NIST resist testing update

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*See also Shannon’s talk Wednesday at 1600h*
Outline

• Overview of NIST EUV-based resist outgas-testing facility
• Observed trends in resist outgassing
• Atomic-H cleaning of C and non-C residuals from EUV and e-beam contamination (preliminary results)
• Comparison of contamination potential from selected resist-outgas-related species.
**ASML Resist-Outgas Testing Protocol at NIST**

1. **Determine E0**
   - Co-expose witness sample & resist-coated 200 mm wafer to E0 in 1 hr.

2. **Measure C**
   - thickness with spectroscopic ellipsometry and scale to 300 mm wafer

3. **Clean C with atomic H**
   - Measure amount of residual non-C {S, P, F, I, Cl, …} with XPS.

4. **Measure C-thickness with**
   - spectroscopic ellipsometry and scale to 300 mm wafer

5. **Measure amount of residual non-C**
   - {S, P, F, I, Cl, …} with XPS.
BL-1B Sample chamber

Witness sample
- Ru-capped
- Mo/Si multilayer
- H-atom cleaned
- 10° angle of incidence

Narrowband (13.5 nm) EUV beam (~2 mW)

Broadband (6 nm - 18nm) EUV beam (~150 mW)

Power (mW/nm @ 300mA)
wavelength (nm)

Incident power

- Witness plate
- Relay mirror
Outgas testing requires “mass-limited” C growth

Witness sample (WS)
Ru-MLM

~50 mW/mm², Bandwidth ~ (7-20) nm

~0.15 mW/mm², In-band 13.5 nm

Relay MLM

Intensity saturation: mass-limited growth

Spectroscopic ellipsometry map

Line profile through spot center

Position (mm)

Intensity on WS (a.u.)

Thickness (nm)
Reproducibility

- 200 mm wafer exposed in 1 hr
- C thickness scaled by 9/4 to get 300 mm wafer exposure equivalent
- Reproducibility within ±10%
Poor correlation of outgas contamination with $E_0$

- Normalized witness sample (WS) C thickness for 11 different resists does not correlate with dose-to-clear ($E_0$). Other parameters dominate:
  - Outgas species
  - Diffusion time

- For low-sensitivity resists, EUV power at some facilities may be insufficient to expose entire wafer in 1 h.
- May need to compensate with scaling.
Some species (e.g., benzene) will diffuse more readily from resist than others (e.g., m=39).

Outgassing for each species will reach steady state once all volatiles have diffused from initially irradiated area.

If steady state not attained by end of exposure, amount of volatiles still trapped in resist (and the contamination they would cause) will vary with exposure time.
Time dependence dominated by diffusion of volatile species out of resist.

Extending exposure time to supply E0 to entire wafer for low-power EUV sources is NOT advised due to complicated, resist-dependent correlation.

Reducing exposure area is likely better approach (under study).

Exposure time decreased by increasing EUV power to maintain E0 exposure of 200 mm wafer in all cases.
Atomic-H cleaning of non-C contaminants

• There is little data on efficacy of atomic H cleaning of non-C contaminants (S, P, I, F, etc.)

• Only two data points on this at NIST
  - In one case when XPS could be performed before and after cleaning of resist outgas sample, ~3 At% of S was completely removed by AH.
  - AH completely removed all C and S from ~6 nm deposit made by exposing TiO$_2$-cap MLM in presence of diphenyl sulfide.

• We have just completed new “high-contamination” facility to make EUV-induced deposits of highly contaminating species with non-C elements of interest.

• We have performed preliminary investigations by AH cleaning of EUV-exposed spin-coated polymers containing appropriate species.
NIST atomic-H cleaning facility

- Base pressure $\sim 10^{-8}$ Torr
- Filament-sample distance = 4.5 cm
- Filament material - W
- $H_2$ pressure $\sim 1$ Torr
- $T_{\text{filament}} = 1850^\circ C$
- $T_{\text{sample}} \leq 60^\circ C$

AH cleaning of EUV-deposited carbon

- Thickness monitored *in situ* by NEIS (Nulling Ellipsometric Imaging System)
- NEIS signal normalized to thickness measured by *ex situ* XPS before cleaning.

Maximum rate $\sim 20$ nm/h
Polymer-based AH-cleaning study of S & F

1) Spin coat <10 nm film of polymer onto Si or Ru-cap MLM substrate
2) Perform EUV exposures with varying dose (1-200 J/mm²)
3) Inspect with spectroscopic ellipsometry (SE) and XPS
4) Clean with atomic-H (AH)
5) Inspect with SE and XPS
Conclusions of polymer-based study

- XPS shows polymeric C is gradually converted to a more graphitic form (C=C) with increasing EUV dose. (Consistent with similar transformations observed in EUV-induced deposits.)
- EUV strongly desorbs F and partially desorbs S.
- AH rapidly cleans S-containing EUV-exposed deposits at rate similar to C-only EUV-deposits.
- AH cleans F-containing EUV-exposed deposits much more slowly (~5x slower) than C-only EUV-deposits.
- Hence F is rarely observed as “non-cleanable” outgas contaminant because it is rapidly desorbed by EUV, not because it is efficiently cleaned by AH.
Contamination rates for various species

In-band contamination rate at 1 mW/mm²

<table>
<thead>
<tr>
<th>Substance</th>
<th>Contamination rate [nm/h]</th>
<th>Exposure pressure [Torr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethyl sulfide</td>
<td>Measured @ 13.5 nm</td>
<td>2×10⁻⁶</td>
</tr>
<tr>
<td>Benzene</td>
<td>Scaled from 10 nm broadband</td>
<td>1×10⁻⁶</td>
</tr>
<tr>
<td>Toluene</td>
<td></td>
<td>1×10⁻⁶</td>
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<tr>
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<td></td>
<td>1×10⁻⁶</td>
</tr>
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<td></td>
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Vapor pressure:
- Diethyl sulfide: 58 Torr
- Benzene: 94 Torr
- Toluene: 27 Torr
- Tetradecane: 3×10⁻³ Torr
- Diethyl benzene: 1 Torr

Contamination rates:
- Diethyl sulfide: ≈(1 to 2) nm/h
- Benzene: 0.30 nm/h
- Toluene: 0.20 nm/h
- Tetradecane: 0.10 nm/h
- Diethyl benzene: 0.00 nm/h

Measured at 13.5 nm, scaled from 10 nm broadband.
Contamination rates for various species

- Presence of S does not necessarily result in high contamination rate
- Vapor pressure is better indicator of contamination potential, but not universal

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In-band contamination rate at 1 mW/mm²
ASML Resist-Outgas Testing Protocol at NIST

ASML announced relaxed XPS detection limit criteria

- 0.1 at% for I (highly absorbing)
- 0.25 at% for all others
- Compared with original (0.1 at% for all), new limits allow acquisition in ¼ of the time without compromising sensitivity to iodine, the most damaging species
- NIST developed spreadsheet tool relating XPS acquisition parameters to desired “detection limit” to improve uniformity in XPS sensitivities at different resist outgas testing facilities.

(1) Determine E0
(2) Co-expose witness sample & resist-coated 200 mm wafer to E0 in 1 hr.
(3) Measure C-thickness with spectroscopic ellipsometry and scale to 300 mm wafer
(4) Clean C with atomic H
(5) Measure amount of residual non-C {S, P, F, I, Cl, …} with XPS.
Ongoing research

1. Establish equivalence of e-beam vs. EUV resist outgas testing
   • C thickness for expanded set of resists - benchmarks
   • AH cleaning efficacy of C and non-C residuals (S, P, halogens)
     ➢ EUV and e-beam induced contamination
     ➢ Spun-on polymers
   • Scaling of WS contamination with exposure time, area and dose

2. Possible new phenomena associated with high-dose EUV exposure in HVM:
   • “graphitization” of contamination and impact on AH cleaning
   • Reflectivity loss due to repeated AH cleaning