Three-Component Negative-Type Photoresist Based on Calix[4]resorcinarene, a Cross-linker, and a Photoacid Generator

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A negative-working photoresist based on calix[4]resorcinarene (C-4-RA), 4,4′-methylenebis-[2,6-bis(hydroxymethyl)phenol] (MBHP) as a cross-linker, and a photoacid generator diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) has been developed. A clear transparent film was obtained from a 25 wt % C-4-RA solution in 2-methoxyethanol. The photoresist consisting of C-4-RA (65 wt %), MBHP (25 wt %), and DIAS (10 wt %) showed a sensitivity of 4.3 mJ/cm^2 and a contrast of 2.9 when it was exposed to 365 nm light and postbaked at 120 °C for 3 min, followed by developing with a 0.1% aqueous tetramethylammonium hydroxide solution at room temperature. The mechanistic study on the formation of images is also discussed.

Introduction

Significant advances have been made in microelectronic technology during the past decade, where radiation-sensitive polymeric materials called "resists" play an important role to produce circuit patterns in substrates.[1]

Now, the 64-Mbit DRAM has been produced in microelectronic industries. Resists consisting of a classical cresol−formaldehyde novolac resin and diazonaphthoquinone (DNQ) have been the workhorse because of their high resolution, high thermal stability, and resistance to dry-etching conditions. The lithographic performance of these resists is profoundly affected by many factors originated from the undefined structures and the wide molecular weight distributions of novolac resins.[2] Therefore, the optimum resist performance is obtained with a complex mixture of different structures and molecular weight novolac resins.

In contrast to novolac resins, macrocyclic oligomers obtained by the reaction of phenols with aldehyde, called "calixarenes", have definite linkages and molecular weights.[3] We are interested in calixarenes for resist materials as the substitute of novolac resin to create monodisperse materials. Recently, hexaacetate *p*-methylcalix[6]arene was successfully used as a high-resolution negative resist in electron beam lithography.[4]

Calixarenes are generally high-melting compounds, insoluble in water and only sparingly soluble in organic solvents. However, a variety of calix[4]resorcinarenes have been reported to have a good solubility in organic solvents and aqueous alkaline solutions.[5]

Recently, we reported a three-component negative-type photoresist based on calix[4]resorcinarene (C-4-RA), 4,4′-methylenebis[2,6-bis(hydroxymethyl)phenol] (MBHP) as a cross-linker, and a photoacid generator diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS).[6] This allows us to develop photoresists with a broad variation of matrixes.

In this paper, we report detailed studies on the preparation and the lithographic evaluation of this three-component negative-working photoresist.

Experimental Section

Materials. Calix[4]resorcinarene (C-4-RA) was prepared by the reaction of resorcinol with acetaldehyde according to the reported procedure and crystallized from methanol.[7] The yield was 50%. IR (KBr): ν 3425 (OH), 1200 cm^{-1} (C−O−C). ^{1}H NMR (DMSO-d_6): δ 1.30 (d, CH$_3$, 12H), 4.44(q, CH, 4H), 6.14 (s, ArH, 4H), 6.76 (s, ArH, 4H), and 8.55(s, OH, 8H). FAB-MS: m/e (%) = 544 (M$^+$, 29).

4,4′-Methylenebis[2,6-bis(hydroxymethyl)phenol] (MBHP) was prepared by the reaction of phenol with formaldehyde in water.[8] The yield was 22%. IR (KBr): ν 3310 (OH), 1211 cm^{-1} (C−O). H NMR (DMSO-d_6): δ 3.70 (s, Ar−CH$_2$−Ar, 2H), 4.50 (d, Ar−CH$_2$−OH, 8H), 5.21 (t, OH, 4H), 6.96 (s, ArH, 4H), and 8.34 (s, OH, 2H). FAB-MS: m/e (%) = 320(M$^+$, 29).

Diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) was prepared by the reaction of diphenyliodonium chloride with sodium 9,10-dimethoxyanthracene-2-sulfonate, which was obtained by the reduction of sodium anthraquinone-2-sulfonate with zinc and aqueous sodium hydroxide solution, followed by the methylation with dimethyl sulfate.[9] The yield was 50%. IR (KBr): ν 2940, 2845 (C−H), 1200 cm^{-1} (C−O−C). ^{1}H NMR (DMSO-d_6): δ 4.00 (s, CH$_3$, 6H), 7.65−7.80 (m, ArH, 9H), 8.24 (m, ArH, 7H), 8.50 (s, ArH, 1H).

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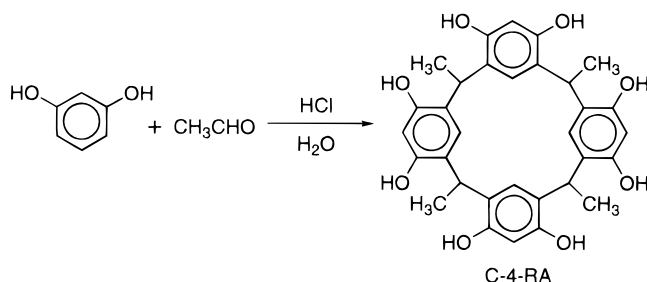(5) Weiner, F.; Schneider, H.-J. *J. Org. Chem.* **1991**, *56*, 5527.
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Scheme 1

C-4-RA

2,4-Dimethyl-6-(hydroxymethyl)phenol (DHP) was prepared from 2,4-dimethylphenol and formaldehyde according to the reported procedure.[10] The yield was 65%. IR (KBr): ν 3402 (OH), 2924(C−H), 1211 cm^{-1} (C−O−C). ^{1}H NMR (DMSO-d_6): δ 2.11, 2.16 (s, CH$_3$, 6H), 4.52 (s, Ar−CH$_2$−OH), 5.22 (s, OH, 1H), 6.77, 6.85 (s, ArH, 2H), 8.15 (s, OH, 1H).

Photosensitivity. C-4-RA was dissolved at 20 wt % in 2-methoxyethyl ether at room temperature, and to this solution were added MBHP and DIAS. Films spin-cast on silicon wafers were prebaked at 80 °C for 10 min and exposed through a filtered super-high-pressure mercury lamp (Ushio USH-200DP). Imagewise exposure through a mask was carried out in a contact-printing mode.

Dissolution Rate. The 1 μm films on a silicon wafer were exposed at 365 nm wavelength to the filtered super-high-pressure mercury lamp, developed in 0.1% aqueous tetramethylammonium hydroxide (TMAH) solution at room temperature, and rinsed in water. The characteristic curve of the normalized film thickness versus exposure energy was obtained.

Model Reaction. C-4-RA (65 wt %), DHP (25 wt %), DIAS (10 wt %) were dissolved in 2-methoxyethanol. The solution was spin-coated onto a silicon wafer and exposed to 365 nm UV light (60 mJ/cm²), followed by heating at 120 °C for 3 min. The sample was dissolved in DMSO-d_6 and analyzed by ^{1}H NMR spectroscopy.

Measurement. The infrared spectra were recorded on a HORIBA FT-210 spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL EX 270 spectrometer. UV spectra were obtained on a JASCO V-560 spectrophotometer. The film thicknesses were measured by a Dectak 3030 system (Vecco Instruments Inc.).

Results and Discussion

Preparation of Calix[4]resorcinarene. Calix[4]-resorcinarene (C-4-RA) was prepared by the condensation of resorcinol and acetaldehyde in aqueous hydrochloric acid at 75 °C and was recrystallized from methanol (Scheme 1).[7]

C-4-RA can in principle exist in the four possible configurations formulated cis−cis−cis, cis−cis−trans, cis−trans−trans, and trans−cis−trans. The obtained C-4-RA was confirmed to have all-cis configuration by a ^{1}H NMR spectrum on the basis of the previous report.[11]


Cis-Cis-Cis
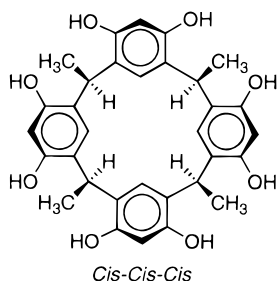
C-4-RA showed good solubility in organic solvents such as dipolar aprotic solvents, acetone, and especially in alcohols at room temperature.

The formation of film and the dissolution behavior of C-4-RA film toward an alkaline solution were studied. C-4-RA was dissolved in 25 wt % in 2-methoxyethanol at room temperature and then spin-coated on a Si wafer. The wafer was prebaked (100 °C for 5 min) to remove the residual solvent. The clear transparent film was obtained and dissolved completely in a 0.1% aqueous tetramethylammonium hydroxide (TMAH) solution at room temperature for 5 s. This solubility of the C-4-RA film toward the 0.1% aqueous TMAH solution was too high to obtain a positive-working photoresist combining with a dissolution inhibitor such as DNQ.

Thus, we decided to develop a negative-working alkaline developable photoresist based on C-4-RA, a cross-linker, and a photoacid generator.

Lithographic Evaluation. The UV spectrum of C-4-RA film is shown in Figure 1. C-4-RA has two strong absorptions at 216 and 285 nm due to $\pi-\pi^*$ transitions and is almost transparent around 250 nm and above 300 nm. Furthermore, this UV spectrum is a very similar to that of novolac resins.

Many onium salts, such as diaryliodonium and triarylsulfonium salts, are well-known as photoacid generators. However, there are few onium salts that have an absorption band at wavelengths longer than 300 nm.[12] In the previous papers, diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS) was successfully applied to the formulation of a positive photoresist composed of bisphenol A protected with a *tert*-butoxycarbonyl group and a novolak resist matrix[13] and a negative photoresist based on poly(hydroxyimide) and a cross-linker.[14] Thus, we decided to employ DIAS having a strong absorption in the range of 300−450 nm as the photoacid generator.

DIAS
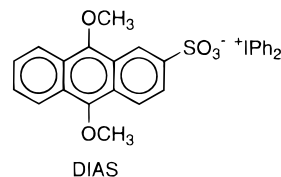
Various cross-linkers are successfully used in the chemical-amplification negative resist system. Recently, Fréchet et al. reported that polyfunctional benzylic alcohols act as good cross-linkers for poly(4-hydroxystyrene) in the presence of acid.[15] On the basis of availability and the sensitivity, 4,4′-methylenebis[2,6-bis(hydroxymethyl)phenol] (MBHP) was selected.

MBHP
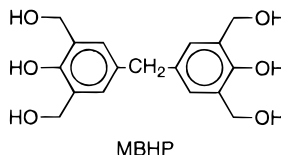
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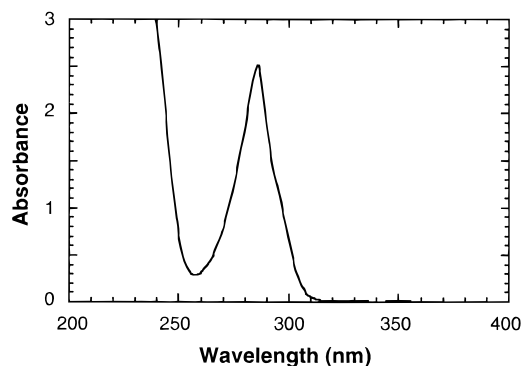(14) Ueda M.; Nakayama, T.*Macromolecules* **1996**, *29*, 6427.

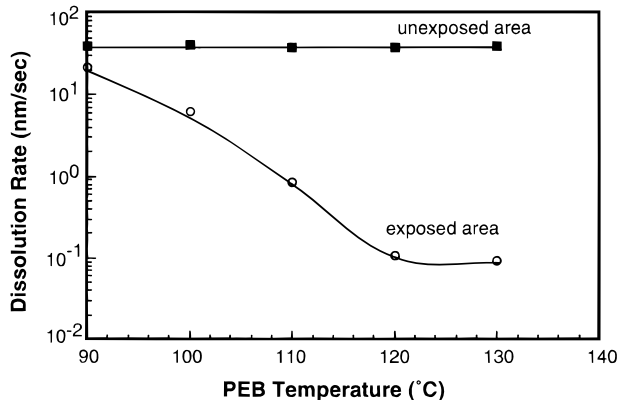**Figure 1.** The UV spectrum of C-4-RA film (0.8 μm).

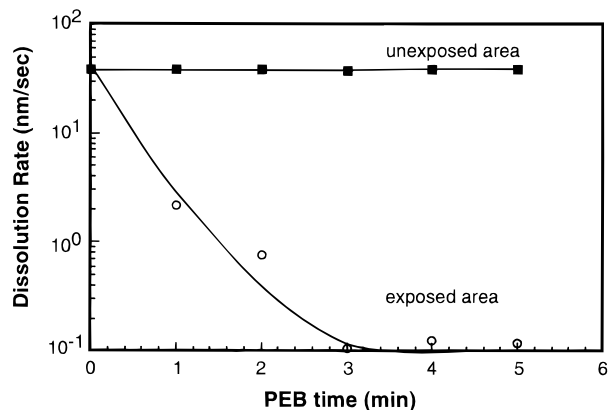**Figure 2.** The effect of postexposure bake temperature on the dissolution rate.

Figure 3. The effect of postexposure bake time on the dissolution rate.

Figure 4. The effect of MBHP loading on the dissolution rate.

Figure 5. Exposure characteristic curve for the system of C-4-RA, BHMP, and DIAS.

Figure 6. A scanning electron micrograph of negative image contact-printed in the resist.

To investigate the dissolution behavior of exposed and unexposed areas, the effects of the postexposure bake (PEB) temperature and PEB time on the dissolution rate were studied. The dissolution rate was estimated by measuring the film thickness after the development. The results in the case of the resist formulated by mixing C-4-RA (65 wt %), MBHP (25 wt %), and DIAS (10 wt %) in 2-methoxyethyl ether are shown in Figure 2, where the film was exposed to 365 nm UV light of 20 mJ/cm^2 intensity, postbaked at ambient temperature for 3 min, and developed with the 0.1% aqueous TMAH solution. The dissolution rate of the exposed part decreased with increasing PEB temperature. On the other hand, the solubility of unexposed area was 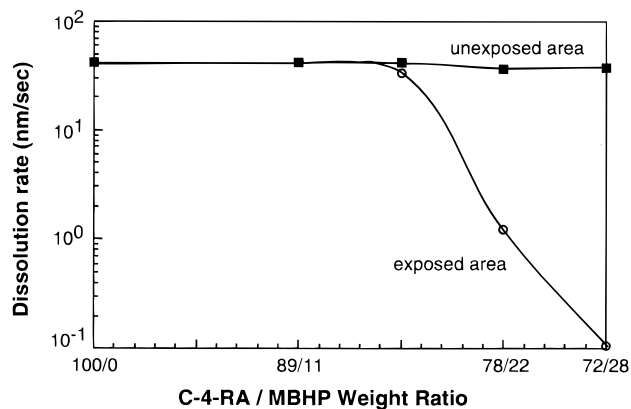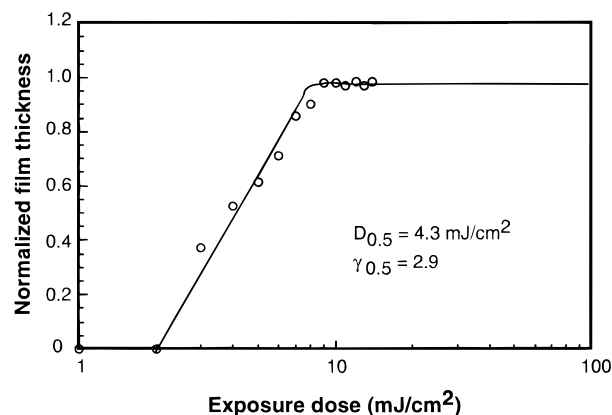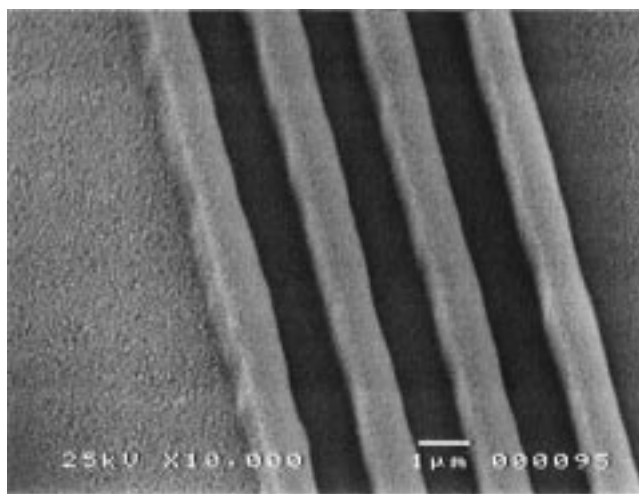almost unchanged. The difference of the dissolution rates between exposed and unexposed parts reached about 400 times after at 120 °C for 3 min. Then, the effect of PEB time on the dissolution rate in 0.1% aqueous TMAH solution after exposure at 20 mJ/cm^2 and PEB at 120 °C was studied (Figure 3). The high dissolution contrast was obtained after 3 min PEB treatment. These results suggest that PEB treatment promotes the cross-linking reaction due to electrophilic aromatic substitution.
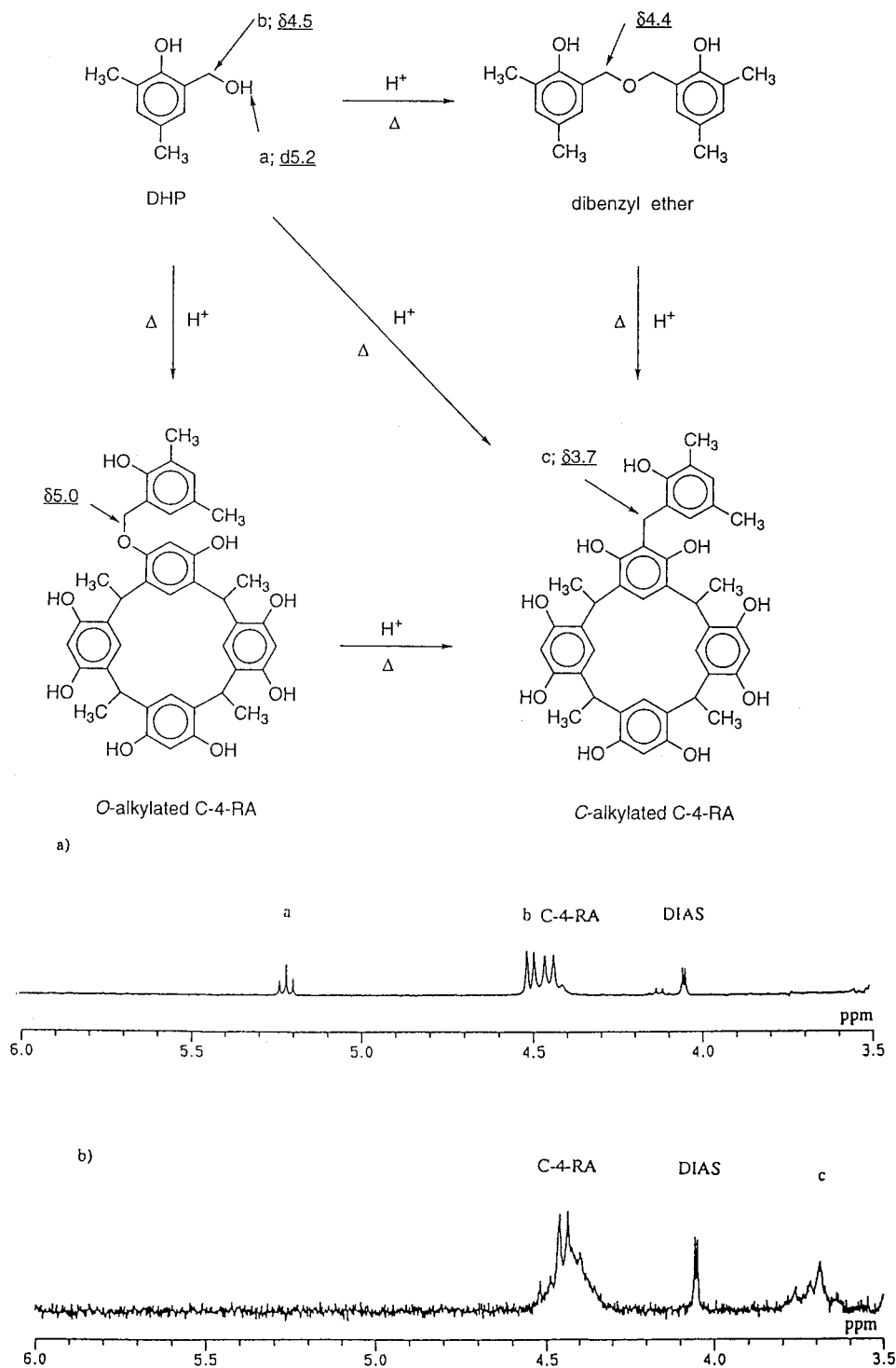
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Figure 7. ^{1}H NMR spectra of model study with C-4-RA, DHP, and DIAS: (a) unexposed film, (b) exposed and postbaked film.

The effect of the MBHP loading on the dissolution rate in the 0.1% aqueous TMAH solution after the exposure at 20 mJ/cm^2 and PEB at 120 °C for 3 min was investigated. The results are shown in Figure 4. It was found that a 25 wt % MBHP loading was necessary to achieve an adequate dissolution contrast.

After these preliminary optimization studies involving MBHP loading, PEB temperature, and PEB time, we formulated a resist system consisting of C-4-RA (65 wt %), BHMP (25 wt %), and DIAS (10 wt %) in 2-methoxyethyl ether. The film spin-cast on silicon wafer was prebaked at 80 °C for 10 min (thickness of 1 μm), ex-

posed to 365 nm UV radiation, postbaked at 120 °C for 3 min, and developed in a negative mode with the 0.1% aqueous TMAH solution at room temperature. The sensitivity curve (Figure 5) was consistent with the dissolution behavior studied above, indicating that the sensitivity ($D^{0.5}$) and contrast ($\gamma^{0.5}$) were 4.3 mJ/cm^2 and 2.9, respectively.

Figure 6 presents a scanning electron micrograph of the contact-printed image that was obtained using the resist described above after exposure to 15 mJ/cm^2, PEB at 120 °C for 3 min, and developing with the 0.1% aqueous TMAH solution. The clear negative pattern

Scheme 2

DIAS

MBHP

C-4-RA

Cross-linked C-4-RA
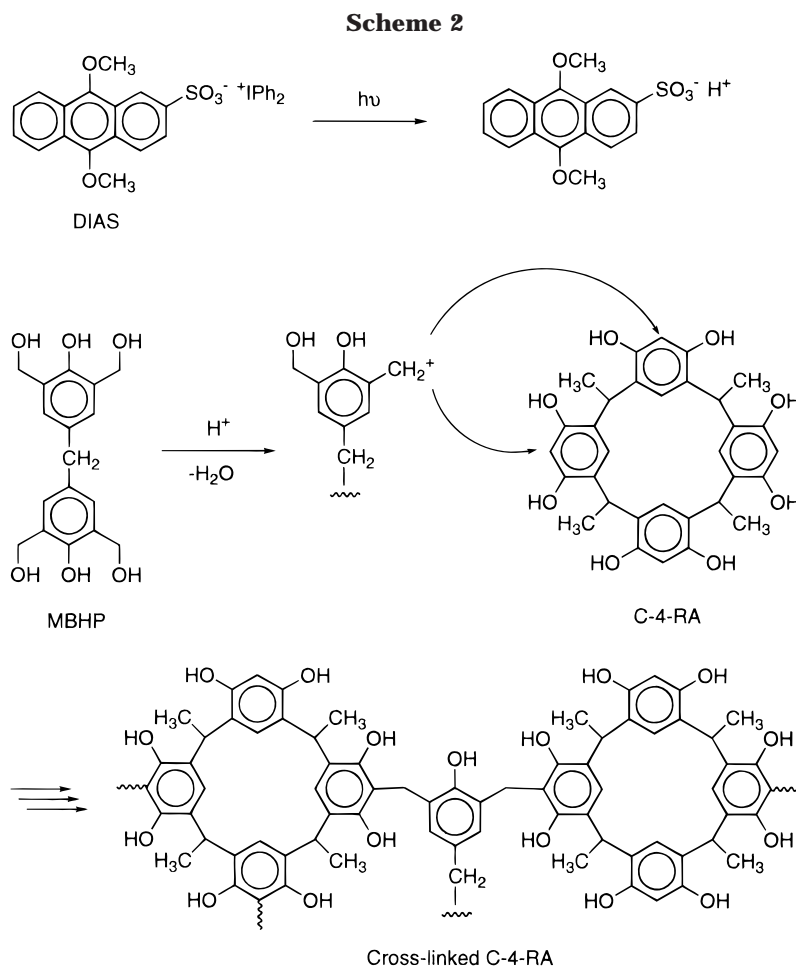
with 1 μm resolution, which is the limitation of our exposure system, was obtained.

Mechanism of the Acid-Catalyzed Cross-Linking. The mechanism of the acid-catalyzed cross-linking of a photoresist based on poly(hydroxystyrene) and polyfunctional benzylic alcohols was studied by ^{1}H NMR spectroscopy and proposed to proceed via a direct *C*-alkylation as well as an initial *O*-alkylation, followed by a subsequent acid-catalyzed rearrangement to the final alkylated product.[16]

To ascertain the mechanism of the acid-catalyzed cross-linking, a model reaction was carried out using C-4-RA (65 wt %), a monofunctional benzyl alcohol, 2,4-dimethyl-6-(hydroxymethyl)phenol (25 wt %, DHP), and DIAS (10 wt %). This solution in 2-methoxyethanol was spin-coated on to a silicon wafer, prebaked at 80 °C for 10 min, and then irradiated at 365 nm light with the exposure dosage of 60 mJ/cm². The exposed sample was then heated at 120 °C for 3 min, and the resulting resist was analyzed by ^{1}H NMR spectroscopy (Figure 7). The unexposed film showed two peaks due to the hydroxy and methylene protons of the benzylic alcohol at 4.5 and 5.2 ppm, respectively. In the film exposed at 365 nm and heated at 120 °C, these peaks derived from DHP decreased rapidly, and several peaks appeared around 3.7 ppm. These peaks were assigned to the benzyl

protons of *C*-alkylated C-4-RA based on the assignment of a previous paper.[16] On the other hand, the peaks (around 4.9 ppm) due to methylene protons in the *O*-alkylated product were not observed. The methylene protons of benzyl ether formed by self-condensation of DHP would be overlapped with the methine protons of C-4-RA.

These experiments show that a photogenerated acid catalyzes the formation of benzylic carbocation species, which undergo electrophilic aromatic substitution to produce *C*-alkylated polymers. This reaction converts soluble C-4-RA to insoluble cross-linked polymers (Scheme 2).

Conclusions. We have successfully designed a new monodisperse material as a matrix for photoresists. That is, the new negative-working photoresist was formulated by mixing C-4-RA (65 wt %), MBHP (25 wt %) as the cross-linker, and the photoacid generator DIAS (10 wt %), and it was found to be an alkaline-developable negative-type photoresist. As various calixarenes are now available, an interesting new photoresist based on calixarenes and their analogues will be developed in near future.

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