

Rational Design in Cyclic Olefin Resists for Sub-100nm Lithography

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Outline



Polymer design

Material properties of Cobra 5K polymers

- Optical density at 157nm and 193nm
- Etch resistance and after etch surface roughness
- Dissolution properties

Lithographic performance of Cobra 5K resists (with 193nm exposure tool)

- PEB sensitivity and CD uniformity
- Line/space performance
- Contact Hole performance

Conclusions

Design of resist for sub-100nm lithography



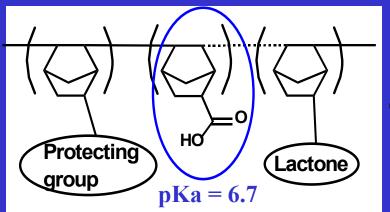
Fluorination (@reduce 157nm O.D.) (@ reduce etch resistance)

Cyclic olefin (intrinsic high etch resistance)

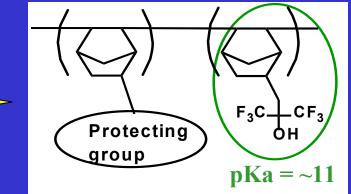
Fluorinated cyclic olefin (low 157nm O.D. + high etch resistance)

New polymer design to improve dissolution properties



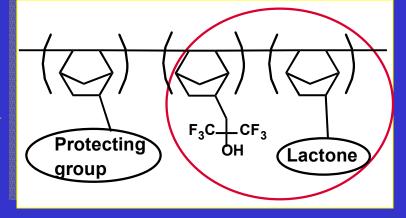


Cobra 1K-4K: Good etch resistance Swelling Limited resolution



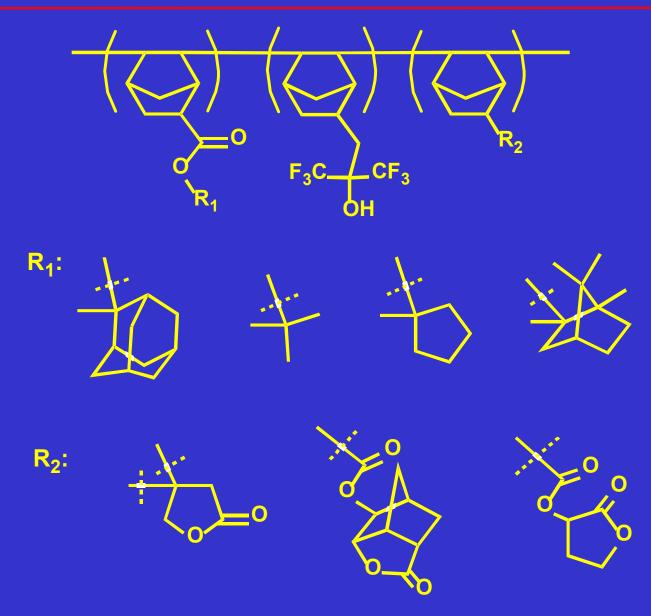
Cobra 5K copolymer: Low 157 nm O.D. Little swelling

Cobra 5K terpolymer: No swelling Much improved resolution Good etch resistance



Structures of Cobra 5K terpolymers





Optical density and contact angle data of Cobra 5K polymers

| Polymer | 157nm O.D. (μm ⁻¹) | 193nm O.D. (µm ⁻¹) | Contact Angle (H ₂ O) | $\overline{\langle \mathbf{x} \rangle}$ |
|------------------------|-----------------------------------|-----------------------------------|--|---|
| Polynorbornene | | | 96° | F ₃ CCF ₃ |
| PNBHFA | 1.7 | 0.05 | 69° | он |
| NBMCP/NBHFA (20/80) | 3.0 | 0.12 | | PNBHFA |
| NBMCP/NBHFA (30/70) | 3.2 | 0.16 | | |
| NBMCP/NBHFA (40/60) | 3.4 | 0.19 | 76° | |
| NBMCP/NBHFA (50/50) | 3.7 | 0.20 | 78° | NBMCP/NBHFA |

HFA effectively reduces the 157nm O.D. of CO polymers
HFA effectively increases the hydrophilicity of CO polymers

Oxide etch rate of Cobra 5K copolymers



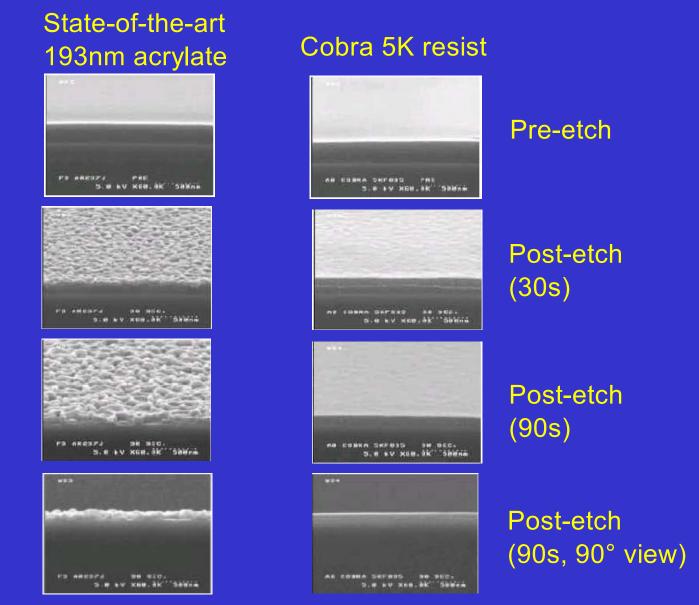
| Polymer | Oxide etch rate (Å/min) | Relative etch rate (vs. PHS) | $(\Box)(\Box)(\Box)$ |
|-----------------------------------|----------------------------|---------------------------------|----------------------|
| Poly(hydroxystyrene) | 998 | 1 | · ↓ · ↓ ↓ · ↓ |
| Poly(t-BOC hydroxystyrene) | 1,147 | 1.15 | Cobra 3K |
| Cobra 3K polymer | 1,076 | 1.08 | () () |
| Cobra 5K (50/50) (NBMCP/NBHFA) | 1,161 | 1.16 | 0 F_3C CF_3 |
| Cobra 5K (20/80) (NBMCP/NBHFA) | 1,216 | 1.22 | он NBMCP/NBHFA |

* Etch chemistry: CF₄/CF₃H/O₂/Ar

Fluorine-containing Cobra 5K polymers maintain good etch resistance

Cobra 5K has much better after etch surface roughness than acrylates





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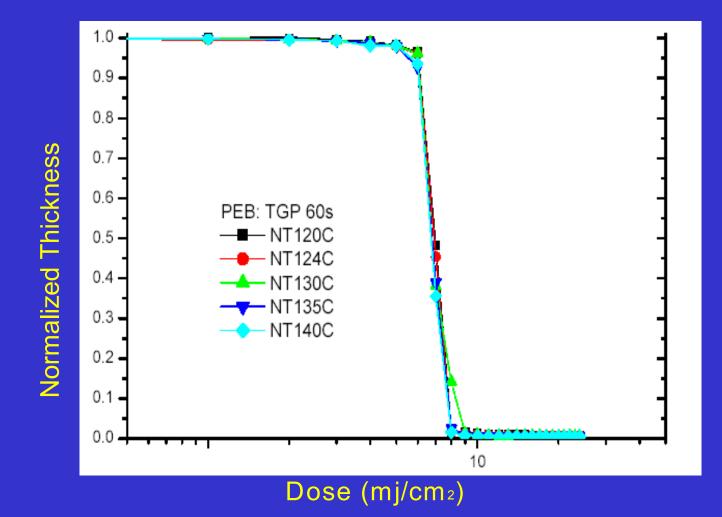
| Polymer | Dissolution rate (Å/s) | |
|----------------------|------------------------|--|
| PNBHFA | 1500-8000 | |
| NBMCP/NBHFA (20/80) | -2.0 | |
| NBMCP/NBHFA (30/70) | -0.9 | |
| NBMCP/NBHFA (40/60) | -0.6 | |
| NBMCP/NBHFA (50/50) | -0.5 | |
| Cobra 5K terpolymers | $-0.2 \sim 0.2$ | |

Wide range of NBHFA concentration cause little swelling
Terpolymers with HFA and lactone combination have better dissolution properties than copolymers

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Contrast curve of Cobra 5K resist at different PEBs



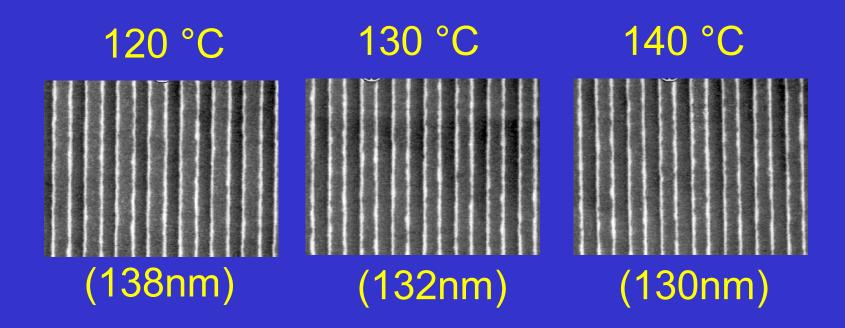


Little change in contrast curve with PEB temperature from 120 °C to 140 °C

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Very low PEB sensitivity of Cobra 5K resists





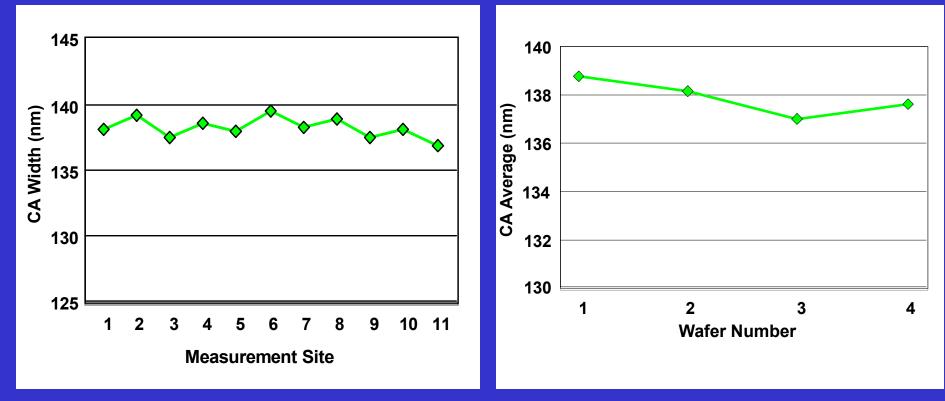
----- PEB sensitivity: <0.5 nm/°C

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CD Uniformity: across wafer

CD uniformity: wafer to wafer



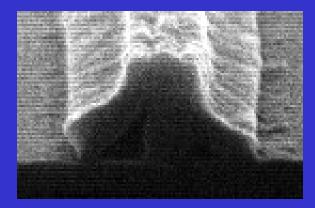
Good CD uniformity possibly due to low PEB sensitivity





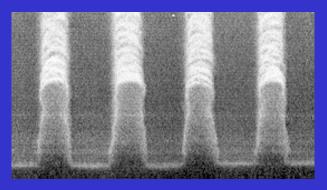
(193nm ASML tool, 0.75 NA, attn. PSM, 3000 Å resist thickness)

Cobra 3K (120nm 1:1)



(limited resolution due to swelling)

Cobra 5K (105nm 1:1)



(improved dissolution properties leads to better resolution)

105nm 1:1 line/space exposure latitude



(193nm ASML tool, 0.75 NA, attn. PSM, 3000 Å resist thickness)



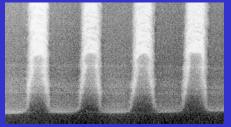
(118nm, 20mj)



(113nm, 20.5mj)



(103nm, 21mj)



(101nm, 21.5mj)



(96nm, 22mj)

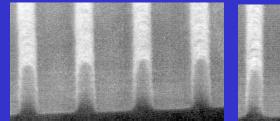
 $> \sim 10\%$ exposure latitude

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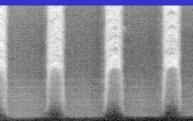
80nm line in 245nm pitch performance



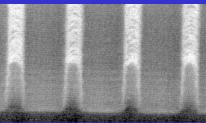
(193nm ASML tool, 0.75 NA, attn. PSM, 2700 Å resist thickness)



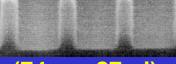
(88nm, 25.5mj)



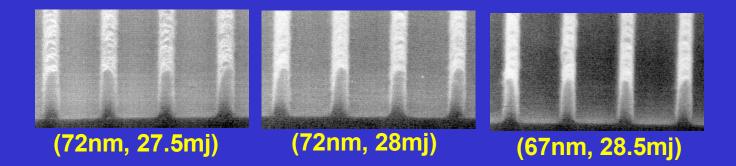
(84nm, 26mj)



(81nm, 26.5mj)



(74nm, 27mj)

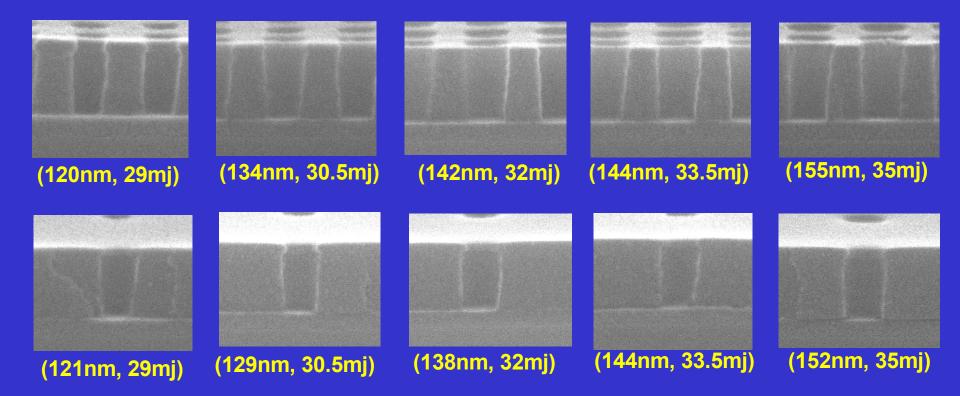


> No line collapse to 67nm, indicating good adhesion to substrate

Exposure latitude of 140nm dense and iso contacts



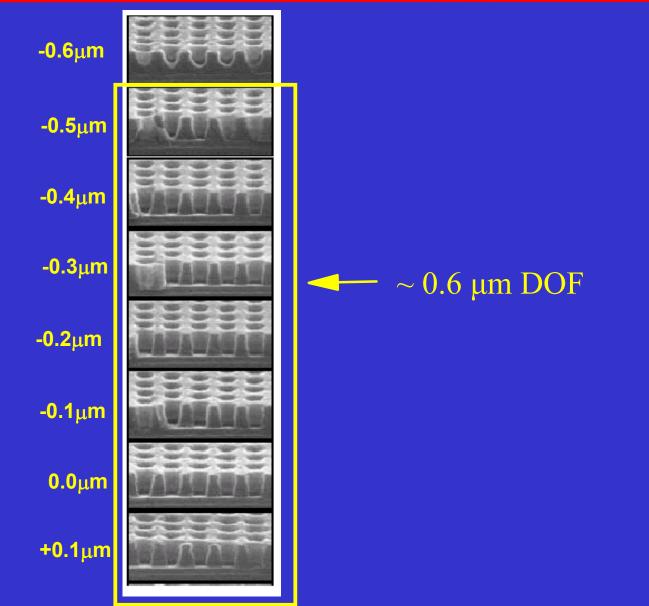
(193nm ASML tool, 0.75 NA, attn. PSM, 3000 Å resist thickness)



~20% exposure latitude for both dense and iso contacts
Small dense-iso bias (< 5nm)

Focus latitude of 140nm dense contacts



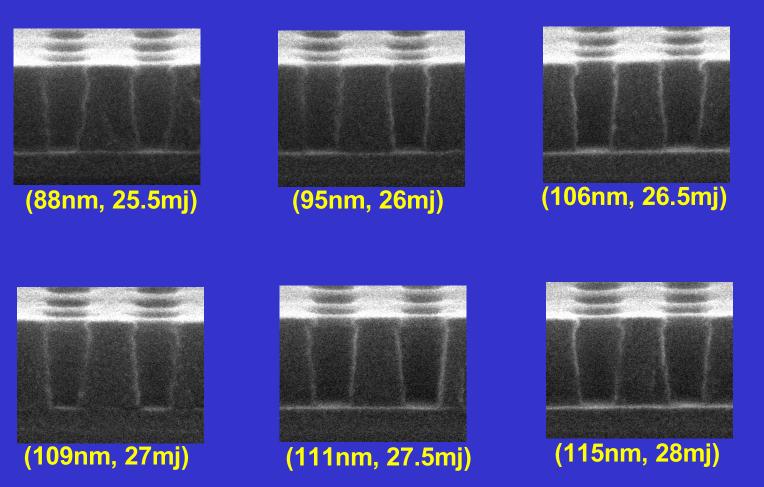


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100nm contact holes in 280nm pitch



(193nm ASML tool, 0.75 NA, attn. PSM, 3000 Å resist thickness)

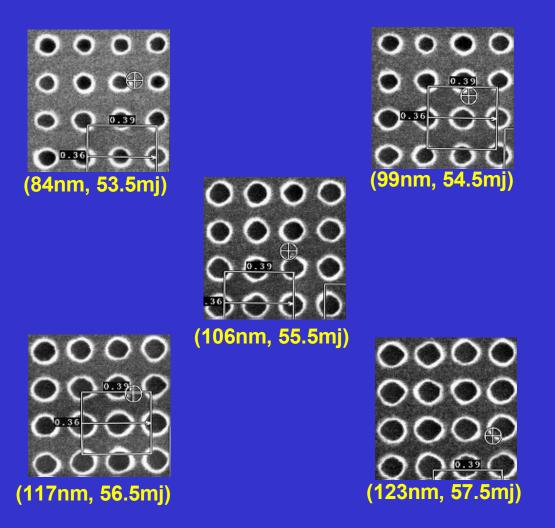


>~8% exposure latitude

100nm dense contact holes



(193nm ASML tool, 0.75 NA, attn. PSM, 2300 Å resist thickness)



Conclusions



The combination of HFA and CO polymer backbone provides:

- Low 157nm and 193nm O.D.
- Good etch resistance and after etch surface roughness
- Improved dissolution properties (vs. COOH)

Cobra 5K resists (commercialized through JSR for 193nm application) demonstrated:

- Low PEB sensitivity (<0.5nm/°C) and good CD uniformity
- Good L/S performance
- Excellent contact hole performance
 - ✓ Large process window
 - ✓ Small dense-iso bias
 - ✓ Sub-100nm resolution capabilities