Tetrahydropyranyl protected polyhydroxystyrene for a chemically amplified deep u.v. resist

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(Received 13 July 1990; revised 25 February 1991; accepted 8 March 1991)

Tetrahydropyranyl (THP) protected poly(*p*-hydroxystyrene) (PHS) was synthesized and its acid-catalysed thermal deprotection utilized in the design of an alkali developable, positive photoresist system incorporating chemical amplification. The solubility of THP-PHS films mixed with the appropriate onium salt photo acid generators in alkaline developers increases upon exposure to deep u.v. radiation and subsequent heating. A resist composed of THP-PHS and bis(tert-butylphenyl)iodonium triflate resolves 0.35 μm line-and-space patterns using a KrF excimer laser (248 nm) stepper (20 mJ cm^{-2}).

(Keywords: tetrahydropyranyl protected polyhydroxystyrene; onium salt; acid-catalysed deprotection; chemical amplification; deep u.v. resist)

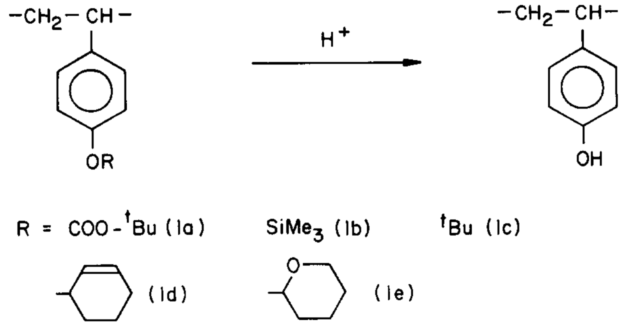
INTRODUCTION

The design requirements of successive generation of very large scale integrated (VLSI) circuits have led to reductions in the lithographic critical dimensions. Among several competing strategies for increasing circuit density is deep u.v. lithography[1], which utilizes shorter wavelength light from an excimer laser (KrF, 248 nm) than g-line (436 nm) or i-line (365 nm) radiation from a mercury lamp in conventional photolithography. The light intensity at the wafer plane of the excimer laser system is not high because of the spectral narrowing utilized to avoid colour aberrations. Therefore, a high sensitivity and high resolution resist system is necessary for the successful implementation of deep u.v. excimer laser lithography.

Recently, there has been increased interest in 'chemical amplification' resist systems for deep u.v. lithography[2] since the pioneering work by Ito and Willson[3,4] and Frechet *et al.*[5]. In the chemical amplification resist, a photosensitive acid generator is decomposed to produce acid during the exposure. The following acid-catalysed thermal reaction renders the exposed parts of the resist soluble in the case of positive resists or insoluble in negative resists.

The protection of the phenolic hydroxyl group of poly(*p*-hydroxystyrene) (PHS) [poly(*p*-vinylphenol)] with tert-butoxycarbonyl (1a)[3,5], trimethylsilyl (1b)[6,7], tert-butyl (1c)[8,9] and cyclohexenyl (1d)[10] has been proven to be useful for imaging in a photoacid-catalysed process to yield a free phenolic polymer with modified polarity and solubility (*Scheme 1*).

The tetrahydropyranyl (THP) protective group was reported to be effective in a similar acid-catalysed imaging in 1973[11]. In this paper we report on an application of a chemical amplification resist utilizing PHS protected by the THP group (THP-PHS) (1e in *Scheme 1*) to microlithography[12].



Scheme 1 Acid-catalysed deprotection of PHS protected with various protective groups

EXPERIMENTAL

Materials

THP-PHS was synthesized according to the reaction sequence shown in *Scheme 2*. The acid-catalysed addition reaction of *p*-hydroxybenzaldehyde with 3,4-dihydropyran yielded *p*-tetrahydropyranyl-oxybenzaldehyde which was then converted to *p*-tetrahydropyranyl-oxystyrene by the Wittig reaction. This monomer was polymerized to THP-PHS by a free radical polymerization using AIBN as an initiator. Details of the polymer synthesis were reported in a previous paper[13].

Onium salts were synthesized using established methods[14]. A halide photoacid generator, 1,3,5-tris(2,3-dibromopropyl)-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)trione (TDB) was obtained from Hitachi Chemical Co.

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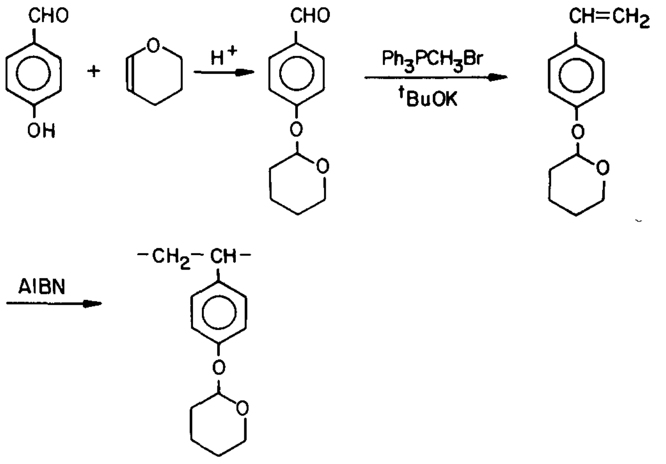


Scheme 2 Preparation of THP protected PHS

Resist composition and processing

Resist formulations were prepared by dissolving THP-PHS polymer along with the photoacid generators (onium salts or TDB) in xylene or ethylcellosolve acetate. Resist films spin-coated from the above solutions on appropriate substrates were exposed to 250 nm radiation from a Xe-Hg lamp through an interference filter to generate an acid. After post-exposure-baking (PEB), the resist films were developed in an aqueous base developer (NMD-3 : 5.0% tetramethylammonium hydroxide obtained from Tokyo Ohka Kogyo Co.) or in a mixture of NMD-3 (2.38%) with n-propyl alcohol. After dipping development, the resist films were rinsed with water. Deep u.v. lithographic evaluation was performed using a Canon KrF excimer laser stepper operating at 248 nm with a numerical aperture of 0.37.

Characterization

^{13}C n.m.r. spectra were taken with a Hitachi R1900 spectrometer. U.v. absorption spectra were measured with a Hitachi U-3410 spectrophotometer. I.r. reflection spectra were recorded on a Hitachi 260-10 i.r. spectrometer using thin films spin-coated on aluminium-deposited glass substrates. The polystyrene equivalent molecular weight and molecular weight distribution were determined by g.p.c. using a Hitachi 635 liquid chromatography system. The solvent was tetrahydrofuran. THP-PHS with $M_n = 20000$ and $M_w/M_n = 1.86$ was used for lithographic applications.

Exposure characteristic curves were obtained from the graph in which film thickness or normalized film thickness after development was plotted as a function of the logarithm of the exposure dose. The thickness of the resist film remaining after development was measured with an Alpha-step 200 (Tencor Instruments).

RESULTS AND DISCUSSION

Polymer characterization

The ^{13}C n.m.r. and i.r. spectra of THP-PHS, synthesized according to *Scheme 2*, are shown in *Figures 1* and *2*, respectively. The ^{13}C n.m.r. spectrum exhibits 11 distinctive peaks as anticipated from the structure of

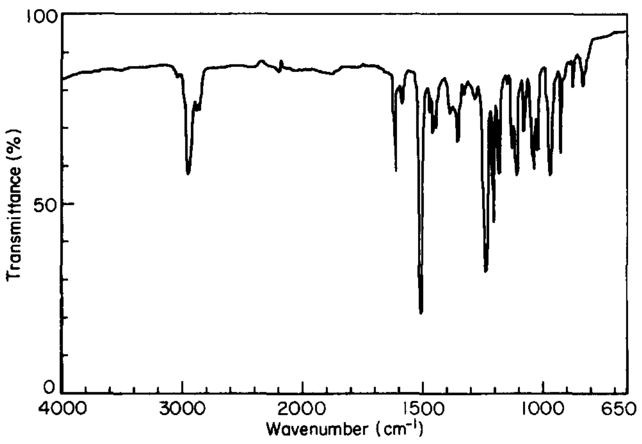


Figure 2 I.r. reflection spectrum of a THP-PHS film

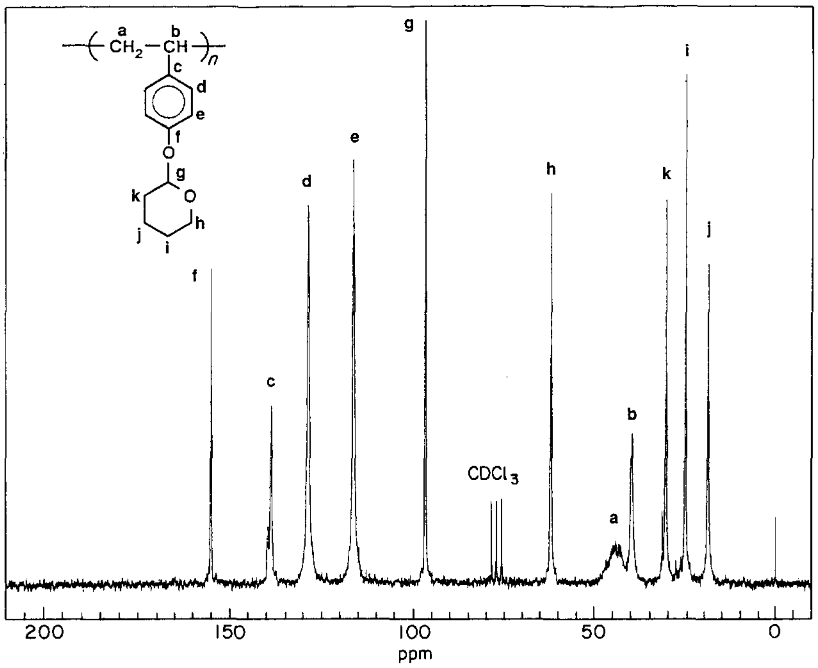


Figure 1 ^1H decoupled ^{13}C n.m.r. spectrum of THP-PHS in $CDCl_3$ solution

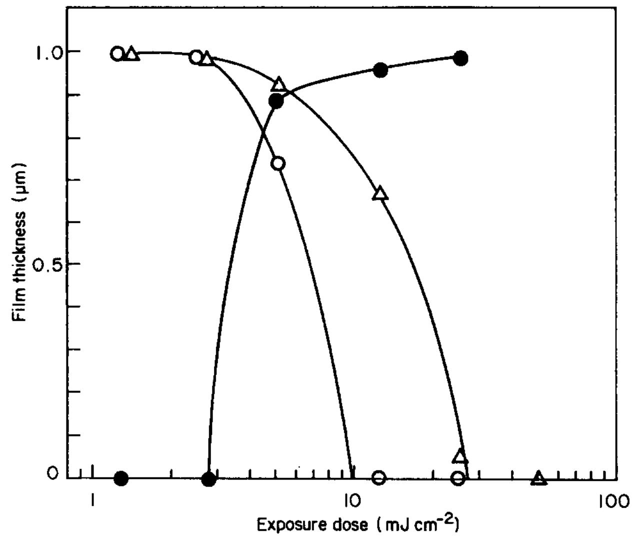
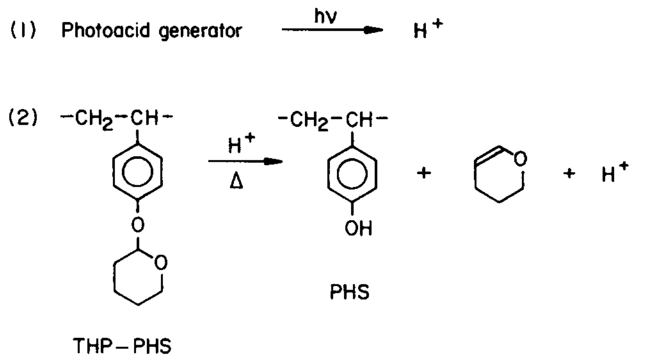


Figure 3 Exposure characteristic curves for the THP-PHS/TBIT resist (100/3 w/w) in different developers: (●) xylene, 10 s; (○) NMD-3 (2.38%)/n-PrOH = 7/1, 60 s; (△) NMD-3 (5%), 90 s. Irradiation at 250 nm, PEB at 100°C for 10 min



Scheme 3 Acid generation and deprotection in the resist composed of THP-PHS and photoacid generator

THP-PHS and the assignment is given in *Figure 1*. The i.r. spectra of the synthesized polymer showed no free hydroxyl group in the range from 3000 to 4000 cm^{-1}. These facts indicate that the THP group completely protects PHS in the polymer prepared using the reaction sequence in *Scheme 2*.

Resist characterization

Exposure characteristic curves for a resist formulated from THP-PHS and a photoacid generator bis(tert-butylphenyl)iodonium triflate (TBIT) are shown in *Figure 3*. The THP-PHS/onium salt TBIT weight ratio in the resist is 100/3. After exposure to the 250 nm radiation with varied doses, the resist film was baked at 100°C for 10 min.

The reaction sequence which is expected in our formulated resist can be summarized in *Scheme 3*. In the first step, acid is generated by the photolysis of a photoacid generator. During the subsequent heating (PEB) process, the acid-catalysed thermal deprotection of the acetal group produces a phenolic polymer (PHS) and dihydropyran. At the same time a proton is liberated ensuring that the process is catalytic and thus chemical amplification is achieved.

As shown in *Figure 3*, the films can be developed as either positive or negative resist simply by choosing the appropriate developer. The phenolic photoproduct PHS in the exposed area (*Scheme 3*) is soluble in polar solvents such as alcohol or aqueous base because of the acidity of the phenolic functionality, whereas the THP-PHS in the unexposed area is completely insoluble in these solvents. Consequently, development in polar solvents generates a positive image of the mask. Conversely, THP-PHS is soluble in non-polar solvents such as xylene or chlorobenzene, in which the phenolic photoproduct is completely insoluble. Therefore, development in these non-polar solvents results in a negative resist response (*Figure 3*).

The THP-PHS/TBIT resist films (100/3 w/w) before exposure and after exposure and PEB were compared in i.r. and u.v. spectra (*Figures 4* and *5*). As shown in *Figure 4*, a broad i.r. absorption at around 3350 cm^{-1}

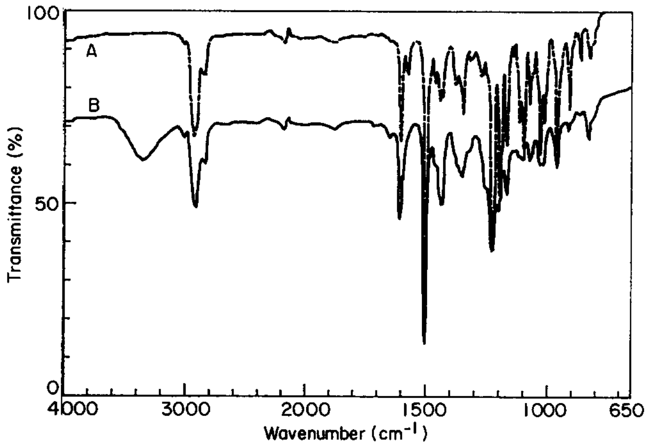


Figure 4 I.r. reflection spectra of the THP-PHS/TBIT resist (100/3 w/w) films (A) before and (B) after exposure (7.5 mJ cm^{-2} at 250 nm) and PEB at 100°C for 10 min

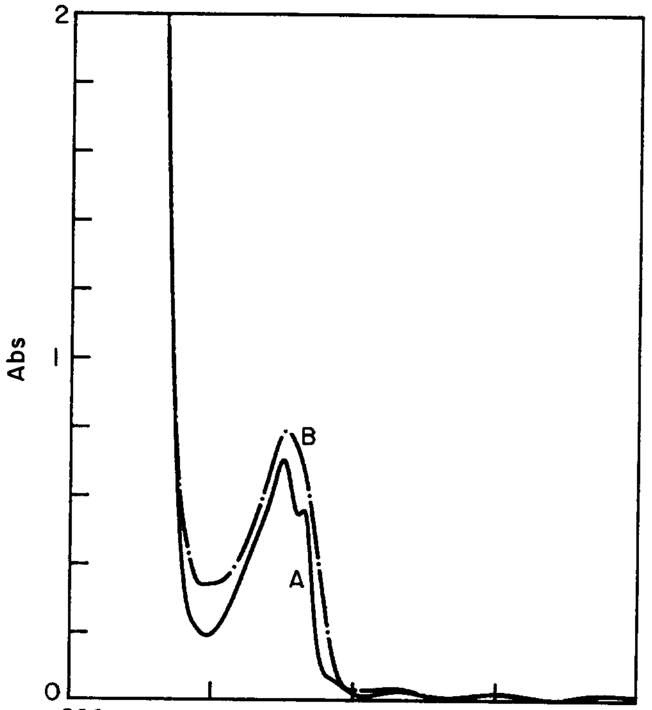


Figure 5 U.v. absorption spectra of a 1 μm thick THP-PHS/TBIT resist (100/3 w/w) film (A) before and (B) after exposure (7.5 mJ cm^{-2} at 250 nm) and PEB at 100°C for 10 min

appears after the resist film was exposed to 7.5 mJ cm^{-2} of 250 nm radiation and post-exposure-baked at 100°C for 10 min, indicating the formation of the hydroxyl functionality. This supports the mechanism depicted in *Scheme 3*. The increase in u.v. absorption after exposure and PEB shown in *Figure 5* is consistent with the fact that the phenolic resin PHS is more absorptive than the THP-PHS precursor.

Photoacid generators

The photoacid generators evaluated in conjunction with THP-PHS are presented in *Table 1* along with their u.v. absorption. Since the photoacid generators except TBIT are not readily soluble in xylene, a good coating solvent for THP-PHS, ethylcellosolve acetate was used as a coating solvent in a series of experiments in which these photoacid generators were evaluated. Exposure characteristic curves for resist films composed of THP-PHS and a photoacid generator (100/3 w/w) are given in *Figure 6*. Each resist film was post-exposure-baked at 100°C for 10 min and then developed in a mixture of NMD-3 (2.38%)/n-propyl alcohol (7/1 v/v) for 1 min. As shown in *Figure 6*, all four onium salts investigated act as good acid generators, while the bromide photoacid generator TDB was found to be ineffective for positive imaging of THP-PHS.

Table 1 Photoacid generators and absorbance at 248 nm of resist films composed of THP-PHS/photoacid generator (100/3 w/w)

	Absorbance at 248 nm[b]		
Photoacid generator[a]	Before exposure	After exposure[c]	After PEB[d]
Diphenyliodonium triflate	0.19(65%)	0.20(64%)	0.32(48%)
Diphenyliodonium hexafluorophosphate	0.24(58%)	0.23(59%)	0.45(36%)
TBIT	0.25(56%)	0.24(56%)	0.43(37%)
Triphenylsulphonium triflate	0.30(51%)	0.31(49%)	0.42(38%)
TBD	0.14(73%)	0.14(73%)	0.13(75%)

[a] Chemical structures of the photoacid generators are given in *Figure 6*

[b] Film thickness: 1 μm. Transmittance in parentheses

[c] Exposure: 7.5 mJ cm^{-2} at 250 nm

[d] PEB at 100°C for 10 min

The u.v. absorbance at 248 nm of these resist films with 1 μm film thickness is summarized in *Table 1*. The combined absorbance of THP-PHS and the photoacid generator at 248 nm is between 0.14 and 0.31 before and after exposure depending on the choice of the photoacid generator. The important feature of this resist system is this low absorbance at the irradiation wavelength before and during exposure, because high absorbance would deteriorate the pattern profiles of the developed resist[2].

When onium salts are employed as the photoacid generator, the absorption at 248 nm increases after PEB as can be seen in *Table 1* and *Figure 5*, indicating the formation of highly absorptive PHS. On the other hand, the absorption at 248 nm after PEB decreases in the case of the bromide photoacid generator TDB, suggesting the failure of the PHS formation, which is consistent with its exposure characteristic curve given in *Figure 6*.

Since differences in both the sensitivity (*Figure 6*) and the u.v. absorbance (*Table 1*) of the THP-PHS/onium salt resist were small among the four onium salts examined, TBIT, which is quite soluble in xylene, was chosen as the photoacid generator. The performance of the THP-PHS/TBIT resist is evaluated in detail and described below.

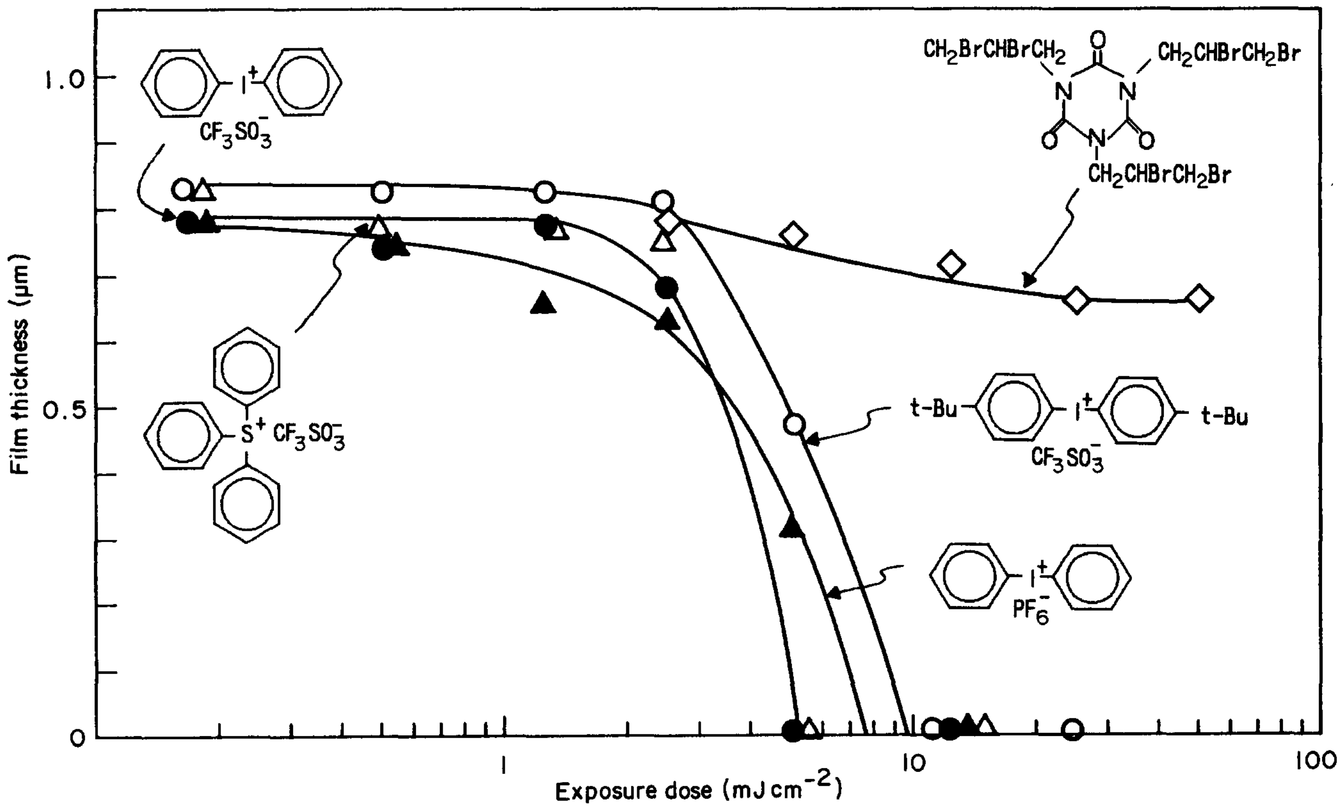


Figure 6 Exposure characteristic curves for resists with different photoacid generators. THP-PHS/photoacid generator = 100/3 (w/w)

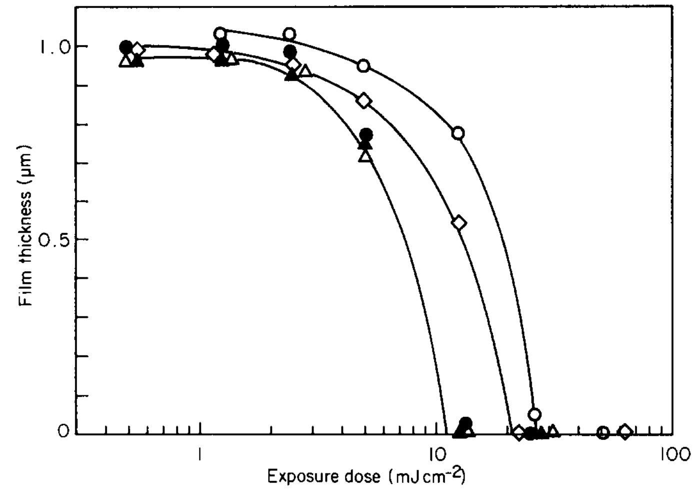


Figure 7 Effect of concentration of photoacid generator TBIT on sensitivity of THP-PHS/TBIT resists (100/x w/w): (◇) 0.5; (▲) 1; (△) 3; (●) 5; (○) 10 wt%

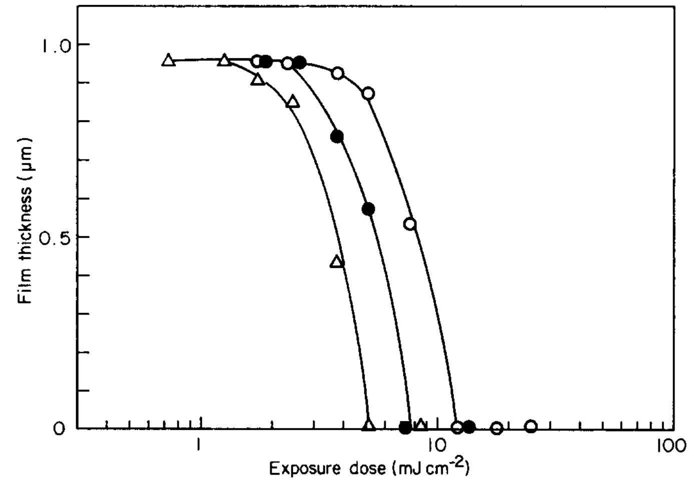


Figure 8 Effect of PEB temperature on the sensitivity of the THP-PHS/TBIT resist (100/3 w/w): (○) 80; (●) 100; (△) 120°C. PEB time: 10 min

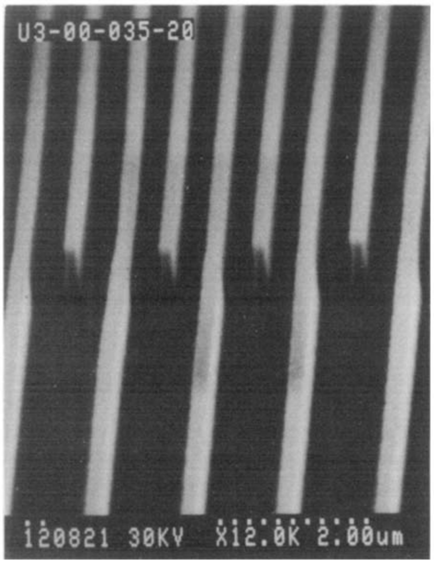


Figure 9 Scanning electron micrograph of a 0.35 μm line-and-space pattern produced with a Canon KrF excimer laser (248 nm) stepper in a resist composed of THP-PHS and TBIT. Exposure dose: 20 mJ cm^{-2}; PEB: 100°C for 10 min; film thickness: 1.0 μm

Resist evaluation

Sensitivity dependence on concentration of onium salt TBIT. The resist sensitivity was measured with varying TBIT concentration using THP-PHS/TBIT = 100/x (w/w, $x = 0.5$–10). As shown in *Figure 7*, the sensitivity increases with increasing TBIT concentration for $x < 1$, saturates for $x > 1$, and then decreases for $x > 5$.

The increase in onium salt concentration leads to the increase in both the u.v. absorbance at the exposure wavelength and the dissolution inhibition. It is considered that the sensitivity decrease in the higher TBIT concentration ($x = 10$) is partly due to the decrease in the amount of radiation at the resist–substrate interface because of the strong absorption and is partly due to the increasing inhibition effect of the onium salt on alkaline development of the exposed areas. The optimum TBIT concentration was chosen to be 3 wt% because of its high sensitivity.

Effect of PEB on sensitivity. Exposure characteristic curves for the THP/TBIT (100/3 w/w) resist with PEB temperatures varied from 80 to 120°C are given in *Figure 8*. The sensitivity increases with a rise in PEB temperature. The rate increase in the thermal deprotection and the increase in the mobility of the photogenerated acid can be assumed to explain this sensitivity increase.

Lithographic evaluation

Patterning of the THP-PHS (100/3 w/w) resist was carried out with a Canon KrF excimer laser stepper (numerical aperture 0.37). As shown in *Figure 9*, 0.35 μm line-and-space patterns were resolved for a resist film with a thickness of 1 μm. The resist was exposed with a dose of 20 mJ cm^{-2}, post-exposure-baked at 100°C for 10 min and then developed in a mixture of NMD-3 (2.38%) and n-propyl alcohol (7/1 v/v) for 1 min. This result demonstrates the potential for high resolution capability with this resist system.

CONCLUSIONS

A chemical amplification resist system composed of THP protected PHS and a photoacid generator was investigated for deep u.v. lithography. It was found that the thermal deprotection reaction of THP-PHS in the presence of the acid generated by deep u.v. irradiation produces a phenolic polymer PHS that is developable in alkaline solutions. Among the photoacid generators evaluated, onium salts acts as good acid generators for positive imaging of THP-PHS in alkaline developers. A resist formulated from THP-PHS and TBIT resolves 0.35 μm line-and-space patterns using a KrF excimer laser stepper with a dose of 20 mJ cm^{-2}.

ACKNOWLEDGEMENTS

The authors would like to thank Drs Saburo Nonogaki, Hiroshi Shiraishi and Leo Schlegel for their helpful discussions and Toshio Sakamizu for n.m.r. measurements.

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