Tetrahydropyranyl- and Furanyl-Protected Polyhydroxystyrene in Chemical Amplification Systems

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SYNOPSIS

Tetrahydropyranyl- (THP) and furanyl- (THF) protected polyhydroxystyrene (PHS) polymers have been investigated for their potential use in conjunction with onium salt acid precursors to yield high-sensitivity resist systems. The synthesized polymers have high transmittance at 248 nm (the wavelength used in next-generation excimer laser, KrF exposure tools). At 248 nm the transmittance for a 1-μm thick film is ~ 80% (Abs = 0.097 μm^{-1}). The acid sensitivity of the acetal functionality at room temperature is high, requiring careful handling of all materials to prevent any premature deprotection of the hydroxy group. The highest lithographic sensitivities obtained so far with a system consisting of poly(*p*-tetrahydropyranyl-oxy-styrene) base resin and 1 mol % of bis(*p*-*tert*-butyl phenyl) iodinium triflate (TBIT) was ~ 2 mJ/cm^2. High-resolution line and space patterns (0.35 μm) were obtained with a system comprising PHS-*p*-THP and an acid precursor, using an excimer laser step and repeat exposure at 248 nm.

INTRODUCTION

The drive toward increased circuit density in microelectronic devices has promoted significant effort aimed at improving the resolution capabilities of optical exposure tools, materials, and processes. One of the candidates for future lithography uses deep UV excimer laser (KrF 248 nm) exposure systems rather than the 436-nm Hg line systems used in conventional lithography. Unfortunately, most commercially available positive photoresists are not well suited for excimer laser lithography due to the low absorbance of typical diazonaphthoquinone dissolution inhibitors and the strong unbleachable absorbance of the novolac-type resins as used in these resists. The light intensity at the wafer plane of the excimer laser system is not high at this moment because of the spectral narrowing utilized to avoid color aberrations.[1] Although efforts have been made to improve the design of the system as to increase the light intensity at the wafer plane, progress has been slow.[2] Therefore, a high-sensitivity resist system is one of the major requirements for the successful implementation of deep UV excimer laser lithography.

Reports on the use of photogenerated acids to increase the sensitivity in lithographic systems go back as far as 1973.[3] However, it was not until after Ito and Willson[4] and Frechet et al.[5] reported on the use of onium salt acid precursors in conjunction with acid labile polymers that there has been a major research effort in this "chemical amplification" concept.[6-11] The basic idea utilizes the initial photogeneration of a proton, followed by a subsequent (catalytic) chemical reaction to induce a change in solubility of the exposed area.

Recently three component positive chemical amplification systems for microlithography composed of dissolution inhibitor, acid generator, and novolac resin have been reported.[12,13] Polymeric and nonpolymeric dissolution inhibitors are investigated in these systems.

In this work we report on the synthesis of hydroxystyrene-based polymers protected by acetal functionalities for chemical amplification systems.[3] We also investigated the lithographic performance

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of a resist system composed of an acetal-protected polymer and an onium salt acid precursor.

EXPERIMENTAL

Dihydropyran, *p*-hydroxybenzaldehyde, potassium *t*-butoxide, and methyl-triphenylphosphonium bromide were purchased from Tokyo Kasei Chemical Industries, Ltd. Solvents were obtained from Wako Chemicals and treated with NaOH before use.

Proton NMR spectra were recorded in deuterated chloroform using an Hitachi model R-24 spectrometer. The H-decoupled C-13 NMR spectra were recorded on an Hitachi model R-90H FT-NMR (22.6 MHz) in deuterated chloroform. IR and UV spectra were recorded on Hitachi model 260-10 and model U-3410 spectrometers, respectively.

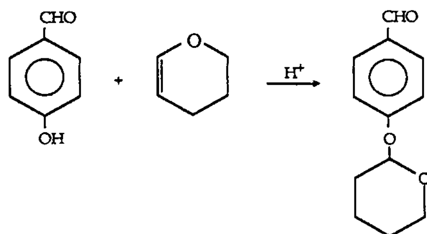
Differential scanning calorimetry was performed on a Rigaku 8240 DSC system at a heating rate of 10 K/min from −40 to 250°C. Thermal gravimetric analysis and differential thermal analysis were performed on an ULVAC Shinku Riko TGD-5000 Differential Thermal Microbalance.

Molecular weights were measured on an Hitachi model 635 GPC system calibrated with polystyrene standards. The system was equipped with Gelpack A150, 140, and 120 columns (Hitachi Chemical) in THF.

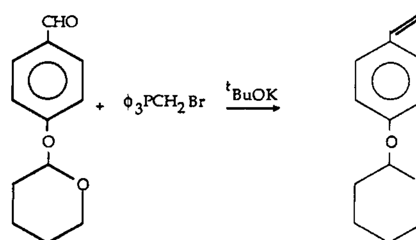
Exposures were carried out using a Hg–Xe deep UV source in combination with a 248-nm narrowband interference filter.

Preparation of Monomers and Model Compound

Tetrahydropyranyl-oxy-styrene was synthesized according to the following procedure: To a solution of 56 g (0.5 mol) of *p*-hydroxybenzaldehyde and 126 g (1.5 mol) of 3,4-dihydropyran in ethyl acetate was added 25 mL of HCl saturated ethyl acetate (Scheme 1).[14] After leaving this solution at room temperature for 2–3 days, the completion of the reaction was checked by thin-layer chromatography.



Scheme 1 Protection of *p*-hydroxybenzaldehyde.



Scheme 2 Synthesis of *p*-tetrahydropyranyl-oxy-styrene.

The mixture is then washed with 3% NaOH twice, distilled water once, and an NaCl saturated solution once. The solution is dried over a mixture of $MgSO_4$ and MgO. After removal of the solvent and excess dihydropyran, the crude protected aldehyde was obtained (yield ~ 90%). This aldehyde could be used directly in the preparation of the monomer.

To a suspension of 140 g (0.4 mol) methyl triphenylphosphonium bromide in 200 mL THF was slowly added a suspension of 100 g (0.9 mol) potassium *t*-butoxide under an N_2 atmosphere. After stirring for one hour at room temperature, the solution was treated with a 70-g solution of the protected aldehyde (0.35 mol); *p*-tetrahydropyranyl-oxybenzaldehyde in 100 mL THF (Scheme 2).

The reaction was exothermic and the color of the solution turned from bright yellow to brown. The solution was stirred for an additional 30 min, poured onto a mixture of ice and NaCl, and then three times extracted with ethyl acetate. The organic layer, which mainly contained triphenylphosphine oxide and monomer, was then poured into 2 liters cold hexane upon which most of the triphenylphosphine oxide would precipitate.

The monomer was concentrated by rotavaporization and further purified by vacuum distillation (bp 82°C at 0.2 mmHg). After distillation a yield of 36 g (50%) pure monomer was obtained. The proton NMR has peaks at 7.1 ppm (5H), 5.3 ppm (3H), 3.8 ppm (2H), and 1.8 ppm (6H).

The *m*-tetrahydropyranyl-oxy-styrene was prepared according to the same procedure starting from dihydropyran and *m*-hydroxybenzaldehyde. IR and NMR spectra both confirmed the structure. The IR spectrum showed characteristic acetal functionalities between 1200 and 800 wave numbers and the NMR spectrum showed peaks at 7 ppm (5H), 5.5 ppm (3H), 3.8 ppm (2H), and 1.8 ppm (6H).

The *m*-tetrahydrofuranyl-protected benzaldehyde was synthesized starting from 2-chlorotetrahydrofurane and *m*-hydroxybenzaldehyde according to the procedure given in the literature.[15] The NMR

spectrum of the monomer showed peaks at 6.9 ppm (5H), 5.5 ppm (3H), 3.8 ppm (2H), and 2.0 ppm (4H).

Bisphenol-A tetrahydropyranyl ether was synthesized according to the following procedure: Approximately 12.5 g (0.05 mol) of bisphenol-A was dissolved in 50 mL (0.55 mol) 3,4-dihydropyran. Upon acidification with 20 mL of HCl saturated ethyl acetate, the temperature of the mixture rose to 50°C, and the mixture was heated gently at 70°C for 30 min.[16]

After cooling of the reaction mixture, the solution was washed with 3% NaOH twice, with distilled water once, and with a saturated NaCl solution once. After drying over $MgSO_4/MgO$, the excess dihydropyran was removed by rotavaporization and high vacuum. The product was then added to approximately 100 mL diethyl ether and stored at −20°C.

After 24 h, 15 g (70%) of the pure tetrahydropyranyl-protected bisphenol-A crystals were recovered (mp 78°C). The proton NMR spectrum has peaks at 7.1 ppm (8H), 5.4 ppm (2H), 3.8 ppm (4H), and 1.8 ppm (18H).

Free Radical Polymerization of the Monomers

A solution of 27 g of *p*-tetrahydropyranyl-oxy-styrene in 27 g of toluene that contained 0.28 g of azobis-isobutyronitrile (AIBN) was heated for 8 h at 60°C under nitrogen atmosphere in a sealed ampoule. The polymer was precipitated in fresh petroleum ether and dried under vacuum. The polymer weighed 16 g (60% yield) and showed no deprotection in the IR spectrum.

The polystyrene equivalent MW as determined by GPC in THF, M_n = 20,000 g/mol, and a polydispersity, M_w/M_n = 1.86. Alternately, the monomer was polymerized with the addition of 60% by weight toluene and 1% AIBN at a temperature of 73°C for 8 h. The polystyrene equivalent MW was determined to be M_n = 10,000 g/mol and a polydispersity of 1.86.

The *m*-tetrahydropyranyl-oxy-styrene was polymerized and purified in a similar manner. The polystyrene equivalent MW as determined by GPC in THF; M_n = 11,000 g/mol and a polydispersity of 1.84.

The *m*-tetrahydrofuranyl analogue was polymerized and purified under the same conditions. The polystyrene equivalent molecular weight from GPC in THF turned out to be M_n = 11,700 g/mol and a polydispersity of 1.57.

Preparation of Onium Salt Acid Precursor

The onium salt used was synthesized according to the literature.[17] In this study, bis(*tert*-butyl phenyl) iodinium triflate (TBIT) was prepared from triflic acid and the appropriate bis(*tert*-butyl phenyl) iodinium chloride salt.

Preparations for Lithographic Evaluation

For the lithographic evaluation of the resist systems, xylene and cyclohexanone solutions of polymer and acid precursor were spin casted onto silicone wafers at 1000–3000 rpm (depending on the viscosity of the solution) to render ~ 1-μm-thick films. These films were baked for half an hour at 80–100°C to remove residual casting solvent that could cut down the transmittance at 248 nm significantly.

The wafers were then cut into small pieces and subsequently exposed to render sensitivity curves. The exposure system consisted of a high-pressure Hg–Xe lamp with a narrow-band 248-nm interference filter.

Deep UV lithography was performed by a stepper with a numerical aperture of 0.35. Micrographs of developed resist patterns were taken with a scanning electron microscope (Hitachi model S-800). The exposed films were post-exposure baked for various lengths of time and developed in a mixture of NMD-3 and *n*-propanol.

RESULTS AND DISCUSSION

Polymer Characterization and Stability

NMR Spectroscopy

The ^{13}C-NMR spectrum for poly(*p*-tetrahydropyranyl-oxy-styrene) (H-1 decoupled) was taken in $CDCl_3$. The spectrum has 11 distinctive peaks at 154.9, 138.5, 128.4, 116.0, 96.5, 61.9, 44.0, 39.6, 30.6, 25.3, and 19.0 ppm, respectively (see Fig. 1). The ^{1}H-NMR spectrum of this polymer in $CDCl_3$ has broad peaks at 6.5 ppm (4H), 5.3 ppm (1H), 3.8 ppm (2H), and 1.8 ppm (9H).

IR Spectroscopy

The IR spectrum of the synthesized polymers showed no free hydroxy groups. However, in Figure 2 the IR spectrum of a freshly synthesized poly(*p*-tetrahydropyranyl-oxy-styrene) polymer before (solid line) and after 2 days in commercial-grade cyclohexanone solution (broken line) is shown. Only

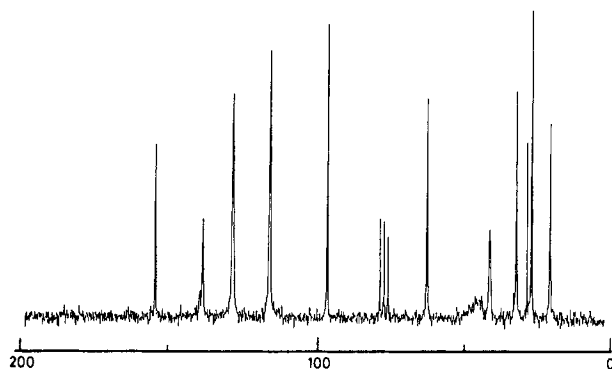


Figure 1 ^{13}C-NMR spectrum of *p*-tetrahydropyranyl-oxy-styrene polymer in $CDCl_3$ (H-1 decoupled).

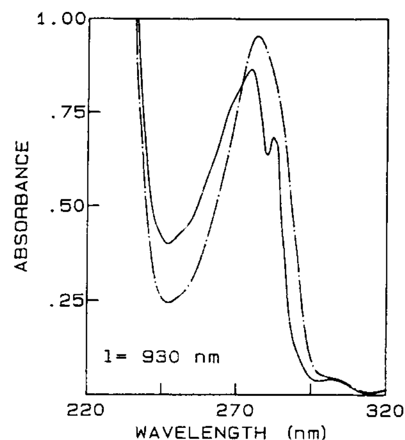


Figure 3 Deep UV spectrum of PHS-*p*-THP film with 5 wt % bis(*tert*-butyl phenyl) iodinium triflate (TBIT) (at 248 nm before exposure A_i = 0.43 μ^{-1}, and after exposure A_f = 0.25 μm^{-1}, the exposure dose is approximately 60 mJ/cm^2).

the slightest amount of acid coming from the spin casting solvent can deprotect part of the polymer (in the case of cyclohexanone the impurity was acetic acid). To avoid any future problems, all solvents used (for polymerization, precipitation, and spin casting) were washed with aqueous NaOH and distilled water before use. Taking these precautions resulted in high stability for the polymers in the prepared resist systems.

UV Spectroscopy

The UV spectrum of the pure *p*-tetrahydropyranyl-oxy-styrene polymer in the solid phase shows a broad band at 275 nm associated with the π-π^* transition. This band has little structure, and upon acidolysis of the polymer it loses all its structure and shifts to slightly longer wavelengths (see Fig. 3). This shift and loss in structure shows that mainly free polyhydroxystyrene is formed.

The absorption coefficient for this polymer at 248 nm in the solid state (of importance for its use in a photoresist) was determined to be 0.097 μm^{-1} (T = 80%). This is higher than both *t*-BOC (T = 65%)[4] and trimethyl silyl (T = 65%)[10] protected polyhydroxystyrene (values were taken from figures; raw data were unavailable). The films for the determination of the deep UV absorption spectrum were spun from a xylene solution and baked at 110°C for 10 min to ensure the removal of any solvent.

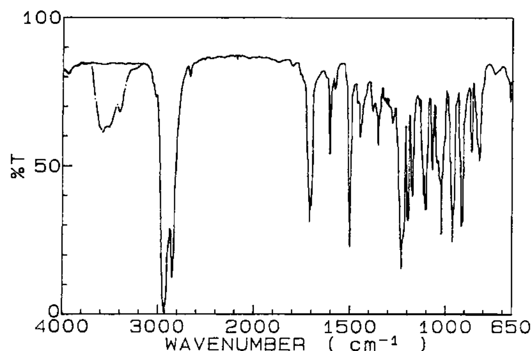


Figure 2 Infrared spectrum of poly(*p*-tetrahydropyranyl-oxy-styrene) in cyclohexanone solution (solid-line; right after dissolution, broken line; after 2 days at room temperature).

In combination with 5 wt % bis(*p*-*tert*-butyl phenyl) iodinium triflate, this polymer gives a resist with high transmittance and high sensitivity. The important features that we can find in the ultraviolet spectrum is the low absorbance and the bleaching ability of this resist system at 248 nm. However, this bleaching ability might depend more strongly on the choice of onium salt acid precursor (its extinction coefficient at 248 nm and its molecular structure) than that it depends on the polymer itself. Moreover, for short exposure times bleaching of the resist will be minimal, thus not having any effect on the resolution.

Thermal Analysis

Thermal gravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) were all performed on the three investigated polymers. The reference material in all three techniques was Al_2O_3 and the heating rate amounted to 10 K/min. The results are given in Table I.

If the polymers would decompose into polyhydroxystyrene and dihydropyran/furan, respectively, than there are some discrepancies in the weight loss for the *p*-THP and *m*-THF analogues. The theoretical weight loss for these polymers should be 41 and 37%, respectively. However, the nonequilibrium

Table I Thermal Analysis of Acetal Protected Polyhydroxystyrene

Polymer	TGA (at *T*, °C)	TDA/DSC
PHS-*p*-THP	−31% (280°C)	Endothermic peak
PHS-*m*-THP	−40% (230°C)	Endothermic peak
PHS-*m*-THF	−29% (210°C)	Endothermic peak

conditions might have caused some inclusion of deprotection products into the polymer matrix (fast heating rate; 10 K/min).

For the *p*-THP analogue the glass transition temperature was observed as an endothermic shift in the base line of the differential scanning calorimeter curve at 110°C (see Fig. 4). This as expected for a styrene-type polymer.

The thermolysis of the tetrahydropyranyl-protected bisphenol-A resulted in an endothermic peak at ~ 80°C corresponding to the melting point and an endothermic peak at ~ 230°C (accompanied with a 40% weight loss) corresponding to the decomposition (see Fig. 4). From these results it follows that these polymers (provided they are clean) are very stable at elevated temperatures (e.g., PHS-*p*-THP: 280°C).

Lithographic Characteristics

The sensitivity of the investigated resist system, PHS-*p*-THP/1 mol % bis(*p*-*tert*-butyl phenyl) iodinium triflate, strongly depends on the specific development conditions. If only an aqueous base developer is used (e.g., NMD-3), concentrations as high as 5% are needed to develop the exposed pattern down to the substrate. However, the addition of *n*-propanol to the base developer makes the development rate faster. Sensitivities of this resist system are dependent on the time one waits after exposure or whether or not a post-exposure bake treatment is given (see Fig. 5 and 6).

The protected polymer used in this resist has a high resistance toward development, the thickness of the unexposed film is unaltered by either the NMD-3 or the *n*-propanol (though SEM photographs of the contact printed line and space patterns show some change near the surface of the resist films). However, once exposed to deep UV and baked at a sufficient high temperature, the development in a mixture of NMD-3/*n*-propanol is fast.

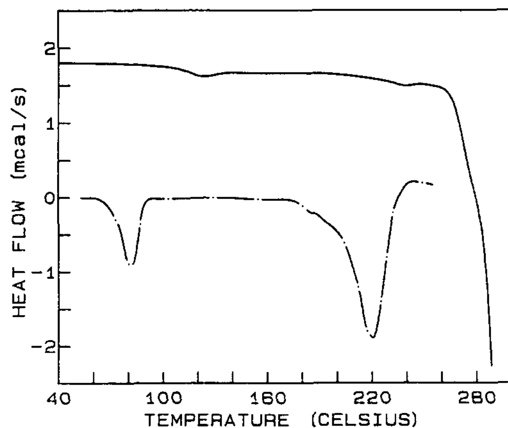


Figure 4 Differential scanning calorimetry curve for *p*-THP-protected polyhydroxystyrene (solid curve) and bisphenol-A (broken curve), heating rate 10 K/min, reference aluminium oxide.

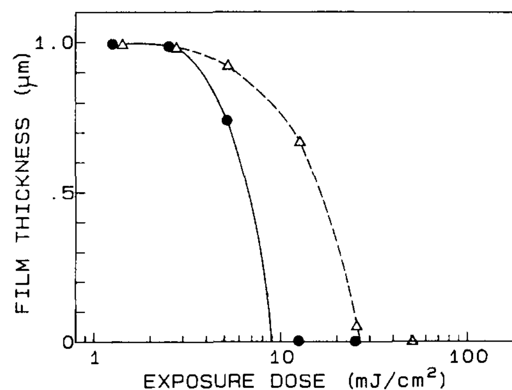


Figure 5 Influence of the developer composition on the sensitivity curve. (1) Solid line: sensitivity curve using a mixture of 3 parts 2.38% NMD-3 and 2 parts *n*-propanol; (2) Broken line: sensitivity curve using 5% NMD-3 developer.

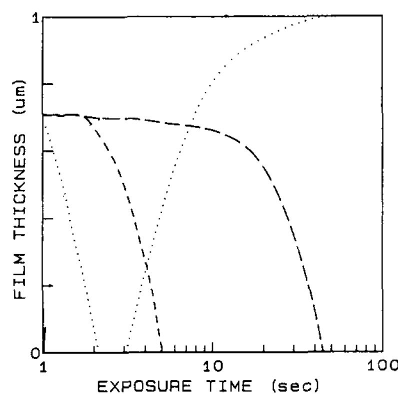


Figure 6 Sensitivity curves for PHS-*p*-THP with 1 mol % bis(*tert*-butyl phenyl) iodinium triflate. (1) Broken negative: RD-2000N (1 μm, 1% NMD-3), the sensitivity of this resist is ~ 50 mJ/cm², 1 s = 1 mJ/cm². (2) Solid positive: PHS-*p*-THP + 1 mol % TBIT (acid precursor), 2.38% NMD-3/*n*-propanol = 5/1, 1 min. Development 1, 10, and 60 min after exposure, respectively; sensitivity: ~ 45, 5, and 2 mJ/cm².

This high contrast in development can be advantageous in lithographic applications since there is no loss of film thickness upon development.

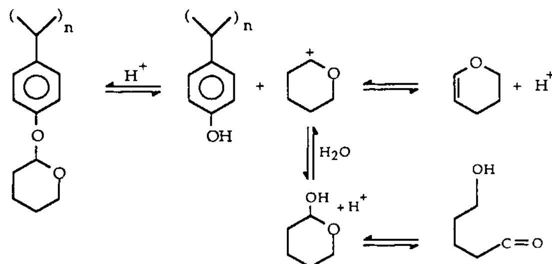
From Figure 5 it can be seen that there is a drastic increase in the sensitivity with the addition of some *n*-propanol to the developer. This fact can be explained in two ways; it can either be an effect from the decomposition of the onium salt acid precursor, or it can be an effect associated with the deprotection of the polymer side chain. Upon deprotection, the proton first attaches itself to the (most basic) phenolic oxygen to produce the free polymer and an oxocarbenium ion (Scheme 3).

This oxocarbenium ion can then react with water from the air to give in first instance 2-hydroxytetrahydropyran[15,18] or it can lose a proton to give 3,4-dihydropyran (depending on the availability of water and the temperature of acidolysis). The 2-hydroxytetrahydropyran is a hemiacetal and is in equilibrium with 5-hydroxypentanal.

In the acid-catalyzed deprotection of poly(tetrahydrofuranyl-oxy-styrene), the protonation again will occur at the most basic oxygen to eventually yield the free phenol and 2-hydroxy-THF[15] or dihydrofuran depending on the exact experimental conditions. The rate of hydrolysis for cyclic acetals is dependent on both the basicity of the acetal and the stability of the intermediate oxocarbenium ions; since the THF group is much more basic than the THP group, its sensitivity as a photoresist is also expected to be higher.[15]

To investigate the PHS-*p*-THP resist system further, 5-hydroxypentanal was used in several experiments. When mixed in an equimolar ratio with polyhydroxystyrene, the 5-hydroxypentanal does inhibit the dissolution of the PHS in aqueous base slightly. However, if the film is baked for successive periods of time at higher temperatures, the dissolution rate of the PHS/HP goes down significantly (Fig. 7).

However, if some acid is introduced, the dissolution rate is almost totally inhibited indicating that there is some reaction of the hydroxypentanal and the matrix. This could be a protection reaction of the polyhydroxystyrene to generate PHS-THP or it might be some kind of crosslinking reaction. The aldehyde could link two hydroxy groups together to form an acetal and water.[19] However, the reaction of hydroxypentanal and the polyhydroxystyrene does not affect the dissolution with these strong development conditions (i.e., *n*-propanol is a very good solvent for PHS). In aqueous base/alcohol developer very high sensitivities can be obtained (Fig. 6).



Scheme 3 Deprotection mechanism for *p*-tetrahydropyranyl-oxy-styrene.

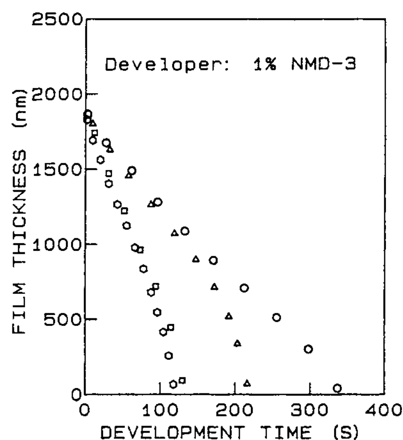


Figure 7 Base dissolution characteristics for an equimolar mixture of 5-hydroxypentanal and polyhydroxystyrene after various baking times at 100°C (hexagonal 100% PHS, square PHS/HP = 50/50, triangle after 5 min at 100°C, circle after 15 min at 100°C, pentagonal exposed to acid, developer 1% NMD-3 at room temperature).

Figure 6 also shows us that the polymer in the presence of acid readily decomposes even at room temperature. By waiting for 60 min after exposure before developing the resist, the sensitivity gradually increases to the value obtained as with a post-exposure bake included (~ 2 mJ/cm^2).

When a mixture of 5 parts 2.38% NMD-3 and 1 part *n*-propanol was used for the development of the exposed resist (comprising PHS-*p*-THP and an acid precursor), a resolution of 0.35 μm (L/S) in a 1-μm-thick film was obtained (see Fig. 8).

CONCLUSIONS

The tetrahydropyran and furan ethers are promising candidates for use in side chain protection of polyhydroxystyrene-type polymers. In combination with low amounts of acid precursor ($\sim$ 1 mol %), the polymers can give a photoresist with high sensitivity, high transmittance, and high resolution.

The highest sensitivity until now was obtained with a resist system comprising poly(*p*-tetrahydro-

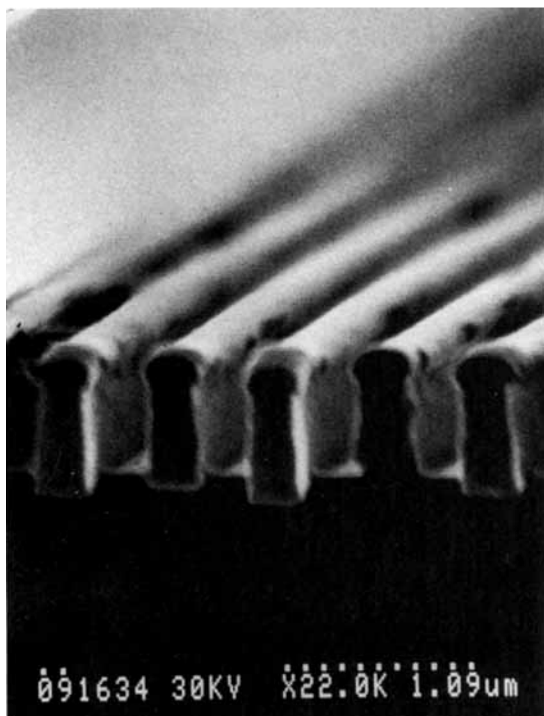


Figure 8 Scanning electron microscope photograph of line and space pattern (0.35 μm L/S) exposed in positive mode at 248 nm (PHS-*p*-THP/acid precursor, film thickness = 1 μm).

pyranyl-oxy-styrene) and 1 mol % bis(*p-tert*-butyl phenyl) iodinium triflate was 2 mJ/cm^2. High-resolution line and space patterns (0.35 μm L/S) were obtained with doses of approximately 10 mJ/cm^2 at 248 nm.

The higher basicity of the THF as compared to the THP-protected PHS makes this polymer more susceptible toward acidolysis.[8,15,19] This higher sensitivity toward acidolysis can later be utilized in a higher sensitivity resist system compared to the THP-protected system. By adding an onium salt that does not inhibit the dissolution of the resist as much as the onium salt used in this study, the sensitivity can be increased even further.

Differential scanning calorimetry rendered a glass transition temperature for the poly(*p*-tetrahydropyranyl-oxy-styrene) of 110°C. This might be too low for actual use in some applications in microlithography. However, by introducing an extra methyl group in the backbone of the polymer one can restrict the movement of the chain and increase the glass transition temperature substantially.

The only disadvantage of the investigated system is the fact that the exposed resist does not develop in pure aqueous base, some *n*-propanol needs to be added.

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