A Novel Chemically Amplified Positive Photoresist for UV Lithography

Liyuan Wang, Na Xu, Jinxing Yu; College of Chemistry, Beijing Normal University; Beijing 100875, P.R.China

Abstract

A novel chemically amplified positive i-line photoresists can be formed by 2,3,4-tris[2-diazo-1-(2H)-naphthalenone-4-sulfonyloxy] benzophenone (2,1,4-DNQ) and an acidolytic acetal polymer. When irradiated with i-line light, the 2,1,4-DNQ sulfonate undergo photolysis not only to give off nitrogen gas but also generate sulfonic acid which can result in the decomposition of the acidolytic polymer. The lithographic performance of the resist materials is evaluated and significant advantages (higher resolution and sensitivity) over conventional novolak/ diazonaphthoquinone (DNQ) resist system can be observed.

1. Introduction

We have reported the preparation and properties of a series of novel ester acetal polymers which were synthesized by the reaction of dicarboxylic acids and divinyl ether compounds [1-3]. These polymers can be easily decomposed by strong acid generated from photoacid generator (PAG) and so new types of positive tone chemically amplified photoresists can be formed by them.

The performance advantages of chemically amplified (CA) photoresists, compared to novolak/DNQ chemistry, are demonstrated by their high sensitivity and resolution. Meanwhile, novolak/DNQ based resists can provide excellent contrast. Combining these two types in one resist composition probably afford new i-line photoresists with high performance. In this paper, we tried to form chemically amplified positive i-line photoresist by 2-diazo-1-naphthoquinone-4-sulfonate and an acetal polymer with high acidolysis activity. When irradiated with i-line light, 2,1,4-DNQ sulfonate can be photochemically transformed to 3-sulfoindenecarboxylic acid[4,5] and so can functions as a photoacid generator

2. Experimental

2.1 Measurements

FT-IR spectra were measured by a Avatar 360 FT-IR (Nicolet, U.S.A.) spectrophotometer.

The UV absorption spectra of the polymers were measured using GBC Cintra 10e UV spectroscopic system.

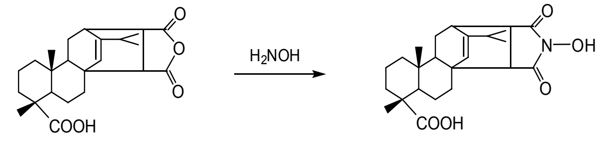
The glass transition temperature (Tg) was detected using a DSC 30 (Mettler, Switzerland) with 10k/min and N_2 protection with the second heating/cooling cycle.

The molecular weight of the polymers was determined by Gel permeation chromatography (GPC) using a Polymer Laboratories GPC50 chromatograph system.

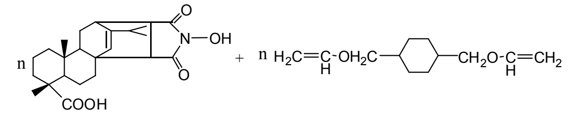
2.2 Materials

2.2.1 Synthesis of acidolytic acetal polymer

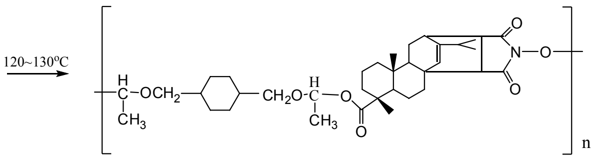
Maleic anhydride pimaric acid (MPA) was prepared by the Diels-Alder reaction of abietic acid and Maleic anhydride. The compound was reacted with hydroxylamine to give N-hydroxy maleimide pimaric acid (NHMPA), which was further reacted with 1,4-cyclohexanedimethanol divinyl ether(CHDDE) to give p(NHMPI-CHDDE):



Maleic anhydride pimaric acid (MPA)   N-hydroxy maleimide pimaric acid(NHMPA)



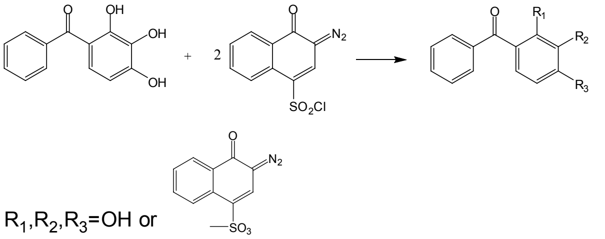
N-hydroxy maleimide pimaric acid (NHMPA)   1,4-cyclohexanedimethanol divinyl ether(CHDDE)



p(NHMPI-CHDDE)

2.2.2 Preparation of 2,1,4-DNQ sulfonate

2,3,4-Trihydroxy benzophenone was reacted with 2-diazo-1-naphthoquinone-4-sulfonyl chloride to give a 2,1,4-DNQ sulfonate:



2.3 Lithographic experiments

Resists were formulated by dissolving the acetal polymer p(NHMPI-CHDDE) and 2,1,4-DNQ sulfonate (3/1 and 9/1,w/w) at 15wt% in propylene glycol monomethyl ether acetate(PGMEA) and then the solution was filtered with a 0.2 μm Teflon membrane filter. Resists were spin coated on waver and soft baked at 90°C for 60s to yield 0.6-0.9 μm thick films. Exposure was carried out using a Nikon NSR-200si9c stepper. After post exposure bake(PEB), exposed resists were developed in a 2.38 wt% tetramethylammonium hydroxide (TMAH) aqueous solution for 60 seconds. The SEM images were taken by a KLA-Tencor 8250 CD-SEM system.

3. Results and Discussion

3.1 Properties of the acetal polymer

3.1.1 Molecular weight

Figure1 was the GPC plot of p(NHMPI-CHDDE) with a Mn of 0.41×104, a Mw of 0.94×104 and a polydispersity(Pd) of 2.3 which was much smaller than that of novolak resin.

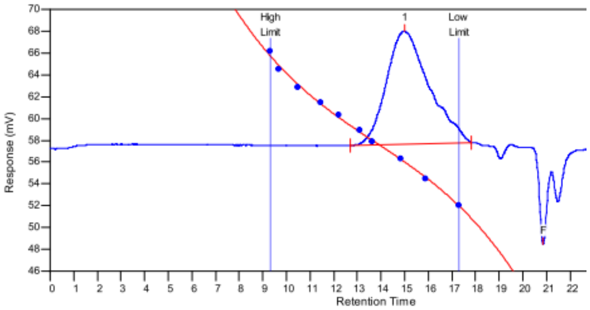


Figure 1 GPC plot of p(NHMPI-CHDDE)

3.1.2 Thermal properties

P(NHMPI-CHDDE) had a glass transition temperature of 82-85 ^{o}C，which can be attributed to the large multiple alicyclic groups and the imide rigid structure of the polymer. The polymer was thermally stable and did not show any apparent decomposition until after 220^{o}C, as evidenced by the DSC measurement (Figure 2).

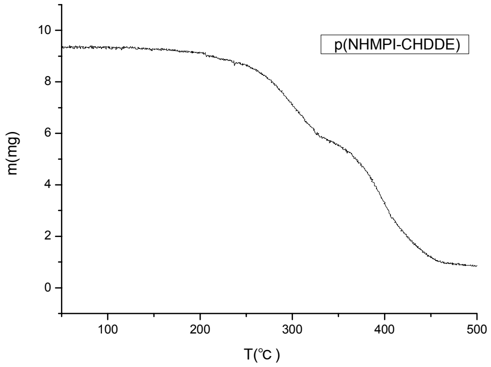


Figure 2 *DSC plot of p(NHMPI-CHDDE)*

3.2 The UV absorption spectra of acetal polymer

The UV absorption spectrum of p(NHMPI-CHDDE) was shown in Figure 3 . It indicates that the polymer is transparent in the region above 230 nm.

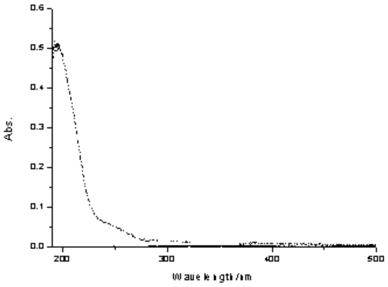


Figure 3 *The UV absorption spectra of p(NHMPI-CHDDE)*

3.3 The acidolysis of the acetal polymer

The ester acetal linkage of the polymers can be cleaved by strong acid generated by PAGs. To investigate the acidolysis activity, the film of the acetal polymer containing 3% PAG (sulfonium salt) on salt slice was exposed to low pressure Hg light (254nm) with the exposure dose of about 50mj/cm^2. The IR spectra of the film were measured before exposure, after exposure without PEB and after exposure with PEB separately. It can be seen from Figure 4 that the IR spectrum of the film displays no apparent change after exposed without post exposure bake indicating little acidolysis reaction at room temperature. After exposed and baked at 100^{o}C for 1 min, the absorption peak of the ester group at 1721 cm^{-1} was partly transformed to that of carboxylic acid at 1692 cm^{-1} indicating that the acidolysis reaction after PEB is rapid and can result in a high dissolution rate of the exposed district.

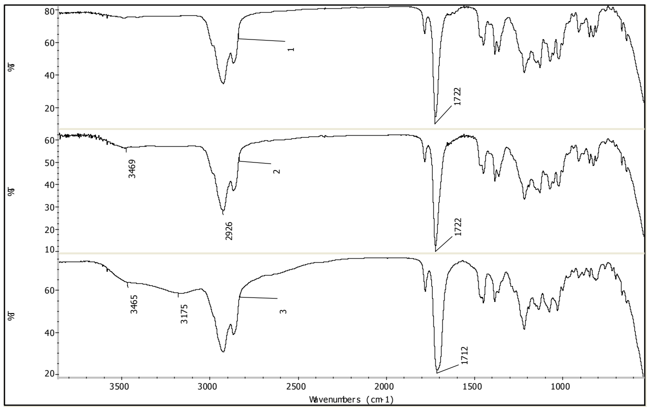


Figure 4 *FT-IR spectrum of p(NHMPI-CHDDE) film containing 3% PAG*

1. before exposure; 2. after exposure; 3. after exposure and PEB

3.4 Lithographic performance

I-line lithographic performances of the resists were investigated. Description of the resist samples are shown in Table 1. Two ratios of acetal polymer to 2,1,4-DNQ sulfonate was chosen. PEB was conducted at 100^{o}C and 110 ^{o}C for comparison.

The CD-SEM images of the obtained patterns were presented in Figure 5. It can be seen that clear patterns with resolution of 0.35μm L/S were achieved in all the resist samples. The high resolution benefits from the narrow molecular weight distribution of the acetal polymer. Increasing the ration of 2,1,4-DNQ sulfonate to acetal polymer will enhance the photosensitivity of the resist, which is much higher than that of common novolak/

diazonaphthoquinone (DNQ) resist. A higher PEB temperature will also benefit to the increasing of photosensitivity. Besides, another advantage of the resists is that the reduction of thickness of the resist film before and after development is less than 2%. This results from the insolubility of the unexposed area in aqueous base.

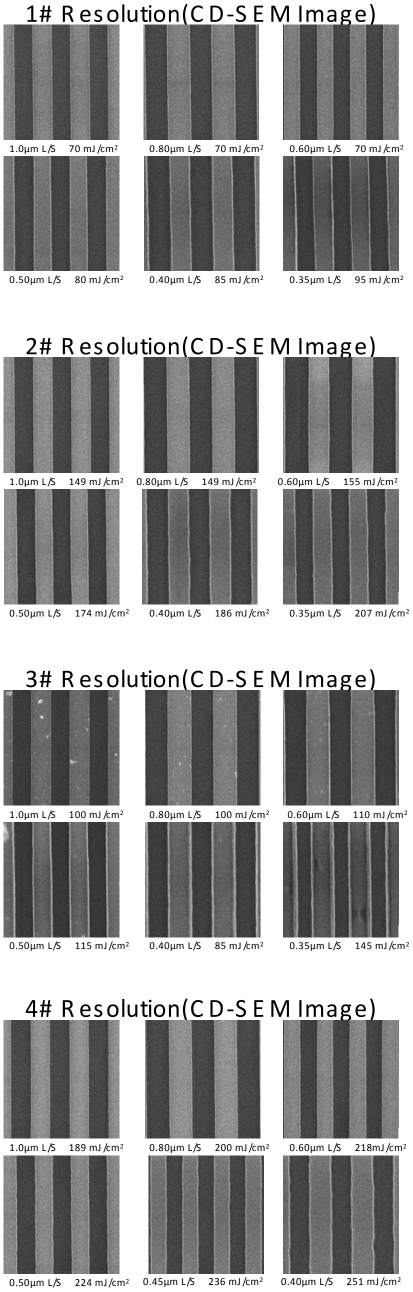


***Figure 5** SEM images of resist pattern (top view)*

However, no pattern can be obtained without post exposure bake (PEB). The exposed film can be developed only after post exposure bake because of the relatively low acidolytic activity of the polymer at room temperature. This also indicates the chemical amplification effect on the DNQ based photosensitive system.

Comparing to common novolak/ diazonaphthoquinone (DNQ) resist, the novel chemically amplified i-line photoresist can readily achieve high photosensitivity, resolution and film thickness remaining.

Table 1 Description of the resist samples

NO.	Sample	Film Thickness (nm)	PEB	Thickness Remaining	E0 (mJ/cm2)
1#	3:1	566	110°C/60S	98%	42
2#	9:1	634	110°C/60S	98%	99
3#	3:1	766	100°C/60S	99%	66
4#	9:1	847	100°C/60S	99%	129

4. Conclusion

2,1,4-DNQ sulfonate can undergo photolysis when irradiated to i-line light not only to give off nitrogen gas but also generate sulfonic acid which can result in the decomposition of the specially designed acetal polymer. Novel chemically amplified positive i-line photoresists can be formed by 2,1,4-DNQ sulfonate and the acidolytic polymer. Excellent performance was investigated in the lithography experiments. Comparing with conventional novolak/ diazonaphthoquinone (DNQ) resist system, the novel CA i-line photoresist can readily achieve high photosensitivity and resolution.

Acknowledgement

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References

[1] L.Wang;X.Zhai; Y.Huo, Novel 193-nm positive photoresist composed of ester acetal polymer without phenyl group, Proc. SPIE, 6519, pg. 65192H (2007)

[2] L.Wang;Z.Chu; L.Cheng, Two-component photoresists based on acidolytic cleavage of novel ester acetal polymer , Proc. SPIE, 6519, 65192I (2007)

[3] L.Wang; Y.Huo; F.Kong, The synthesis of novel ester acetal polymers and their application for chemically amplified positive i-line photoresist, Proc. SPIE, 6923, pg.69233R. (2008)

[4] G.Buhr; H.Lenzt; S.Scheler, Image reversal resist for g-line exposure: chemistry and lithographic evaluation, Proc. SPIE, 1086, 6,117. (1989).

[5] B.aumbach; J.Bendig; T.Nagel, Synthesis and characterization of substituted 2-diazo-1-oxo-1,2-dihydronaphthalenes and their products of photolysis and thermolysis, Journal fuer Praktische Chemie (Leipzig), 333(4), 625(1991).

Biography

Dr. Liyuan Wang is currently an Associate Professor in the College of Chemistry, Beijing Normal University. He received his B.S. in Chemistry, his M.S. in Physical Chemistry and Ph.D. degree in Material Chemistry from BNU. His research group focuses on the research and development of new photopolymer materials and their application in IC manufacture and printing plates.