EUV resist material study for the outgassing reduction and LWR improvement

October 18, 2006

FUJIFILM Corporation

Research & Development Management Headquarters

Electronic Materials Research Laboratories

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New Company & Logo design

FUJI PHOTO FILM Co., Ltd.

FUJIFILM Corporation

We have changed company name and logo since October 1, 2006.

Outline

- Introduction
- Reduction of the outgassing segment from polymer
- Sensitivity enhancement by optimizing protection ratio
- PAG sensitivity improvement
- Reduction of the outgassing segment from PAG
- LWR improvement study
- Conclusion

Requirements for EUV resist - ITRS 2005 -

Specification	ITRS 2005
Sensitivity	5 - 15 mJ/cm^2
Resolution 1:1 L/S	32 nm
Resolution Iso line	21 nm
LWR (low frequency)	1.7 nm
Outgassing	< 5 x 10^{13}molecules/cm^2-s

Table . 1 Required lithographic performance in EUV resist based on ITRS 2005

- Regarding with outgassing measurement, we use GC-MS method with thermal desorption tube (unit: molecules/cm^2) in this presentation.

Outgassing segment from polymer

- Deprotection of the polymer

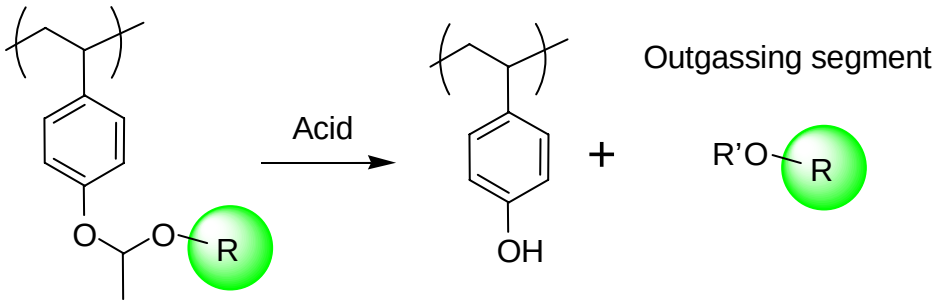
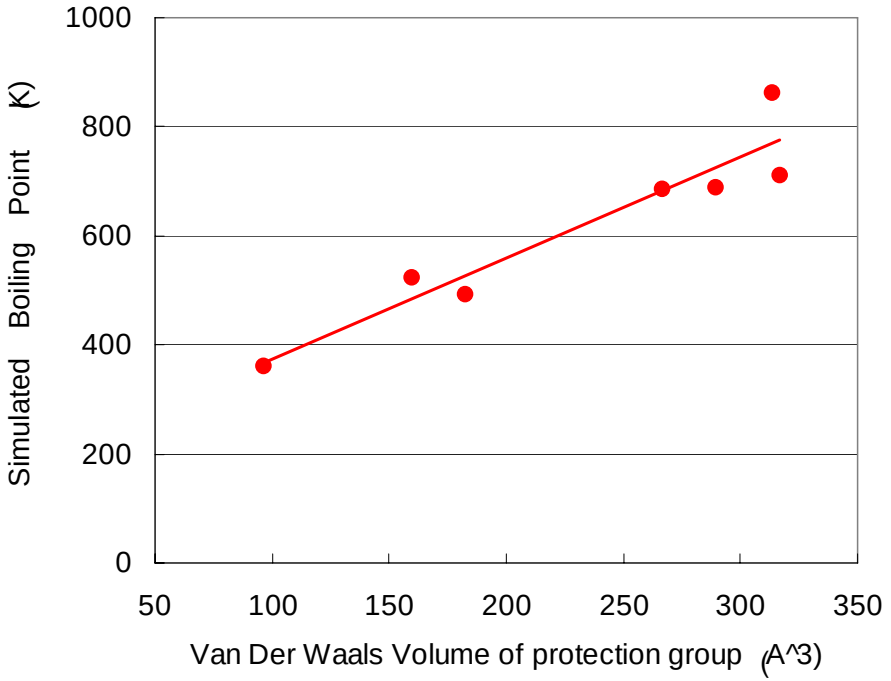


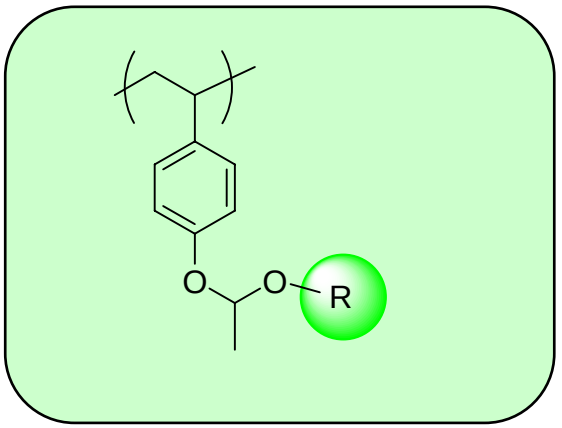
Fig. 1 The outgassing segment from the acetal protected polymer

- Protection group design
  - The size of protection group size was important to improve inhibition efficiency.
  - Large size protection group could raise boiling point of decomposed segment, but need to be optimized.

Simulated the size of the protection group

- Van der Waals volume vs. Boiling point





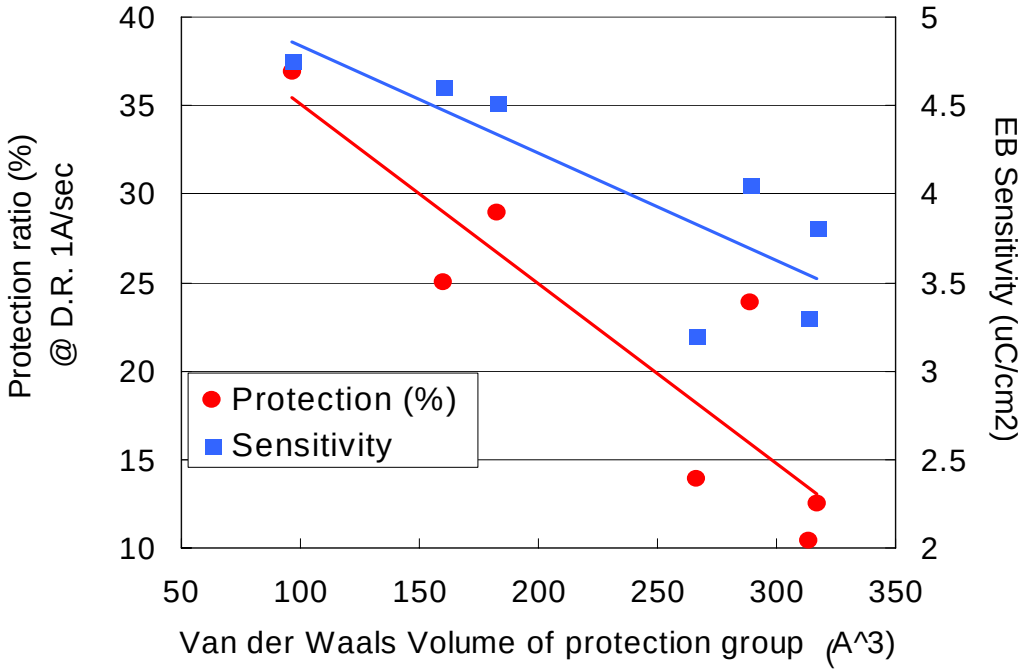
VDW volume of the acetal protection was calculated by CAChe (Fujitsu)

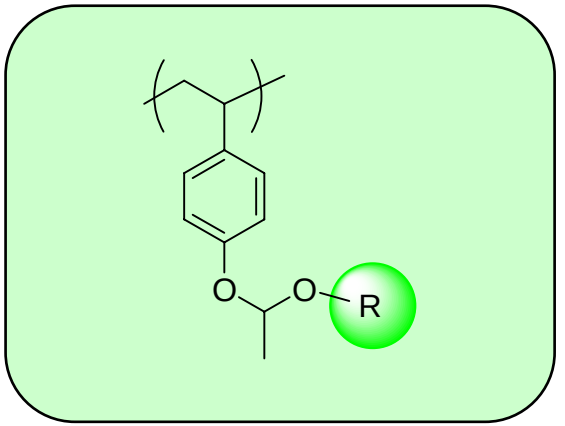
Fig. 2 The Van der Waals volume size dependence on the simulated boiling point of the deprotected alcohol.

- The size of the protection group (VDW volume) is one of the key to raise boiling point of the deprotected segment from polymer.
- Outgassing level from the polymer could minimize by changing the size of the acetal protection group.

Sensitivity enhancement by optimizing acetal protections ratio

- Inhibition efficiency and resist sensitivity





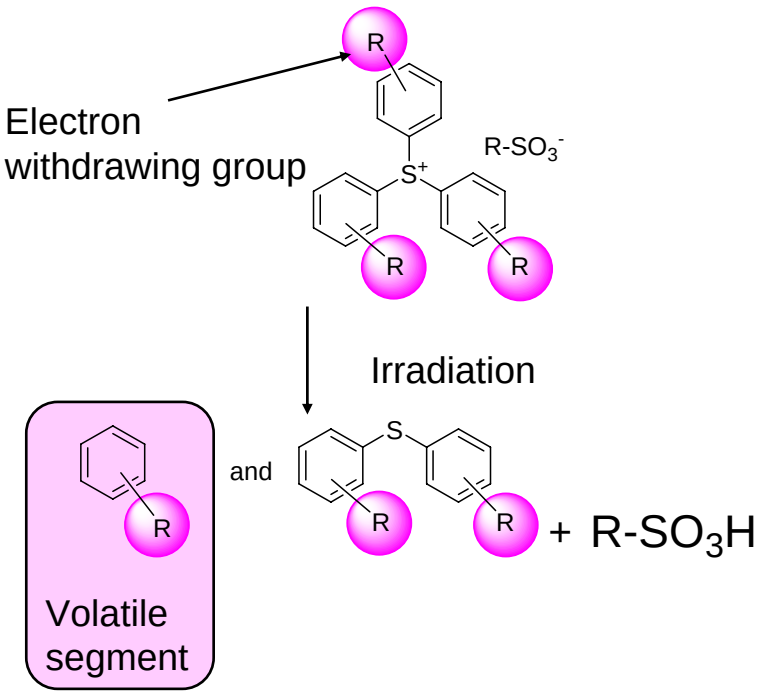
Bulky acetal protected polymer

Fig. 3 The protection size dependence on both a) protection degree and b) resist sensitivity.

- The bulkiness of acetal protection group could also reduce the protection ratio of the polymer to achieve about 1 angstrom / second of the dark erosion while development.
- The low amount of protection group in inside of the polymer improved the resist sensitivity.

PAG sensitivity improvement

- Relative acid generation efficiency



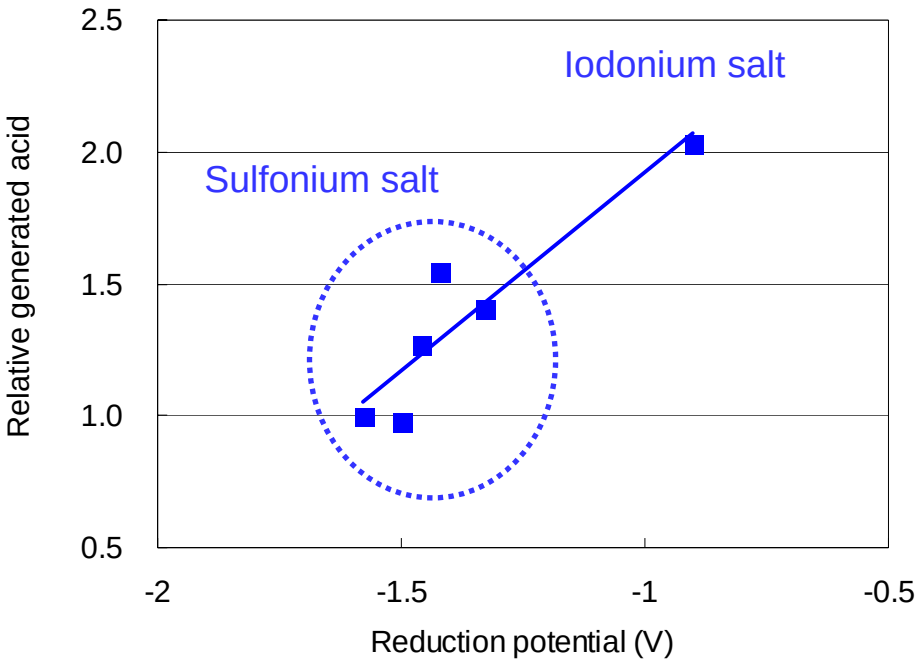
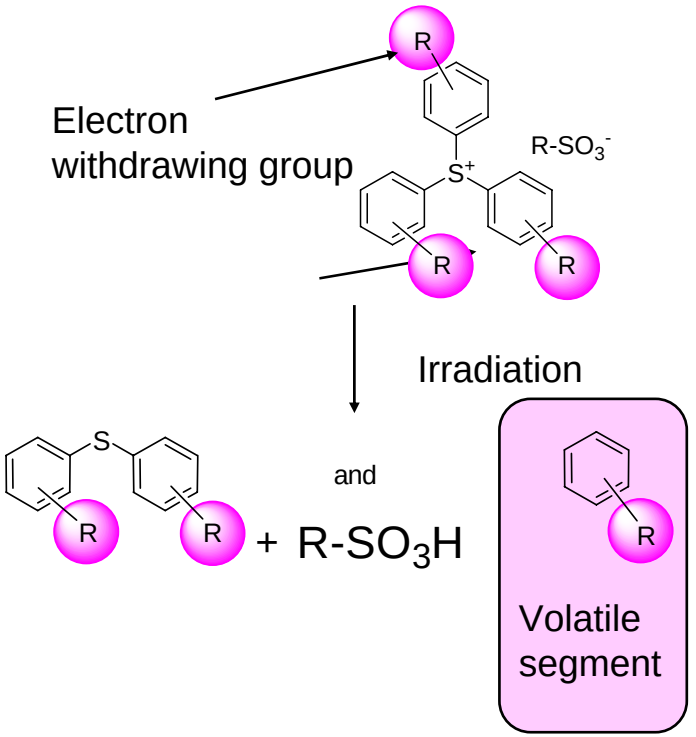


Fig. 4 The correlation between reductive potentials and relative generated acid by E-beam

- Reduction potential voltage of PAG has been measured with cyclic voltammetry.
- Acid generation efficiency was improved by loading electron withdrawing group on the PAG's cation.

Outgassing

- In early version of acetal based resist…



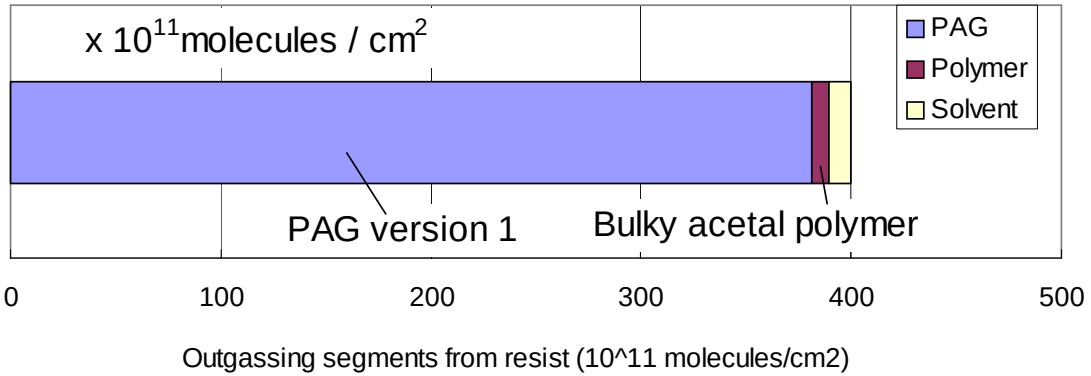
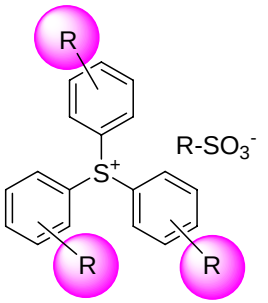


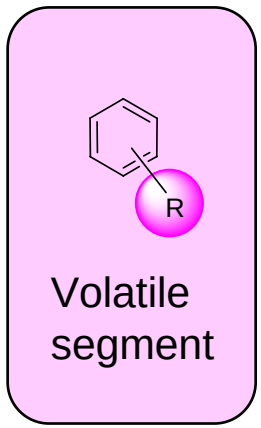
Fig. 5 Typical outgassing segments by EUV irradiation in early version of EUV resist

- The most of the outgassing segment was from PAG.
- Bulky acetal protected polymer gave a few amount of outgassing during EUV exposure.

Outgassing from PAG

- Minimizing outgassing segment from PAG





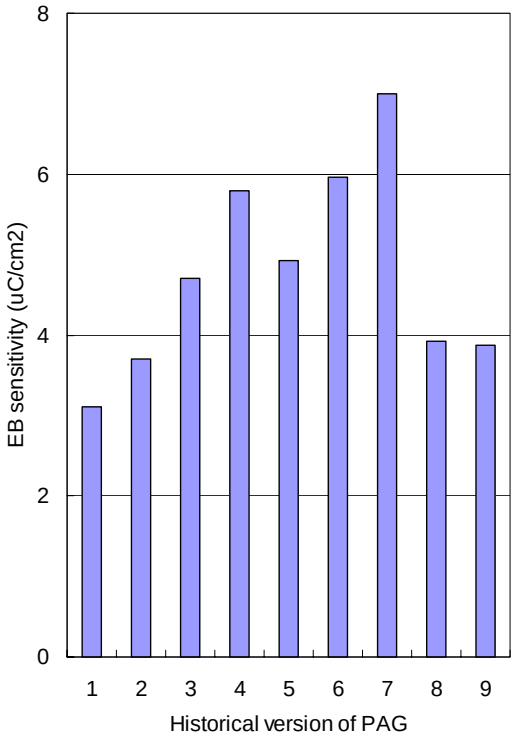


Fig. 6 PAG sensitivity

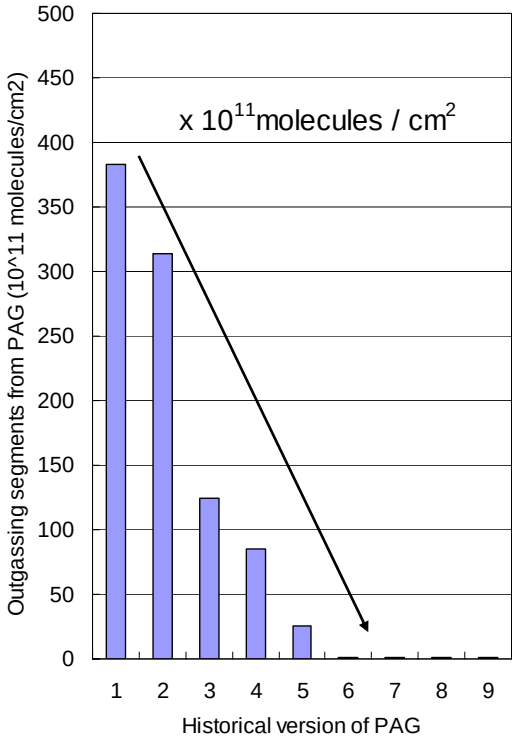
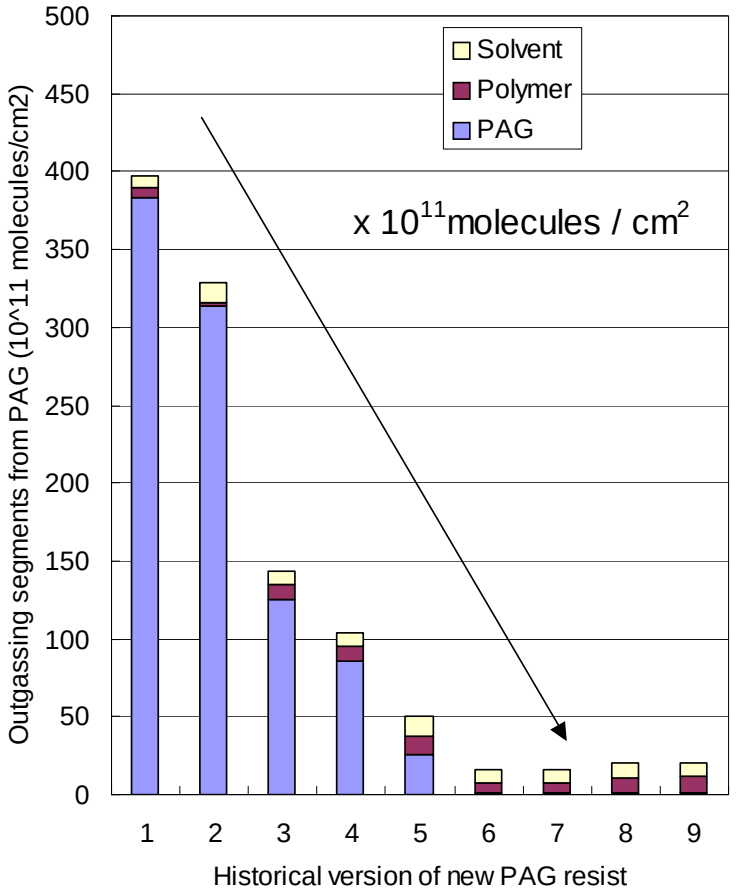


Fig. 7 Outgassing from PAG by EUV exposure

- The outgassing segment for PAG could be reduced by modifying PAG cation group, maintaining high sensitivity.

Total amount of outgassing from resist

- Historical improvement of the EUV resist



Minimizing total amount of outgassing segments

PAG	< 10^{11} molecules/cm^2
Polymer	1-9 x 10^{11} molecules/cm^2
Solvent	1-9 x 10^{11} molecules/cm^2
Total	ca. 10-20 x 10^{11} molecules/cm^2

- The outgassing materials from the resist could be minimized by utilizing the bulky protection group together with newly developed low outgassing PAG in acetal based chemically amplified resist.

Fig. 8 Historical improvement of the outgassing reduction in EUV resist

LWR improvement study

- Polymer Molecular weight study
  - The surface roughness was measured with various kinds of polymer Mw at half exposed area by using open frame e-beam exposure.
  - Resolution capability was observed by EUV exposure.
- Sensitivity vs. LWR measurement
  - LWR was measured at various base loading ratio.

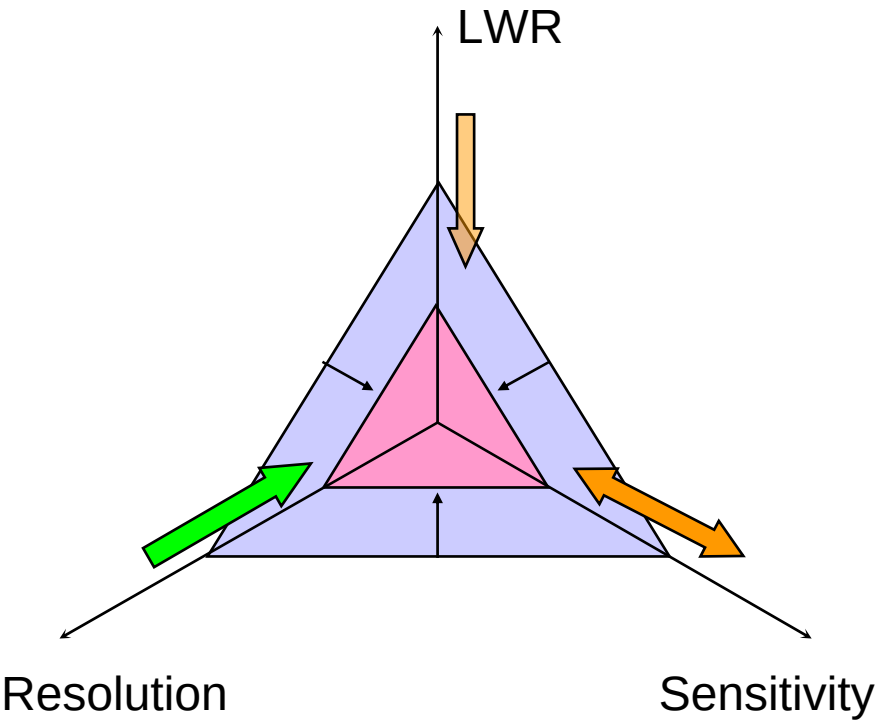
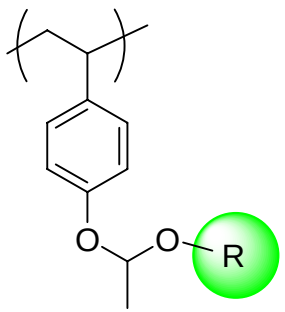


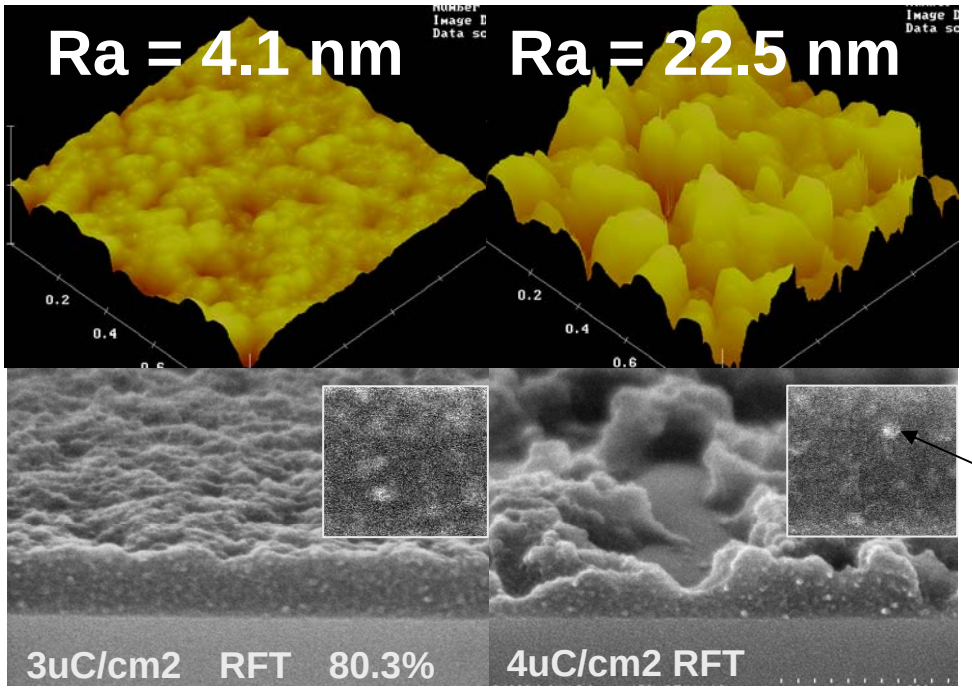
Fig. 9 Resolution, Sensitivity and LWR trade-off.

AFM and X-SEM analysis

Conventional resin



High Mw



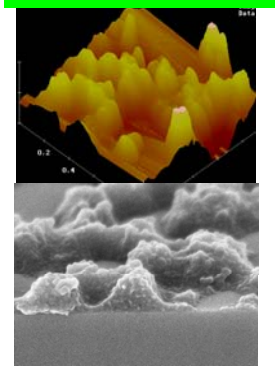
Polymer grain size = 6-13 nm

Fig. 10 AFM study

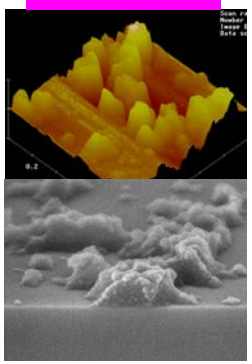
- Grain size can be visible by using special formulation resist.
- Polymer grain size is around 6-13 nm.
- Grain size is not changed at half exposed area.
- Relatively large area (>100 nm) are fully opened, but some area remains ca. 80% of film thickness at the half exposed area.

Surface roughness – AFM -

Very High Mw



High Mw



Molecular weight order VH > H > M > L

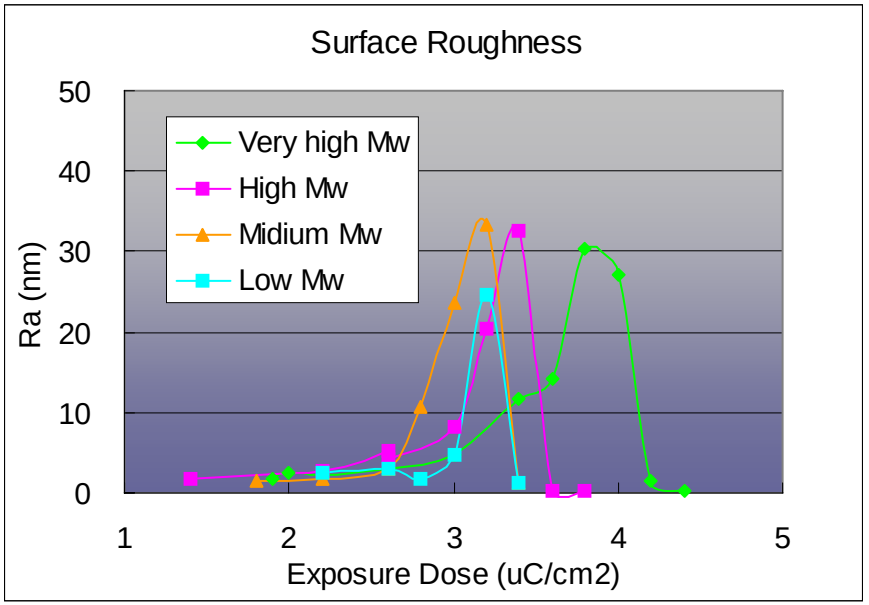
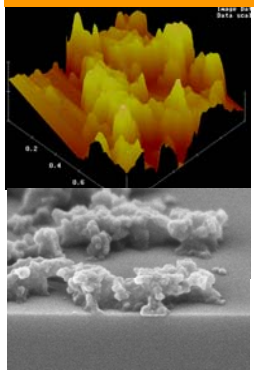
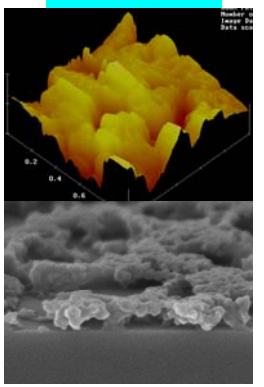


Fig. 11 Ra max vs. exposure dose

Medium Mw



Low Mw

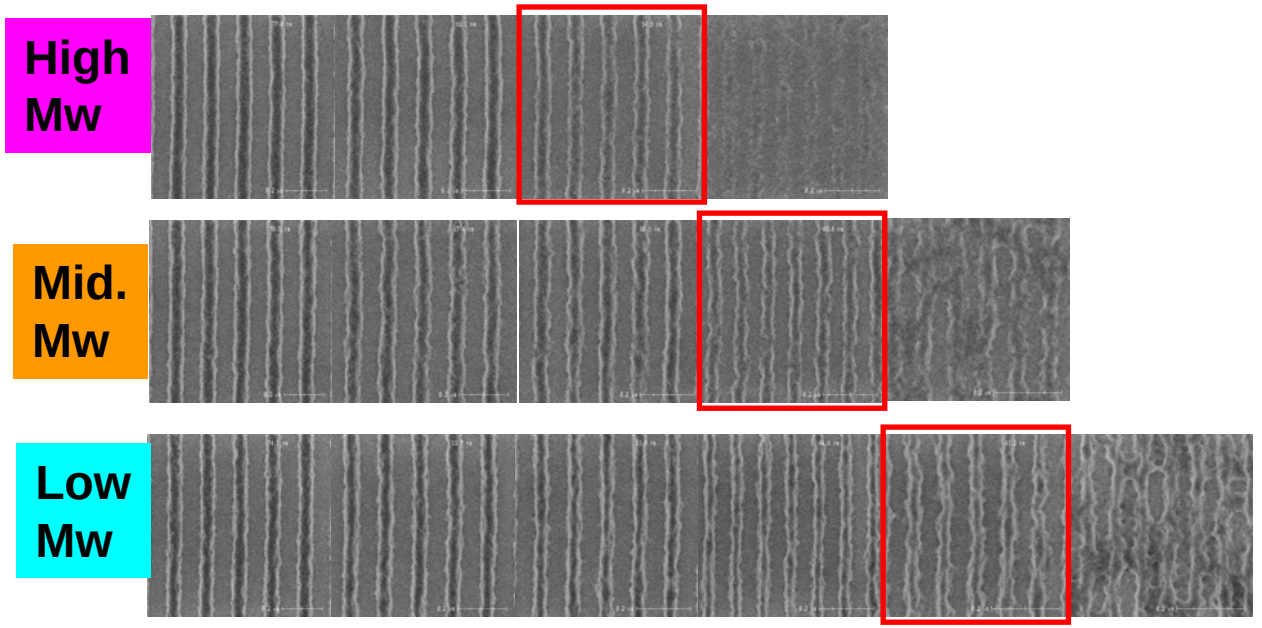


- The surface roughness (Ra) value at the half exposed area has a peak around 30-40 % of the remaining film thickness.
- The Ra Max values are not depends on the polymer molecular weight.

Resolution vs. Polymer Molecular Weight

EUV exposure

80 nm 70 nm 60 nm 50 nm 45 nm 40 nm



Process Condition: FT=125 nm, PB = 120 oC/ 90 sec, MS-13 Microstepper (NA=0.3), PEB = 110 oC/90sec, Deve.= TMAH 2.38% 60 sec,

Fig. 12 Resolution capability dependence on polymer molecular weight

EB exposure

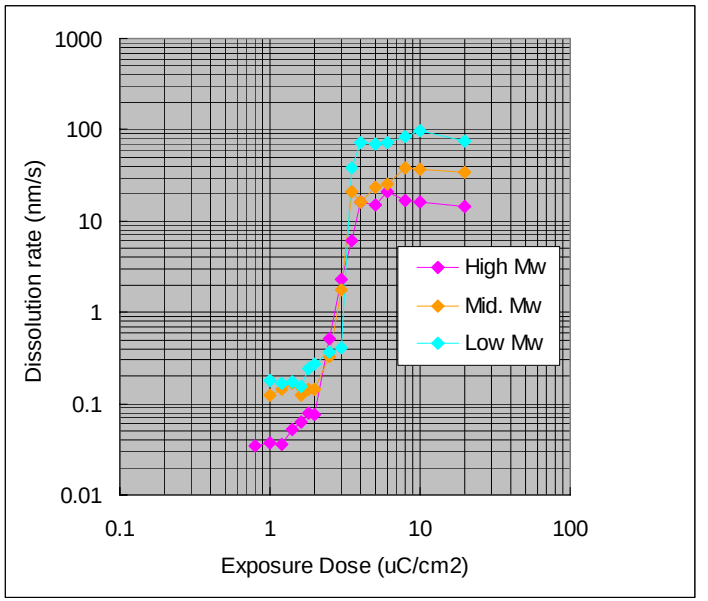
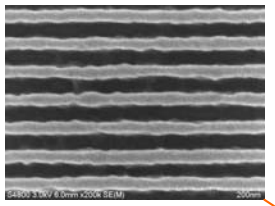


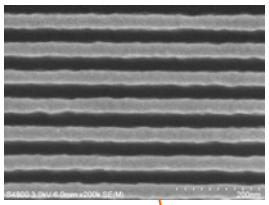
Fig. 13 Dissolution rate property of various kinds of molecular weight of polymer

- Resolution capability is slightly improved by minimizing polymer molecular weight.
- Lower Mw polymer gives higher dissolution contrast, which can enhance resolution capability.

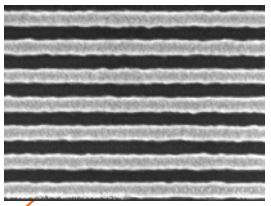
LWR vs. Sensitivity @ 35 nm lines



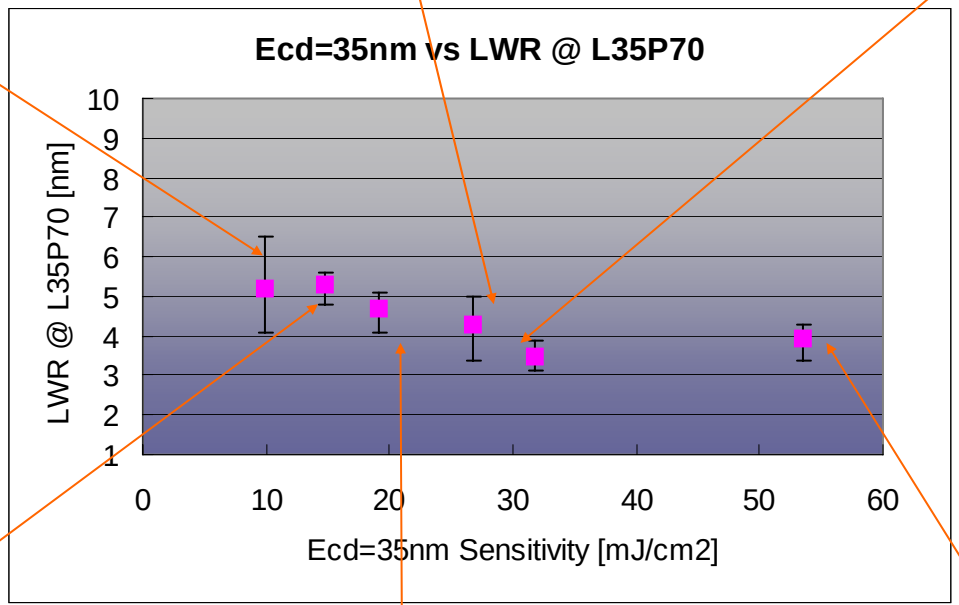
Resist E
10.4 mJ/cm²
LWR = 5.2 nm

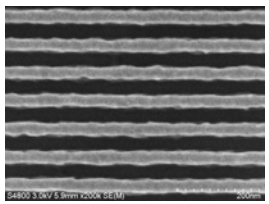


Resist G
26.8 mJ/cm²
LWR = 4.3 nm

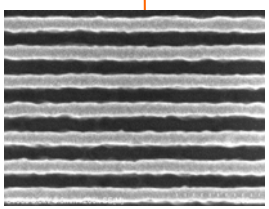


Resist I
31.9 mJ/cm²
LWR = 3.5 nm

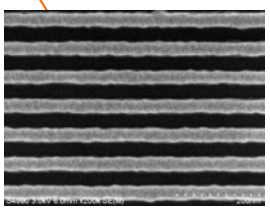




Resist F
9.9 mJ/cm²
LWR = 5.3 nm



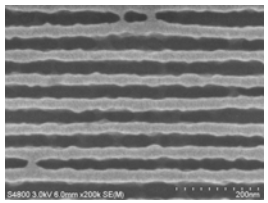
Resist H
19.1 mJ/cm²
LWR = 4.9 nm



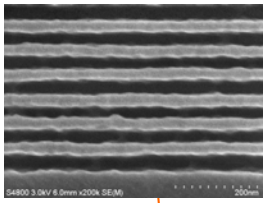
Resist J
53. 5 mJ/cm²
LWR = 3.9 nm

Fig. 14 Resolution capability of the acetal type resist (MET@ALS, Y- monopole)

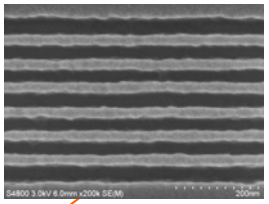
LWR vs. Sensitivity @ 30 nm lines



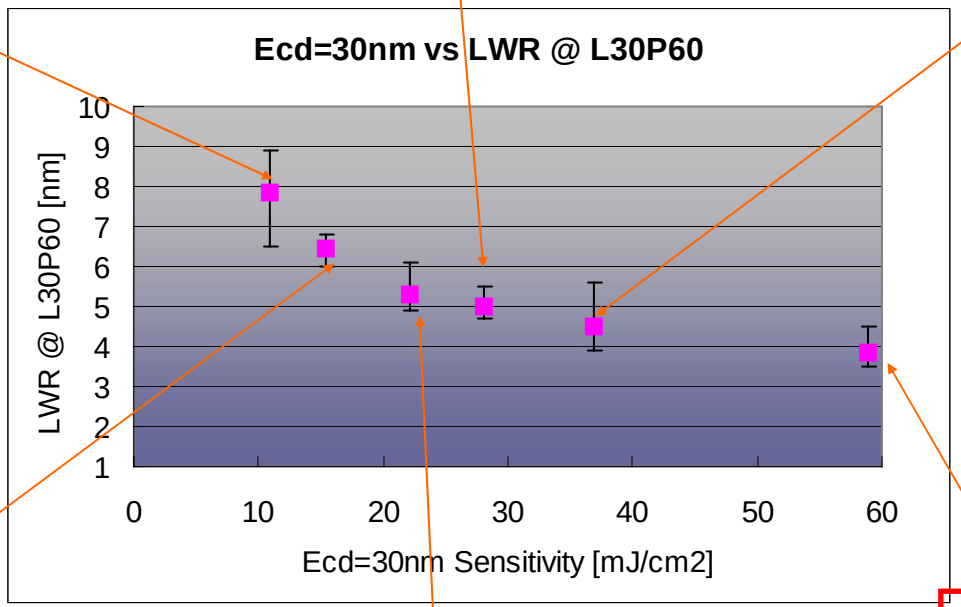
Resist E
11.5 mJ/cm²
LWR = 7.9 nm

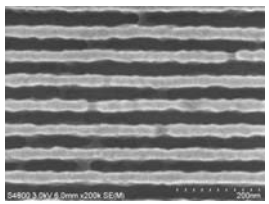


Resist G
28.1 mJ/cm²
LWR = 5.0 nm

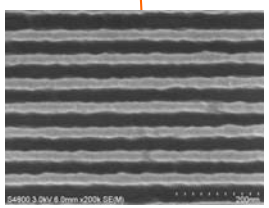


Resist I
36.9 mJ/cm²
LWR = 4.5 nm

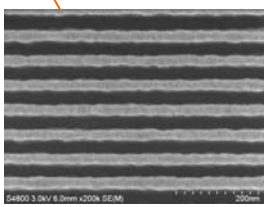




Resist F
10.9 mJ/cm²
LWR = 6.4 nm



Resist H
22.1 mJ/cm²
LWR = 5.3 nm

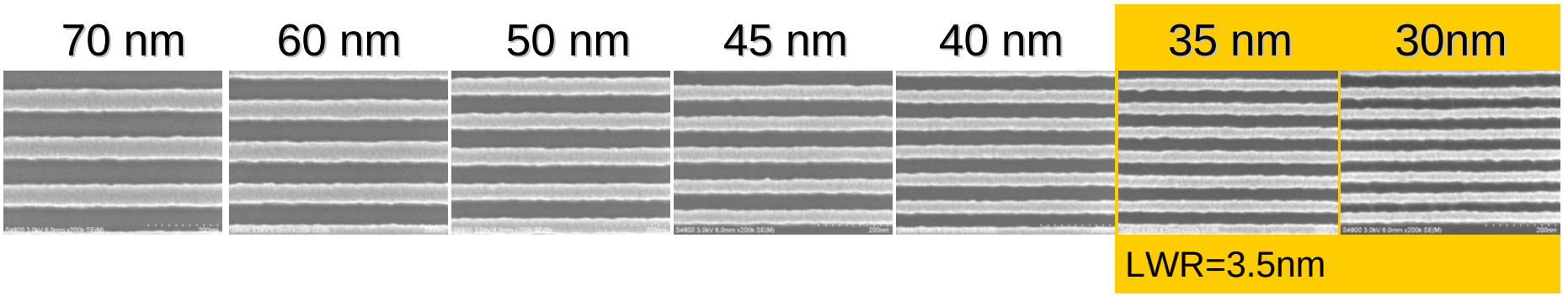


Resist J
59.0 mJ/cm²
LWR = 3.9 nm

Fig. 15 Resolution capability of the acetal type resist (MET@ ALS, Y- monopole)

EUV lithographic performance (1)

- MET @ ALS exposure (SEMATECH EUV program)
  - Sensitivity : 36.8 mJ/cm^2, Y-monopole

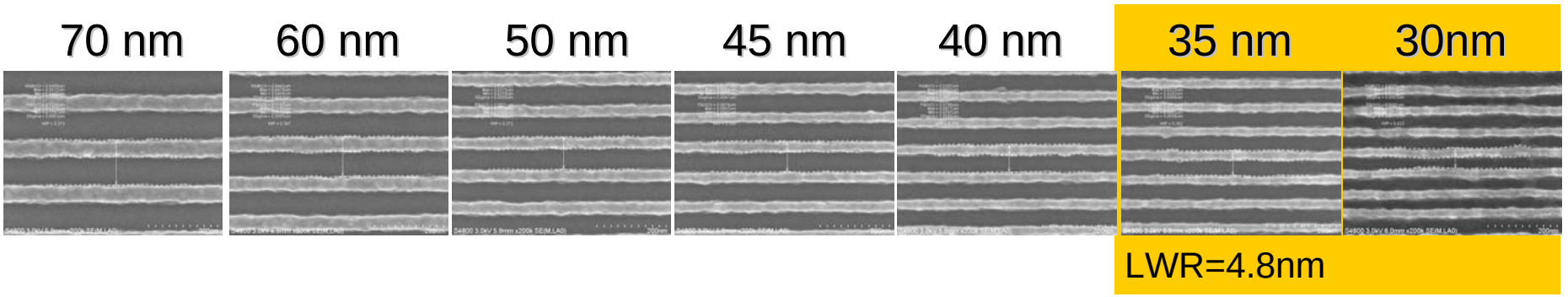


  - EL 22.2% @ 35 nm lines
  - LWR 3.5 nm @ 35 nm lines

Fig. 18 Resolution capability of the acetal type resist with MET at LBNL

EUV lithographic performance (2)

- MET @ ALS exposure (SEMATECH EUV program)
  - Sensitivity : 7.4 mJ/cm^2, Y-monopole



  - EL 17.0 % @ 35 nm lines
  - LWR 4.8 nm @ 35 nm lines

Fig. 17 Resolution capability of the acetal type resist with MET at LBNL

MET @ ALS result summary

- **Historical LWR improvement with our EUV resist**

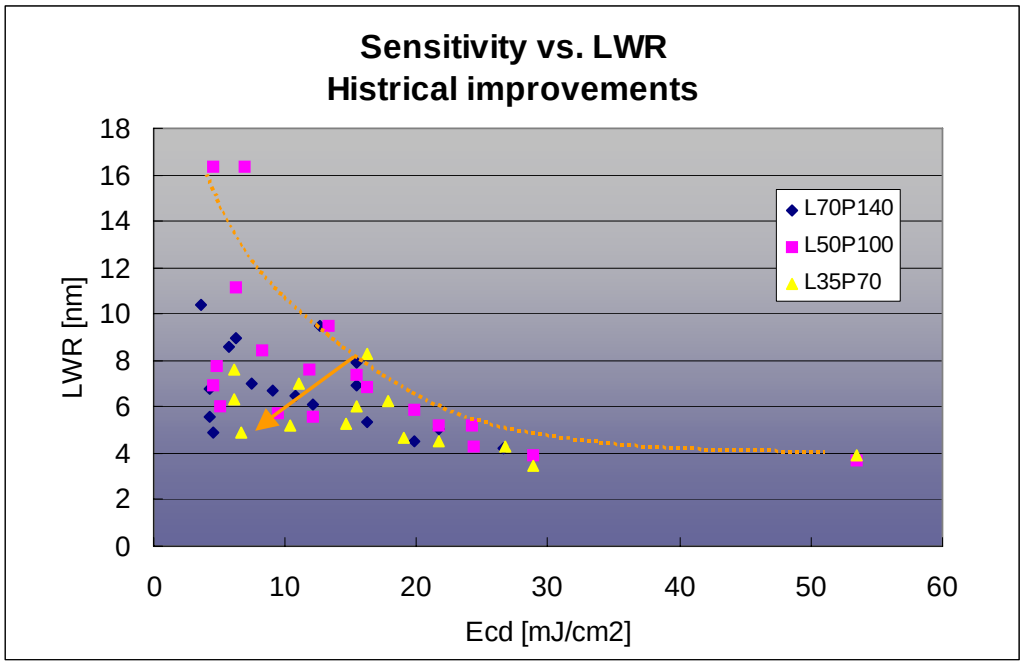


Fig. 16 LWR vs. sensitivity trade-off at various line width

– It is difficult but may be possible to improve LWR at the very high sensitivity region below 10 mJ /cm².

Conclusion

- The resist sensitivity has been improved by modifying bulkiness of acetal protection group and its ratio.The bulkiness of acetal group is effective to reduce outgassing segment from the polymer.
- The acid generation efficiency of the PAG have been successfully improve by loading electron withdrawing group into the PAG cation, that could also minimize the amount of the outgassing from PAG.
- Reduction of polymer molecular weight is not effective to decrease surface roughness at half exposed area.
- Low Mw polymer shows slightly better resolution capability, and which could improve LWR around the resolution limit.
- Resolution, Sensitivity and LWR trade-offs could be improved with this acetal based low molecular weight polymer approach.

Acknowledgement

- University of Wisconsin
- Lawrence Berkeley National Laboratory
- SEMATECH