Aqueous Ammonium Sulfide Passivation and $Si_{1-x}Ge_x$ MOSCaps

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Motivation

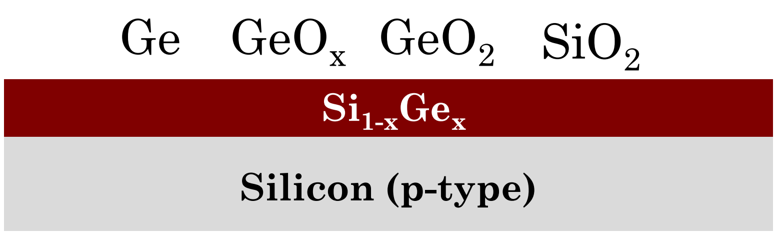
- Ge and SiGe are alternatives to Si for CMOS devices owing to their smaller bandgap and increased hole mobility.
- Incorporating Ge into SiGe films can be used to tune material properties.
- Ge oxides form readily and the interface contains a high density of defects.
- SiGe with $<$ 50% Ge has been integrated into current Si semiconductor manufacturing.
- SiGe with $>$ 50% Ge has been difficult to integrate.
- Sulfur chemistry is accepted by industry for passivation.

Chemistry on the SiGe surface lead to poor MOSCap performance

Surface Chemistry

Dangling Bonds

Native Oxides



Electrical/Device Defects

Electronic states appear between band gap

Poor nucleation of oxide layer

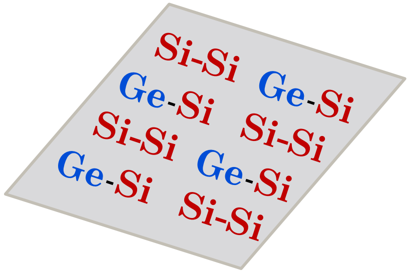
Poor control and repeatability in device manufacture

Multiple dielectrics

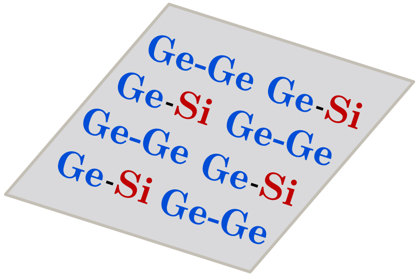
Goals

1. Remove oxides from SiGe surface and passivate Ge dangling bonds with $(NH_4)_2S$ chemistries to:
    - Reduce interface defects between SiGe and high k dielectric
    - Minimize defects in bulk layer of dielectric
    - Minimize electric oxide thickness

2. Compare 25% and 75% Ge substrates



$Si_{1-x}Ge_x$ (x = 0.25)



$Si_{1-x}Ge_x$ (x = 0.75)

Removing Oxides and Forming Ge-S

Remove oxides through wet chemistry clean*

Control Treatment

SC-1: 1:1:500, RT, 2 min
UPW, 1 min,
Slow dry with N_2 (~30 s)

↓

$HF:HCl:H_2O$ (1:3:300)
5 min

Bond Ge dangling bond to S with $(NH_4)_2S$*

$(NH_4)_2S$ Treatment

(Control)

↓

$(NH_4)_2S:H_2O$ (1:100) 20 min

Acidic Treatment

(Control)

↓

$(NH_4)_2S:HF:HCl:H_2O$ (1:0.15:0.15:100) 20 min

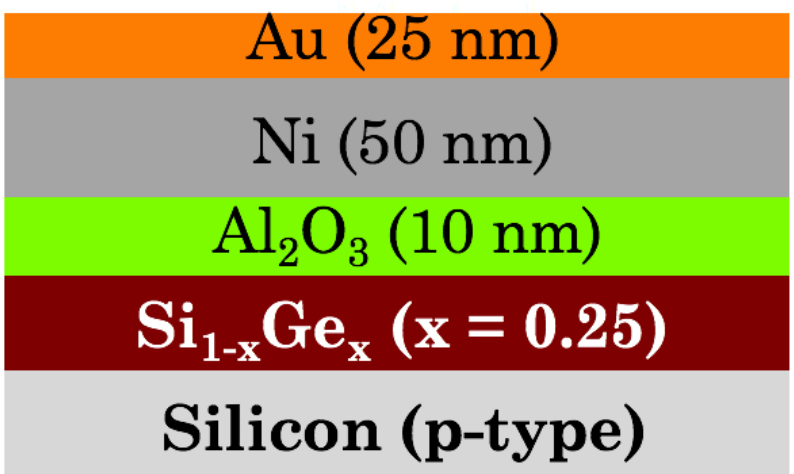
*Coupon Size Samples: 1 x 1 cm^2

A Study of Two Surfaces and Two MOSCaps

$Si_{1-x}Ge_x$ (x = 0.25)

Surface

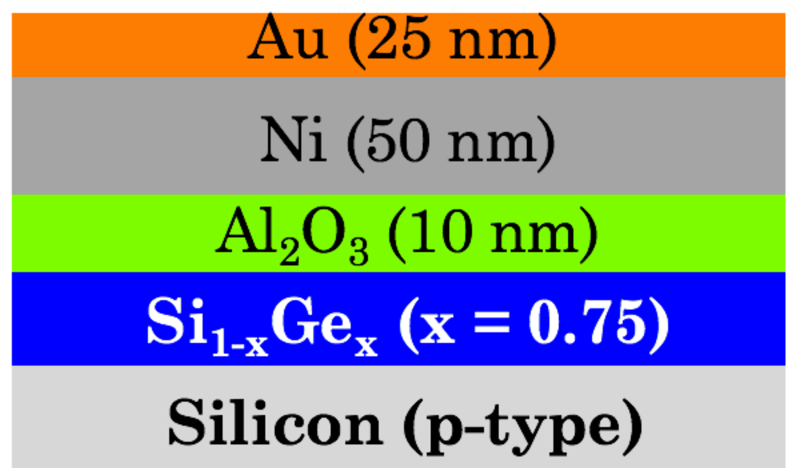
MOSCap



$Si_{1-x}Ge_x$ (x = 0.75)

Surface

MOSCap



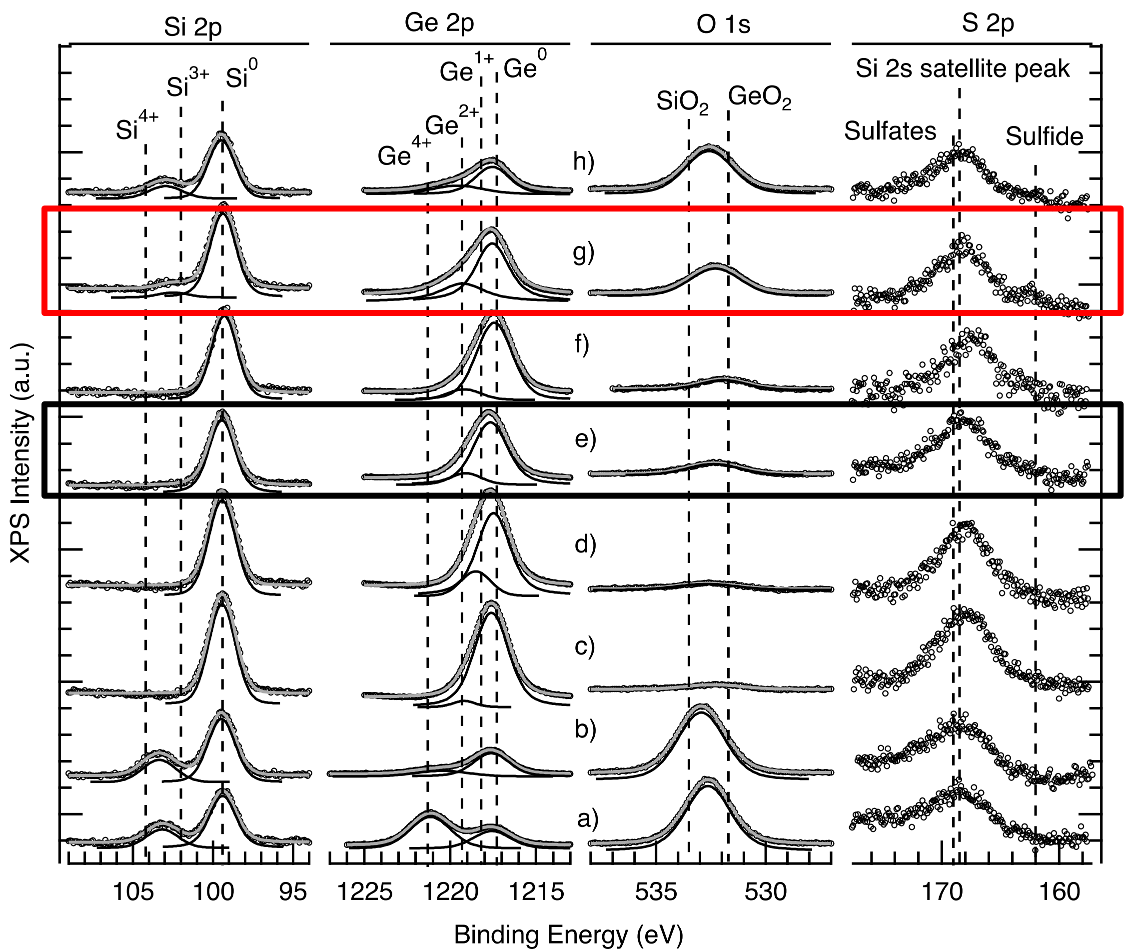
$Si_{1-x}Ge_x$ (x = 0.25)

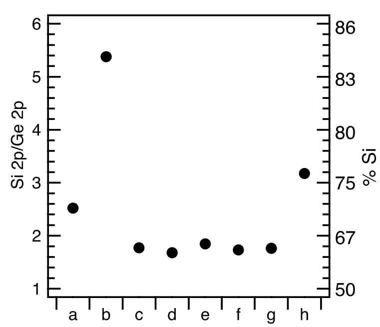
Chemical & Electrical Characterization

On $Si_{1-x}Ge_x$ (x = 0.25) Ge-S not detected with $(NH_4)_2S$ treatment.

$(NH_4)_2S$ Treatment

Control Treatment

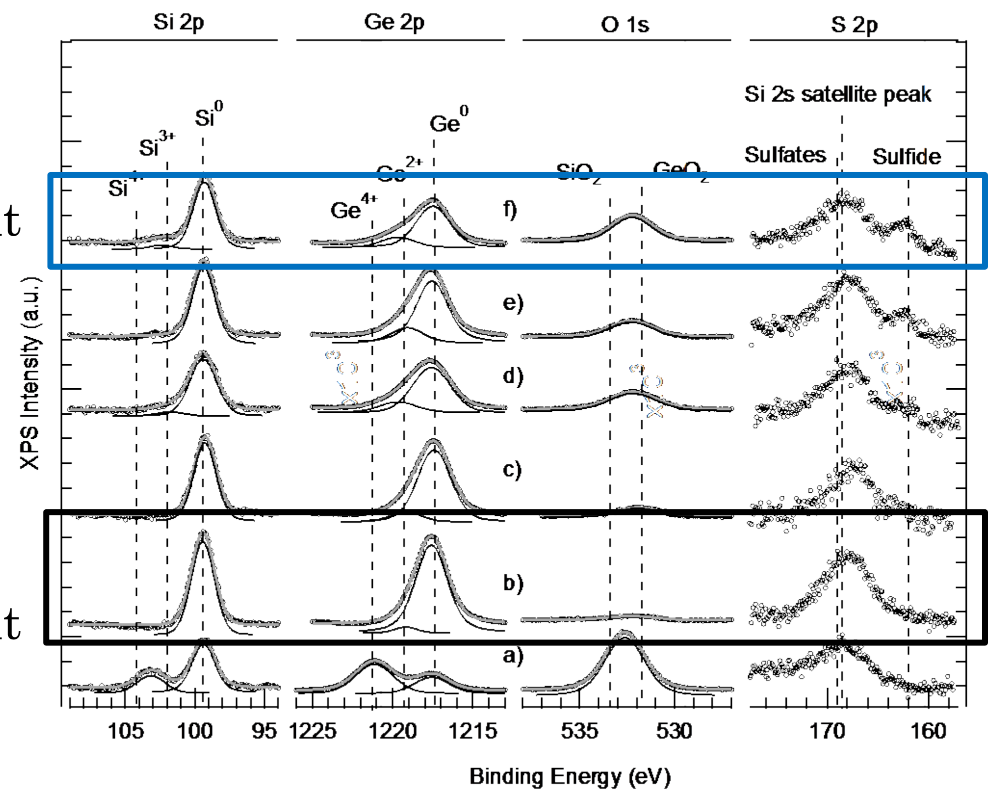


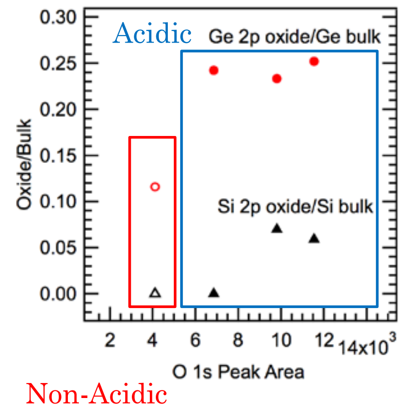


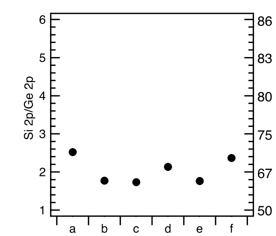
Ge-S is detected with acidic $(NH_4)_2S$ (1:100 v/v) treatment, as well as oxides.

Acidic Treatment

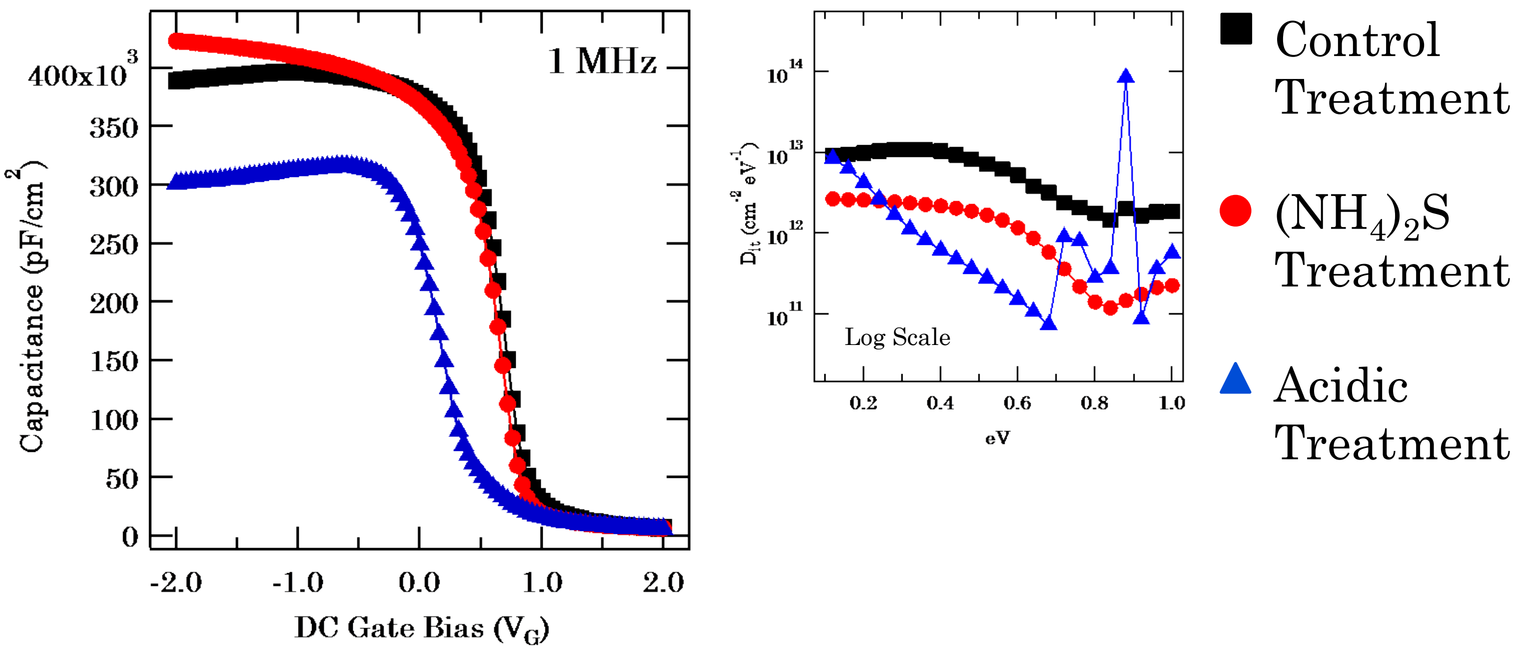
Control Treatment







Acidic treatment reduces defects and capacitance.

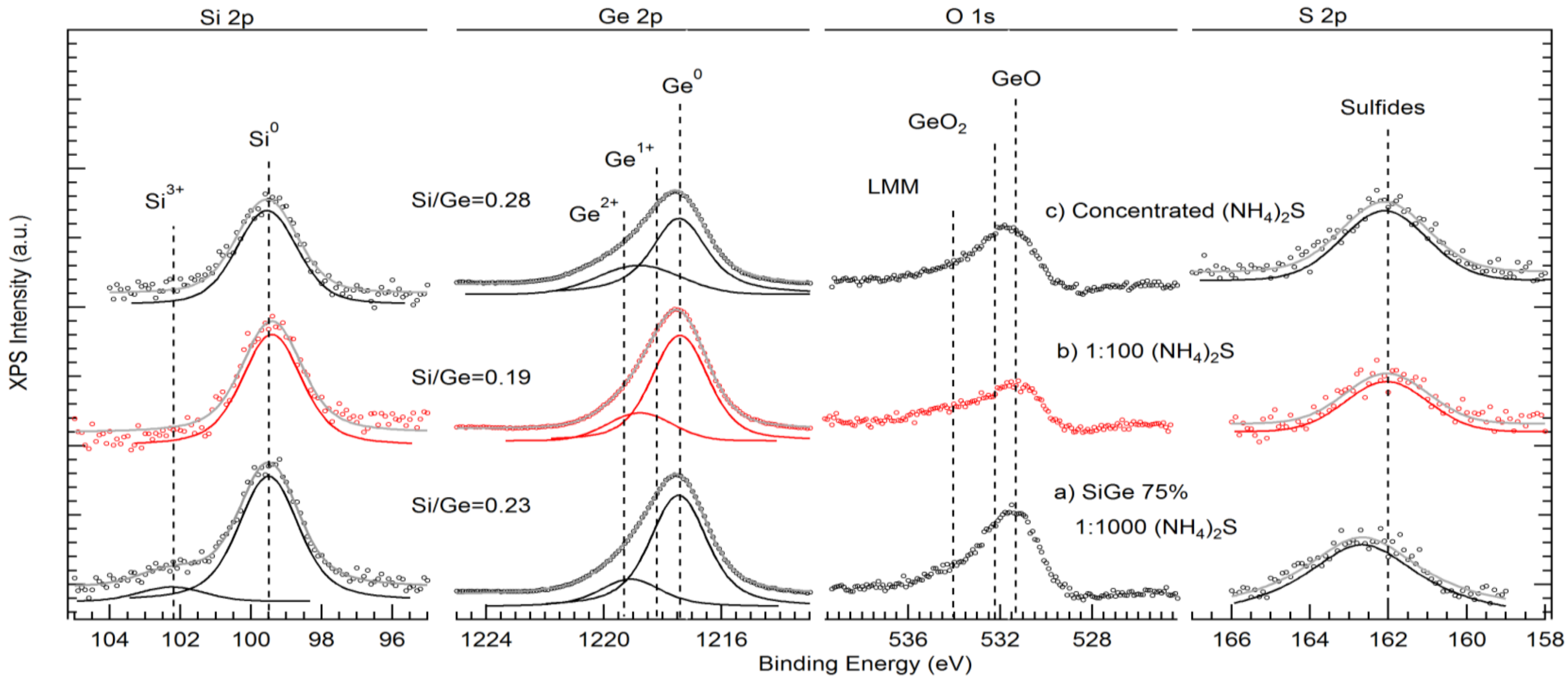


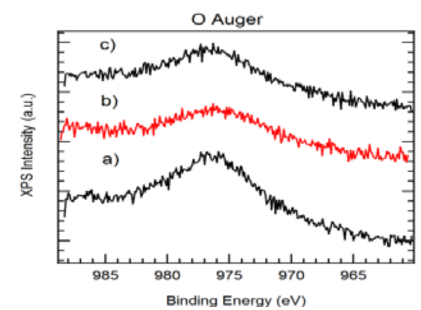
Flatband shift possibly due to thickness of dielectric layer.

$Si_{1-x}Ge_x$ ($x = 0.75$)

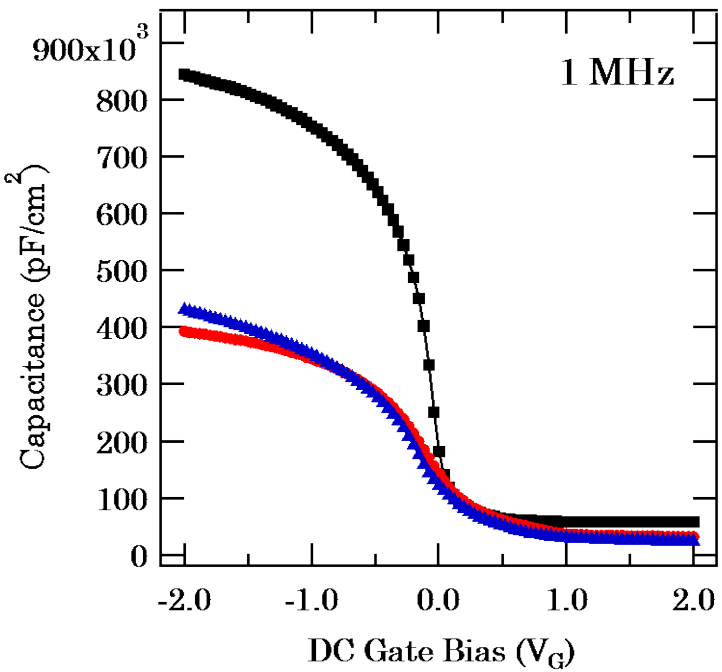
Chemical & Electrical Characterization

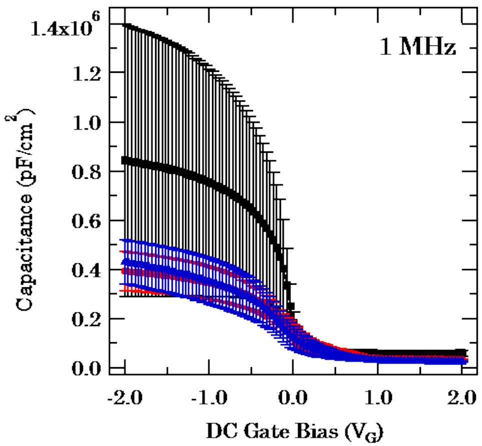
On $Si_{1-x}Ge_x$ (x = 0.75) Ge-S and oxides detected after $(NH_4)_2S$ treatment.





Ge-S and oxides correlate to less capacitance.



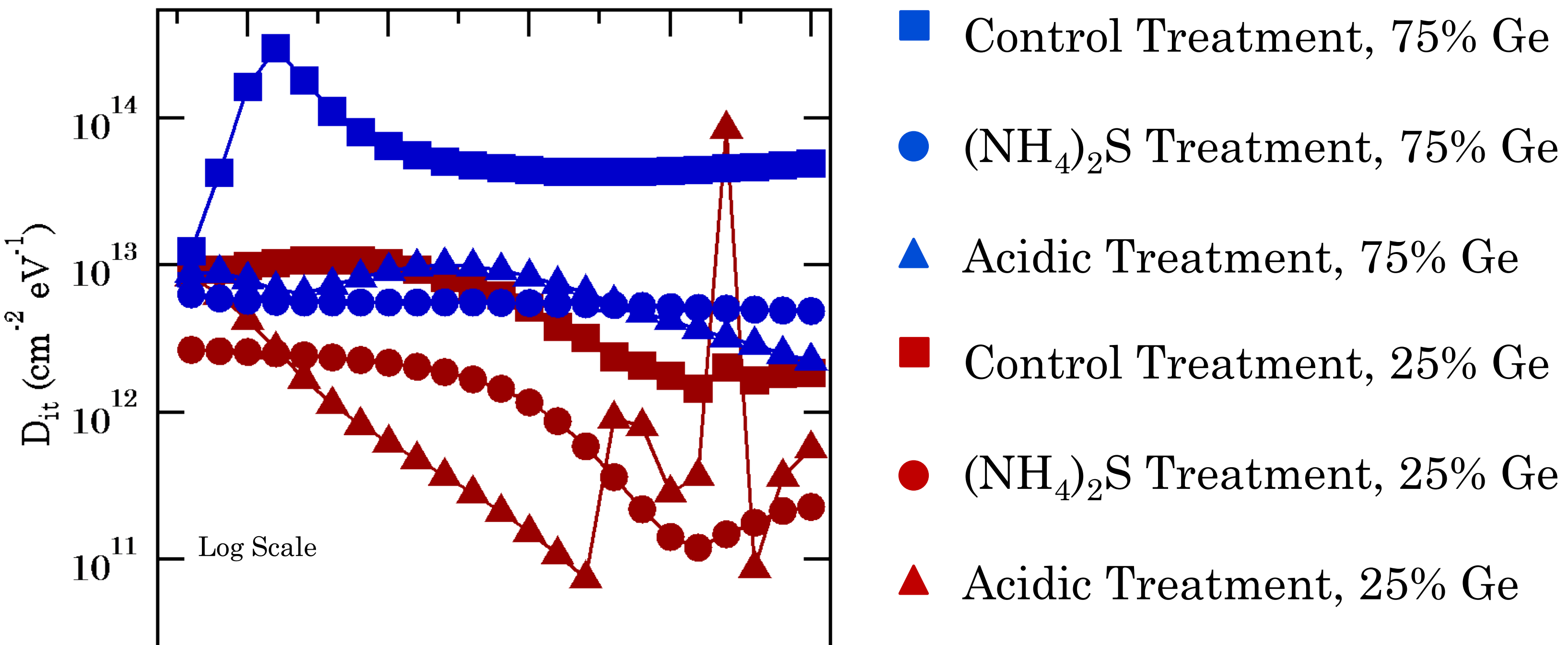


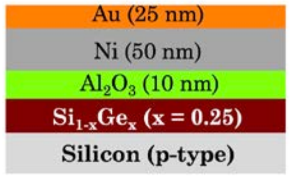
■ Control Treatment, 75% Ge

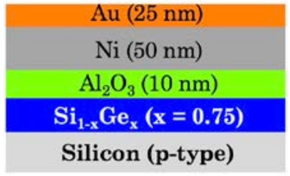
● $(NH_4)_2S$ Treatment, 75% Ge

▲ Acidic Treatment, 75% Ge

$(NH_4)_2S$ treatments decrease interface defects at valence band edge for both substrates.

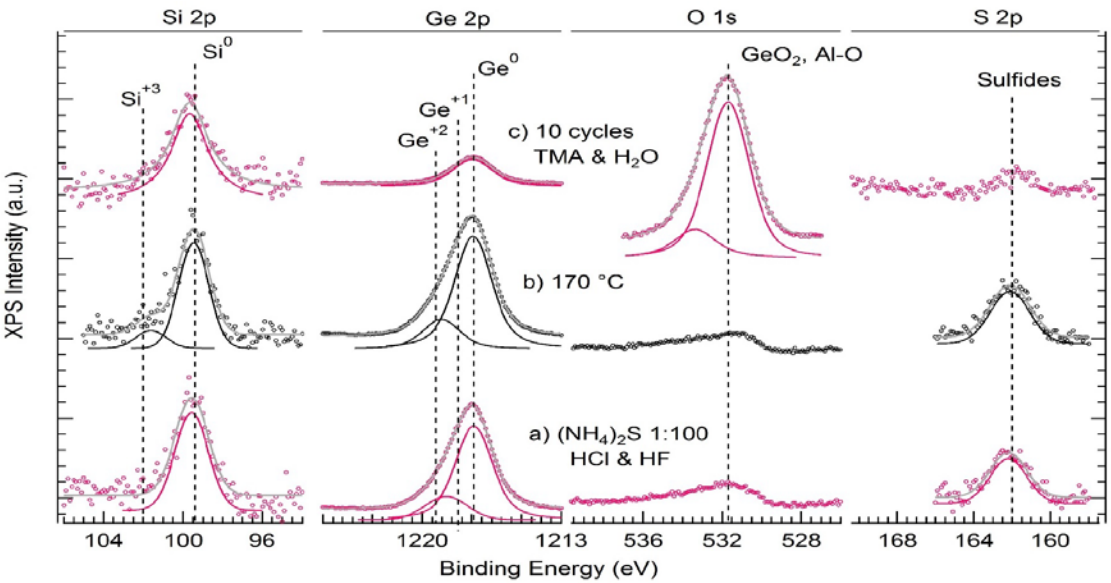


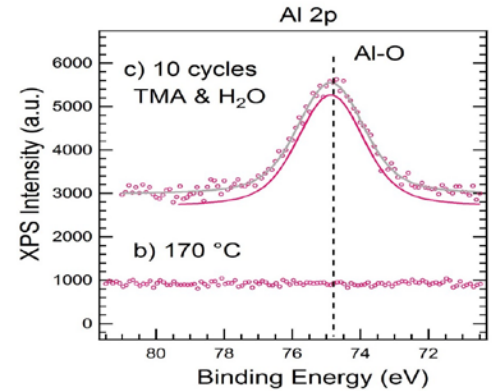




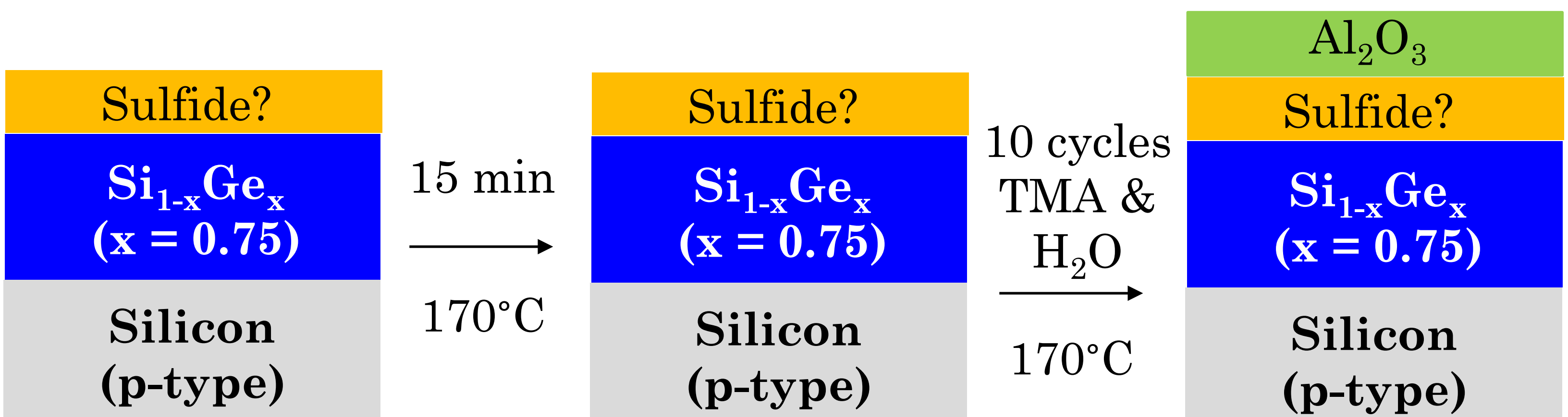
Additional Studies on S Desorption, Surface Variation, Repeatability, and Time

Checking S desorption after ALD

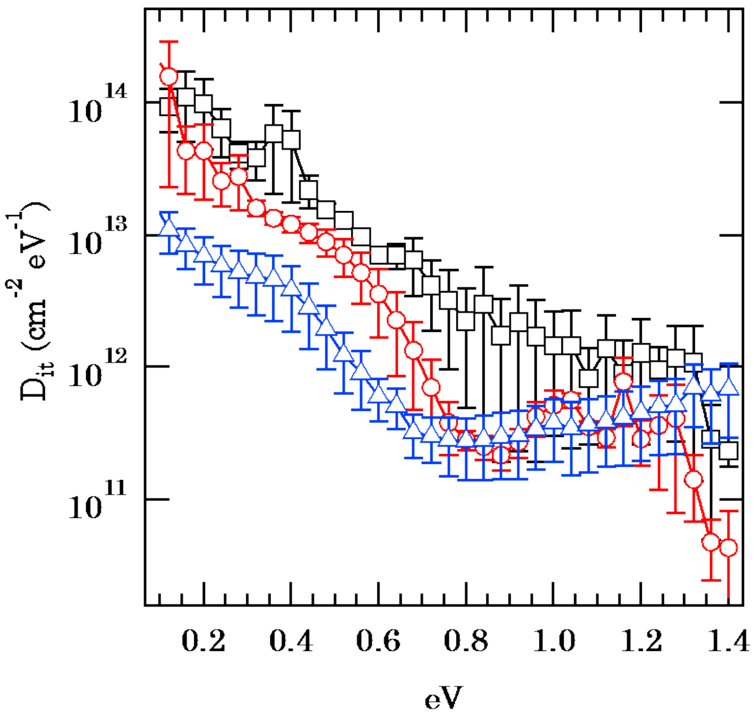


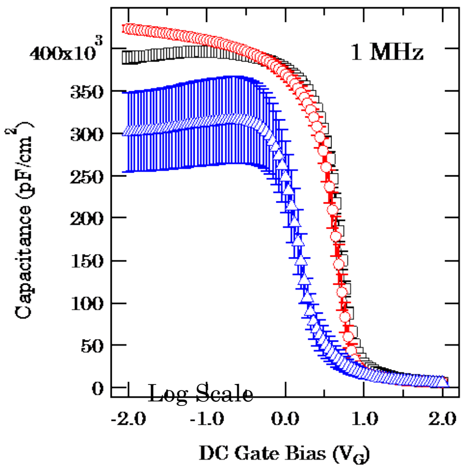


Al/O = 0.71



Surface variation on $Si_{1-x}Ge_x$ (x = 0.25) observed through D_{it}



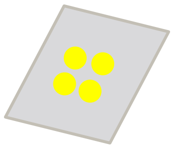


□ Control Treatment

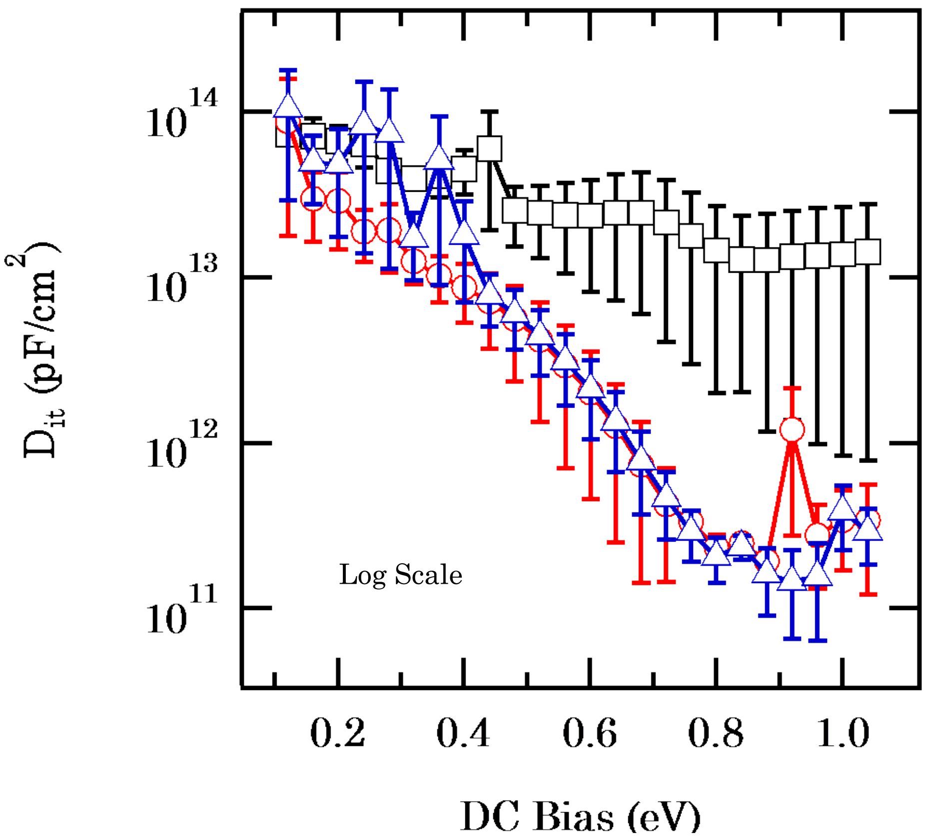
○ $(NH_4)_2S$ Treatment

△ Acidic Treatment

Micron scale capacitors on coupon



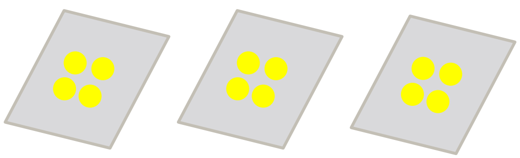
Between three sets of $Si_{1-x}Ge_x$ (x = 0.25) MOSCaps D_{it} trend does not hold.



Control Treatment

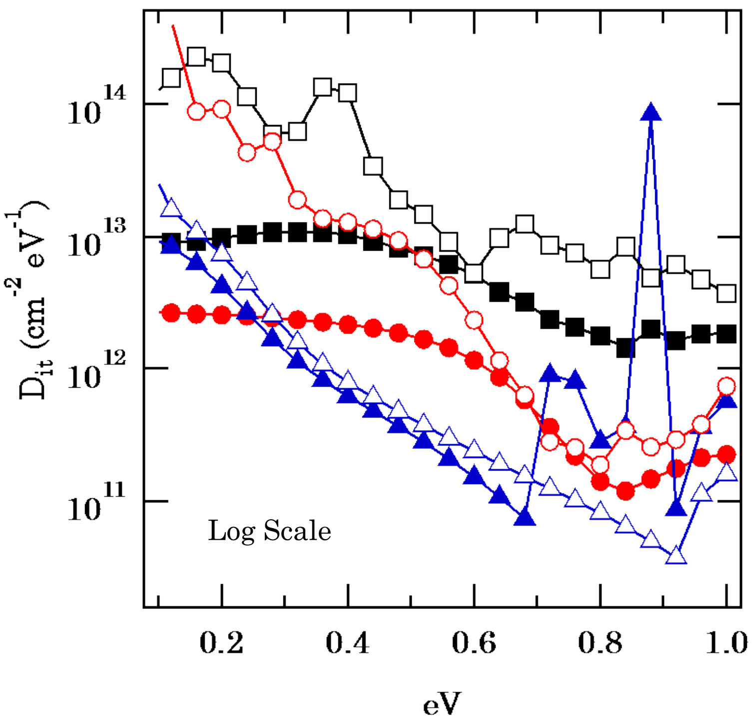
$(NH_4)_2S$ Treatment

Acidic Treatment



Three sets of coupons

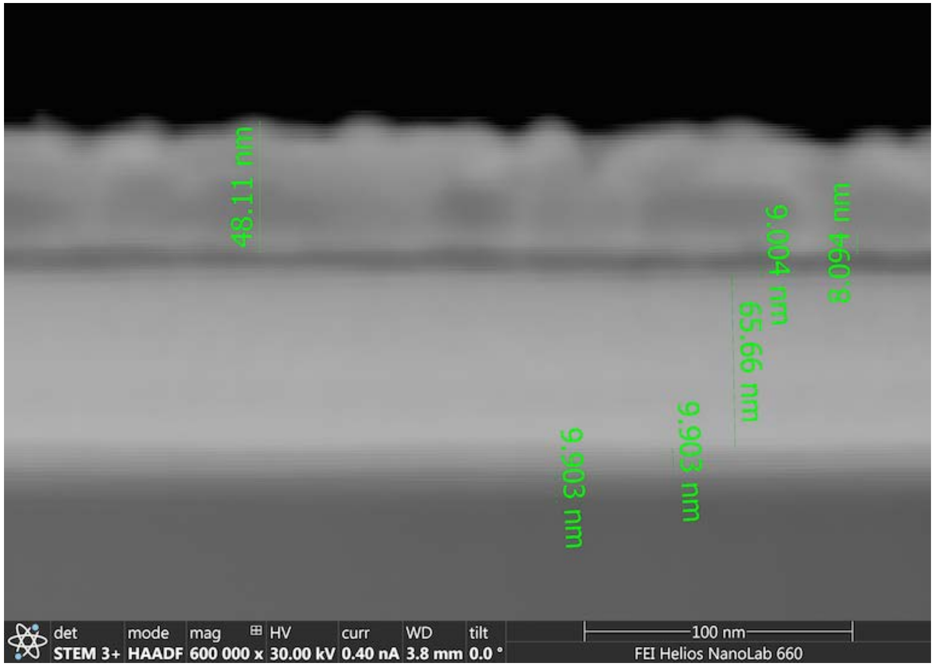
Interface defects increase with time.



- ■ Control Treatment, Time 1
- □ Control Treatment, Time 2
- ● $(NH_4)_2S$ Treatment, Time 1
- ○ $(NH_4)_2S$ Treatment, Time 2
- ▲ Acidic Treatment, Time 1
- △ Acidic Treatment, Time 2

Time 2 – Time 1 = 5 months

SEM Image of $Si_{1-x}Ge_x$ (x = 0.25) MOSCap



Control treatment

Pre annealing

Thicknesses for metal layers are not expected.

Metal layers are indistinguishable.

Conclusions

- Ge-S forms on both $Si_{1-x}Ge_x$ ($x = 0.25, 0.75$) in either the $(NH_4)_2S$ or the $(NH_4)_2S$ + Acid solution.
- Oxides regrow faster on both $Si_{1-x}Ge_x$ ($x = 0.25, 0.75$) when S is present on the surface.
- D_{it} reduction could be caused by Ge-S bond and/or oxide formation.
- MOSCap repeatability and surface homogeneity varies significantly between the two SiGe substrates.
- Interface defects increase with age on the $Si_{1-x}Ge_x$ ($x = 0.25$) surface.

Future Work

- Form Ge-S without oxide regrowth by non-aqueous solutions and gas phase deposition.
- Improve D_{it} analysis with series resistance correction.
- Improve metal contact deposition with calibration and switch to thermal deposition.
- Deposit thinner layers of high k to reduce flat band shift.