Chemical Bonding Transformation Mapping to Optimize Low-k Dielectric Nanostructure Fabrication and Post-etch Residue Clean

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University of North Texas

Kanwaljit Singh

Components Research, Intel Corporation

Ian Brown, Jacques Faguet

US-Technology Development Center,
TEL Technology Center
> 42,000 Students,
> $1 billion annual budget
Goal: Explore the underlying fundamental science that leads to real engineering solutions for important interfacial issues in microelectronic fabrication.

Group members:
Alex Lambert, Issac Goutham, Muthappan Asokan, Seare Berhe

Alumni:
Dr. Sirish Rimal (JSR-Micro)
Dr. Tamal Mukherjee (LAM)
Dr. Nick Ross (Intel)
Dr. Kyle Yu (TEL)
Dr. Karthik Pillai (TEL)
Dr. Simon Koskey (Intel)
**Interfacial Electrochemistry & Materials Research Lab**

**Front end (FEOL):** Silicon surface preparation, H-passivation, SC1/SC2 cleaning, Silicon oxide etching, metal (Cu) and organic contamination control/detection.


**Back end (BEOL):** Cu ECD, Ru-based liner/barrier, Cu cleaning chemistry, Cu bimetallic corrosion mechanism, Post etch residue, Porous Low-k damage control.


**IC Packaging:** Cu vs. Au wire bonded device, Al pad corrosion prevention, molding compounds, Subtractive Cu Etching.

Requirements for BEOL Cleans

Removal of:
- Litho materials
- Etch polymers
- Sacrificial hardmasks

Compatibility with:
- Low-\(k\) dielectric
- Lower-layer metals

Complex interactions:
- Plasma-etch modified materials
- Galvanic corrosion
- Interfacial adhesion

BEOL Patterning & Damascene Processing

(Cu plating):
\[ \text{Cu}^{+2}_{(aq)} + 2e^- \rightarrow \text{Cu}_{(s)} \]

C. Weng, Materials Science in Semiconductor Processing, 13, 376 (2010)
Invent Ru Barrier/liner

Micro-pattern Corrosion Screening Cu/Ru, Co/Cu

Co on Cu without inhibitor

Co on Cu with inhibitor

Applied Physics Letter, 2005, 86, 083104
BEOL Patterning & Damascene Processing

Etch/Clean Process optimization

→ MIR-IR Chemical Bonding Mapping

C. Weng, Materials Science in Semiconductor Processing, 13, 376 (2010)
Attenuated total reflection (ATR) Infrared Spectroscopy (ATR-IR)

- Not-reproducible
  - sample elasticity
  - flatness, position
  - fragile ILD damage
- Low sensitivity
  - miss max evanescent wave interaction
Multiple Internal Reflection Infrared Spectroscopy (MIR-IR)

Patterned Si wafer = IR waveguide

MIR-IR

Detector

[(d_p) = 1-2 μm]

MIR-IR Advantages

- No sample-contact problem
- Reproducible
- Max Evanescent Wave Interaction
- Superior Sensitivity (<10% monolayer)


Not-reproducible
- sample elasticity
- flatness, position
- fragile ILD damage

Low sensitivity
- miss max evanescent wave interaction
MIR-IR Application:
Ultra-clean Silicon Wafer Surface Preparation
Surface Bonding Transformation on Si(100) by Trace Cu$^{+2}$ impurity

Trace Cu$^{+2}$ induced early oxide and pitting

MIR-IR : Optimize $\alpha$-Si:H Microbolometer for Night Vision Camera

PECVD Production of $\alpha$-Si:H wafer.

Fabricate into IR waveguide

PECVD Production of $\alpha$-Si:H wafer.

$\alpha$-Si:H Microbolometer Pixel

Optimize PECVD Hydrogen Dilution, BCl$_3$ dosage, Temperature, etc

Data Analyses

MIR-IR Characterization
Comparing MIR vs Transmission (TIR) Sensitivity on $\alpha$-Si:H

MIR-IR: Optimizes $\alpha$-Si:H Thin Film Quality

Bonding to Hydrogen is the key

Chemical Bonding Data Accelerates PECVD Process Optimization
**Objective:** Utilize MIR-IR to optimize RIE etching and post RIE cleaning with minimum dielectric damages
Current Metrology for Trench ILD Nano-structures

SEM and TEM
• Electron beam based metrology
• Cross sectional profiling
• **Destructive analysis, limited chemical bonding info**
• Laborious and time consuming

XPS and TOF-SIMS
• Evaluate depth of carbon depletion
• Provides elemental composition
• Based on x-ray, ion bombardment
• **Can’t reach deep-sidewalls and bottoms**

Spectroscopic Ellipsometry
• For unpatterned films
• Technique based on refractive index
• Requires modeling

IR – traditional
• Provide chemical bonding structure
• **Weaker signal and limited resolution**
MIR-IR is a Powerful Substantive Tool --
Isolate Low-k Film Stack only Spectra

Oxide (50nm)
Dense Low-k (50nm)
Porous Low-k (300nm)
Si sub

Low-k Stack

Sample Spectrum

Vs.

Background Spectrum

→

Si substrate

Low-k stack only Spectrum

New IR Metrology

Prepare directly from patterned ULK/Resist wafer
Chemical Bonding Transformation Map for Porous Low-k Nanostructure

MIR-IR: Evaluating Plasma-induced Damages on Trench ILD


<table>
<thead>
<tr>
<th>Wafers</th>
<th>SiOH @ 3430 cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) pristine</td>
<td>13 mabs</td>
</tr>
<tr>
<td>(2) post-etch</td>
<td>16 mabs</td>
</tr>
<tr>
<td>(3) post-strip</td>
<td>24 mabs</td>
</tr>
<tr>
<td>(4) +60 sec over-etch</td>
<td>43 mabs</td>
</tr>
</tbody>
</table>

Post-Strip (O₂ plasma) more ILD damages

Confirmed by DHF etch

60 sec Over-Etch After dHF etch
Four oxidative plasma strip processes screened by either adjusting process gases or by modulating chamber pressure for reduced O radical content.

Strip process 1 induces minimal damage (lowest silanol) retaining maximal C-doping (highest CH₃).

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**MIR-IR: Minimize Low-κ Damage of Manufacture Strip Processes**

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**Absorbance**

**Wavenumber (cm⁻¹)**

**Peak Heights (mabs)** Si-OH

**Strip 1** Lowest Water Sensitivity

**Strip 1** Highest Carbon Dopping

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**Interfacial Electrochemistry & Material Research Lab**

**UNT**
Chemical Bonding Transformation Map for Porous Low-k Nanostructure

Absorbance

3000
3500
4000

Wavenumber cm⁻¹

Low-k Damage

Si-OH

a-CH₃

Carbon Doping

Low-k Damage

Residue removal

Si-O cage

Carbon Doping

Si-CH₃ (bend)

Si-CH₃ (rock)

Low-k

Etch residue

FC=CF

C=CF

CH₃, CH₂, CH (def.)
MIR-IR: Evaluating Plasma Damages and Etch Residue Removal

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</tr>
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</table>

Evaluate Post-etch Residue Removal Efficiency

MIR-IR: Identify Chemical Bonding Structure for Post-Etch Residues

Kanwaljit Singh, Intel
Alan M Myers, Intel
XPS Data: Difficult to Assign Chemical Bonding

Curve Fitting

XPS: Elemental Info
(C, F, O, H)
C-F, C-H, C-O, C-C

But, no reliable chemical bonding structure info

Chemical Bonding Structure of Etch Residues

- Mainly fluoropolymer backbone
- Significant branching/cross-linking
- Olefinic unsaturation (fluorinated)
- Carbonyl functional groups

Polytetrafluoroethylene (Teflon)

$\square = \{\text{CF}_2 - \text{CF}_2\}_n$

Identify Chemical Bonding Structure by Functional Group Specific Surface Derivatization

Brady's test
Confirmation of C=O by DNPH Reaction

DNPH
2,4-Dinitrophenyl Hydrazine

Hydrazine
C=O
1710
C=N
1619
Hydrazone

≈ - 2 mabs
Assignments
C-H stretching (aromatic) 3000-3100 3108
C-H wagging (aromatic) 795-880 870-910
C-H scissoring (aromatic) 1000-1600 1000-1230
Aromatic ring sextant out of plane deformation (ring pucker) 680-720 746
NO$_2$ stretching (sym) 1318-1357 1341
NO$_2$ stretching (asym) 1485-1555 1505
C=C stretching (aromatic ring) 1500-1555 1510-1555
N-H stretching 3300-3500 3314
N-H bending 1580-1650 1596
C=N stretching 1610-1680 1619

**Hydrazone absorption peak table:**

<table>
<thead>
<tr>
<th>#</th>
<th>Exp (ref)</th>
<th>#</th>
<th>Exp (ref)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>3314 (3313)</td>
<td>13.</td>
<td>1380 (1359)</td>
</tr>
<tr>
<td>2.</td>
<td>3108 (3106)</td>
<td>14.</td>
<td>1341 (1336)</td>
</tr>
<tr>
<td>3.</td>
<td>2976 (organics)</td>
<td>15.</td>
<td>1316 (1312)</td>
</tr>
<tr>
<td>4.</td>
<td>2945 (2946)</td>
<td>16.</td>
<td>1216 (1236)</td>
</tr>
<tr>
<td>5.</td>
<td>2882 (2882)</td>
<td>17.</td>
<td>1175 (1136)</td>
</tr>
<tr>
<td>6.</td>
<td>1619 (1616)</td>
<td>18.</td>
<td>1140 (1136)</td>
</tr>
<tr>
<td>7.</td>
<td>1596 (1595)</td>
<td>19.</td>
<td>1102 (1102)</td>
</tr>
<tr>
<td>8.</td>
<td>1546 (1542)</td>
<td>20.</td>
<td>1044 (1062)</td>
</tr>
<tr>
<td>9.</td>
<td>1525 (1525)</td>
<td>21.</td>
<td>923 (922)</td>
</tr>
<tr>
<td>10.</td>
<td>1505 (1508)</td>
<td>22.</td>
<td>886 (855)</td>
</tr>
<tr>
<td>11.</td>
<td>1454 (1458)</td>
<td>23.</td>
<td>834 (831)</td>
</tr>
<tr>
<td>12.</td>
<td>1431 (1420)</td>
<td>24.</td>
<td>746 (744)</td>
</tr>
</tbody>
</table>

Confirm all 24 spectroscopic features of Hydrazone modified Post-Etch Residues.

2 x 10$^{-3}$ mabs

**Differential:** (before) – (after)
Identification of C=C by Br$_2$ Reaction

Before

After

Differential

Identify Fluoropolymer Backbone \[ \left\{ \text{CF}_2-\text{CF}_2 \right\}_n \]
By Reductive Defluorination on C-F bond

Naphthalenide Anion Radicals attack C-F bonds

Generate reactive radicals on Fluoro-polymer

Sodium Naphthalenide

Reductive Extraction of F

MIR-IR : UV-assisted Cleaning on Post-etch Residues

Kanwaljit Singh  Intel
Ian Brown  TEL
Jacques Faguet  TEL

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SEM Images of UV & UV+Wet Clean Samples

- No UV
- Hydrophobic
- No Wet Clean
- Deposit
- 5X Polymer
- #265_no Ash

Kanwal Jit Singh
SEM Images of UV & UV+Wet Clean Samples

- No UV
- 10sec UV
- 30sec UV
- 60sec UV
- 120sec UV
- 180sec UV
- 300sec UV

- Hydrophobic
- Hydrophilic

UV induced Polymer Residue Removal

Deposit
5X Polymer

#265_no Ash

Kanwal Jit Singh
SEM Images of UV & UV+Wet Clean Samples

No UV

Hydrophobic

No Wet Clean

Deposit 5X Polymer

10sec UV

30sec UV

60sec UV

120sec UV

180sec UV

300sec UV

UV induced Polymer Residue Removal

Hydrophilic

10sec UV + Wet Clean

30sec UV + Wet Clean

60sec UV + Wet Clean

120sec UV + Wet Clean

180sec UV + Wet Clean

300sec UV + Wet Clean

Complete removed by Wet Clean

#265_no_Ash

intel

Kanwal Jit Singh

TEL

Ian Brown
C=O Chromophore Required for UV-assisted Clean

With -C−O, no UV clean

Need -C=O, for UV clean

O₂ is required
Chemical Bonding Transformation Mapping - UV Radiation

- Fluorocarbon polymer backbone \(-(CF_2)_n\) steadily decrease as UV treatment time increases
- Gradual reduction of \(CF_x=CF_x\) band
- Fluoro-carbonyl \(F_xC=O\) forms by photo-cleavage of \(CF_x=CF_x\) bonds

Provide Critical Process Evolution Info for Engineering Optimization
Summary of Chemical Bonding Transformation with UV Radiation

Volatile Fragments

<table>
<thead>
<tr>
<th>Compound</th>
<th>BP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonyl Fluoride (CF₂O)</td>
<td>-84.57</td>
</tr>
<tr>
<td>Trifluoroacetyl Fluoride (C₃F₇O₂)</td>
<td>-59</td>
</tr>
<tr>
<td>Hexafluoroacetone (C₄F₆O)</td>
<td>-28</td>
</tr>
<tr>
<td>Octafluorobutan-1-one (C₄F₈O)</td>
<td>7-9</td>
</tr>
<tr>
<td>Nonfluoropentanal fluoride (C₅F₁₀O)</td>
<td>52.2</td>
</tr>
<tr>
<td>Perfluoro (2-methyl-3-pentanone) (C₆F₁₃O)</td>
<td>49</td>
</tr>
</tbody>
</table>

[2+2] Cycloaddition

Post-Etch Residues

Low-k modification

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IR Spectroscopic Evidence for Hydroxyl Formation during UV/Air Treatment

Chemical Bonding Transformation Insights – UV Clean Optimization More Efficient

Cleaning mechanism

Chemical Bonding Structure

Effective Post-etch cleaning with minimum dielectric damages
BEOL Etch and Cleans Process Integration

ULK Materials Engineering
- Low $K_{eff}$
- UV cured PECVD
- HF resistant

Reactive Ion Etching
- CD control
- Clean friendly
- Damage control

Post Etch Cleans
- Less damage
- Fast clean
- Keep CD, $K_{eff}$

Chemical Bond Formation & Bond Breaking - Highly Selective in time & space!

BEOL Integration Challenges

Metrology Tools
- Physical
- Electrical
- Chemical

Not complete
Costly

7 nm finFETs

Chemical bonding transformation map

PI: Oliver Chyan*, Chyan@unt.edu

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MIR-IR Applications in Advanced IC Fabrication

- FEOL (Ge, SiGe etc), BEOL etching and cleaning, formulation
- Monitor Post-etch residue removal & minimize Low-k damages
- Optimize Plasma Etch/Strip/Clean Process integration
- Monitor Low-k damages and optimize restoration process
- UV curing on porous Low-k dielectrics materials
- Evaluate TiN hard mask for Low-k pattern fabrication
- Flowable low-k dielectrics for gap filling in nanostructure
- Atomic Layer Deposition/Etching: provide critical interfacial chemical bonding info for better atomic layer control.

PI: Oliver Chyan*, Chyan@unt.edu
Goal: Achieve better understanding of fundamental materials properties at the critical interfaces of practical applications.

Group members:
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END