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Analysis of acid-generating action of PAG in an EUV resist using acid-sensitive dyes

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Outline

1. Introduction
2. The equipment of experiment
3. Effect of the amount of quencher added
4. Simulations accounting for the effects of quencher amounts
5. Conclusion

1. Introduction

Researchers are currently examining various methods for determining the quantity of acid generated by a photoacid generator (PAG) and for analyzing acid-generating reactions using acid-sensitive dyes that react with acid and generate a color. Adding an acid-sensitive dye to the resist gives a clear grasp of the acid-generating action. The process involves applying a resist containing an acid-sensitive dye to a quartz substrate; exposing the substrate; and measuring and evaluating the absorbance of a chromogenic substance near 530 nm using a spectroscope. The method determines the rate constant for acid generation (Dill C parameter) during exposure based on the relationship between transmissivity at 530 nm and exposure dose. Using this method, we obtained and compared rate constants for acid generation (C parameters) as part of our study of dependence on the quantity of quencher in the EUV resist. Our results indicate a new model that accounts for the quencher concentration parameter would be useful in analyzing dependence on the quantity of quencher. This paper presents these findings, together with the results of studies of profile simulations using the quencher concentration parameter obtained in the experiments.

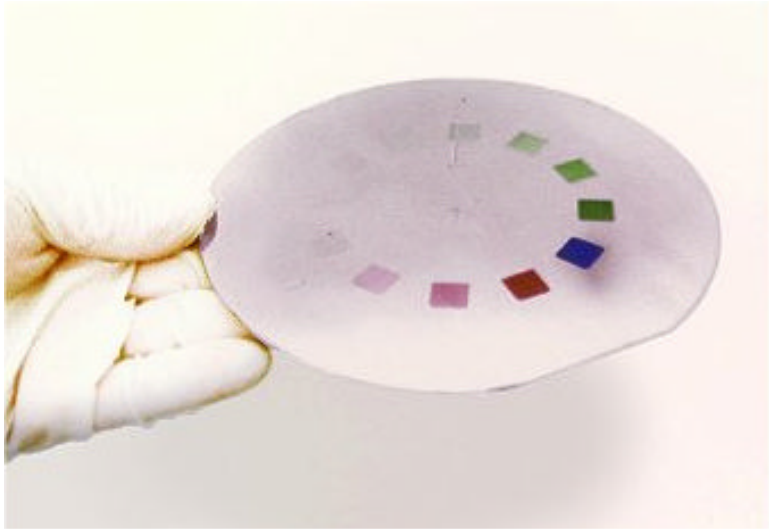


Figure 1 EUV open frame exposure tool (EUVES-7000) and exposed pattern

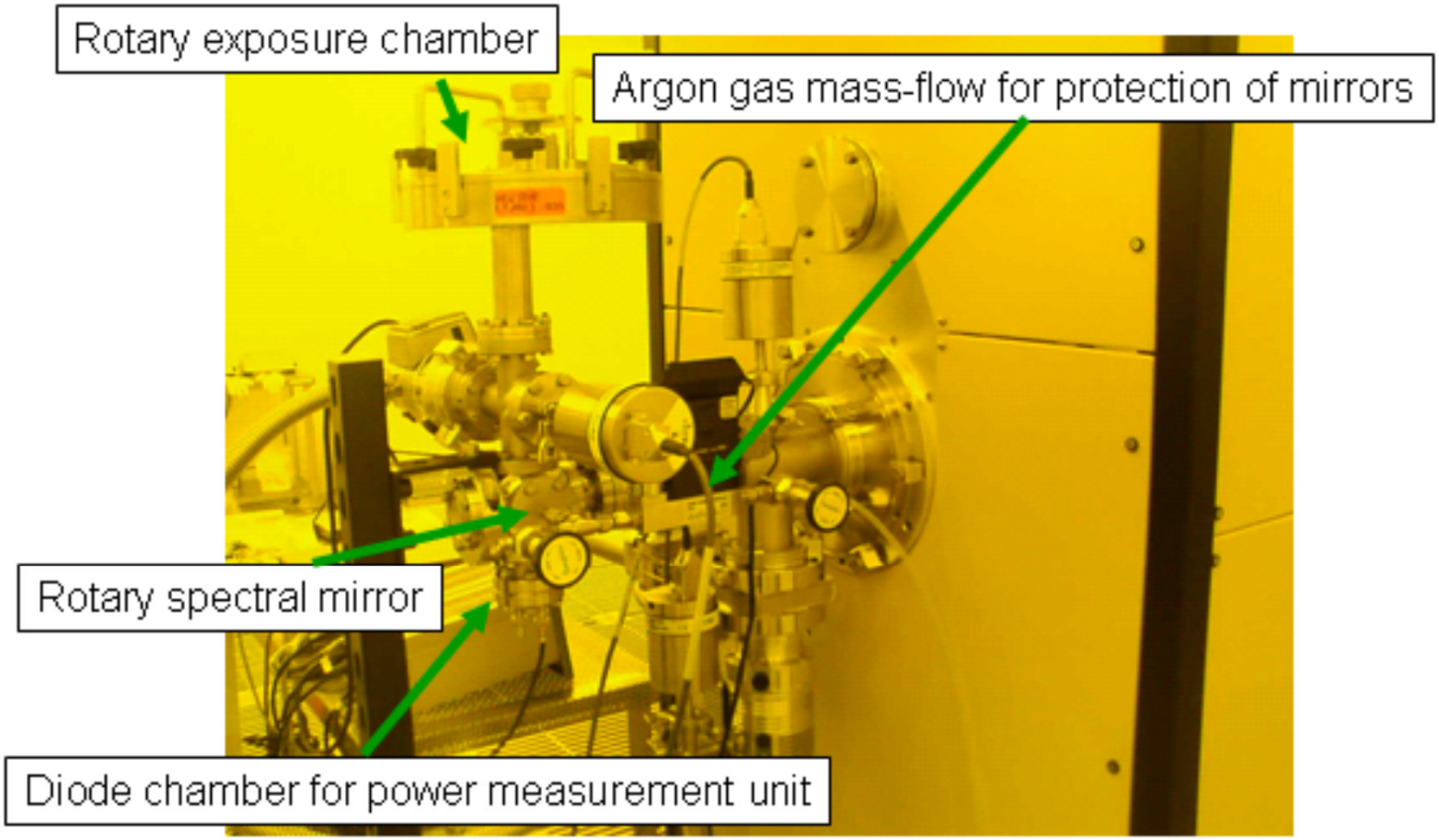
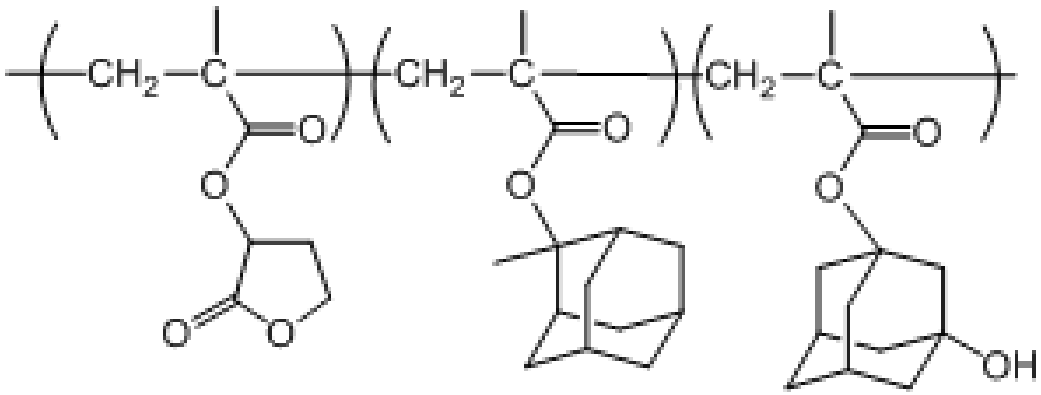
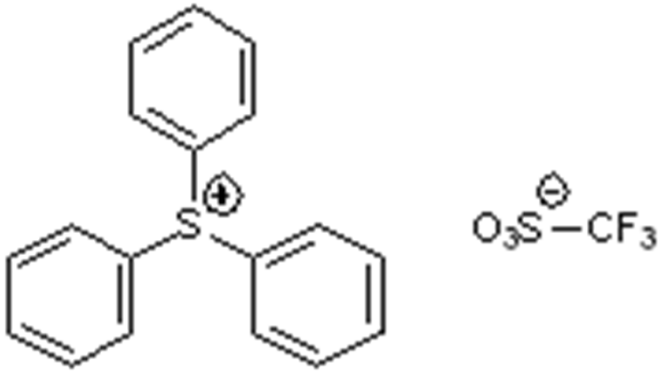


Figure 2 13.5nm beam line



(a) GMH (With blocking group)



(b) PAG (TPS-TF)

Figure 3 Polymer structures (a) and PAG structures (b)

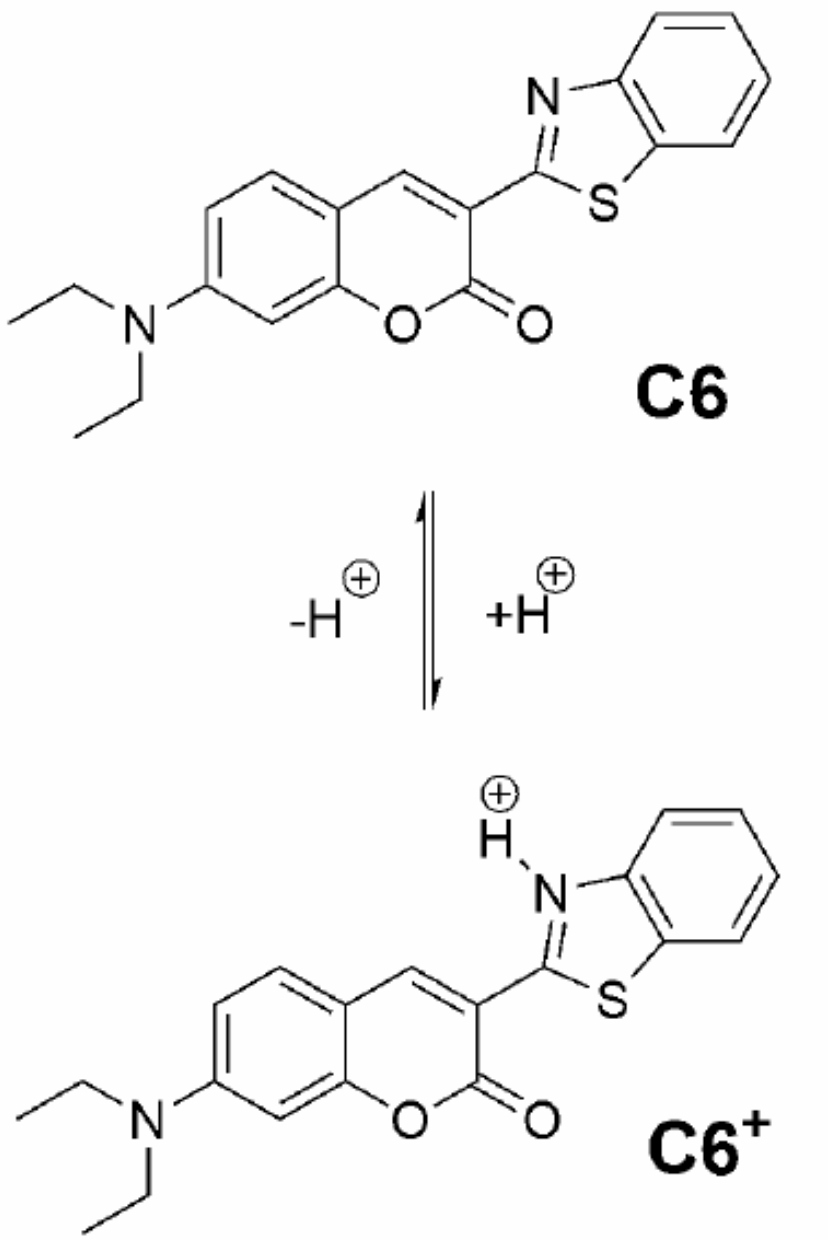


Figure 4 Structure of coumarin 6 and its chromogenic reaction

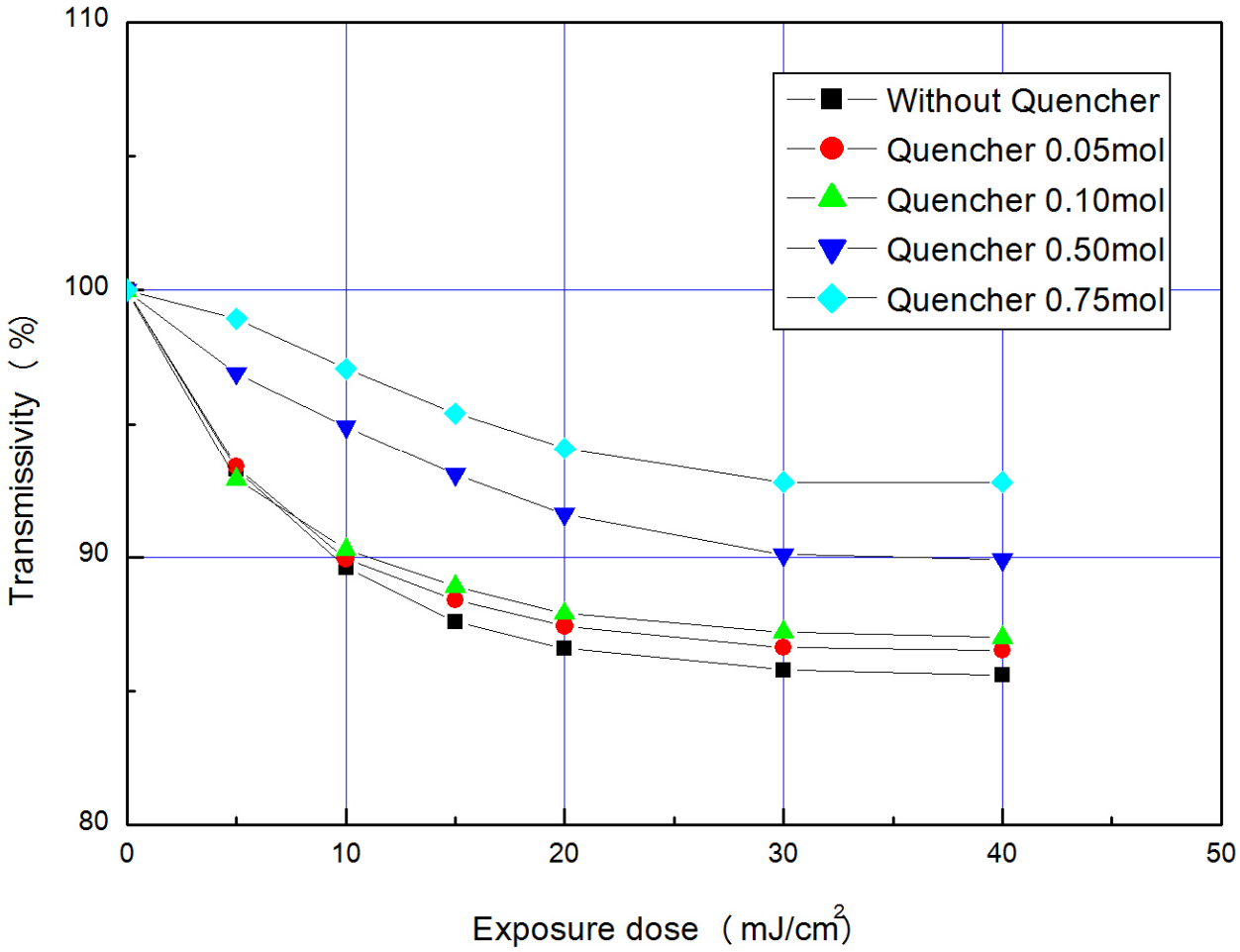


Figure 5 Relationship between transmissivity (at 530 nm) and exposure dose obtained with different amounts of quencher

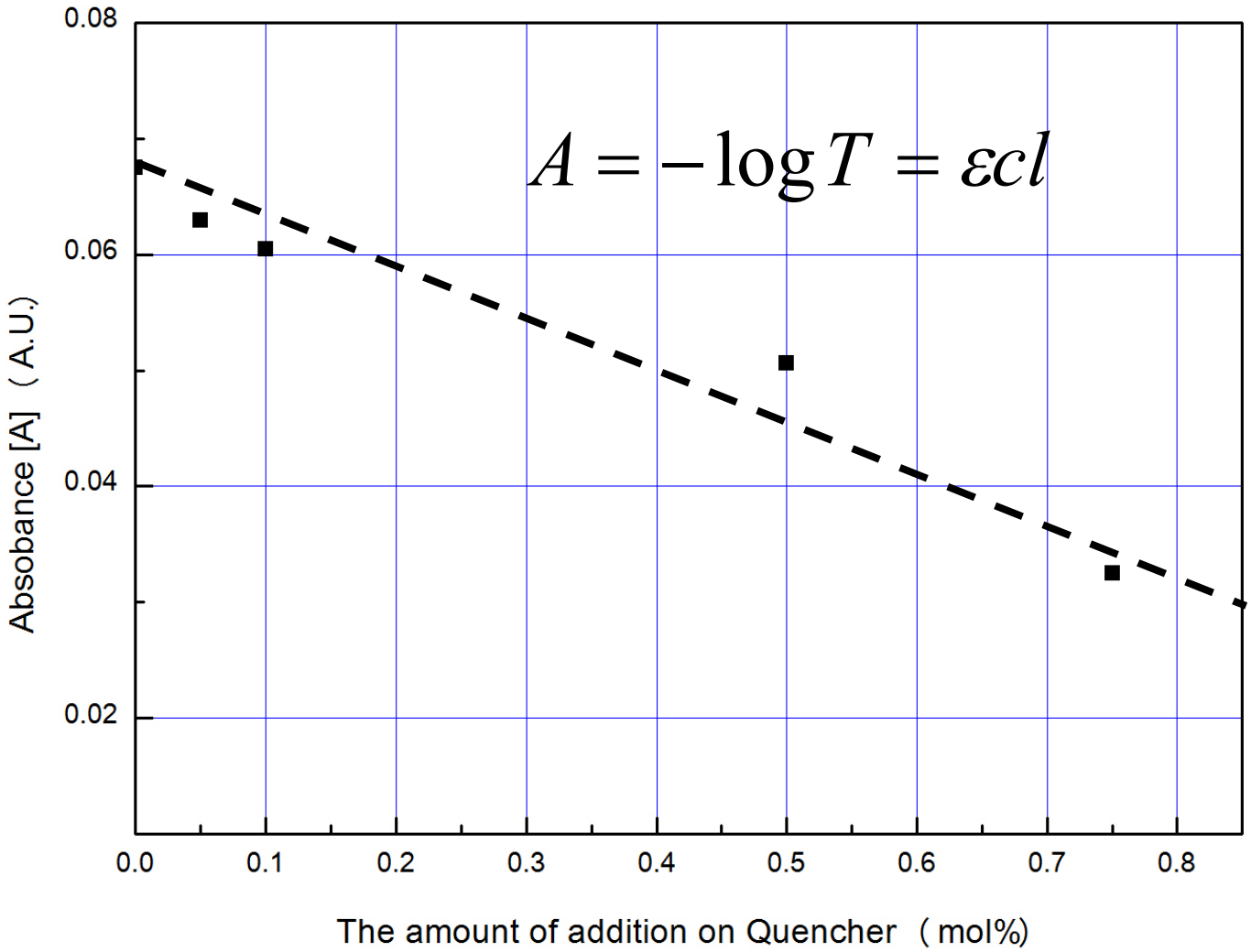


Figure 6 Relationship between absorbance [A] and amount of quencher added

$$[H^+] = 1 - \exp(-C \bullet E)$$

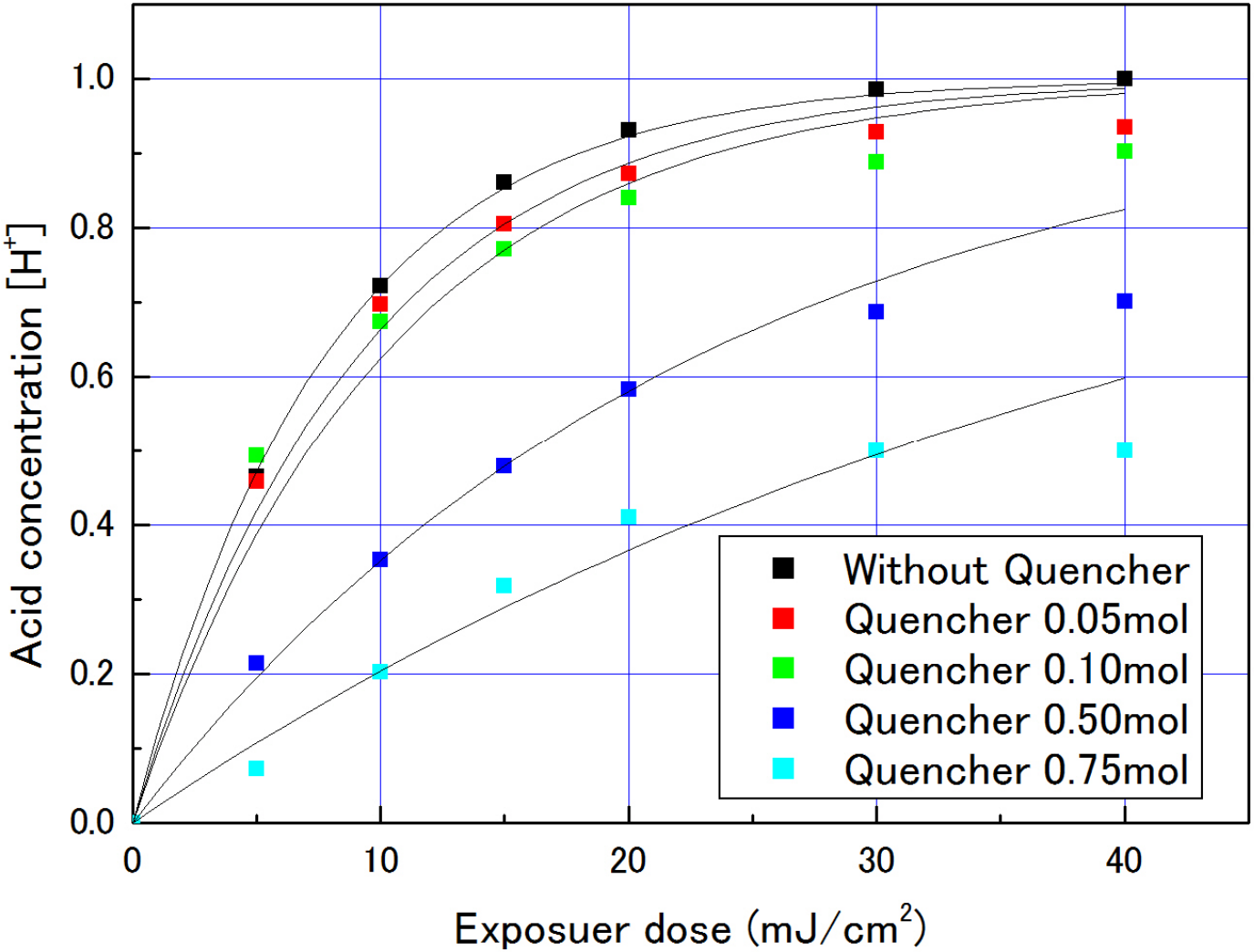


Figure 7 Relationship between acid concentration $[H+]_q$ after neutralization reaction and exposure dose obtained with varying amounts of quencher; results of fitting given by conventional formula (Black lines indicate fitted results)

Table 1 C parameters obtained using varying quencher concentrations (conventional model)

PAG	Polymer	The amount of Additional of quencher (mol%)	Dill's C parameter) (cm^2/mJ)
A	GMH	0.00	0.1280
A	GMH	0.05	0.1090
A	GMH	0.10	0.0982
A	GMH	0.50	0.0435
A	GMH	0.75	0.0228

$$[H^+]_q = \frac{\left([H^+]_0 - [Q]_0\right)}{\left(1 - \left(\frac{[Q]_0}{[H^+]_0}\right) \cdot e^{\left(-k_q \cdot \left([H^+]_0 - [Q]_0\right) \cdot E\right)}\right)}$$

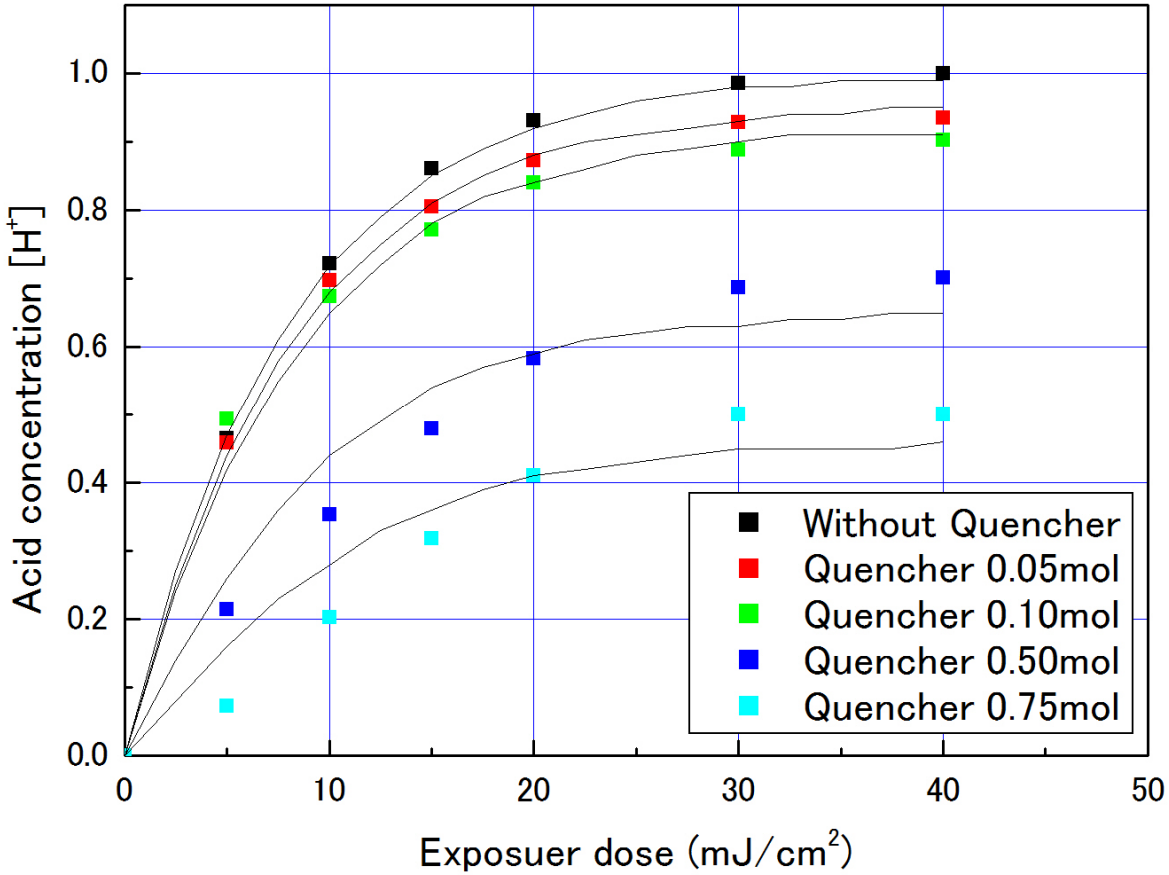


Figure 8 Relationship between acid concentration $[H+]_q$ after quenching and exposure rate obtained with varying amounts of quencher; results of fitting using new model (Black lines indicate fitted results)

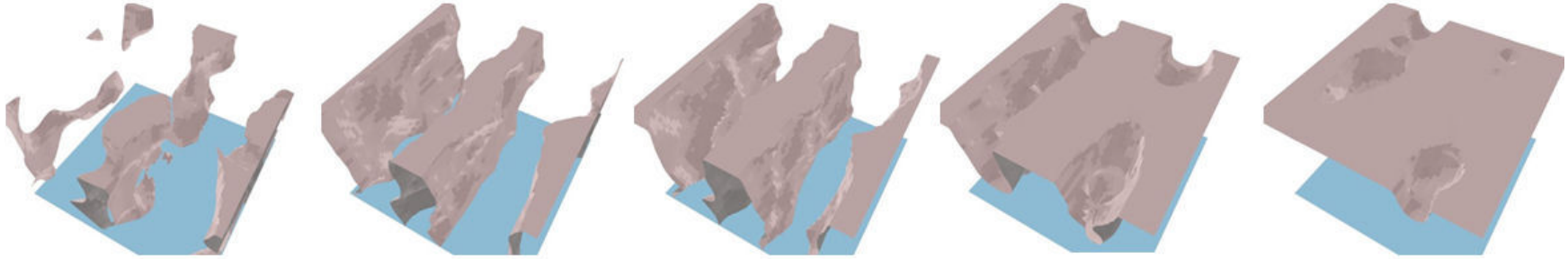
Table 2 Quencher concentration parameters obtained using varying quencher concentrations (new model)

C=0.1280(mJ/cm^2)

PAG	Polymer	The amount of addition of quencher (mol%)	Concentration of quencher parameter $[Q]_0$
A	GMH	0.00	0.000
A	GMH	0.05	0.116
A	GMH	0.10	0.253
A	GMH	0.50	0.603
A	GMH	0.75	0.798

Simulation condition

λ=13.5nm
NA=0.3
Annular illumination (Outer σ=0.7/Inner σ=0.3)
Pattern: L&S 1:1 24nm
Exposure dose=4.7mJ/cm^2
Dev. Time=60sec (TMAH)



[Q]=0 mol% [Q]=0.05mol% [Q]=0.10mol% [Q]=0.50mol% [Q]=0.75mol%

Figure 9 Results of simulations accounting for the quencher concentration parameter

5. Conclusion

We obtained Dill C parameter with varying amounts of added quencher. The results indicate that applying the conventional model formula changed the Dill C parameter due to a dependency on quencher quantity. This is because the quencher consumes the acid generated from the PAG, reducing the apparent amount of acid generated. Based on this finding, we developed a new acid-quencher neutralization reaction model that accounts for the quencher concentration parameter $[Q]_0$. The new model allows us to calculate the acid concentration while accounting for the quencher concentration parameter. We performed simulations using the obtained quencher concentration parameter. The simulation results indicated that increasing the amount of quencher significantly reduces pattern resolution.

Acknowledgements

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