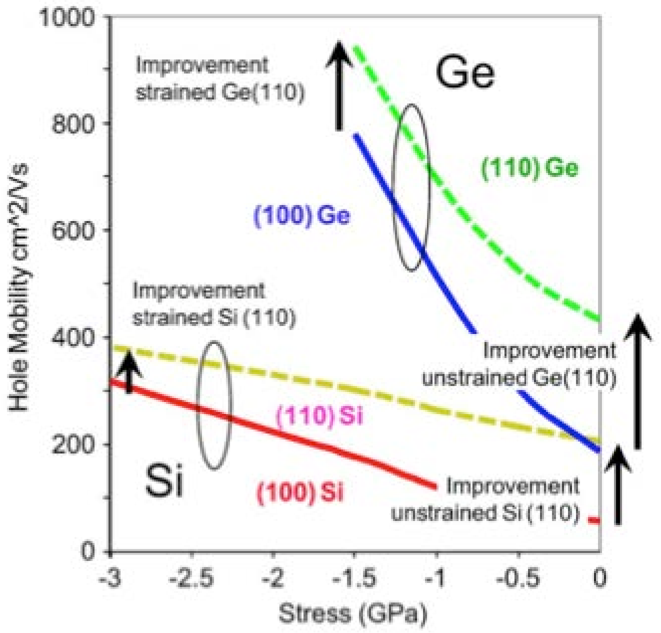
A Comparison of Sulfur-Based Chemistries to Passivate the (100) Surfaces of SiGe 25% and 75%

Zhonghao Zhang, Stacy L. Heslop, and Anthony J. Muscat

Department of Chemical and Environmental Engineering
University of Arizona, Tucson, Arizona, 85721

Contact Info:
muscat@email.arizona.edu
520-621-6162

Prospect and Challenge on SiGe



K.J. Kuhn, *IEEE Trans. Electron Devices*, **59**(7), 1813 (2012)

Prospect:

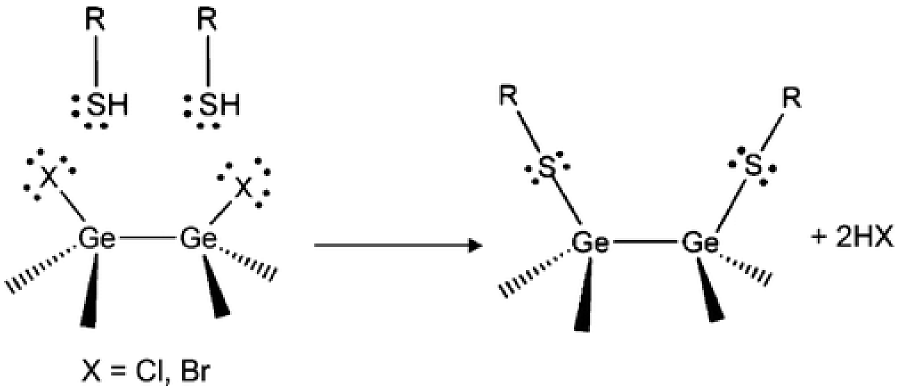
- Bandgap and carrier mobility of SiGe alloys can be tuned by varying Ge content.
- SiGe can be more easily integrated into Si processes.

Challenge:

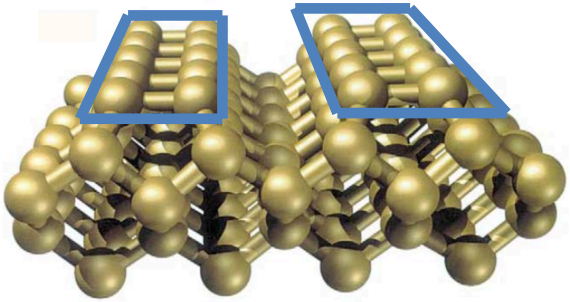
Unstable Ge oxides formed on SiGe surfaces are detrimental to device performance.

Solution:

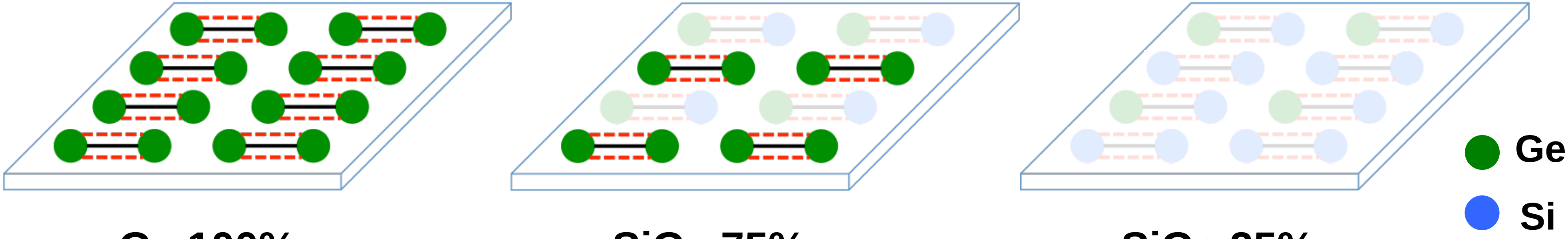
Passivate Ge and SiGe with Sulfur



P. Ardalan *et al.*, *Langmuir*, **26**(11), 8419(2010)



Ge (100) Surface



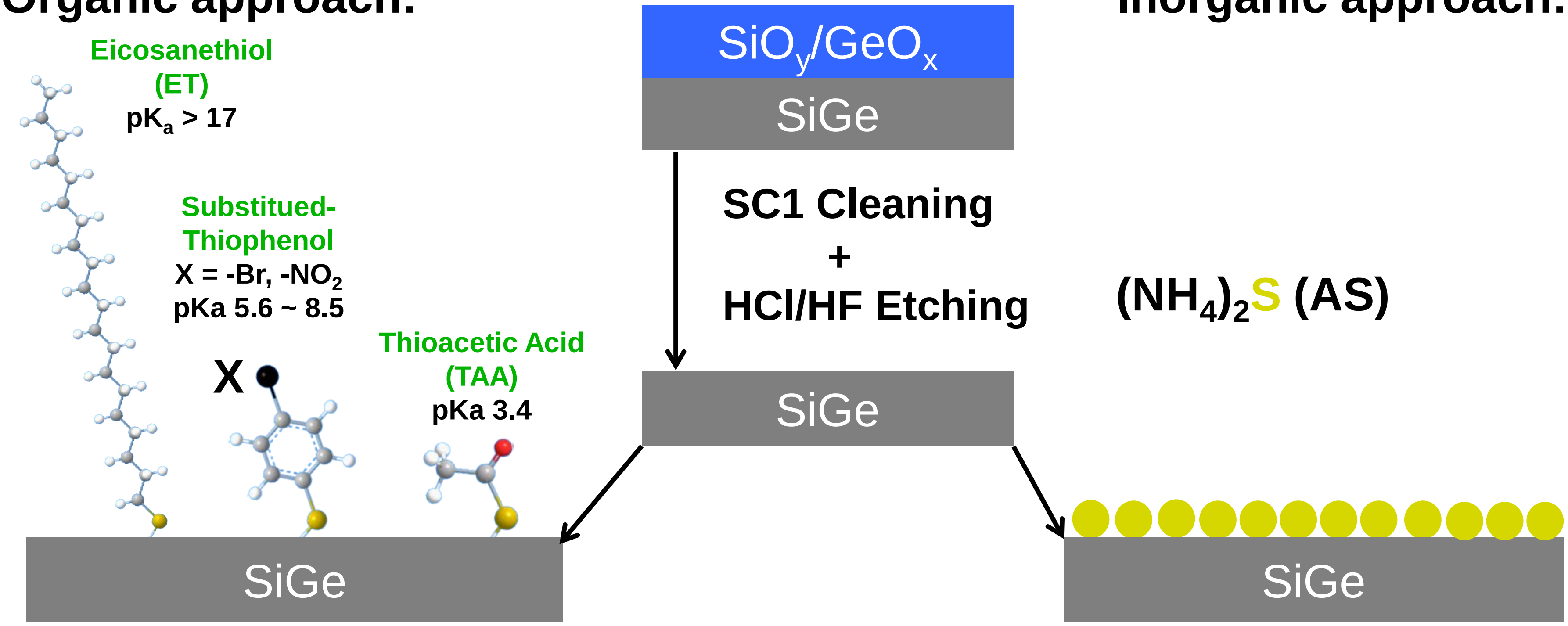
Ge 100% **SiGe 75%** **SiGe 25%**

Goal: Explore sulfur chemistries to passivate SiGe 25% and 75% surface.

- Deposit sulfur on SiGe 25% and 75% (100) surface .
- Avoid surface re-oxidation during chemical treatment.

SiGe Cleaning and Passivation Strategy

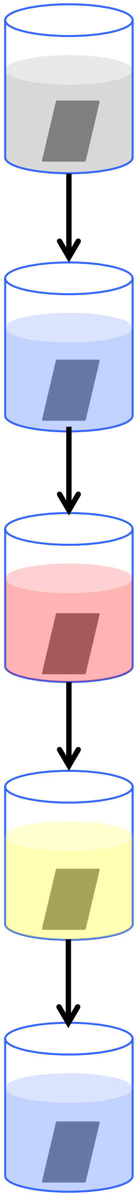
Organic approach: **Inorganic approach:**



- **Long-Chain Alkylthiols:**
  Can potentially form a self-assembled monolayer on surface.
- **Low pK_a Thiols:**
  Generate higher concentration of active sulfur species in solution.

Good compatibility with aqueous process.

Experimental Procedures



SC1 Cleaning (25 °C): Immerse sample in SC1 solution (H_2O_2:NH_4OH:Water = 1:1:500) with stirring for 2 min.

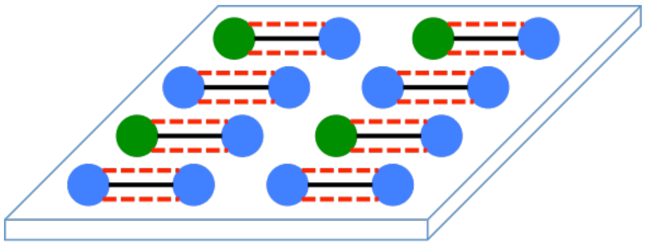
Rinse (25 °C): Immerse sample in ultra pure water for 1 min without stirring. Dry slowly with N_2 afterward.

HF/HCl Clean (25 °C): Immerse sample in HF/HCl solution (HF:HCl:Water = 1:3:300) with stirring for 5 min. No rinse or dry afterward. Immediately immerse sample into passivation solution.

Passivation Treatment (25 °C): Immerse sample in passivation solution with stirring for desired time (24 hr in ET solution, 20 min in AS solutions and low pK_a thiol solutions).

Rinse (25 °C): Rinse the sample in water (for ammonium sulfide passivation) or ethanol (for thiol passivation) for 30 s.

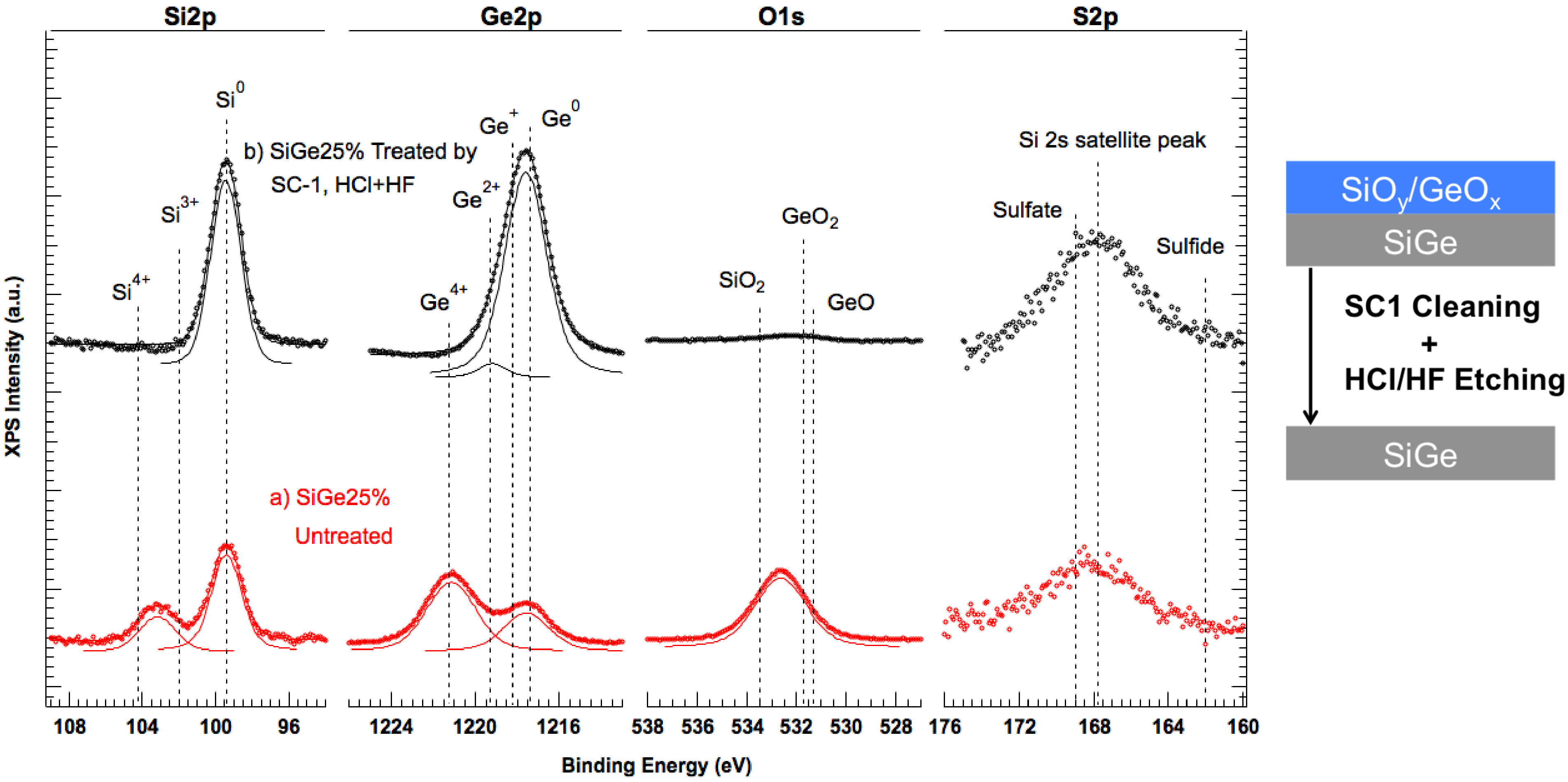
Passivation on SiGe 25% Surface (Inorganic Approach)



SiGe 25%

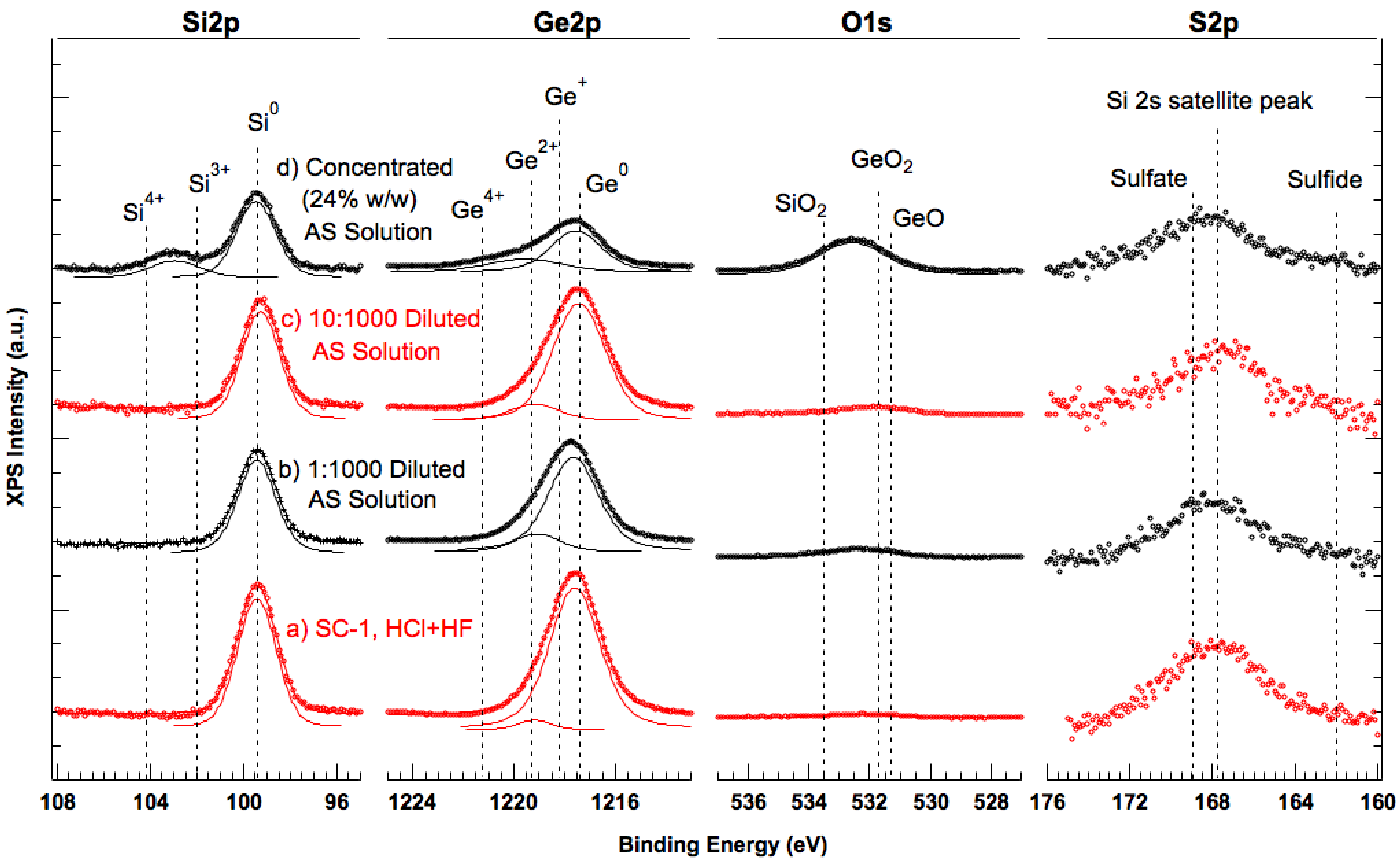
SiGe 75%

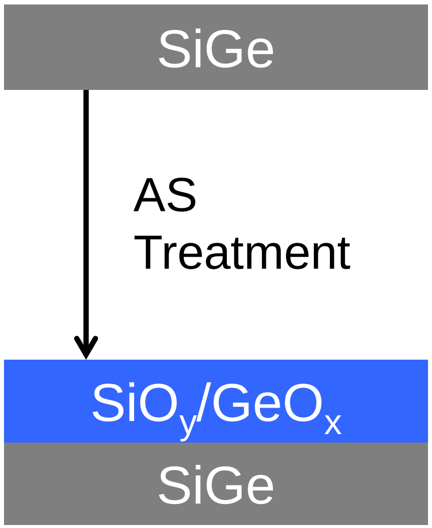
Effect of SC-1 and HF/HCl Cleaning



- Surface oxide was successfully removed by SC-1 cleaning followed by HF/HCl cleaning.

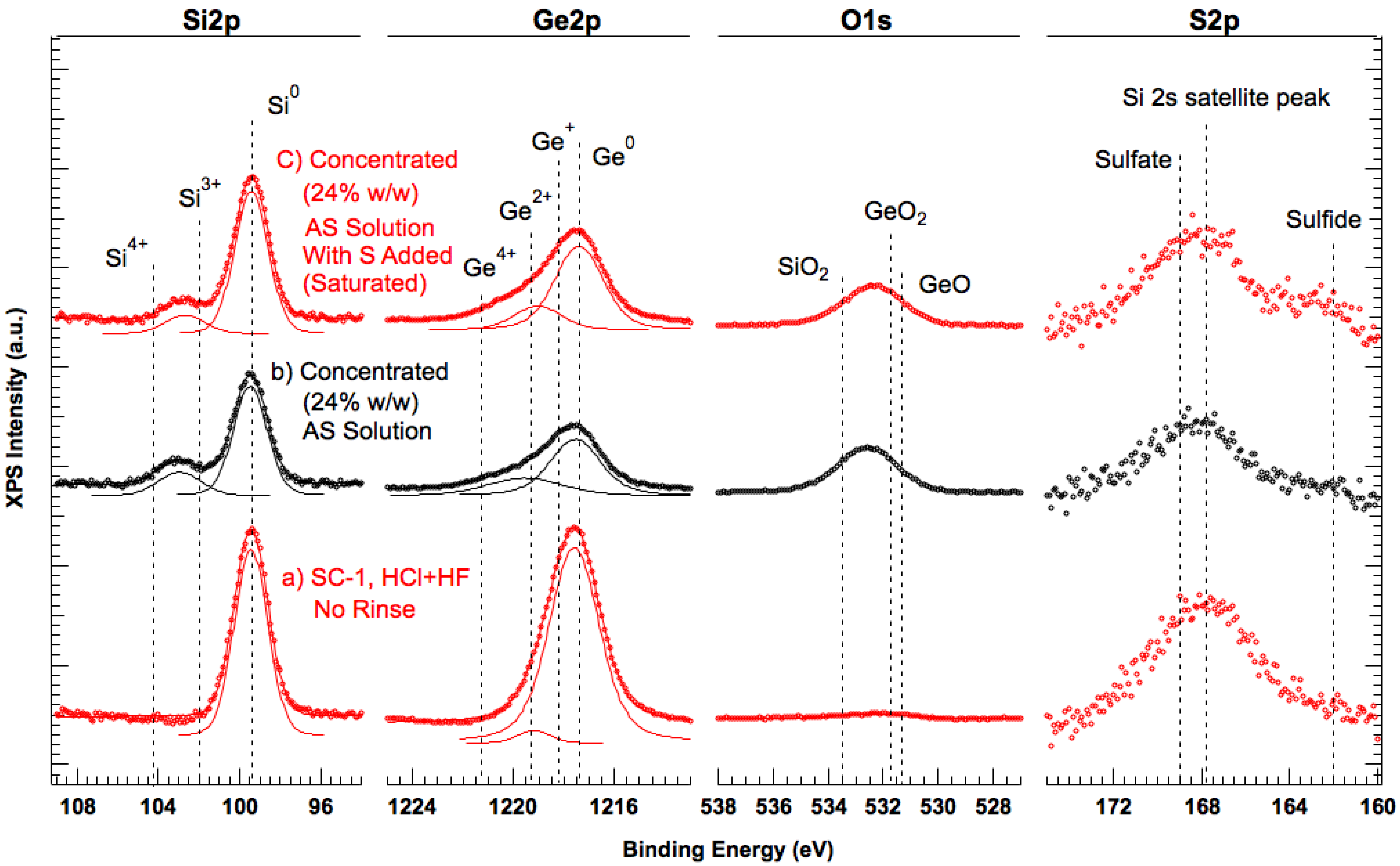
$(NH_4)_2S$ (AS) Treatment (20 min) on SiGe 25%

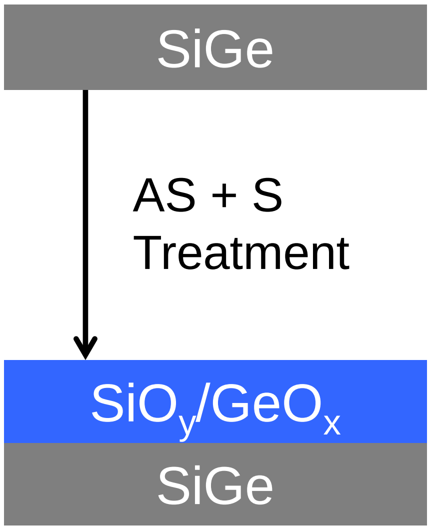




- No covalent Ge-S bond formation was observed.
- Instead of passivation, the surface was re-oxidized during treatment.

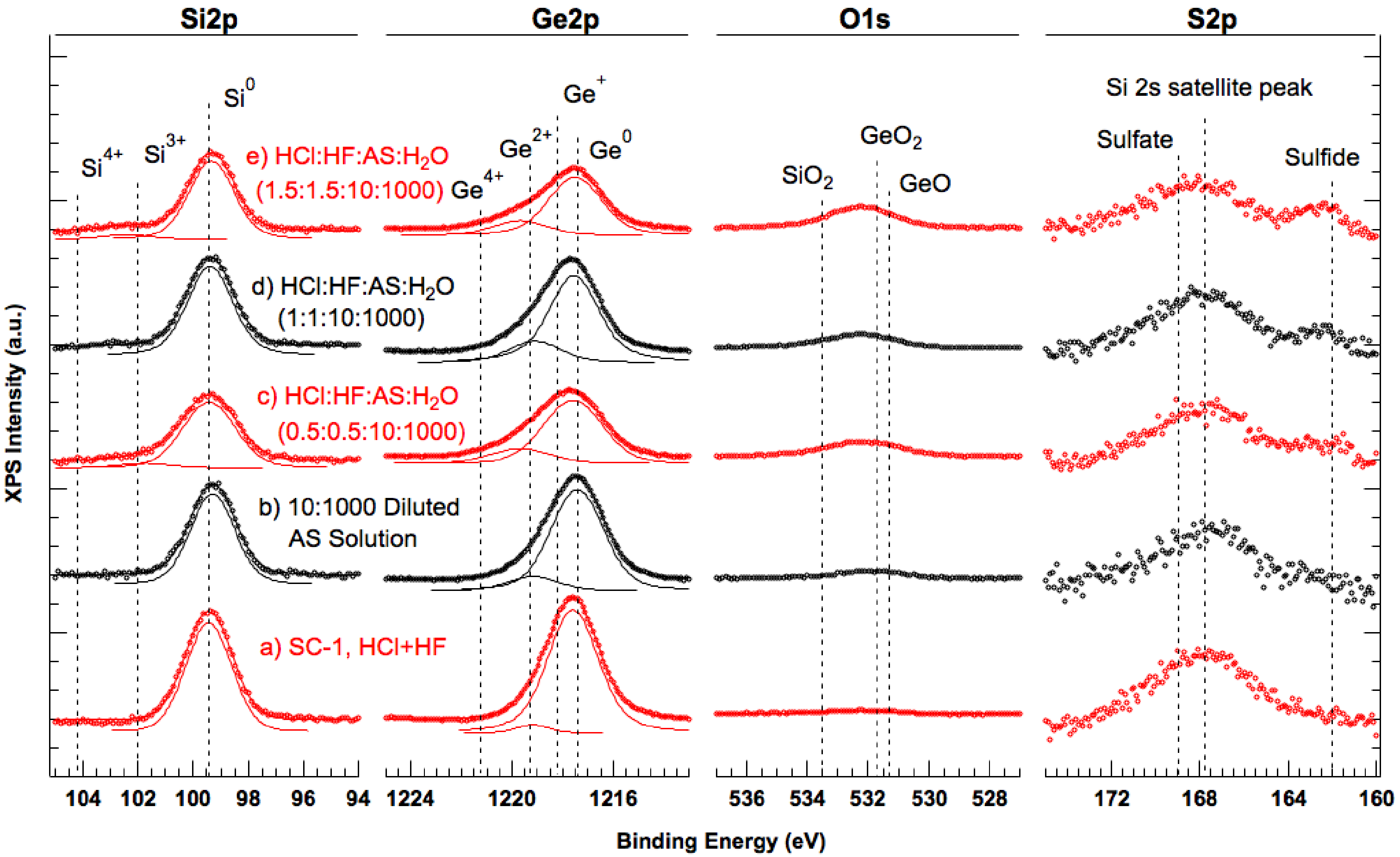
$(NH_4)_2S$ Treatment with Elemental S Added (20 min) on SiGe 25%

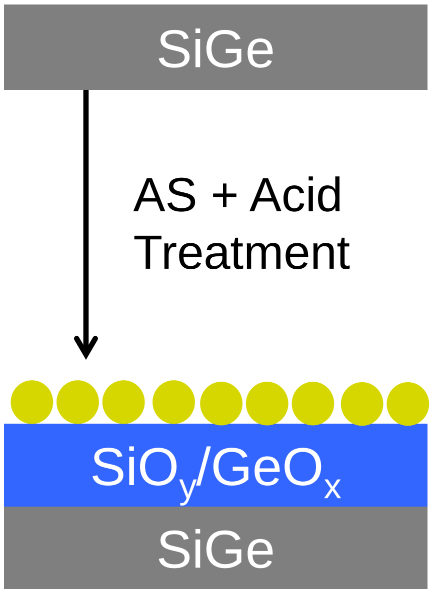




- Very weak sulfide peak was observed in S2p region.
- The surface was re-oxidized during treatment

$(NH_4)_2S$ Treatment with Acid Added (20 min) on SiGe 25%





- Sulfide bond formation was observed.
- The surface was re-oxidized during treatment.

Summary of Inorganic Approach on SiGe 25%

Experiment	**Final Effect**	
	Sulfur Deposition	Surface Re-oxidation
$(NH_4)_2S$ Only	No	Yes
$(NH_4)_2S$ + Elemental S	Minimal	Yes
$(NH_4)_2S + H^+$ (Acid)	Yes	Yes

Sulfur Deposition Hypothesis:

$$(NH_4)_2S + 2H^+ \longrightarrow H_2S + 2(NH_4)^+$$

Surface Re-oxidation Hypothesis:

- **Oxidation of $(NH_4)_2S$ Solution During Storage**

$$2(NH_4)_2S + 2O_2 + H_2O \longrightarrow (NH_4)_2S_2O_3 + 2(NH_4)OH$$

- **Hypothesis: NH_3 Promotes Si Oxidation**

$$(NH_4)_2S \longrightarrow 2NH_3 + H_2S$$

Future Work of Inorganic Approach on SiGe 25%

- **Use aqueous H_2S (prepared by bubbling H_2S into water).**

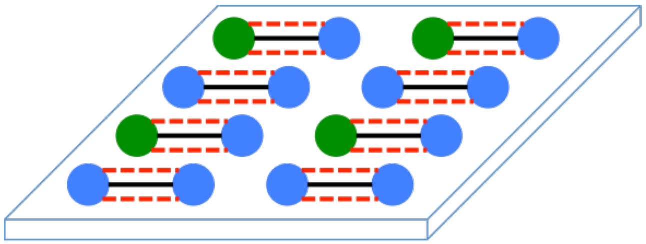
- **Purify ammonium sulfide to remove $(NH_4)_2S_2O_3$:**

$$S_2O_3^{2-} + 2H^+ \longrightarrow S(\text{Solid Precipitate}) + SO_2 + H_2O$$

$$SO_2 + 2S^{2-} + 4H^+ \longrightarrow 3S(\text{Solid Precipitate}) + 2H_2O$$

- **Use alternative sulfide molecules.**

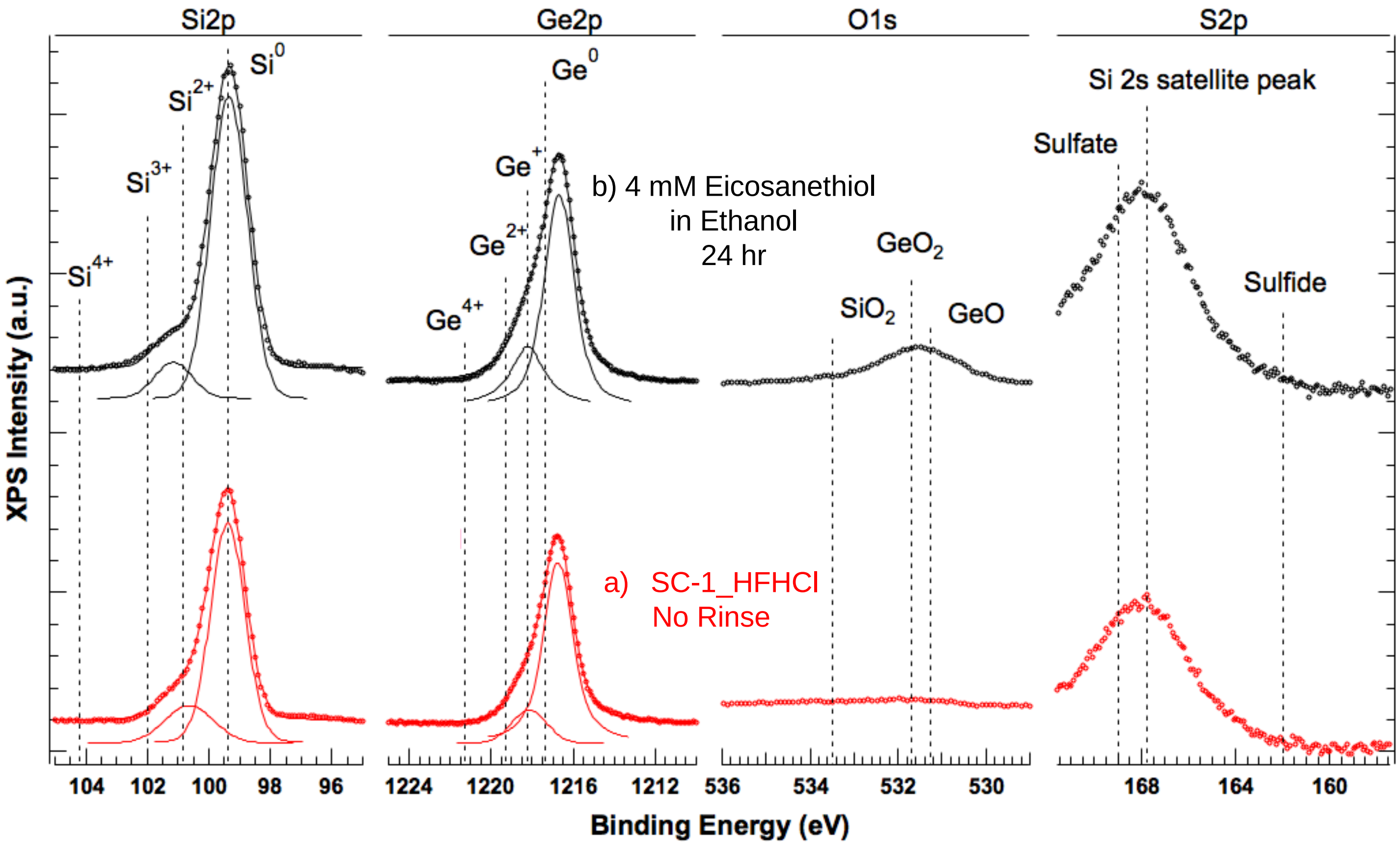
Passivation on SiGe 25% Surface (Organic Approach)



SiGe 25%

SiGe 75%

Long Chained Alkylthiol Treatment (24 hr) on SiGe 25%



Eicosanethiol (ET)
$pK_a > 17$

- ET did not deposit on SiGe 25% surface.
- Surface was re-oxidized during treatment.

S-H Bond Dissociation and pK_a of Thiol Molecules

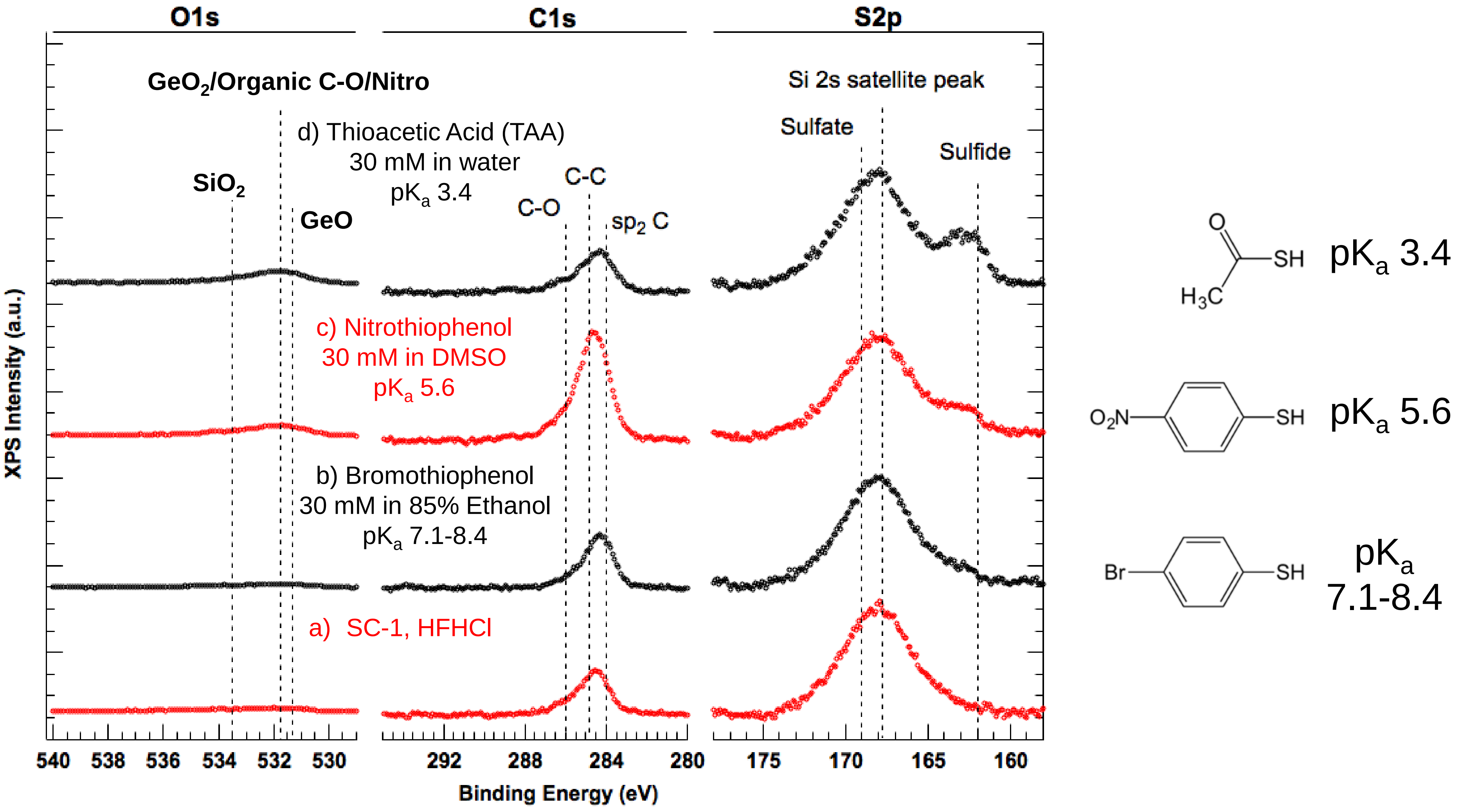
$$\underset{\text{(Thiol Molecule)}}{R\text{-}SH} \longrightarrow \boxed{R\text{-}S^-} + H^+$$

Active Species for S Deposition

$$K_a = \frac{[RS^-][H^+]}{[RSH]} \qquad pK_a = -log_{10}K_a$$

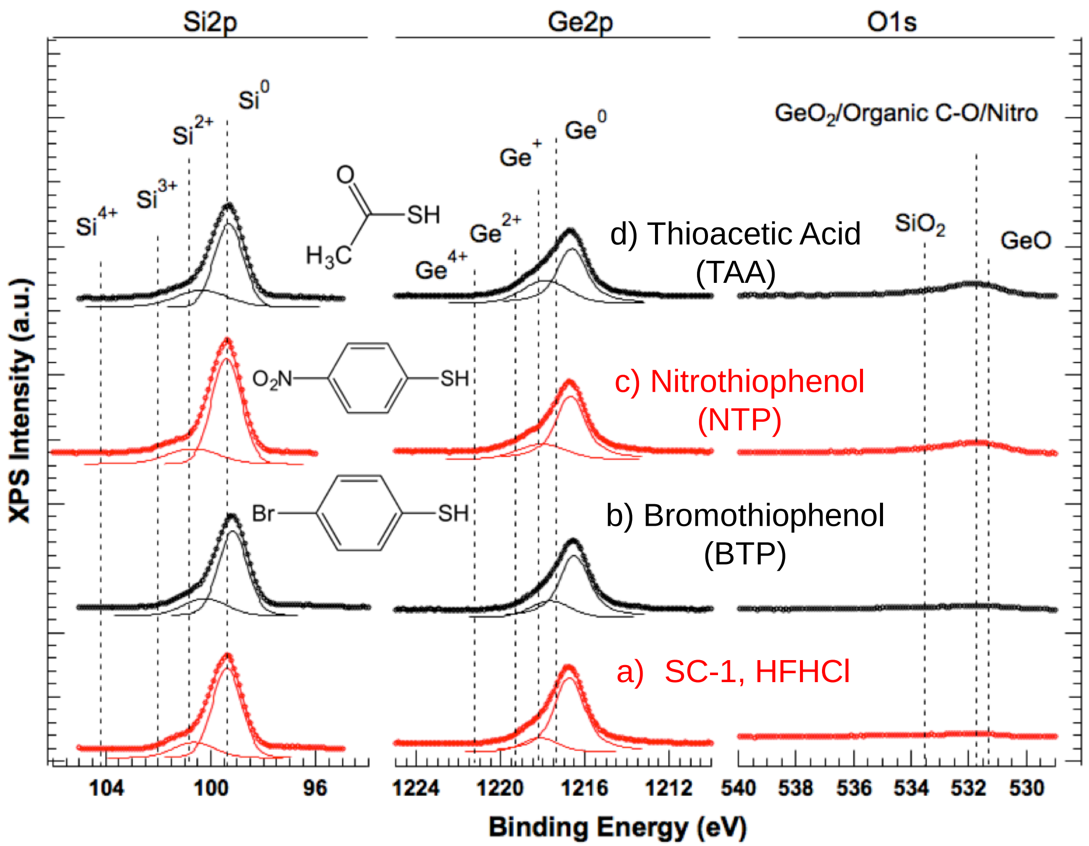
- **Thiol molecules with lower pK_a values have higher tendency for S-H bond dissociation.**
- **Higher tendency of S-H bond dissociation can potentially facilitate Ge-S bond formation.**

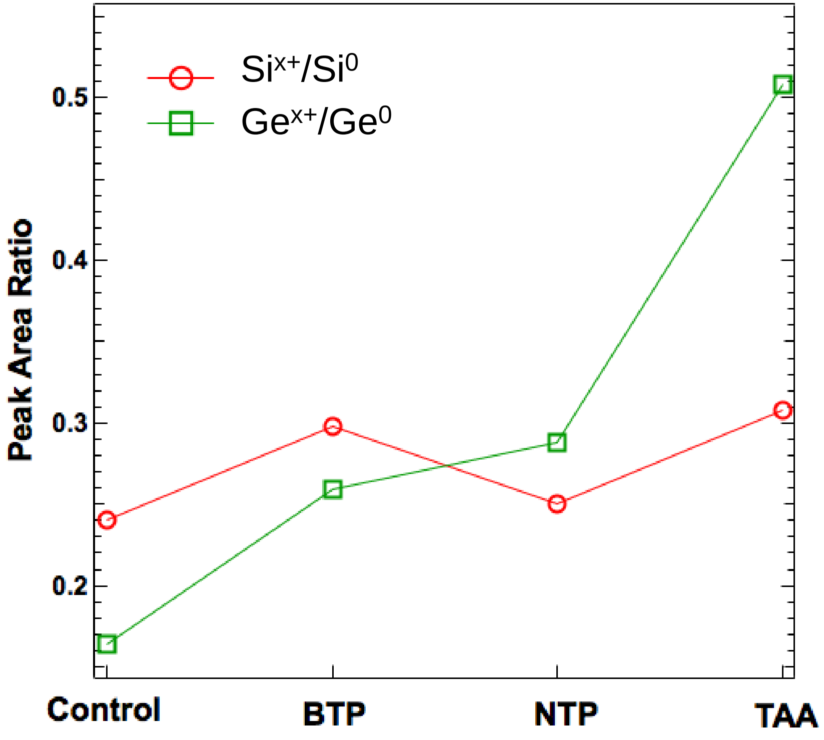
Low pK_a Thiol Treatment (20 min) on SiGe 25%



- Thiol molecules with lower pK_a values deposited more S on SiGe 25%.
- Oxygen was observed after treatment.

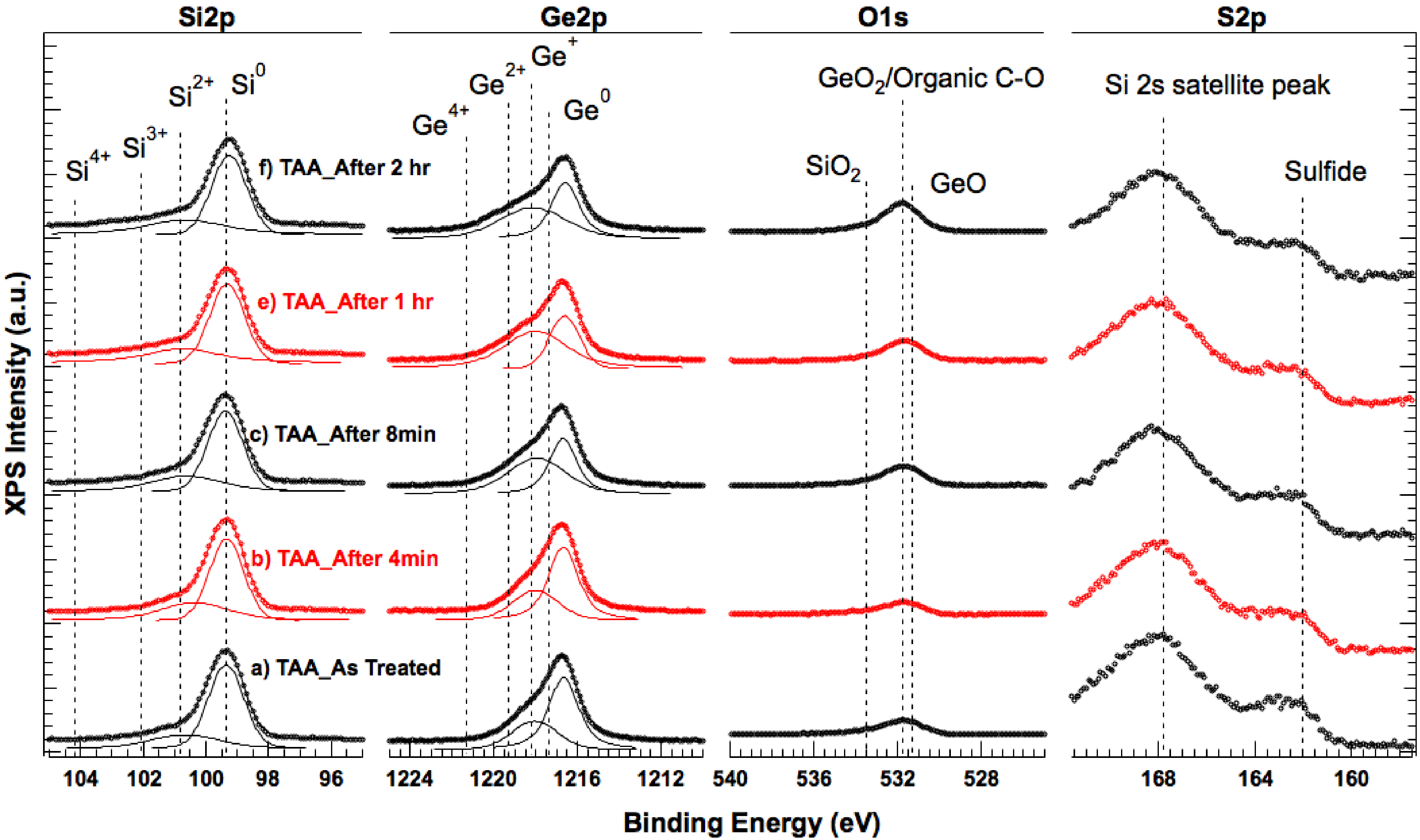
Where did the Oxygen Come From





- Oxygen mainly came from oxygen containing groups in thiol ligands.

Surface Re-Oxidation on TAA Treated SiGe 25%



- Surface was re-oxidized over time after treatment.
- The short chain of TAA cannot protect the surface.

Conclusion of Organic Approach on SiGe 25%

- **Long alkyl chain eicosanethiol (ET) did not deposit on SiGe 25% surface even after prolonged (24 hr) treatment, possibly due to its high pK_a value.**

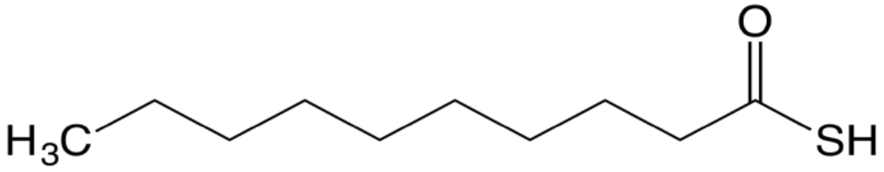
- **Thiol molecules with lower pK_a values more efficiently deposited onto SiGe 25% surface.**

- **Thioacetic acid (TAA) did not protect SiGe25% surface against oxidation after treatment, possibly due to its short carbon chain.**

Future Work of Organic Approach on SiGe 25%

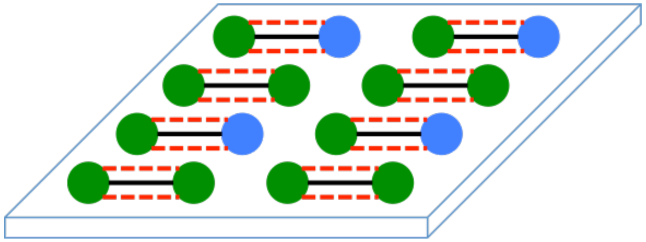
- **Study surface re-oxidation on nitrothiophenol (NTP) treated SiGe 25% surface.**

- **Explore low pK_a thiol molecules with long alkyl chain, which can both effectively deposit on SiGe 25% surface and potentially form thicker and/or denser organic layer.**



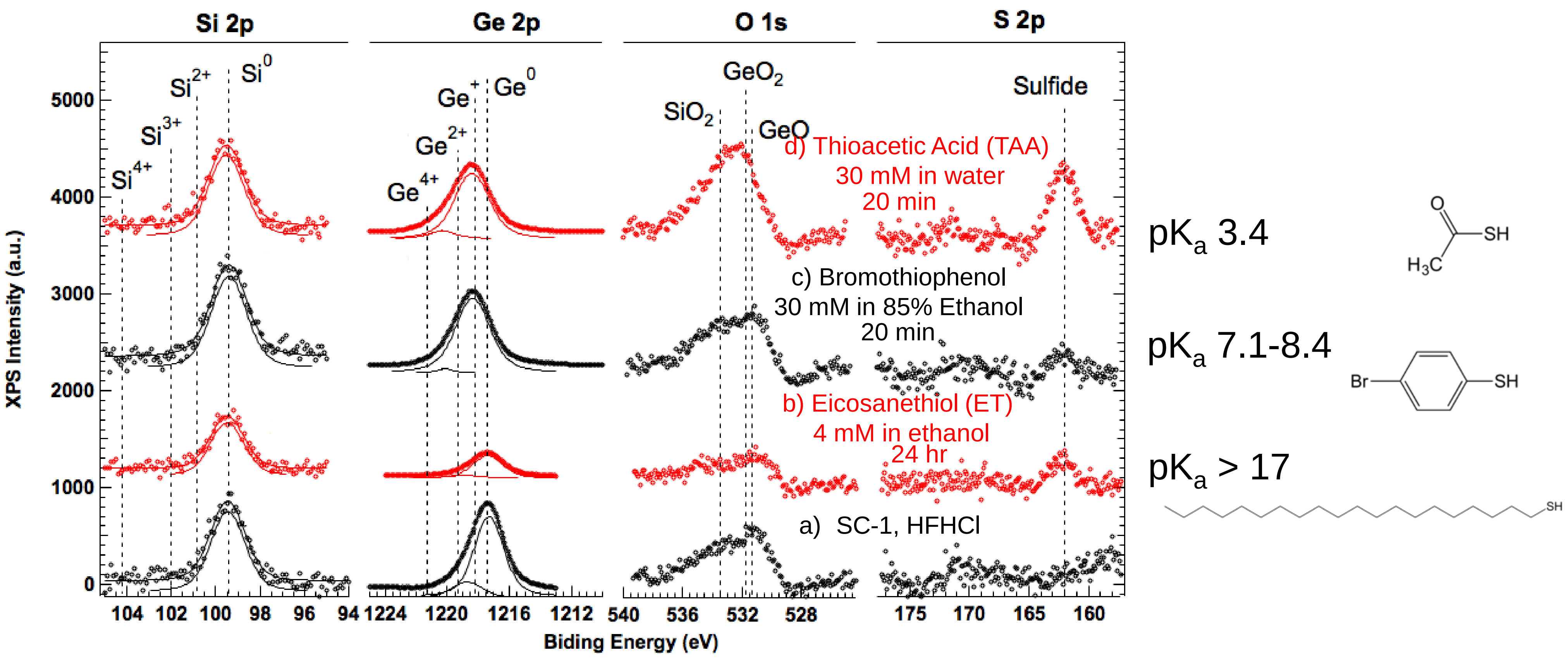
Passivation on SiGe 75% Surface (Organic Approach)

SiGe 25%



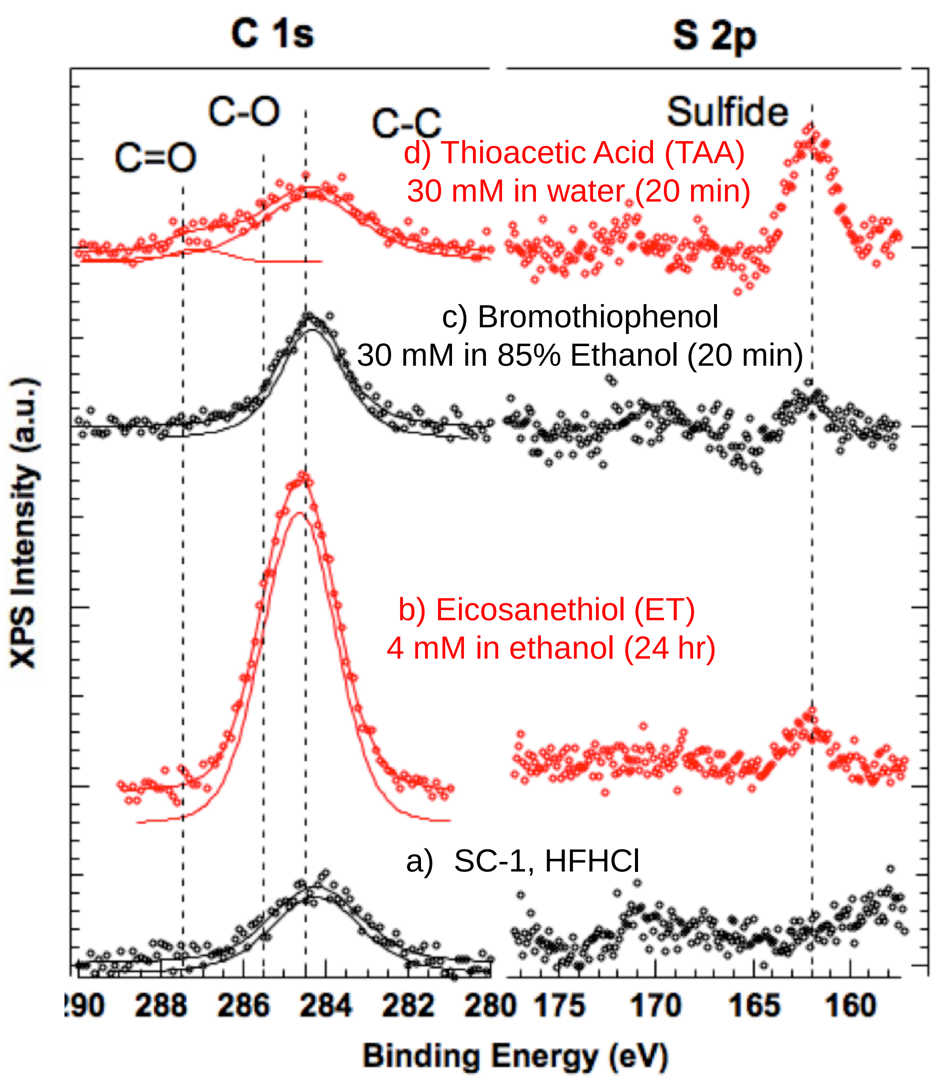
SiGe 75%

Organic Thiol Treatment on SiGe 75%

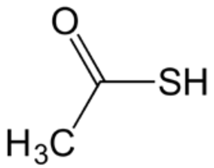


- ET successfully deposited on SiGe 75% surface.
- Lower pK_a thiols deposited more sulfur on SiGe 75% surface.

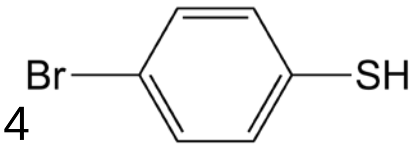
Organic Thiol Treatment on SiGe 75%



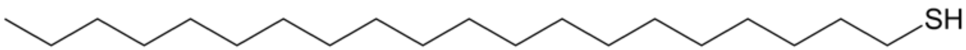
TAA
pK_a 3.4



BTP
pK_a 7.1-8.4



ET
pK_a > 17



- ET deposited the thickest and/or most dense organic layer.

Conclusion and Future Work of Organic Approach on SiGe 75%

Conclusion:

- Thiol molecules with lower pK_a values deposited more sulfur on SiGe 75% surface.
- Although eicosanethiol did not deposit the most sulfur on SiGe 75% surface due to its high pK_a, it deposited the highest amount of organic layer on SiGe 75% surface due to its long alkyl chain. This can potentially provide the best protection on SiGe 75% surface against oxidation.

Future Work:

- Study SiGe 75% surface re-oxidation after ET treatment.

Acknowledgement

Muscat Research Group

- Yissel Contreras
- Lauren Peckler
- Pablo Mancheno
- Shawn Miller
- Adam Hinckley
- Gabriela Diaz
- Jimmy Hackett
- Lance Hubbard
- Shuo Yang
- Ruoyun Xiao

Lam Research Corporation

- Dr. Nerissa Draeger
- Dr. Reza Arghavani

THE UNIVERSITY OF ARIZONA

Lam RESEARCH