Modification of Chemically Amplified Resists by Radical Copolymerization

S. Bulgakova, M. Johns, E. Kiseleva*

Summary: Modification of a phenolic resist has been carried out by copolymerization with methacrylic monomers. Influence of irradiation source and its intensity has been studied by analyzing sensitive curves of a various resist composition. Inversion of imaging type at varying post exposure bake temperature has been investigated for resists based on copolymers containing methacrylic acid units, which has been related with crosslinking of macromolecules.

Keywords: chemically amplified resists; image type inversion; methacrylic monomers; radical copolymerization

Introduction

The polymeric materials, used in microelectronics as resists for manufacturing of semiconductor devices, should have high sensitivity, resolution and etch resistance parameters. Chemically amplified resists which most fully satisfy to these requirements have been intensively studied over the last decades. The image in such resists is formed by means of acid-catalyzed deprotection of functional groups of polymeric matrix caused by a Brönsted acid formed from photoacid generator (PAG) at exposure. The acidolysis causes the changes of the polarity and hence the solubility of the polymer.

The classical chemical amplification resist is a poly(4-*tert*-butoxycarbonyloxystyrene) (PTBOCS), which converts to hydrophilic of poly(4-hydroxystyrene) (PHOST) in result of acidolysis.[1] Thus, it would be possible to receive a positive and a negative image in case of developing the latent images in an aqueous-base and an organic solvent, respectively. However it appears to be impossible to develop a positive image due to PTBOCS's high lipophility and its weak adhesion to the silicon wafer. The developer that has penetrated under the film from the wafer edges by overcoming weak adhesion forces of interaction of a highly hydrophobic polymer with the hydrophilic substrate surface creates a disjoining pressure, and the resist film is lifted off. It is known [2] that adhesion of a resist to a wafer can be enhanced by varying the resist composition toward increasing the polar component of its surface tension. Herein the modification of PTBOCS resist by copolymerization with methacrylic monomers and the substitution of lipophilic TBOCS moieties by ethoxyethyl methacrylate (EEMA) parts was carried out.

Experimental Part

Methylmethacrylate (MMA) was purified by vacuum recondensation, and methacrylic acid (MAA) was freed of water by freeze-drying and then distilled under vacuum. TBOCS and EEMA purchased from Aldrich was used without further purification, the initiator AIBN was purified by recrystallization from isopropyl alcohol (IPA), and THF was dried over CaH_2 and distilled. Isopropanol, diglyme, methyl ethyl ketone and toluene were purified according to conventional procedures.[3]

The copolymers of TBOCS and EEMA were prepared by radical polymerization in a THF solution with a concentration of

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Research Institute of Chemistry N.I. Lobachevsky State University of Nizhny Novgorod, pr.Gagarina 23, bldg.5, Nizhny Novgorod 603950, Russia
E-mail: sbulg@mail.ru

30 vol% at 70 °C and 50 vol% at 60 °C respectively in the presence of 0.005 mol/l AIBN to a 90–96% conversion. The copolymers were purified by three-fold reprecipitation from acetone to hexane. The precipitated copolymers were dried under vacuum at room temperature to a constant weight. The amount of acid in the copolymers was determined by potentiometric titration with a TV-6L1 instrument, and the content of TBOCS by FT-IR spectroscopy according to absorbance of C=O at 1756 cm^{-1} and 1730 cm^{-1} corresponding to TBOCS and MMA, respectively (Figure 1).

The molecular-mass characteristics of the copolymers were determined by means of GPC at 40 °C on a "Shimadzu" Prominence LC-20VP liquid chromatograph with a set of columns packed with polystyrene-divinylbenzene standards with pore sizes of 10^5 and 10^6 Å. A differential refractometer was used as a detector, and THF was used as an eluent. Narrow dispersed PMMA and PS standards were used for calibration.

Resist films were applied onto silicon wafers from diglyme solutions that had been preliminarily filtered using 0.45 μm filters by spin coating. Film thickness was monitored using a MII-4 microinterferometer. As a PAG, we used the triarylsulfonium salt Cyracure® UVI 6974 SbF_6^- $[Ar_2{-}S^+{-}C_6H_4{-}S{-}C_6H_4{-}S^+{-}Ar_2]SbF_6^- + [Ar{-}S{-}C_6H_4{-}S^+{-}Ar_2]SbF_6^- = 90{:}10$ (PAG-1) and 4,4′-di(*tert*butylphenyl)iodonium *p*-toluenesulfonate $[C(CH_3)_3C_6H_4J^+C_6H_4C(CH_3)_3]$-$[C_6H_4CH_3SO_3]^-$ (PAG-2) prepared in-house according to a procedure described in.[4]

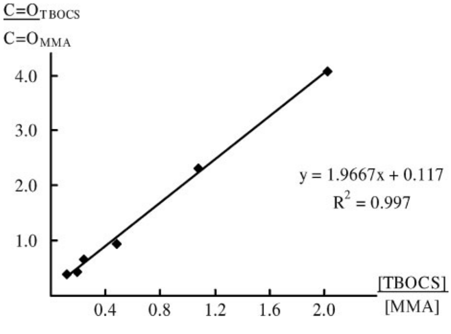


Figure 1.
Calibration plot between ration of absorbance bands intensity of C=O groups corresponding to TBOCS and MMA and molar ration of these units.

The resists were exposed in air to UV light from a BUF-15 lamp (λ ≈254 nm) with intensity 1 mW/cm^2 and KrF-laser irradiation (λ =248 nm). Post apply and post exposure baking of these resists was performed on a hot plate. The sensitivity and the contrast γ of a resist were determined from the sensitivity curves as a minimal dose required for resist solubility change over the entire initial thickness, and as a slope of linear portion of the curve.

IR spectra were measured on Infralum FT-801 spectrometer using 1 μm polymer films applied on ZnSe substrates.

Results and Discussion

With the purpose of increase of a PTBOCS resist adhesion we modified it by TBOCS copolymerization with MMA taken in an amount of 10, 41, or 61 wt %. Lithographic studies have shown that all three resists with the PAG-1 operate in the chemical amplification mode. The addition of even 10 wt % MMA units ensures the formation of a stable positive image in an aqueous base developer alongside with the negative image in toluene with a contrast $\gamma = 8$ and 2.7 respectively. However to reach the required hydrophilic–hydrophobic balance in the complex substrate–resist–developer system, it was necessary to add a small amount of IPA to aqueous solution of tetraethyl ammonium hydroxide (TEAH). The experimental data presented in the Table 1 show that than less content of MMA units in the copolymer the above resist sensitivity and more poorly erosion of the exposed resist (loss in resist thickness) during post exposure bake which is associated with the release of carbon dioxide and isobutylene, the volatile hydrolysis products of TBOCS units. It was also found that the resist sensitivity depends on the type of UV radiation used. It is seen from the Table 1 that the sensitivity of the resists

Table 1.
Influence of the copolymer composition TBOCS:MMA with 2 wt % PAG-1 on the sensitivity (*D*) to continuous UV radiation ($\lambda = 254$ nm) and KrF laser radiation ($\lambda = 248$ nm), an energy per pulse of 5 mJ/cm^2, a pulse duration of 25 ns) and on the loss in thickness of exposed resist films (Δd), post apply bake, 90 °C/60 s; post exposure bake, 120 °C/30 s; developer, 0.3 N TEAH + IPA = 1:1

Copolymer characteristics				D, mJ/cm^2		Δd, %
Content of TBOCS, wt %	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	254 nm	248 nm	
90	69	39	1.78	1.5	12	30
59	90	44	2.03	4.5	45	14
39	69	39	1.78	12.5	168	0

exposed to pulsed KrF laser radiation is almost an order of magnitude lower than that in the case of continuous UV light from a lamp. Assuming that this difference is due to a higher intensity of laser radiation, we studied the influence of the dose per pulse on the sensitivity of the 59:41 TBOCS–MMA copolymer resist. The results presented in Figure 2 show that the resist sensitivity indeed deteriorates with an increase in radiation intensity.

The further researches of this resist have shown that the negative image can be received not only in toluene but also in an aqueous base solution if it will be baked post exposure at high temperature. As shown from Figure 3 at the aqueous base development the positive image is formed after post exposure bake at 120 °C while the negative tone is received at 150 °C.

It is visible also that the sensitivity of a resist depends on catalyst concentration: than more concentration the above sensitivity. Thus the negative resist shows a higher sensitivity in comparison with a positive formulation. For an explanation of the image inversion effect depending on post exposure bake temperature the IR spectroscopy studies were carried out. The received results presented on Figure 4 show that for heating a resist at 150 °C both thermal and acid-catalyzed deprotection of polymer occurs and phenolic functionality is formed. Thus both processes proceed with identical efficiency as the absorption of OH groups at 3423 cm^{-1} slightly differs (Figure 4a). Despite of it the solubility of exposed film in an aqueous base developer is reduced. In our opinion it is connected to a large contribution of side reactions proceeding in a film at the presence of the photogenerated acid at high temperatures as Ito has reported in review.[5] These

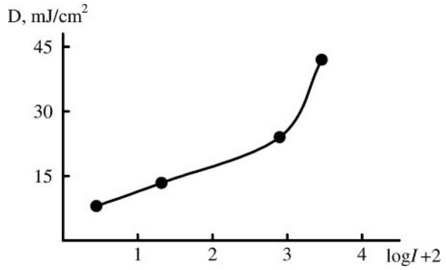


Figure 2.
Sensitivity *D* of the resist based on TBOCS–MMA (59:41) and 2 wt % PAG-1 to KrF laser radiation as a function of the dose per pulse. The post apply and post exposure baking were set at 80 °C/60 s and 120 °C/ 30 s respectively; developer, 0.4 N TEAH–IPA = 1:1 v/v.

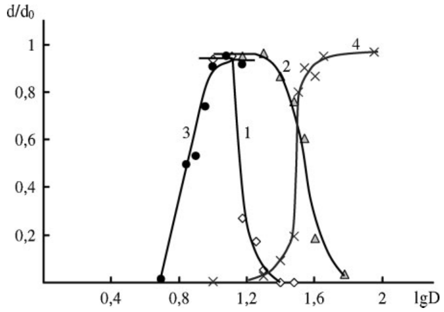


Figure 3.
Sensitivity curves for resist based on TBOCS-MMA = 59:41 wt % with 2 wt % (*2*, *4*) and 8 wt% PAG-1 (*1*, *3*) at different post exposure bake temperature: 120 °C/15 s (*1*, *2*), 150 °C/60 s (*3*, *4*). UV radiation (248 nm), post apply bake at 60 °C/5 min, development in 0.3 N TEAH-IPA = 1:1

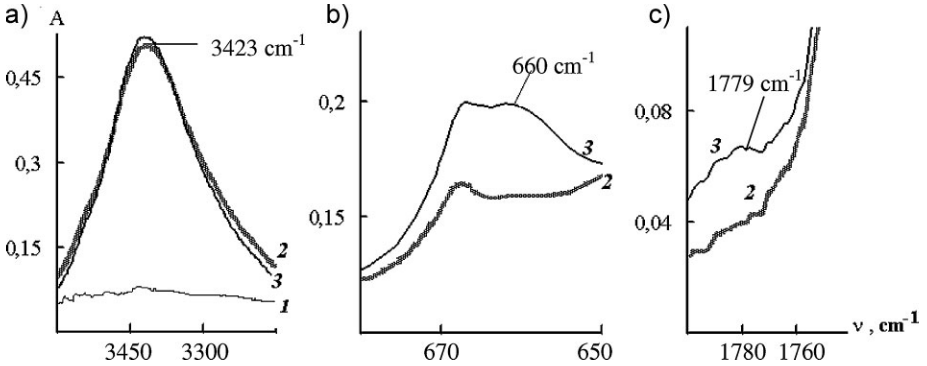


Figure 4.
IR spectra of TBOCS-MMA copolymer resist before (*1*) and after bake at 150 °C: *2*- unexposed film, *3*- exposed film

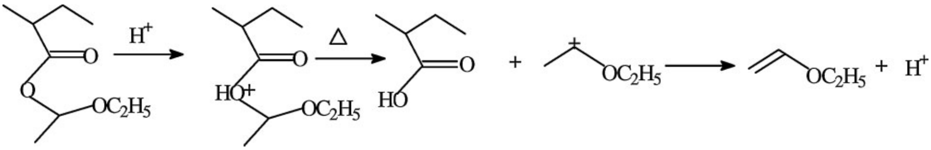
side reactions are caused by scisson of O-C or CO-O bonds in TBOCS group to produce *tert*-butyl and *tert*-butoxy intermediates, respectively. The result of these processes in our case is *C*-alkylation benzene ring and crosslinking of macromolecules through formation of fragment ArOC(O)OAr which could reduce the dissolution rate of the exposed film in TEAH–IPA solution. It is proved by appearance of absorption bands in IR spectra of polymer film after PEB at 150 °C at 660 cm^{-1} and at 1779 cm^{-1} corresponding to 1,3,4 – substituted aromatic compounds and valence vibration of C=O in ArOC(O)OAr fragments, respectively (Figure 4b, 4c).

For increase of this resist liophility the modification by *tert*-copolymerization of TBOCS-MMA- MAA was carried out and in this case it was found the positive image pass to negative type at the development in the aqueous-base solvent at the post exposure bake temperature above 130 °C also (Table 2).

Table 2.
Sensitivity to UV (254 nm) and contrast of TBOCS-MMA-MAA = 60:20:20 wt% ($M_w = 192000$, $M_w/M_n = 2.0$) + 2 wt% PAG, at the development in a 0.025N TEAH – IPA = 5:1 v/v

Type of image/Post exposure bake temperature	D, mJ/cm^2	Contrast (γ)
Positive/80 °C	38	9.4
Negative/150 °C	20	9.6

The similar effect of the reversal imaging in an aqueous-base developer is observed and for another resist on a basis of *tert*-copolymer EEMA with MMA and MAA. Image formation in this resist is based on the amenability of EEMA to acid hydrolysis according to the following mechanism:



Kinetic researches showed that the resist solubility depends on the post exposure bake temperature (Figure 5): in the region of 60–80 °C, the rate of dissolution of exposed areas exceeds that of unexposed areas; at temperatures above 80 °C, the reverse is observed— up to the complete loss of *tert*-polymer solubility in the exposed area

Therefore, in this case, either a positive or negative image can be formed in the resist depending on the baking temperature. Note that the temperature point of solubility inversion of exposed and unexposed areas depends on the developer concentration, namely, a higher baking temperature is required in more concen-

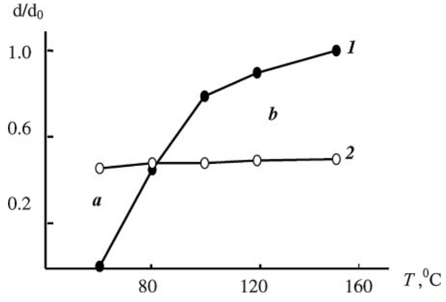


Figure 5.
Relative residual thickness d/d_0 of films of copolymer EEMA-MMA-MAA = 53:27:20 wt% ($M_w = 101000$, $M_w/M_n = 2.3$) with 8 wt % PAG-1 (*1*) exposed UV dose of 120 mJ/cm^2 at 254 nm and (*2*) unexposed as a function of the post exposure bake temperature: development in a 0.01 N TEAH solution. (*a*) Positive image region; (*b*) negative image region.

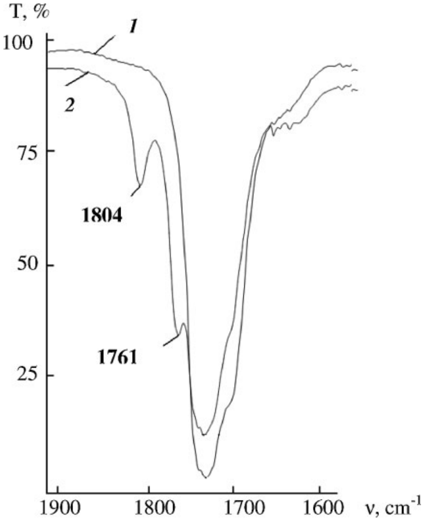


Figure 7.
IR spectra of EEMA-MMA-MAA copolymer resist with 8 w.% of PAG-1 exposed by UV at 254 nm before (*1*) and after bake at 150 °C (*2*)

trated developers. However similar effect is not observed for iodonium salt PAG-2 as shown from Figure 6. In our opinion, such behavior of the resists is explained by a difference in structure of the acids $HSbF_6$ and $C_6H_5SO_3H$ produced by photoacid generators. The highly reactive acid $HSbF_6$ presumably causes the crosslinking of macromolecules via carboxylic groups in the exposed area when a baking temperature of the order of 120–150 °C is attained. This assumption is confirmed by the results of IR-spectroscopy on the Figure 7: the absorption bands at 1761 and 1804 cm^{-1} assigning to anhydride groups are appeared.

As results from the Figure 8, the exposure of this resist to laser radiation has revealed the same relation between the sensitivity and radiation intensity as it was established for TBOCS-MMA resist; according to this relation, a decrease in energy per pulse by a factor of 4 leads to an eightfold increase in resist sensitivity.

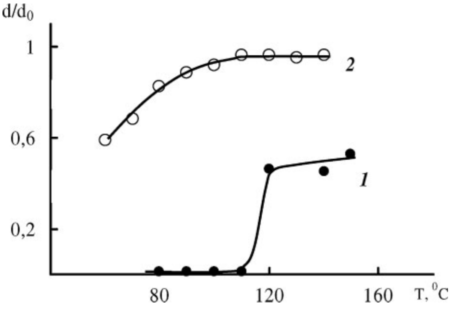


Figure 6.
Relative residual thickness d/d_0 of films of copolymer EEMA-MMA-MAA with 8 w. % PAG-2 (*1*) exposed (UV dose of 120 mJ/cm^2 at 254 nm) and (*2*) unexposed to UV irradiation as a function of the post exposure bake temperature. Development in a 0.1 N TEAH solution.

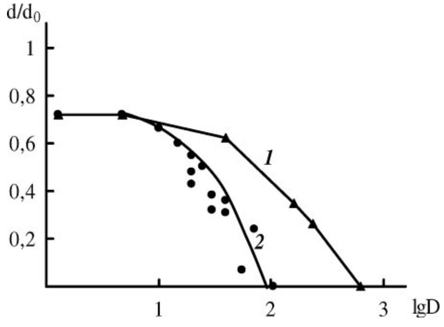


Figure 8.
Sensitivity curves for resist EEMA-MMA-MAA with 2 wt % PAG-2 at different intensities of laser radiation (248 nm) per pulse (**1**) I_1 and (**2**) $I_2 = 1/4I_1$. Post apply bake, 110 °C/60 s; post exposure bake, 100 °C/60 s. Development in 0.05 N TEAH solution, 35 s.

Conclusion

As a result of the conducted researches it was found that the lithographic characteristics of resists depend on PAG type, intensity and kind of UV-radiation type, than above energy of radiation the worse sensitivity of a resist. Inversion of image type in an aqueous base developer is observed at high post exposure bake temperatures and depends on PAG type.

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