

High-Resolution Negative Photoresists Composed of Phenolic Resin and Aromatic Azide

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(Received October 31, 1986)

ABSTRACT: A group of negative photoresists has been developed by sensitizing poly(vinylphenol), or more exactly, poly(*p*-hydroxystyrene) with aromatic azides. The resists exhibit high resolution capability because they do not swell in aqueous alkaline developers. Examples of azides used are 3,3'-diazidodiphenylsulfone (I), 4-azidochalcone (II), 3-(*p*-azidostyryl)-5,5-dimethyl-2-cyclohexen-1-one (III), 3-(4-(*p*-azidophenyl)-1,3-butadienyl)-5,5-dimethyl-2-cyclohexen-1-one (IV), and 2-(*p*-azidostyryl)-4-benzylideneoxazolone (V). Sensitization of poly(vinylphenol) with I gives a deep UV resist. Photoresist composed of poly(vinylphenol) and II or III is suited for exposure to *i* line (365 nm) of mercury lamp. It resolves 0.6 μ m line and space patterns. When IV or V is used as a sensitizer, the resist is sensitive to visible light such as *g* line (436 nm).

KEY WORDS Photoresist / Poly(vinylphenol) / Aromatic Azide /

The minimum feature size of microelectronic devices has been steadily reduced and is now entering submicron region. Corresponding to this, the photoresists used to fabricate such devices are required to have a high resolution capability. As conventional positive-tone photoresists meet this requirement, they are now being used in large quantities to fabricate the most advanced semiconductor devices such as one-megabit dynamic random access memories.

Negative-tone photoresists composed of cyclized rubber and aromatic bisazide were used in semiconductor industry almost exclusively in the past. However, they are now being gradually replaced by positive photoresists, because the resolution capability of this type of negative photoresists is lower than that of positive photoresists.

The fact that the bisazide-rubber resist system has a relatively low resolution does not necessarily imply that all kinds of negative photoresists have lower resolutions. In the case

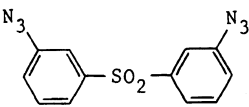
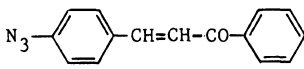
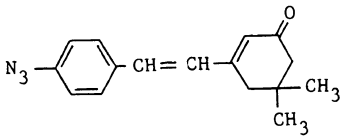
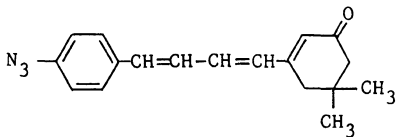
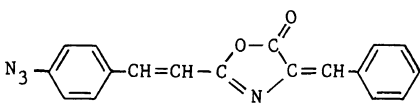
of bisazide-rubber resists system, the resolution can not be very high because of the swelling of photo-insolubilized resist films during development. However, this is not always the case. If a resist does not swell in a developer, its resolution can be high. A typical example for such resists is positive photoresist. Other examples are also found among negative photoresists.

The present paper outlines some examples of such high-resolution negative photoresists developed in our laboratory.

PHOTORESIST COMPOSITION

To formulate a photoresist which does not swell in a developer, one should use a polymer which dissolves in a developer without swelling. In the case of positive photoresist, cresol novolac is commonly used as a non-swelling polymer matrix. In our work, we used poly(vinylphenol), or more exactly, poly(*p*-hydroxystyrene). Like the novolac used in

Table I. Aromatic azides used as photosensitizers

No.	Structure	λ_{\max} in methanol or ethanol
I		240 nm
II		337 nm
III		346 nm
IV		368 nm
V		400 nm

positive photoresists, this polymer dissolves in an aqueous alkaline solution without swelling. The polymer was obtained from Maruzen Oil Company under the trade name of Resin M. Its weight-averaged molecular weight is 7000.

Aromatic azides used to sensitize the polymer, poly(vinylphenol), are exemplified in Table I together with their maximum absorption wavelengths in methanol or ethanol.

In most of our experiments, the resist solution was prepared by dissolving poly(vinylphenol) and azide in cyclohexanone. The weight ratio of azide to the polymer was 0.2, and the concentration of the polymer in the solution was 20 wt%.

PREPARATION OF AZIDES

3,3'-Diazidodiphenylsulfone (I in Table I) was obtained by diazotizing the corresponding diamine with nitrous acid, and converting the resulted tetrazonium salt into diazide by add-

ing sodium azide to the reaction mixture.

4-Azidochalcone (II) was obtained by Claisen condensation of *p*-azidobenzaldehyde with acetophenone in alcohol containing a small amount of sodium hydroxide as a catalyst.

3-(*p*-Azidostyryl)-5,5-dimethyl-2-cyclohexen-1-one (III) was obtained by Claisen condensation of *p*-azidobenzaldehyde with isophorone.

3-(4-(*p*-Azidophenyl)-1,3-butadienyl)-5,5-dimethyl-2-cyclohexen-1-one (IV) was obtained by Claisen condensation of *p*-azidocinnamaldehyde with isophorone.

2-(*p*-Azidostyryl)-4-benzylideneoxazolone (V) was obtained by condensation of *N*-*p*-azidocinnamoylglycine with benzaldehyde. This reaction is a modification of azlactone synthesis¹ where hippuric acid is condensed with benzaldehyde to give 2-phenyl-4-benzylideneoxazolone. The reaction was carried out in hot acetic anhydride containing a

small amount of sodium acetate as a catalyst. The azlactone synthesis is a very versatile reaction. By using this, we have synthesized a large number of azidoazlactones. Unfortunately, however, many of them are sparingly soluble in organic solvents.

PHOTOABSORPTION SPECTRA OF RESIST FILMS

We have developed several kinds of negative photoresists utilizing poly(vinylphenol) and aromatic azides described above. Transmission spectra of these resists are shown in Figure 1 together with that of poly(vinylphenol). The weight ratio of azide to polymer in each resist is 0.2, and the film thickness is 1 μm .

We named the photoresist comprising poly(vinylphenol) and azide I MRS,² which is an abbreviation of Micro Resist for Shorter wavelength. As seen in Figure 1, poly(vinylphenol) has a transmission window at about 250 nm, and azide I in MRS strongly absorbs the light around this wavelength. So that, MRS is sensitive to deep UV light in this window region.

The resist comprising poly(vinylphenol) and

azide II was named MRL,³ which is an abbreviation of Micro Resist for Longer wavelength. As seen in Figure 1, this resist strongly absorbs the light in near UV region, especially i line (at 365 nm) of mercury arc. It has been found that azide II is somewhat unstable in resist solution. So that, this azide has been replaced with more stable 4-azido-4'-methoxychalcone in a present formulation for MRL.⁴

Using azide III, we formulated MRL(N). The name MRL(N) means a new type of MRL. This resist is also sensitive to the light in near UV region, and especially suited for i-line photolithography.

The resist comprising poly(vinylphenol) and azide IV was named MRG,⁵ which is an abbreviation of Micro Resist for g line. Mercury arc has a strong emission line at 436 nm. This line is called g line. As seen in Figure 1, MRG absorbs this line and is applicable to g-line photolithography.

By replacing azide IV with azide V, we obtained MRG(N). The name MRG(N) means a new type of MRG. This resist is also sensitive to g line.

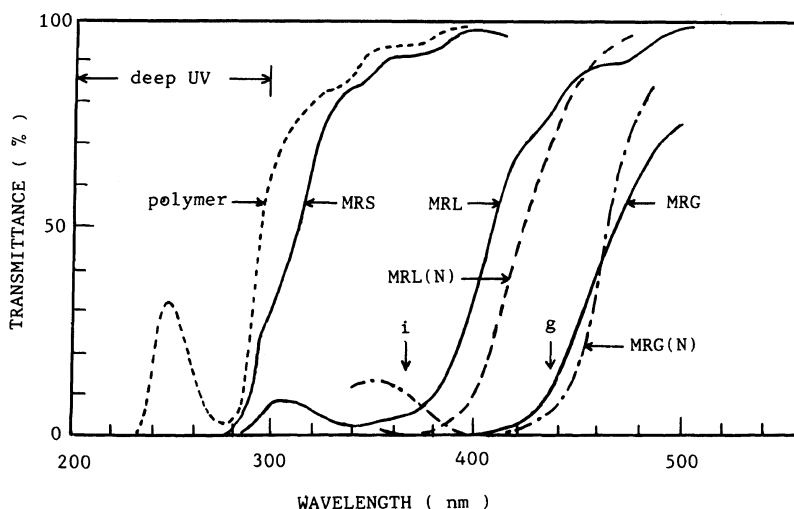


Figure 1. Transmission spectra of MR resists (film thickness: 1 μm).

EXPOSURE CHARACTERISTICS

To measure the exposure characteristics of the resists, a silicon wafer was spin-coated with a resist solution and dried. The resist film thus obtained was exposed to light spotwise successively with increasing or decreasing dose. The film was then developed with an aqueous

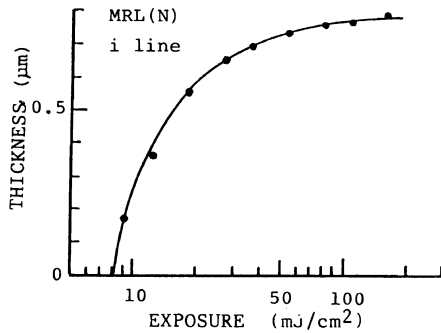


Figure 2. Exposure characteristic of MRL(N). The resist film was exposed to i line (at 365 nm).

alkaline solution and the thickness of the film remaining on the wafer was measured either by an interference microscope or by a mechanical stylus. The exposure characteristic curve was obtained by plotting the remaining film thickness against the dose. Examples of the curves obtained in this way are shown in Figures 2 and 3.

The exposure characteristic of MRL(N) shown in Figure 2 was obtained by exposing a $0.83 \mu\text{m}$ thick resist film to i line (at 365 nm), and then develop it with a 0.95% aqueous solution of tetramethylammonium hydroxide. The sensitivity required for photoresists used in semiconductor device fabrication is about 50 mJ cm^{-2} . As seen in Figure 2, MRL(N) meets this requirement.

The exposure characteristic of MRG(N) shown in Figure 3 were obtained by exposing $0.75 \mu\text{m}$ thick resist films to g line (at 436 nm), and then develop them with two different

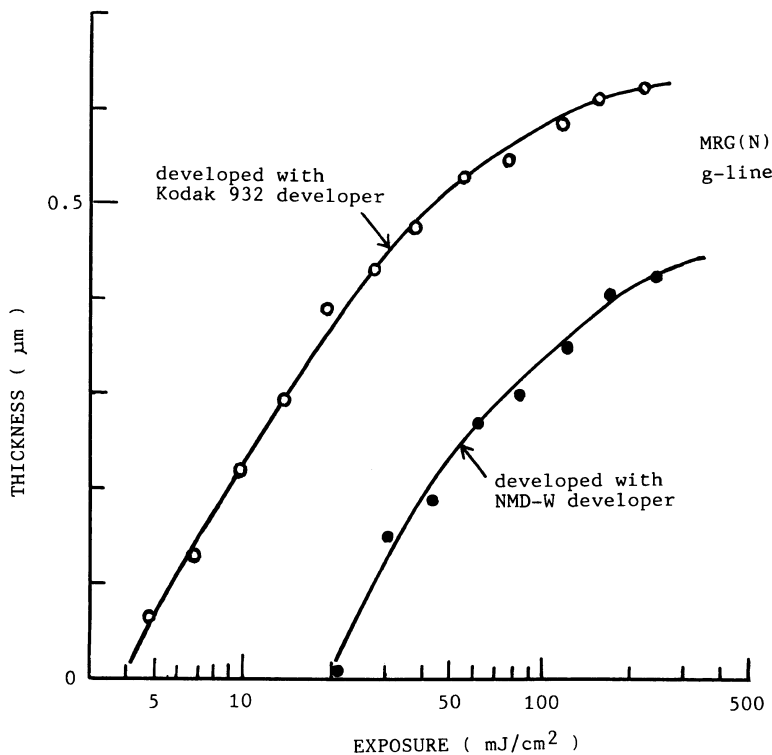


Figure 3. Exposure characteristic of MRG(N). The resist film was exposed to g line (at 436 nm).

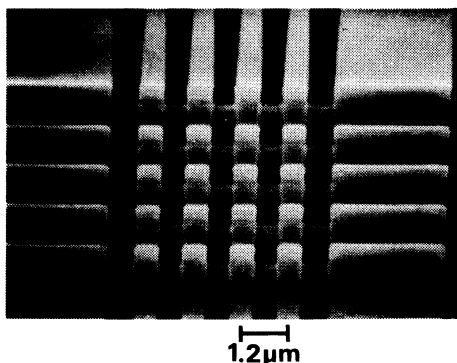


Figure 4. Line and space patterns of MRL formed on a stepped aluminum surface.

Figure 4 shows $0.6\ \mu\text{m}$ line and space patterns of MRL formed on a stepped aluminum surface. These patterns were delineated by an i-line reduction projection printer.

CONCLUSION

1. Resist systems composed of poly(vinylphenol) and aromatic azides have been proved to be high-resolution negative photoresists.
2. Their spectral sensitivities range from

deep UV to visible region, depending on the molecular structure of azide used.

3. Photoinsolubilization of the system is attributed to the increase in molecular weight of poly(vinylphenol) by the recombination of polymer radicals produced by the reaction of photo-generated nitrenes with the polymer molecules.

Acknowledgments. The author thanks Drs. Takao Iwayanagi, Michiaki Hashimoto, and Ryotaro Irie for their collaboration and Mr. Hiroshi Shiraishi for his help in analysing the reaction mechanism of the resists.

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