A Negative-Working Alkaline Developable Photoresist Based on Calix[4]resorcinarene, a Cross-linker, and a Photoacid Generator

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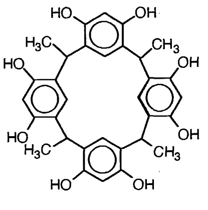
A negative working photoresist based on calix[4]resorcinarene, 4,4'-methylenebis[2,6-bis(hydroxymethyl)phenol] (MBHP) as a cross-linker, and a photoacid generator, diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS), has been developed. A clear negative pattern was obtained when it was exposed to 365 nm UV light and postbaked at 130 °C, followed by developing with a 0.5% aqueous tetramethylammonium hydroxide solution at room temperature.

The microelectronics technology has shown an astounding progress for the past decade, where radiation-sensitive polymeric materials called "resist" play an important role to produce circuit patterns in substrates.[1] The classical diazonaphtoquinone/novolac resist is still the "workhorse" of the microelectronics industry. The lithographic performance of the resist is profoundly affected by the molecular weight distribution of novolac resin.[2] The optimum resist performance was obtained with a complex mixture of different molecular weights novolac fractions.

In contrast to novolac resins, cyclic oligomers of phenols derived from the condensation *p*-alkyl phenols with formaldehyde, called "calixarenes" have definite molecular weights.[3] We are interested in calixarenes for resist materials as the substitute of novolac resin because of monodisperse materials. Quite recently, *p*-methylcalix[6]arene hexaacetate 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 has been reported to have a good solubility for organic solvents and aqueous alkaline solution.[5] So, we decided to use calix[4]resorcinarenes as the matrix material.

In a previous paper, we reported a new negative working photosensitive polyimide based on poly(hydroxyimide) (PHI), 2,6-bis(hydroxymethyl)-4-methylphenol (BHMP) as cross-linker, and photoacid generator, diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate (DIAS).[6] This finding promoted us to employ the approach for the development of the new negative working alkaline developable resist based on calix[4]resorcinarene (C-4-RA), because C-4-RA containing a hydroxyphenyl unit reacts easily with electrophilic benzyl carbocation.



C-4-RA

We now report the new negative working alkaline developable resist based on calix[4]resorcinarene.

Calixarene, C-4-RA was prepared by the condensation of resorcinol and acetaldehyde in water and is soluble in dipolar aprotic solvents, acetone and especially in alcohols at room temperature.[7]

The UV spectrum of C-4-RA in methanol (Figure 1) indicates that C-4-RA has two strong absorptions at 216 nm and 285 nm due to π-π* transitions and is almost transparent around 250 nm and above 300 nm. This means DIAS having a strong absorption in the range of 300-450 nm can be used as the photoacid generator.

In order to study on the formation of film and the dissolution behavior of C-4-RA film toward an alkaline solution, C-4-RA was dissolved in 25 wt% in 2-methoxyethanol at room temperature,

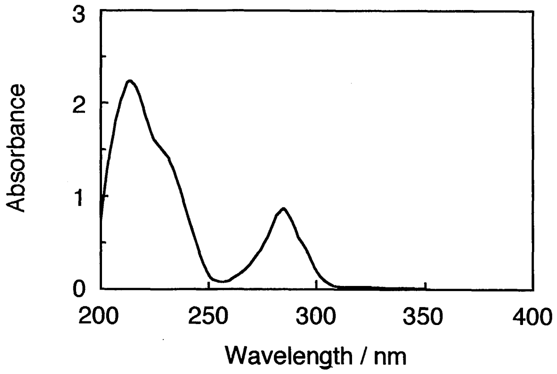


Figure 1. UV spectrum of C-4-RA in methanol. Sample concentration was 6.5×10^{-5} mol•l^{-1}.

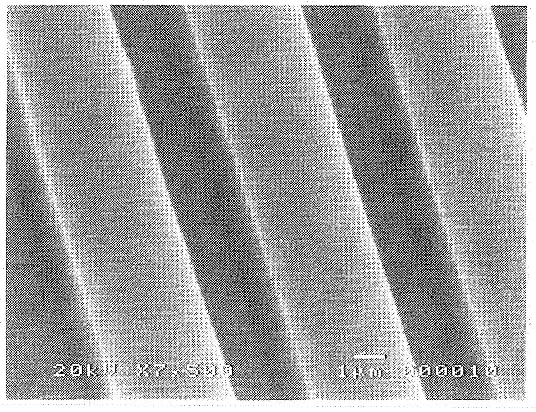
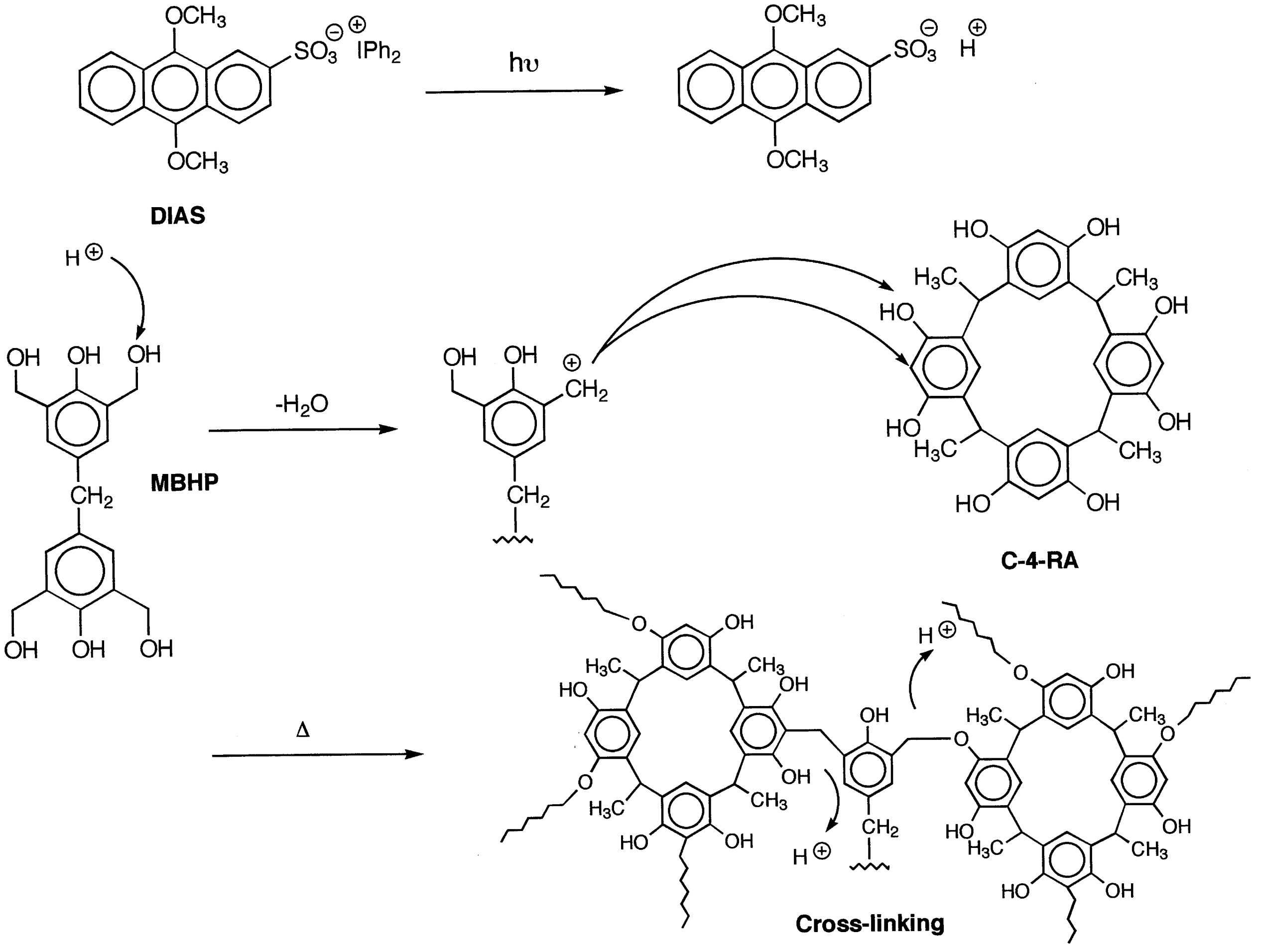


Figure 2. A scanning electron micrograph of negative image printed in the resist.



Scheme 1.

then spin-coated on Si wafer (thickness of 2 μm). Then the wafer was prebaked (100 °C for 5 min) to remove the residual solvent. The resulting clear transparent film was dissolved completely in 0.1 % tetramethylammonium hydroxide (TMAH) at room temperature for 5 sec.

Then we formulated a resist consisting of C-4-RA (70 wt%), 4,4'-methylenebis[2,6-bis(hydroxymethyl)phenol] (MBHP) (22 wt%), and DIAS (8 wt%) in 2-methoxyethyl ether. The film spin-cast on silicon wafer was prebaked at 80 °C for 10 min (thickness of 2 μm), exposed 200 mJ/cm^2 to 365 nm UV radiation, postbaked at 130 °C for 2 min, and developed in a negative mode with 0.5% TMAH aqueous solution at room temperature.

Figure 2 shows a scanning electron micrograph of the contact-printed image. The clear negative pattern was obtained.

The mechanism of this negative pattern formation is outlined in Scheme 1.

A photogenerated acid catalyzes the formation of benzylic carbocation species, which undergo electrophilic aromatic substitution to produce a C- and O-alkylated polymers. This reaction converts the soluble C-4-RA to insoluble cross-linked polymer.[6]

To achieve an excellent resolution, a more detailed optimization study involving MBHP and DIAS loading, and pre- and post bake conditions is in progress.

References and Notes

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