

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

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**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  $\mu$ 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 | $\lambda_{\max}$ 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-(4-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 synthesis<sup>1</sup> 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  $\mu\text{m}$ .

We named the photoresist comprising poly(vinylphenol) and azide I MRS,<sup>2</sup> 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,<sup>3</sup> 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.<sup>4</sup>

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,<sup>5</sup> 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.

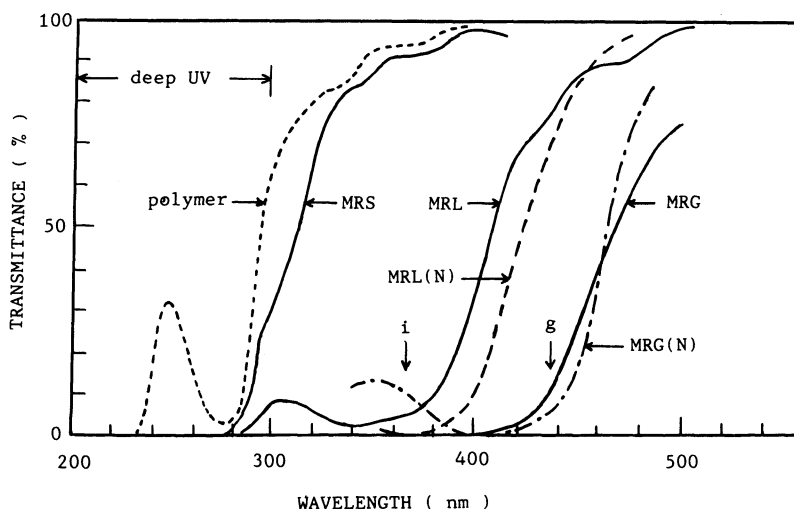
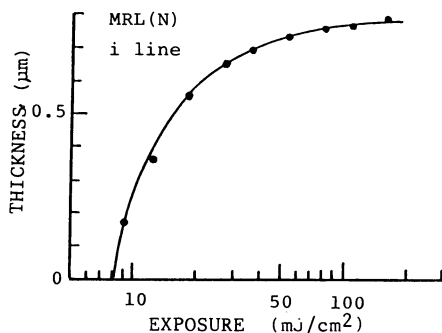


Figure 1. Transmission spectra of MR resists (film thickness: 1  $\mu\text{m}$ ).

## 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

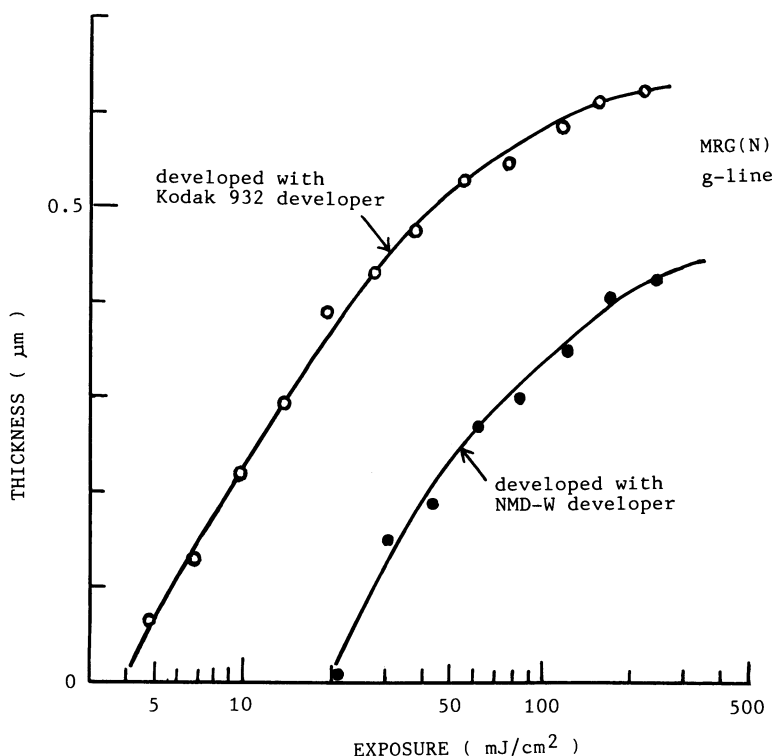
alkaline solution and the thickness of the film remaining on the wafer was measured either by an interference microscope or by a mechanical stylus. The exposure characteristic curve was obtained by plotting the remaining film thickness against the dose. Examples of the curves obtained in this way are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



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

The exposure characteristic of MRL(N) shown in Figure 2 was obtained by exposing a  $0.83\text{ }\mu\text{m}$  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  $50\text{ mJ cm}^{-2}$ . As seen in Figure 2, MRL(N) meets this requirement.

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

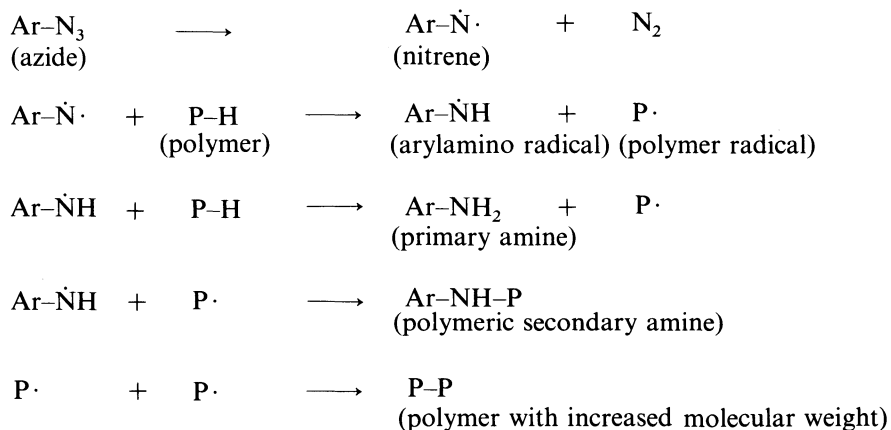


**Figure 3.** Exposure characteristic of MRG(N). The resist film was exposed to g line (at 436 nm).

kinds of aqueous alkaline developers. One of the developers was Kodak 932 developer, and the other was Tokyo Ohka NMD-W developer. Both developers were diluted with water so as to develop the resist films in one to two minutes. The difference between two curves in Figure 3 encourages us to look for more suitable developers for this type of photoresists.

### PHOTOINSOLUBILIZATION MECHANISM

To elucidate the photo-induced chemical



Upon exposure to light, azide decomposes into nitrene and nitrogen. Nitrene abstracts hydrogen from the polymer to form arylamino radical and polymer radical. If arylamino radical abstracts hydrogen from the polymer, primary amine and polymer radical are formed. The recombination of arylamino radical with polymer radical gives polymeric secondary amine. And the recombination of polymer radicals with each other gives the polymer with increased molecular weight.

The generation of the polymer with increased molecular weight is considered to be the origin of photo insolubilization of the resist. In fact, it has been found experimentally that the dissolution rate of the polymer in an

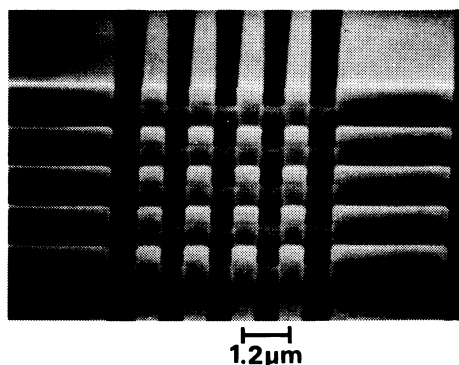
aqueous alkaline developer is strongly dependent on the molecular weight of the polymer.<sup>4</sup> Outline of the results and discussion is as follows.

The main reaction products identified are primary amine, polymeric secondary amine and poly(vinylphenol) with increased molecular weight. And, the primary amine was identified to be aminochalcone. A series of chemical reactions considered to take place to give these reaction products is shown below.

aqueous alkaline developer is strongly dependent on the molecular weight of the polymer.<sup>4</sup>

### APPLICATIONS

All the resists described above do not swell during the development process and exhibit high contrast characteristics. Therefore, they are capable of forming very high resolution resist patterns. To add to this, the resists have a good resistance to dry etching. So that, they are suited to fine line lithography in semiconductor device fabrication. An example of resist patterns obtained by using this type of photoresist is shown in Figure 4.



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

Figure 4 shows  $0.6\text{ }\mu\text{m}$  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.

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