Absolute Total Ion Yield and the Relative Extent of Ionic Outgassing of Photoresists and Underlayer Materials upon Irradiation at 13.5-nm

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1. Introduction
Outgassing studies by different approaches

<table>
<thead>
<tr>
<th>Method</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal desorption tube + GC/MS</td>
<td>Accumulation (high sensitivity)</td>
<td>TD material dependent</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Not real-time products</td>
</tr>
<tr>
<td>Pressure rise + filament ionizer/QMS</td>
<td>Independent on chemical analysis (Partial Pressure)</td>
<td>Calibrations needed for:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pressure gauge gas correction factor</td>
</tr>
<tr>
<td></td>
<td></td>
<td>QMS ionizer efficiency</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Mass filter efficiency</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pumping speed</td>
</tr>
<tr>
<td>Summing + filament ionizer/QMS</td>
<td>Direct counting / summing</td>
<td>Calibrations needed for:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>QMS detection sensitivity</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ionizer efficiency</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pumping speed</td>
</tr>
</tbody>
</table>

Outgassing results of the round-robin resist differ by an order of $10^4$.

1. Introduction
Outgassing studies by witness plate


Time consuming!
1. Introduction
Outgassing studies by pressure rise
- Achieving measurement precision to a factor of two.

The repeatability results for the resists in a span of six months.

1. Introduction – Less studied but critical

1. Reactive neutrals: fluorine-containing outgassing

<table>
<thead>
<tr>
<th>References</th>
<th>Reactive Neutrals</th>
</tr>
</thead>
</table>

2. Reactive and dominant F⁺ outgassing:

(1) F⁺ and most ions react at collision rates \( \sim 10^{-9} – 10^{-10} \) cm³ s⁻¹.

(2) F⁺ outgassing is the major ion products of PAG upon 13.5 nm irradiation.
1. Introduction – 13.5 nm = 91.84 eV, $\Gamma_{\text{ion}} \geq 1$

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_{\text{abs}}$ (Mb)$^a$</th>
<th>Photoionization cross section$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_{\text{cross}}$ (Mb)$^a$</td>
<td>$\sigma_{\text{cross}}$ (Mb)$^a$</td>
</tr>
<tr>
<td>He</td>
<td>0.49</td>
<td>$M^+$</td>
</tr>
<tr>
<td>Ne</td>
<td>4.44</td>
<td>$M^+$</td>
</tr>
<tr>
<td>Ar</td>
<td>1.35</td>
<td>$M^+$</td>
</tr>
<tr>
<td>Kr</td>
<td>0.7</td>
<td>$M^+$</td>
</tr>
<tr>
<td>Xe</td>
<td>25.3</td>
<td>$M^+$</td>
</tr>
</tbody>
</table>

\[ 13.5 \text{ nm} = 91.84 \text{ eV}, \quad \Gamma_{\text{ion}} \geq 1 \]

---


2. Experimental

(1) Synchrotron radiation at 13.5 nm (91.84 eV) at BL-08A-LSGM, NSRRC.

(2) Equipments:
(a) Double ion chamber
   - Absolute photon flux per second by Ar photoionization

\[
\text{photon flux} = \frac{i_1 N_A}{96500 e^{-\sigma_{\text{abs}[Ar]} L_1}} \left(1 - e^{-\sigma_{\text{abs}[Ar]} (L_2 - L_1)}\right)
\]

Photon flux = $3 \times 10^{12}$ photon s\(^{-1}\)
Photon intensity = 0.88 mW s\(^{-1}\)
2. Experimental

(2) Equipments:

(a) Double ion chamber (DI)
   - Absolute total ion yield (ATIY)

\[
ATIY = \frac{i_2 N_A}{96500 \times (\text{photon flux})}
\]

- Exposure kinetics:
  Processes include
  (1) direct ionic outgassing.
  (2) ionic outgassing by diffusion.
2. Experimental

(b) Quadrupole Mass Spectrometer (QMS)
- Mass spectrum of outgassed ions
- The relative extent of $F^+$ and $C_nH_m^+$ outgassing

- Exposure kinetics:
  Processes include
  (1) direct ionic outgassing.
  (2) ionic outgassing by diffusion.
2. Experimental

(3) Samples:

(a) Thirteen underlayer materials, round-robin resist, and PMMA provided by Nissan Chemical Industries, Ltd.

Polyester: A, B, C
Methacrylate: A (low carbon), B (high carbon), C (medium carbon)
PAG – attached - methacrylate: A, B, C
Novolac: A, B, C, D
Photoresist: PMMA, Round-robin photoresist

(b) NUK:
PMMA
PMMA + 10wt% PAG
3. Results – Absolute total ion yield (ATIY by DI)

- For a given sample, an identical ATIY value can be obtained from different beamline conditions.
- For fifteen sample measured, the ATIY value is slightly proportional to the absorbance.
- The ATIY value is thickness independent.
- The ionic escape depth 
  \[ ATIY \sim \text{absorbance} \times \text{escape depth} \]

\[ \text{Ionic escape depth} \sim 0.2 \text{ nm} \]
3. Results – Mass spectra by QMS

<table>
<thead>
<tr>
<th>Major</th>
<th>Medium</th>
<th>Minor</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_3^+ )</td>
<td>( \text{CF}^+ )</td>
<td>( \text{C}_4\text{H}_9^+ )</td>
</tr>
<tr>
<td>( \text{F}^+ )</td>
<td>( \text{C}<em>3\text{H}</em>{3,5,7}^+ )</td>
<td>( \text{CF}_3^+ )</td>
</tr>
<tr>
<td>( \text{C}<em>2\text{H}</em>{3,5}^+ )</td>
<td>( \text{CH}_3\text{CO}^+ )</td>
<td>( \text{C}_2\text{F}_4^+ )</td>
</tr>
</tbody>
</table>

F+ outgassing
### 3. Results

Relative extent of \( \text{CH}_3^+ \) outgassing (by QMS)

<table>
<thead>
<tr>
<th>Type of Materials</th>
<th>Photoresist</th>
<th>Polyester</th>
<th>Methacrylate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Name</td>
<td>Round-robin</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>( \text{CH}_3^+ )</td>
<td>0.8 ± 0.4</td>
<td>0.9 ± 0.1</td>
<td>0.25 ± 0.04</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Type of Materials</th>
<th>PAG-attached-methacrylate</th>
<th>Novolac</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Name</td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
<tr>
<td>( \text{CH}_3^+ )</td>
<td>4.4 ± 0.4</td>
<td>4.0 ± 0.5</td>
<td>5.4 ± 0.5</td>
</tr>
</tbody>
</table>

- The extent of \( \text{CH}_3^+ (\text{C}_m\text{H}_n^+) \) outgassing:
  - **Polyacrylate** > **Polyester** > **Novolac**
  - Novolac is stable upon 13.5 nm irradiation confirmed by the EUV reflectometer study.
3. Results

Relative extent of F⁺ outgassing (by QMS)

<table>
<thead>
<tr>
<th>Type of Materials</th>
<th>Photoresist</th>
<th>Polyester</th>
<th>Methacrylate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Name</td>
<td>Round-robin</td>
<td>A B C</td>
<td>A B C</td>
</tr>
<tr>
<td>F⁺</td>
<td>1.8 ± 0.4</td>
<td>1 ± 0.16</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>0.05 ± 0.02</td>
<td>1.0 ± 0.2</td>
<td>0.24 ± 0.05</td>
</tr>
</tbody>
</table>

<table>
<thead>
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<th>Type of Materials</th>
<th>PAG-attached-methacrylate</th>
<th>Novolac</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Name</td>
<td>A B C</td>
<td>A B C D</td>
</tr>
<tr>
<td>F⁺</td>
<td>7.9 ± 0.9</td>
<td>0.19 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>8.5 ± 1.1</td>
<td>0.66 ± 0.08</td>
</tr>
<tr>
<td></td>
<td>11.2 ± 1.6</td>
<td>0.59 ± 0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.49 ± 0.08</td>
</tr>
</tbody>
</table>

- F⁺ outgassing is dependent on fluorine photoabsorption

\[ R_F = 100\% \times \frac{F \text{ photoabsorption}}{\text{overall photoabsorption}} \]
3. Results – Exposure kinetics

Round-robin resist (by QMS)

Two decay processes of ionic outgassing with different rates:

1. **Direct photochemistry**: first-order decay for dose \( \leq 50 \text{ mJ cm}^{-2} \).

2. **Diffusion processes**: log (ion intensity) - log (dose) correlation.

**Dill's C parameter for ionic outgassing**:

\[
\ln \frac{I}{I_0} = -CIt
\]
3. Results – Exposure kinetics

Round-robin resist (by DI chamber)


Three decay processes of ATIY with different rates:

1. **Fast, direct photochemistry:**
   - First-order decay for dose \( \leq 3 \text{ mJ cm}^{-2} \). \( \Rightarrow \) reactive ionic outgassing

2. **ATIY rise:** only correlated to iodine-containing compound.

3. **Diffusion processes:** log (ion intensity) - log (dose) correlation.
3. Results – Exposure kinetics

(1) $C_{\text{ATIY,0-3 mJ cm}^{-2}} > 1 \times 10^{-2} \text{ cm}^2 \text{ mJ}^{-1}$ for PMMA, PAG-MM-C.

(2) $C_{F^+} \approx C_{\text{CmHn}^+}$ for PAG-MM-A, B, C.

(3) $C_{F^+} > C_{\text{others}}$ for most tested samples other than (2).

4. Conclusion

1. **F⁺ outgassing** is important for **F-containing** compounds.

2. For samples tested, **methacrylate-type** polymers give off the most **CH₃⁺ (CₘHₙ⁺)** outgassing.

3. The **absolute total ion yield** is dependent on the **absorbance** value, and is in the order of **10⁻³**.

   ⇒ the ion escape depth ~ 0.2 nm

4. The **F⁺ outgassing** can be satisfactorily correlated to **fluorine-photoabsorption**.

5. The exposure kinetic study shows the following:

   (1) In the **first few mJ cm⁻²** dose, the ionic outgassing follows a **first-order decay**. ⇒ Dill’s C parameter can be derived.

   (2) Ionic outgassing by diffusion is not important for dose < 10 mJ cm⁻².
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