

Chapter 19

Synthesis of New Metal-Free Diazonium Salts and Their Applications to Microlithography

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New metal-free diazonium salts have been synthesized and applied to microlithography as photobleachable dyes for a contrast enhancing layer (CEL), negative working photoactive compounds, and photoacid generators. 4-N,N-dimethylaminobenzenediazonium trifluoromethanesulfonate (D1) is the most suitable photobleachable dye. Upon i-line (365nm) exposure, 0.4- μ m line-and-space patterns were obtained using a positive resist in conjunction with the D1-CEL. D1 also shows good properties as a negative working sensitizer for a two-layer resist system formed by means of a "doping" process, in which the diazonium salt is distributed in the top and bottom layers. 4-Methoxybenzenediazonium trifluoromethanesulfonate can be used as a photoacid generator for acid catalyzed cross-linking. Submicron resolution can be achieved with high sensitivity.

In recent years, demands on microlithographic techniques have become much more severe along with the reduced sizes of semiconductor devices. Various techniques to enhance the performance of microlithographic resist systems have been developed. Contrast enhanced lithography (CEL) is one technique which improves resist resolution(1,2). The CEL process involves spin-coating a CEL layer containing a photobleachable dye on top of a conventional photoresist. This CEL layer is opaque before exposure, but during exposure, the most highly exposed regions bleach first while the least exposed regions bleach later. Therefore, optical images that are degraded by the lens system of the exposure apparatus are sharpened by passing through the CEL layer. The photobleachable dyes used in contrast enhancing materials can be classified into four categories: nitrones(1,2), polysilanes(3), styrylpyridiniums(4), and diazonium salts(5-9).

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The relationship between resist contrast and optical properties (extinction coefficient and bleaching quantum yield) of photobleachable dyes was previously described by a simple model(9), and water-soluble diazonium salts with good optical properties were developed for the CEL process(9).

Diazonium salts are also useful as a photosensitive material in a photobleachable two-layer resist system based on a "doping process"(10). High-resolution resist patterns were obtained using this two-layer resist scheme and an i-line reduction projection aligner.

As mentioned above, the conventional diazonium salts have good optical properties as CEL dyes and negative working sensitizers for the two-layer resist system. However, almost all diazonium salts are stabilized with metal-containing compounds such as zinc chloride, tetrafluoroborate, hexafluoroantimonate, hexafluoroarsenate, or hexafluorophosphate, which may not be desirable in semiconductor fabrication because of potential device contamination. To alleviate the potential problem, new metal-free materials have been sought for.

In this paper we report on the use of trifluoromethanesulfonates (Table 1) of 4-N,N-dimethylamino-benzenediazonium (D1) and 4-methoxybenzene-diazonium (D2) as CEL dyes, negative working sensitizers, and photoacid generators for chemical amplification resist systems(11).

Experimental

Synthesis of diazonium salts. The details of the synthesis of 4-N,N-dimethylaminobenzenediazonium trifluoromethanesulfonate (D1) are described below. N,N-Dimethyl-*p*-phenylenediamine (27.7 g, 0.2 mole) was dissolved in acetic acid (150 ml). Trifluoromethanesulfonic acid (30.6 g, 0.2 mole) was added to the solution in an atmosphere of nitrogen. The solution was kept at room temperature while isopentyl nitrite (26 g, 0.22 mole) was added dropwise. The solution was allowed to react for half an hour. After completion of diazotization, tetrahydrofuran (400 ml) was added to the solution and the precipitated D1 (55 g) was filtered. D1 (20 g) was recrystallized from acetone (90 ml)/tetrahydrofuran (260 ml). Precipitated D1 crystals (14 g) were filtered and dried. The melting point of D1 is 127°C and the maximum absorption in water appears at 376 nm. 4-Methoxybenzenediazonium trifluoromethanesulfonate (D2) was synthesized similarly.

Lithographic evaluation.

CEL dye. A CEL solution was obtained by dissolving poly(N-vinylpyrrolidone) (PVP) (7 g) and D1 (5.8 g) in 50 wt% aqueous acetic acid. (87.2 g). The CEL layer was spin-coated onto a photoresist, RI-7000P (Hitachi Chemical Co.), and baked at 80°C for 20 minutes. Exposure was performed with an in-house i-line reduction projection aligner. The resist was developed in a 2.38 wt% tetramethylammonium hydroxide aqueous solution. The film thickness was measured with an Alpha-step 200 (Tencor)

profilometer. Spectroscopic measurements were performed on a Hitachi 340 UV spectrophotometer and a Hitachi 260-10 IR spectrophotometer.

Negative two-layer resist. A cresol novolac resin (Alnovol PN-430) was spin-coated on a silicon wafer and baked at 80°C for one minute on a hot plate. The silicon wafer was set on a spin-coater and a photosensitive solution consisting of D1 (3 wt%), PVP (5 wt%), acetic acid (46 wt%), and water (46 wt%) was deposited so as to contact the phenolic resin film on the silicon wafer. The solution on the phenolic resin film stood for 2 minutes. The residual solution on the phenolic resin film was spun to form a D1-PVP top layer and baked at 80°C for two minutes. By this process, a two-layer resist was formed (10).

The resist was exposed with an in-house i-line reduction projection aligner or a 600-W Xe-Hg lamp (Cannard Hanovia) in conjunction with a UVD2 band pass filter (Toshiba glass Co.). After removing the top layer by rinsing in water, the resist was developed with a 2.38 wt% tetramethylammonium hydroxide aqueous solution.

Photoacid generator. D1 (4 wt%) was mixed with poly(glycidyl methacrylate) (PGMA) (20 wt%) in ethyl cellosolve acetate. The mixture was spin-coated on a silicon wafer and baked at 80°C for 1 minute. Exposure was performed with a 600-W Xe-Hg lamp in conjunction with a UVD2 filter. The resist was developed in a mixture of methyl ethyl ketone to ethanol (7/1 w/w).

In another application, the diazonium salt (D1 or D2) (2.5 wt%) was dissolved in a mixture of cyclohexanone and acetic acid containing 12.5 wt% poly(4-hydroxystyrene) and 2.5 wt% Methylone resin (GE 75108). The resist was exposed with a 600-W Xe-Hg lamp through a 313-nm interference filter. After exposure the resist was baked at 80°C for 3 minutes and developed in a 1 wt% tetramethylammonium hydroxide aqueous solution.

Results and discussion

Synthesis of diazonium salts. The conventional diazotization of amino compounds is performed as described below. An amino compound is dissolved in acidic water, then aqueous sodium nitrite is added dropwise to the solution, while the solution temperature is kept below 0°C. After completion of diazotization, a diazonium ion stabilizer such as zinc chloride, sodium tetrafluoroborate, or sodium hexafluorophosphate is added to the reaction solution. Therefore, diazonium salts that are synthesized by the conventional process contain metal ions that may contaminate semiconductor devices. In addition, because some diazonium salts are extremely soluble in water, it is often difficult to isolate them from the aqueous reaction solution.

To avoid the above mentioned problems, diazonium salts were synthesized by diazotizing amino compounds with isopentyl nitrite in acetic acid containing a strong acid such as trifluoromethanesulfonic acid. After completion of diazotization, the reaction solution was poured into an organic solvent. The precipitated crystals were filtered and dried.

This process makes it possible to remove metal ions from the diazonium salts and also provides easy isolation of the diazonium salts that are highly soluble in water.

Thermal stability of D1. The thermal stability of the D1 in 50 wt% acetic acid aqueous solution was evaluated by kinetic analysis. The thermal decomposition of diazonium salts in an aqueous solution is a first-order reaction. The thermal decomposition constants of D1 at 25, 75, and 90°C are 9.1×10^{-5} , 2.9×10^{-3} , 1.3×10^{-1} /hr, respectively. The Arrhenius plot of D1 in acetic acid solution is shown in Figure 1. The activation energy of D1 (23.0 kcal/mol) and the decomposition rate constant at 5°C were obtained from Figure 1. This decomposition rate constant ($k_{5^\circ\text{C}} = 3.7 \times 10^{-7}$ /hr) indicates that 1% of the D1 in the acetic acid aqueous solution will decompose in about 3 years at 5°C.

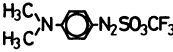
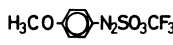
Photoproduct of D1 in solid state. Major photoproduct from D1 in the solid state was isolated by silica gel column chromatography and analyzed by IR and NMR spectroscopy (Figures 2 and 3). NMR spectrum shows that a photoproduct of D1 has the absorption band of the N,N-dimethylamino group (2.86 ppm) and the symmetric absorption band of aromatic protons (6.57-7.10 ppm). The strong IR absorption of the sulfonyl group (1210 and 1420 cm^{-1}) can be seen in Figure 3. From NMR and IR spectra, the main photoproduct of the D1 was identified as trifluoromethanesulfonic acid 4-N,N-dimethylaminophenyl ester.

Application to a CEL dye. The UV spectra of D1 in a PVP matrix before and after bleaching are shown in Figure 4. The absorption maximum of D1 lies at 376 nm. The photobleaching curve of the D1-CEL layer consisting of D1 and PVP is shown in Figure 5. The transmittance of the unbleached layer is less than 1% and that of the completely bleached layer is about 90%. Contrast and resolution of the photoresist are expected to be greatly improved with the use of the D1-CEL.

The exposure curves of the positive photoresist Hitachi Chemical RI-7000P with and without the D1-CEL are shown in Figure 6. The resist contrast with the D1-CEL ($\gamma=3.9$) is three times higher than that without the D1-CEL ($\gamma=1.3$). Scanning electron microphotographs of submicron resist patterns printed with and without the D1-CEL are shown in Figure 7. The photographs show that the CEL layer containing D1 enables imaging of 0.4- μm line-space patterns on an i-line reduction projection aligner.

Application to the two-layer resist system. Photobleachable resist systems that have a strong absorption before exposure and that bleach completely upon UV exposure alleviate the light reflection from the substrate. A photobleachable resist system formed by means of the "doping process" was reported in our previous paper(9). This resist system consists of two layers in which a diazonium salt is distributed in both the top and bottom layers. When exposed to i-line, the diazonium salt in

Table 1. Newly synthesized diazonium salts and chemical structure of Methylene used in this experiment

NAME	CHEMICAL STRUCTURE	λ_{\max} (nm)	ϵ_{\max} $\times 10^4$
D 1		376	3.37
D 2		312	2.37

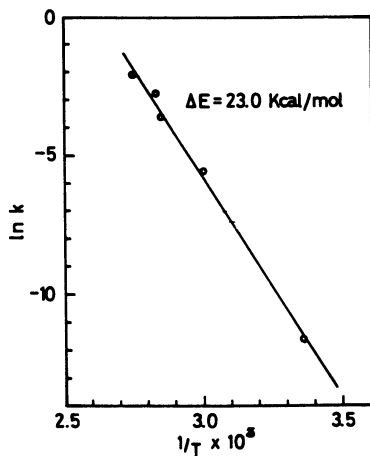
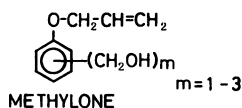


Figure 1. Arrhenius plot of D1 thermal decomposition in a 50 wt% acetic acid aqueous solution.

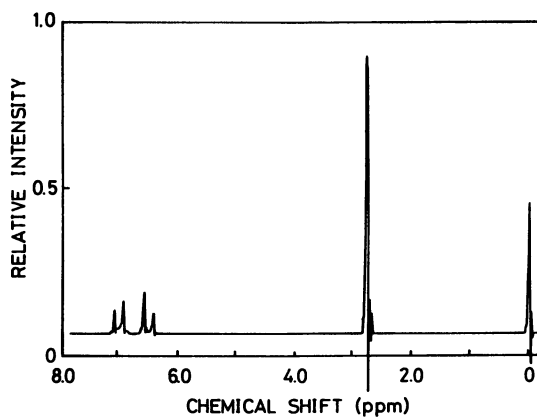


Figure 2. NMR spectrum of the main photoproduct from D1.

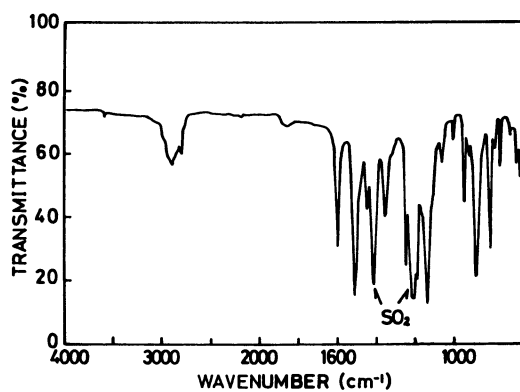


Figure 3. IR spectrum of the main photoproduct from D1.

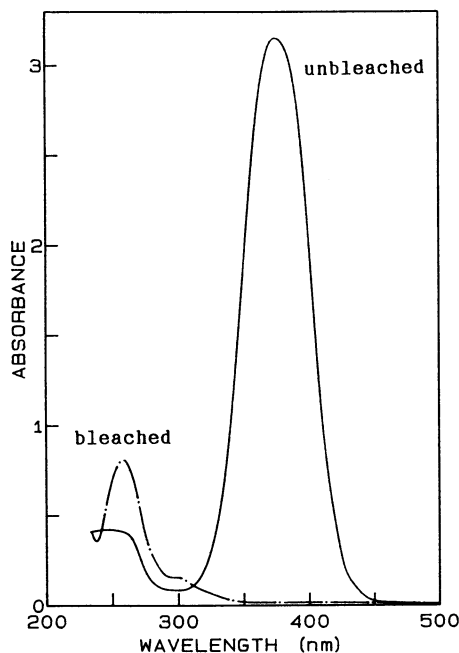


Figure 4. UV absorption spectra of a D1-CEL layer consisting of 4-*N,N*-dimethylaminobenzenediazonium trifluoromethanesulfonate and PVP. The solid line is the unbleached layer, and the broken line is the completely bleached layer.

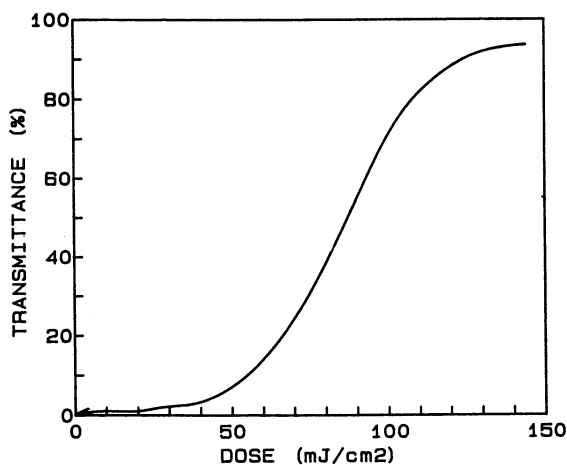


Figure 5. Photobleaching curve of the D1-CEL layer exposed at the *i*-line (365 nm).

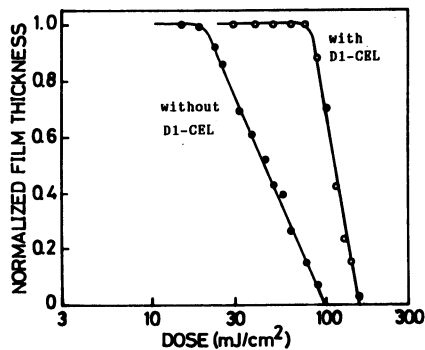


Figure 6. Exposure curves of positive resist Hitachi Chemical RI-7000P with and without the D1-CEL. The contrast (γ -value) of the D1-CEL resist is three times of that of the non-CEL resist.

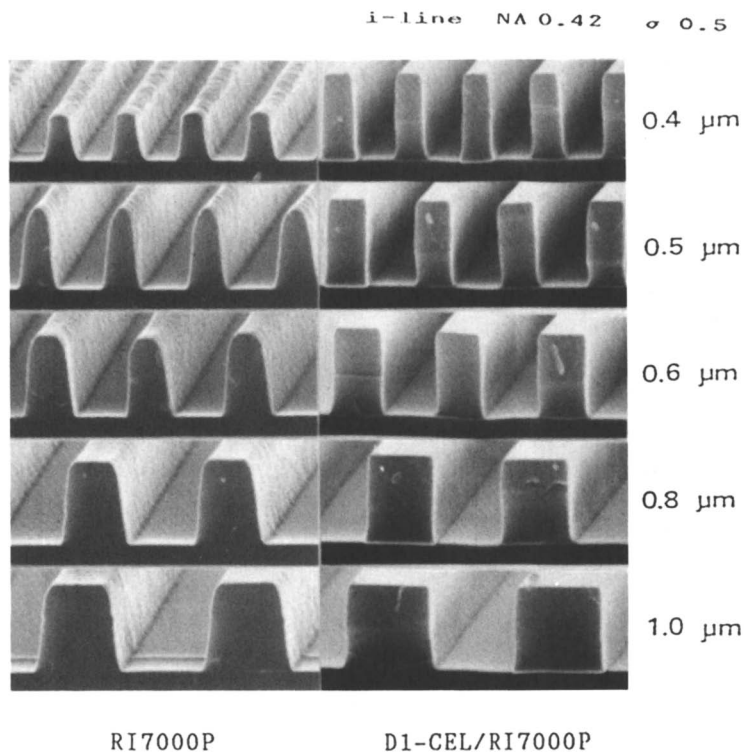


Figure 7. SEM photographs of resist patterns printed with and without the D1-CEL on commercially available resist (Hitachi Chemical RI-7000P).

the top layer bleaches to act as a contrast enhancing material, while the diazonium salt in the bottom layer decomposes to cause insolubilization of the phenolic resin in the base developer.

The exposure curve of the two-layer resist based on the doping process is shown in Figure 8. The two-layer resist system has a high contrast and high resolution capability. Submicron line-and-space patterns are obtained using this two-layer resist system (Figure 9).

Application to photoacid generators. Recently much attention has been focused on chemically amplified resist systems using onium salts(11), halogen compounds(12), or nitrobenzyl ester(13) as photoacid generators. Since the newly synthesized diazonium salts have trifluoromethanesulfonic acid anion as the counter ion, they generate a strong protonic acid upon UV exposure. D1 and poly(glycidyl methacrylate) (PGMA) were mixed and exposed to i-line. The exposure curve of the D1-PGMA resist system is shown in Figure 10. Here it can be seen that the D1-PGMA resist works as a highly sensitive negative resist. The newly synthesized diazonium salts might be useful as photoacid generators for chemical amplification resist systems. However, the D1-PGMA resist system did not show excellent image quality because of swelling during the development process.

Another acid-catalyzed cross-linking type resist system devoid of swelling was evaluated, which consisted of a phenolic resin, Methylone resin, and the diazonium salt. Both D1 and D2 were used. The exposure curve of the resist system containing D2 as the photoacid generator is shown in Figure 11. The sensitivity and contrast of the resist dramatically improved with post exposure baking. An SEM photograph of the submicron pattern of the acid catalyzed resist system using D2 as the photoacid generator is shown in Figure 12. The resist system which contains D1 does not show high sensitivity and high contrast characteristics. It is probable that the photogenerated acid is wasted by the protonation of the N,N-dimethylamino group of D1. The details of the reaction mechanism are under investigation.

Conclusion

New metal-free diazonium salts were synthesized and applied to microlithography. A CEL layer consisting of D1 and PVP has good optical properties for i-line exposure and resolves 0.4- μ m line-and-space positive resist patterns. D1 is also a useful material as a negative working sensitizer for phenolic resins. 4-Methoxybenzenediazonium trifluoromethanesulfonate can be used as a photoacid generator for the design of mid-UV resist system based on acid-catalyzed cross-linking. Submicron resist patterns are resolved using this highly sensitive resist system.

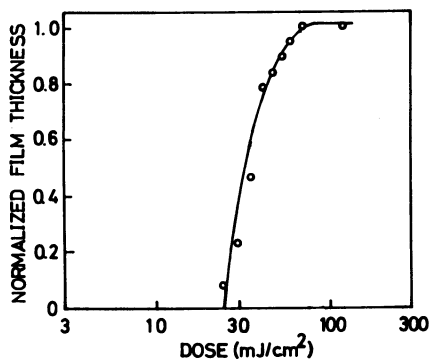
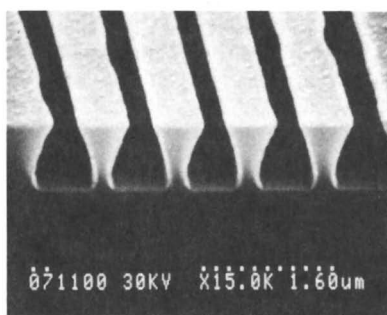
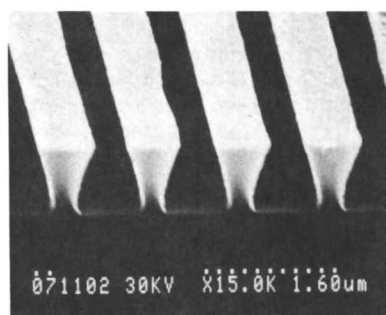


Figure 8. Exposure curve for a negative two-layer resist system formed by "doping." Exposure was performed at the i-line (365nm).



(A)



(B)

Figure 9. SEM photograph of the negative two-layer resist formed by means of "doping." Exposure was performed at the i-line. (A) 0.5- μ m L&S, (B) 0.6- μ m L&S.

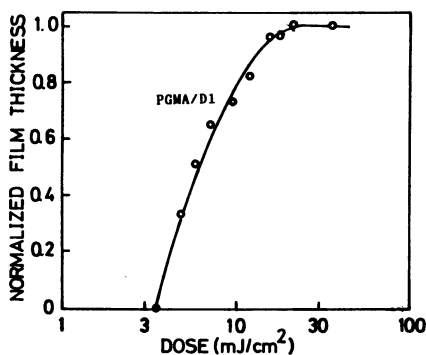


Figure 10. Exposure curve of PGMA sensitized with D1. Exposure was performed at the i-line.

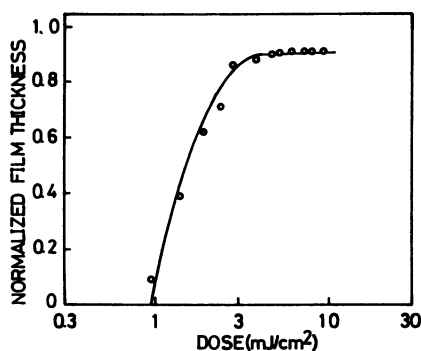
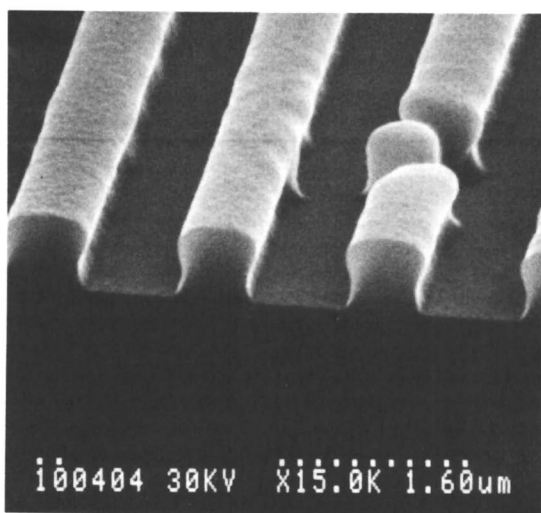


Figure 11. Exposure curve of the acid-catalyzed resist system consisting of poly(4-hydroxystyrene), D2, and Methylone. Exposure was performed using a Xe-Hg lamp equipped with a 313-nm interference filter.



0.7 μm L & S

Figure 12. SEM photograph of the acid-catalyzed resist system exposed at 313 nm with an exposure energy of 5 mJ/cm².

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