This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Azide-Containing Phenolic Resin as a Negative Deep Uv Resist

Saburo Nonogaki[a]; Minoru Toriumi[a]
[a] Central Research Laboratory Hitachi, Ltd., Tokyo, Japan

To cite this Article Nonogaki, Saburo and Toriumi, Minoru(1988) 'Azide-Containing Phenolic Resin as a Negative Deep Uv Resist', Journal of Macromolecular Science, Part A, 25: 5, 617 — 626
To link to this Article: DOI: 10.1080/00222338808053388
URL: http://dx.doi.org/10.1080/00222338808053388

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. MACROMOL. SCI.–CHEM., A25(5-7), pp. 617-626 (1988)

AZIDE-CONTAINING PHENOLIC RESIN AS A NEGATIVE DEEP UV RESIST

SABURO NONOGAKI and MINORU TORIUMI

Central Research Laboratory
Hitachi, Ltd.
Kokubunji, Tokyo 185, Japan

Downloaded At: 18:10 24 January 2011

ABSTRACT

A negative photoresist has been developed by partial esterification of poly(*p*-hydroxystyrene) with *p*-azidobenzenesulfonyl chloride. About 10% of esterification is sufficient to sensitize the polymer to light in the wavelength region between 240 and 300 nm. The dose required to insolubilize the polymer was 80 mJ/cm^2. The resolution capability is not as high as expected because of the swelling of photoinsolubilized resist films in an aqueous alkaline developer.

INTRODUCTION

The minimum feature size of microelectronic devices has been steadily reduced and is now entering the submicron region. Corresponding to this, the photoresist used to fabricate such devices is required to have a high resolution capability. Since conventional positive-tone photoresists meet this requirement, they are now being used in large quantities to fabricate the most advanced semiconductor devices such as 1 Mbit dynamic random access memories.

Negative-tone photoresists composed of cyclized polyisoprene and aromatic bisazide, which were used in the semiconductor industry almost exclusively in the past, are now being gradually replaced by positive photoresists because the resolution capability of this type of negative photoresist is lower

Copyright © 1988 by Marcel Dekker, Inc.

than that of positive photoresist. The loss in resolution results from the swelling of photoinsolubilized resist films during the development process.

If a resist does not swell in a developer, its resolution can be high. A typical example of such resists is the positive photoresist composed of Novolac and diazoquinone. Another example is a group of negative photoresists obtained by sensitizing poly(*p*-hydroxystyrene) with various kinds of aromatic azides [1-4]. The spectral sensitivity of these negative photoresists is dependent on the kind of azide used. For example, a resist named MRS and composed of poly(*p*-hydroxystyrene) and 4,4′-diazidodiphenylsulfone is sensitive to light in the deep UV wavelength range from 240 to 320 nm.

Recently, the use of excimer lasers, which emit light in the deep UV region, in photolithography has been proposed to improve the resolution of exposure. High-resolution photoresists are sensitive to deep UV light. However, they are not necessarily suited for excimer laser lithography because most of them strongly absorb the light in the deep UV region.

We have recently developed a new type of photosensitive polymer by partial esterification of poly(*p*-hydroxystyrene) with *p*-azidobenzenesulfonyl chloride. The polymer thus obtained is insolubilized by exposure to light in the wavelength range from 240 to 300 nm. Photoabsorption of the polymer in this wavelength range is not as strong as that of MRS. Therefore, the polymer is considered to be a suitable photoresist for deep-UV lithography. The present paper describes the synthesis and characterization of this polymer.

Downloaded At: 18:10 24 January 2011

EXPERIMENTAL

Preparation of Sodium *p*-Azidobenzenesulfonate

Ten grams sulfanilic acid, 2.9 g sodium carbonate, and 4.2 g sodium nitrite were dissolved in 100 mL water and cooled with ice. To the solution, 7 mL concentrated HCl diluted with 10 mL water was added dropwise. The precipitated diazonium salt was separated from the solution by filtration, washed with 40 mL cold water, and then dispersed in 20 mL cold water. To the dispersion, an aqueous solution of sodium azide (4 g dissolved in 10 mL) was added dropwise until no further nitrogen gas liberation took place on addition of one more drop. The sodium salt was salted out by adding 7 g sodium chloride to the solution, separated from the solution by filtration, and then dried. Yield was 8.6 g, including some sodium chloride.

Preparation of *p*-Azidobenzenesulfonyl Chloride

Four grams sodium *p*-azidobenzenesulfonate, prepared as above, was suspended in 6 g *N,N*-dimethylformamide. To this suspension, 4 mL thionyl chloride was added. The mixture was allowed to stand for 45 min and then poured into 100 mL water. The precipitated white crystals were separated by filtration, washed with water, and then dried. The yield was 3.7 g.

Esterification of Poly(*p*-Hydroxystyrene)

Poly(*p*-hydroxystyrene) with a weight-average molecular weight of about 7000 was purchased from Maruzen Oil Co. and used without further purification. Six grams of the polymer and 1.07 g *p*-azidobenzenesulfonyl chloride were dissolved in 60 mL 1,4-dioxane. To the solution, 0.6 g potassium hydroxide dissolved in 1 mL water was added under vigorous agitation. The mixture was warmed at 60°C for 20 min to complete the reaction. After the reaction, 250 mL water and a small amount of acetic acid to neutralize the remaining alkali were added to the mixture, and the deposited polymer was collected, washed with water, and then dried. The yield was 6.6 g. By assuming the reaction to be completed quantitatively, the degree of esterification is calculated to be 10%.

Downloaded At: 18:10 24 January 2011

Preparation of *p*-Ethylphenyl *p*-Azidobenzenesulfonate

Two grams *p*-ethylphenol and 3.66 g *p*-azidobenzenesulfonyl chloride were dissolved in 40 mL 1,4-dioxane. To the solution, 1.7 g potassium hydroxide dissolved in 3 mL water was added under stirring. After being warmed by hot water for a few minutes, the mixture was allowed to stand for 30 min, and then poured into 250 mL water. The oily deposit from the mixture was crystallized by adding a seed which can be prepared by rubbing a drop of the oil on a glass plate with a glass rod. The resulting white solid was separated from the solution, washed with water, and then dried. The yield was 4.7 g.

Spectroscopic Characterization

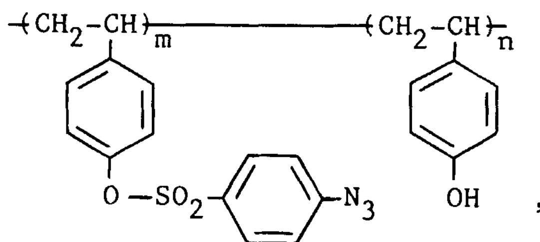
The infrared spectra of polymer films were measured with a Hitachi 260-10 infrared spectrophotometer. To measure the UV spectra of the films, a Hitachi 340 recording spectrophotometer was used.

Lithographic Evaluation

Silicon wafers were coated with a conventional positive photoresist, baked at 200°C for 20 min, and used as substrates for polymer film deposition. The polymer was dissolved in cyclohexanone and spread onto a substrate by spinning and dried. The polymer film thus formed was baked at 80°C for 20 min. To irradiate the film, a 1-kW Xe-Hg lamp with a 248-nm interference filter was used. After the exposure, the film was developed with an aqueous solution of tetramethylammonium hydroxide. The thickness of the film remaining on the substrate was measured by a stylus-type surface tracer (Alpha-step 200, Tencor Instruments) and plotted against irradiation dose.

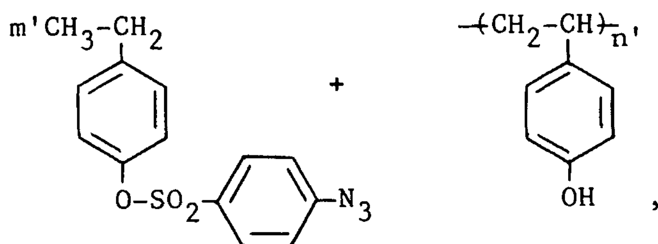
RESULTS AND DISCUSSION

As described above, 0.1 mol sulfonyl chloride to 1 mol *p*-hydroxystyrene monomer unit was used to esterify the polymer. Therefore, if the yield is 100%, the structure of the polymer is as follows:



where $m/(m+n) = 0.1$.

To estimate the yield of esterification, we prepared a polymer-azide mixture with the following composition and compared its infrared spectrum with that of esterified polymer.



Downloaded At: 18:10 24 January 2011

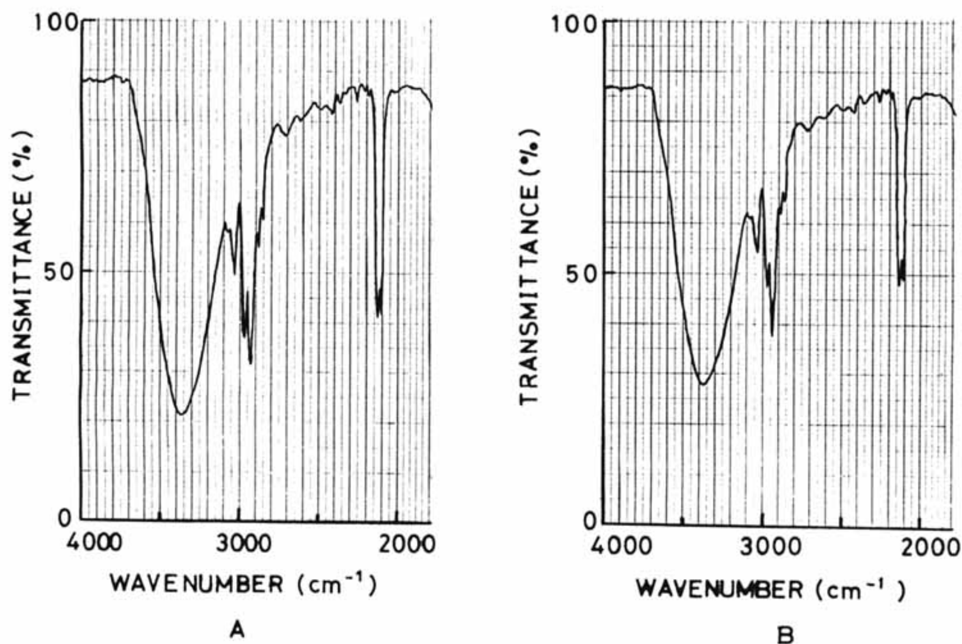


FIG. 1. Infrared spectra of partially *p*-azidobenzenesulfonated poly(*p*-hydroxystyrene) (A) and a mixture of *p*-ethylphenyl *p*-azidobenzenesulfonate and poly(*p*-hydroxystyrene) (B).

Downloaded At: 18:10 24 January 2011

where $m'/(m' + n') = 0.1$. The result is shown in Fig. 1. The absorption peak at about 2140 cm^{-1} corresponds to the $-N_3$ group, and that at about 3375 cm^{-1} corresponds to the –OH group. The ratios of absorbance of the former to the latter are 0.57 and 0.58 for esterified polymer and polymer-azide mixture, respectively. This good agreement indicates that both the yield and the degree of esterification is nearly 100%.

Ultraviolet spectra of esterified polymer before and after exposure to light from a 500-W high-pressure mercury lamp are shown in Fig. 2. The change in spectral absorption indicates the photodecomposition of azido ($-N_3$) groups in the polymer. The absorption spectrum of unexposed polymer shown in Fig. 2 does not strictly represent the spectral sensitivity of the polymer because the unesterified polymer also absorbs light in this wavelength region.

The change in spectral absorption by esterification is shown in Fig. 3,

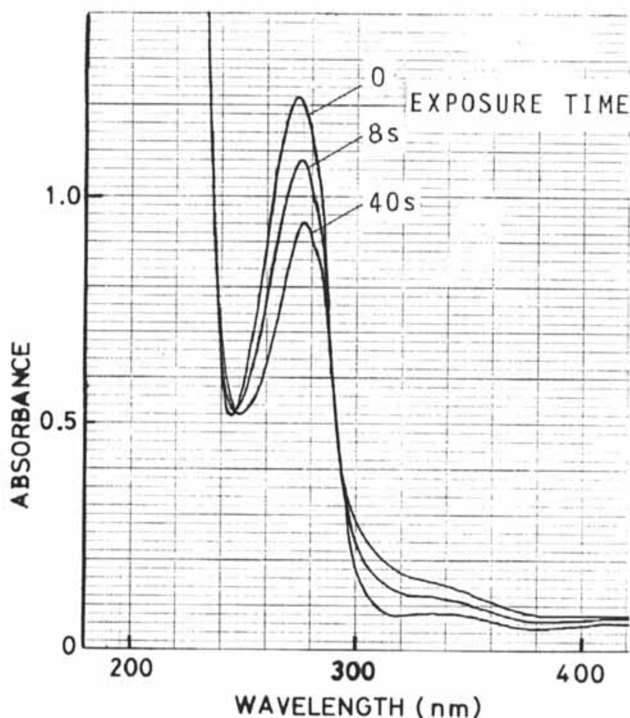


FIG. 2. Ultraviolet absorption spectra of partially *p*-azidobenzenesulfonated poly(*p*-hydroxystyrene) before and after exposure to light. The film thickness is 0.47 μm.

Downloaded At: 18:10 24 January 2011

where the absorbance per 1 μm film thickness calculated from the experimental data is plotted against wavelength for both polymers before and after esterification. The difference between two spectral curves corresponds to the absorption by the acidophenyl groups. From this difference, the averaged percentage of photon energy absorbed by azidophenyl groups to the total energy absorbed by the polymer in the wavelength region between 240 and 300 nm is calculated to be 56%.

The photosensitivity characteristics of the esterified polymer are exemplified by Fig. 4, where the remaining film thickness after development in a 1.8% aqueous solution of tetramethylammonium hydroxide for 70 s is plotted against the irradiation dose.

Downloaded At: 18:10 24 January 2011

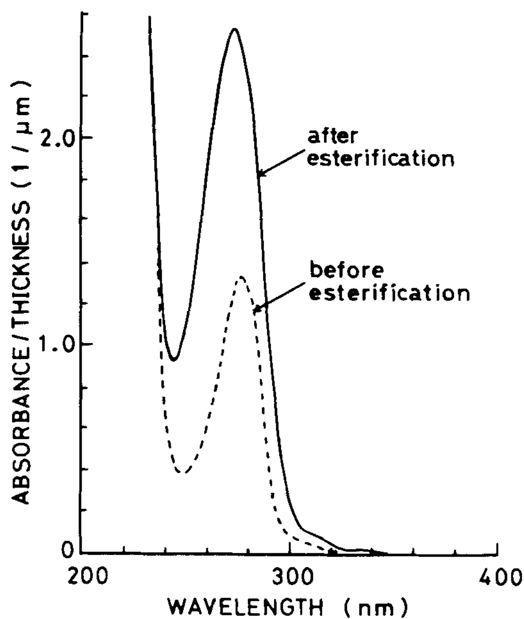


FIG. 3. Spectral change in poly(*p*-hydroxystyrene) by partial esterification with *p*-azidobenzenesulfonyl chloride.

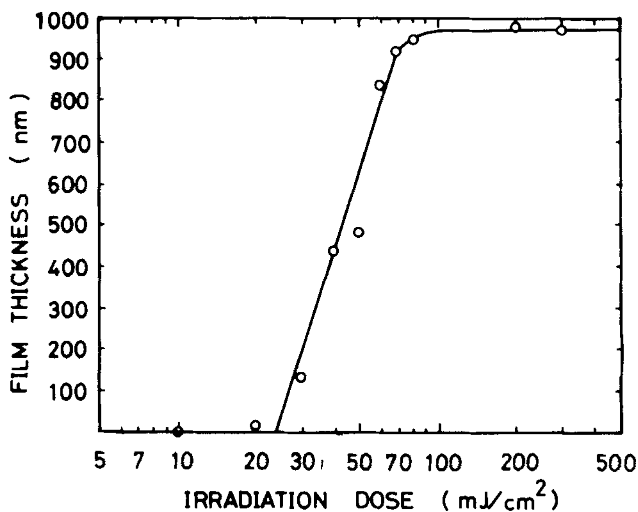
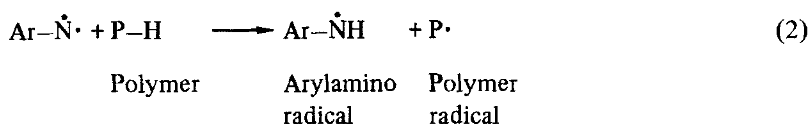
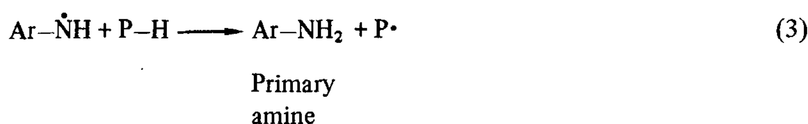
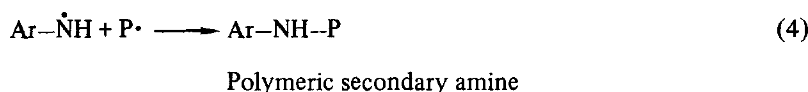


FIG. 4. Photosensitivity characteristic of partially *p*-azidobenzenesulfonated poly(*p*-hydroxystyrene).

The photoinsolubilization mechanism in a photoresist consisting of poly-(*p*-hydroxystyrene) and an aromatic monoazide has been investigated in detail [3]. The reaction scheme experimentally confirmed in this study is as follows.







In this case, only one kind of reaction, Reaction (4), leads to insolubilization of the polymer by crosslinking. However, in the present case, where azide molecule and polymer molecule are identical, crosslinks are formed by Reaction (4) as well as by Reaction (5). Therefore, more efficient photoinsolubilization is expected in this case.

Films of the esterified polymer 1-μm thick were exposed patternwise to light at wavelength 248 nm by contact printing and then developed with an aqueous solution of tetramethylammonium hydroxide. An example of an SEM photograph of the resist patterns thus formed is shown in Fig. 5. Although resist lines with widths of 1.5 and 1.0 μm were also resolved, they are wobbly on the substrates. This "wobbling" is evidence of the swelling of the resist patterns in the developer. Since the swelling of resist patterns greatly reduces the resolution capability, it must be eliminated. In the present case a relatively strong alkaline developer is used to dissolve the unexposed polymer which has been rendered less alkali-soluble by esterification. This probably results in the swell-

Downloaded At: 18:10 24 January 2011

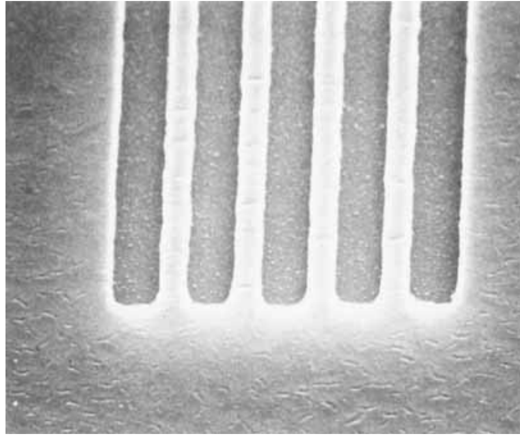


FIG. 5. Scanning electron microscope photograph of resist patterns obtained by contact printing. Irradiation dose is 300 mJ/cm^2 at 248 nm. The resist lines are 2 μm wide and with 4 μm spaces.

Downloaded At: 18:10 24 January 2011

ing of the resist patterns. Therefore, it seems possible to obtain a polymer with an acceptable photosensitivity and nonswelling character by optimizing the degree of esterification between 0 and 10%.

CONCLUSION

An alkali-developable negative deep-UV resist has been obtained by azidobenzenesulfonylation of poly(*p*-hydroxystyrene). The resist has been proved to be highly sensitive to deep UV light. Resist patterns with feature sizes less than 2 μm swell in an aqueous alkaline developer. This swelling character can possibly be eliminated by optimizing the degree of esterification between 0 and 10%.

REFERENCES

[1] T. Iwayanagi, T. Kohashi, S. Nonogaki, T. Matsuzawa, K. Douta, and H. Yanazawa, *IEEE Trans. Electron Devices, ED-28,* 1306 (1981).

[2] T. Iwayanagi, M. Hashimoto, S. Nonogaki, S. Koibuchi, and D. Makino, *Polym. Eng. Sci.*, *23*, 935 (1983).

[3] M. Hashimoto, T. Iwayanagi, H. Shiraishi, and S. Nonogaki, *Ibid.*, *26*, 1090 (1986).

[4] S. Nonogaki, *Polym. J.*, *19*, 99 (1987).

Downloaded At: 18:10 24 January 2011