GeSn SURFACE PREPARATION BY WET CLEANING AND IN-SITU PLASMA TREATMENTS PRIOR TO METALLIZATION

SPCC 2018 | Raynal Pierre-Edouard|

- Source/Drain compressive stressor in Ge channel MOS transistors (hole mobility increase)

- Direct-band gap materials (photonics applications) between 2.5 and 3.1 um wavelengths with GeSn 10% to 16%

Efficient Ohmic contact mandatory

Native oxide free surface
EXPERIMENTAL PROTOCOL

Stack

Ge$_{85}$Sn$_{15}$ 60 nm
Ge 2,5 µm buffer
Silicon (001)

Characterization

1) Morphology: atomic force microscopy
   Roughness of the surface, pitting…

2) Chemical composition: Plural angular XPS
   $\Theta \approx 75^\circ$ thickness analyzed $\approx 2$ nm

XRD Analysis
GeSn 15%
OUTLINE

GeSn characterization surface

Roughness and native oxidation

WET Surface Preparation

Diluted HF: Morphological impact and oxide removal efficiency

DRY Surface Preparation

Plasma He, Argon: Morphological impact and oxide removal efficiency

WET and DRY Surface Preparation

Alternative WET and DRY combination for surface preparation
OUTLINE

GeSn characterization surface

Roughness and native oxidation

WET Surface Preparation

Diluted HF:
Morphological impact and oxide removal efficiency

DRY Surface Preparation

Plasma He, Argon:
Morphological impact and oxide removal efficiency

WET and DRY Surface Preparation

Alternative WET and DRY combination for surface preparation
Low surface roughness

Sn oxidation almost immediate (<15 min air exposure)
SnO_x oxidizes to SnO_2 with air exposure

Ge oxidation slower than that of Sn
No evolution of the oxide in samples older than 14 days
**MOTIVATION: SURFACE PREPARATION PRIOR TO METALLIZATION**

**Silicon**

- \( \text{Ge}_{0.85}\text{Sn}_{0.15} \) \( 60 \text{ nm} \)
- Ge \( 2.5 \mu\text{m} \)

Native oxide GeO\(_x\) and SnO\(_x\)

- Oxide grows almost immediately
- Oxide deleterious for Ni and NiPt ohmic contacts
- This oxide should be removed without degrading the surface
- GeSn is a new material: *surface preparation should be investigated*

**WET treatment**
- HF-Last + \( \text{N}_2 \) gun drying
- HF + \( \text{H}_2\text{O} \) rinse

**DRY treatment**
- He
- Argon
OUTLINE

GeSn characterization surface

- Roughness and native oxidation

WET Surface Preparation

- Diluted HF: Morphological impact and oxide removal efficiency

DRY Surface Preparation

- Plasma He, Argon: Morphological impact and oxide removal efficiency

WET and DRY Surface Preparation

- Alternative WET and DRY combination for surface preparation
IMPACT OF DILUTED HF ON GESN 15%

- No pitting
- Slight roughness increase

Grazing XPS quantification

<table>
<thead>
<tr>
<th></th>
<th>Aged GeSn</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn/(Sn + Ge)</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>GeOx/Ge</td>
<td>0.5</td>
<td>0.3</td>
</tr>
<tr>
<td>SnOx/Sn</td>
<td>0.9</td>
<td>0</td>
</tr>
</tbody>
</table>

- [Sn] surface depletion
- Ge top oxide layer
- Oxide free Sn
IMPACT OF DILUTED HF + H₂O RINSE ON GESN 15%

- **No pitting**

**Grazing XPS Spectra**

- Surface is Sn depleted (as after a dip in HF)

**H₂O rinse post HF step oxidizes slightly Ge and Sn**

**Grazing XPS quantification**

<table>
<thead>
<tr>
<th></th>
<th>Aged GeSn</th>
<th>HF</th>
<th>HF + H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn/(Sn + Ge)</td>
<td>0.2</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>GeOₓ/Ge</td>
<td>0.5</td>
<td>0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>SnOₓ/Sn</td>
<td>0.9</td>
<td>0</td>
<td>0.1</td>
</tr>
</tbody>
</table>

RMS = 0.8 nm

AFM

1 µm
WET surface preparation:

Ex-situ WET cleaning chamber → Metallic deposition TOOL

Air break unavoidable

DRY surface preparation:

In-Situ DRY plasma chamber → Metallic deposition TOOL

No Air Break

➢ DRY surface preparation useful for air sensitive material
OUTLINE

GeSn characterization surface

Roughness and native oxidation

WET Surface Preparation

Diluted HF: Morphological impact and oxide removal efficiency

DRY Surface Preparation

Plasma He, Argon: Morphological impact and oxide removal efficiency

WET and DRY Surface Preparation

Alternative WET and DRY combination for surface preparation
Air break of 15 minutes between the dry treatment and XPS analysis

<table>
<thead>
<tr>
<th></th>
<th>Native oxide</th>
<th>He</th>
<th>Argon soft</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn/(Sn + Ge)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>GeOx/Ge</td>
<td>0.5</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>SnOx/Sn</td>
<td>0.9</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

- Air break has an impact on native oxide regrowth
- He and Argon plasma seem to reduce Sn oxide

AFM

Native oxide
RMS = 0.48 nm
1 µm

He
RMS = 0.63 nm
1 µm

Argon soft
RMS = 0.54 nm
1 µm

- He: no pitting
- Argon soft generates pitting
TUNING THE ARGON PROCESS ON GESN 15%

Grazing XPS quantification

<table>
<thead>
<tr>
<th></th>
<th>Oxyde natif</th>
<th>Argon soft</th>
<th>Argon super soft</th>
<th>Argon extra soft</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn/(Sn + Ge)</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>GeOx/Ge</td>
<td>0.5</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>SnOx/Sn</td>
<td>0.9</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

➢ Plasma still reduces oxide

AFM

Native oxide

Argon soft

Argon super soft

Argon extra soft

➢ Fine process tuning: pits are avoided

Plasma power reduction

RMS = 0.48 nm

1 µm

RMS = 0.54 nm

1 µm

RMS = 0.50 nm

1 µm

RMS = 0.50 nm

1 µm
OUTLINE

GeSn characterization surface

Roughness and native oxidation

Diluted HF: Morphological impact and oxide removal efficiency

 Plasma He, Argon: Morphological impact and oxide removal efficiency

Alternative WET and DRY combination for surface preparation

WET Surface Preparation

DRY Surface Preparation

WET and DRY Surface Preparation
WET DRY SURFACE PREPARATION COMBINATION

HF Surface preparation

Results in a thin layer of GeO$_x$ without SnO$_x$

DRY Surface preparation

Reduces Ge and Sn oxides

Combine WET and DRY surface preparation to increase the oxide removal

WET and DRY treatments
- HF - He
- HF - Argon
### Grazing XPS quantification

<table>
<thead>
<tr>
<th></th>
<th>Native oxide</th>
<th>HF-rinse</th>
<th>HF-He</th>
<th>HF-Argon extra soft</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn/Ge</td>
<td>0.2</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>GeOx/Ge</td>
<td>0.5</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>SnOx/Sn</td>
<td>0.9</td>
<td>0.1</td>
<td>0.6</td>
<td>0.6</td>
</tr>
</tbody>
</table>

- Surface oxide still present
- Air break re-oxidation
- XPS Analysis needs to be without air break (in progress)

### AFM

<table>
<thead>
<tr>
<th>Surface oxide</th>
<th>HF-rinse</th>
<th>HF-He</th>
<th>HF-Argon extra soft</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native oxide</td>
<td>RMS = 0.48 nm</td>
<td>RMS = 0.54 nm</td>
<td>RMS = 0.45 nm</td>
</tr>
<tr>
<td>HF</td>
<td>RMS = 0.54 nm</td>
<td>RMS = 0.45 nm</td>
<td></td>
</tr>
<tr>
<td>HF-He</td>
<td>RMS = 0.45 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HF-Argon extra soft</td>
<td>RMS = 0.45 nm</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- WET and DRY combinations increase pitting
- Shorter exposures to plasma might cure that
1) **GeSn 15%** is very sensitive to air exposure:
   - Formation of a native oxide almost immediately

2) **Diluted HF:**
   - removes the Sn oxide and leaves a thin layer of Ge oxide
   - Does not change the surface roughness

3) **He and Ar plasmas:**
   - reduce the amount of oxide
   - with a fine tuning: no pitting and no roughening

4) **Diluted HF + plasma sequence:**
   - reduces the amount of surface oxide
   - Limits pitting
ACKNOWLEDGMENT

Thanks to:

LTM: PHD supervisor
L. Vallier

WET: PHD supervisor
V. Loup, P. Besson

Sample
J. Aubin, J.M. Hartmann

DRY
Ph. Rodriguez, A. Quintero

This work was partially supported by:
- the LabEx Minos ANR-10-LABX-55-01
- the French National Research Agency (ANR) under the “Investissements d'avenir” programs: ANR 10-AIRT-0005 (IRT NANOELEC)
- ANR 10-EQPX-0030 (EQUIPEX FDSOI 11) and by Nano2017 project

THANKS YOU FOR YOUR ATTENTION