Negative Working Resist by Photosensitization of Onium Salts

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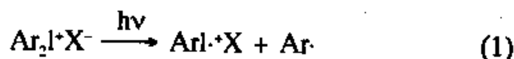
ABSTRACT

A negative resist system is described which is sensitive to wavelengths above 310 nm. The resist is formulated from poly(p-methoxystyrene), photosensitizer and a cationic photoinitiator such as diaryliodonium salt. Upon irradiation at wavelengths absorbed by the photosensitizer, the photoresist undergoes facile cross-linking via a sequence of electron transfer reactions.

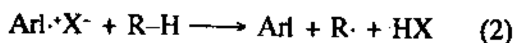
KEY WORDS: Negative resist, photosensitization, poly(*p*-methoxystyrene), crosslinking, onium salt.

INTRODUCTION

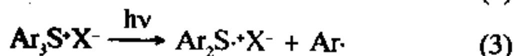
Thermally stable onium salts, such as iodonium salts and sulphonium salts ($Ar_2I^+X^-$ and $Ar_3S^+X^-$) with non-nucleophilic counter anions ($X^- = PF_6^-$, SbF_6^- AsF_6^- and BF_4^- etc.) have been widely used as photoinitators[1] for cationic polymerization Recently, onium salts have found application in photoresist technology with high chemical amplification[2-4] Upon irradiation these compounds produce strong Brønsted acids which provide a unique opportunity to design novel imaging systems which rely on various acid catalyzed process for their action.



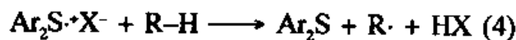
$$Ar_2I^+X^- \xrightarrow{h\nu} ArI^{\cdot +}X + Ar^{\cdot} \quad (1)$$



$$ArI^{\cdot +}X^- + R\text{–}H \longrightarrow ArI + R^{\cdot} + HX \quad (2)$$

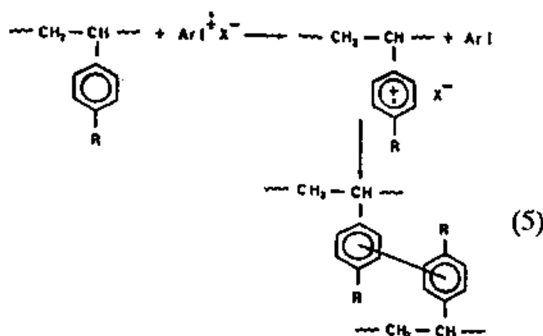


$$Ar_3S^+X^- \xrightarrow{h\nu} Ar_2S^{\cdot +}X^- + Ar^{\cdot} \quad (3)$$



$$Ar_2S^{\cdot +}X^- + R\text{–}H \longrightarrow Ar_2S + R^{\cdot} + HX \quad (4)$$

Recently, a new class of photoresist consisting of vinyl aromatic polymers with electron donating substituents or halogens together with todonium and sulphonium salts have been described[5]. In this process, the aryliodinium and the diarylsulfinium cation radicals are shown in Eq (2) and (4) undergo electron transfer reactions which lead to efficient crosslinking in polymer resist systems, according to the following reactions.



R = –OCH$_3$, –OH, –CH$_3$, –Cl etc.

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J. Polym. Mater. 9 (1992) 55–58
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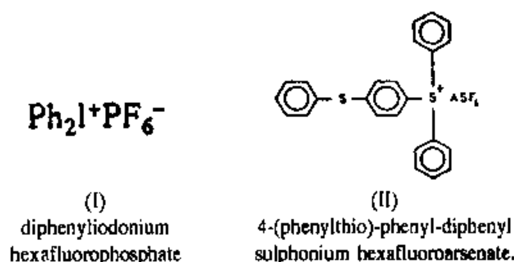
This report describes the similar photoresist system consisting of poly (*p*-methoxy styrene) in combination with onium salts such as diaryliodonium and complex sulphonium salt and photosensitizers such as antracene.

EXPERIMENTAL

Materials

Poly (*p*-methoxystyrene) was obtained by polymerizing the commercially available monomer cationically after purification with conventional drying and distillation procedures. The preparation of diphenyliodonium hexafluorophosphate (I) and 4-(phenylthio)-phenyldiphenyl sulphonium hexafluoroarsenate (II) were prepared according to the described procedures[6-7]. Photosensitizers were purified by recrystallization and sublimation procedures.



Photoimaging of Poly (*p*-methoxy styrene)

0.5 g of polymethoxystyrene together with 0.05 g of onium salt and 0.05 g of sensitizer when indicated were dissolved in 5 mL of dichloromethane. The solutions were spin coated onto 2 in silicon wafers (from Wacker Chemitronic GmbH) which were previously cleaned chemically and oxidized to increase adhesibility, and dried at 70°C for 30 min. The films were then irradiated through mask (perforated Kodak High resolution plate using KSM-MJ3-3 model Mask Aligner 250 W super pressure Hg lamp at standard distance. After baking the exposed fotoresist in an oven for 1 min at 1.25°C, the wafers were developed using the mixture of dichloromethane/*n*-hecane(1/1; v:v).

Analysis

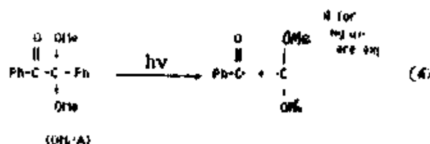
Scanning electron micrographs were taken by using Scanning Electron Microscope Model T-3 30 JOEL equipped with Trocor 5400 EDS system U.V. spectra were taken using a Perkin-Elmer 550 S spectrophotometer.

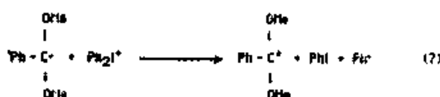
RESULTS AND DISCUSSION

In order to extend the spectral response of onium salts to longer wavelengths several photoactivators were tested in the photoresist system. In Table 1 are presented the result obtained using benzophenone (BP), 2,2-dimethoxy-2-pheylacetophenone (DMPA) and antrancene (A) in combination with diphenyliodonium hexafluorophosphate; or 4-(phenylthiophenyl-diphenyl sulphonium hexafluoroarsenate as light-sensitive components in the proposed negative photoresist. Poly(*p*-methoxystyrene) was used as polymer substrate since it was found to be the most efficient substituted vinyl aromatic polymer which undergoes facile electron transfer upon direct photolysis of onium salts leading to crosslinking. As it can be seen, DMPA is inefficient photoactivator which precludes the possibility of the participation of cations in the imaging process. Radicals produced photochemically with free radical photoinitiators such as DMPA, have been shown[8] to participate in the generation of reactive cations by the reduction of diaryliodonium salts as illustrated below.

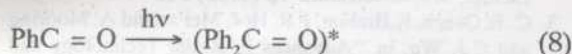
TABLE 1. Sensitized Nagative Image Formation on Irradiation of Poly (*p*-methoxystyrene) the Presence of Onium Salts.

Photoactivator	Onium Salt	Irradiation Time	Result
—	I	5′	–
DMPA	I	5′	–
Benzophenone	I	2′	–
Antracene	I	55″	+
—	II	5′	–
Benzophenone	II	3′	–
Antracene	II	1′	+

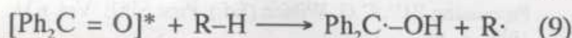




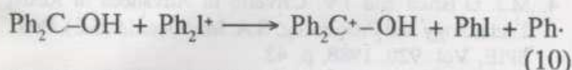
Similarly benzophenone does not participate efficiently in this process. In the case of benzophenone sensitized reactions, a hydrogen donor is required[9].



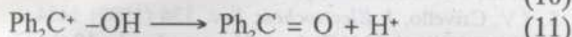
$$PhC = O \xrightarrow{h\nu} (Ph_2C = O)^* \quad (8)$$



$$[Ph_2C = O]^* + R{-}H \longrightarrow Ph_2C{\cdot}{-}OH + R{\cdot} \quad (9)$$



$$Ph_2C{-}OH + Ph_2I^+ \longrightarrow Ph_2C^+{-}OH + PhI + Ph{\cdot} \quad (10)$$

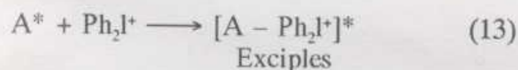


$$Ph_2C^+ {-}OH \longrightarrow Ph_2C = O + H^+ \quad (11)$$

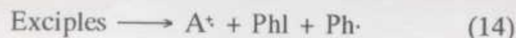
Ketyl radicals formed upon hydrogen abstraction are oxidized by the iodonium salt to produce carbocations (protonated ketones) which dissociate to yield protons. Protons were found to be incapable of acting as species for the crosslinking of poly (*p*-methoxystyrene) which is in accordance with Crivello's results[5].

In contrast to DMPA and BP, antracene is useful for this type of negative resist. Poly(*p*-methoxystyrene) resist containing antracene and iodonium salt is irradiated, sensitizer radical cations are expected to form according to the following reactions.

$$\underset{\text{(Antracene)}}{A} \xrightarrow{h\nu} A^* \quad (12)$$



$$A^* + Ph_2I^+ \longrightarrow \underset{\text{Exciples}}{[A - Ph_2I^+]^*} \quad (13)$$



$$\text{Exciples} \longrightarrow A^{+\cdot} + PhI + Ph{\cdot} \quad (14)$$

The antracene radical cation (A^+) may then induce crosslinking by electron transfer in a manner similar to that described for iodonium radical cations (see equation 5). Detailed mechanism of the generation of photosensitizer radical cations in the presence of onium salts was described elsewhere[10]. In our system, direct photolysis of the onium salts is precluded by the use of pyrex mask. As can be seen from Fig. 1, the mask absorbs the light at wavelengths below 310 nm where onium salts main absorbtions appear. Fig. 2 shows a scanning electron micrograph of 10 μm line and space pattern produced using poly (*p*-methoxystyrene), onium salt (diphenyl iodonium hexafluorophosphate) and antracene which were spin coated onto silicon wafers. After bake drying the wafers, they were subjected to imagewise exposure at above 310 nm and then baked for 60 seconds at 125°C. Finally, the unexposed portions of the resist were removed by mixture of *n*-hexane/dichloromethane (1/1, v/v). Some loss of line profiles may be due to the postbake temperature which is considerably above the T_g temperature of the polymer (89°C)[11].

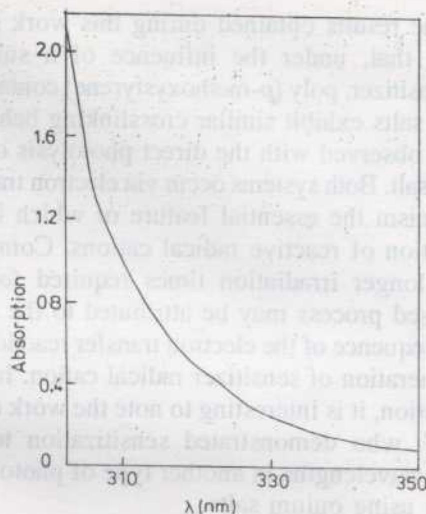


Fig. 1. Absorbtion characteristics of the mask employed in photoimaging studies.

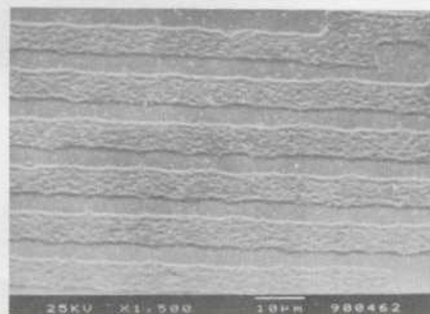


Fig. 2. Scanning electron microscope (SEM) micrograph of 7μm lines and 3.5 μm space pattern obtained after irradiation of poly (*p*-methoxystyrene), antracene and diphenyliodionium hexafluorophosphate negative photoresist system.

The results obtained during this work show clearly that, under the influence of a suitable phtosensitizer, poly (*p*-methoxystyrene) containing onium salts exhibit similar crosslinking behavior to that observed with the direct photolysis of the onium salt. Both systems occur via electron transfer mechanism the essential feature of which is the generation of reactive radical cations. Comparatively longer irradiation times required for the sensitized process may be attributed to the additional sequence of the electron transfer reaction for the generation of sensitizer radical cation. In this connection, it is interesting to note the work of Ito *et al.*[12]. who demonstrated sensitization to the longer wavelengths in another type of photoresist system using onium salts.

Acknowledgement. The autuors are grateful to Prof. Duran Leblebici at Faculty of Electrical and Electronics Engineering, Istanbul Technical University for his comments and suggestions. We wish also to thank Prof. Adnan Tekin at Department of Metallurgy, Istanbul Technical University for taking scanning electron micrographs.

Received: 15 March 1991
Accepted: 16 January 1992

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