Study of Germanium Surface for Wet Cleaning Applications

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Background

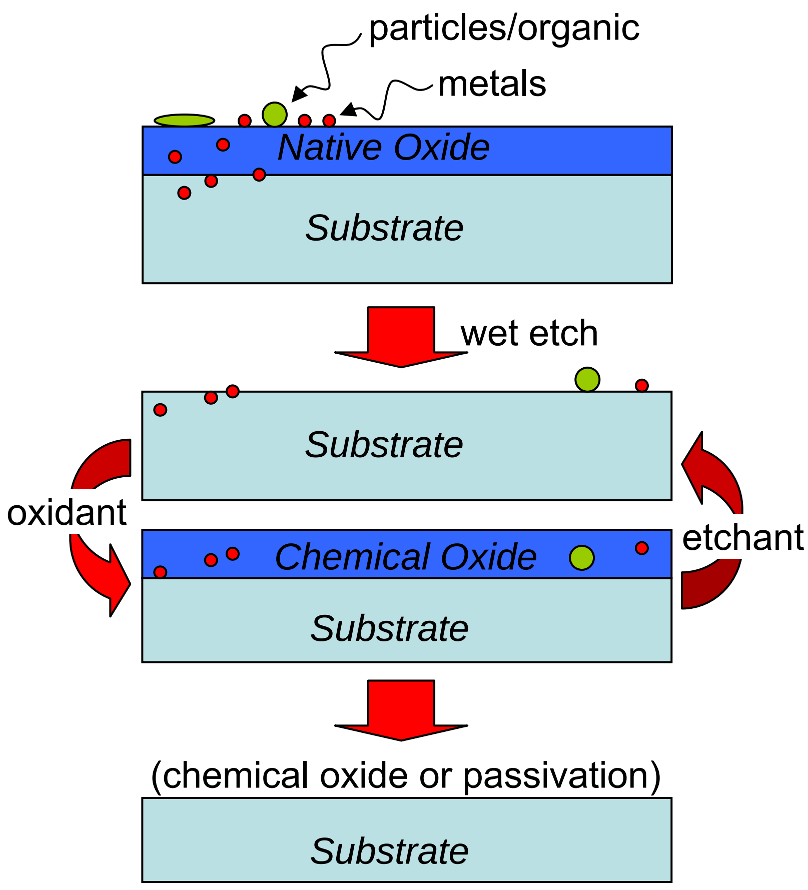
- Ge is gaining interest as a substrate for high mobility applications because of higher carrier mobility.
  (2X electron & 4X hole mobility of Si)

$(cm^2V^{-1}s^{-1})$	Si	Ge
Electron	1450	3900
Hole	505	1800

Schäffler et al, *Semiconductor Sci. Tech.* (1997)

- Therefore effective cleaning solution is required to fully utilize the high mobility properties of Ge in process integration.

Basics of Cleaning Process Development



Typical cleaning process flow

- Pre-requisite for Efficient Clean Process

1. Minimal Consumption of the Substrate
   - Study of etch rates of Ge in various chemicals
2. Minimal Increase in Surface Roughness
   - Effect of various chemicals on surface roughness with AFM
3. Efficient Metal Removal Efficiency
   - Intentional contamination and metal removal efficiency using ICP-MS
4. Efficient Passivation Characteristics
   - Timed passivation study with XPS

- Evaluation of the pre-requisites will allow us to set-up guidelines to develop an integrated cleaning process for Ge.

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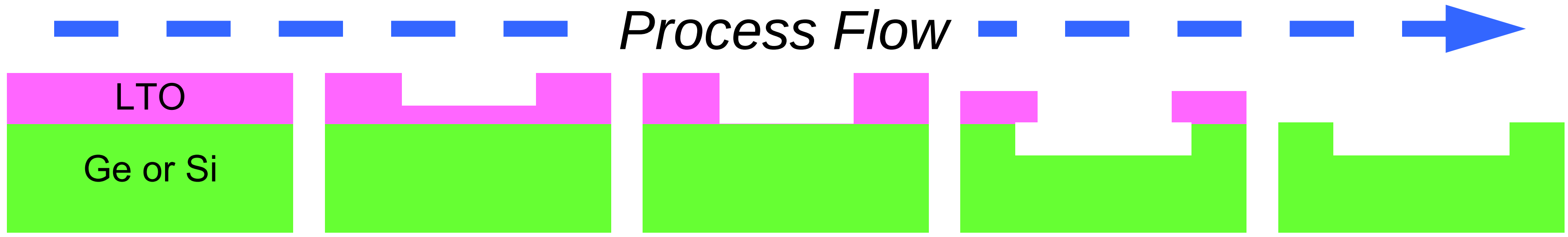
2. Etch Rate Study
3. Surface Roughness Study
4. Surface Passivation Study
5. Metal Removal Efficiency
6. Conclusions

Etch Rate Study



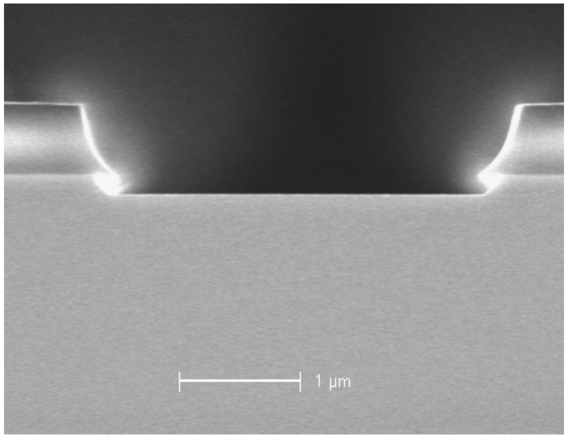
LTO Deposition

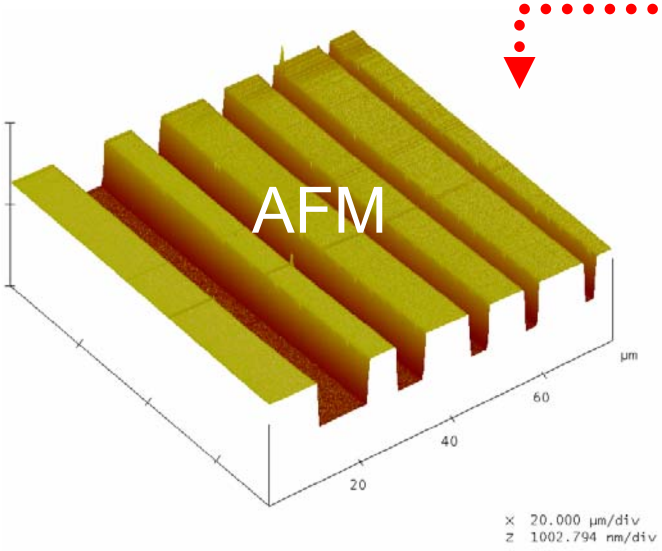
Litho & Dry Etch

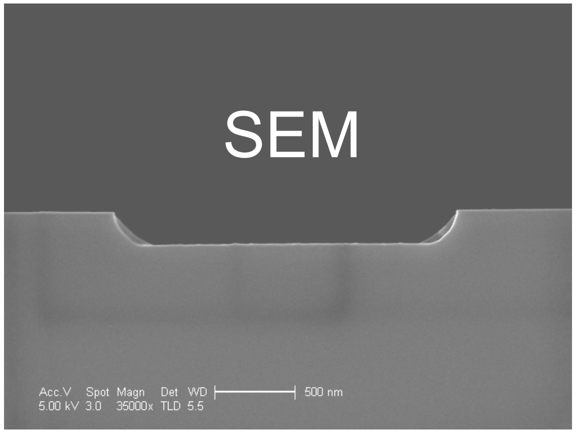
Wet HF(50:1) Etch (selective LTO etch)

Chemical etch

LTO Removal & Step Height Measurement

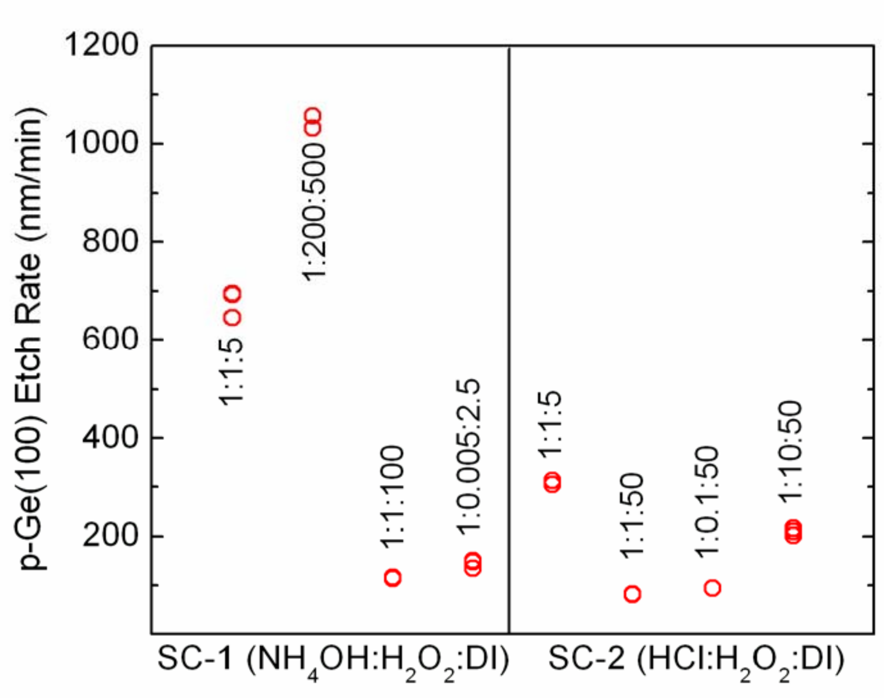


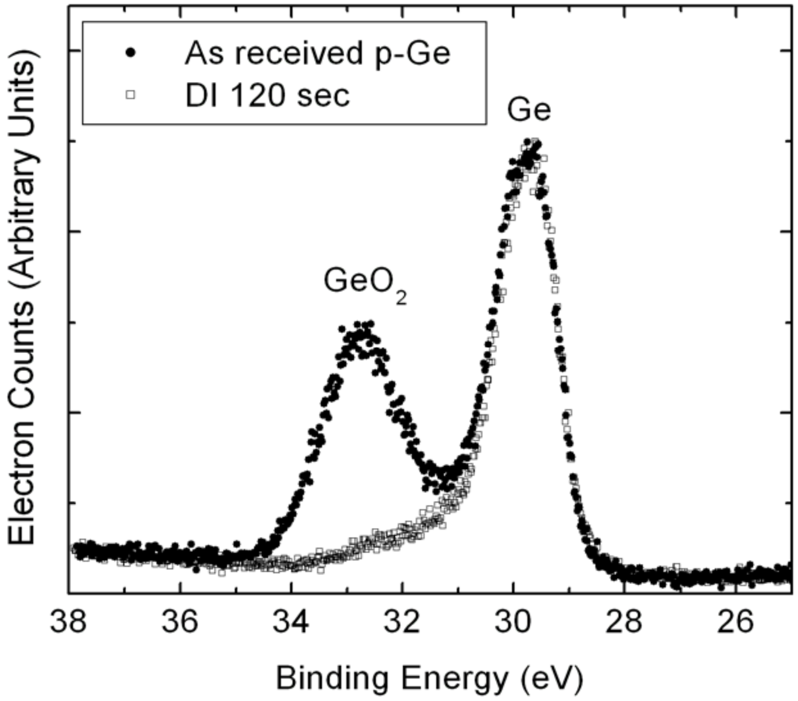




- Templates were used to measure etch rates by AFM and SEM

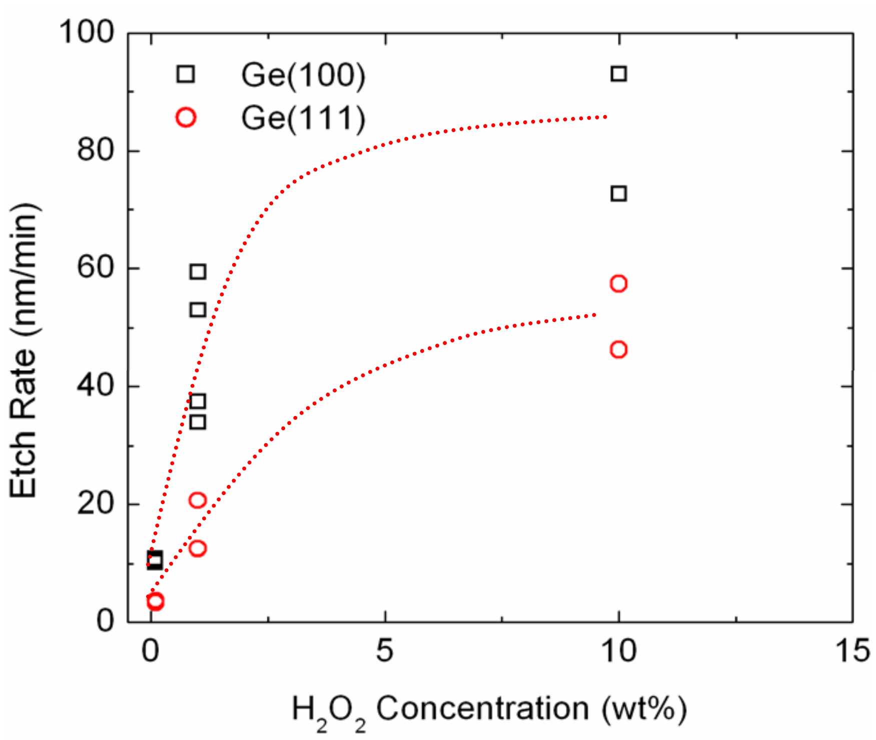
Etch Rate Study

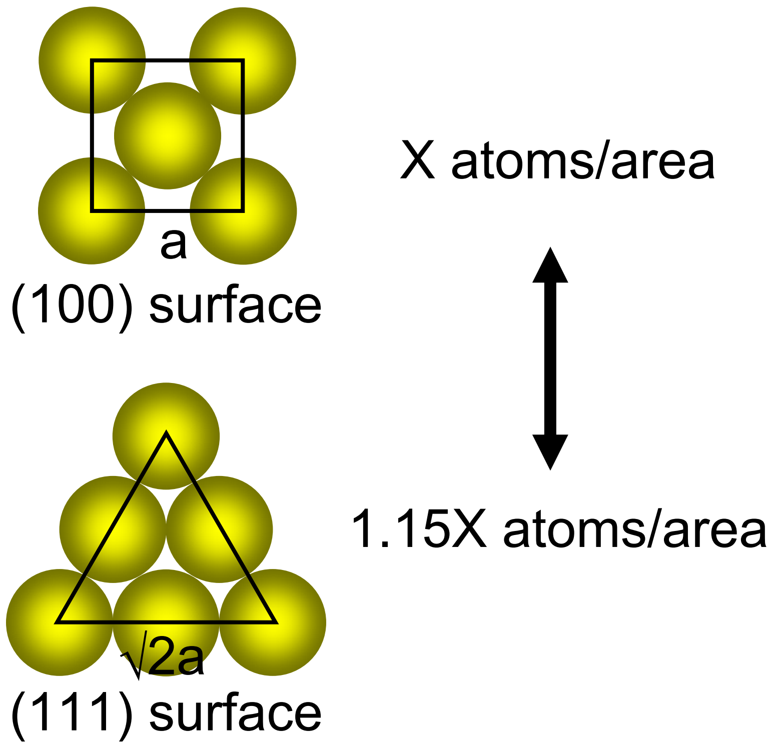




- ▶ High etch rates are observed for room temp SC-1 & SC-2. This is due to the fact that GeO_2 is soluble in DI. XPS study reveals that GeO_2 dissolves in DI water.

Etch Rate Study





- High etch rates are observed for H_2O_2 and saturates at high conc. H_2O_2 oxidizes the surface and DI water etches the formed oxide. For minimum consumption and etch controllability, very dilute H_2O_2 need to be studied. Ge(111) has lower etch rates than Ge(100).

Etch Rate Study - Conclusions

1. Ge has very high etch rates in oxidizing aqueous cleaning solutions (700 nm/min in 1:1:5 SC-1 @room temp)
2. Ge has negligible etch rates in DI water. (0.007nm/min)
3. GeO_2 is soluble in DI water.
4. Ge has concentration & crystallographic dependent high etch rates in H_2O_2 solutions.

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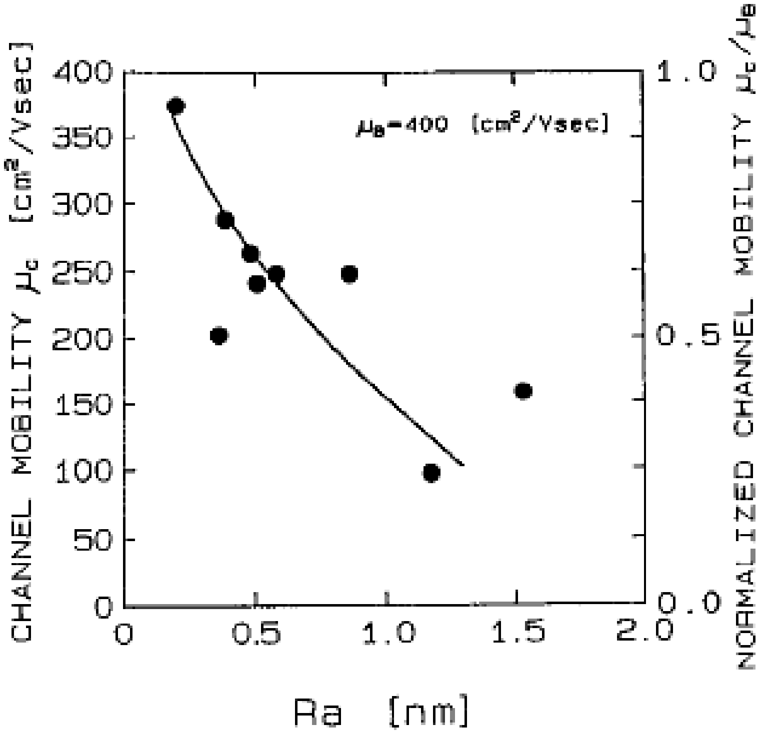
Surface Roughness

- Surface Roughness Effects

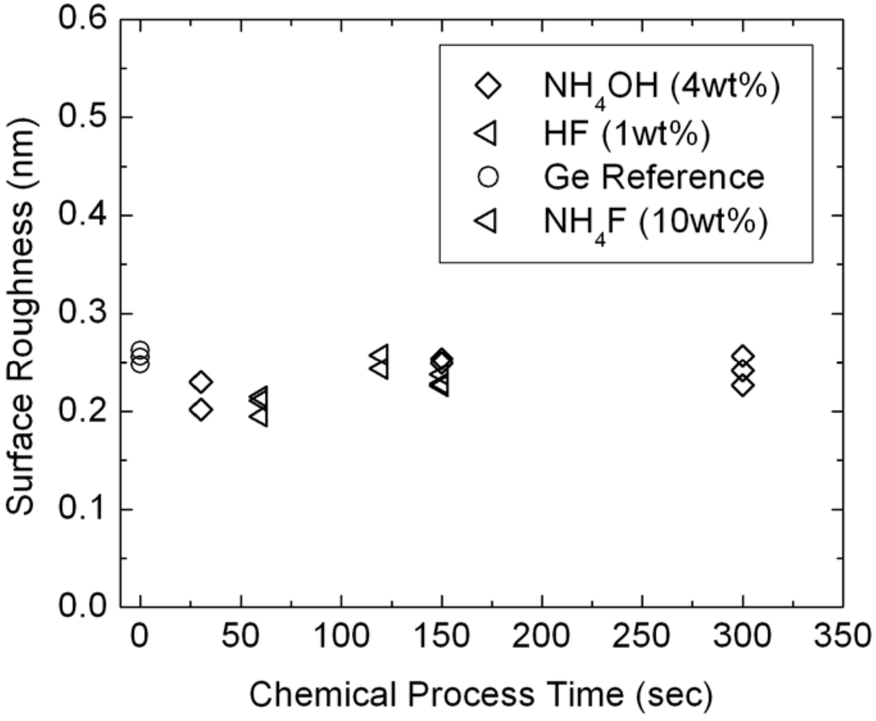
1. Degradation of mobility
2. Q_{bd} degradation
3. Metrology difficulties (unable to distinguish between particles and surface roughness)

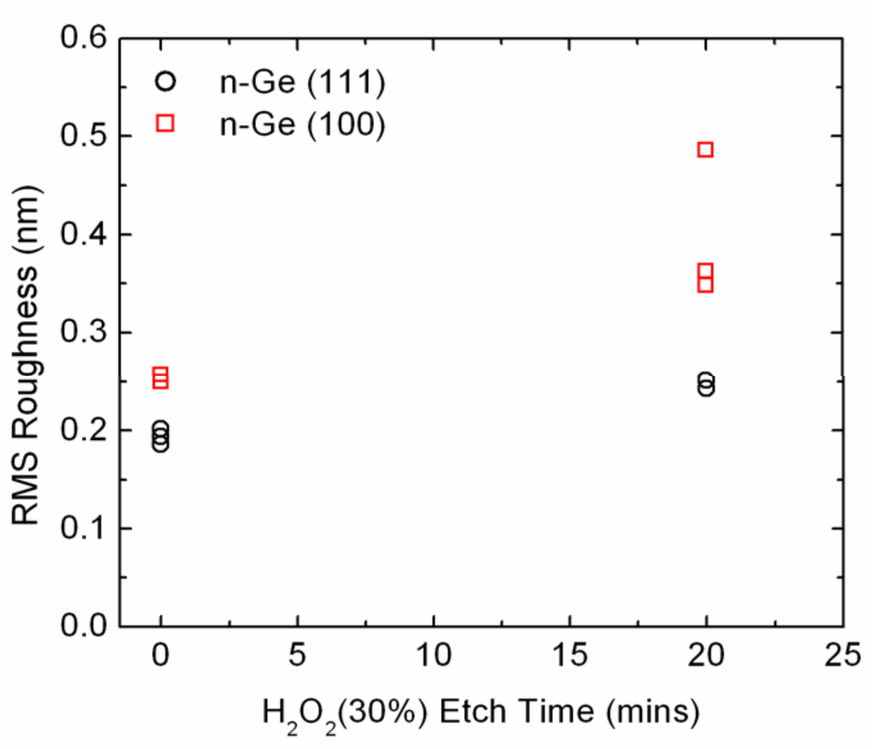


Degradation of Mobility due to surface roughness

(Ohmi et al, *IEEE Trans. on Electron. Devices* (1992))

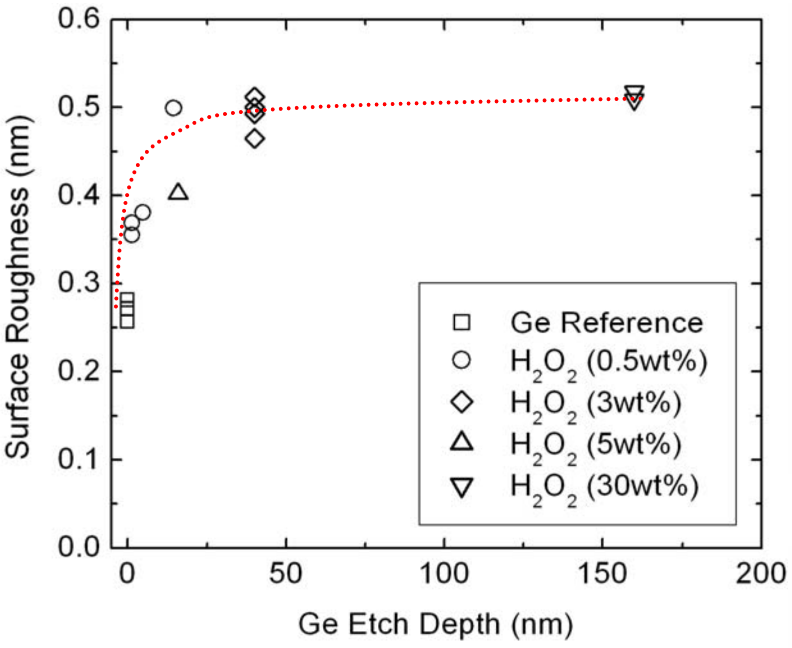
Surface Roughness



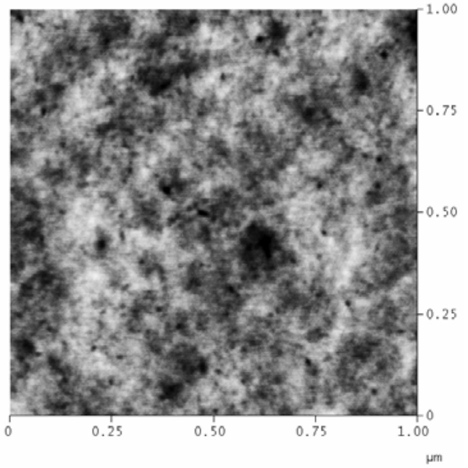


- Surface roughness does not increase in non-etching solutions (NH_4F, HF, NH_4OH and DI water). Surface roughness can be minimized by minimizing the etch amount.
- Surface roughness is direction dependent. Ge(111) has lower surface roughness than Ge(100)

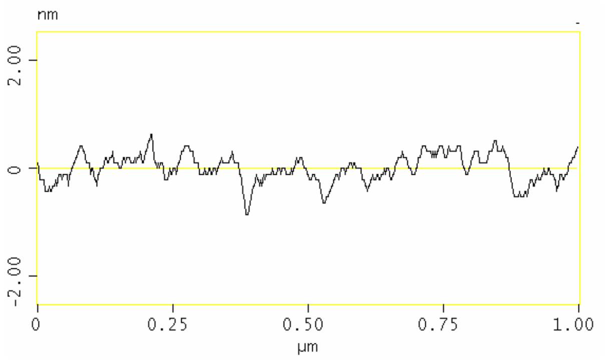
Surface Roughness



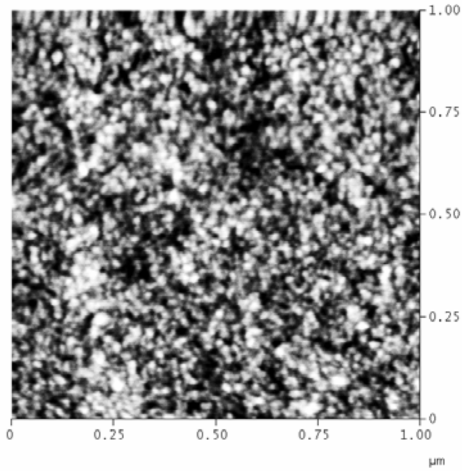
- Surface roughness increases with etch amount and saturates at a steady state value of 0.5nm.



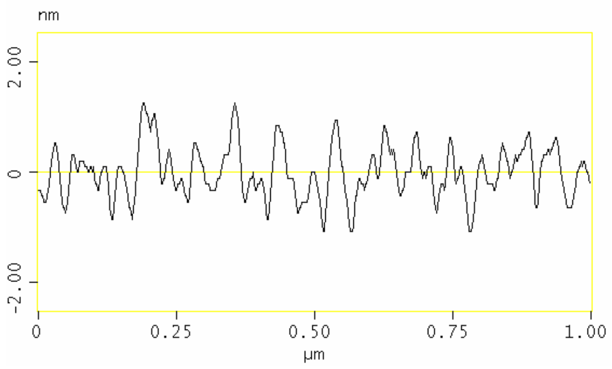
As received Ge



Cross-section

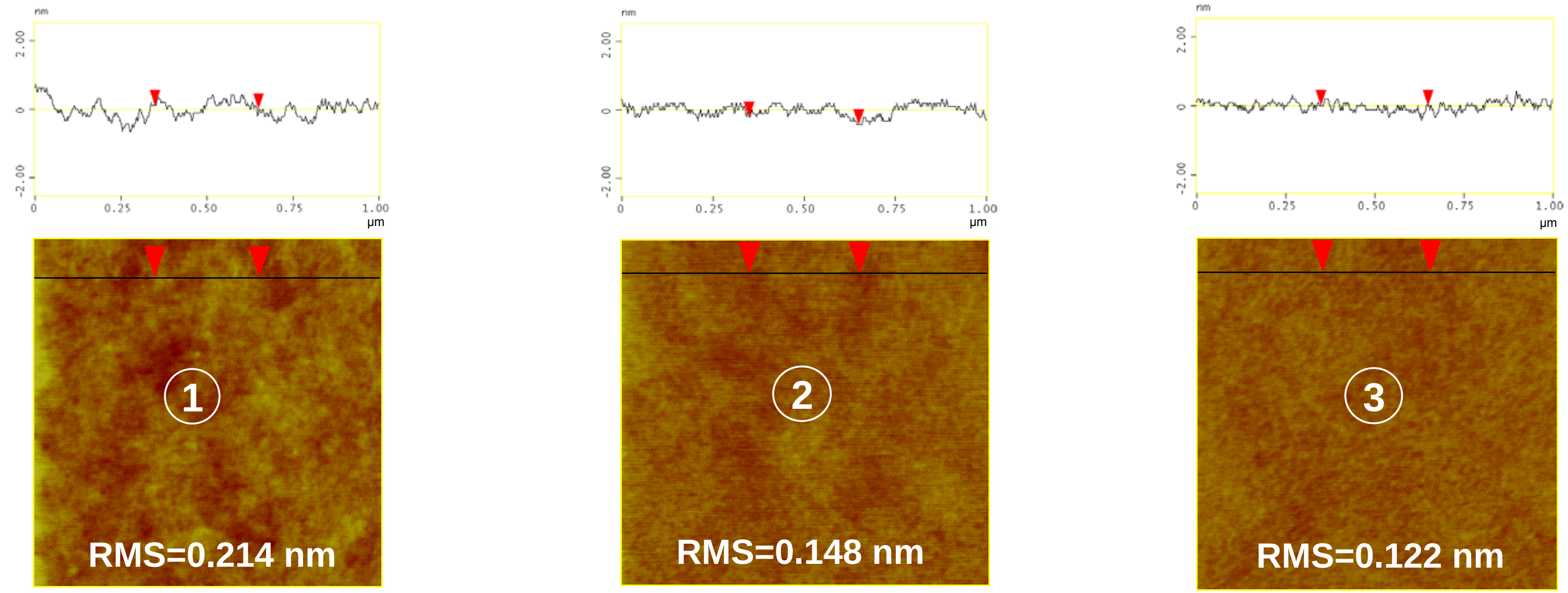


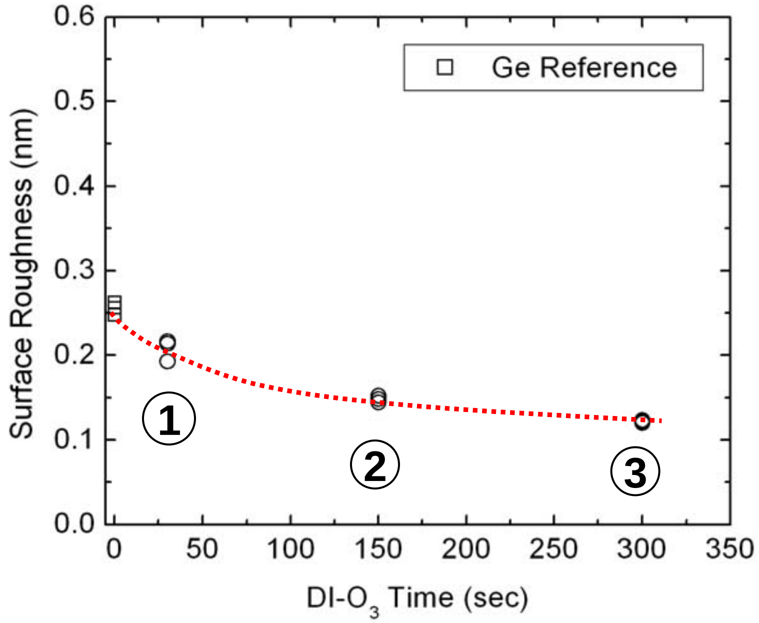
H_2O_2(3wt%) 10min



Cross-section

Surface Roughness





- Surface roughness decreases with time in DI-O_3 (ozonated DI). Similar phenomenon observed with ozone processes for Si surfaces

(*Tardiff et al, Solid State Phenomena (1999)).*

DI-O_3 Process

1. DI-O_3 10”(organic removal)
2. DHF 60” (native oxide removal)
3. DI-O_3 Process (oxide re-growth)

Surface Roughness - Conclusions

1. Surface roughness increases with etching amount in H_2O_2 and saturates at RMS=0.5nm.
2. Surface roughness increases with etching amount and does not change in non-etching solutions such as HF, NH_4F, NH_4OH and DI (0.007 nm/min).
3. Surface roughness is less for Ge(111) crystallographic direction.
4. Surface roughness decreases with DI-O_3 process time and reaches that of prime Si wafers (RMS=0.12nm).

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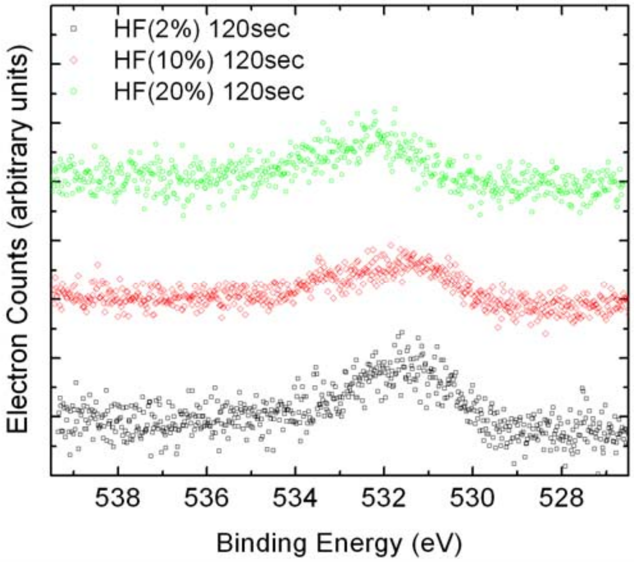
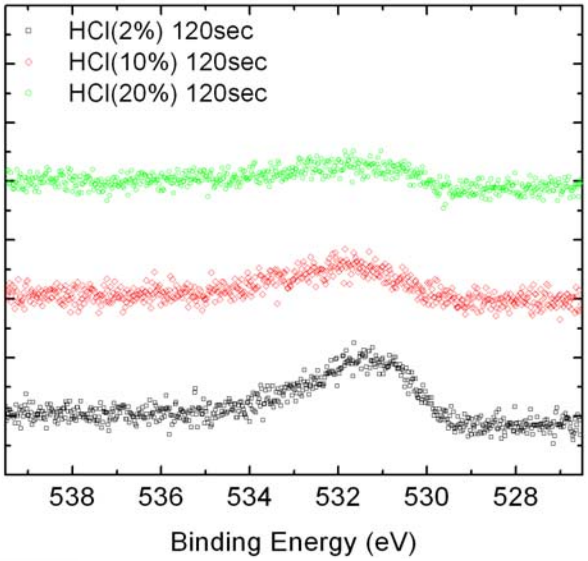
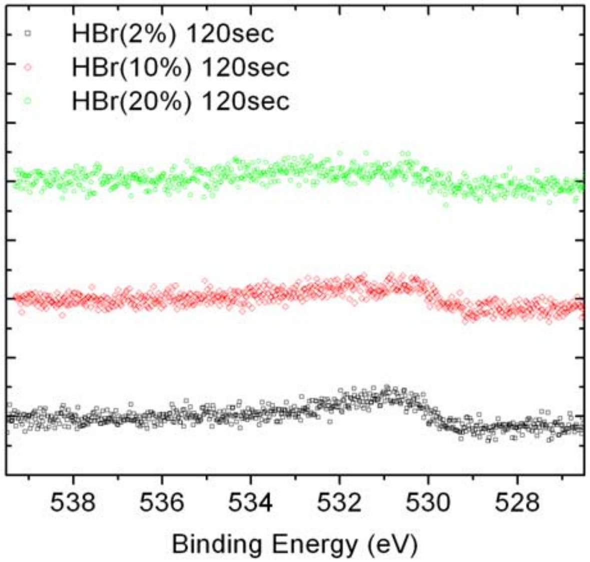
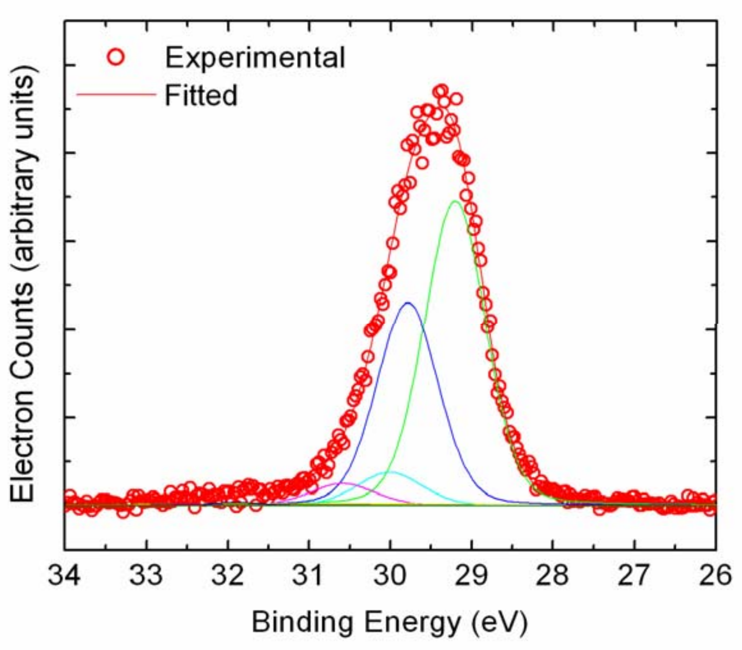
Surface Passivation



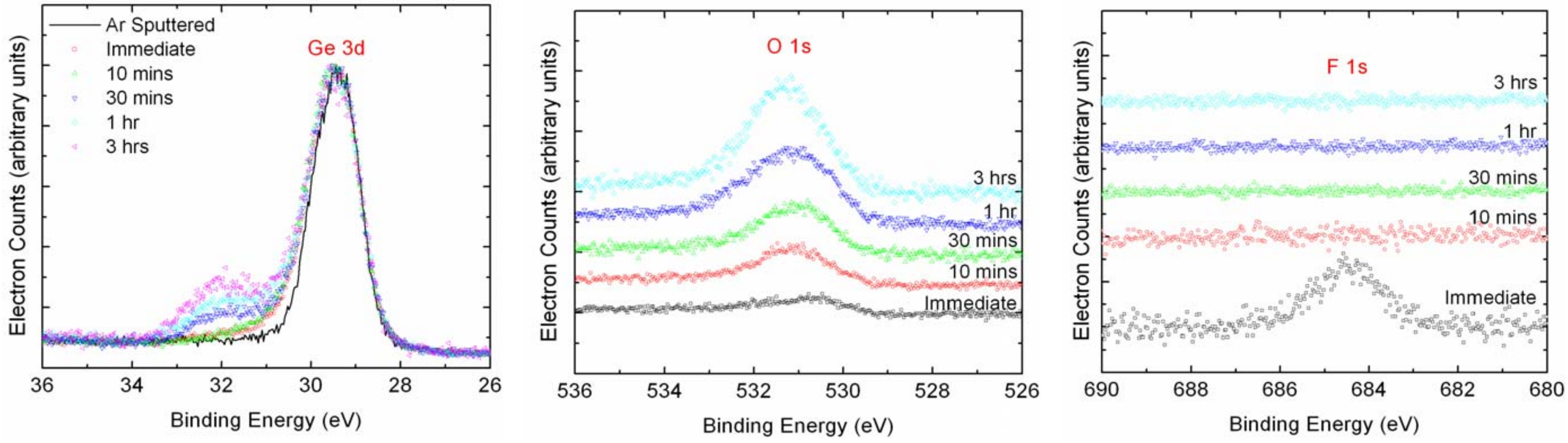




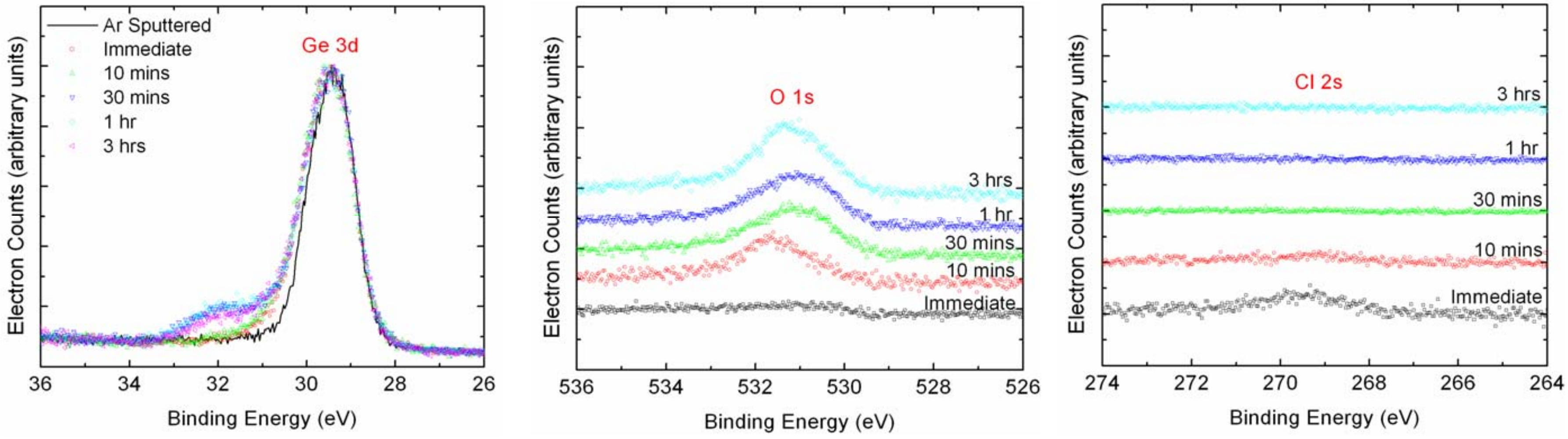


- ▶ Higher concentration solutions removes more oxide from the surface.
- ▶ HF cannot completely remove oxygen species on Ge.

Ambient Stability of HF & HCl Treated Surface

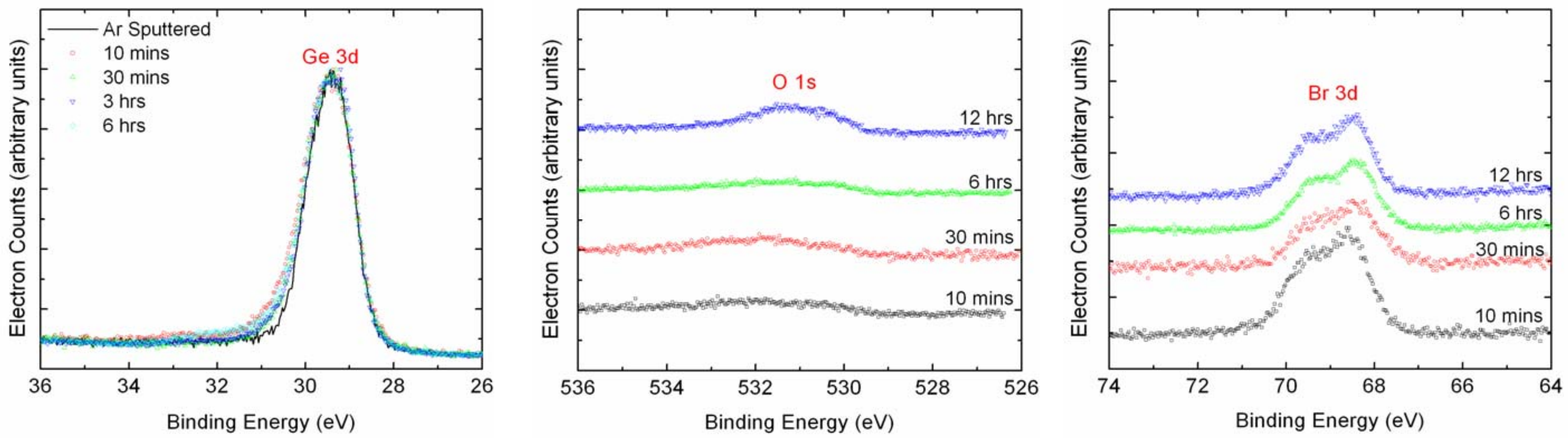


- HF treated surface re-oxidizes in 10 mins. (desorption of fluorine)

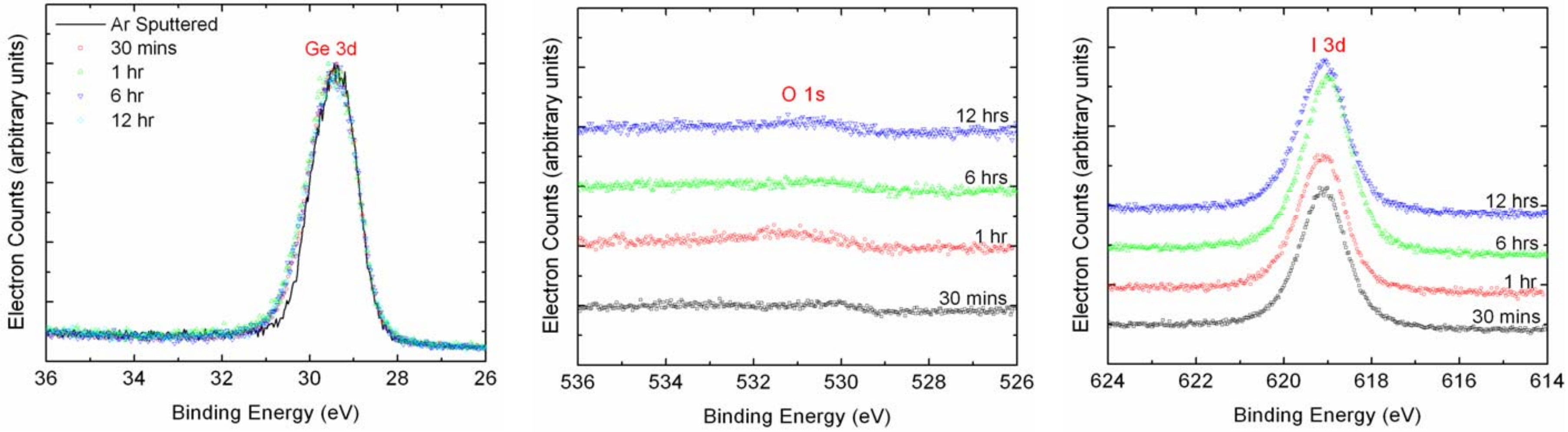


- HCl treated surface re-oxidizes in 10 mins. (desorption of chlorine)

Ambient Stability of HBr & HI Treated Surface



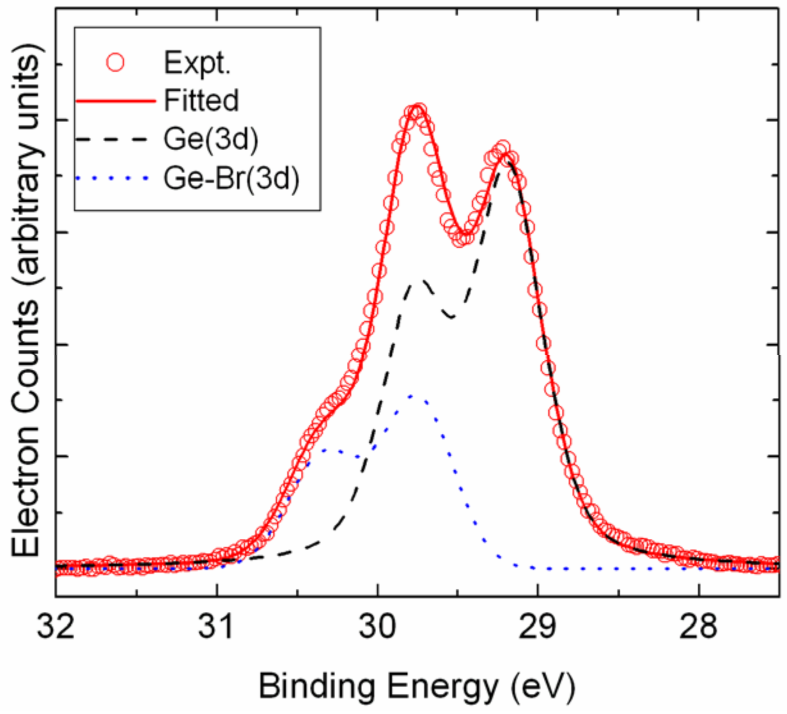
- ► HBr treated surface stays passivated for 6 hours.



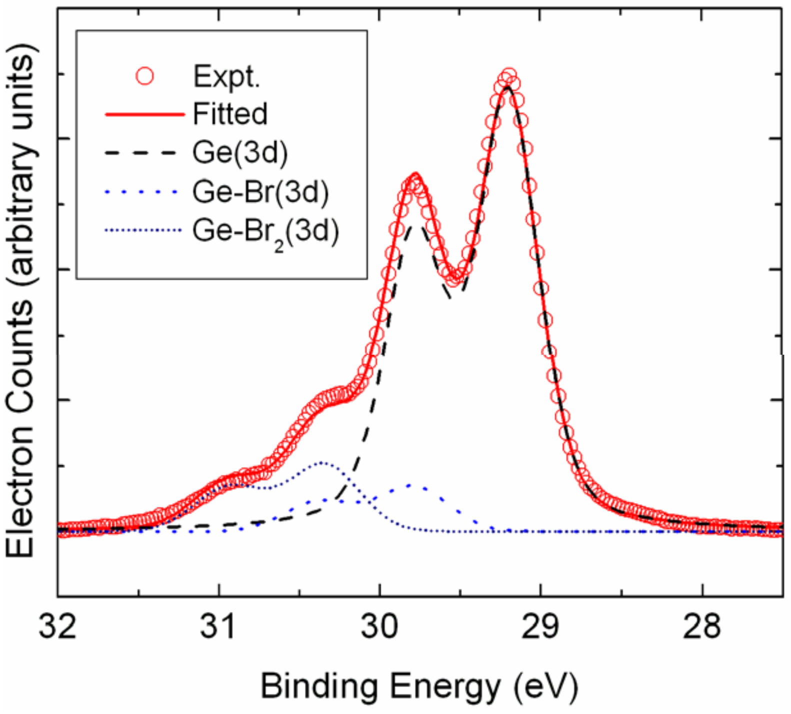
- ► HI treated surface stays passivated for 12 hours.

Synchrotron XPS Study of HBr Treated Surfaces

p-Ge(111)



p-Ge(100)



- Ge surfaces are bonded to either 1 or 2 Br atoms depending on the crystallographic direction. Quantitative calculation show that the surface dangling bonds are passivated by the Br atoms.

(Beam Energy = 80eV)

Surface Passivation – Conclusions

1. Higher concentration solution of HCL, HBr and HI remove more oxide from the surface. Concentrated HF leaves behind a sub-oxide layer.
2. HBr & HI passivation of Ge(100) is stable up to 6 hrs & 12 hrs in ambient, respectively .
3. Synchrotron XPS results show that Br passivates the dangling bonds of the Ge(100) and Ge(111) surfaces,

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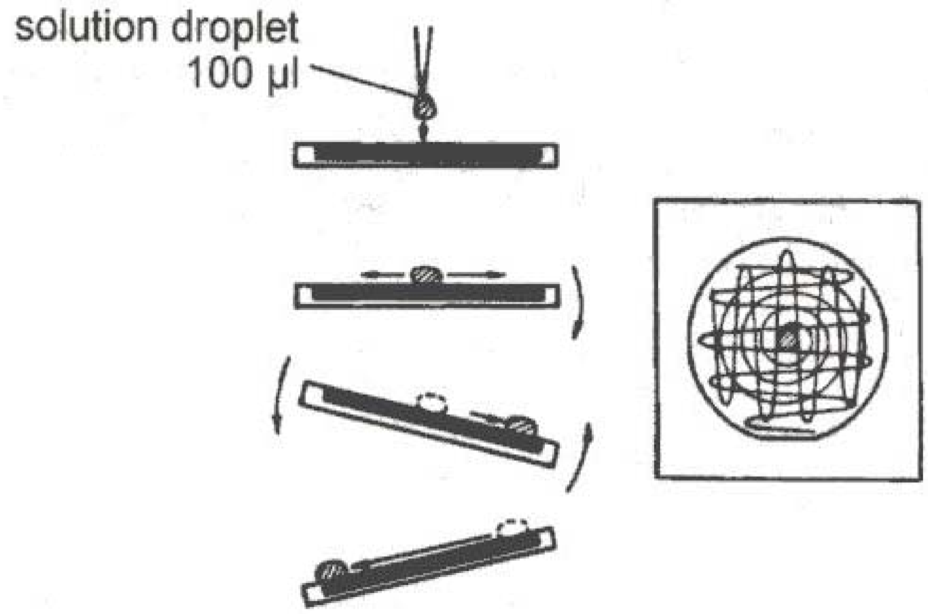
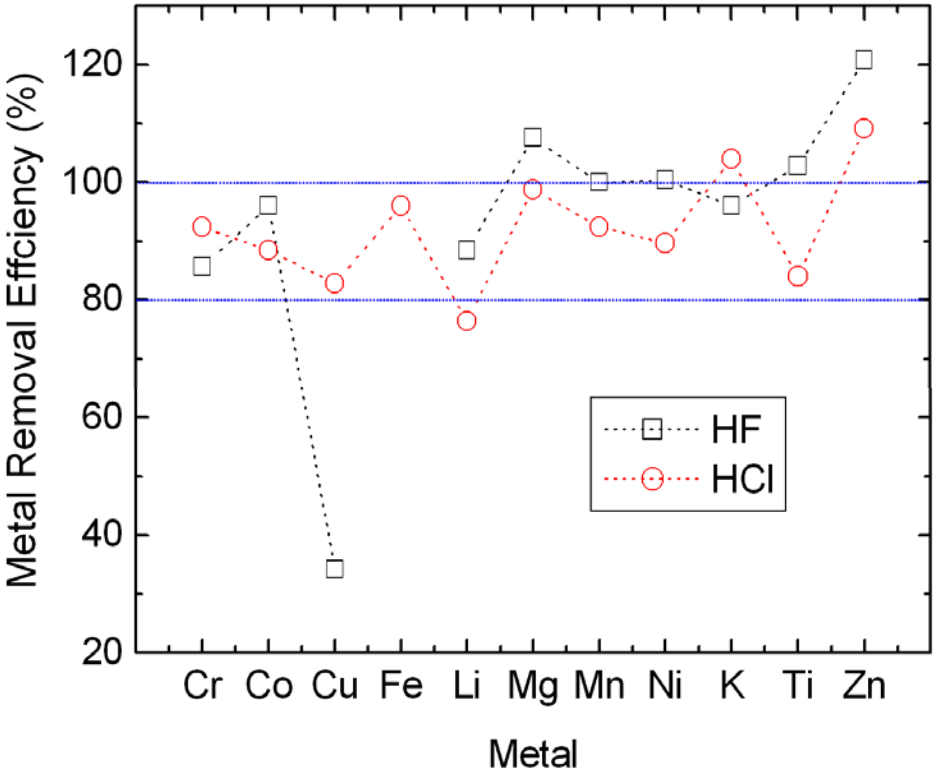
Metal Removal Efficiency – Method



(Ultraclean surface processing of silicon wafers : secrets of VLSI manufacturing / Takeshi Hattori (ed.) (1998))

- Clean Ge wafers were intentionally contaminated and contaminant containing native oxide layer is stripped by a cleaning solution droplet allowing one to measure the metal removal efficiency of a particular solution.

Metal Removal Efficiency – Results & Conclusion



- Both HF and HCl metal removal efficiencies of greater than 80%. Both HF and HCl is efficient in removing metals from the surface but previous XPS results show that HCl can completely remove the sub-oxide and is relatively more stable in ambient than HF.

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Conclusions

1. Ge has crystallographically dependent high etch rates in oxidizing (H_2O_2) aqueous cleaning solutions.
2. RMS surface roughness increases with etching amount in H_2O_2 and saturates at 0.5nm.
3. Surface smoothening effect is observed in DI-O_3 solutions.
4. HBr & HI is effective in passivating Ge(100) surface up to 6 hrs & 12 hrs in ambient, respectively.
5. HCl is a promising candidate in effectively removing metal contamination from Ge surface.

Future Works

1. Using the results from the individual experiments; optimization of a fully integrated process looking at the substrate consumption, metal removal efficiency, surface roughness and surface passivation.
2. Effect of cleaning on the electrical properties of the gate stack on Ge surface.