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by

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NOVEL CHEMICALLY AMPLIFIED DRY-DEVELOPING IMAGING MATERIALS FOR HIGH RESOLUTION MICROLITHOGRAPHY.

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Several new polymers, copolymers, and polyfunctional crosslinkers that can be used to formulate chemically amplified resist materials have been prepared, characterized, and tested in combination with suitable photoactive compounds. All of the materials operate on the basis of acid catalyzed processes involving alkylation, dehydration, or isomerization reactions. Sensitivities below 0.1 mJ/cm^2 have been measured with deep-UV irradiation, while most of the materials also operate very effectively with E-beam or X-ray exposure. The resist materials are useful in dry development and top-surface imaging processes. Depending on the nature of the matrix polymer and the design of the resist material, both positive and negative tone images can be obtained. Dry development using an oxygen plasma can be achieved following selective silylation of the resists after exposure and post-baking. Those areas of the films that are silylated resist etching by the oxygen plasma providing access to high resolution images that also benefit from the high sensitivity of the chemically amplified resists.

1. Introduction.

Chemically amplified resists have attracted much attention due to their very high sensitivities and versatility allowing imaging through the use of a variety of radiation sources, from deep ultraviolet, to electron-beam, to synchrotron X-ray. It has been more than thirteen years since Fréchet and Willson first designed in 1979 chemically amplified resist materials based on the thermolysis of poly(p-t-BOC-styrene) [1-2] and on the depolymerization of poly(phthalaldehyde) [3-4]. In particular, numerous resists systems based on the very versatile t-BOC chemistry and the photogeneration of acid have emerged in recent years [5-6]. Several other families of chemically amplified resists, also based on processes catalyzed by radiation-generated acid, have been described. Of particular interest, in the context of this report, are the resists that operate via electrophilic aromatic substitution [7-9]. For example, we have described a negative resist that involves a copolymer of 4-hydroxystyrene and 4-acetoxymethylstyrene in combination with radiation-sensitive acid precursors. This resist shows extremely high sensitivities to deep UV, E-beam as well as X-ray radiation [8]. The same resist material has recently been shown to operate in positive-tone mode through an image reversal process involving photogenerated base [10].

While all of these materials can usually be developed with aqueous base, an alternate approach to image development based on dry etch processes has emerged. In all cases, development of the resist after imaging is carried out in a plasma environment where an etch rate differential between exposed and unexposed areas of the resist results from the exposure process itself or from a subsequent modification of the resist image. A most attractive approach to achieve the desired etch rate differential between exposed and unexposed areas of the resist film, is to incorporate an oxygen etch resistant element such as tin, silicon, or boron into the resist *after imaging* and prior to development. For example, Taylor and Stillwagon [11] succeeded in the selective incorporation of diborane into the unexposed areas of a cyclized rubber, while MacDonald et al. [12] used a silylation process to incorporate silicon into resist images obtained from the poly(t-BOC-styrene) resist. In both cases, exposure of the hydroborated or silylated material to an oxygen plasma afforded dry-developed images, as the areas of the resist film that contained boron or silicon became protected by etch resistant layers of B_2O_3 or SiO_2 respectively, while other areas of the film were etched away. Mechanistic studies of the MacDonald poly(t-BOC-styrene) silylation process have been reported [13-14]. In particular, these studies have shown that the gas phase functionalization rates are influenced by a number of variables, including the vapor treatment temperature and pressure. Further variations of the gas phase silylation process, such as the so-called "DESIRE" process of Rolands and Coopmans [15], as well as a variety of three component systems

[16] have appeared.

An interesting feature of plasma developable systems is their adaptability to top-surface imaging (TSI) [17]. An advantage of the TSI approach is that radiation need not penetrate through the entire thickness of the resist film. This is particularly important to solve problems associated with substrate reflectivity or to overcome the problem of printing small images over existing substrate topography. In addition, the TSI scheme facilitates the use of the new high numerical aperture UV exposure tools which only have limited depth of focus.

Plasma developable resists suitable for TSI have recently been evaluated for their potential use in manufacturing [18].

2. Experimental Design.

Our experimental design for these studies rests on a chemically amplified system that operates on the basis of acid-catalyzed changes in solubility within a resist film. In all cases the acid will be generated photochemically by irradiation of an appropriate triaryl sulfonium salt or equivalent radiation-sensitive proton source. We have already demonstrated that this approach is extremely versatile as excellent results can be obtained with a great variety of radiation sources. For example, we have used a deep-UV lamp, an electron beam, or a VUV synchrotron (X-ray) as the source of radiation.

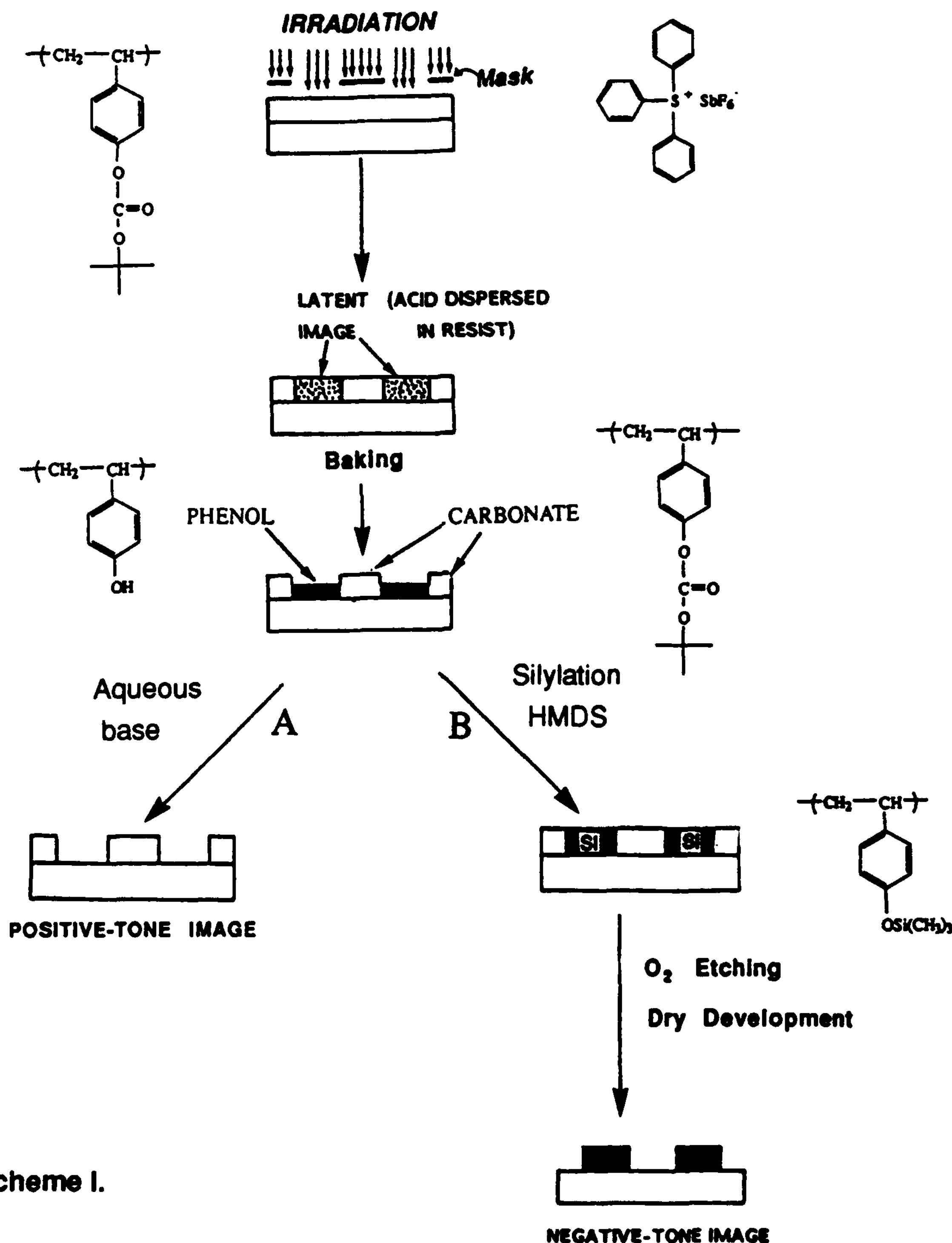
The chemistry of the resist material itself is based on acid catalyzed electrophilic processes including carbon-carbon or carbon-oxygen bond forming reactions, as well as acid-catalyzed rearrangements.

The silylation reactions were carried out in a specially designed gas-phase functionalization chamber providing for good control of pressure and temperature of the silylation reagent, as well as other important variables. In a typical process the exposed wafer is inserted onto the heated base of the silylation chamber and secured in place by vacuum suction. After evacuation, the system is allowed to reach thermal equilibrium and the silylation reagent, hexamethyldisilazane is introduced at the appropriate pressure. Once the silylation reaction has taken place, the chamber is evacuated and the treated wafer is removed for examination or dry-development in an oxygen plasma etcher.

In order to calibrate our experiments the gas-phase silylation procedure was first checked with our well known poly(t-BOC-styrene) / onium salt resist [1, 2, 12]. The chemistry that occurs during imaging is outlined in Scheme I. After exposure and post-bake, the unexposed areas of the film contain the unchanged polymer while the exposed areas contain poly(4-hydroxystyrene).

Wet development with aqueous base (path A) can be used at this stage to produce a positive tone image [2]. In order to accomplish dry-development (path B), the

exposed resist is first exposed to an atmosphere of a silylating agent [12]. During silylation with hexamethyldisilazane (HMDS), the phenolic groups are converted to the corresponding trimethylsilyloxy groups. Oxygen plasma etching of the silylated film then affords a negative tone image (Scheme I). The silylation process is readily monitored by difference FT-IR spectrometry as shown in Figure 1 which features prominent peaks at 850, 920, 1250 and 1500 cm^{-1} resulting from silylation of the free phenolic groups of the resist.



Scheme I.

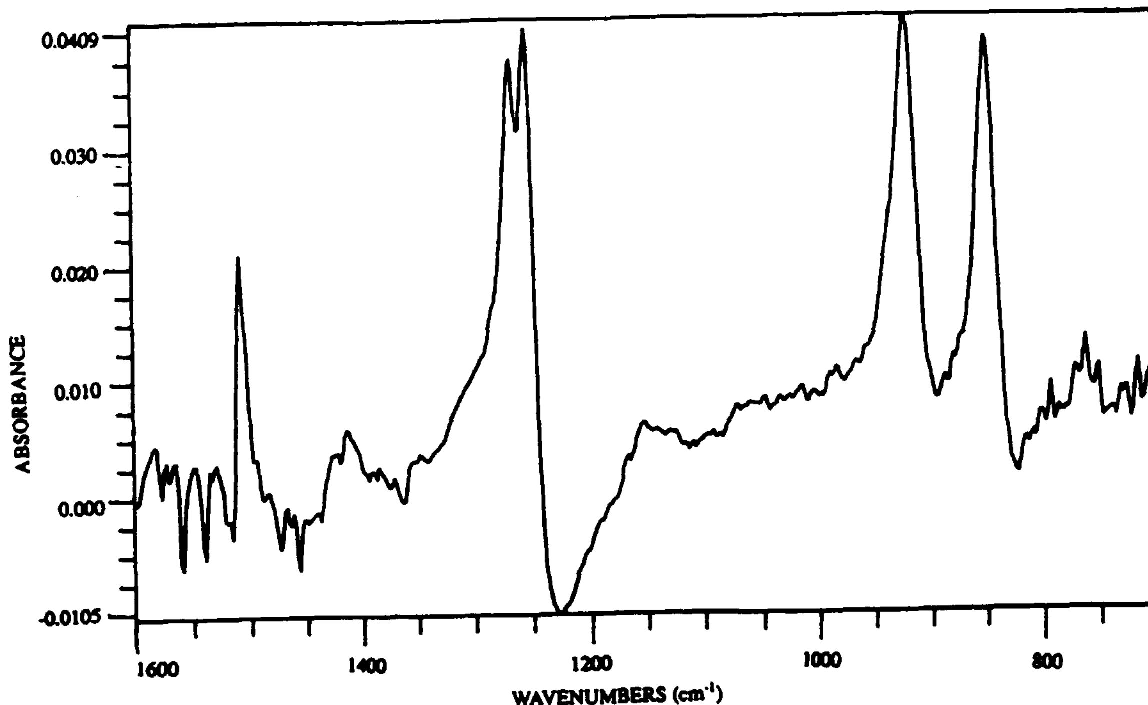


Figure 1. IR difference spectrum of poly(t-BOC-styrene) resist before and after silylation

3. Results and Discussion.

Several systems, all based on acid-catalyzed electrophilic processes, were tested in this study. For example, a three component system consisting of poly(4-hydroxystyrene), a polyfunctional alkylating agent such as 1,2,4,5-tetraacetoxymethylbenzene and an acid photogenerator was tested. Upon exposure to radiation, acid catalyzes the crosslinking of the resist (Figure 2) and a negative-tone image can be obtained by wet development with aqueous base.

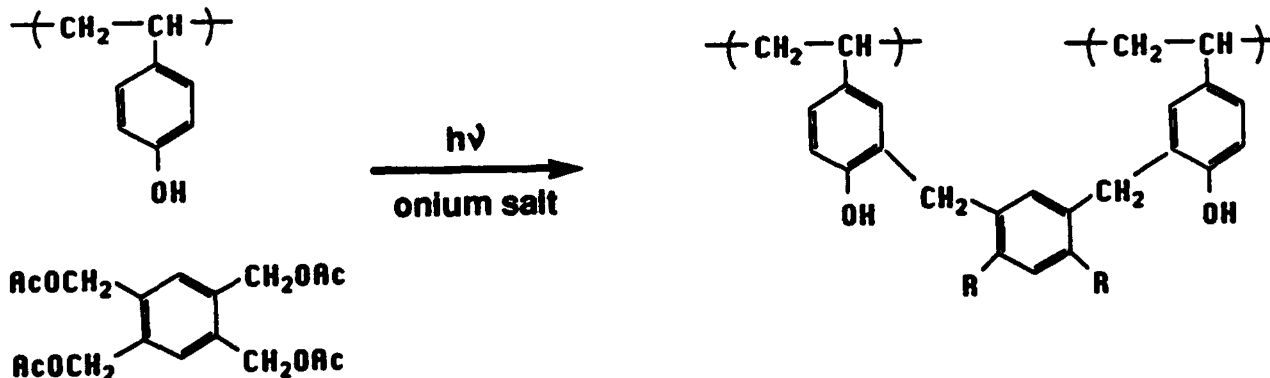


Figure 2. Photocrosslinking of poly(4-hydroxystyrene) using a polyfunctional reagent.

However the crosslinking reaction also results in an induced change in permeability of the resist film to external reagents. Therefore, a silylating reagent such as HMDS is

only able to penetrate effectively those areas of the film that are not crosslinked resulting in incorporation of silicon, as trimethylsilyloxy groups, only in the unexposed areas of the resist. Dry-development with an oxygen plasma is therefore possible as a thin coating of refractory silicon dioxide forms at the surface of those areas of the resist that have been silylated, protecting them from further etching, while the unsilylated areas are etched away. Overall, this process affords a positive-tone image with very steep vertical sidewalls.

Numerous processing variables such as the silylation time, silylation temperature, as well as the partial pressure of silylating reagent in the reaction chamber have a great effect on the quality of the final images.

In particular, it is not necessary to effect complete silylation of the unexposed areas of the polymer film as incorporation of silicon in the top surface is sufficient to protect the underlaying material. The gas-phase silylation process is effectively monitored by FT-IR techniques as shown in Figure 3. The increase in the absorption bands at 845 and 920 cm^{-1} can be used to quantify the extent of silicon uptake. Although Figure 3 shows silylation times of up to two hours at a constant pressure of HMDS of 120 torrs and at 100°C, a silylation time of 3-5 min was found to be sufficient in top surface imaging conditions to provide for good oxygen plasma etch selectivity.

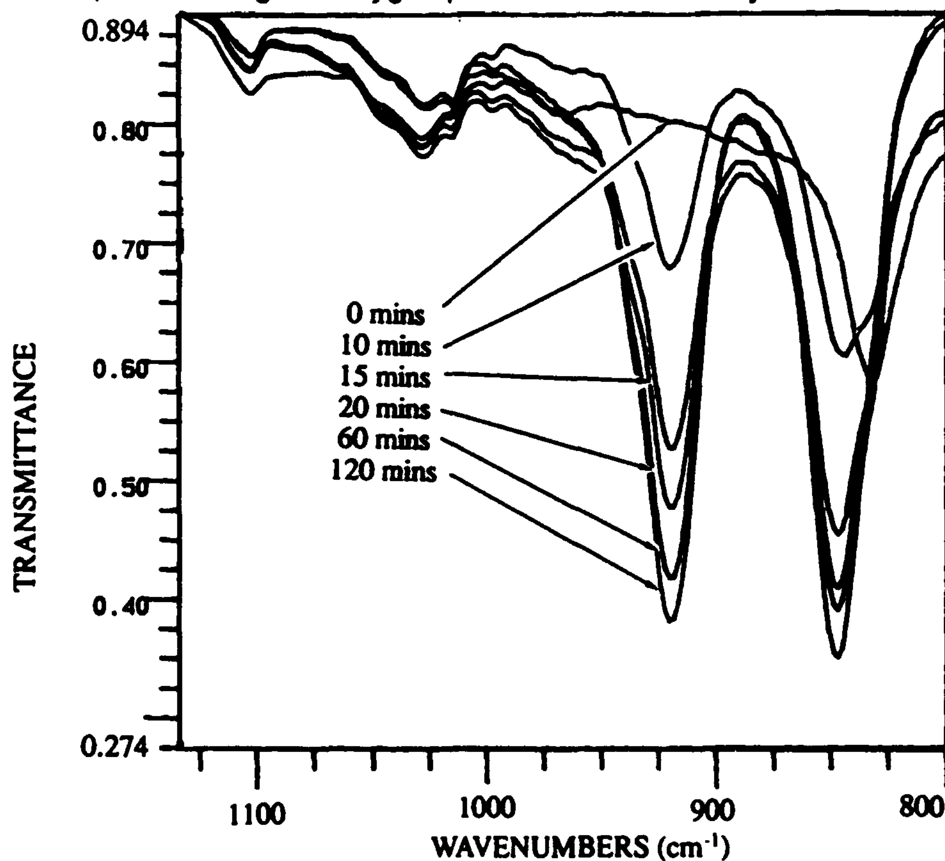
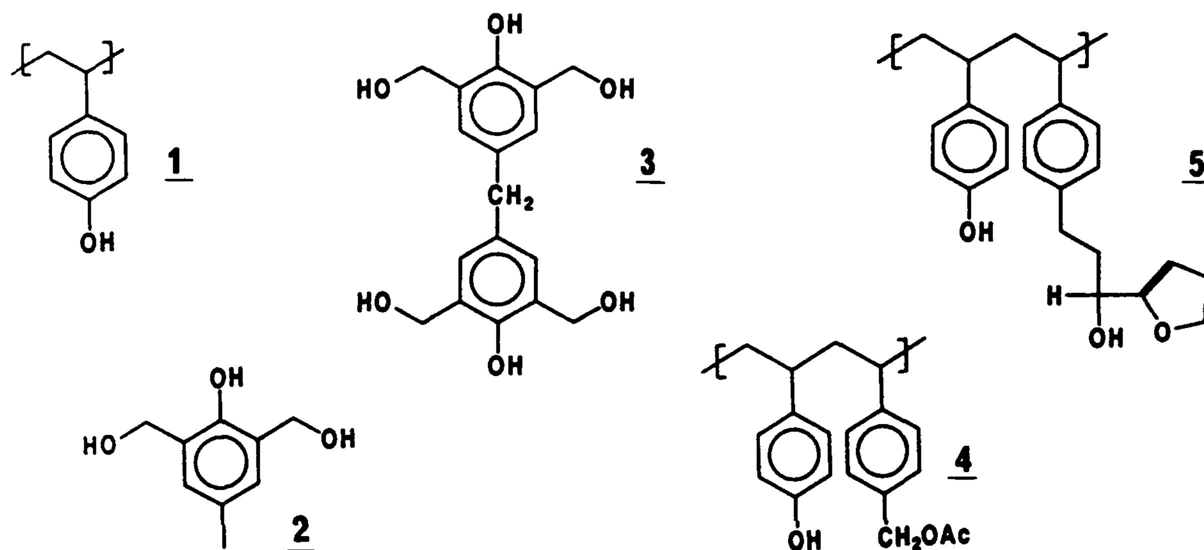


Figure 3. Silicon uptake as a function of silylation time (100°C @ 120 torrs HMDS).

The same principles can be applied to a great variety of three-component resists based on a photoacid generator, poly(4-hydroxystyrene) 1 or novolac, and a polyfunctional latent electrophile [19]. For example, a chemically amplified negative resist with a sensitivity higher than 0.1 mJ/cm^2 at 254 nm is obtained using a combination of 1 with a photoacid generator and phenolic crosslinkers 2 or 3. As was the case for the resist shown above in Figure 2, image reversal with dry development is possible through silylation of the crosslinked polymer obtained after exposure to UV light and post-baking.



A two-component system may also be used to achieve image reversal and dry development through silylation of a lightly crosslinked polymer containing free phenol or alcohol groups. Therefore, polymers 4 and 5 which contain activated aromatic rings, free hydroxyl groups, and latent electrophiles, are readily crosslinked upon irradiation under conditions that produce and acid within the exposed areas of the polymer film. This process, outlined in Figure 4, has been used to produce negative images using deep-UV, E-beam, or X-ray radiation [8, 20].

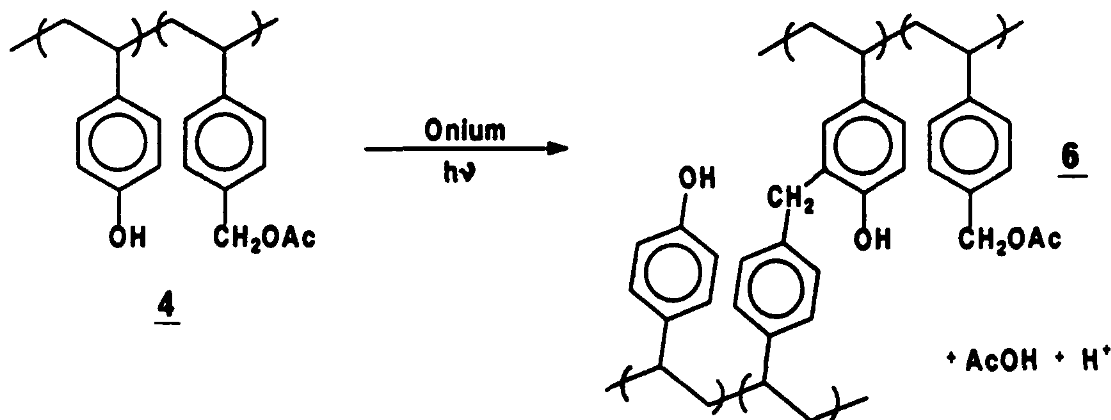


Figure 4. Chemically amplified photocrosslinking of two-component resist system.

With both polymers **4** and **5**, gas-phase silylation following post-exposure bake leads to incorporation of silicon into the unexposed areas of the polymer film due to the higher permeability of the resist in its non-crosslinked areas. Oxygen plasma etching following the silylation process affords excellent images with good sidewall profiles. Figure 5 shows positive-tone images obtained with resist **4** containing 80% 4-hydroxystyrene repeating units and triphenylsulfonium hexafluoroarsenate as the photoacid generator. These images were obtained using a top-surface imaging process with gas-phase silylation (HMDS at 200 torrs, 70°C, 2 min.) after post-exposure bake at 90°C for 1.5 min. Exposure was done at 248nm with a dose of 3mJ/cm^2.

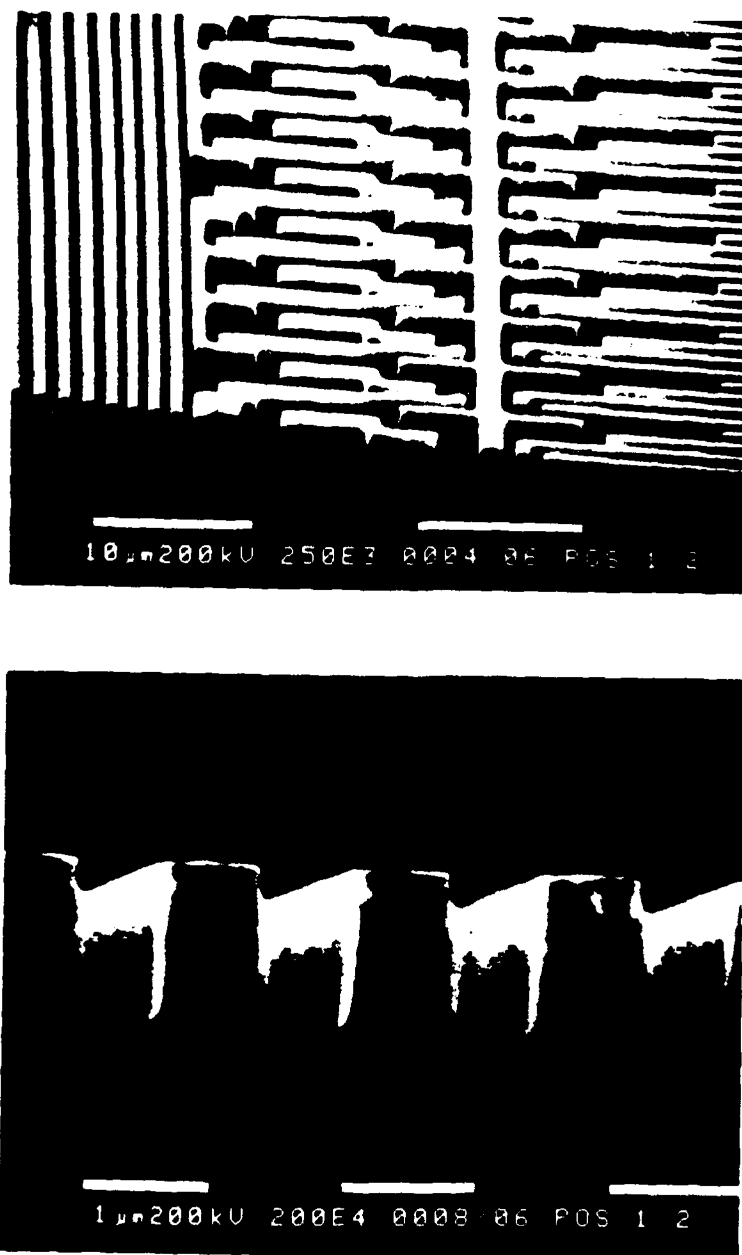
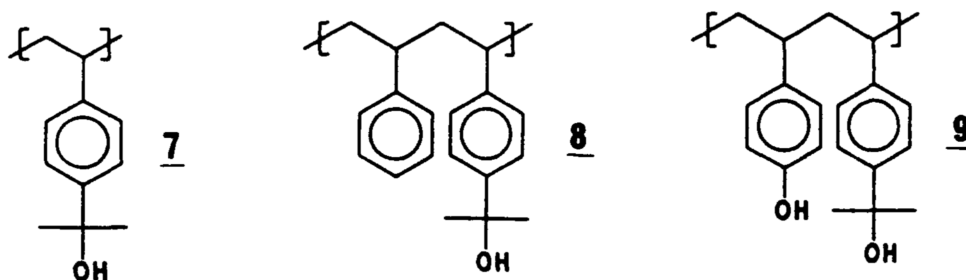


Figure 5. Dry-developed images obtained by top-surface imaging / silylation of resist **4**.

Resists based on polymers 7, 8, and 9 also operate on the basis of chemical amplification with electrophilic crosslinking. Structures 7 and 8 have been used earlier in the preparation of comb polymers via living cationic polymerization processes [21].



This early work had shown that in the presence of strong acid polymers 7 and 8 lost water readily and afforded a crosslinked product as shown in Figure 6. In the case of copolymer 8 the crosslinking reaction is predominantly due to an electrophilic aromatic substitution process similar to that observed with polymer 4. Protonation on oxygen results in the loss of water with formation of a stabilized tertiary benzylic carbocationic intermediate that can eliminate to the isopropenyl structure 10 or alkylate a neighboring aromatic ring in a crosslinking process. Since both processes result in regeneration of a proton, chemical amplification is achieved.

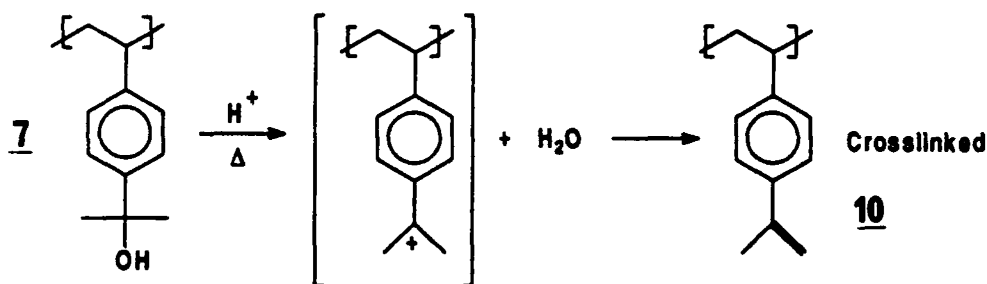


Figure 6. Acid-catalyzed dehydration and crosslinking of polymer 7.

When formulated with an onium salt or similar photoacid generator, copolymer 8 containing a high proportion of the tertiary alcohol moiety is a useful chemically amplified resist material with high sensitivity. Irradiation of a film of the resist followed by post-bake at 125°C for 3 min. results in loss of water as well as crosslinking of the polymer (Figure 7). Image reversal by gas-phase silylation is also possible in this case as the unexposed polymer contains a large amount of hydroxyl groups while the exposed polymer is both dehydrated and crosslinked. In an attempt to improve the quality of images obtained with this family of materials, resists based on structure 9 are under investigation.

It should be emphasized here that structure 12, shown for the crosslinked product obtained after exposure and post-bake, is only a schematic representation of one of the several types of crosslinking processes that are believed to occur upon heating of resist 8 and photogenerated acid. Other crosslinking processes involving the double bonds, obtained upon loss of water and subsequent deprotonation of intermediate 11, are also possible depending on the exact reaction conditions, including the post-bake temperature, as well as the copolymer composition. The facile sequence of reactions involved with this type of imaging material provides for a very high sensitivity. For example, doses well below 0.5mJ/cm^2 are sufficient to image polymer 8 in the negative-tone, though image quality is affected by some swelling in the case of solvent developed systems.

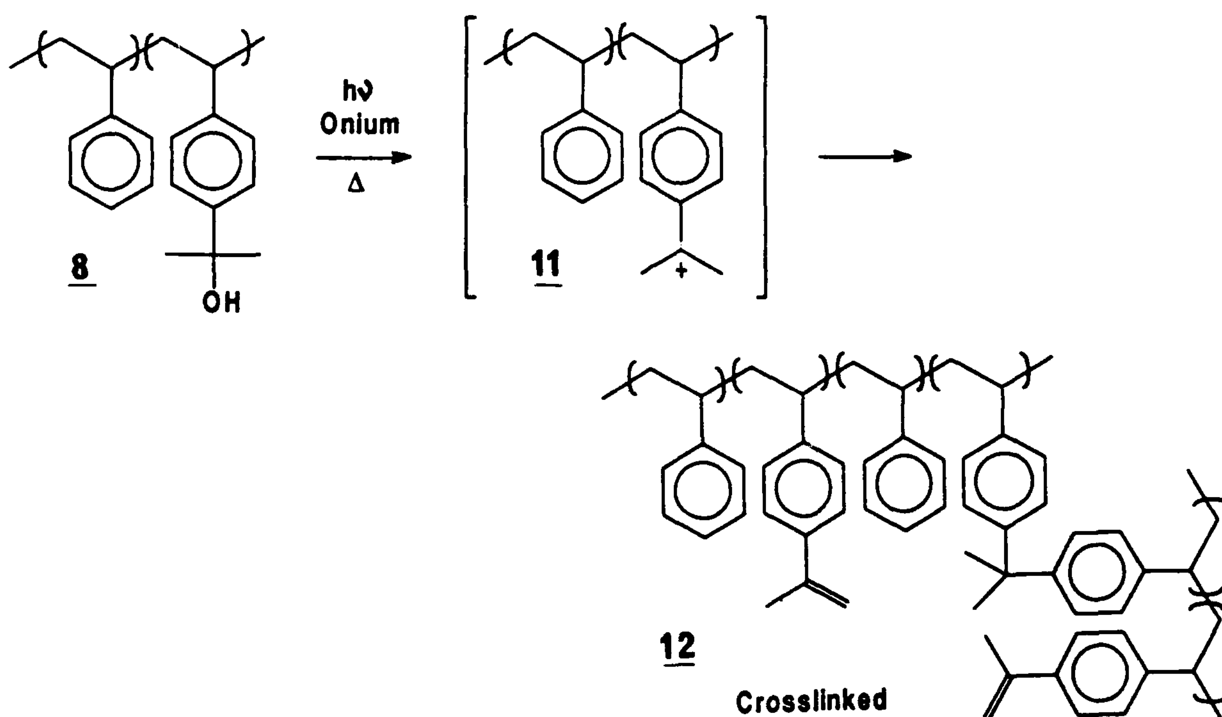


Figure 7. Chemically amplified resist based on copolymer 8

Finally, we have also explored a totally different electrophilic reaction involving the isomerization of an O-alkylated benzyl phenyl ether into the corresponding C-alkylated phenol as an imaging process [20]. The basic design of this family of imaging materials shown in Figure 8 would also apply to analogous novolac-based ethers and partially etherified systems.

Once again, formulation of the resist requires that polymer 13 be used in combination with a triarylsulfonium salt or another suitable photoacid generator. Exposure to radiation (UV, E-beam or X-ray) causes the release of protons within the polymer film with protonation of the ether groups leading to 14. The electrophilic isomerization of 14 into

15 occurs during the post-bake step as the activation energy necessary for this thermal process becomes available. C-alkylation of the aromatic ring proceeds with release of a proton providing for chemical amplification. This simple system is suitable for the production of both negative and positive-tone images using solvent development with appropriate developers [20]. In both modes of imaging, sensitivities of the order of 2 mJ/cm^2 have been obtained. Negative-tone images can also be obtained with dry-development through silylation of the exposed and post-baked material to vapors of hexamethyldisilazane. Silylation occurs only in those areas of the film that have undergone isomerization to the free phenolic structure 15, while unexposed areas of the film (structure 13) remain totally unaffected by the silylating agent. Following HMDS treatment, oxygen plasma etching of the resist film affords a negative-tone image as the silylated areas of the film (structure 16) are not etched away, while unexposed areas are removed under the action of the oxygen plasma.

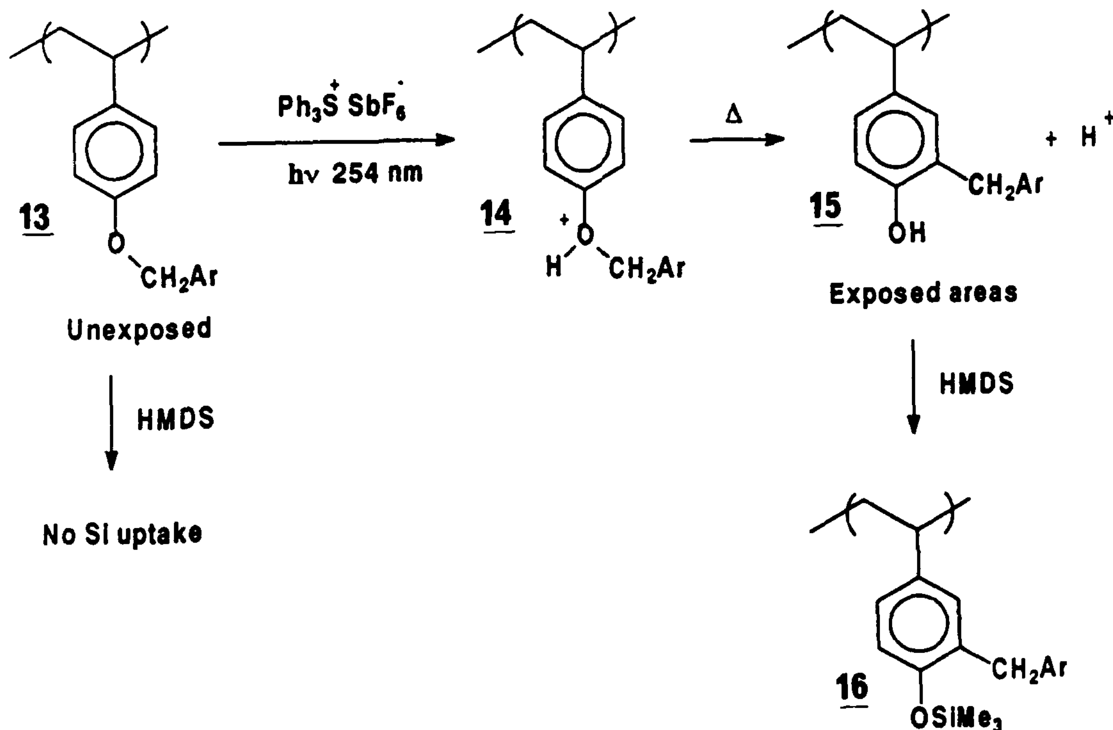


Figure 8. Acid-catalyzed electrophilic isomerization of phenyl benzyl ethers.

4. Conclusion.

All of these examples have demonstrated the versatility of the resist designs based on acid-catalyzed electrophilic processes. Extremely high sensitivity materials are obtained as the various processes are chemically amplified. In all cases, the protons which

are responsible for the initial formation of electrophilic moieties are regenerated in the alkylation, dehydration, or isomerization step. While the structures shown have all involved polymers or copolymers containing 4-hydroxystyrene, application to novc ,ac or other phenolic-type resins are easily implemented.

All of these systems are also well suited for top surface imaging via gas phase silylation using a simple reagent such as HMDS to introduce silicon, either in the exposed areas, or in the unexposed areas of the resist film. In those cases where crosslinking is observed, selective silylation results from differences in permeability of the crosslinked and non-crosslinked areas of the films. The availability of the highly anisotropic dry-development process via oxygen plasma etching provides for high resolution images. We are currently refining the chemistry and processing conditions for a number of these systems and our detailed results will be reported elsewhere.

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