

Negative-tone Cycloolefin Photoresist for 193 nm Lithography

S. C. Fu^a, K. H. Hsieh^{a,*}, and L. A. Wang^b

a. Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan

b. Graduate Institute of Electro-Optical Engineering, National Taiwan University, Taipei 106, Taiwan

ABSTRACT

The chemistry of acid-catalyzed dehydration reaction and followed by crosslinking of the *tert*-alcohol group in the cycloolefin photoresists was used to tailor the performance of the photoresists for 193 nm lithography. A radiation-sensitive photoacid generator (PAG) in this chemically amplified photoresist (CAMP) can change the polarity of the exposed area of the resist and exhibit a negative-tone behavior. The cycloolefin resists are synthesized by the free radical copolymerization of alicyclic monomer and maleic anhydride, and/or by the cationic polymerization of alicyclic monomer *via* Pd catalyst followed by the attaching of *tert*-alcohol group into the resist. The side reaction of cycloolefin copolymer was observed at the temperature below the post exposure baking (PEB) temperature, but this problem can be eliminated by the introduction of isobornyl methacrylate into the polymer. The lithographic performance of the resists was investigated by using isopropyl alcohol as a developer under various processing conditions. The results demonstrate that these resists are the promising candidates for being used in 193 nm lithography.

Keywords: CAMP, 193 nm lithography, cycloolefin, negative-tone resist

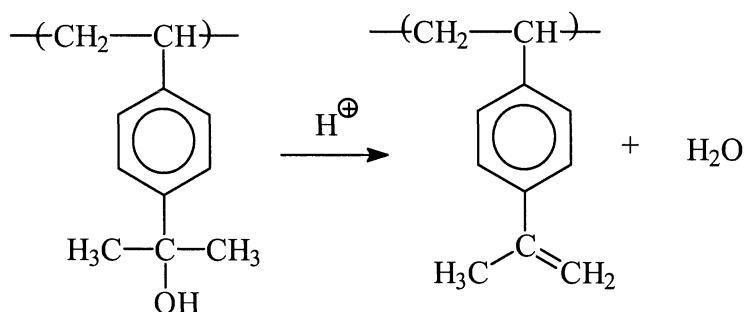
1. INTRODUCTION

Optical lithography has been utilized for a long time to fabricate the IC patterns for its high throughput and low cost comparing to other techniques. Nowadays, with the help of phase shift mask (PSM) and other illumination enhancement techniques, the KrF 248 nm lithography is capable to produce pattern with 0.18 μm design rule. But a thinner critical dimension (CD) is still desired to suit the requirements that more units needed in a chip and faster conversation between units.

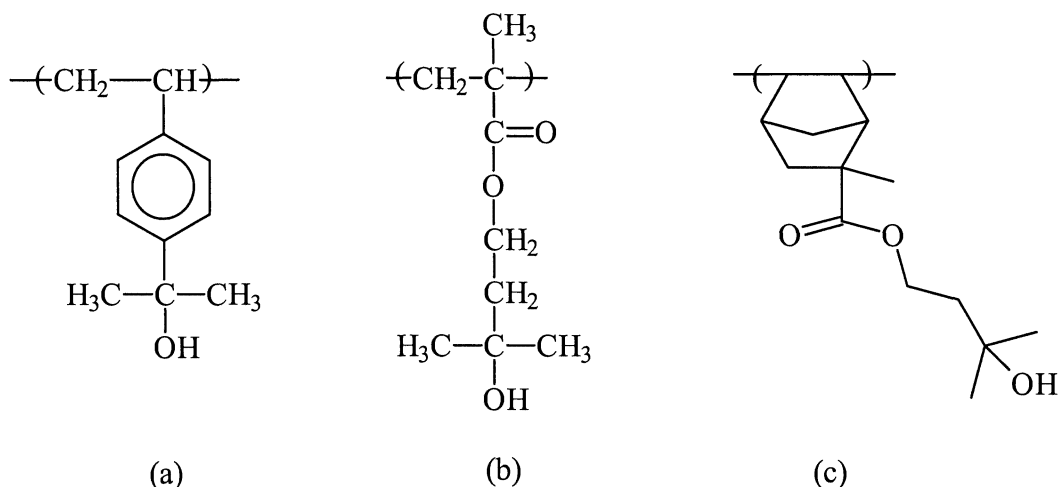
According to the Rayleigh equation, the shorter wavelength can have a higher resolution. The ArF 193 nm lithography, for its shorter wavelength than KrF, is well believed to substitute for KrF lithography in coming days. ArF lithography may extend the life of optical tools and is planned to produce pattern with CD below 100 nm. Some problems remained to be resolved before ArF lithography can be used for commercial production, and the resist is one of the most important issues. The chemical amplified (CAMP^{1,2,3}) design rule is used in ArF resist. Radiation-sensitive photoacid generator (PAG) in the CAMP can catalyze the deprotection or crosslinking²⁻⁵ reactions, and change the polarity of the exposed area during the microlithographic process. Wet developing using organic solvent or basic solution can transfer the latent image to concrete patterns. But the Poly(4-hydroxystyrene) (PHS) resist used in KrF cannot be used as ArF photoresists owing to the low sensitivity and strong phenolic absorption at the 193 nm wavelength. The first ArF resist is reported by IBM Co., "Version 1", based on the MMA, MAA and TBMA copolymer⁴. A non-benzene structure meets the absorption requirement, but problems such as the low RIE resistance, processing stability, and developer compatibility arise many other inventions. Methacrylate^{5,6}, cycloolefin-maleic anhydride copolymers^{7,8,9,10} and vinyl ether-maleic anhydride copolymer¹¹ are synthesized, and some commercial products can be purchased from vendors.

ArF resists are mainly designed as the positive-tone single layer resist (SLR). The negative-tone resist, for its intrinsic swelling properties, does not easily delineate the sub-micron pattern. But when using PSM as tools to breakthrough the optical limitation, the negative-tone resist is preferred to eliminate the phase edge problem¹². For the 248 nm resist, Ito^{13,14} synthesized the PHS derivatives with pendant tertiary alcohol for using as negative-tone resist. A pinacol-pinacolone rearrangement or an intramolecular dehydration reaction (Scheme I) induce a reverse polarity transformation from a polar alcohol to a non-polar olefin. The negative-tone resist using the pinacol rearrangement was recently reported by Willson¹⁵. For the acid-catalyzed dehydration route with water released in PEB, we have developed the acrylate resist with 3-Hydroxy 3-methylbutyl methacrylate (HMMA) for using as a negative-tone ArF resist, and the kinetics of dehydration of the resist was proved suitably to be used as a resist¹⁶. However, the acrylate resist, though it has good quality control and high polymerization yield, is rarely resistant to oxide etching. We extend the polymer design as shown in Scheme II. The

cycloolefin resists are synthesized. The copolymerization of cycloolefin monomer (HMMBC) containing *tert*-alcohol group with maleic anhydride, or the homopolymerization of cycloolefin monomer following the attachment of the *tert*-alcohol group in the polymer side chain, were studied (Scheme III). The physical properties, RIE resistance, and the lithographic capabilities of the cycloolefin resists are described in the paper.



Scheme I. Polarity reversal mechanism in PHS system



Scheme II. The design concept of the negative-tone resists (a) PHS resist (b) acrylate resist (HMMA) (c) cycloolefin resist (HMMBC)

2. EXPERIMENTAL

2.1 MATERIALS

Cyclopentadiene (CPD) were prepared from dicyclopentadiene by cracking prior to use. 3-Methyl-1,4-butanediol, triethylamine, thionyl chloride, methacrylic acid, norbornene (NB), maleic anhydride (MA), 2,2'-azobisisobutyronitrile (AIBN), ethyl lactate, Pd sponge, nitrosonium tetrafluoroborate (NOBF_4), acetonitrile (MeCN) were purchased from Acros without further purification. The photoacid generator (PAG), triphenylsulfonium triflate, was purchased from Midori Kagaku Company. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled for the experiment. Isobornyl methacrylate (IBMA) was purchased from Aldrich and was vacuum distilled to remove the inhibitor.

2.2 MEASUREMENT INSTRUMENTS

^1H NMR spectra were analyzed on a Bruker DMX-500SB. FTIR spectra were obtained using a BIO-RAD FTS-40. UV-VIS spectra were performed on Hitachi U-3501. Thermal properties were assessed on Perkin-Elmer DSC-7 and TGA-7. Gel

permeation chromatography (GPC) was conducted on Showa Shodex RI-71 using THF as solvent. The lithographic performance of the resists was investigated using a Hitachi S-4000H SEM. Lambda Physik ArF excimer lasers was used as the exposure tool. RIE resistance was conducted using a Roth&RAU Unilab RIE. Film thickness was measured by Dektak 3030ST.

2.3 SYNTHESIS METHODS

3-hydroxy-3-methylbutyl 2-methyl-bicyclo[2.2.1]hept-5-ene-2-carboxylate (HMMBC)

Fresh cracked CPD (1 mol) was added drop-wise to methacrylic acid (1 mol). The reaction proceeded for 2 h and was refluxed for 3 hours. 2-methyl-bicyclo[2.2.1]hept-5-ene-2-carboxylic acid (MBC) was collected at 100 °C by vacuum distillation. Purification was carried out by recrystallization in petroleum ether. 2-methyl-bicyclo[2.2.1]hept-5-ene-2-carbonyl chloride, prepared from MBC and thionyl chloride, was dropped into 3-methyl-1,4-butanediol (1.1 mol), triethylamine (1.05 mol), and THF mixture. The HMMBC were separated by extraction using ether, and collected at 135 °C by vacuum distillation. FTIR (cm⁻¹): 3450 (O-H), 3020 (C-H), 2900 (C-H), 1712 (C=O), 1150 (C-O-C), 721 (C=C). ¹H NMR (δ, ppm): 0.88-0.89 [1H, bm, bridgehead], 1.10 [3H, s, -CH₃], 1.28 [6H, s, -C(OH)(CH₃)₂], 1.38-1.42 [2H, m, -CH₂-], 1.86 [2H, t, -C(OH)CH₂-], 2.14 [1H, br, OH], 2.38-2.46 [1H, m, bridgehead], 2.82-3.01 [2H, bm, -C=CCH-], 4.27 [2H, t, -O-CH₂CH₂-], 6.08-6.21 [2H, bm, olefinic].

Poly (2-methyl-bicyclo[2.2.1]hept-5-ene-2-carboxylic) (Poly(MBC))

The Pd(II) catalyst, [Pd(MeCN)₄](BF₄)₂ was synthesized according to the method by Sen¹⁷. The [Pd(MeCN)₄](BF₄)₂ was made from Pd sponge and NOBF₄ in the MeCN solution. Poly(MBC) was prepared by dissolving MBC (1 mol) and [Pd(MeCN)₄](BF₄)₂ (0.004 mol) in ethyl lactate. The mixture was stirred at room temperature for 72 hours, and the Poly(MBC) was separated as light yellow powder by precipitation in petroleum ether. Yield 21%. FTIR (cm⁻¹): 3440 (O-H), 2960 and 2880 (C-H), 1710 (C=O), 1190 (C-O-C). ¹H NMR (DMSO-*d*₆) δ (ppm): 1.0-3.0 [br, bridgehead], 11.9 [br, COOH]. EA: C, 71.65; H, 7.71 (*calc.* C, 71.07; H, 7.89). Thermal decomposition temperature (Td): 270 °C.

Poly (3-hydroxy-3-methylbutyl 2-methyl-bicyclo[2.2.1]hept-5-ene-2-carboxylate-alt-maleic anhydride) copolymer (Poly(HMMBC/MA))

HMMBC/MA alternative copolymers were prepared by adding an equal amount monomer in dried THF, with AIBN as initiator (Table I). The mixture were degassed three times, and the polymerization were performed at 65 °C under a nitrogen atmosphere over 24 hours. After the reaction, the polymers were precipitated twice in petroleum ether and then dried in a vacuum. FTIR (cm⁻¹): 3460 (OH), 2970 (C-H), 1860 and 1780 (C=O, cyclic anhydride), 1730 (C=O, ester), 1160 (C-O-C), 910 (C-O-C, cyclic anhydride). ¹H NMR (DMSO-*d*₆) δ (ppm) 1.0-3.0 [br, bridgehead and main chain]. EA: C, 63.50; H, 6.62 (*calc.* C, 64.31; H, 7.14). Td: 115 °C.

Poly (3-hydroxy-3-methylbutyl 2-methyl-bicyclo[2.2.1]hept-5-ene-2-carboxylate-alt-maleic anhydride-co-isobornyl methacrylate) terpolymer (Poly(HMMBC/MA/IBMA))

Poly(HMMBC/MA/IBMA) was synthesized by adding different amount monomer in dried THF, with AIBN as initiator (TABLE I). The mixture were degassed three times, and the polymerization were performed at 65 °C under a nitrogen atmosphere over 24 hours. After the reaction, the polymers were precipitated twice in petroleum ether and then dried in a vacuum. FTIR (cm⁻¹): 3460 (OH), 2970 (C-H), 1860 and 1780 (C=O, cyclic anhydride), 1730 (C=O, ester), 1160 (C-O-C), 910 (C-O-C, cyclic anhydride).

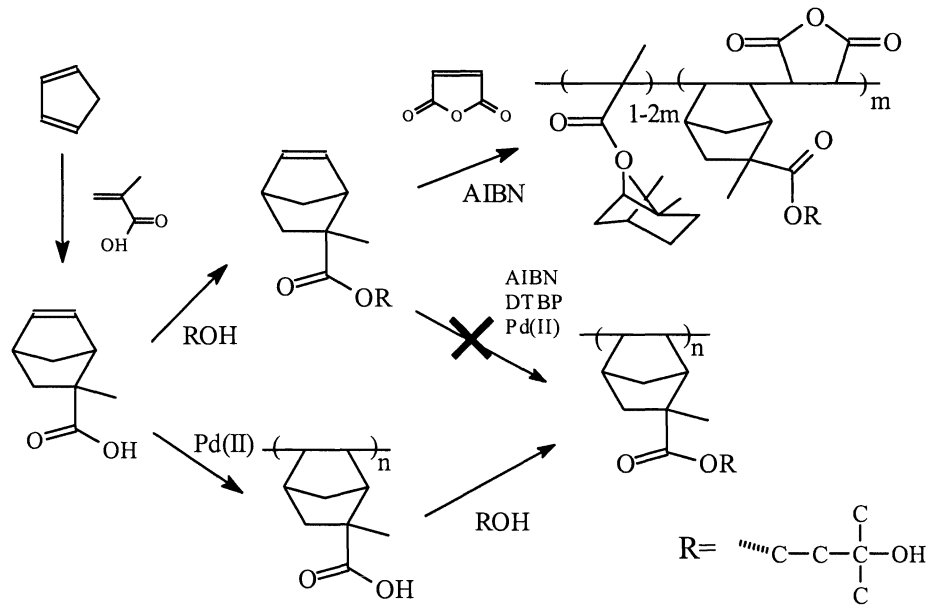
Poly (3-hydroxy-3-methylbutyl 2-methyl-bicyclo[2.2.1]hept-5-ene-2-carboxylate) (Poly(HMMBC))

The Poly(HMMBC) is synthesized by the esterification of Poly(MBC) with 3-methyl-1,4-butanediol using the method similar to the synthesis of HMMBC. FTIR (cm⁻¹): 3440 (O-H), 2960 (C-H), 2880 (C-H), 1720 (C=O), 1160 (C-O-C). ¹H NMR (DMSO-*d*₆) δ (ppm): 1.0-3.0 [br, bridgehead, main chain]. EA: C, 69.88; H, 9.02 (*calc.* C, 70.61; H, 9.24). Td: 190 °C.

2.4 LITHOGRAPHIC EVALUATION OF THE RESISTS

Polymers and 2 wt % PAG were dissolved in ethyl L-lactate and filtered through 0.2 μm Teflon filter. Wafers were cut to the size about 15mm*15mm. Resists were spin-coated on the wafers and then pre-baked at 100 °C for 1 minute. Thickness was controlled by adjusting the resist concentration (about 1.8 g resist / 10 g ethyl L-lactate for 1 μm thickness). Samples

were exposed through a 1 μm line and space (L/S) contact mask, and were then subjected to a post exposure baking (PEB) at 120 $^{\circ}\text{C}$. Finally, the resists were developed on IPA solution and then rinsed with water.



Scheme III. The design of cycloolefin negative-tone resist

3. RESULTS AND DISCUSSION

3.1 PROPERTIES OF POLYMERS

The copolymerization of HMMBC with MA was conducted because the MA monomer is believed to proceed an alternative copolymerization with the alicyclic monomer⁹. The copolymer was synthesized and characterized as described in the previous experimental section. However, when the copolymer (Resist A) was tested for its thermal calorimetry, an exothermic reaction at about 110 $^{\circ}\text{C}$ is observed in Figure 1(a). This copolymer was excluded as a resist because of its thermally unstable during the PEB processing temperature. On the contrary, the other copolymers were stable through the processing temperature. To understand the thermal behavior of the copolymers, the copolymer film was heated at a constant temperature, the IR analysis was conducted at various times. The results are depicted as spectrum in Figure 2. The disappearance of the OH group around 3450 cm^{-1} and the tertiary alcohol around 1170 cm^{-1} , and some variations of C=O group around 1710 cm^{-1} are observed at a longer time. Besides, the disappearance of the CH_3 group in $^1\text{H-NMR}$ is also found at about 1.28 ppm. Comparing with the thermal calorimetry of homopolymer Poly(HMMBC) in Figure 2(d), we can infer that the acid-labile *tert*-alcohol group may be dehydrated by acidic anhydride at elevated temperature. The Poly(HMMBC/MA) film was degraded during PEB process and therefore the Poly(HMMBC/MA) was unsuitable for pattern transferring.

The alicyclic moiety, such as isobornyl or adamantyl group, is usually used to enhance the thermal stability and anti-etching resistance of the acrylate resist^{18,19}. Based on this idea, Poly(HMMBC/MA/IBMA) was synthesized. The physical properties of the resists are listed in Table I. With the introduction of IBMA monomer into the polymer, the thermal stability of the copolymer is greatly increased to well above PEB temperature as shown in Figure 2(b) and 2(c). The lower T_g of the resists comparing with the other NB/MA resists in the published literature is attributed to the long carbon branch in the resist, and this low T_g character may induce the thermal instability of the Poly(HMMBC/MA) resist. The T_g s of the resists increase with an increase of the IBMA content in the composition. However, due to the hydrophobic property of IBMA monomer, the copolymer containing more than 30% IBMA in composition loses its adhesion property on the wafer and thus can not be used as resists.

Homopolymerization of HMMBC by using free radical initiator or Pd catalyst was not successful in the experiments. Resist *D* can only be obtained by synthesizing the Poly(MBC) and then grafting the 3-methyl-1,4-butanediol to the homopolymer.

Figure 3 illustrates the UV absorbance of the resists. The lower absorbance of the resist at 193 nm is required for using as a 193 nm photoresist. The high absorbance of Resist *A* is probably due to the degradation of the resist during the baking process. Resist *B, C* and *D* have low absorbance at 193 nm and are applicable to be used as resists.

Table 1. The physical properties of the resists

Feed ratio	Mw	PDI	Abs ¹	T _g (°C)	RIE ²
A HMMBC/MA=50/50	2360	1.59	0.993	----	----
B HMMBC/MA/IBMA=45/45/10	3190	1.72	0.601	87.6	0.45
C HMMBC/MA/IBMA=40/40/20	2820	1.58	0.644	92.5	0.42
D Poly(HMMBC)	27700	1.50	0.347	----	0.38

¹ Absorbance of 1 μm film at 193 nm.

² RIE etch rate of the resist relative to the PMMA under oxide etch condition. (CHF₃ 25 sccm, 0.31 mTorr).

3.2 LITHOGRAPHIC PERFORMANCE

As the film of the Resists *B~D* was exposed with different doses, the remaining film thickness after developing in IPA was displayed as the contrast curve shown in Figure 4. The sensitivity and the contrast of the resists have similar tendency to that of the acrylate resist in our previous report¹⁶. Resist *D* was found to be more sensitive to the exposure light than Resists *B* and *C*. This high sensitivity of Resist *D* can be attributed to the high content of acid-labile group in the resist. Therefore, less amount of acid is required to catalyze the crosslinking reaction of the Resist *D*.

The microphotographs of lithographic performances by Resists *B* and *C* are shown in Figure 5. It was observed in both resists that the resin remained in the space area, and the rounding shape and softening-like of the exposed lines. However, the pattern by Resist *C* is little better than that by Resist *B*, and may be attributed to its higher T_g, which contributing to the higher dimensional stability of the exposed pattern. The reducing of PEB temperature had been tried to avoid the melting of the resist at the PEB temperature, but it still did not result in better patterns. The reason for this is the chemical reaction of the PAG with the *tert*-alcohol group is very slow at this PEB temperature in our previous report¹⁶. Therefore, the resist with low T_g limits its processing temperature range of PEB. However, the further elevation of T_g with introducing higher IBMA content is not always useful because of the poor film quality resulted from the high IBMA content copolymer. The increasing stiffness of Poly(HMMBC/MA) resist by incorporation of other thermal stable monomer is prospective for a better lithographic performance.

Poly(HMMBC) can only be obtained by the modification of Poly(MBC) for our investigation as shown in Scheme III. However, the property of the resist from polar to nonpolar characteristics results in the decrease of adhesion strength of the resist to the wafer, and some investigation indicated that the Pd(II) catalyzed resist has very low adhesion²⁰. The IPA developer of low surface energy will penetrate into the interface of the resist and wafer, and will result in the distorted pattern as shown in Figure 6(d). The developer with various IPA concentrations was tested and the resulting lithographic patterns are shown in Figure 6. Using a developer with IPA/water ratio of 1/1, the unexposed area was found swelling and not dissolved away as shown in Figure 6(a). As the increase of IPA concentration in developer, the interface between the exposed and unexposed area is clearly observed. Higher IPA concentration in developer can enhance the solubility of the unexposed resist. However, the adhesion of exposed resist to the wafer may decrease during the developing process. A developer with IPA/water ratio of 8/2 is demonstrated to the balance between the solubility and adhesion of the resist from Figure 6.

Based on the developer with IPA/water ratio of 8/2, the dosage effect on the pattern of resist *D* was investigated. As shown in Figure 7, the more dosage of deep UV light was applied, the width of the exposed line increased from the central part of the line to the edge. Thus, Resist *D* has better lithographic performance than Resists *B* and *C*. A dosage of 30 mJ/cm² for Resist *D* is suitable for effectively transferring the image.

3.3 DRY-ETCHING RESISTANCE

According to the Ohsishi's²¹ study, the etch rate can be expressed as:

$$\text{Rate} = k \left(\frac{N_T}{N_C - N_O} \right)$$

where N_T , N_C and N_O represents the number of total atom, carbon atom, and oxygen atom respectively. The k value was measured to be 0.29 for noncyclic component and 0.42 for cyclic component²². The RIE etching resistance of the resists relative to that of PMMA resin was investigated under CHF_3 atmosphere for silicon oxide etching condition. The resultant etching rates of the resists are shown in Figure 8. It is apparent that the cycloolefin resists (Resists *B*, *C* and *D*) are more resistant to RIE than the acrylate resists (Resists *E* and *F*). Especially, the Resist *D* of all alicyclic structure shows the lowest etching rate among the resists.

4. CONCLUSION

The dehydration and post-crosslinking reactions of the *tert*-alcohol group in the cycloolefin negative-tone resists are proved to work well as the reactions in the acrylate resist. The polarity change after PEB processing, from polar to non-polar property, makes the exposed resist insoluble in isopropyl alcohol. The alternative polymer, Poly(HMMBC/MA) resist, is unstable at elevated temperature because the acidic maleic anhydride would result in the dehydration and other side reaction at the PEB temperature. The incorporation of isobornyl methacrylate monomer in the resist is found to increase the thermal stability of the resist. The process for the resist post-exposure-baking at 120 °C for 2 minutes and then developing in isopropyl alcohol for 40 seconds, is found suitably to define a 1 μm L/S pattern. For the homopolymer resist, Poly(HMMBC), developer with IPA/water ratio of 4/1 and a dosage of 30 mJ/cm² is found to have optimistic lithographic performance. The RIE resistance of the polycycloolefin resists are proved to be superior to that of the acrylate resist, and Poly(HMMBC) has the lowest etching rate under CHF_3 atmosphere.

5. ACKNOWLEDGMENT

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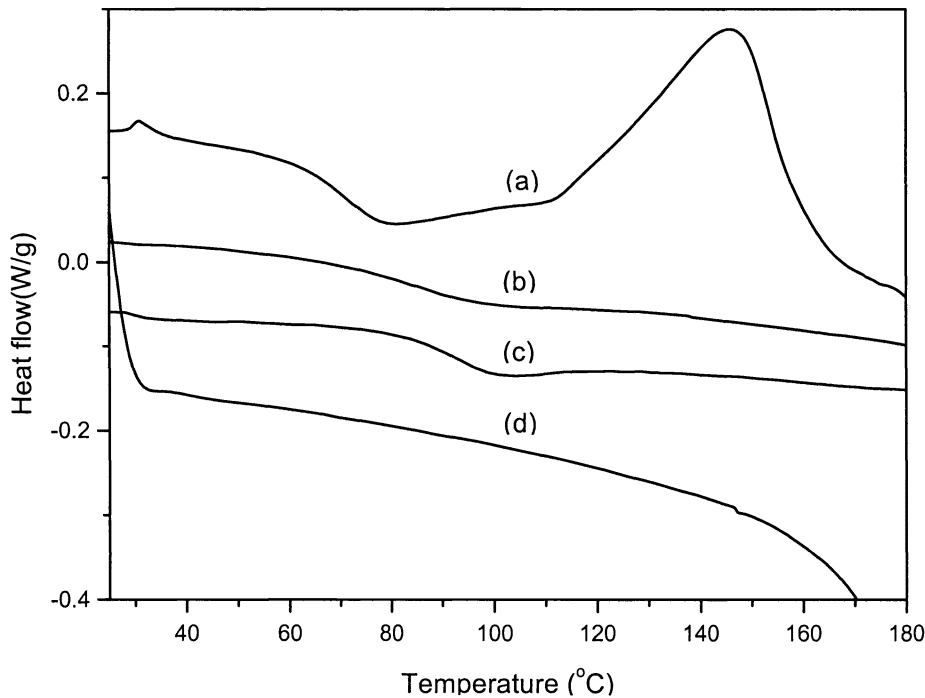


Figure 1. The DSC curves of (a) Resist A (b) Resist B (c) Resist C (d) Resist D at heating rate: 10 °C/min.

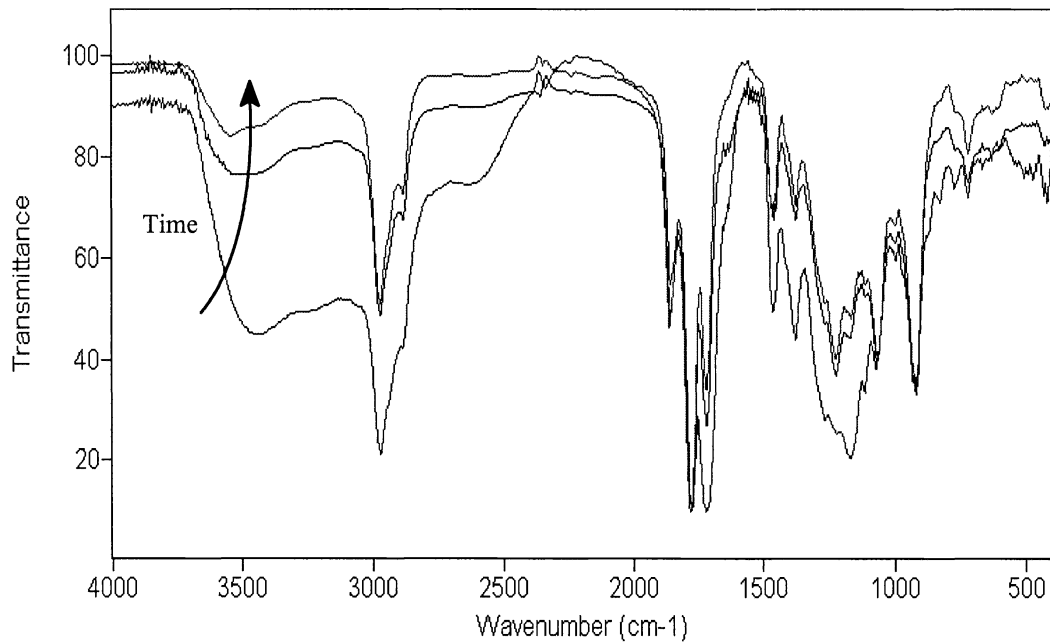


Figure 2. Time dependence of FT-IR spectrum for Resist A baked at 120 °C.

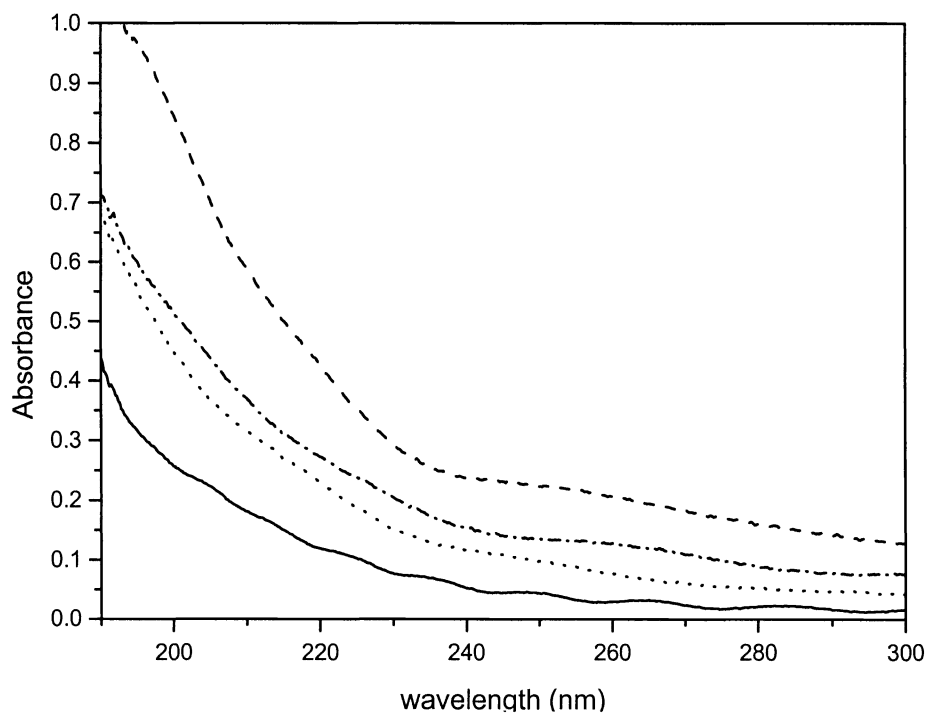


Figure 3. UV absorption by 1 μm film of resists --- Resist A, Resist B, - - - - Resist C, ——— Resist D.

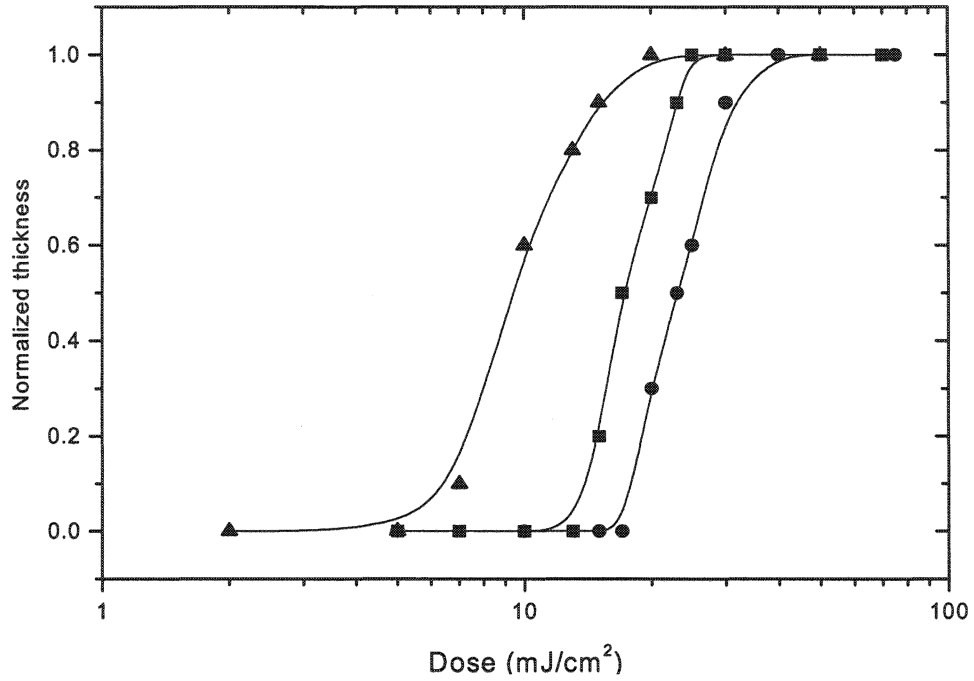
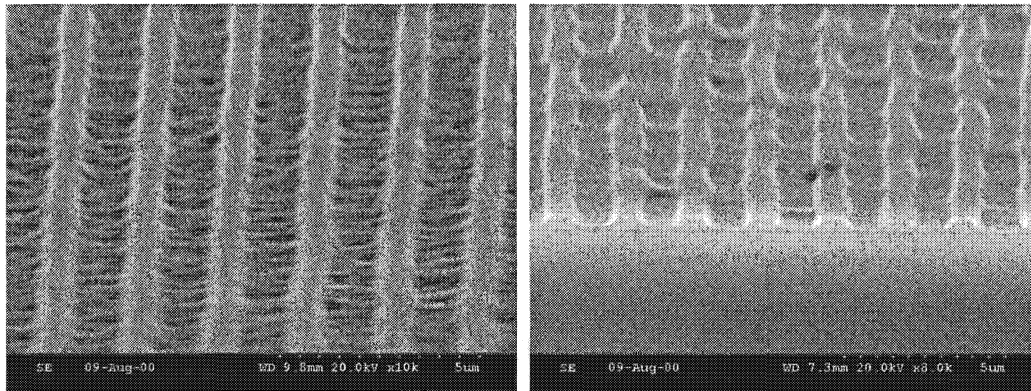
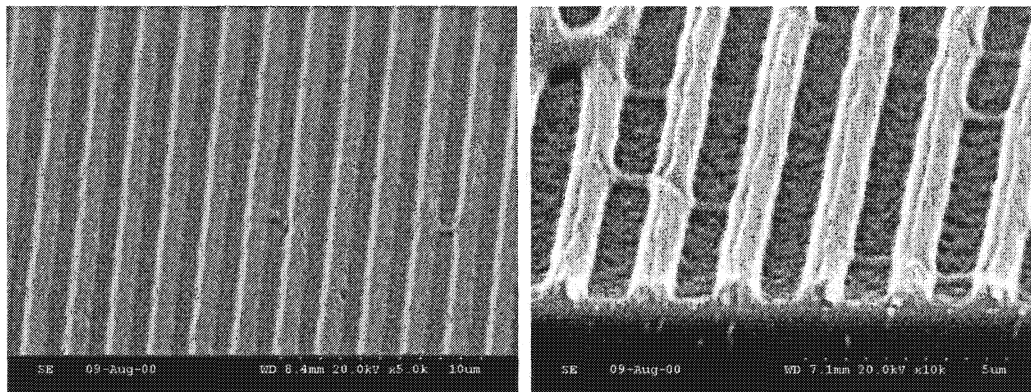


Figure 4. Contrast curves of resists : ■ Resist B, ● Resist C, ▲ Resist D.



(a)



(b)

Figure 5. Lithographic performance of (a) Resist B, (b) Resist C. Conditions: Dose 50 mJ/cm², PEB 120 °C for 2 minutes, developed in IPA for 30 seconds and rinsed in water for 10 seconds.

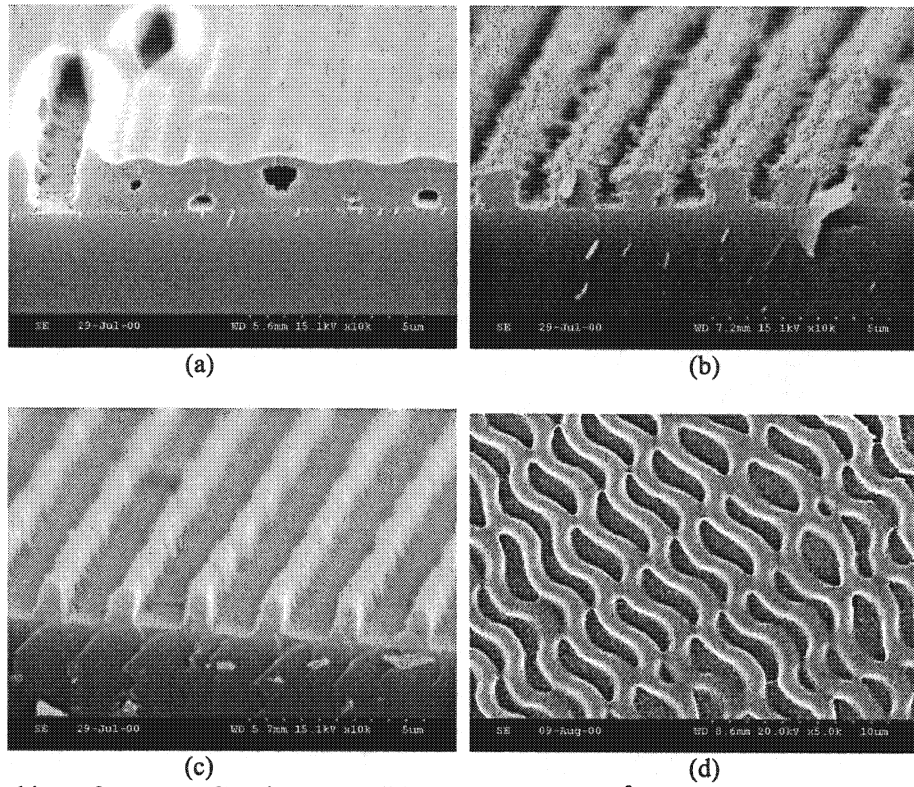


Figure 6. Lithographic performance of Resist *D*. Conditions: Dose 25 mJ/cm², developed with water/IPA solution at a ratio of (a) 5/5 (b) 7/3 (c) 8/2 (d) 10/0, for 30 seconds and rinsed with water for 10 seconds.

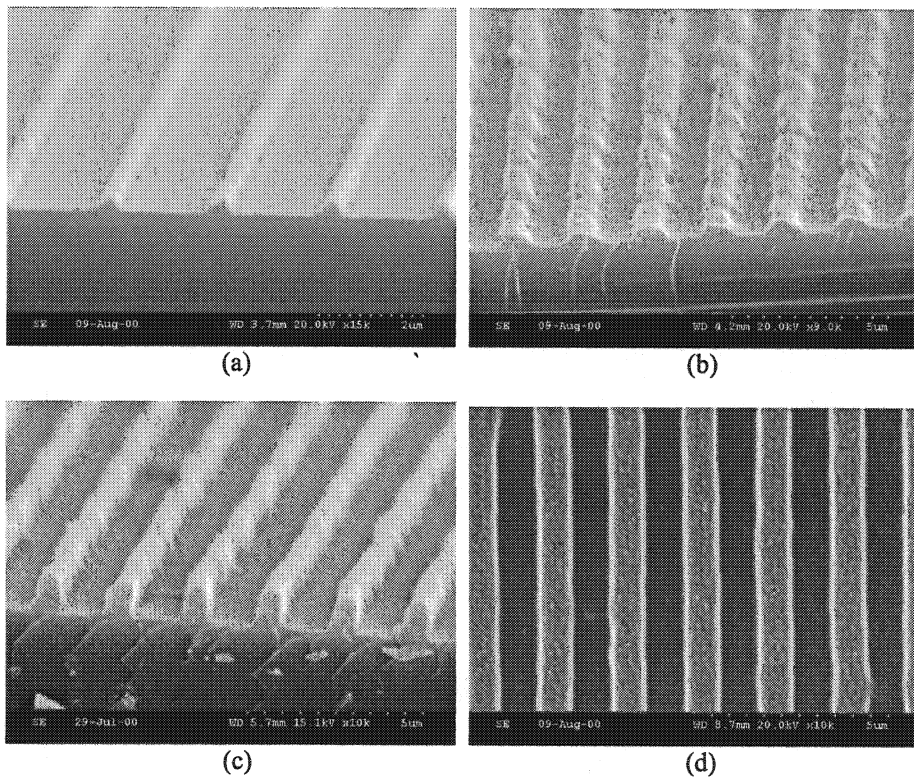


Figure 7. Lithographic performance of Resist *D*. Conditions: Dose (a) 15 mJ/cm² (b) 20 mJ/cm² (c) 25 mJ/cm² (d) 30 mJ/cm², developed in IPA for 30 seconds and rinsed with water for 10 seconds.

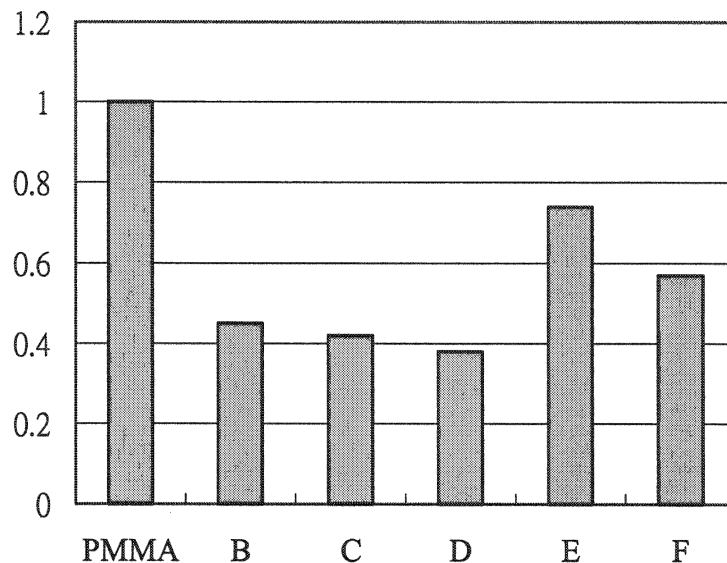


Figure 8. The reactive ion etch rate of resists. (E: Poly (HMMA) and F: Poly(HMMA_{0.5}/IBMA_{0.5}))

6. REFERENCE

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