Lecture 16

Chemical Engineering for Micro/Nano Fabrication

Next: 193nm Lithography
Absorption of Photoresist Polymers

Impact of Photoresist Absorbance on Developed Image Profile

Exposure Step

Final Profile

Moderate absorbance

High absorbance
Relative Etch Rate of Polymers

- Aliphatic
- Aromatic
- Carbon
The Ohnishi Number

An empirical law discovered by Ohnishi states that the RIE etch rate of polymers is a linear function of the Ohnishi number O.N., i.e., the number of atoms in the polymer repeat unit, divided by the number of carbon minus the number of oxygen atoms:

$$O.N. = \frac{N}{N_C - N_O}$$

The higher percentage of carbon in aromatic structures leads to improved etch resistance, e.g.

PolyStyrene \((C_8H_8)_n\)  
ON = 16/8 = 2.0

PMMA \((C_8H_{18}O_2)_n\)  
ON = 15/3 = 5.0

193 nm Resist Materials

Challenge:

• 248 and 365 nm resists are unsuitable for 193 nm imaging because they are opaque at this wavelength.

• Etch resistance requires high carbon/hydrogen ratio but aromatics are precluded because of their absorption.

• How do you achieve both 193nm optical transparency and etch resistance?
High C:H Ratio of Alicyclic Hydrocarbons

The key!

Structure:

\[
\begin{align*}
\text{C}_6\text{H}_6 & \quad \text{C}_{12}\text{H}_{16} & \quad \text{C}_7\text{H}_{10} & \quad \text{C}_n\text{H}_{2n+2} \\
\text{CH}_3(\text{CH}_2)_n\text{CH}_3
\end{align*}
\]

Formula:

\[
\begin{align*}
\text{C}_6\text{H}_6 & \quad \text{C}_{12}\text{H}_{16} & \quad \text{C}_7\text{H}_{10} & \quad \text{C}_n\text{H}_{2n+2} \\
4 & \quad 5 & \quad 3 & \quad 0
\end{align*}
\]

Unsaturation Number:

\[
\begin{align*}
\text{C}_n\text{H}_{2n+2} - \text{C}_n\text{H}_x & \quad \text{C}_6\text{H}_{14} \\
\Delta H /2 = \text{Unsaturation Number} & \quad \text{C}_6\text{H}_8 \\
6/2 = 3
\end{align*}
\]
APEX 248nm Resist Design

CH–CH₂

O–tBOC

OH

Tethering Function  Acid Lability  Base Solubility  Etch Resistance
UTexas193nm Design

- Tethering Function
- Acid Lability
- Base Solubility
- Etch Resistance
Early Lithography

Resist

\[
\begin{align*}
\text{C} &= \text{O} \\
\text{CH}_3 &\quad \text{0.80} \\
\text{C} &= \text{O} \\
\text{OH} &\quad \text{0.20}
\end{align*}
\]

\[
\text{poly(NBCA-co-CBN)} + \text{Ø}_3\text{SSbF}_6
\]

- Synthesis requires metal catalyst!
- Excellent image quality
- Adhesion failure
Trading Etch Resistance for Adhesion: Alternating Systems: COMA

\[
\text{V601} \quad \begin{array}{c}
\text{COOCH}_3 \quad \text{COOCH}_3 \\
\text{H}_3\text{C} \quad \text{N} = \text{N} \quad \text{CH}_3 \\
\text{CH}_3 \quad \text{CH}_3
\end{array}
\]

Waco Chemical
No Metal!

Yield: 60%
\( M_n : 4,660 \)
\( M_w : 6,860 \)
\( Pd : 1.472 \)

Shelf Life issues?
Images in UT 193nm COMA Resist

Alternating co-polymer

Uzo Okoroanyanwu, Jeff Byers
Improving Etch Resistance

\[
\text{DNBC} + \text{carboxylic acid} \xrightarrow{\text{V601, Dioxane, 70°C}} \text{polymers}
\]

UV Absorbance
0.44 \(\mu\text{m}^{-1}\)
@ 193 nm

Yield: 55%
\(M_n: 3,400\)
\(M_w: 4,340\)
Pd: 1.276

With JSR
ChE 384T / 323
Resist and Process Development

- Basic Chemistry
- Formulation and Process Development
- Optimization

Time

Performance

248nm

193nm Issues!

I-line
Fujitsu’s Acrylic Platform

Acrylate Copolymers …
Free radical polymerizations
No metal
Acrylic Polymer Platform

Fujitsu

IBM, JSR, etc.
Types of PAGs Used For 193 nm Lithography

**IONIC**

- TPS
- DPI
- ALS
- NEALS
- NAT·OTf

**VOLATILE**

- AsF$_6^-$
- Rf–SO$_3^-$
- F$_3$C–SO$_3^-$

**NON-VOLATILE**

- "nonaflate"

**NON-IONIC**

- SIT
- MDT
- MBT
- NIT

: too weak for 193 nm
193nm Resist Challenges

- Pattern Collapse
- Line Edge Roughness (LER)
- Etch Resistance
- Heisenberg Principle issue
- New Defect Types
Line edge Roughness

193

248
Simulation of a PE Bake

Blocked sites

Unreacted polymer

Latent Image Edge

Gerard Schmid
Influence of Base on LER

Base quencher can decrease the acid sphere of influence in low contrast regions, thereby reducing LER.

Exploring Base Effects

To add base quencher seems to make the contrast higher, thereby LER reducing.

0% base
6.61 nm RMS

15% base
5.47 nm RMS

30% base
3.89 nm RMS

Comparison of ArF and KrF

**Typical KrF system always shows dramatic variation of DR** …

- **No DR @ Unexposed area**
- **No DR changes until this point**
- **Suddenly the dissolution begins**
- **The contrast is very high**
- **Quite high Rmax**
- **Different DR inside film**

**Comparison of ArF and KrF**

- **ChE 384T / 323**
Dissolution behavior

This difference in the contrast amplifies small variations in the blend region. “Digital” On/Off switching phenomenon makes the line edge rough.
Is there such a thing as too much contrast?

- The KrF system has lower contrast
- Small fluctuations cause small changes in dissolution rate.

- The ArF system changes from insoluble to soluble over a very narrow dose range
- Small fluctuations are amplified and cause huge changes in dissolution rate.
- Stochastic process noise becomes line edge roughness
Could have been

Can “it” be done again at 157nm???

Perhaps....but
This time it would have been really hard!!
### Absorption ($\mu$m$^{-1}$) of Common Polymers

<table>
<thead>
<tr>
<th>Transmission</th>
<th>Wavelength (nm)</th>
<th>157.6</th>
<th>193</th>
<th>248</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00001%!!!</td>
<td>248 resist</td>
<td>6.84</td>
<td></td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>193 resist</td>
<td>6.86</td>
<td>0.47</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polystyrene*</td>
<td>6.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Polynorbornene*</td>
<td>6.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>PMMA*</td>
<td>5.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fluorocarbon*</td>
<td>0.70</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Vacuum UV
- $\text{O}_2$, $\text{H}_2\text{O}$ absorbs at this wavelength
- Even hydrocarbons like butane and polyethylene absorb strongly

Fluorination of Norbornane Skeleton

Opaque

\[
\begin{align*}
\text{248 nm} & \quad \rightarrow \quad \text{193 nm} & \quad \rightarrow \quad \text{157 nm}
\end{align*}
\]

Transparent

How many fluorines and where to fluorinate?
Selective Fluorination of Norbornane

Geminal substitution at the two carbon bridge is the most effective fluorination pattern $\alpha$-CF$_3$ acrylates.
Surprising Serendipitous Discovery

\[ A_{157} = 2.57 \, \mu m^{-1} \quad A_{157} = 1.15 \, \mu m^{-1} \]

NBHFABOC and NBHFA are surprisingly transparent

Absorbance of Fluorinated Polymers

Hexafluoroisopropyl and $\alpha$-trifluoromethylcarboxylic acid are groups surprisingly transparent!
Some Imaging Results

100nm

90nm

80nm

60nm

40nm
Resist and Process Development

- Basic Chemistry
- Formulation and Process Development
- Optimization

Performance

Time

- 60nm
- 157 nm
- 248nm
- 193nm

We are well off the base line

ChE 384T / 323
Images in UT 157nm Resists

Issues include: Pace, Resist, Pellicles, CaF$_2$, Birefringence, Cost, etc.

Intel Announcement