Development of Selective SiGe Etchants

Glenn Westwood and Rebecca Duffy

Avantor, 1013 US Highway 202/206, Bldg. JR-1, Bridgewater,
NJ 08807

glenn.westwood@avantorinc.com,
rebecca.duffy@avantorinc.com

©2019 Avantor, not to be reproduced or used without permission

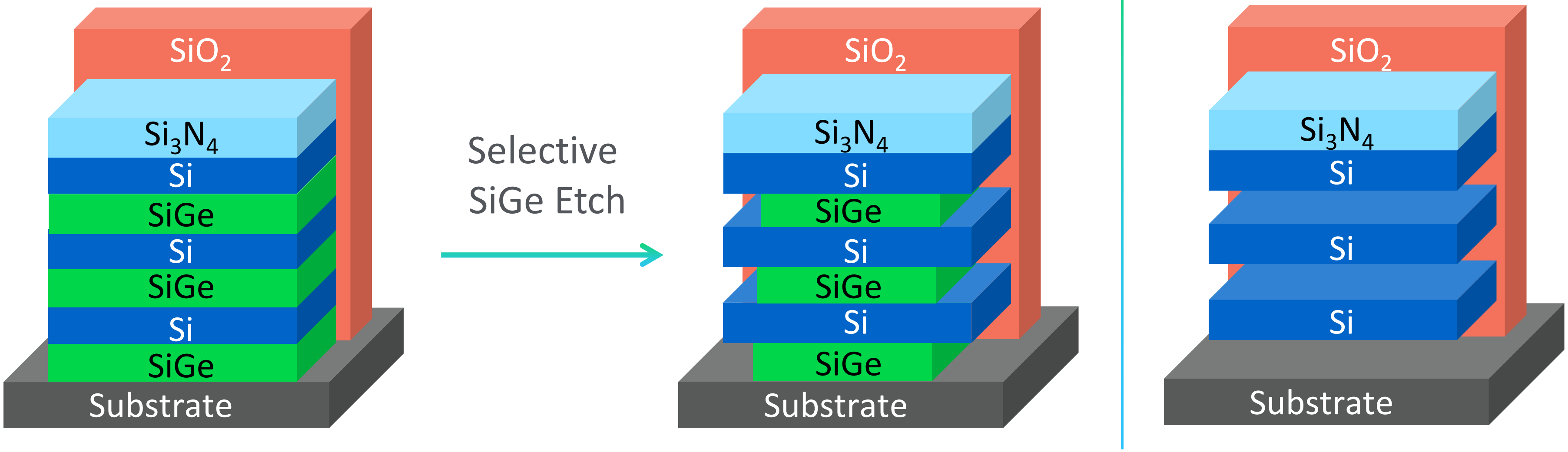
Introduction

- **Goals**
  - Develop SiGe etchants with high selectivity to Si, SiO_2, and Si_3N_4.
  - Target etchants for SiGe with <30% Ge.
  - Target Gate-All-Around (GAA) Si applications.

- **Outline of Presentation**
  - Applications
  - Approaches to SiGe/Si Etch Development
  - Etchant Development work – Inhibitor identification, Clouding
  - Performance – Aging effect, Bath life
  - SiGe Thickness Effects – Etch rates and interfacial Ge content.
  - Conclusions and Future work

©2019 Avantor, not to be reproduced or used without permission

Applications – Gate All Around (GAA) Transistors



Selective SiGe Etch

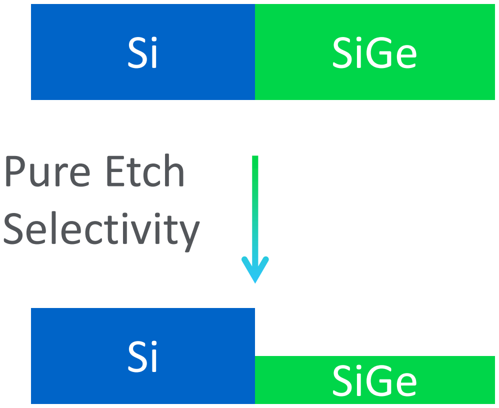
Option 1: Cavity Etch
Partial Release

Option 2: Full Release

1. Alternating deposition of Si and SiGe layers
2. Partial or full release of the SiGe layers
3. Si nanosheets or nanowires remain

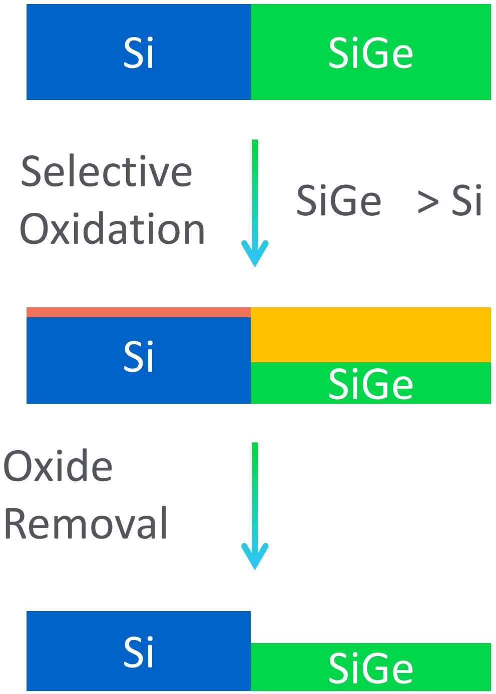
©2019 Avantor, not to be reproduced or used without permission

Approaches to Selectively Etching SiGe (20%) vs. Si



Pure Etch Selectivity

- Effective at Si>>SiGe with TMAH-based chemistries.
- Avantor efforts unsuccessful to date.
- Achieved Si ≈ SiGe with highly alkaline chemistries.

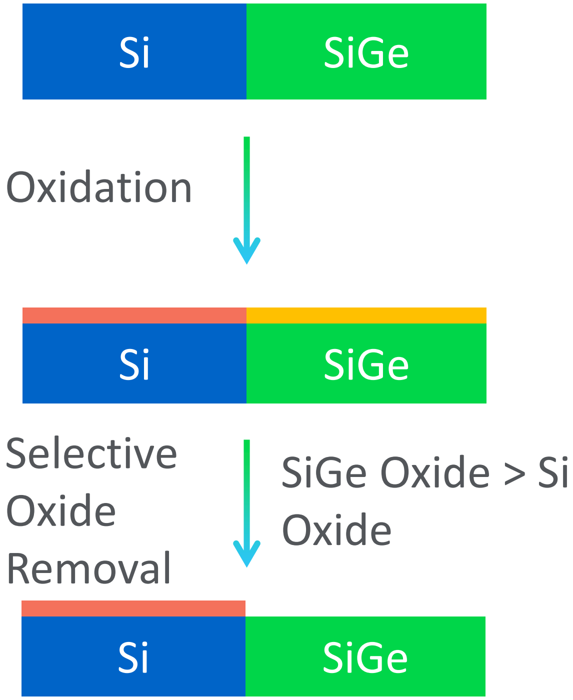


Selective Oxidation

SiGe > Si

Oxide Removal

- Limiting step is surface oxidation.
- Proven approach for SiGe>Si etch.
- SiO_2 and Si_3N_4 compatibility is inconceivable.



Oxidation

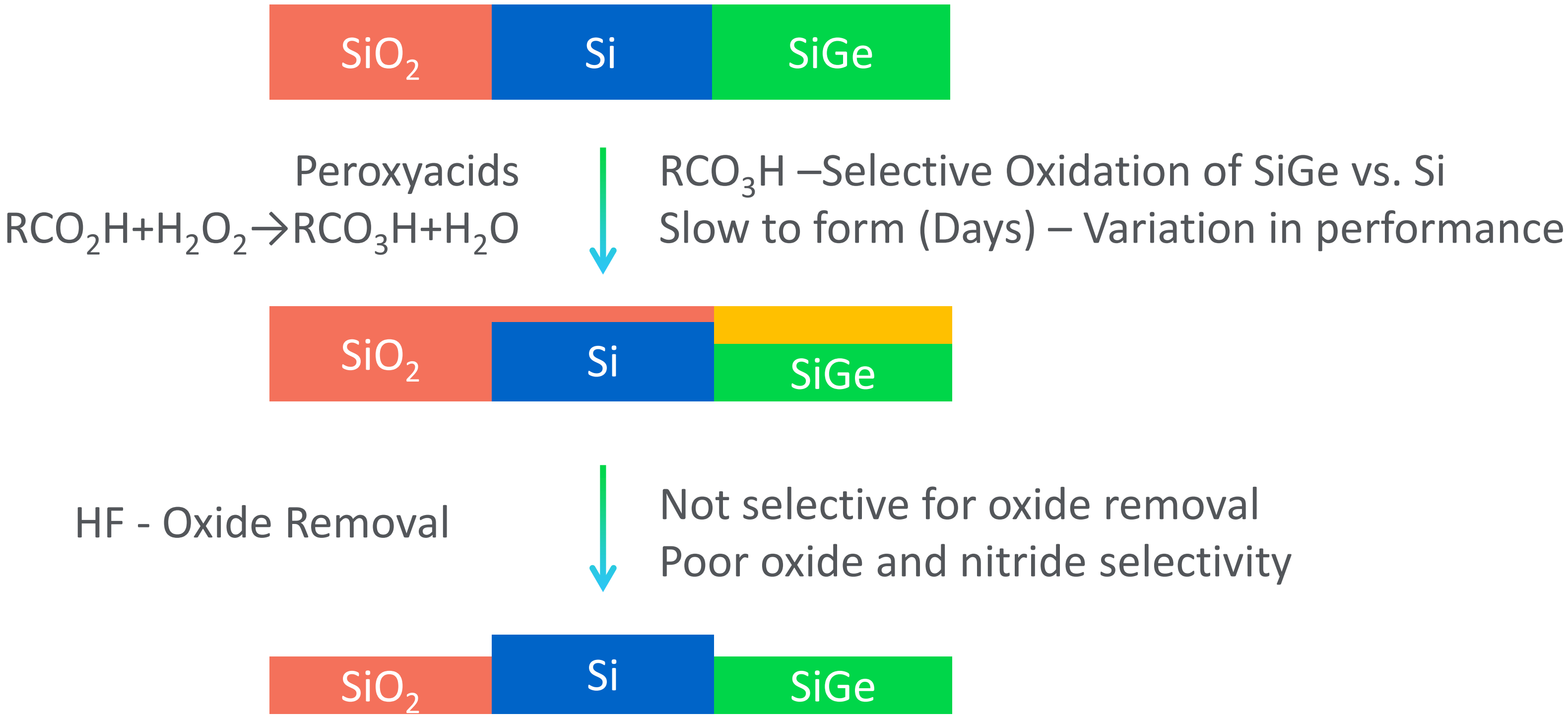
Selective Oxide Removal

SiGe Oxide > Si Oxide

- Limiting step - oxide removal.
- Necessary to achieve SiO_2 and Si_3N_4 compatibility.

©2019 Avantor, not to be reproduced or used without permission

HF/Acetic Acid/H2O2 Selective SiGe Etchant



Peroxyacids
$RCO_2H + H_2O_2 \rightarrow RCO_3H + H_2O$

RCO_3H –Selective Oxidation of SiGe vs. Si
Slow to form (Days) – Variation in performance

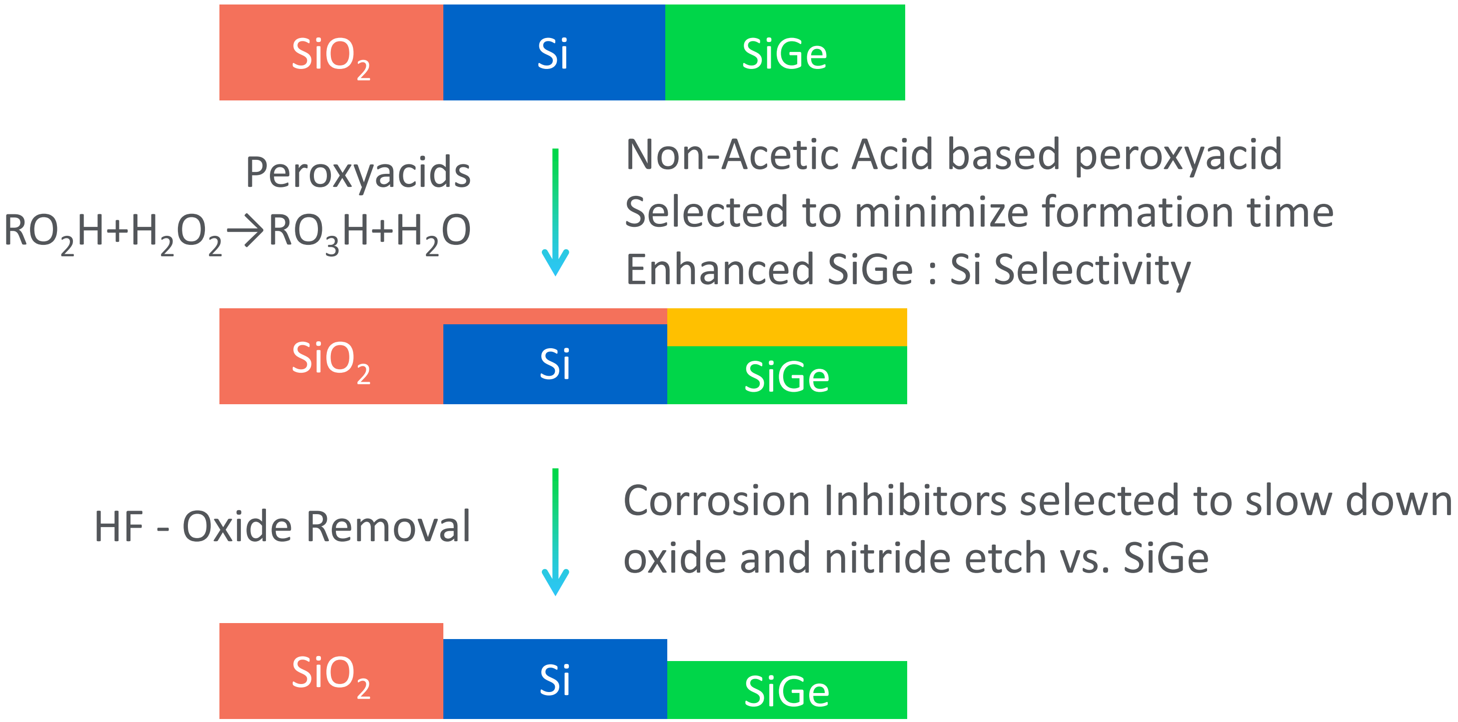
HF - Oxide Removal

Not selective for oxide removal
Poor oxide and nitride selectivity

Very high SiGe etch rates achieved,
but reported SiGe:Si Etch selectivity of ~20:1 is still not ideal.

©2019 Avantor, not to be reproduced or used without permission

Avantor Approach to Developing New SiGe Etchant



Peroxyacids

$RO_2H+H_2O_2 \rightarrow RO_3H+H_2O$

Non-Acetic Acid based peroxyacid
Selected to minimize formation time
Enhanced SiGe : Si Selectivity

HF - Oxide Removal

Corrosion Inhibitors selected to slow down oxide and nitride etch vs. SiGe

Formulation Evaluated

- >95% Water
- Hydrofluoric Acid
- SiGe/Si selectivity enhancer
- Chelator
- Etch Inhibitor Added
- Mixed 5:1 H2O2

©2019 Avantor, not to be reproduced or used without permission

SiO_2 Etch Inhibitor Screening – First Attempt

Formulation Evaluated

- >95% Water
- Hydrofluoric Acid
- SiGe/Si selectivity enhancer
- Chelator
- Etch Inhibitor Added
- Mixed 5:1 H_2O_2

Results

- No clear winners.
- Many improved pSi selectivity.
- Cationic surfactants (A1-A3) - worse selectivity.
- Picked 4 select additives for further testing.

Etch Inhibitors	SiO_2 Etch Rate (Å/min)	pSi Etch Rate (Å/min)
None	6.3	13.3
A1	130.5	20.7
A2	17.9	61.3
B1	11.1	3.1
B2	4.9	1.9
B3	6.5	1.6
C1	5.8	4.8
C2	5.7	3.3
D1	5.2	1.1
D2	6.6	1.9
D3	10.8	1.7
D4	2.7	1.3
E1	11.1	1.1
E2	6.0	1.5
E3	10.9	1.5
E4	10.9	3.3
E5	26.1	0.2
F1	11.7	2.8

avantor™

©2019 Avantor, not to be reproduced or used without permission

SiO_2 Etch Inhibitor Screening – Second Attempt

Formulation Evaluated

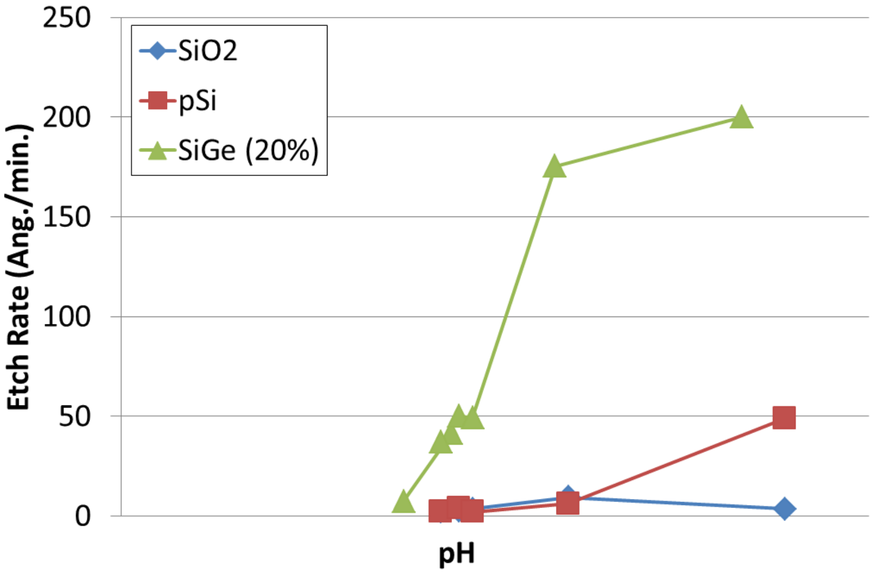
- >95% Water
- Reduced Hydrofluoric Acid
- SiGe/Si selectivity enhancer
- Chelator
- Increased Etch Inhibitor

Mixed 5:1 H_2O_2

Etch Inhibitors	SiO_2 Etch Rate (Å/min)	pSi Etch Rate (Å/min)	SiGe (20%) Etch Rate (Å/min.)	SiGe (20%) / pSi Etch Selectivity
B1	1.1	0.6	12.1	20
D4	1.8	0.6	17.9	30
E3	1.0	0.5	12.4	25
F1	1.5	1.3	41.6	32

Results

- Formulation w/ F1
- Increasing pH dramatically increases SiGe etch rate.
- pSi etch rates also increase with pH.



©2019 Avantor, not to be reproduced or used without permission

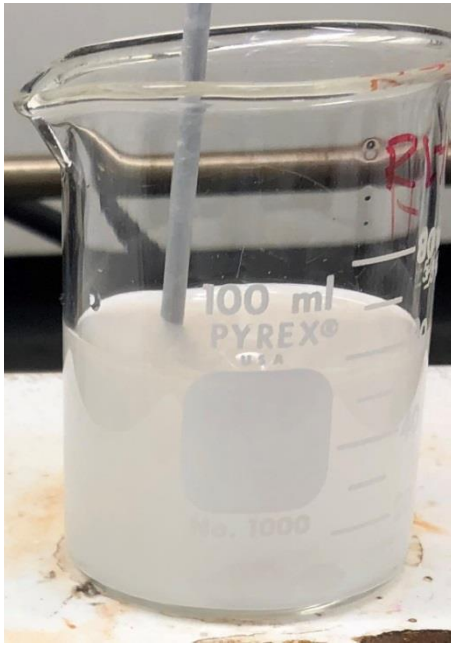
RL-1 and RL-1B – Cloudy Formulations

Formulation	XM-529-V3 + Etch Inhibitor	SiO_2 Etch Rate (Å/min)	Si_3N_4 Etch Rate (Å/min.)	pSi Etch Rate (Å/min)	SiGe (20%) Etch Rate (Å/min.)	SiGe (20%) / pSi Etch Selectivity
RL-1*	F1	2	63	2	80	40
Rl-1B*	F1 + B3	2	3	3	58	20

* Mixed 5:1 H_2O_2 at 35 C

- All high selectivity etchants in initial stages of this study were cloudy.
- Cloudiness – precipitation of:

Etch Inhibitor + Ge/Si Selectivity Enhancer

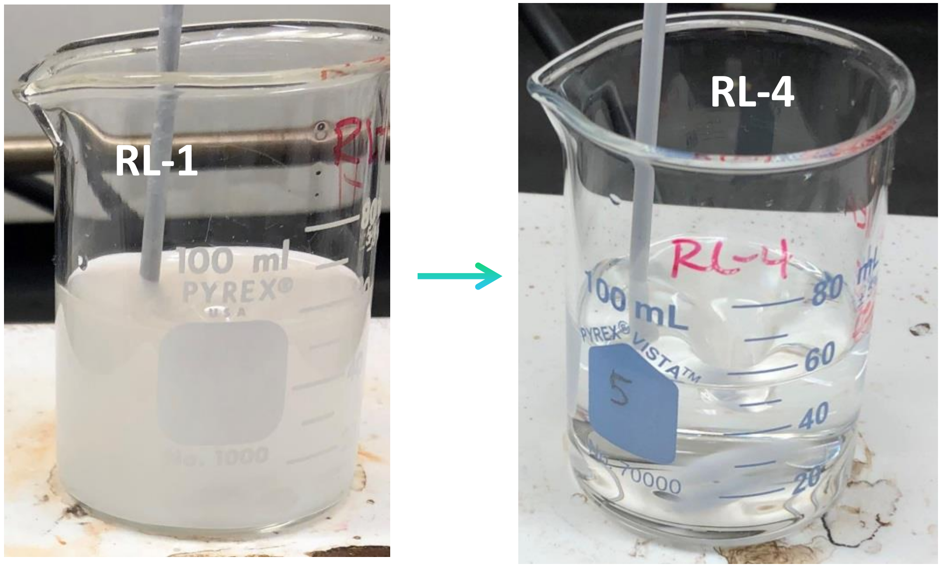


©2019 Avantor, not to be reproduced or used without permission

Formulations without Clouding

Prevented clouding by:

1. Reducing SiGe/Si Selectivity Enhancer – RL-3
2. Modified Etch Inhibitor – RL-4 – Best Etch solution to date.
3. Comparable selectivity, but lower SiGe etch rates.

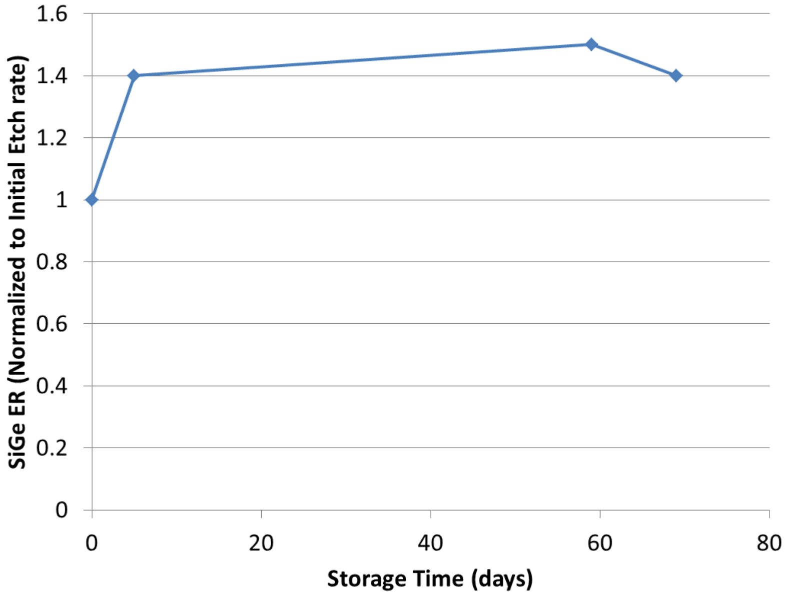


Formulation	XM-529-V3 + Etch Inhibitor	SiO_2 Etch Rate (Å/min)	Si_3N_4 Etch Rate (Å/min.)	pSi Etch Rate (Å/min)	SiGe (20%) Etch Rate (Å/min.)	SiGe (20%) / pSi Etch Selectivity
RL-3*	F1	3.4	1.8	3.2	45	15
RL-4*	F2	0.8	1.3	1.2	34	28

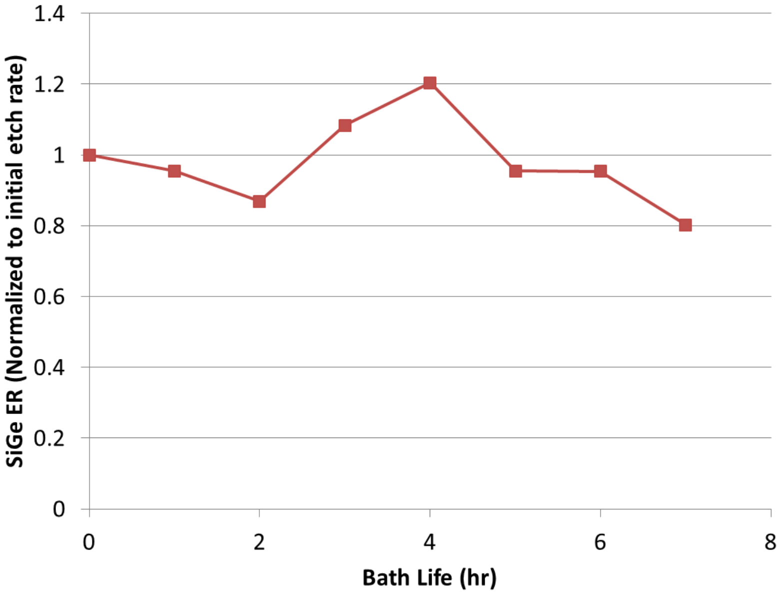
* Mixed 5:1 H_2O_2 at 35 C

©2019 Avantor, not to be reproduced or used without permission

RL-4: Bath Performance Data



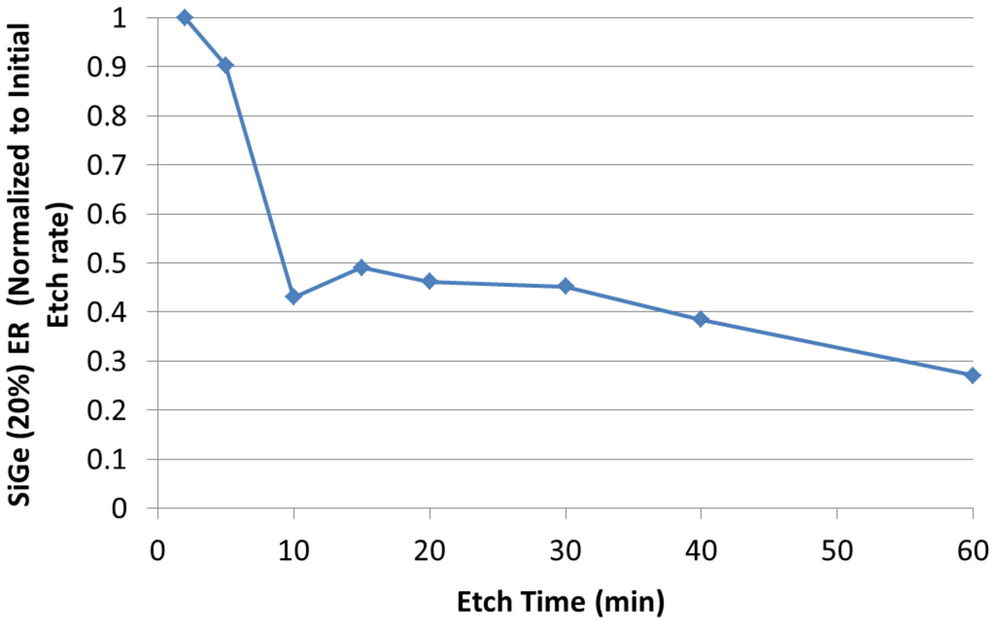
- RL-4 was mixed with H_2O_2 (5:1) and tested after days of storage.
- ~50% increase in SiGe etch rates.
- Less increase over time than acetic acid based blends.
- Stable



- 5 RL-4 : 1 H_2O_2 at 35 C, 650 rpm.
- RL-4 bath life stable out to 7 hrs.

©2019 Avantor, not to be reproduced or used without permission

Etch Rate Dependence on Etch Times



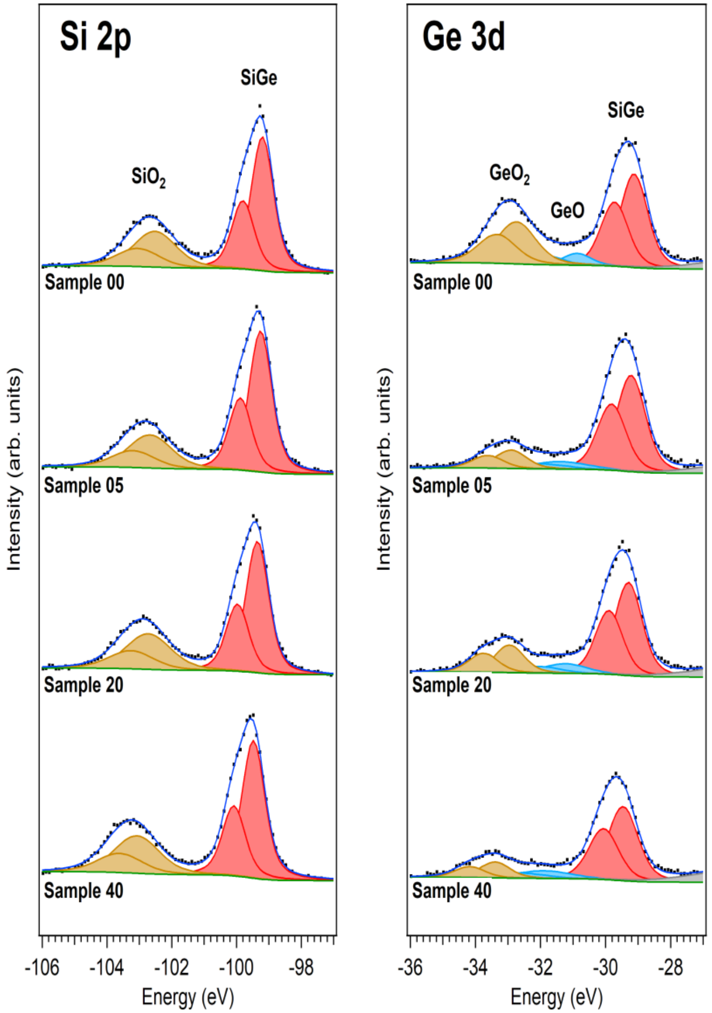
- RL-4 : H_2O_2 at 35 C, 650 rpm. Etched SiGe wafers for different etch times.
- The longer the etch time, the lower the etch rate.
- SiGe etch rate does not decrease with bath life, instead the SiGe (20%) etch is slowing because the SiGe thickness is decreasing.

©2019 Avantor, not to be reproduced or used without permission

Etch Time Effect (XPS)

SiGe Etch Depth (Å)	SiGe ER (Normalized)	% Ge
0	1.00	12.9
156	0.90	11.3
519	0.46	11.0
917	0.38	9.2

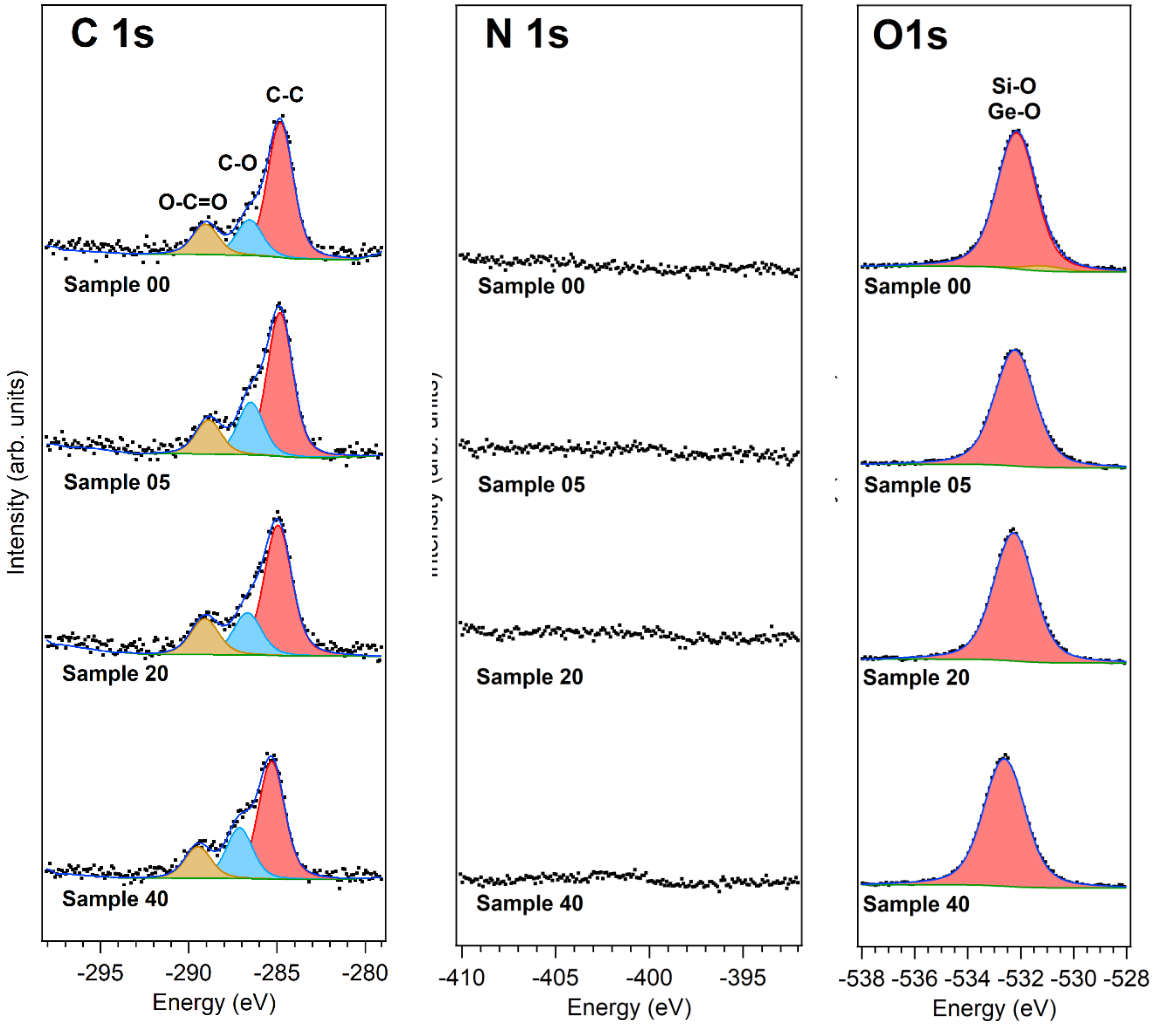
- Longer etch times result in decreased Ge and GeO_2 at the interface.
- Etch rates decrease with thinning of SiGe films because of reduced Ge content
- Possible explanations
  - Uneven starting Ge content in SiGe films.
  - Interface becomes depleted in Ge due to the etch Ge>Si.



XPS collected by Ryan Thorpe, Rutgers K-Alpha XPS Facility

©2019 Avantor, not to be reproduced or used without permission

Additional XPS Results



- Carbon – Only adventitious carbon identified
- No nitrogen detected
- No indication that components from chemistry remain on the SiGe

XPS collected by Ryan Thorpe, Rutgers K-Alpha XPS Facility

©2019 Avantor, not to be reproduced or used without permission

Conclusions

- **SiGe Etchant Development**
  - Achieving high SiGe:Si selectivity is not difficult.
  - High SiGe:SiO_2 selectivity without clouding is a challenge.

- **Best Solution**
  - RL-4
  - Identified SiO_2 etch inhibitor that doesn’t reduce SiGe etch rates.
  - Etch Rates for partial release not full release.
  - Stable bath life and stable when storing mixed with H_2O_2.
  - SiGe etch rate slows with increased SiGe removal due to decrease in Ge at interface.

Formulation	SiO_2 Etch Rate (Å/min)	pSi Etch Rate (Å/min)	SiGe (20%) Etch Rate (Å/min.)	SiGe (20%) / pSi Etch Selectivity
RL-4	0.8	1.2	34	28

©2019 Avantor, not to be reproduced or used without permission

Next Steps

- Improvements based on cloudy formulations – High SiGe etch rate and selectivities
  - Clear solution separated from cloudiness.

SiO_2 Etch Rate (Å/min)	pSi Etch Rate (Å/min)	SiGe (20%) Etch Rate (Å/min.)	SiGe (20%) / pSi Etch Selectivity
<0.5	1.4	53	38

  - Use a cloudy solution

SiO_2 Etch Rate (Å/min)	pSi Etch Rate (Å/min)	SiGe (20%) Etch Rate (Å/min.)	SiGe (20%) / pSi Etch Selectivity
9	6	175	29

- Test Application on devices
- Related GAA etch solutions
  - Si/SiGe, Si/Ge, and SiGe/Ge.
  - III-V release chemistries – InGaAs/GaAs

©2019 Avantor, not to be reproduced or used without permission