EUV Negative Resist Using Thiol-Yne Stepwise Radical Reaction

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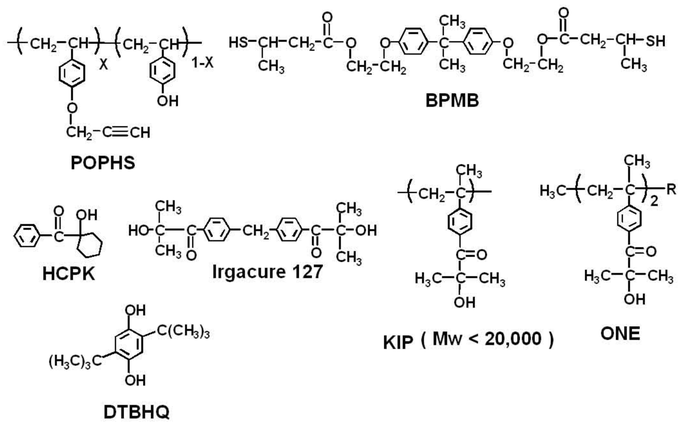
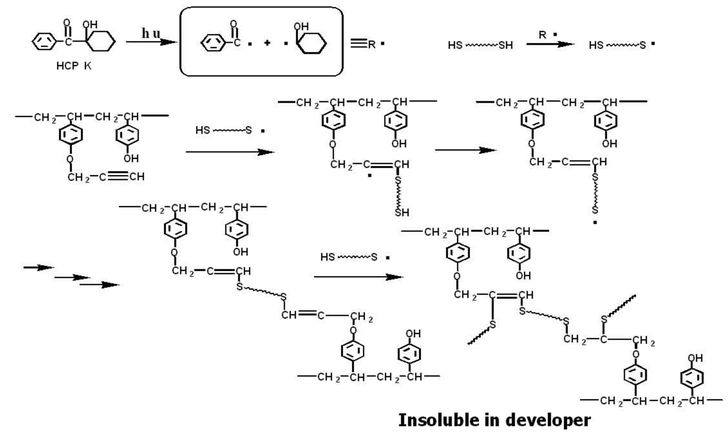
Introduction

Design concept reported for EUV resist is basically the extension of the chemically amplified (CA) system developed for ArF and KrF resists. In CA resists, homogeneous distribution of photoacid generator (PAG) in resist film is essentially important. Furthermore, control of the diffusion length of the photo-induced acid during post-exposure-bake (PEB) treatment is also very important. Although large diffusion length of acids gives high photo-speed, it also induces large LER and/or LWR. Photo-speed and LER and/or LWR are in a trade-off relationship. To improve LER and/or LWR for EUV lithography, it is a good challenge to develop non-conventional CA resist systems with high sensitivity. Here, we report a highly sensitive negative type resist based on the thiol-yne radical reaction. This system is not the conventional CA resist. In this system, PEB treatment is not necessary.

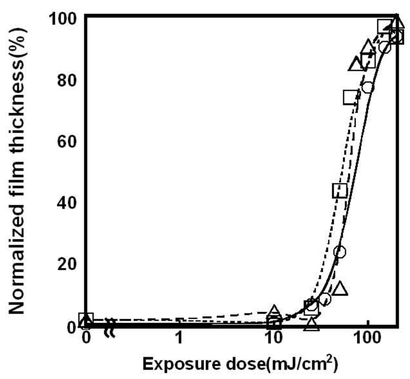
Structures of Chemicals Used



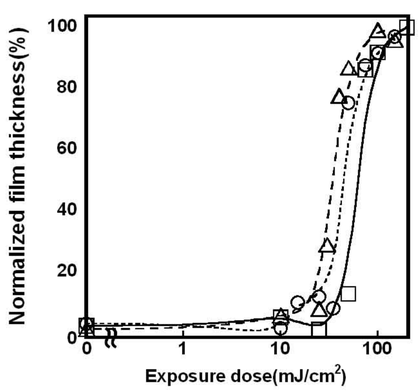
Crosslinking Mechanism



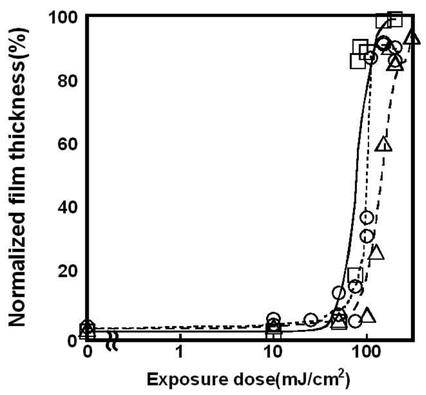
Effect of Several Factors on Sensitivity



Effect of BPMB added on sensitivity.
Exposure: 254 nm.
Resist formulation: POPHS (Mn=3,100, x=0.26, PDI=1.13) / BPMB / HCPK (5 wt %).
BPMB added (wt %): (□) 6, (○) 12, (△) 24.

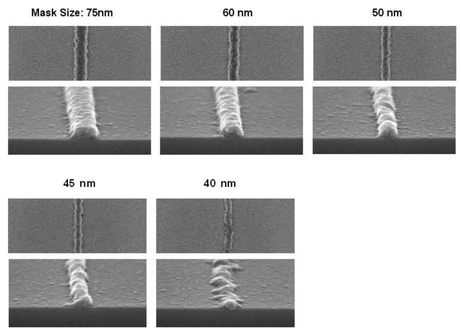


Effect of HCPK added on sensitivity.
Exposure: 254 nm.
Resist formulation: POPHS (Mn=3,100, x=0.26, PDI=1.13) / BPMB (24 wt %) / HCPK.
HCPK added (wt %): (□) 5, (○) 10, (△) 15.

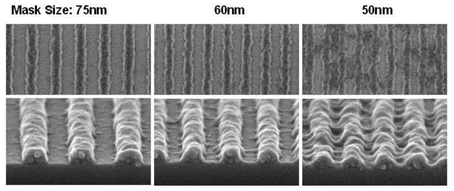


Effect of DTBHQ added on sensitivity.
Exposure: 254 nm. Resist thickness: 80-95 nm.
Development: 2.38 wt% TMAHaq for 90 sec.
Resist formulation: POPHS (Mn=3,100, x=0.26, PDI=1.13) / BPMB (24 wt %) / HCPK (5 wt%) /DTBHQ.
DTBHQ added (wt %): (□) 2, (○) 4, (△) 6.

Imaging

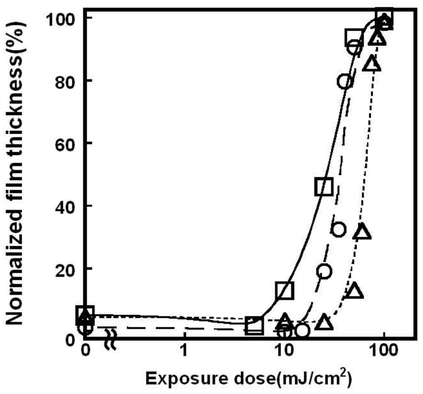


SEM photographs for isolated line images.
Resist: POPHS (Mn=8,000, x=0.26) / BPMB (23 wt%) / HCPK (15 wt%) / DTBHQ (2 wt%).
Substrate: Si treated by HMDS.
Resist thickness: 60 nm.
Exposure: Small Field Exposure Tool (SFET), 16 mJ/cm^2 .
Development: 2.38 wt% TMAHaq for 60 sec.

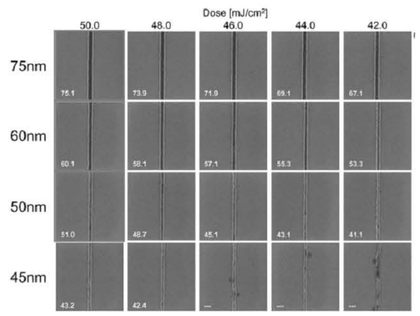


SEM photographs for L/S images.
Resist: POPHS (Mn=8,000, X=0.26) / BPMB (23 wt%) / HCPK (15 wt%) / DTBHQ (2 wt%).
Substrate: Si treated by HMDS.
Resist thickness: 60 nm.
Exposure: Small Field Exposure Tool (SFET), 16 mJ/cm^2.
Development: 2.38 wt% TMAHaq for 60 sec.

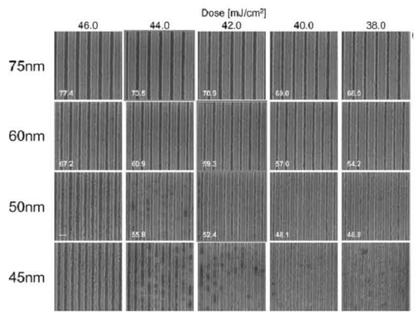
Effect of Radical Initiators



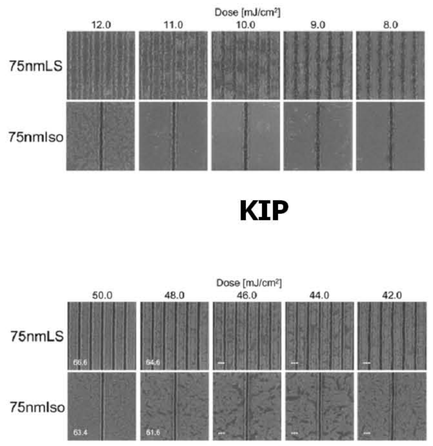
Effect of radical initiators on sensitivity.
Exposure: 254 nm.
Resist formulation: POPHS (Mn=4,400, x=0.25, PDI=1.08) / BPMB (22wt%) / Radical initiator (15 wt %).
Radical initiator: (□) KIP, (○) ONE, (△) Irgacure 127.



ONE



ONE



SEM photographs for L/S and Iso images.
Resist: POPHS (Mn=4,400, X=0.25) / BPMB (22wt%) / Radical initiator (15 wt%) / DTBHQ (2 wt%).
Substrate: Si treated by HMDS.
Resist thickness: 60 nm.
Exposure: Small Field Exposure Tool (SFET).
Development: 2.38 wt% TMAHaq for 60 sec.

Summary

Highly sensitive negative resist for EUV lithography was investigated. OH groups of PHS were modified with propargyl units and the modified-PHS was used as a resist base polymer which was developable with 2.38wt% TMAH aqueous solution. A formulation of the resist was a mixture of modified-PHS, difunctional thiol compound, photoradical generator, and hydroquinone derivative. This resist was highly sensitive because the photo-induced radical chain reaction effectively occurred at room temperature under vacuum atmosphere. Sensitivity was strongly dependent on the concentration of radical initiators and structure of radical initiators. Addition of radical scavenger to the resist system effectively improved the lithographic performance. Outgassing from the present resist was thoroughly low compared to the Selete standard resist.

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