RE-P17

EUVL 2010, Kobe (10/18/10)

Acid Proliferation Reaction in EUV Resists

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3) Tokyo University of Science

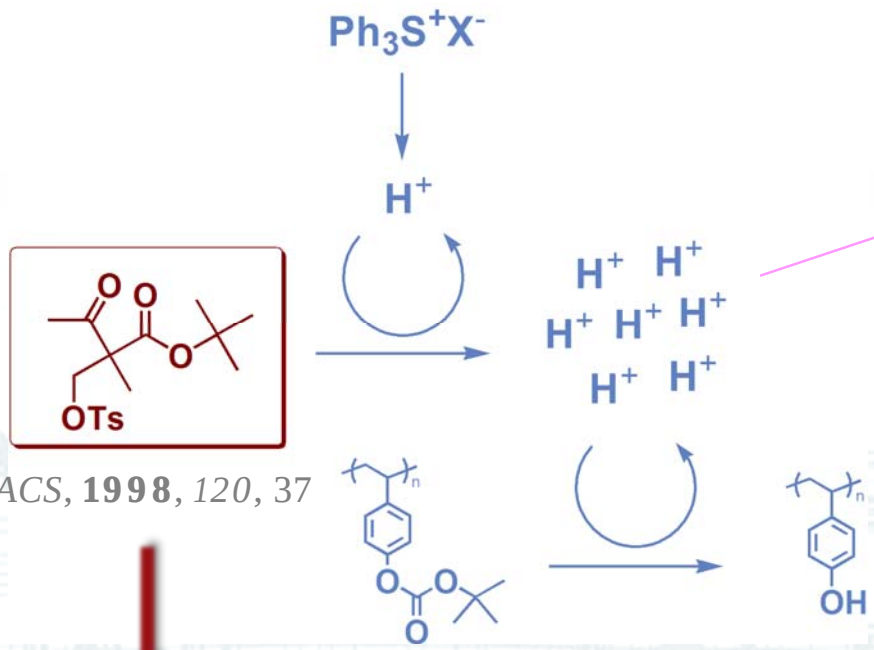
Abstract

Highly sensitive EUV resists are strongly needed to compensate for the low productivity of EUV lithography due to the low power of the EUV light source. Herein we report the efficient acid generation by the control of acid proliferation processes in order to improve the sensitivity of EUV resists.

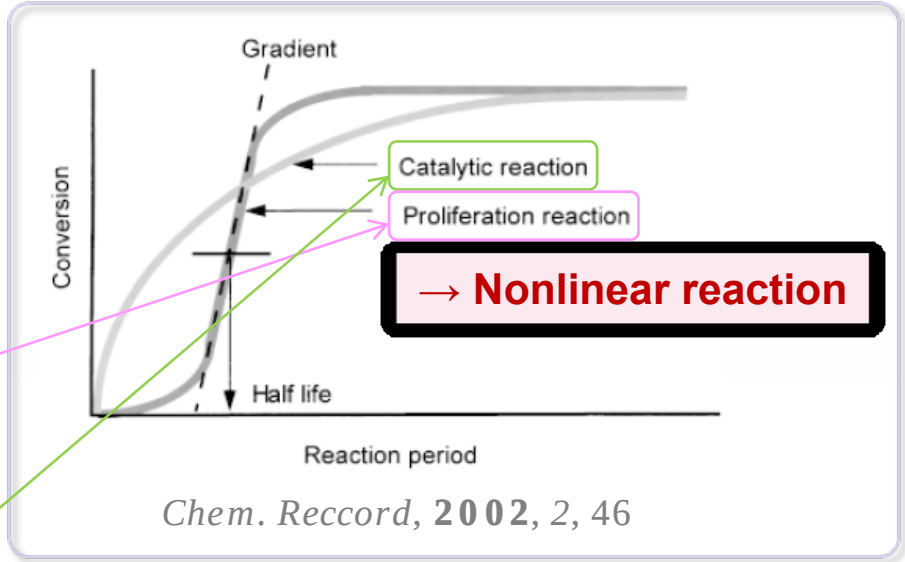
Thin polymer films of UV3 containing pinanediol-monotosylate (PiTs) as an acid amplifier were employed. Irradiation was performed by using EUV radiation. The dose to clear (E_0) values for 5, 10, 20 wt% of PiTs loading were 1.8, 1.3, and 0.5 mJ cm^{-2}, respectively. It is suggested that the PiTs decomposed autocatalytically in the presence of acids generated from acid generator to give corresponding acids; subsequently, the *tert*-butyl group was cleaved effectively by the acids.

Introduction

■ Acid Proliferation



JACS, **1998**, *120*, 37



Chem. Reccord, **2002**, *2*, 46

Acid amplifiers (AA) give additional acid generation through the autocatalytic decomposition in the presence of a strong acid.

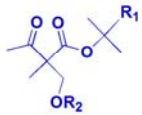
Requirements of AA

- Acid-sensitive
- To generate strong acids
- To exhibit autocatalytic fragmentation
- Thermally stable in the absent of acid

Acid amplifiers

Ichimura and Arimitsu Lab

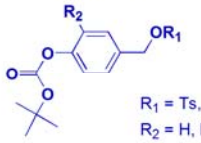
Acetoacetates (7)



R_1 = CH_3, C_6H_5
R_2 = Ts, Ms (Cl_2CHCO, C_6H_5CO)

JACS **1998**, *120*, 37

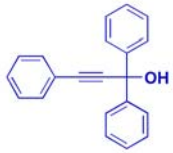
Benzyl Sulfonates (3)



R_1 = Ts, Cl_2CHCO
R_2 = H, NO_2

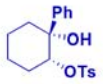
MCP **2000**, *201*, 132

Propaergyl alcohol (1)

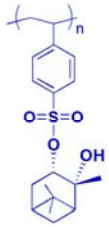


JPST **1996**, *9*, 25

1,2-Diol Monosulfonates (8)



JPST **1997**, *10*, 315



ChemLett **2000**, 1036

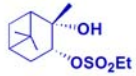
R_1 = Ts

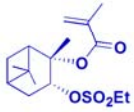
ACS PMSE **1999**, *81*, 63

R_1 =

$O_2S-C8H17$

JPST **1999**, *12*, 509



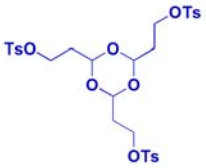


Macromol Rapid Commun **2000**, *21*, 1050

AAs Generating Multiple Acid Molecules (3)

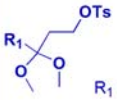
R_1 = CF_3, CF_3CH_2

JPST **2000**, *13*, 215



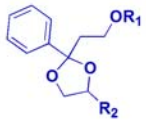
ChemLett **1998**, 823

β-Ketals (7)



R_1 = CH_3, C_6H_5

ChemMater **1999**, *11*, 2119



R_1 = Ts, Ms, 2,4,6-$Me_3C_6H_2SO_2$, 2,4,6-$^iPr_3C_6H_2SO_2$
R_2 = H

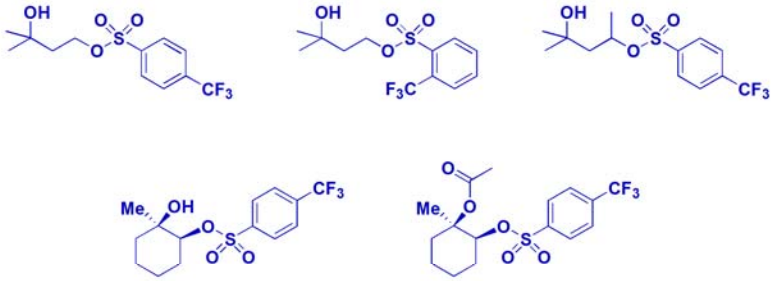
ChemMater **1999**, *11*, 2127

R_1 = Ts; R_2 = *o*-NOPh

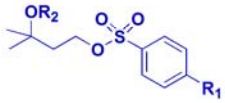
MCP **2000**, *201*, 132

Brainard Lab

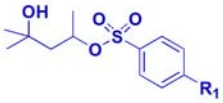
Fluorinated AAs (5)



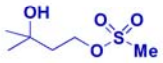
JACS **2009**, *131*, 9862

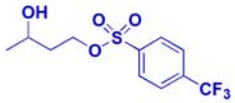


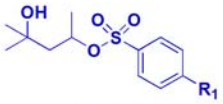
R_1 = CF_3, CH_3 (Ts)
R_2 = H, Ac



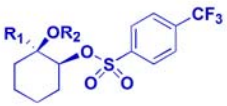
R_1 = CF_3, CH_3 (Ts)







R_1 = CF_3, CH_3 (Ts)

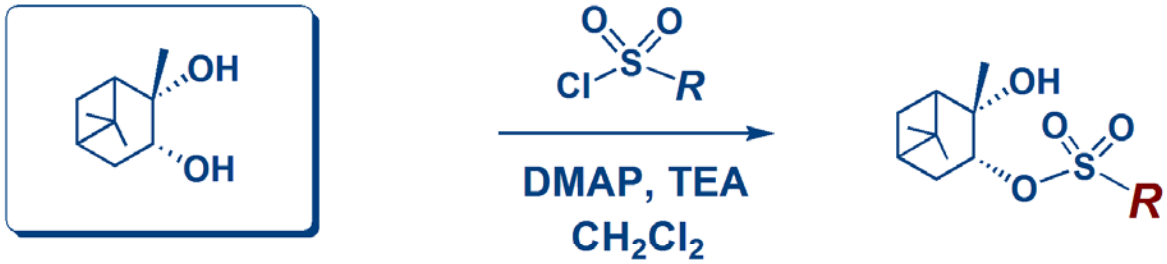


R_1 = Me, Ph
R_2 = H, Ac

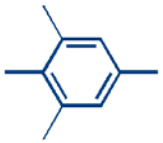
SPIE **2009**, *7273*, 72733Q-1

Synthesis of Pinandiol Monosulfonates

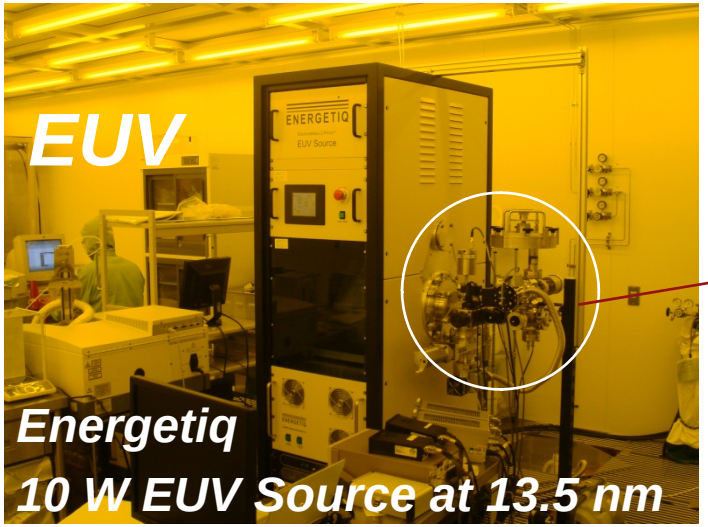
Arimitsu Lab Acid Amplifiers

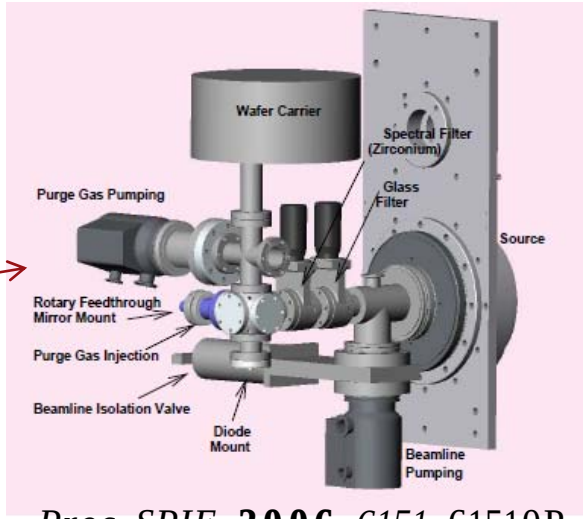


(1S, 2S, 3R, 5S)-(+)-Pinanediol

R					
	PiTs	PiMe	Pi1F	Pi3F	Pi5F
Yield (%)	87	82	83	98	17

Facilities at Tagawa Lab

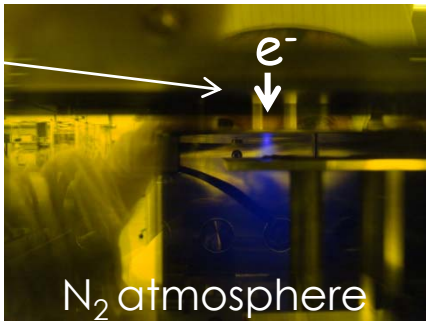




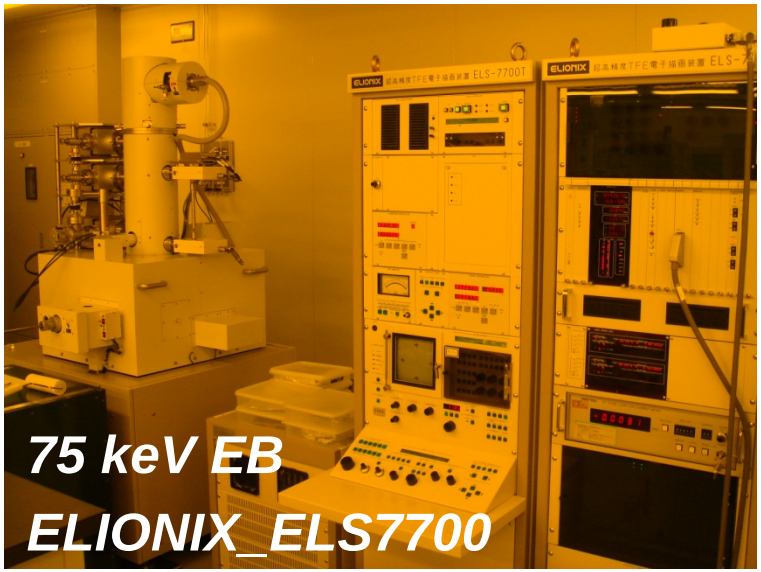
Proc. SPIE, **2006**, *6151*, 61510P

EB-ENGIN

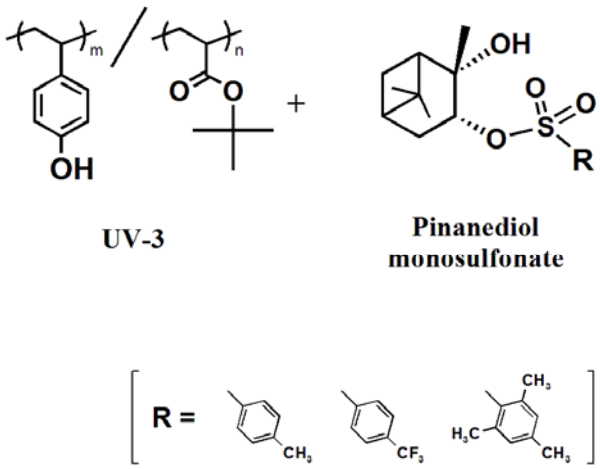
(Hamamatsu)

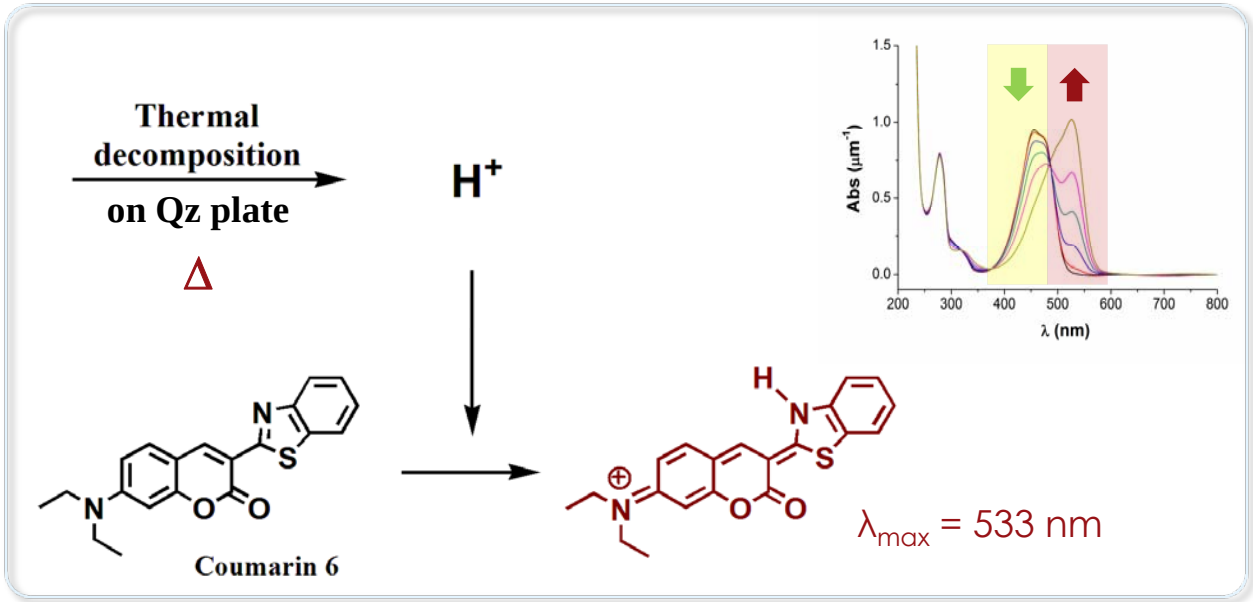


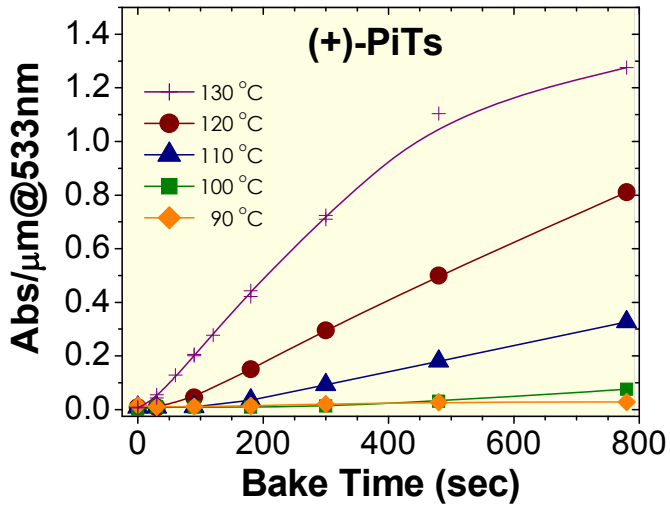
- 40 ~ 110 keV
- 0 ~ 200 μA

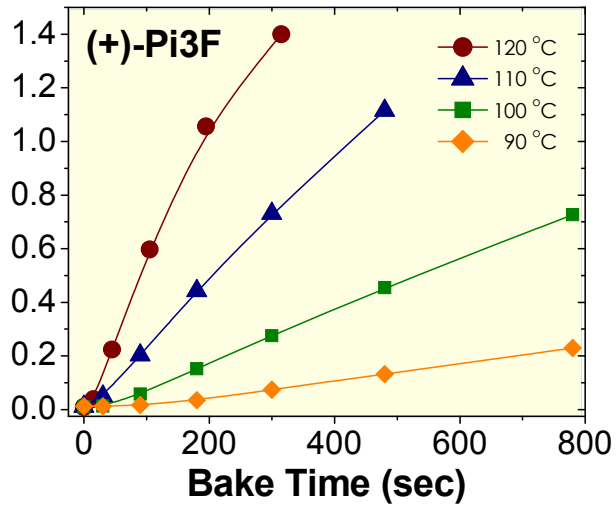


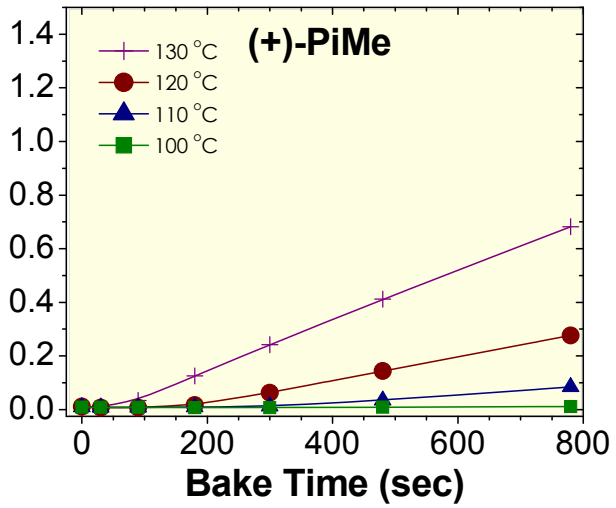
Thermal Stability









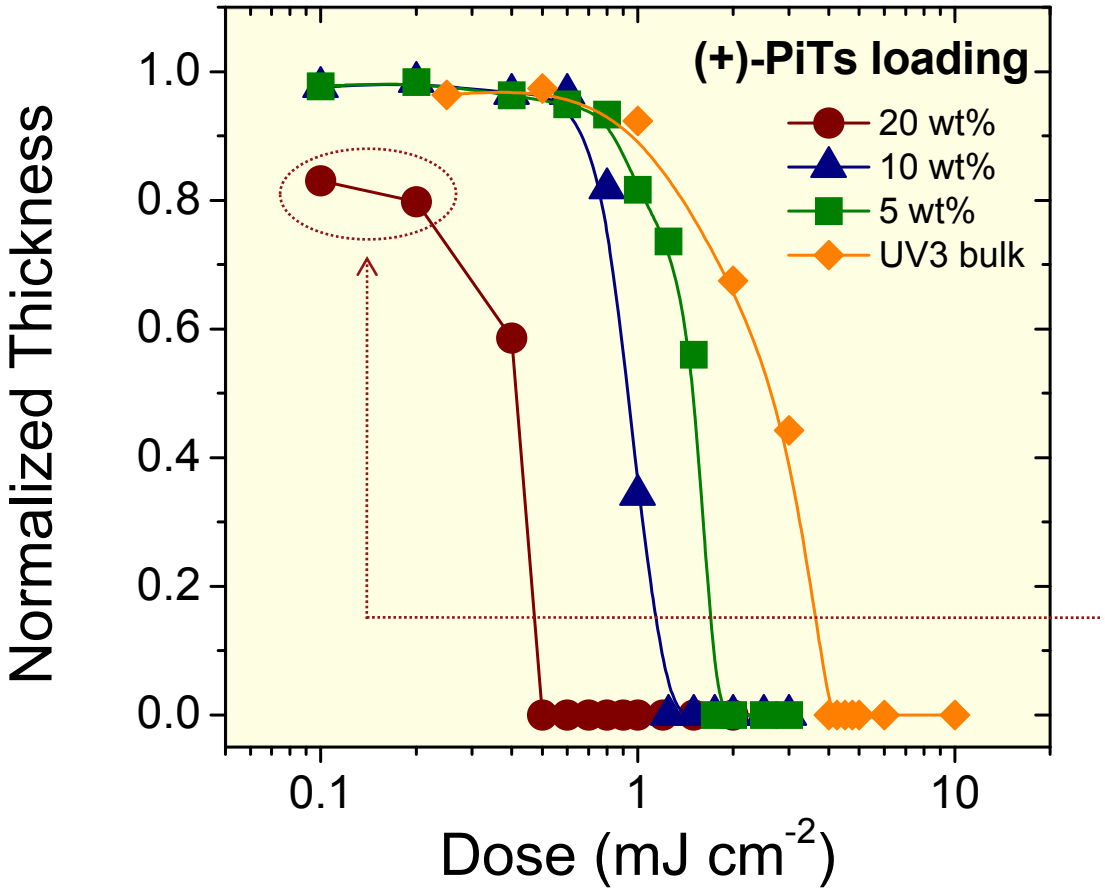


AA stability is due to the acid strength

Contrast curve of the UV3 with (+)-PiTs

EUV

■ Effect of the acid amplifier (AA) loading



■ **Increasing (+)-PiTs loading leads to improve sensitivity of the resist.**

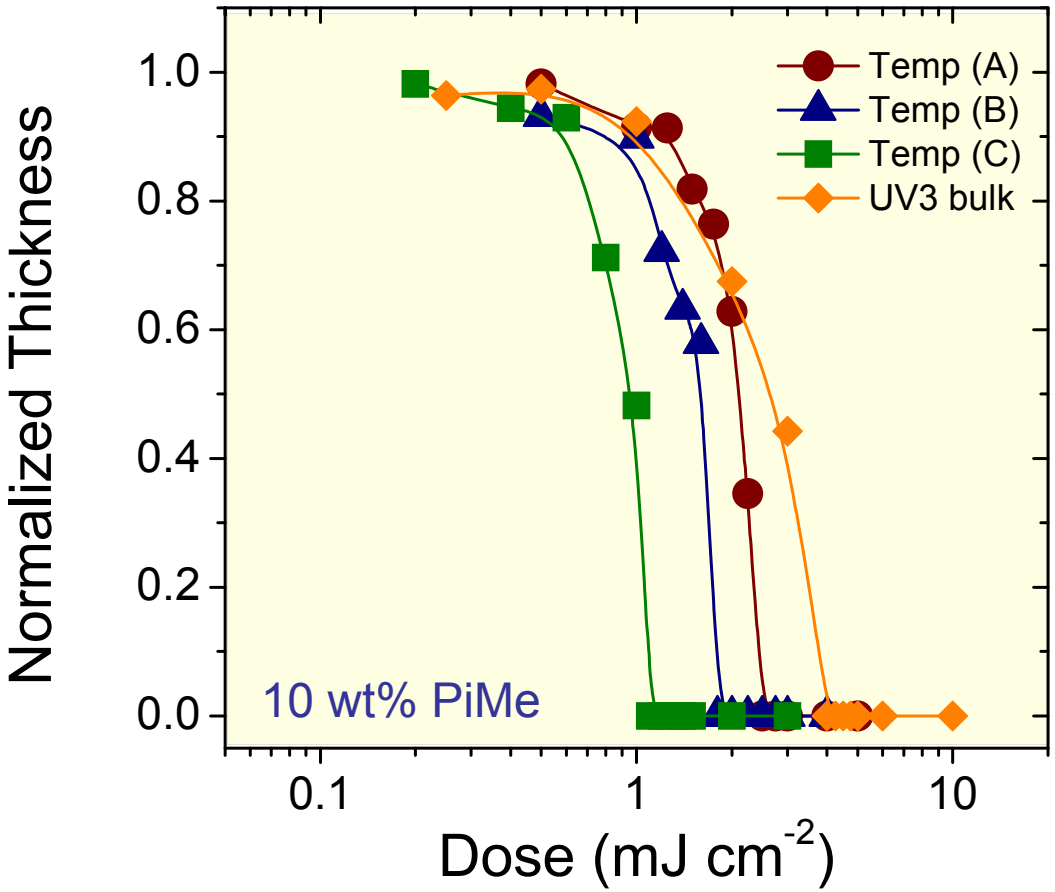
→ The similar trend was observed with PiMe, excepted with Pi3F.

● Due to a self decomposition

Contrast curve of the UV3 with (+)-PiMe

EUV

■ Control of the PEB temperature



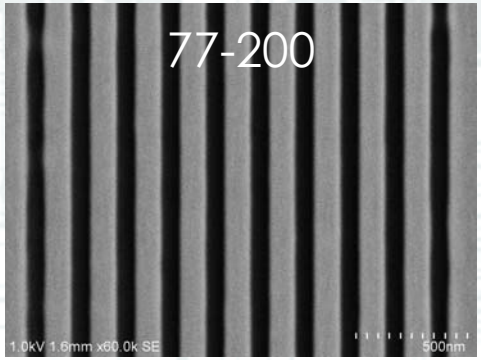
■ The E_0 values for the UV3 film containing 10 wt% of (+)-PiMe after development were 2.5, 1.8, and 1.1 mJ cm^{-2} with a post exposure bake.

Line-Space Lithographic Patterning

75 keV EB

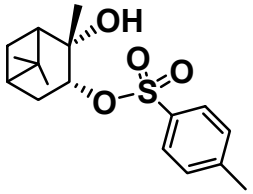
UV3 only

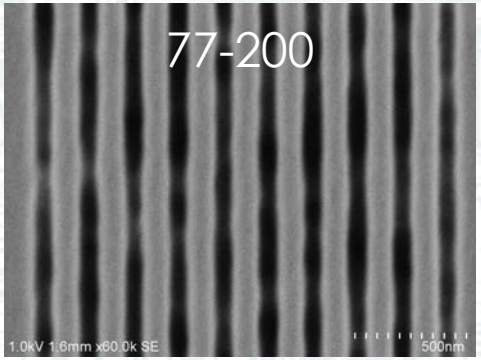
w/o AA



40 μC cm^{-2}

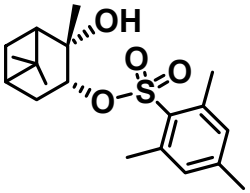
10 wt% (+)-PiTs

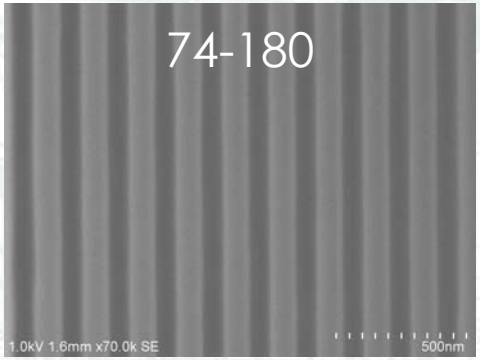




19 μC cm^{-2}

10 wt% (+)-PiMe





25 μC cm^{-2}

* Line – Pitch (nm)

Summary

1) **Thermal stability of AAs**
   – PiTs, Pi3F, and PiMe were stable up to 110 ^{o}C, 90 ^{o}C, and 120 ^{o}C for at least 90 sec, respectively.

2) **Improved sensitivity**
   – E_0 values for 5, 10, 20 wt% of PiTs loading were 1.8, 1.3, and 0.5 mJ cm^{-2}, respectively. Such an enhancement of sensitivity indicates the importance of the control of acid proliferation during PEB.

3) **Clear 75 keV EB imaging achieved**

Acknowledgments

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Japan Science and Technology Agency

CREST
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