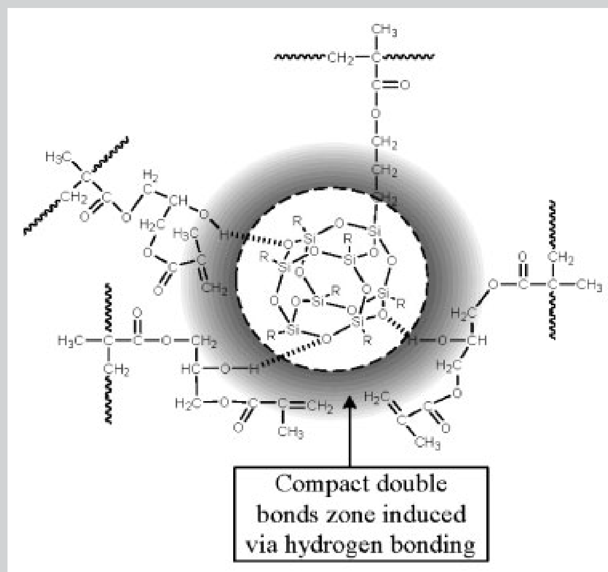
Summary: A series of methacrylate copolymers containing polyhedral oligomeric silsesquioxane (POSS) was synthesized from the free radical copolymerization of methacrylic acid, methyl methacrylate, and isobutyl propylmethacryl polyhedral oligosilsesquioxanes, and then were modified with glycidyl methacrylate to serve as negative-type photoresists. The UV/Vis spectroscopy reveals that the incorporation of POSS moiety into the copolymer results in a slight decrease in transparency from 99 to 92.5% (at wavelength = 365 nm). The photosensitivity in terms of resist sensitivity ($D_n^{0.5}$), contrast (γ), and photopolymerization rate are significantly increased with increase in the POSS content. In addition, the induction time is reduced from 0.520 to 0.515 min after incorporating the POSS unit based on photo-DSC analyses. These observed results can be rationalized as due to hydrogen bonding interactions between siloxane and hydroxyl groups in copolymers which tend to attract the methacrylate double bonds surrounding POSS units to crosslink, thereby enhancing the photopolymerization rate and sensitivity. We further evaluate the lithographic property of a photoresist under a collimated exposure.



Compact double bonds zone induced via hydrogen bonding.

Polyhedral Oligomeric Silsesquioxane Containing Copolymers for Negative-Type Photoresists

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Introduction

Over the past decades, applications of photosensitive resins in microelectronics, optoelectronics, printed circuit boards, printing plates, photo-fabrications, imaging, stereo-lithographies, adhesives, and inks have grown rapidly. Acrylate monomers have been widely used in photocuring applications due to their high reactivity. However, the effect of incorporating polyhedral oligomeric silsesquioxanes (POSS) structure into these photosensitive resins has rarely been investigated. It has been widely discussed in the literature[1–6] that the inorganic–organic hybrid architecture of POSS can be easily copolymerized or blended with other common polymers. The POSS-containing polymers generally possess improved thermal stability, mechanical property, and surface hardening, and have attracted considerable interest in versatile applications. Several POSS-based photoresists have also been widely reported.[7–14] Positive tone POSS containing photoresists have been investigated for electron beam,[7,8] extreme ultraviolet,[9] 157 and 248 nm lithography.[10,11] The results showed high resolution and improved reactive ion etching resistance. Alternatively, octavinylsesquioxane dry resist has been performed as a negative tone resist that exhibits high sensitivity for deep UV-lithography, electron-beam, and X-ray lithography.[12] Photocurable inorganic–organic hybrid materials with functionalized POSS unit have been

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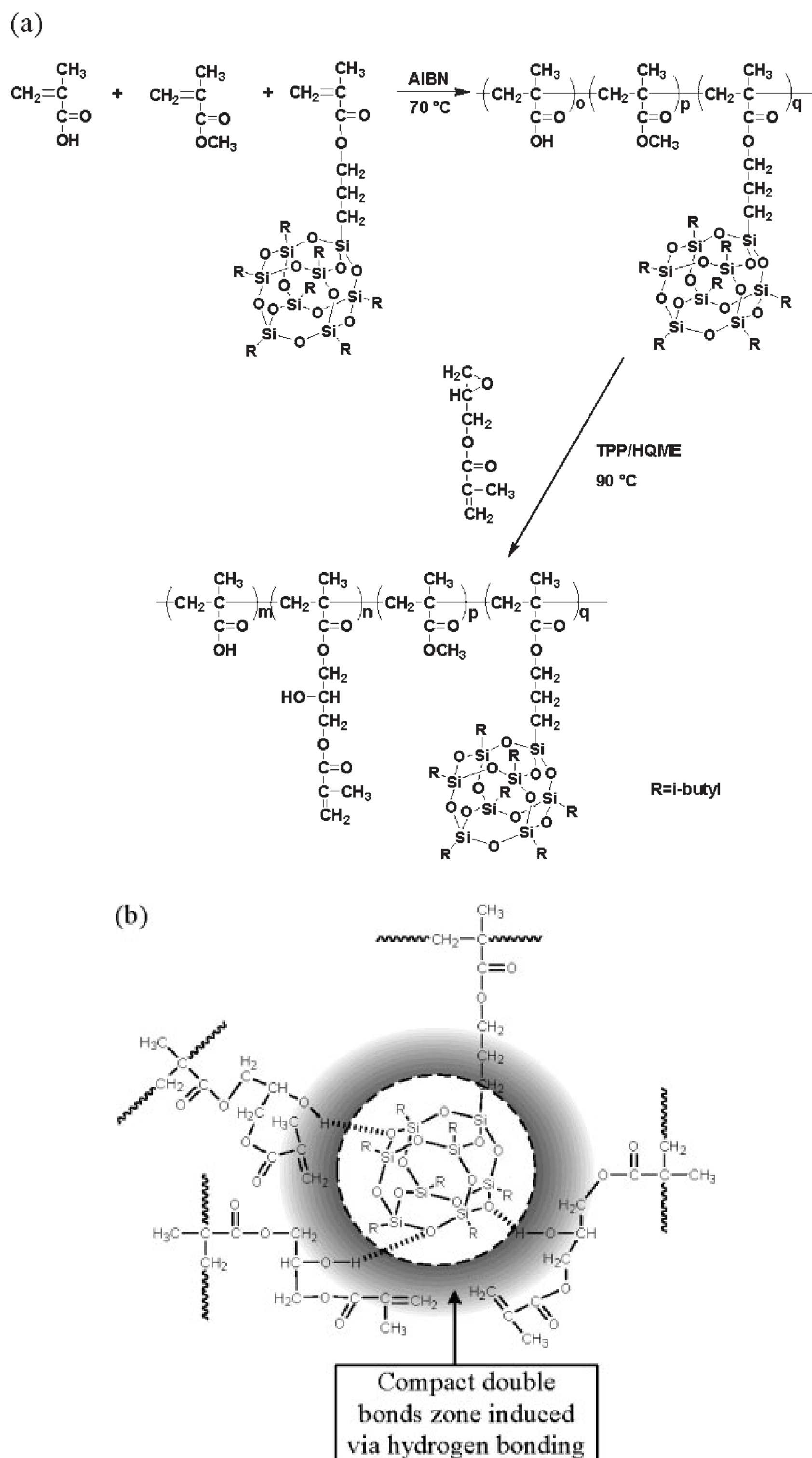
studied in methacrylate,[13] coumarin,[14] and thiol-ene[15] systems.

Properties of photoresists are directly related to the monomer structure. It has been reported that the polymerization rates of photoresists capable of forming hydrogen bonding are significantly higher than those conventional photoresists due to the pre-organization via hydrogen bonding to bring reactive bonds closer to each other, and thus enhance the rate of



Scheme 1. (a) Synthetic routes of POSS-containing photosensitive copolymers and (b) the proposed microstructure via hydrogen bonding interaction of POSS copolymers.

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photopolymerization.[16–18] In our previous study,[19–22] we have observed the existence of hydrogen bonding interaction between the siloxane of the POSS moiety and the hydroxyl groups. Accordingly, we would like to extend our previous works to develop POSS-containing photoresist materials for UV-lithography with enhanced sensitivity, higher contrast, and better resolution. Here, we have prepared photocurable methacrylate-based copolymers with various POSS contents. These POSS-containing copolymers were utilized as negative-type photoresists and the resultant photoresist properties were investigated in terms of sensitivity, contrast, and pattern resolution. The exotherms for photopolymerization of the photoresists was investigated by photo-DSC.

Experimental Part

Chemicals

2,2′-Azoisobutyronitrile (AIBN, TCI) was recrystallized in methanol before use. Isobutylpropylmethacryl polyhedral oligosilsesquioxane (MI-POSS, Hybrid Plastics), methyl methacrylate (MMA, Lancaster), methacrylic acid (MAA, Showa), glycidyl methacrylate (GMA, TCI), diethylene glycol monomethyl ether (DEGME, Tedia), triphenylphosphine (TPP, Lancaster), hydroquinone monomethyl ether (HQME, Lancaster), trimethylolpropane triacrylate (TMPTA, Sartomer), 4′-methylthio-2,2-dimethyl-2-morpholinoacetophenone (Irgacure 907, Ciba), and isopropylthioxanthone (ITX, Lamberti) were used as received.

Syntheses of POSS-Containing Photosensitive Copolymers

These POSS-containing methacrylate copolymers were prepared in DEGME using AIBN (1 wt.-% of monomers) as initiator at 70 °C for 5 h under nitrogen atmosphere. After adding TPP as catalyst and HQME as free radical polymerization inhibitor to the above copolymer solution, GMA was added and reacted for 3 h at 90 °C. The acid value of the copolymer solution was monitored to ensure that all the GMA underwent the ring-opening reaction of epoxide group. The POSS-containing photosensitive copolymer was isolated in excess hexane, filtered and washed thoroughly by hexane. The product was purified by reprecipitation from THF/hexane. Finally, the sample was dried under vacuum at 60 °C for 1 d.

Characterizations

Infrared spectrum was recorded on a Bio-Rad FTS 3000 FT-IR Spectrometer. ^{1}H NMR spectra were obtained using a Varian INOVA500 (500 MHz) Spectrometer in acetone-d_6. UV/Vis spectra were recorded on a film (ca. 15 μm) on quartz plates with a Perkin-Elmer Lambda 900 Spectrophotometer. The molecular weights and polydispersities were determined in THF by a Waters gel permeation chromatography (GPC) system using a calibration curve of PS standards. The calorimetric measurement was performed on a Perkin-Elmer DSC 7 instrument. Approximately 10 mg of sample was held for 15 min at 150 °C to evaporate the residual solvent. The sample was then quickly cooled and then scanned between 25 and 250 °C with a scan rate of 20 °C · min^{-1} to obtain the glass transition temperature (T_g). A Perkin-Elmer Thermal Gravimetric Analyzer 7 was used to study the thermal stability of the copolymer. All samples were treated at 150 °C for 15 min to remove the solvent. Around 10 mg of the samples were heated under air atmosphere from 25 to 600 °C at the heating rate of 20 °C · min^{-1}. The heat of photopolymerization exotherm was detected by photo-DSC (Perkin-Elmer DSC 7 with Perkin-Elmer DPA 7 Photocalorimeter) under a nitrogen flow at 30 °C. Approximately 1 mg of photoresist was placed in the aluminum DSC pan. The photoresist was formulated by dissolving 2 g of POSS-containing photosensitive copolymer, 1 g of TMPTA, 0.5 g of Irgacure 907, and 0.125 g of ITX in 3 g of DEGME. The photoresist was spin-coated onto 10 × 10 cm^2 copper-clad laminate and the solvent was removed at 80 °C for 30 min. The film was exposed with a collimated exposure, developed by dipping in a 1 wt.-% Na_2CO_3 aqueous solution at 25 °C for 3 min, and rinsed by water. The image of the photoresist was obtained by a Hitachi S-4200 scanning electron microscope. The characteristic curve was determined by normalizing the film thickness against exposure dose.

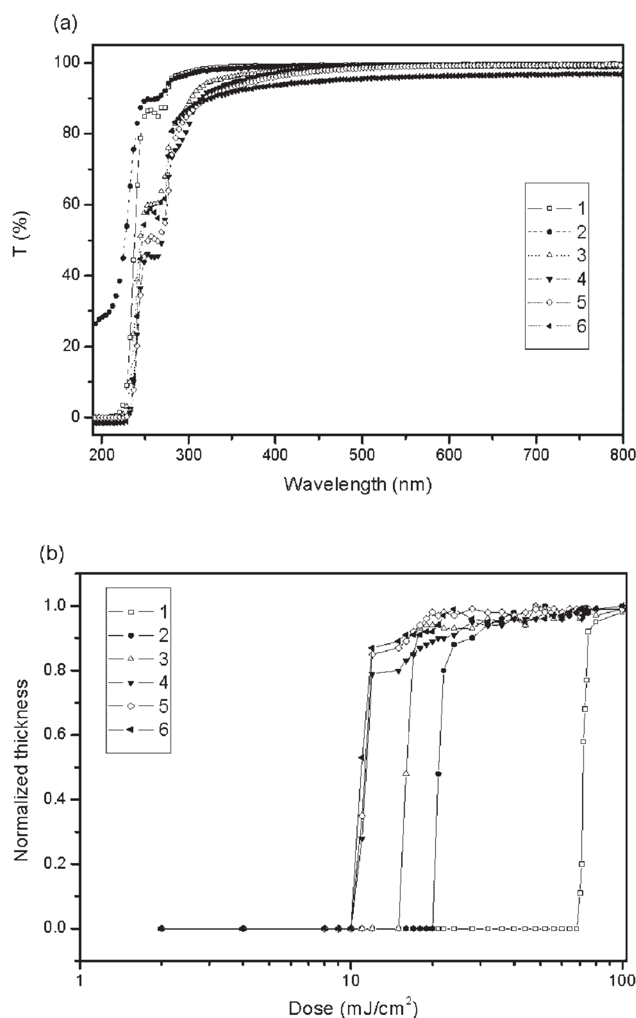

Figure 1. (a) UV/Vis spectra of POSS-containing photosensitive copolymers; (b) characteristic curves of the POSS-containing photoresists [MI-POSS wt.-% in photoresists: 1 (0%), 2 (0.9%), 3 (5.9%), 4 (8.7%), 5 (24.6%), 6 (35.3%)].

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Results and Discussion

The POSS-containing photosensitive copolymer was prepared in two steps according to the synthetic route shown in Scheme 1(a). According to Lichtenhan,[5] the POSS monomer has reactivity similar to MMA in POSS/MMA system. The loading of MI-POSS contents were varied from 0 to 37 wt.-%, and the obtained $\overline{M}_w$ values of these copolymers were greater than 35 000 $g \cdot mol^{-1}$ with a PDI of about 2.0 (Table 1). The infrared characteristic peaks of these POSS-containing photosensitive copolymers are assigned as follows: the peak at 1 620 cm^{-1} as the C=C stretch vibration, 1 726 cm^{-1} as the C=O stretch vibration and 1 111 cm^{-1} as the Si–O–Si stretch vibration. The peak assignments of the ^{1}H NMR spectrum for the POSS-containing photosensitive copolymer are: –C=C$\boldsymbol{H}_2$ protons at 5.68 and 6.12 ppm, –COOC$\boldsymbol{H}_3$ protons at 3.60 ppm, and –SiC(C$\boldsymbol{H}_3$)$_3$ protons at 1.0 ppm. Table 1 summarizes compositions and properties of these copolymers. The decomposition temperature and glass transition temperature of these copolymers increase with the increase in the POSS content. The Si–O–Si bond of POSS structure has high bond dissociation energy of 462 $kJ \cdot mol^{-1}$,[23] and the incorporation of POSS moiety is able to effectively improve the thermal stability of the copolymer. In addition, the increase of POSS content results in significant increase in the copolymer T_g due to the bulkiness and rigidity of the POSS structure, which have been reported to increase T_g of POSS-containing copolymers.[7] In our previous study,[19–22] we also demonstrated the hydrogen bonding interaction between the siloxane group of POSS and the hydroxyl groups. In these photocurable copolymers, competitive hydrogen bonding formations within POSS moiety exist between hydroxyl–siloxane and carboxylic acid–siloxane, while these hydrogen bonding interactions play an important role in causing significant increase in T_g.

Figure 1(a) shows the UV/Vis spectra of POSS-containing photosensitive copolymer films of around 15 µm thickness on quartz plates. The transmittance of the copolymer slightly decreases with the increase in POSS content because these POSS units tend to aggregate in the copolymer and cause slight decrease in transparency of the copolymer.[11,24–26] Overall, these copolymers all show acceptable transmittances ranging from 99 to 92.5% at 365 nm wavelength as listed in Figure 1(a) and Table 1. The characteristic curves of the photoresists for exposure doses ranging from 2 to 100 $mJ \cdot cm^{-2}$ are shown in Figure 1(b). The parameters of sensitivity ($D_n^{0.5}$) and contrast (γ) were determined from these characteristic curves to evaluate the photoresist performance and the results are also summarized in Table 1. The sensitivity ($D_n^{0.5}$) is defined as the dose that retains 50% of the original film thickness after development.[27] The contrast (γ) was obtained as the slope of the initial tangent to the characteristic curve.[28] The sensitivity of the POSS-free photoresist 1 is 71.8 $mJ \cdot cm^{-2}$ while the POSS-containing photoresists, photoresists 2–6, are significantly decreased ranging from 20.0 to 10.8 $mJ \cdot cm^{-2}$. The contrasts of the photoresists also show the same trend as sensitivities. These results indicate that the presence of POSS unit plays an important role in the negative-type photoresist properties. The bulky POSS structure and the hydrogen bonding between POSS-containing photosensitive copolymers tend to restrict polymer chain motion, and result in changing the characteristics of photoresists. The influence of physically cross-linked POSS structure on photopolymerization of photoresists was studied by photo-DSC. Figure 2 shows the exothermal curves of photopolymerizations for these photoresists. It has been reported[29] that the heat flux is related to the rate of photopolymerization. According to the photo-DSC results, the maximum peak of heat flux shifts to a shorter time with higher POSS content, implying that the photopolymerization rate of the photoresist is accelerated by the increase in the POSS content. We also observed the same trends in the heat of reaction (ΔH) relating to the POSS content. As mentioned before, competitive hydrogen bonding formations within POSS moiety exist between hydroxyl–siloxane, and carboxylic acid–siloxane. However, hydrogen bonding interaction of hydroxyl–siloxane majorly influences the methacrylate double density. Therefore, it is

Table 1. Characterizations of POSS-containing photosensitive copolymers and photoresists.

No.	Composition loading (in copolymer) wt.-%				$\overline{M}_w$	PDI	T_g	T_d a)	Transmittance b)	Sensitivity($D_n^{0.5}$)	Contrast
	MI-POSS	MMA	MAA	GMA	$g \cdot mol^{-1}$		°C	°C	%	$mJ \cdot cm^{-2}$	
1	0 (0)	64.51 (66.92)	27.64 (26.16)	7.85 (6.93)	35 400	1.90	85.3	269	99.0	71.8	21.6
2	0.92 (0.87)	63.59 (64.73)	27.64 (27.11)	7.85 (7.29)	41 200	2.26	88.6	282	98.7	20.0	19.3
3	6.40 (5.90)	58.11 (60.89)	27.64 (25.40)	7.85 (7.81)	42 000	1.96	94.6	285	96.7	16.0	15.6
4	9.20 (8.69)	55.31 (57.64)	27.64 (26.01)	7.85 (7.66)	41 900	1.85	116	294	95.3	11.4	10.0
5	23.0 (24.6)	41.51 (42.69)	27.64 (26.64)	7.85 (7.07)	42 900	2.06	122	303	94.1	11.3	10.7
6	36.9 (35.3)	27.61 (32.71)	27.64 (24.97)	7.85 (7.02)	39 400	1.88	139	309	92.5	10.8	11.0

a) Temperature at 10 wt.-% loss under air atmosphere.
b) Transmittance was observed at 365 nm wavelength.

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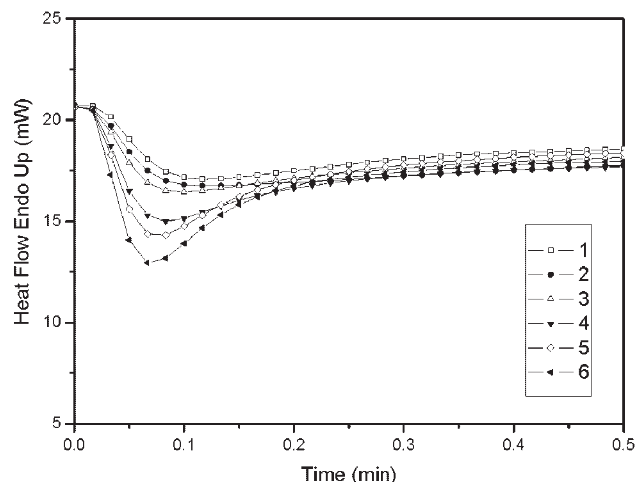

Figure 2. Photo-DSC exothermal curves for the photopolymerization of photoresists.

reasonable to explain that higher photopolymerization rate and higher heat of reaction from these POSS-containing photoresists come from the strong hydroxyl–siloxane hydrogen bonding interaction between the POSS moieties and hydroxyl groups in the double bond side chain of these photosensitive copolymers. The strong hydrogen bond interaction tends to make these methacrylate double bonds dense in the vicinity of POSS moieties and result in higher concentration of these methacrylate double bonds around POSS units and thus enhances the rate of photopolymerization. The proposed schematic microstructure via hydrogen bonding interaction between POSS moieties and hydroxyl groups which resulted in higher concentration of double bonds side chains is shown in Scheme 1(b). Table 1 shows that the sensitivities ($D_n^{0.5}$) for photoresists 4–6 are nearly constant at 10–11 mJ · cm^{-2}, even though the photopolymerization rate is faster for the photoresist with higher POSS content. It is probably due to photoresist 4 (8.7 wt.-% MI-POSS) which has already reached its minimum induction energy for this series of POSS-containing photoresists. As shown in Figure 3, the negative pattern of photoresist 4 was used in UV-lithography. One concern about POSS is that it may cause decrease in sensitivity of photoresist because of its inorganic nature. The results indicate that this is not a problem in our system. Figure 3 shows a nice line pattern (25 μm) with a thickness of 25 μm after a dose of 40 mJ · cm^{-2}.

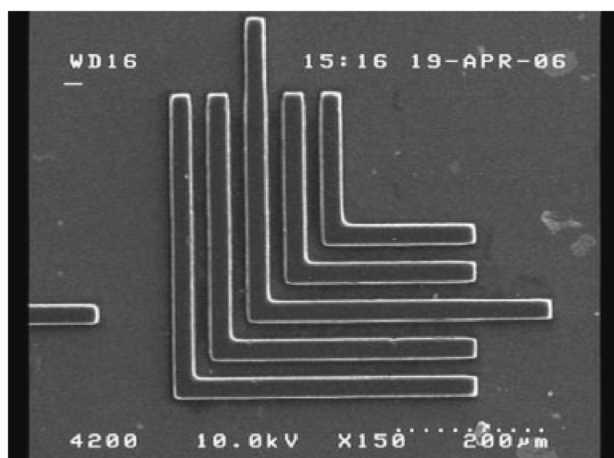

Figure 3. SEM image (line pattern) for photoresist 4 at a dose of 40 mJ · cm^{-2}.

Conclusion

A series of acrylate copolymers with various POSS contents were prepared and characterized. The presence of POSS units plays an important role in enhancing the thermal stability, glass transition temperature, and to maintain the optical properties on these POSS-containing copolymers. The sensitivity and photopolymerization rate are significantly enhanced by the presence of POSS, even with a small amount of POSS. Hydrogen bonding interaction between the POSS moiety and the hydroxyl groups in methacrylate side chain of POSS-containing photosensitive copolymers not only forms a physically cross-linked bond, but also raises the density of methacrylate double bonds around POSS units and enhances the chemically cross-linked photopolymerization rate. Further, we evaluated the lithographic property of a photoresist under collimated exposure. High sensitivity photoresists made by this method have potential utility for UV-lithography.

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