**Accelerating the next technology revolution**

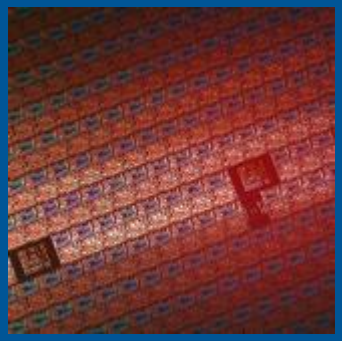
# *Understanding the mechanism of capping layer damage and development of a robust capping material for 16 nm HP EUV mask*

Il-Yong Jang [1], Arun John [1], Frank Goodwin [1]

Su-Young Lee[2], Seong-Sue Kim[2]

[1] SEMATECH

[2] Samsung Electronics



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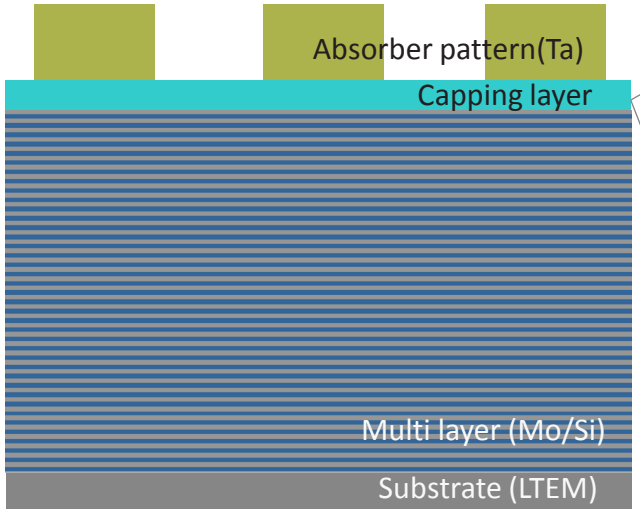
# Outline

- Current status
- Experimental conditions
- Cause of Ru damage
- Simulation results
- How to mitigate Ru damage
  - Process improvement
  - Development of new material
- Summary

# Ru damage

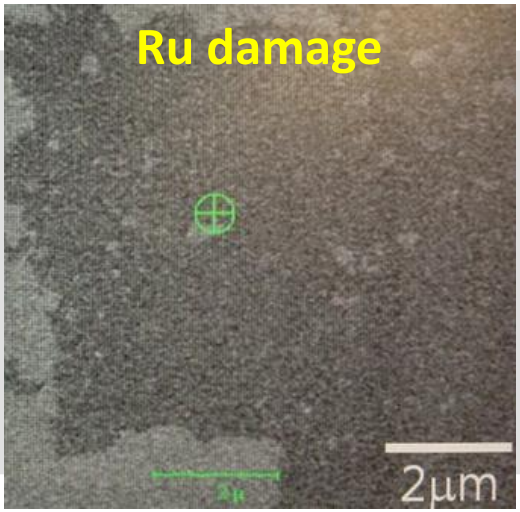



. **Protect ML from damage**
: Dry Etch, Repair, Cleaning

. **Requirements**
: High EUV reflectance
: Oxidation resistance
: Durability in plasma and chemical
: Stability in high temperature

→ **Ru/Ru-compound for capping layer**

. **Mask process**
: Physical force
: Chemical reaction
: High temperature
: UV radiation
: Oxidation




. **Results**
: ML oxidation
: Reflectivity drop
: CD change in WF

# Ru damage during mask process

**Blank Supplier**

Substrate → ML deposition → Capping layer deposition ① → Annealing ② → Absorber deposition

**Maskshop**

Resist patterning → Absorber etch ③ → Cleaning ④ → Inspection → Repair

① Properties of capping layer
: Properties of material in mechanical and chemical stress

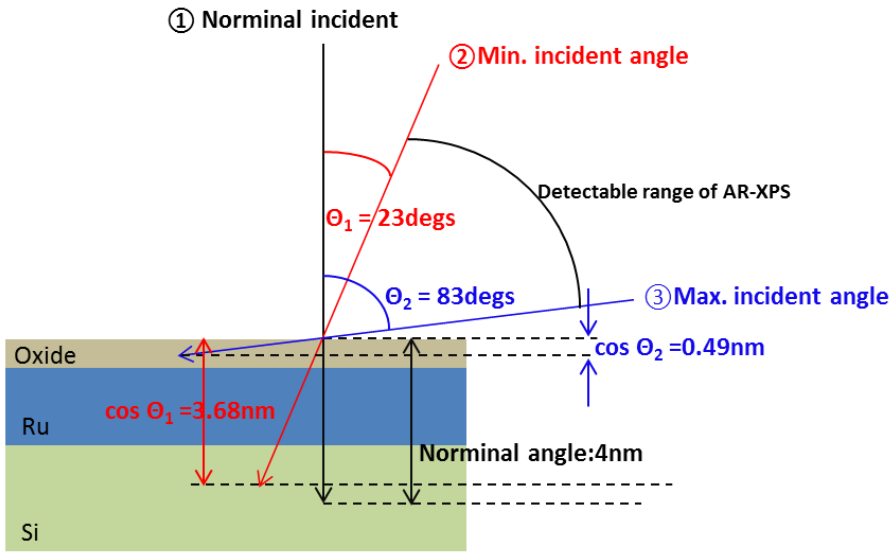
② Annealing in High temperature
: Oxidation, change in material properties

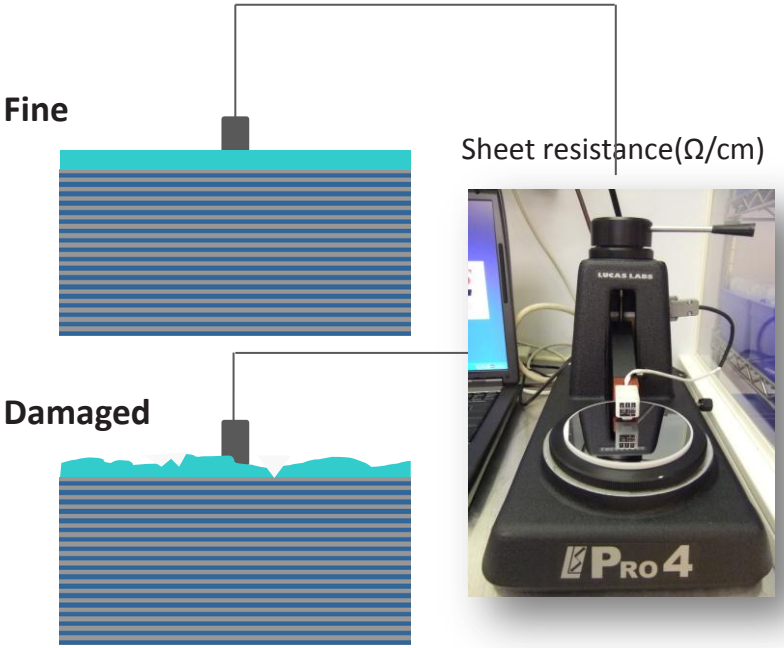
③ Plasma etch : oxidation, erosion by corrosive gas, stress by ion bombardment

④ Cleaning process
: Oxidation, change in material properties

# Experimental

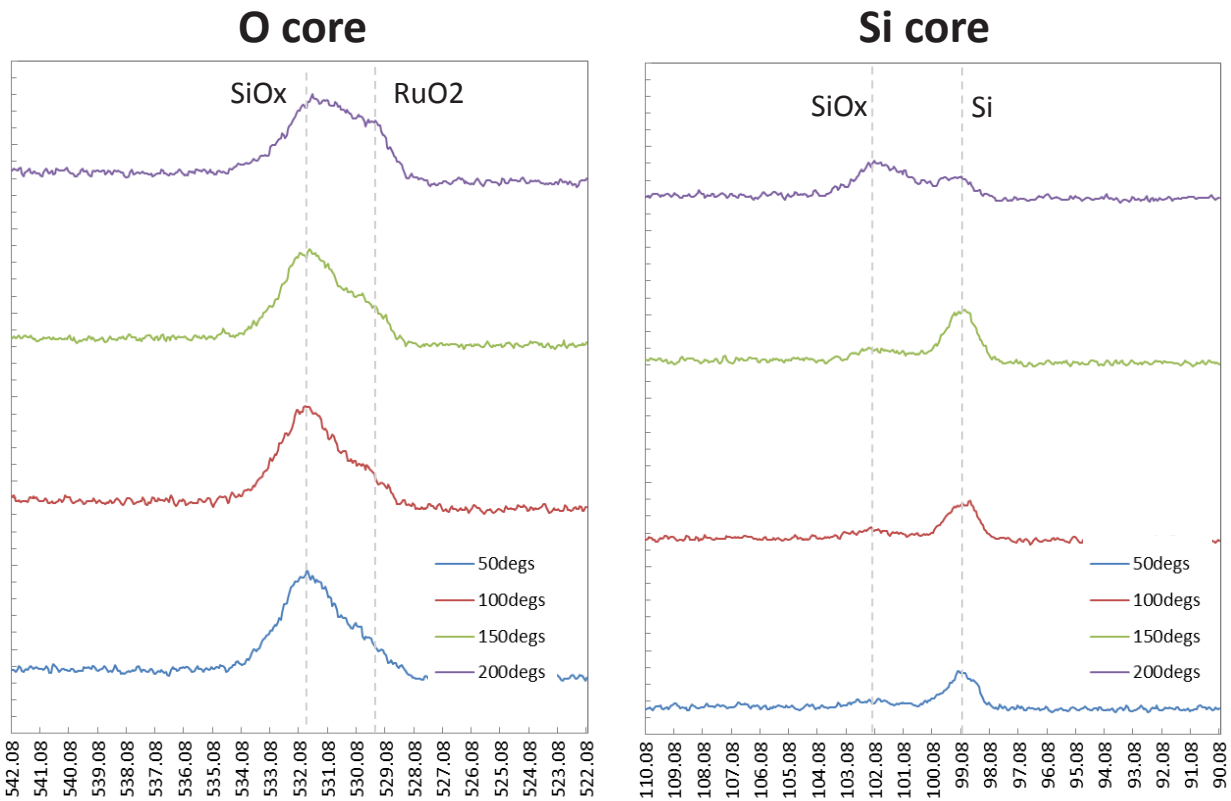
- Material
  - 6 inches sq. wafer for deposition of Ru and new capping material
  - Reactive sputtering using SEMATECH's IBD chamber
- Process
  - In-situ. UV(IUV) cleaning at Mask Track, Anneal on hotplate
- Analysis : Angle Resolved XPS, Four point probe

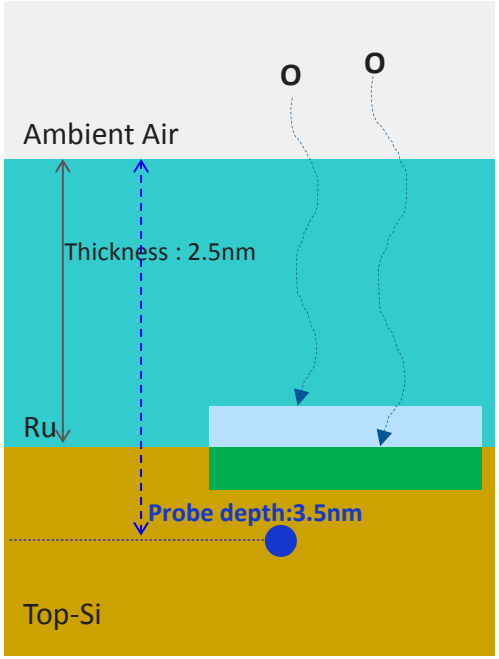


# Change in film properties

# Oxidation by annealing



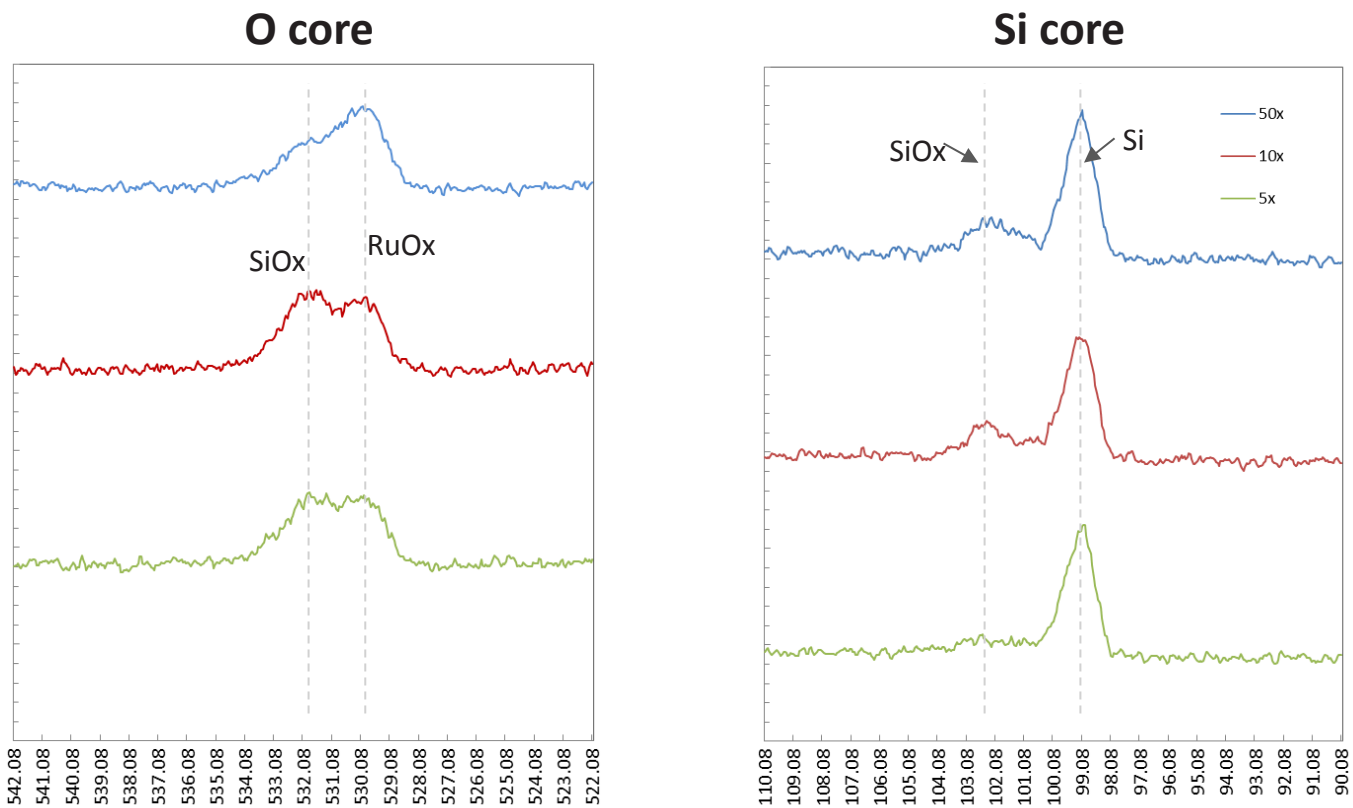




- **Conditions :** 2.5nm-Ru, 10 min annealing, 3.5nm-probing depth
- **O core** : Annealing Temp ↑ → RuOx gradually ↑ → **Ru oxidation ($RuO_2$)**
- **Si core** : The SiOx peak (101.97eV) abruptly increase from 200°C.

  Si has been changed to SiOx by oxygen penetration

➔ **Ru and Si are oxidized by high temperature annealing process**

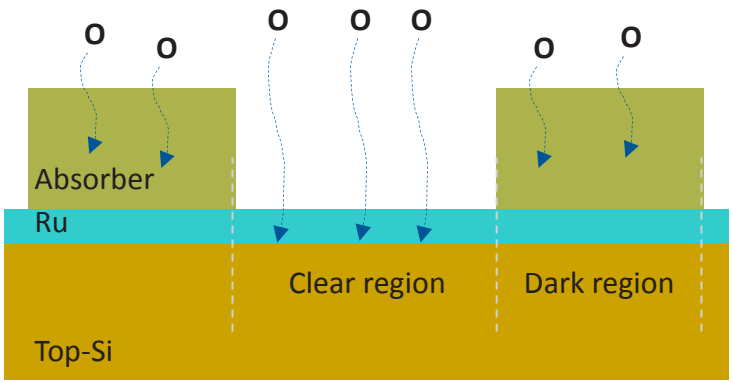
# Oxidation by IUV cleaning




- **Conditions** : 2.5nm-Ru, IUV cleaning (5X, 10X, 50X cycles), 3.5nm-probing depth
- Ru appears to be strongly oxidized by IUV cleaning
- Si under the Ru is also oxidized by IUV cleaning

➔ **During IUV process, oxygen penetrates Ru and finally reacts with Si**

# Mechanism of Ru damage




. **Mask is annealed in Air with HT and cleaned in IUV+DI**

. **Oxygen diffuses to the surface**

. **Clear region**

- Oxygen penetrates Ru film and reaches Si surface
  : Ru → RuOx (ductile → brittle)
  **: Si → SiOx**

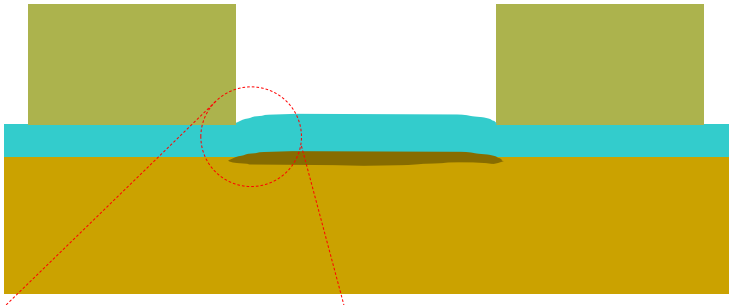
. **Dark region**

- Absorber protects oxygen penetration

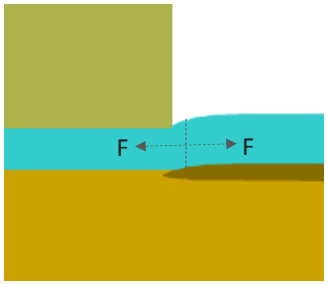
. **Volume expansion when Si → SiOx**

$$x_{si} = x_{ox} * \frac{N_{ox}}{N_{si}}$$

$$= x_{ox} * \frac{2.3*10^{22}\ molecules/cm^3}{5*10^{22} molecules/cm^3} = 0.46 x_{ox}$$



. **Tensile stress**




. **Properties change**

- RuOx : brittle in stress
- SiOx : Poor adhesion to Ru

# Simulation of the Ru damage

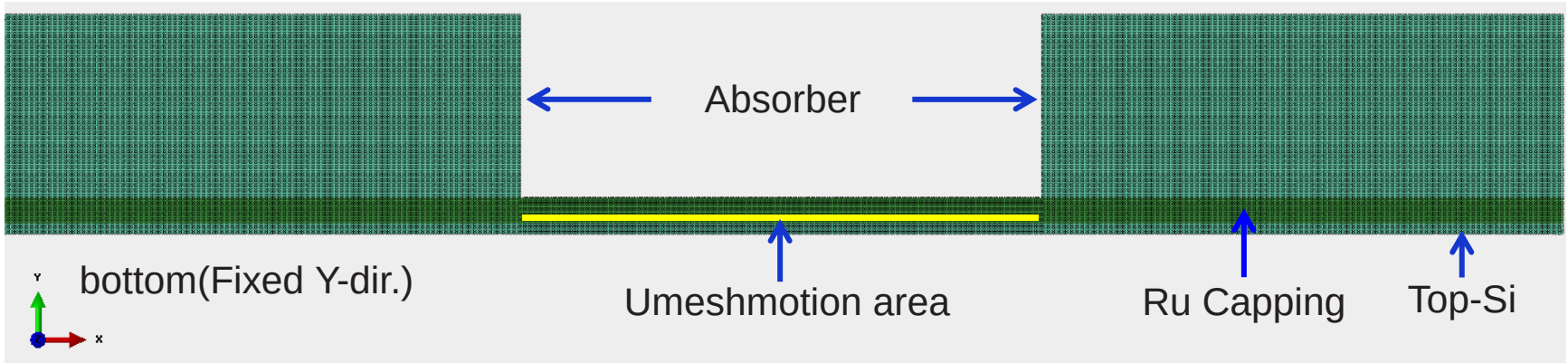
## Simulation parameter

- S/W: ABAQUS (Finite Element Method)
- Element: four-node quadrilateral elements
- Unit element size(W x H): 1 nm x 1 nm
- Total number of Nodes: 37,756ea
- Total number of elements: 37,000ea
- Total Degree of Freedom: 75,512ea

| Layer | Mate-rial | Thick (nm) | Width (nm) | Young's Modulus (GPa) | Poisson's ratio |
|---|---|---|---|---|---|
| Abs | TaN | 70 | 200 | **186** | **0.34** |
| Cap | Ru | 2.5 | - | **447** | **0.30** |
| Si | Si | 4.1 | - | **188** | **0.28** |

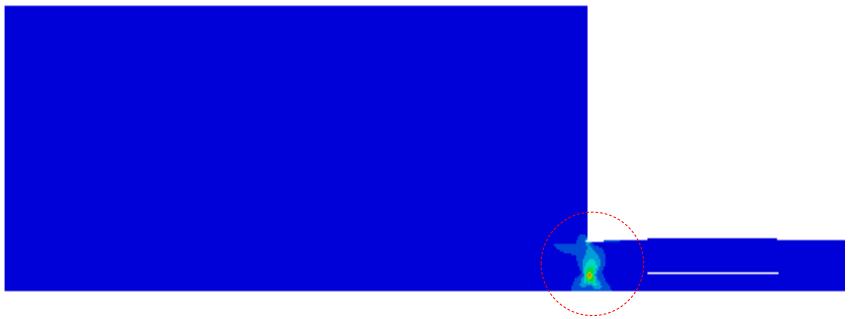
## Boundary condition

Boundary condition: 1-D D-G model $x \cong \frac{B}{A}(t+\tau)$

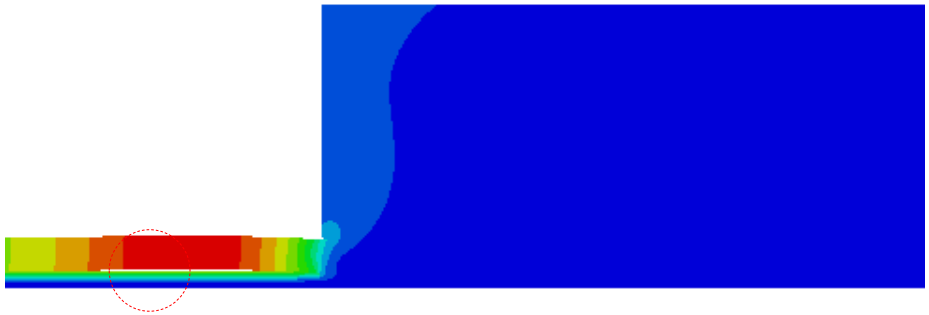


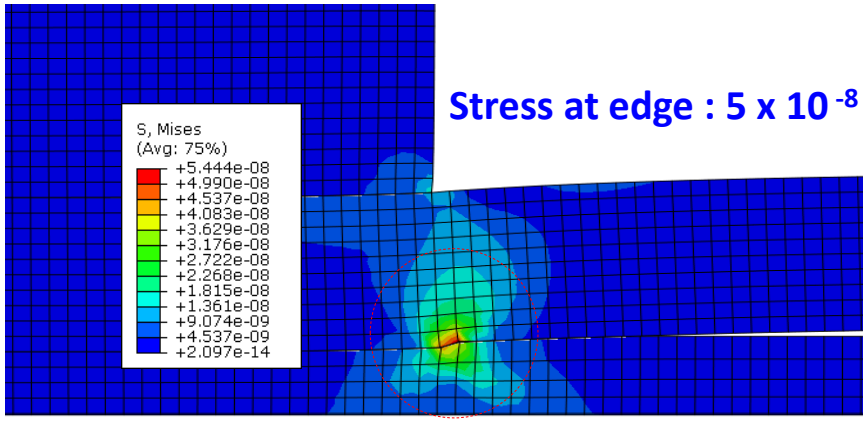
# Simulation of the Ru damage

Film stress



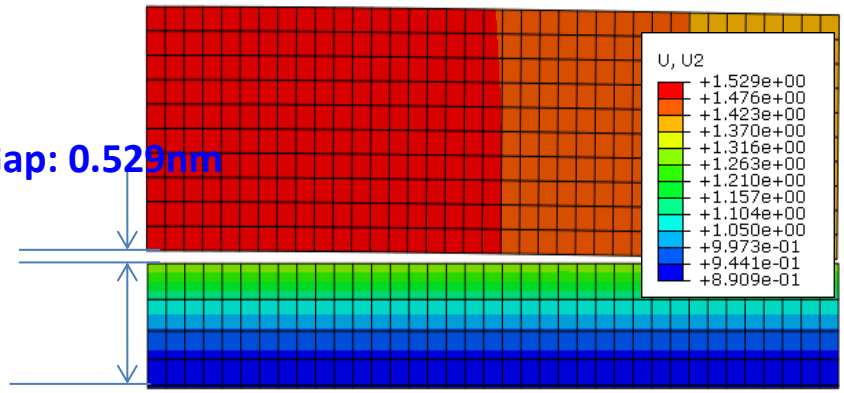
Displacement






**Stress at edge : 5 x 10 $^{-8}$ Pa**

***Gap: 0.529nm**




***umeshmotion: 1 nm (4.1→5.1 nm)**

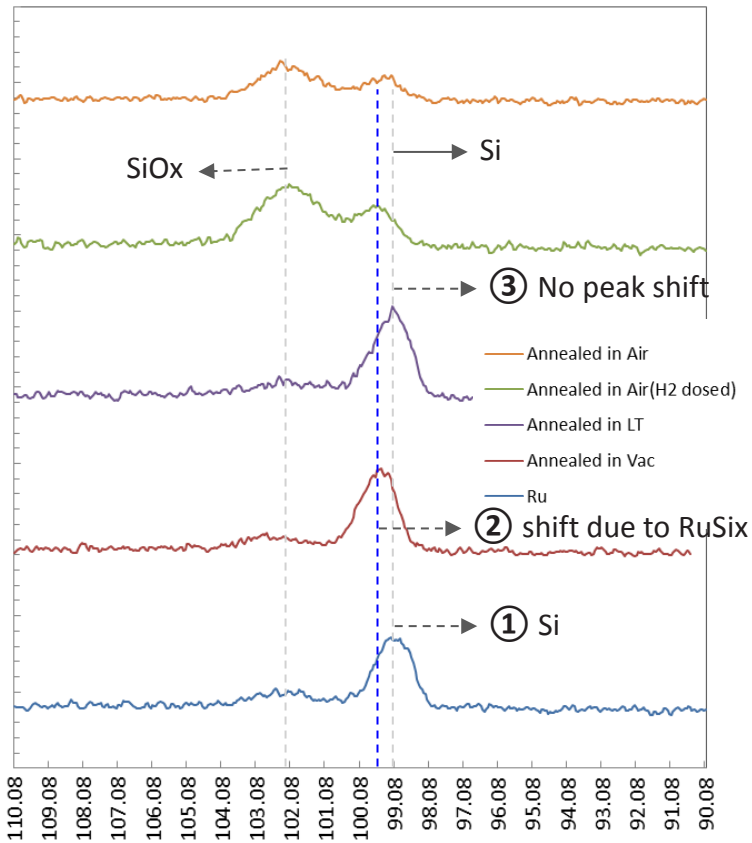
# How to mitigate?

# Mitigation of Ru damage – by process

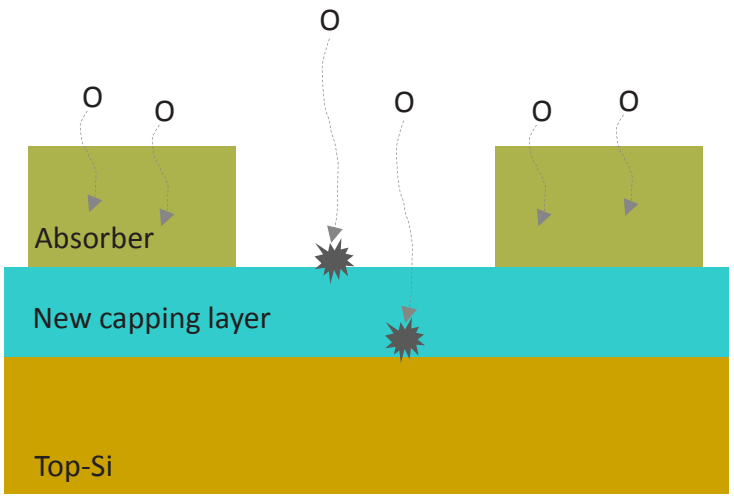
. **Annealing in vacuum**
- No significant SiOx peak
  → suppress Si oxidation
- Slight shift of Si peak due to RuSix formation

. **Annealing in Low Temp. (@150°C)**
- No significant SiOx peak
- Critical Temp. trigger oxidation of Si should be between 150°C and 200°C
- Less RuSix formation

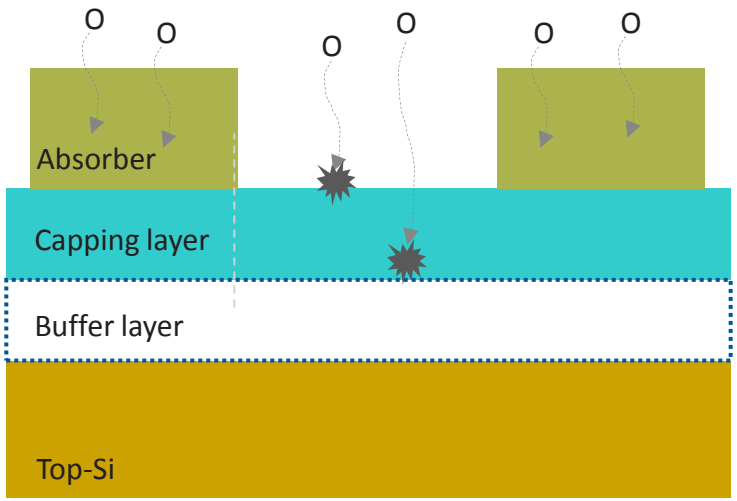
. **$H_2$ dosing**
- Impossible to reduce the oxidized Si by $H_2$ flow
- Increases in peak intensity due to removal of carbon contamination



# Mitigation of Ru damage – by new material

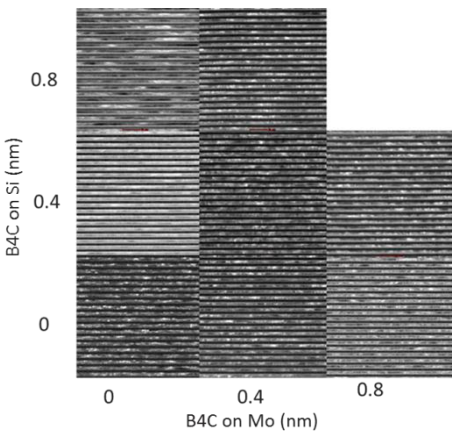


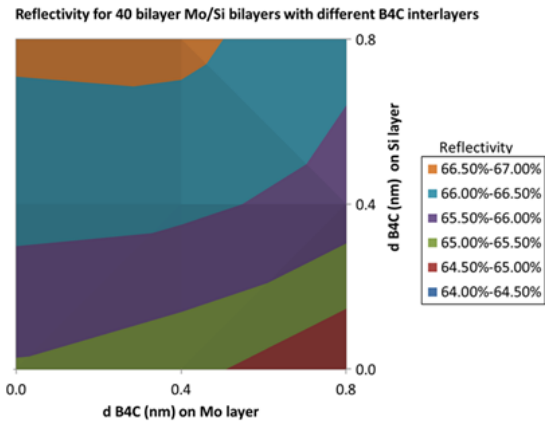

. **Capping layer**
- Suppress oxygen penetration
- Less oxidation
- Stable in chemical / plasma
- Ductile in mechanical stress
- No deterioration of optical properties
- Robust in mask process
- $B_4C$, new Ru compound




. **Buffer layer**
- Suppress oxygen penetration
- Less oxidation
- Robust in mask process
- Good adhesion btw Si and capping layer
- No deterioration of optical properties
- Ru/BL/top-Si

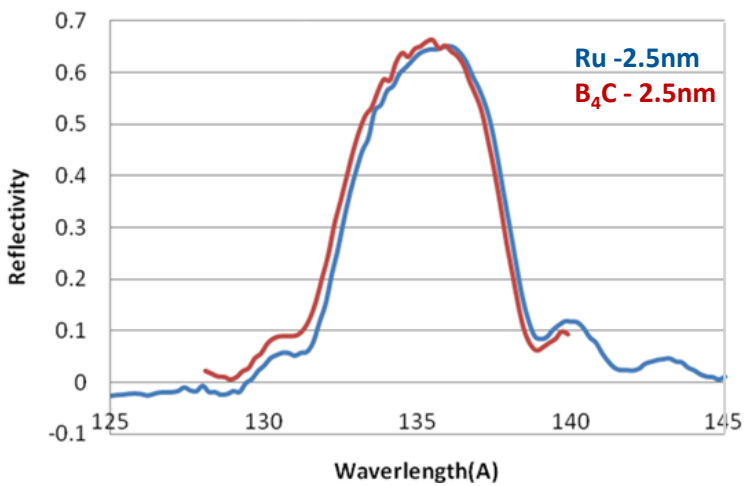
# $B_4C$ capping layer

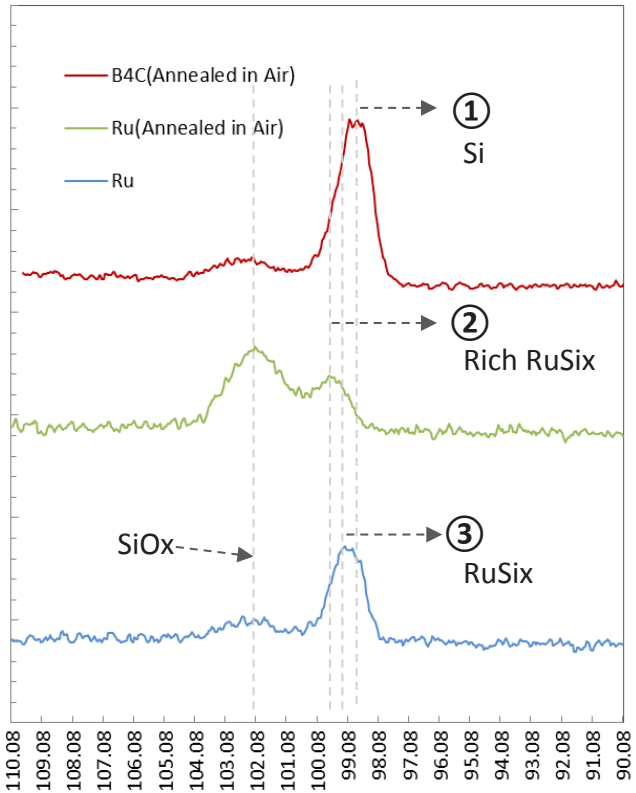



. Good barrier layer to suppress the inter-diffusion

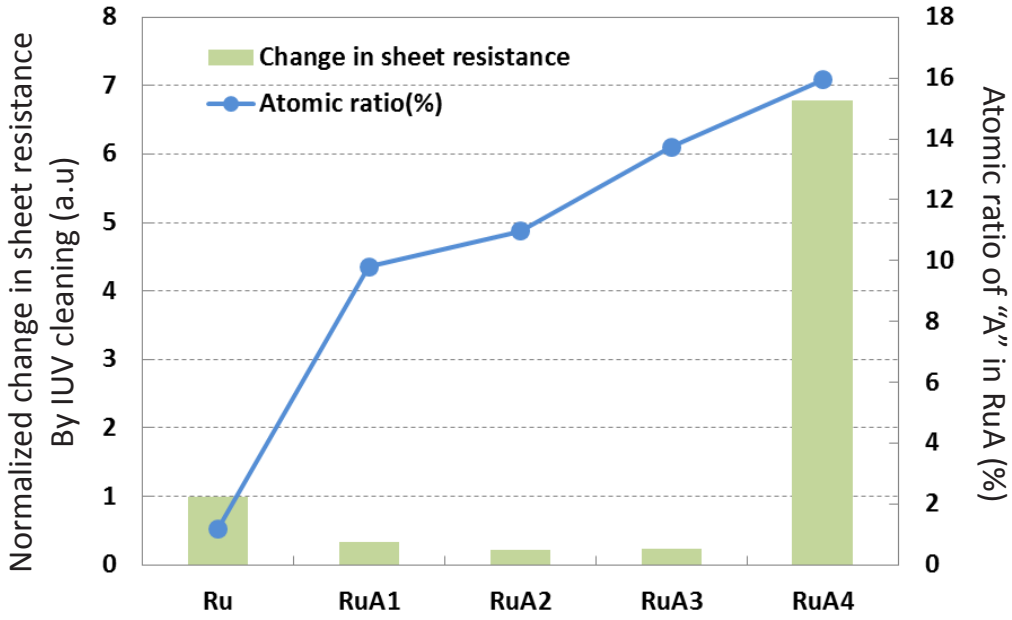
. No silicide formation → increase in 2% of EUVR

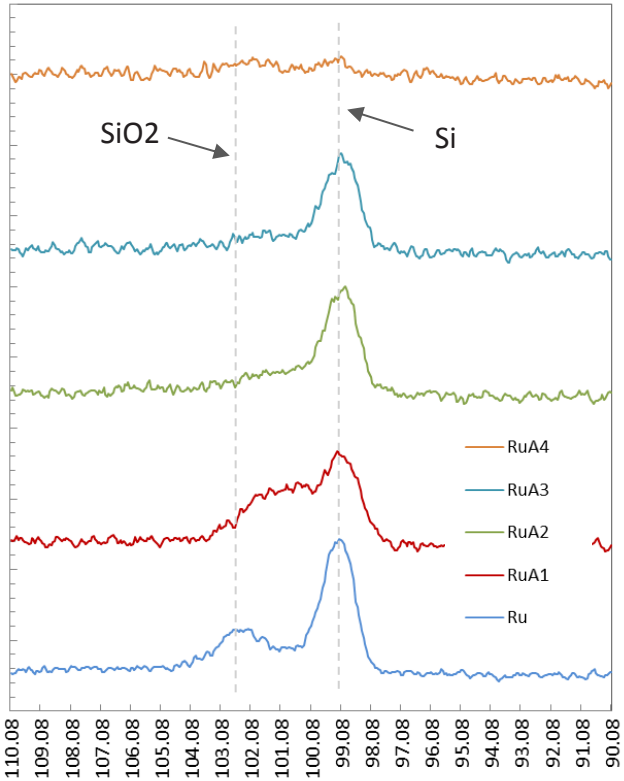



**. No EUVR deterioration is observed once $B_4C$ is used as a capping layer instead of Ru**

# New Ru compound capping layer

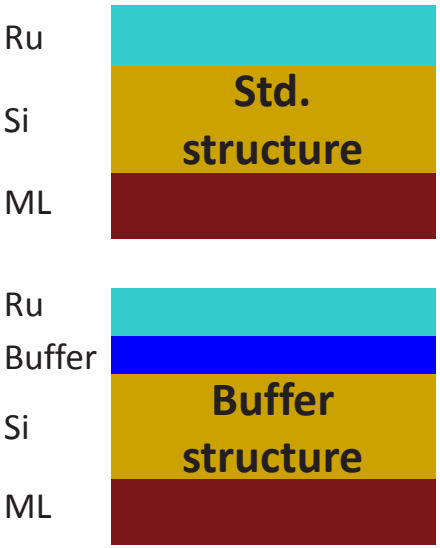


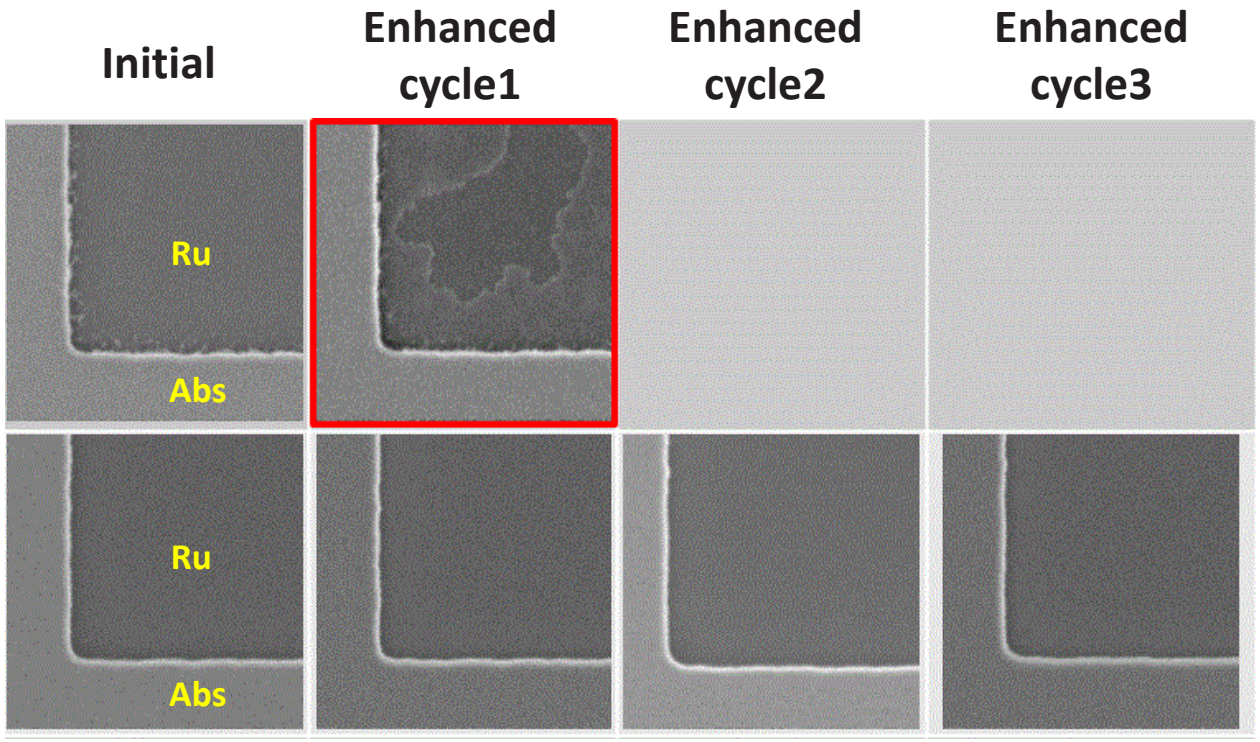




. Dosed "A" atom in Ru to suppress change in film property

. The amount of Si oxidation is inversely proportional to the amount of incorporated "A" atom in RuA

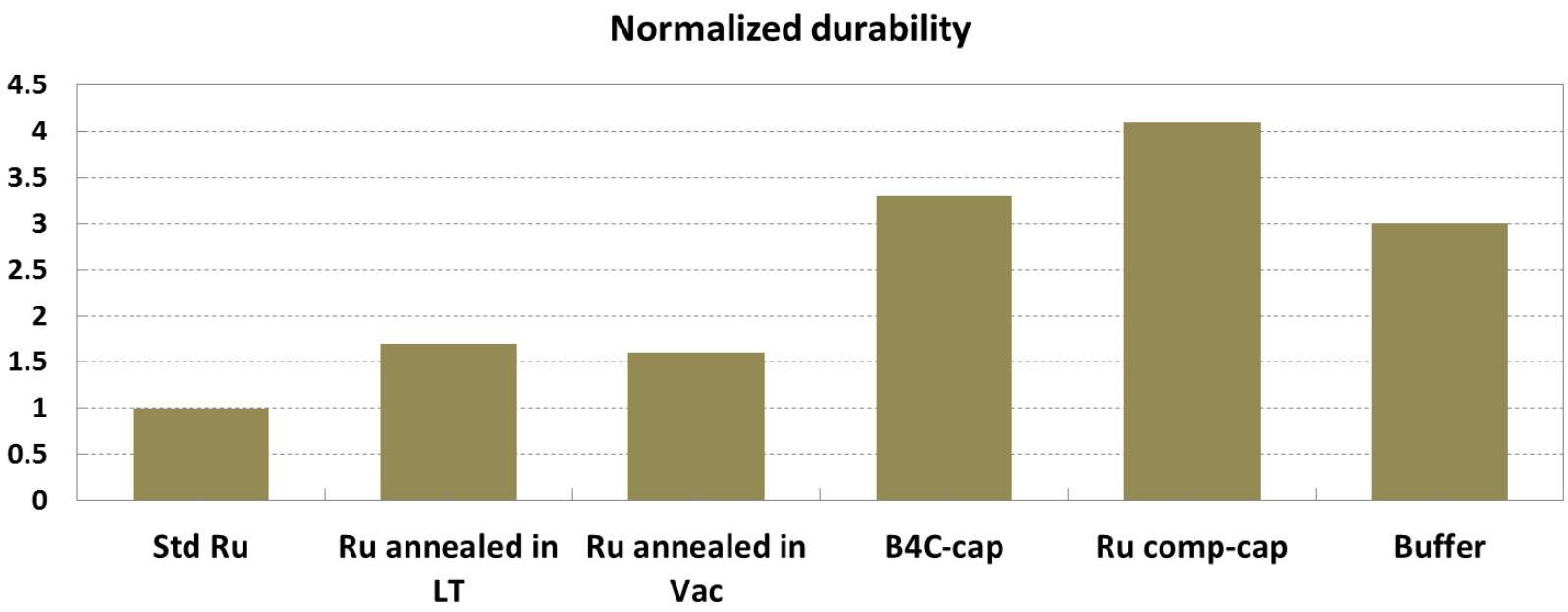
# Inserting buffer layer




. SEMATECH has developed a buffer layer between Ru and Si
. The purpose of buffer layer is to suppress the oxygen diffusion to Si
. The Ru/BL/top-Si structure increases the durability of Ru in IUV process
. Further optimization should be necessary for this structure.

# Summary




. SEMATECH has disclosed the root cause of Ru damage and been developing a new material with state-of-the art IBD tool to solve the problem.

. The most promising method will be verified on 6 in. sq. mask using mask shop's infrastructure in near future.

# Acknowledgement


. **Deposition** : Patrick Kearney and Alin Antohe from SEMATECH

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# Thank you !