Radiation Chemistry of Fluorinated Polymers for Extreme-Ultraviolet Resist

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Abstract

We investigated radiation chemistry of fluorinated polymers (FPs) using the pulse radiolysis. It is suggested that radical anion of FPs is produced through the reaction between FP and electron. Also, acid yields of FPs after Extreme-Ultraviolet (EUV) exposure were measured. The acid yield of FPs was smaller than that of poly (4-hydroxystyrene) (PHS).

Introduction

In semiconductor industry, miniaturizing the circuit pattern is an important issue for high performance of electronics.

Lithography is conventional method to form the circuit pattern.

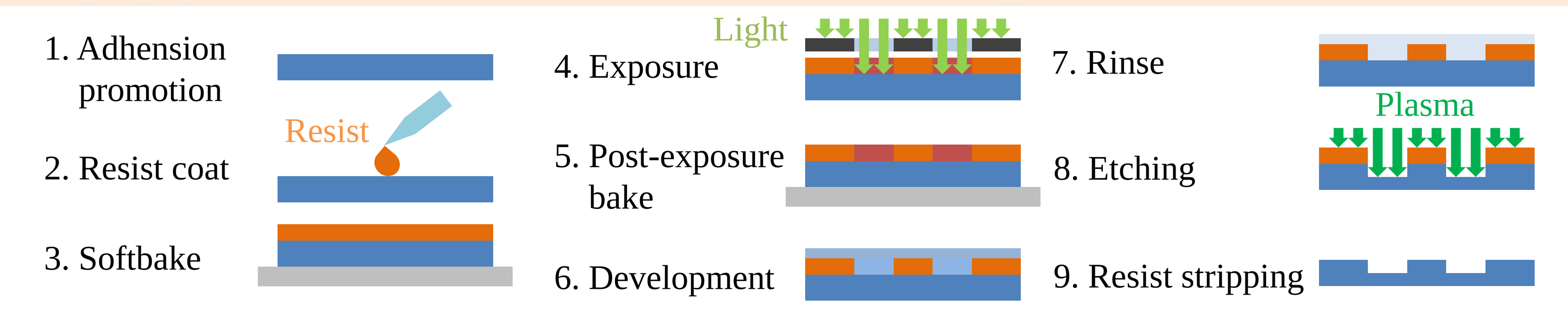

Fig.1. Lithography process.

EUV (92.5 eV) lithography has been investigated for below 11 nm node lately.

Reaction of EUV resist

EUV (92.5 eV) > ionization potential of resist (~10 eV)

$RH \rightsquigarrow RH^{\cdot+} + e^-$

$AX + e^- \rightarrow A^{\cdot} + X^-$ ……★

$RH^{\cdot+} + RH \rightarrow RH(H^+) + R^{\cdot}$

$RH(H^+) + X^- \rightarrow RH + HX$

RH:Polymer

AX:Photo-acid generator (PAG)

Fluorination of polymer for EUV resist

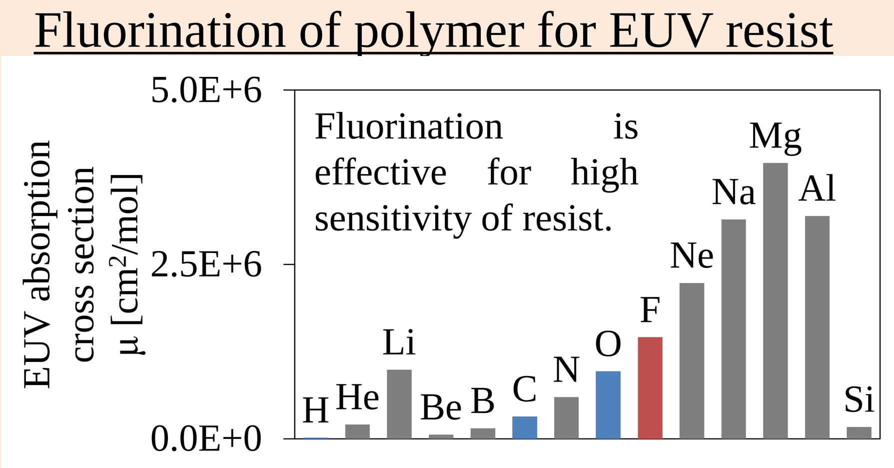

Fig.2. EUV energy absorption cross section of different atoms [1].

It was suggested that dissociative electron attachment prevent reaction ★ in FPs'. [2]

$RF + e^- \rightarrow R(-F)^{\cdot} + F^-$

$F^- \xrightarrow{H^+} HF$

Purpose

Using the pulse radiolysis, we investigated radiation chemical reaction of fluorinated polymers (FPs) which have bicyclo ring or benzene ring. The acid yields were estimated, then compared to conventional resist polymer.

Experimental

Pulse radiolysis

Solutes: FPs

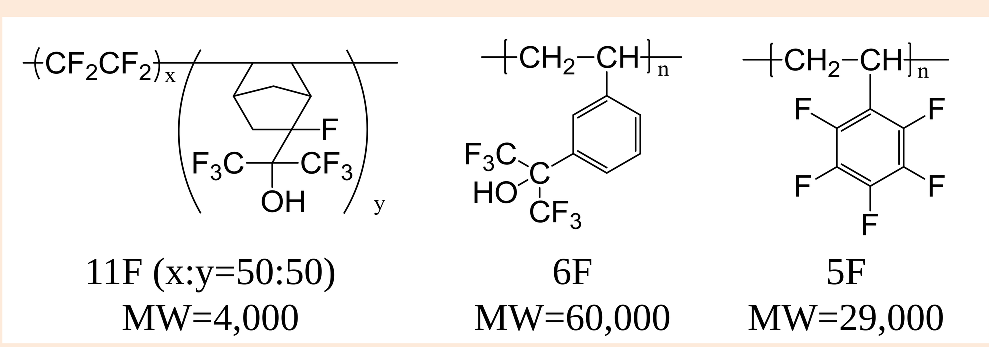

Fig.3. Structure of FPs.

Solvents: Tetrahydrofuran (THF) and Dichloroethane (DCE)

Argon bubbling (5 min)

Source of electron beam: ISIR, Osaka Univ. (28 MeV, 8 ns pulse width)

Acid yields quantification

Solutes: FPs and PHS

Solvent: THF

PAG: Triphenylsulfonium triflate

Acid sensitizer: Coumarin 6 (C6)

[Solute]:[PAG]:[Acid sensitizer] =10:1:0.5

EUV exposure tool: EQ-10M (ENERGETIQ).

Spectroscopy: V-570 (JASCO).

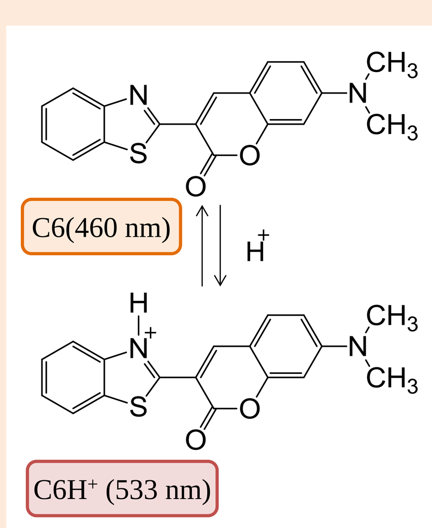

Fig.4. C6 and C6H⁺.

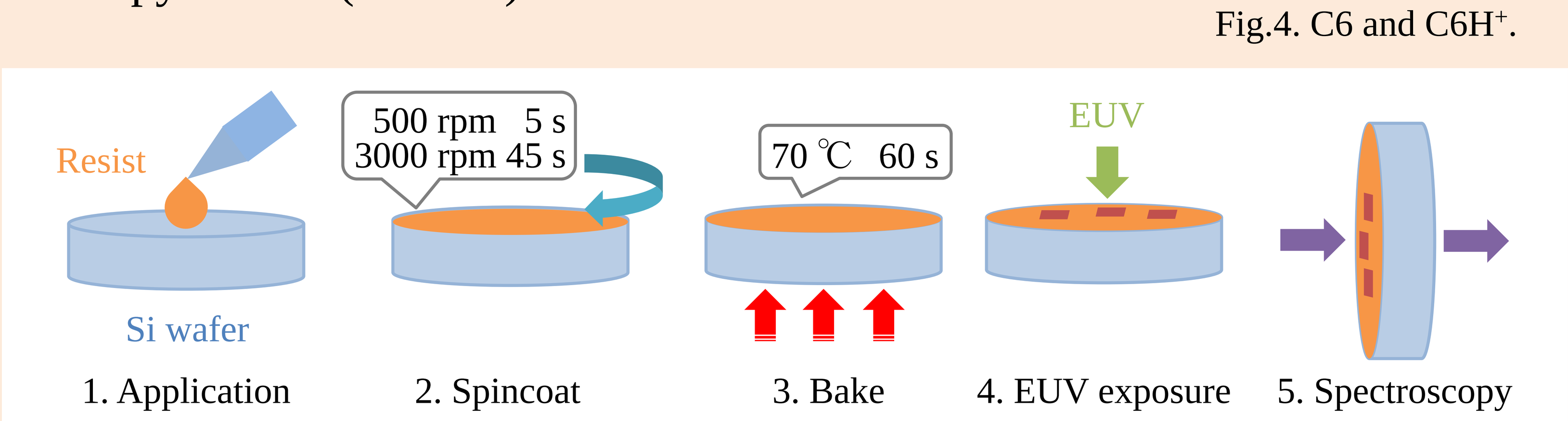

Fig.5. Acid yield quantification method.

Results and Discussion

Pulse radiolysis

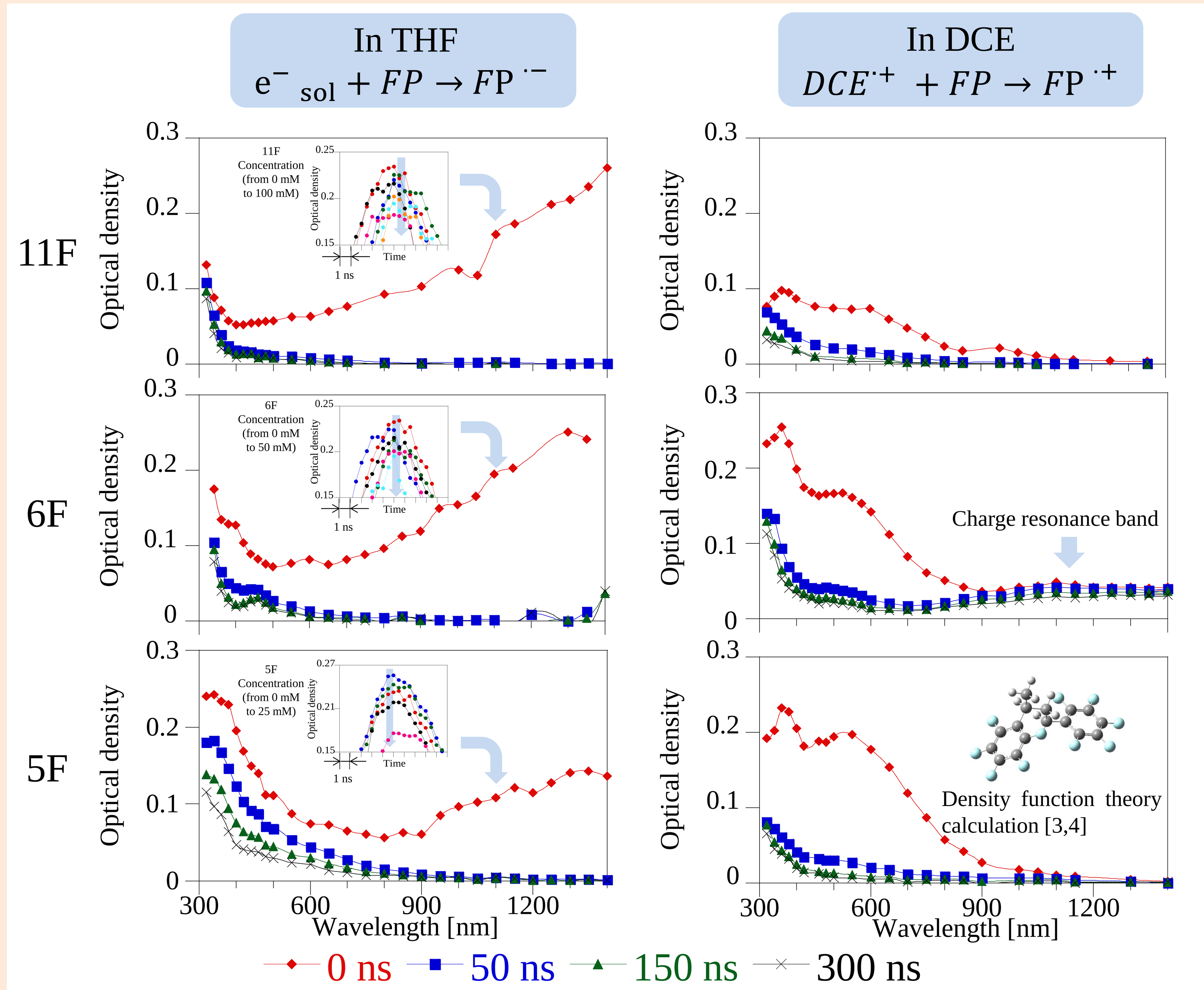

Fig.6.Transient absorption spectra of 11F, 6F, and 5F in THF (100, 50, and 100 mM unit concentration), and time profile of 11F, 6F, and 5F at 1100 nm in THF.

Fig.7.Transient absorption spectra of 11F, 6F, and 5F in DCE (100, 50, and 100 mM unit concentration).

Acid yields quantification

The effect of increase of EUV absorption coefficient by fluorine was not observed clearly.

It was reported that radical anion of fluorinated naphthalene reacts with PAG [5]. However, this reaction has not been clarified in this study.

Secondary electrons react with both photo-acid generator and FPs. The reaction between electron and FP produces radical anion.

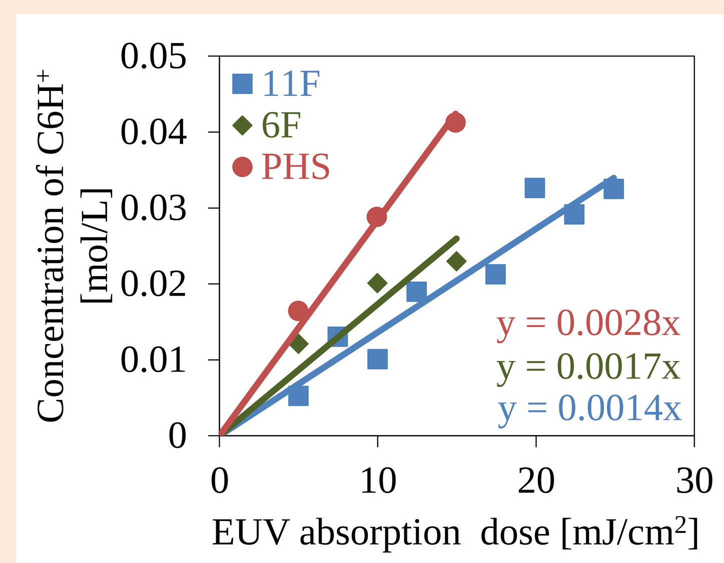

Fig.8. Acid yields related absorbed EUV energy.

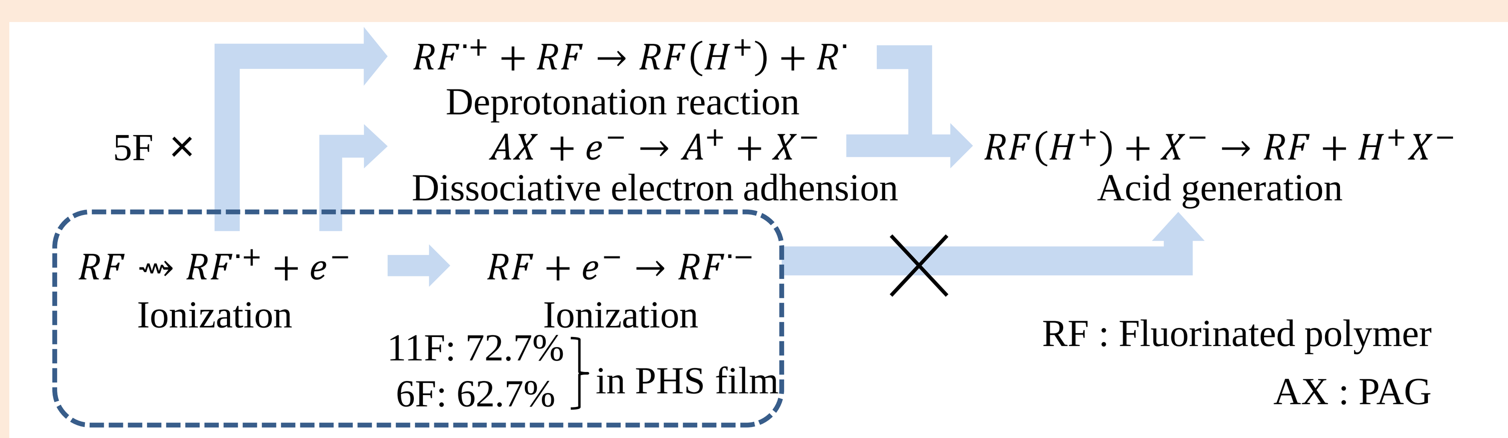

Fig.9. Reaction of resist polymer after EUV exposure.

Summary

Using the pulse radiolysis, radiation chemical reactions of FPs were investigated. The radical anion is produced through the reaction between FP and electron. Acid yields were also estimated by the titrimetry. It is supposed that EUV energy absorption of FPs was smaller than that of PHS because secondary electrons react with FPs.

Acknowledgments

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References

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