Aqueous Ammonium Sulfide Passivation and Si$_{1-x}$Ge$_x$ MOSCaps

Lauren Peckler$^1$, Stacy Heslop$^2$, and Anthony Muscat$^1$

$^1$Department of Chemical & Environmental Engineering, University of Arizona

$^2$Department of Chemistry, University of Arizona
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

Si$_{1-x}$Ge$_x$

Silicon (p-type)
Goals

1. Remove oxides from SiGe surface and passivate Ge dangling bonds with (NH₄)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

\[ \text{Si}_{1-x}\text{Ge}_x \ (x = 0.25) \]

\[ \text{Si}_{1-x}\text{Ge}_x \ (x = 0.75) \]
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 N₂ (~30 s)

HF:HCl:H₂O (1:3:300)
5 min

Bond Ge dangling bond to S with
(NH₄)₂S*

(NH₄)₂S Treatment

(Control)

Acidic Treatment

(NH₄)₂S:HF:HCl:
H₂O
(1:0.15:0.15:100)
20 min

*Control Treatment

*Coupon Size Samples: 1 x 1 cm²
A Study of Two Surfaces and Two MOSCaps

**Si$_{1-x}$Ge$_x$ (x = 0.25)**

- Surface
  - ~40 nm
  - Si$_{1-x}$Ge$_x$ (x = 0.25)
  - Silicon (p-type)

- MOSCap
  - Au (25 nm)
  - Ni (50 nm)
  - Al$_2$O$_3$ (10 nm)
  - Si$_{1-x}$Ge$_x$ (x = 0.25)
  - Silicon (p-type)

**Si$_{1-x}$Ge$_x$ (x = 0.75)**

- Surface
  - ~180 nm
  - Si$_{1-x}$Ge$_x$ (x = 0.75)
  - Silicon (p-type)

- MOSCap
  - Au (25 nm)
  - Ni (50 nm)
  - Al$_2$O$_3$ (10 nm)
  - Si$_{1-x}$Ge$_x$ (x = 0.75)
  - Silicon (p-type)
$\text{Si}_{1-x}\text{Ge}_x \ (x = 0.25)$

Chemical & Electrical Characterization
On \( \text{Si}_{1-x}\text{Ge}_x \) \((x = 0.25)\) Ge-S not detected with \((\text{NH}_4)_2\text{S}\) treatment.
Ge-S is detected with acidic (NH$_4$)$_2$S (1:100 v/v) treatment, as well as oxides.
Acidic treatment reduces defects and capacitance.

Flatband shift possibly due to thickness of dielectric layer.
$\text{Si}_{1-x}\text{Ge}_x \ (x = 0.75)$

Chemical & Electrical Characterization
On $\text{Si}_{1-x}\text{Ge}_x$ ($x = 0.75$) Ge-S and oxides detected after $(\text{NH}_4)_2\text{S}$ treatment.
Ge-S and oxides correlate to less capacitance.

- **Control Treatment**, 75% Ge
- **(NH₄)₂S** Treatment, 75% Ge
- **Acidic** Treatment, 75% Ge
(NH₄)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

Sulfide?  
**Si$_{1-x}$Ge$_x$**  
(\(x = 0.75\))  
Silicon (p-type)  
15 min  
170°C  

Sulfide?  
**Si$_{1-x}$Ge$_x$**  
(\(x = 0.75\))  
Silicon (p-type)  
10 cycles  
TMA & H$_2$O  
170°C  

Sulfide?  
**Si$_{1-x}$Ge$_x$**  
(\(x = 0.75\))  
Silicon (p-type)  

Al/O = 0.71
Surface variation on Si$_{1-x}$Ge$_x$ (x = 0.25) observed through D$_{it}$

![Graph showing variation in D$_{it}$ with eV vs. control, treatment, (NH$_4$)$_2$S treatment, and acidic treatment.](image)

- Control Treatment
- (NH$_4$)$_2$S 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.

![Graph showing $D_{it}$ vs DC Bias (eV) with different treatments: Control, (NH$_4$)$_2$S, Acidic. The y-axis is in a log scale with values ranging from $10^{11}$ to $10^{14}$ pF/cm$^2$. The graph includes three sets of coupons.]
Interface defects increase with time.

Time 2 – Time 1 = 5 months
SEM Image of $\text{Si}_{1-x}\text{Ge}_x$ ($x = 0.25$) 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$_4$)$_2$S or the (NH$_4$)$_2$S + 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.