occurs by altering the polarizabilities of the bridging and framework Ti–O bonds without necessarily involving TiO_6 deformation.

The $KTiOPO_4$ structure field presents an unusual opportunity to evaluate structure/property relationships at the atomic level and to use this information to develop a predictive paradigm to create new nonlinear optic compositions in other metal oxide structural fields. The known isomorphs of KTP, of which there are already more than 40, have been made by both direct synthesis and inclusion tuning, in which cations are exchanged with a melt or, in the case of NH_4TiOPO_4 derivatives, are desorbed into or resorbed from the gas phase. The demonstrated possibility of *selective* siting for ion-exchangeable cations and the potential ability to do this for framework atoms add an unusual dimension to the value of the KTP structure field in correlating electronic and structural properties with NLO behavior. Replacing K and P with elements of greater or lesser atomic refractivity relocates the phase-matchable wavelengths in the resulting isomorphs. Replacing Ti with other elements shifts the LMCT absorption edge or eliminates it altogether, but probably at the cost of significantly reduced nonlinear susceptibility.

This multifaceted tuning is being exploited to investigate the finer details of the electronic and structural properties responsible for the unusually favorable NLO response in the KTP family. Already, KTA's electrooptic and nonlinear optic properties compare favorably with KTP's, and KTA may become more desirable than KTP for certain applications. It seems very probable that with the multidimensional compositional and structural space available to this family additional improvements in selected NLO properties will be obtained in the future.

Acknowledgment. This work was supported by the National Science Foundation. We also thank Drs. Nancy Keder and Bill Harrison for their assistance in preparing the crystallographic data.

Articles

Deep-UV Lithographic Response and Quantum Efficiency Calculations of Poly((trimethylsilyl)methyl methacrylate–(chloromethyl)styrene) Copolymers

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The random copolymer comprised of (trimethylsilyl)methyl methacrylate, SI, and (chloromethyl)styrene, CMS, is known to function as a negative acting deep-UV and electron-beam resist. A range of copolymer compositions, from 0% CMS to 100% CMS, was synthesized to define a working range of sensitivity and weight percent silicon incorporation for use in bilevel applications. The Charlesby–Pinner relationship is used to determine the quantum efficiencies of cross-linking, Φ_{cl}, and chain scission, Φ_s, over the range of copolymer compositions. A preliminary study on the photochemistry of the poly(SI-CMS) copolymers as a function of composition, using either a pulsed KrF laser or a continuous-wave mercury vapor lamp, is presented.

Introduction

As integrated circuit technology becomes more sophisticated, greater demands are placed on the resist materials used in the lithographic pattern definition process. Necessary material requirements include sufficient sensitivity to exposure to ensure appropriate throughput and adequate resolution to enable VLSI device fabrication. Dry etching resistance has become increasingly desirable in pattern-transfer processes, especially for features <1 μm,[1] and for defining features on existing topography.

The incorporation of organometallic elements into resist materials as a mechanism for providing oxygen reactive ion etching resistance (RIE) has captured the attention of research chemists for several years. A wide range of organosilicon resist materials in which are organosilicon component has been incorporated into the polymer main chain as well as into pendent groups has appeared in the literature.[2-6] In addition to improved O_2 RIE resistance, organosilicon polymers allow a reduction in overall process complexity from a trilevel to a bilevel scheme. Unfortunately, this technology cannot be extended to most silyl-

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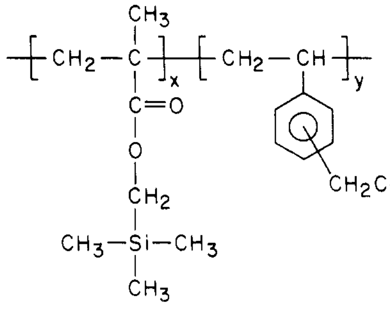
containing homopolymers because they frequently lack necessary characteristics such as a high glass transition temperature and aqueous base solubility essential in the processing of conventional positive photoresists.

There are a number of negative acting resist materials that have evolved from chlorinated derivatives of polystyrene.[5-9] All are highly susceptible to cross-linking upon exposure and are capable of providing resolution in the 0.5-μm regime. A copolymer of (trimethylsilyl)methyl methacrylate (SI) and *m,p*-(chloromethyl)styrene (CMS) is a particularly attractive material. SI-CMS copolymers, **1**, respond to both electron-beam and deep-UV irradiation,



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and they are negative acting because the dose requirements for cross-linking CMS are below those for degrading most substituted methacrylates. The chloromethyl group is known to afford the largest improvement in sensitivity among various halogen groups in polystyrene derivatives,[10] and loss of resolution due to the occurrence of a postirradiation polymerization reaction is not a problem.[11]

A previous study has shown that a 90/10 SI-CMS composition provided good sensitivity to deep-UV radiation ($D_g^{0.5}$ = 20 mJ/cm^2 at $\langle M_w \rangle$ = 1.87 × 10^5 g/mol polystyrene equivalent weight) and that the ratio of etching rates of this material to a planarizing material, HPR-206, was 1:12 in an O_2 plasma.[5] More sensitive resists should result from copolymers with greater CMS content; however, the reduced silicon content would serve to lower the O_2 RIE resistance.

One objective of this ongoing investigation is to substantiate the effect of polymer composition on the sensitivity of this class of negative resist. A second objective is to evaluate the effect of the incident exposure mode, pulsed versus continuous wave, on the chemistry of these materials. The recent availability of excimer laser exposure tools with production capability raises the question as to whether there are differences in the photochemical response of polymeric resists upon pulsed vs conventional mercury vapor lamp exposure. These differences could arise from localized sample heating effects, reciprocity effects, or multiphoton processes when high-energy, pulsed-laser sources are used. Additionally, the instantaneous power difference between a pulsed laser and mercury arc can lead to differences in radical concentrations that could in turn affect the efficiency of bimolecular processes such as cross-linking.[12,13] An investigation into the effect of this incident exposure source on the quantum efficiencies of cross-linking, Φ_{cl}, and scission, Φ_s, is presented.

Experimental Section

Materials. (Trimethylsilyl)methyl methacrylate (Petrarch Systems) and *m,p*-(chloromethyl)styrene (Dow Chemical Co.) were distilled under reduced pressure to remove inhibitors. Irganox 1010 was also used in the distillation of CMS to prevent thermal polymerization. Benzoyl peroxide and toluene (Aldrich, Gold Label) were used as received.

Method. Poly((trimethylsilyl)methyl methacrylate-*co*-(chloromethyl)styrene) was prepared by free-radical solution polymerization under a nitrogen atmosphere. A feed stock solution of benzoyl peroxide in toluene (6.1 × 10^{-4} g/mL) was added via syringe pump to the reaction mixture at a rate of 5.1 mL/h. Copolymer compositions were controlled by adjusting the initial monomer feed ratio. All reactions were run at 80–85 °C until conversions of 45–60% were obtained. Termination of the reaction was accomplished by the addition of 5 mL of ethanol per 100 mL of toluene used in the polymerization and rapid cooling to room temperature. Each polymer was precipitated into a rapidly stirred solution of methanol:water (1:1) in a Waring blender. The fibrous, white polymer was collected by filtration, washed several times with methanol, and dried under vacuum. The copolymers were redissolved in 2-methoxyethyl acetate (MEA), filtered, reprecipitated into the methanol:water solution, and dried to a constant weight under vacuum at 50 °C.

Characterization. Copolymer compositions were determined by ^{1}H NMR spectroscopy on a Varian T-60A spectrometer using 12 wt/v % polymer solutions in $CDCl_3$. CMS content was determined by comparison of the integrated region of either the aromatic or chloromethyl protons to the protons on the (trimethylsilyl)methyl group.

Copolymer molecular weights were determined in THF at 28 °C by high-pressure size exclusion chromatography (HPSEC) using a Waters Model 510 pump (flow rate = 1.0 mL/min), 401 differential refractometer detector, Viscotek Model 100 differential viscometer detector, and a set of Du Pont bimodal silanized columns. A universal calibration curve was obtained by using a kit of 10 narrow molecular weight linear polystyrene standards purchased from the Toyo Soda Co. Data acquisition and analysis were performed on an AT&T 6312 computer using an ASYST Unical 2.71 software system supplied with the Viscotek instrument.

All thickness measurements were performed on a Dektak IIA profilometer. UV spectra were obtained on a Hewlet Packard 8452A spectrometer. Elemental analyses were performed by Galbraith Laboratories.

Preliminary Lithographic Evaluation. Resist films (0.5 μm thick) were spun from 10–12% (wt/v) solutions of the polymer in 2-methoxyethyl acetate onto 4-in. Si substrates. Substrates used were either bare or precoated with 1.8-μm Hunt photoresist (HPR-206) baked at 210 °C for 2 h in air (hard-baked). Resist-coated substrates were prebaked for 1 h at 90 °C, in air, prior to exposure. A postbake of 1 h at 90 °C was performed on all samples.

Samples for the quantum efficiency study were exposed to either a low-pressure mercury lamp (continuous wave (CW) radiation) or a KrF excimer laser. A typical 0.5-μm resist film on 1.8-μm hard-baked HPR-206 was given a series of 12–15 exposures through a 7-mm-diameter circular contact mask approximately 1.5 cm from the wafer's edge. The CW lamp output was 22–26 mJ/(cm^2 min). The power was measured with an Epply copper constantan thermopile and calibrated meter. The fluence for the KrF laser (Questek) at 248.7 nm was 5–7 mJ/(cm^2 pulse) at 1 Hz over a 0.6-cm-diameter spot size. Power was measured with a Scientek calorimeter and calibrated meter. Intensities were varied by using a combination of circular apertures and focusing lenses and/or by changing distances between the sample and laser. No corrections were made for reflective losses. Lithographic exposures were performed by using an optical 5× reduction projection step and repeat exposure tool (λ emission = 248 nm). A Karl Suss Model MA 56M contact aligner equipped with a Lambda Physik KrF laser at 248 nm and a fluence of 0.12–0.14 mJ/(cm^2 pulse)

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Table I. Development Conditions for Poly(SI-CMS) Copolymers[a]

sequence	time, s	spray pressure, psi	spin speed, rpm
developer	60	30	100
developer/rinse I	10	20/20	100
rinse I	20	30	100
rinse I/rinse II	10	20/20	100
rinse II	40	30	100
hot N_2 dry	45		1400

[a] Initial development temperature = 23 °C; environmental chamber temperature = 18 °C; relative humidity = 34–36%.

at 100 Hz was used for further studies. The output was measured with a calibrated thin-film thermopile.

Resist-coated wafers were spray-developed by using an APT Model 915 resist processor under standard development conditions (Table I) with either of two different developers. The first consisted of a developer/rinse I/rinse II combination of methyl ethyl ketone (MEK)/methyl ethyl ketone–methanol (50:50 v/v %)/methanol. The second, and preferential, developer used was an isopropyl alcohol/isopropyl alcohol–water (70:30 v/v %)/water sequence as reported earlier.[14] Bilevel wafers prepared from the 90/10 SI-CMS copolymer were exposed and developed by using each developer system. Thickness measurements of the gel fraction remaining at several doses were made and found to be consistent between the two samples. The MEK/MeOH developer system was used for this portion of the investigation. The isopropyl alcohol developer was used to obtain coded line/space patterns with a minimum of swelling and/or distortion.

Quantum Efficiency Study. Calculations of the quantum efficiency of cross-linking, Φ_{cl}, from exposure response curves required determination of the dose absorbed by the resist film for a given incident dose. It was calculated by measuring the optical density, A, at 248 nm for a given initial film thickness (IFT) and substituting to obtain K, the amount of energy absorbed per thickness of resist film:

$$K = 1 - 10^{-A}$$

Once K is found, the energy absorbed by the sample, E, expressed in einsteins, can be found by substitution:

$$E = DK(8.326 \times 10^{-9})\lambda \times \text{area}$$

where D is the dose in J/cm^2 and λ is the wavelength of the incident radiation expressed in nanometers. The total energy absorbed per gram of resist, r, was found by assuming a density of 1 g/cm^3 over a 1-cm^2 area. The cross-linking efficiencies were determined by using the Charlesby–Pinner relationship:[15]

$$S + S^{1/2} = \frac{p_0}{q_0} + \frac{1}{\Phi_{cl}\bar{M}_w^0 r}$$

In this equation, S is defined as the soluble fraction after a dose, r. $\bar{M}_w^0$ is the initial weight average molecular weight, p^0 is the proportion of main-chain units cleaved per unit radiation dose, and q_0 is the proportion of monomeric units cross-linked per unit radiation dose. The ratio p_0/q_0 is defined as $\Phi_s/2\Phi_{cl}$. A plot of $S + S^{1/2}$ versus r^{-1} yields a straight line, with the slope containing information on Φ_{cl} while the y intercept yields Φ_s values.

Results and Discussion

A series of poly(SI-CMS) copolymers ranging from 0 to 100% CMS were prepared to determine the optimum bilevel lithographic composition and, furthermore, to determine the effect of the UV radiation source on the photochemical response of the system.

The silicon content in the copolymers was varied by altering the charge ratio of the monomers in accordance with published reactivity ratios.[5] The weight percent silicon incorporated was determined by ^{1}H NMR spectroscopy and was confirmed by elemental analysis (Table II). The $\langle M_w \rangle$'s for several samples were too large for proper comparison of resolution and sensitivity, and consequently lower molecular weight samples at the same copolymer compositions were prepared.

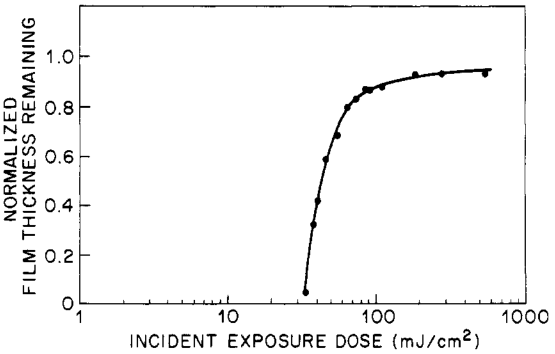

Figure 1. Exposure–response curve for the 85/15 poly(SI-CMS) sample exposed to 248-nm excimer laser radiation at 100 Hz.

An important consideration in achieving uniform exposure throughout the thickness of the resist film is a low optical density (OD) in the wavelength region of interest. The SI homopolymer has an OD at 248 nm of 0.006 AU for a 0.5-μm-thick film while the CMS homopolymer has a value of 0.33 (Table II). As expected, a linear relationship exists between the optical density and mole percent CMS in the copolymers.

Exposure–response curves were generated for each resist, and a representative plot for an 85/15 poly(SI-CMS) is shown in Figure 1. The sensitivity, expressed as the 50% gel dose or $D_g^{0.5}$, and the contrast, γ, were determined for each composition and are listed in Table III. These exposures were performed with an excimer laser at a fluence of either 0.12–0.14 mJ/(cm^2 pulse) at a rate of 100 Hz or 5 mJ/(cm^2 pulse) at 1 Hz or with a continuous wave mercury vapor lamp. Since the CMS portion affords the radiation sensitivity for the copolymer, $D_g^{0.5}$ is expected to decrease as CMS content increases. This general trend can be seen in the data. The CMS homopolymer and the 7% CMS samples were, however, inconsistent with this trend due to differences in molecular weight. The former material has a much lower $\langle M_w \rangle$ than the other copolymers, while the 93/7 SI-CMS copolymers are both higher molecular weight materials and, therefore, show much greater sensitivites. The SI homopolymer did not form a gel fraction in exposures up to 500 mJ/cm^2 by using a step tablet mask and in fact has been demonstrated to degrade upon irradiation.[16]

The effect of molecular weight on the $D_g^{0.5}$ value for the 100-Hz laser exposures can be shown by evaluating copolymers of different molecular weights at the same composition (Table III, Figure 2). A 75/25 SI-CMS sample at a $\langle M_w \rangle = 2.71 \times 10^5$ g/mole (sample 7) exhibited a $D_g^{0.5}$ of 14.5 mJ/cm^2, while at a lower molecular weight, 1.00 $\times 10^5$ g/mol (sample 8), $D_g^{0.5} = 26.2$ mJ/cm^2. The contrast was also seen to increase from 2.2 to 3.0 as the molecular weight decreased (Figure 2, Table III). Additionally, higher contrast was observed with narrower molecular weight distributions.

The results of the 1-Hz laser and mercury vapor lamp exposures (or continuous wave) are also shown in Table III (Figure 3). The $D_g^{0.5}$ values for these copolymers under

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Table II. Properties of Poly(SI-CMS) Copolymers

sample	X_{SI}[a]	X_{SI}[b]	SI/CMS[c] NMR	wt % Si	$10^{-4}\bar{M}_w$, g/mol	MWD	opt density[d] 248 nm	opt density[d] 254 nm
1	1.000	1.000	100/0	16.3	9.61	2.01	0.006	0.004
2	0.976	0.953	93/7	15.2	38.1	1.85	0.017	0.004
3	0.976	0.959	93/7	15.2	41.4	2.12	0.018	0.004
4	0.945	0.901	90/10	14.7	11.3	1.78	0.030	0.017
5	0.945	0.903	90/10	14.7	14.2	1.87	0.031	0.017
6	0.917	0.859	85/15	13.8	14.4	2.00	0.043	0.026
7	0.842	0.766	75/25	12.2	27.1	2.13	0.064	0.037
8	0.842	0.780	75/25	12.3	10.0	1.75	0.067	0.037
9	0.526	0.509	40/60	6.5	25.5	2.10	0.187	0.118
10	0.502	0.485	30/70	5.4	14.8	1.90	0.202	0.129
11	0.000	0.000	0/100	0.0	7.11	1.74	0.325	0.207

[a] Mole fraction SI monomer in monomer feed. [b] Mole fraction SI monomer in polymer, calculated from the weight percent Si. [c] Calculated from NMR ratios. [d] Measured for 0.5′μm films.

Table III. Lithographic Response of Poly(SI-CMS) Copolymers

sample	% CMS	$10^{-4}\bar{M}_w$, g/mol	$D_g^{0.5}$, mJ/cm^2 100 Hz[a]	$D_g^{0.5}$, mJ/cm^2 1 Hz[b]	$D_g^{0.5}$, mJ/cm^2 CW[c]	γ 100 Hz[a]	γ 1 Hz[b]	γ CW[c]
1	0	9.61						
2	7	38.1	45.0		52.0	2.8		3.0
3	7	41.4	44.0	29.0	51.0	3.1	2.9	2.8
4	10	11.3	65.0		82.0	3.0		3.1
5	10	14.2	67.0	55.0	83.0	2.9	2.5	2.4
6	15	14.4	43.5		40.5	2.9		2.2
7	25	27.1	14.5	8.4	15.0	2.2	2.9	2.1
8	25	10.0	26.2		33.5	3.0		2.4
9	60	25.5	12.2	7.7	12.5	2.4	2.3	1.9
10	70	14.8	11.4		14.5	2.4		2.1
11	100	7.11	19.2		25.0	1.9		1.8

[a] Excimer laser exposure at 100 Hz. [b] Excimer laser exposure at 1 Hz. [c] Continuous-wave mercury vapor exposure. [d] SI homopolymer does not exhibit cross-linking behavior.

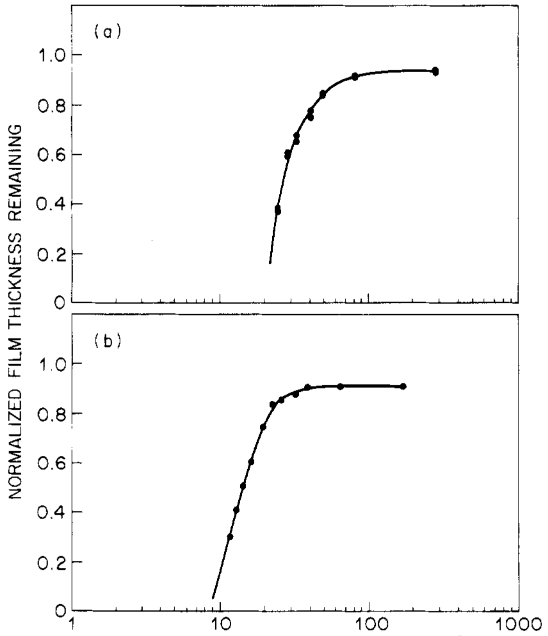


Figure 2. Exposure–response curves for the 75/25 poly(SI-CMS) sample exposed to 248-nm excimer laser radiation at 100 Hz: (a) high molecular weight; (b) low molecular weight.

both exposure conditions show the same trend of increased sensitivity as percent CMS incorporation increased. The CW exposures exhibit $D_g^{0.5}$ values closer to those of the 100-Hz laser exposures than the 1-Hz samples. The 1-Hz experiments were performed at 5 mJ/(cm^2 s), and as a result a greater degree of uncertainty exists in the accurate measurement of dose delivered at low exposure times. This effect is exacerbated at high percent CMS content because

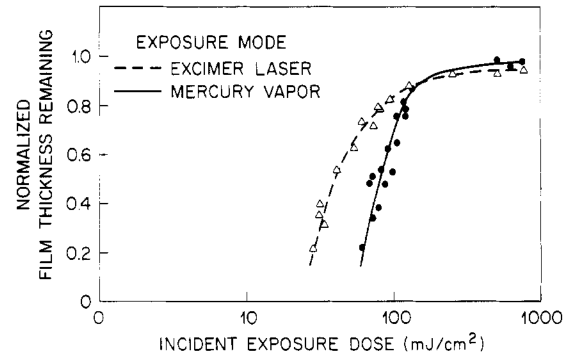


Figure 3. Exposure–response curves for the 90/10 poly(SI-CMS) sample, exposed to 248-nm excimer laser irradiation at 1 Hz and exposed to a CW mercury lamp.

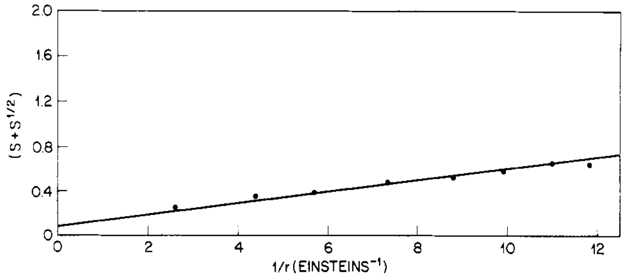


Figure 4. Charlesby–Pinner plot of the 93/7 poly(SI-CMS) sample exposed to 248-nm excimer laser radiation at 100 Hz.

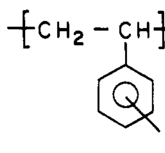
only one or two pulses are needed to achieve the 50% gel dose.

The absolute values for the quantum efficiencies of crosslinking, Φ_{cl}, and chain scission, ϕ_s, can be determined by using the Charlesby–Pinner relationship. Using equations previously discussed, plots of $(S + S^{1/2})$ (soluble

Table IV. Quantum Efficiency Values of Cross-Linking (Φ_{cl}) and Scission (Φ_s) for Poly(SI-CMS) Copolymers by Using Laser Exposure at 100 Hz

sample	% CMS	$10^2\Phi_{cl}$	$10^3\Phi_s$	Φ_s/Φ_{cl}
1	0			
2	7	1.06	1.34	0.122
3	7	1.29	1.57	0.126
4	10	1.20	0.63	0.053
5	10	1.24	0.66	0.052
6	15	1.22	0.55	0.045
7	25	1.26	0.51	0.034
8	25	1.30	0.44	0.041
9	60	1.20	0.36	0.030
10	70	1.19	0.31	0.026
11	100	0.61	0.07	0.011

fraction) versus $1/r$ ((absorbed dose)$^{-1}$) were prepared for each polymer composition by using the normalized film thickness data from the corresponding exposure–response curves.[17] A representative curve is shown in Figure 4. The nonzero intercepts indicate the occurrence of main-chain scission events concomitant with the cross-linking reactions. The values for the slope and intercept were determined by linear regression, and correlation coefficients of >95% were obtained in all cases. When the value of Φ_s/Φ_{cl} is <4, gel formation that leads to negative resist behavior is observed.[17] As seen from Table IV, this case encompasses all the copolymers examined here. Increased CMS content results in increased absorption and more effective cross-linking as judged by improved resist sensitivity (Table III). However, the Φ_{cl} values for the 248 nm laser exposures at 100 Hz show essentially no change throughout the poly(SI-CMS) compositional range (Table IV). Effectively, this means that when Φ_{cl} is normalized to the percent CMS in the polymer, Φ_{cl} *decreases* with increasing CMS content. While this result is counterintuitive, it may be explained given the following. As demonstrated by Tagawa,[6] the predominant species formed upon irradiation of CMS are aromatic methylene radicals (2) and other species, tentatively identified as 3. Clearly, as the concentration of CMS in the polymer increases, the concentration of reactive species within a given polymer chain will increase. Concomitantly, the probability of intramolecular radical combination reactions will also increase. As such reactions do not lead to gel formation and yet deplete the number of reactive species, Φ_{cl} is seen to decrease with increasing CMS content.



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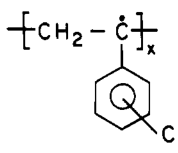

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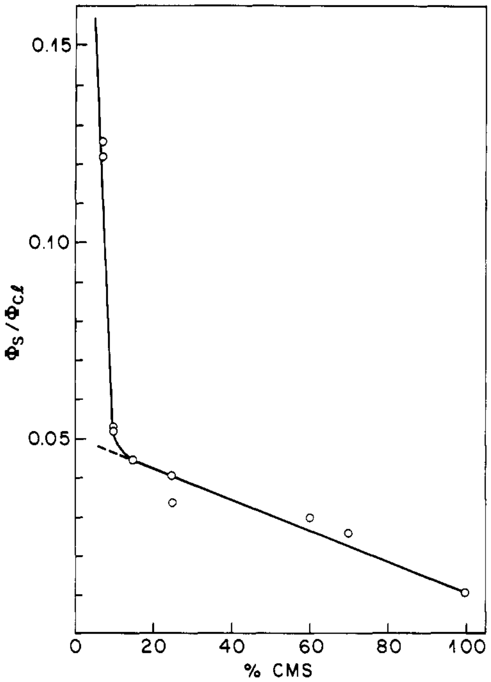

Figure 5. Plot of Φ_s/Φ_{cl} vs percent CMS for poly(SI-CMS) exposed to 248-nm excimer laser radiation at 100 Hz.

Table V. Quantum Efficiency Values of Poly(SI-CMS) Copolymers from Continuous-Wave Exposures

sample	% CMS	$10^2\Phi_{cl}$	$10^3\Phi_s$	Φ_s/Φ_{cl}
2	7	5.56	5.53	0.099
3	7	4.09	3.87	0.095
8	25	2.65	3.33	0.125
10	70	1.52	2.28	0.150
11	100	1.15	2.15	0.186

The change in Φ_s/Φ_{cl} derives from the decrease in the total number of chain-scission events as the SI content decreases. This clearly results from a decrease in the concentration of chain-scission-type monomer units. Examination of Figure 5 shows that the relationship between Φ_s/Φ_{cl} and percent CMS is approximately linear when the concentration of CMS in the polymer is >15%. Below this value, there is a rapid increase in the scission to cross-linking ratio. This is not surprising in view of the fact that the silyl methacrylate homopolymer is known to undergo radiation-induced chain scission,[16] and no gel formation was observed in our experiments. Additionally, methacrylates undergo "unzipping" reactions,[18] so that as the concentration of monomer units (CMS) that would block this process decreases, the propensity of the molecule to continue to undergo scissioning would increase; thus the observed increase in Φ_s/Φ_{cl} and Φ_s.

Quantum efficiency results for the mercury vapor lamp exposures are listed in Table V. It is observed that both the Φ_s and Φ_{cl} values decrease as a function of composition. The ratio Φ_s/Φ_{cl} for the 93/7 poly(SI-CMS) samples (~0.1) are comparable to those obtained by KrF laser exposure (0.12); however, the Φ_s/Φ_{cl} ratio increases with increasing CMS content in the continuous-wave experiments. The CMS homopolymer exhibits a quantum yield ratio of 0.186, which is still well within the $\Phi_s/\Phi_{cl} < 4$ criterion necessary for gel formation to be observed. The increased absolute values of Φ_s and Φ_{cl} upon CW vs pulsed laser exposure is not surprising in view of literature reports that the quantum efficiencies of many radical reactions decrease with increasing radiation intensity.[12] The trends observed in Φ_{cl} and Φ_s also differ for the CW exposures of poly(SI-CMS). While differences in radiation chemistry have been observed for pulsed laser vs Hg lamp exposure for various systems,[12,13] the direction and magnitude of these trends for the poly(SI-CMS) materials examined here cannot be explained at this point and require further investigation.

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(18) Ranby, B.; Rabek, J. F. *Photodegradation, Photo-oxidation and Photostabilization of Polymers*; Wiley: New York, 1975; pp 156–159.

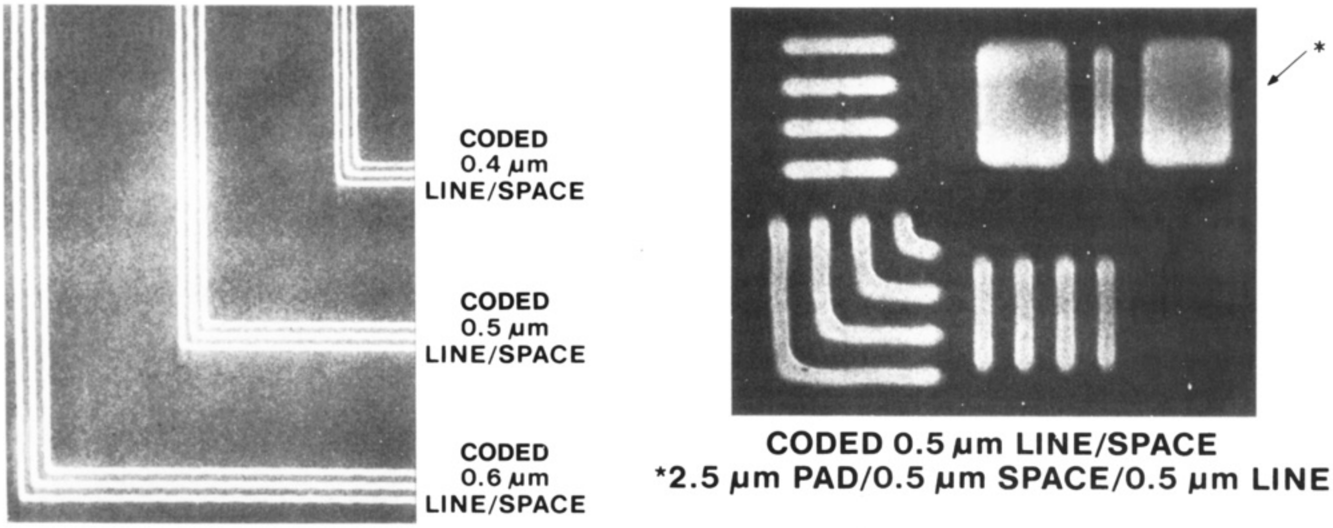

Figure 6. Scanning electron micrograph of the 93/7 poly(SI-CMS) after 150 mJ/cm^2 exposure to 248-nm excimer laser radiation at 100 Hz and isopropyl alcohol development.

Quantum efficiency values for the 1-Hz laser exposures could not be calculated to a high degree of confidence due to insufficient data available from the exposure–response curves at doses below $D_g^{0.5}$.

The sensitivities of all the poly(SI-CMS) materials are quite high and increase with increasing CMS content. For lithographic evaluation, we chose to work at low percent CMS incorporation for several reasons. First, a low CMS content will maximize the percent silicon in the copolymer; second, a lower optical density results from less CMS, ensuring uniform exposure through the thickness of the film; third, copolymers containing <15% CMS can be developed with 2-propanol, a nontoxic solvent; fourth, the doses necessary to obtain lithographically useful features did not affect process throughput.

Figure 6 (left) shows images obtained with a 93/7 poly(SI-CMS) copolymer, $\langle M_w \rangle = 4.0 \times 10^5$ g/mol, exposed at 150 mJ/cm^2, and developed by using 2-propanol. Clearly, 0.4-μm coded line/space patterns can be resolved with a minimum of distortion. Figure 6 (right) shows the same material in a pad/space/line feature. The absence of bridging between these features indicates minimum swelling in the resist by the developer—a key requirement for high-resolution negative resist systems. Initial work in the pattern transfer of submicron features through thick planarizing photoresist has yielded coded 0.75-μm L/S images[5] and more recently, 0.4-μm L/S patterns[14] with little line-width loss.

Conclusions

Poly(SI-CMS) has been found to function as a negative resist throughout the compositional range 7–100% CMS. With either a continuous or pulsed radiation source, the sensitivity of the copolymers decreased with decreasing CMS content. Good agreement between the lithographic sensitivity data obtained from the 100-Hz laser and CW exposures was observed. Values for the quantum efficiencies of cross-linking, Φ_{cl}, and chain scission, Φ_s, indicated the cross-linking reaction to be the predominant photoinduced event. Both Φ_s and Φ_s/Φ_{cl} for the laser exposure data decreased as the proportion of SI monomer, i.e., the concentration of species capable of undergoing scission in the copolymer decreased. Low CMS content, ≤10%, was effective for lithographic purposes, because low optical density and high silicon contents could be achieved. With isopropyl alcohol as a developer, 0.4-μm L/S images could be resolved at an exposure dose of 150 mJ/cm^2 by using an excimer laser.

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