Use of Water-Soluble Sugars as Novel Cross-Linkers in Electrophilic Processes: Application to Negative-Tone Photoresists Based on Poly(4-hydroxystyrene)

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The use of water-soluble sugars as latent cationic cross-linkers for polymers such as poly(4-hydroxystyrene) has been explored. Photogeneration of acid within thin films of the phenolic resin containing the sugars results in their conversion into reactive furan moieties that lead to thermal cross-linking of the phenolic resin via electrophilic aromatic substitution in a chemically amplified process. These resist materials have demonstrated high sensitivities and resolving capabilities with both deep-UV and electron-beam radiation.

Introduction

The ever-increasing demand for high-resolution imaging drives the microlithography industry toward the use of short-wavelength radiation. In general, these radiation sources have much lower output power than the conventional 360 or 435 nm mercury emission lines. The resist materials that have been designed for use with conventional sources are noncatalytic in nature, and their use in combination with the lower power radiation sources leads to a drop in throughput as the time required for exposure of each wafer increases. To alleviate this problem, new resists with much higher sensitivities have been developed. One approach to increasing the sensitivity is to use a chemically amplified system, such as the acid-catalyzed thermolysis of (*tert*-butyloxy)carbonyl- (*t*-BOC) protected poly(4-hydroxystyrene).[1] The increased sensitivities of these catalytic imaging materials (about 1–10 mJ/cm^2) relative to conventional novolak–diazonaphthoquinone resists (100–500 mJ/cm^2) has enabled the implementation of deep-UV lithography[2] and also contributed greatly to advances in e-beam lithography.

In the last decade, a large number of new imaging materials based on chemical amplification have been designed.[3-9] Most of the modifications containing *t*-BOC or *t*-butyl ester active groups afford either positive or negative-tone images as a function of the choice of developer (aqueous base or organic solvent, respectively)[4,5] Alternatively, cross-linking through electrophilic aromatic substitution followed by aqueous base development has been used to create negative-tone resists that afford nonswollen images.[6-9] This design relies on the acid-catalyzed formation of carbenium moieties from latent electrophilic groups. Their alkylation of the aromatic rings of the matrix polymer leads to cross-linking. Chemical amplification arises as the photogenerated proton that is consumed in the initial formation of the carbenium species is regenerated in the subsequent aromatic substitution process.

Two different types of systems have been used: a two-component system consisting of a mixture of a matrix polymer that incorporates the latent electrophile and the photoacid generator, or a three-component system, containing a mixture of the matix polymer, the photoacid generator, and a small-molecule cross-linker. One example of a two-component system is poly[4-(acetoxymethyl)styrene-*co*-4-hydroxystyrene] and triphenylsulfonium hexafluoroantimonate (**1**, resist A).[8] An analogous three-component system includes **1**, poly(4-hydroxystyrene), and the polyfunctional small-molecule cross-linker 1,3,5-triacetoxymethylbenzene (resist B).[9]

We have recently described a new negative-tone resist consisting of poly[4-hydroxystyrene-*co*-4-(3-furyl-3-hydroxypropyl)styrene] (**2**) and the photoacid generator **1**

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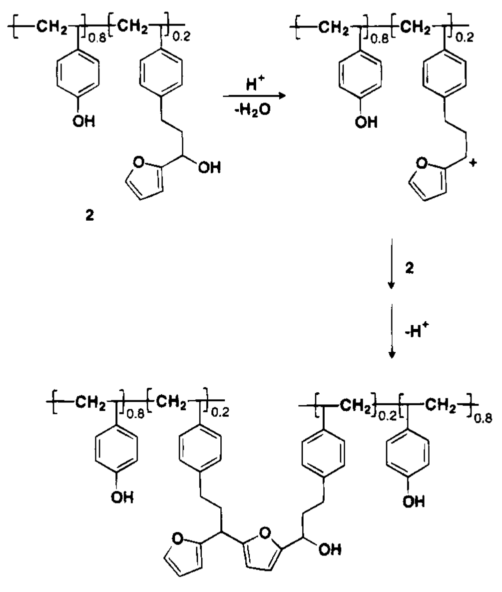
Scheme 1



(resist C).[10] Protonation of the furfuryl alcohol unit on the polymer results in the formation of a carbocation stabilized by the furan ring. Subsequent electrophilic aromatic substitution reaction between the carbocation and adjacent furan moieties forms the cross-link (Scheme 1). This cross-linking process is extremely efficient due to the high reactivity of furans in electrophilic aromatic substitution, leading to high resist sensitivities with both deep-UV and electron beam radiaton.[10]

Work with resists A and B has revealed that, in this instance, the two-component system A has a slightly higher sensitivity. Nevertheless, the three-component approach is much more versatile, allowing for easy exploration of many combinations of components.[8,9] This report describes our design of the three-component equivalent of resist C, using small-molecule cross-linkers based on simple sugars that react through chemistry analogous to that of furans.

Experimental Section

Materials. Poly(4-hydroxystyrene) and triphenylsulfonium hexafluoroantimonate were obtained from IBM Corp. Xylose and glucose were purchased from Aldrich Chemical Co., Inc., and were used without further purification.

Instruments. Infrared spectra were obtained on a Nicolet FTIR/44 spectrometer. Resist film thickness was measured on a Tencor Alpha-Step 200 surface profiler. Deep-UV exposures were performed by contact printing either using a Canon HTG Systems III Contact Aligner or an Optical Associates Inc. exposure system comprising of a low-pressure mercury lamp with a shutter system, an intensity controller, and an exposure timer. Photon flux was measured using an Optical Associates Inc. 354 exposure monitor. The output of the mercury lamp was filtered through a 254 nm narrow-bandwidth interference filter from Oriel Corp. Varying dosages of light for deep-UV sensitivity measurement were obtained with a Series 1 Multidensity resolution target, Ditric Optics Inc. Sensitivities reported are accurate to ±0.05 mJ/cm^2. E-beam exposures of the resist films were conducted with a Cambridge Instruments Electron Beam Microfabricator 10.5/CS. Scanning electron micrographs are recorded on a Cambridge Instruments Stereoscan 200 microscope.

Resist Formulation and Processing. Resist formulations examined are listed in Table 1. Methyl cellosolve was used as the casting solvent for spin coating onto silicon wafers. Preexposure bake was done at 110 °C for 2 min to give 1.0 ± 0.05 μm films. Solvent development of the exposed and postbaked resists was done by dipping the wafer into a beaker of rapidly stirred 30–40% aqueous AZ312MIF solution.

Table 1. Sensitivity Testing of Resists Formulated from Xylose (4) and Glucose (6)

resist	sugar	wt % of 1	postexposure bake temperature,[a] °C	sensitivity,[b,c] mJ/cm^2
D	**4** (5 wt %)	5	120	19.0
D	**4** (5 wt %)	5	130	12.0
D	**4** (5 wt %)	5	140	7.5
E	**4** (15 wt %)	5	120	13.0
E	**4** (15 wt %)	5	130	10.0
E	**4** (15 wt %)	5	140	9.0
F	**4** (5 wt %)	10	120	5.5
F	**4** (5 wt %)	10	130	5.5
F	**4** (5 wt %)	10	140	4.3
G	**4** (10 wt %)	10	120	8.0
G	**4** (10 wt %)	10	130	8.0
G	**4** (10 wt %)	10	140	4.7
H	**6** (5 wt %)	10	120	7.1
H	**6** (5 wt %)	10	130	5.1
H	**6** (5 wt %)	10	140	4.5
F	**4** (5 wt %)	10	140	10.0 μC/cm^2 [d]
H	**6** (5 wt %)	10	140	10.0 μC/cm^2 [d]

[a] All samples postexposure baked for 3 min. [b] Unless otherwise stated, sensitivity data was obtained with 254 nm radiation. [c] Aqueous base development is done by dipping the sample into a beaker of rapidly stirred 20–30% AZ312MIF developer for 25–35 s. [d] Sample exposed with electron beam.

Results and Discussion

In copolymer **2**, the furfuryl pendant groups act as both the latent electrophile and in the nucleophile, while the phenol moieties do not participate the electrophilic aromatic substitution.[10] The furfuryl carbocation has a preference to alkylate another furan moiety rather than the phenolic group. For this reason furfuryl alcohol **3** is not suitable for cross-linking poly(4-hydroxystyrene) in the three-component design. Instead of cross-linking the poly(4-hydroxystyrene) matrix, furfuryl alcohol **3** may simply react with itself resulting in the formation of a furan based polymer. In addition, furfuryl alcohol **3** is not soluble in water or aqueous base and, thus, may have an undesirable inhibitory effect on the dissolution of poly(4-hydroxystyrene) in classical aqueous base developers.

Instead, a variety of sugars such as xylose (**4**) may be used as "latent" cross-linkers. In this design, the desired carbocationic moiety is generated in situ from **4** in the resist film. Xylose is ideal for use in both 248 and 254 nm lithography since it does not have any UV absorption above 190 nm. In addition, it is highly soluble in water and can act as a dissolution promoter for poly(4-hydroxystyrene). This may result in an increased contrast due to enhanced solubility differences between the un-cross-linked and the cross-linked regions.

Acid-catalyzed dehydration of xylose readily affords 2-furaldehyde (**5**, Scheme 2).[11] Although 2-furaldehyde is less reactive than furfuryl alcohol **3**, it also polymerizes readily under acidic conditions.[12] However, the electrophile generated in the system is expected to react with poly(4-hydroxystyrene) rather than **5** since the aromatic system of **5** is less electron rich because of the

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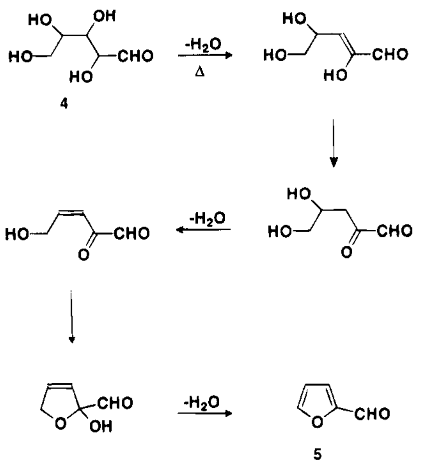
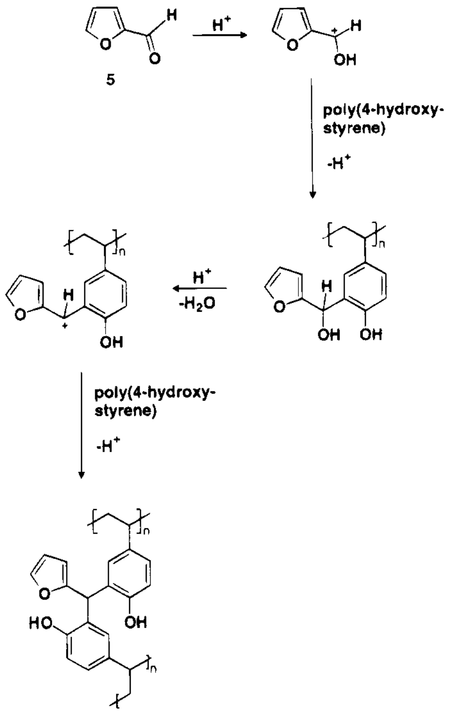
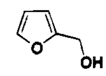
Scheme 2



Scheme 3



negative mesomeric effect of the formyl substituent. Therefore, under acidic conditions, the 2-furaldehyde generated in situ is expected to be a crosslinker of poly(4-hydroxystyrene) (Scheme 3). Because of their ability to afford active carbocationic species, a large number of other sugar molecules, such as glucose (**6**), can be used in the resist formulation. For example, glucose undergoes an acid-catalyzed dehydration reaction similar to that for xylose affording 5-(hydroxymethyl)-2-furaldehyde **7**.[13]



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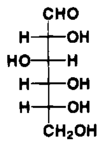

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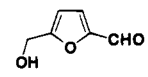

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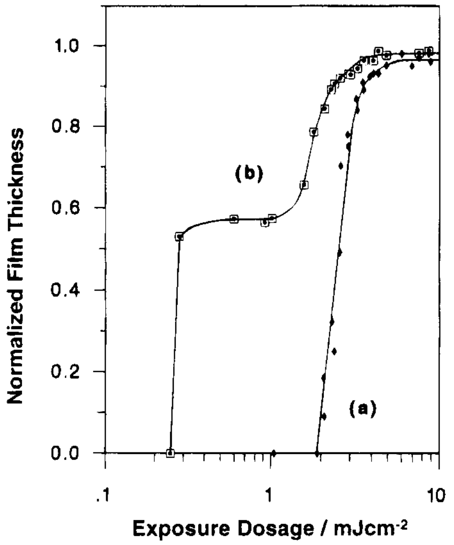

Figure 1. Sensitivity curves of (a) resist F and (b) resist G with postexposure bake performed at 140 °C.

Several different combinations of photoacid generator **1**, poly(4-hydroxystyrene) and sugars **4** or **6** were tested in three-component resist systems. The compositions and resist sensitivities with deep-UV and e-beam radiation are summarized in Table 1. While normal sigmoid-shaped sensitivity curves (Figure 1, curve a) are observed for resists containing 5 wt % of sugar, higher loading of sugar, e.g., in resists E and G, results in "two-step" sensitivity curves (Figure 1, curve b) which may be the result of two distinct insolubilizing mechanisms that operate at different concentrations of the crosslinker. However, the exact cause is not clear. A possible explanation may be that at high sugar concentration in situ polymerization of the furaldehyde occurs resulting in partial insolubilization. As the concentration of sugar becomes depleted, full insolubilization is only achieved once electrophilic aromatic substitution involving the large amount of phenolic pendant groups of the polymer takes over. The best results, in terms of sensitivity and contrast, are obtained with samples loaded with 5 wt % of sugar (**4** or **6**) and 10 wt % of **1**, postexposure baked at 140 °C for 3 min (resists F and H). The contrast values, γ, are about 5.

To monitor the reactions, the resist films were examined before and after irradiation and postbaking by both UV and IR spectroscopies. However, UV spectroscopy could not be used to observe the formation of furan moieties since the furan ring absorption (maximum at 216 nm) is completely masked by the intense absorption of poly(4-hydroxystyrene). In contrast, IR spectra show a significant decrease in the xylose and glucose C$-$O bond stretching at 1050 cm^{-1}, suggesting the formation of **5** and **7**, respectively.

To confirm that the resist functions through crosslinking of the polymer matrix, the temperature at which the resist begins to flow was observed by optical microscopy. Resist F was spin-coated onto silicon wafers to form 1 μm films. The radiation-exposed and postbaked samples were heated on a hot stage and observed under an optical microscope to determine the temperature at which the polymer matrix started to flow. Although the temperatures recorded are not as precise as measurements by DSC, they reveal the trend for the change that results from the irradiation and subsequent postexposure bake steps. The results obtained are as follows: 160 °C for a radiation-unexposed

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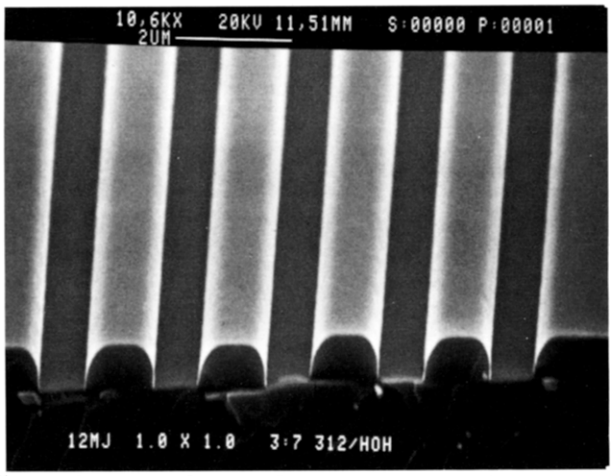

Figure 2. 1.0 μm lines and spaces in 1.0 μm thick resist H using 248 nm projection printing (12mJ/cm^2) and postexposure bake at 140 °C.

sample; 190 °C for a sample exposed to 5 mJ/cm^2; 215 °C for a sample exposed to 10 mJ/cm^2. Because cross-linking of a polymer is known to increase its glass transition temperature, these results are in agreement with the mechanism of operation of this resist.

To demonstrate imaging, a preliminary experiment using 248 nm projection printing was performed with resist G. Figure 2 shows the scanning electron micrograph of 1 μm features obtained after aqueous base development. These results demonstrate the versatility of the concept of radiation-induced cross-linking via electrophilic aromatic substitution. The fact that simple and inexpensive water-soluble sugars can be used as cross-linkers opens a new avenue toward more environmentally friendly cross-linkers not only for resists and imaging materials but also for any system in which electrophilic curing is desirable. We are currently exploring the design of new water soluble resist materials.

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