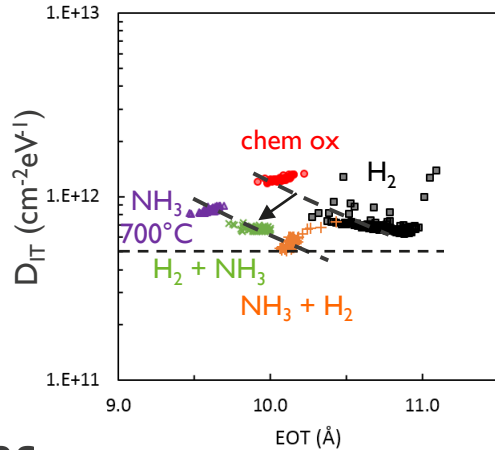
NH₃ ANNEAL + H₂ ANNEAL ON CHEMOX

[H. Arimura et al. IEDM Tech Dig (2019) p. 667 and K. Wostyn et al. presented at ISTD/ICSI 2019]

- Limited delay
- SiGe 25-30% epi
 - Chem ox.
 - NH₃ anneal (700°C, 5 torr, 60 s)
 - **H₂ anneal (775°C, 40 torr, 2 min)**
 - Water rinse
 - HfO₂ (2 nm)
 - PVD TiN/W gate
 - HPA: 400C, 20 ATM, H₂



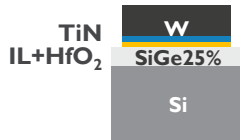
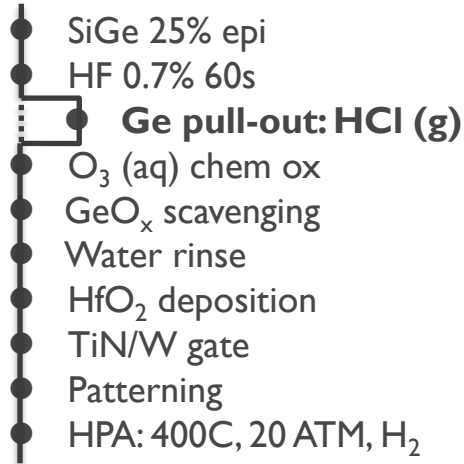
- H₂ anneal at high-T on SiO₂ (775°C, 40 torr, 2 min)
 - SiO vs GeO thermal stability difference
 - **GeO₂(s) + Si(s) → Ge(s) + SiO₂(s)**
- Additional NH₃ anneal on SiO₂ (700°C, 5 torr, 60 s)
 - Nitridation to suppress O / Vo diffusion and GeOx formation [J. Huang et al., APL 88, 143506 (2006.)]
 - Increase in k-value (SiON)



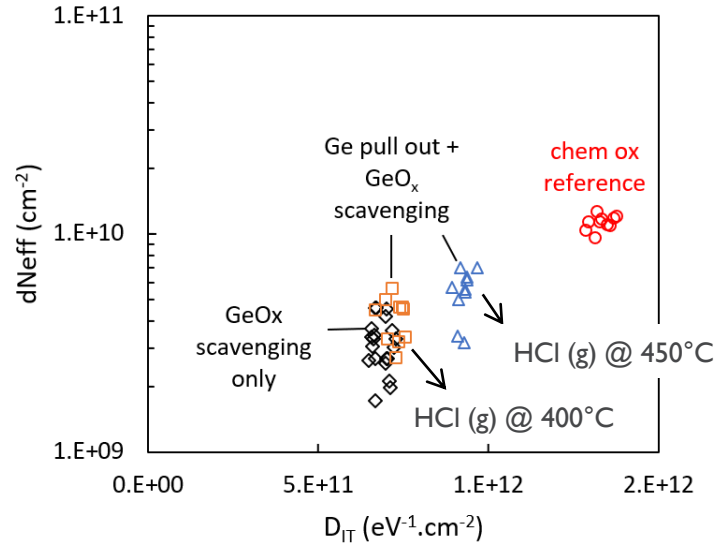
IMPACT OF GE PULL-OUT ON $\text{Si}_{0.75}\text{Ge}_{0.25}$ PASSIVATION

Ge PULL-OUT IN HCl (G) AMBIENT

SiGe passivation



C-V hysteresis measurements at RT



- GeO_x scavenging improves SiGe passivation.
- Combining Ge oxide scavenging with Ge pull-out using HCl (g) shows no or small detrimental impact on dN_{eff} vs D_{IT} .

CONCLUSIONS

- Ge pull-out observed for SiGe < 50% in
 - Aqueous HF solutions, HCl (g) and Cl₂ (g) on oxide-free surface
 - Ge pull-out most efficient using Cl₂ (g)
- Si-cap-free SiGe passivation
 - Improved SiGe passivation by combining chem oxide with Ge-oxide scavenging
 - No or small detrimental impact observed when Ge pull-out in HCl (g) combined with Ge-oxide scavenging
- Future: impact of Ge pull-out on SiGe oxidation → come and see at UCPSS!

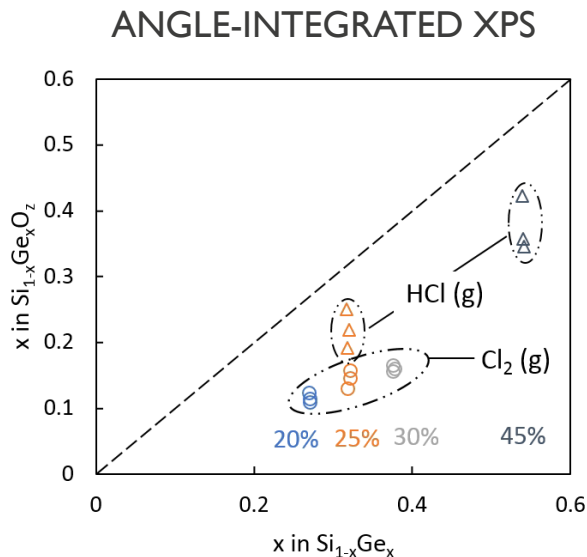
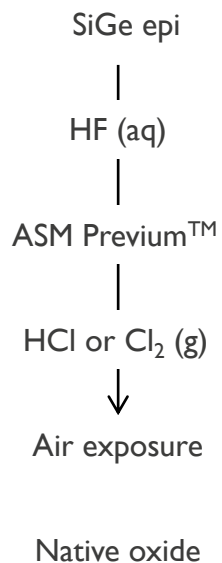


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Ge PULL OUT – SELECTIVE Ge REMOVAL

NATIVE OXIDE COMPOSITION AFTER SURFACE TREATMENT



DESORPTION OF HCL (ADS) ON GE (100)

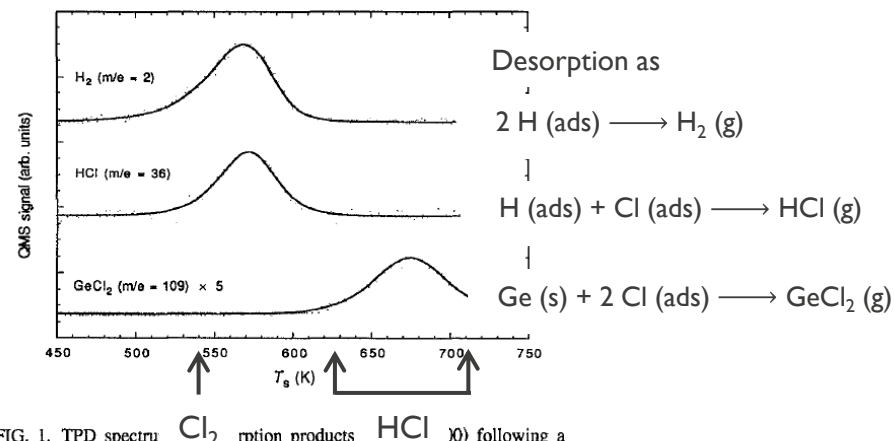


FIG. 1. TPD spectra of H₂, HCl, and GeCl₂ following a saturation dose of HCl. For GeCl₂ the GeCl⁺ cracking reaction was actually detected.

[D'Evelyn et al. J. Chem. Phys. 101 (1994) 2463]

Difference in surface Ge conc between HCl and Cl₂ possibly (partially) related to difference in T during surface preparation step.