Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Characterization of negative-type photoresists containing polyhedral oligomeric silsesquioxane methacrylate

Ho-May Lin [a,b], Kuo-Hung Hseih [c], Feng-Chih Chang [a,*]

[a] *Department of Applied Chemistry, National Chiao Tung University, 300 Hsinchu, Taiwan*
[b] *Material and Chemical Research Laboratories, Industrial Technology Research Institute, 310 Chutung, Taiwan*
[c] *Institute of Polymer Science and Engineering, National Taiwan University, 106 Taipei, Taiwan*

ARTICLE INFO

ABSTRACT

A series of negative-type photoresists made by blending with various contents of polyhedral oligomeric silsesquioxane (POSS) methacrylate were prepared and characterized. These POSS macromers tend to crystallize or aggregate to form their own domains within the photoresist matrix. Sensitivity of the POSS modified photoresist is significantly improved with the increase of the POSS content. Results from photo-DSC analyses indicate that both induction time and peak maximum of heat flux are reduced by blending with POSS macromer. Addition of the proper amount (<13 wt%) of POSS can effectively increase photo-polymerization rate and exothermic heat. Hydrogen bonding interaction between the hydroxyl of photo-resist and the siloxane of POSS tends to attract methacrylate double bonds surrounding POSS particles locally and thus enhances the rate of photo-polymerization and sensitivity.

1. Introduction

Negative-type photoresists have been widely adopted in electronics [1,2], printing plates [3], liquid crystal displays [4], microfabrications [5], nanoimprints [6], and optics [7]. In the future, novel negative-type photoresists will be continually developed through new materials and new processes.

Combining different materials, such as organic and inorganic compounds, to obtain improved performance is an important trend for developing new materials [8]. Polyhedral oligomeric silsesquioxanes (POSS) contain inner inorganic cage structure with rigidity and high thermal stability. The outer surface of POSS molecule can be substituted by certain organic groups which are solvent soluble or polymer compatible. POSS-containing polymers usually result in improved mechanical strength and thermal stability [9], better dimensional stability [10], high glass transition temperature [11], and low dielectric constant [12]. POSS-based photosensitive resins have also attracted considerable interest, however, most prior studies have concentrated on the applications of positive-type photoresists [13–17] and UV curable resins [18–21], research on negative-type photoresist has been relatively rare [22,23].

In our previous study [23], the POSS moiety was incorporated into negative-type photoresists by a copolymerization method. The POSS-containing photosensitive copolymer formulated negative-type photoresist for UV-lithography is able to accelerate the photopolymerization significantly even with small amount of POSS. However, the viscosity of the POSS-containing photosensitive copolymer solution increases with the increase of POSS content and thus causes handling difficulty. The tendency of forming hydroxyl–siloxane hydrogen bonding interaction within the POSS-containing photosensitive copolymer attracts those methacrylate groups close together surrounding POSS units but tends to retard molecular chain movement.

In this study, a blending method has been adopted to overcome the viscosity problem. A series of negative-type photoresists are prepared by blending a general negative-type photoresist with various POSS contents. POSS macromer of isobutylpropylmethacryl polyhedral oligosilsesquioxane (MI-POSS) with one methacrylate group is utilized. Characterizations of this blending system of the general negative-type photoresist were carried out by Fourier transform infrared spectroscopy (FT-IR), ^{1}H nuclear magnetic resonance spectroscopy (^{1}H-NMR), gel permeation chromatography (GPC), differential scanning calorimetry (DSC) and ultraviolet/visible spectroscopy (UV/vis). Photoresist performances were investigated in terms of sensitivity, contrast and pattern resolution. The scanning electron microscope (SEM) was used to observe the morphology and line pattern of photoresists. The exotherms for photo-polymerization of photoresists were also investigated by using photo-differential scanning calorimetry (photo-DSC).

* Corresponding author. Tel./fax: +886 3 5131512.
 E-mail address: changfc@mail.nctu.edu.tw (F.-C. Chang).

2. Experimental

2.1. Chemicals

N,N′-azobisisobutyronitrile (AIBN, TCI) was recrystallized in methanol before use. Isobutylpropylmethacryl polyhedral oligosilsesquioxane (MI-POSS, Hybrid Plastics), methyl methacrylate (MMA, Lancaster), methacrylic acid (MAA, Showa), 2-ethylhexyl acrylate (2-EHA, TCI), glycidyl methacrylate (GMA, TCI), styrene (SM, TCI), diethylene glycol monomethyl ether (DEGME, TEDIA), triphenylphosphine (TPP, Lancaster), hydroquinone monomethyl ether (HQME, Lancaster), trimethylolpropane triacrylate (TMPTA, SARTOMER), 2-methyl-1-[4-(methylthio)phenyl] -2-(4-morpholinyl)-1-propanone (Irgacure 907, Ciba) and isopropylthioxanthone (ITX, Lamberti) were used as received.

2.2. Syntheses of the photosensitive copolymer

The MAA/MMA/2-EHA/styrene 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 (1 wt% of monomers) as catalyst and HQME (0.1 wt% of monomers) 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 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 one day.
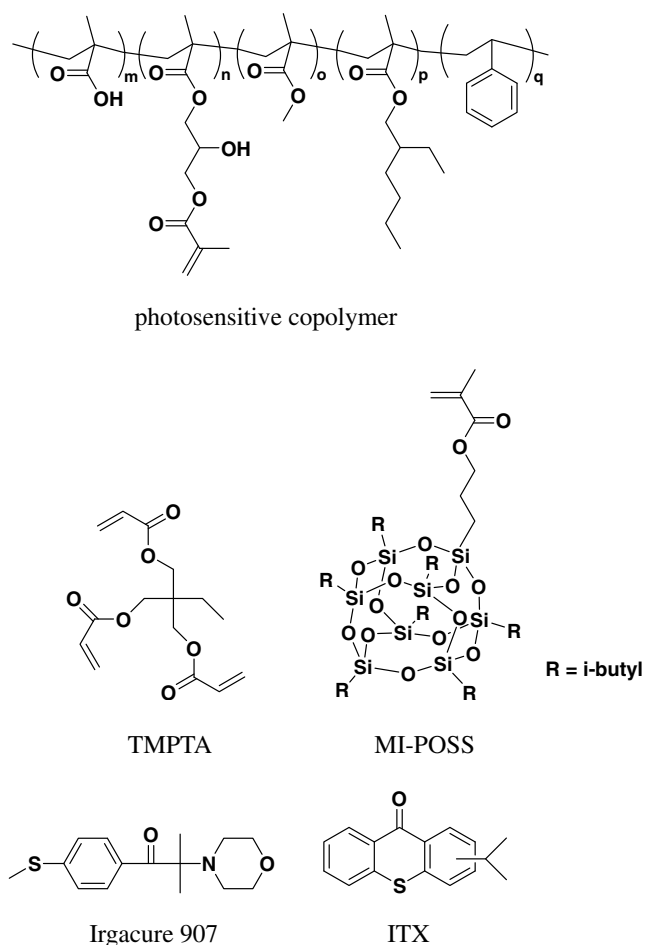
2.3. Characterizations

Infrared spectrum was recorded on a Bio-Rad FTS 3000 FT-IR spectrometer. ^{1}H-NMR spectrum was obtained using a Varian INOVA500 (500 MHz) spectrometer in acetone-d_6. UV/vis spectra were recorded on films (ca. 25 μm) on quartz plates with a Perkin-Elmer Lambda 900 spectrophotometer. The molecular weight and polydispersity 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 residual solvent. The sample was then quickly cooled and then scanned between 25 °C and 250 °C with a scan rate of 20 °C min^{-1} to obtain the glass transition temperature (T_g). The general photoresist was formulated by dissolving 5 g of photosensitive copolymer, 2 g of TMPTA, 1 g of Irgacure 907 and 0.25 g of ITX in 5 g of DEGME. MI-POSS of 0 g, 0.05 g, 0.25 g, 0.5 g, 1.25 g, or 2.5 g was added to the general photoresist and coded from photoresist 1 to photoresist 6. 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 to broadband UV radiation with a collimated exposure (Tamarack 161-OA containing a 5 kW mercury short arc lamp and an internal UV integrator to control exposure dose), developed by dipping in a 1 wt% Na$_2$CO$_3$ 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 film thickness against exposure dose in logarithmic scale. The photopolymerization exotherm curves were detected by a photo-DSC (Perkin-Elmer DSC 7 with Perkin-Elmer DPA 7 Photocalorimeter) under a nitrogen flow at 30 °C. Approximately 1.5 mg photoresist was placed in the aluminum DSC pan. The heat of photopolymerization was calculated by integrated the peak area over the curve using the horizontal baseline (Scheme 1).

3. Results and discussion

The methacryloyl-containing photosensitive copolymer was prepared by free radical copolymerization and glycidyl–carboxyl reaction. The obtained M_w of the copolymer is 75,600 with a polydispersity ca. 2.32 (Table 1). The infrared characteristic peaks of the photosensitive copolymer are assigned as follows: 1620 cm^{-1} as the C=C stretch vibration, 1726 cm^{-1} as the C=O stretch vibration, 758 cm^{-1} and 700 cm^{-1} as the C–H out-of-plane bending vibration of the phenyl ring. The peak assignments of the ^{1}H-NMR spectrum for the photosensitive copolymer are: –C=C$\textbf{H}_2$ protons at 5.68 and 6.12 ppm, –COOC$\textbf{H}_3$ protons at 3.60 ppm, and –C–C$_6$$\textbf{H}_5$ protons at 7.20 ppm. Table 1 summarizes compositions and properties of the copolymer. The glass transition temperature of the copolymer is 128.6 °C.

Fig. 1 displays the UV/vis spectrum of the photosensitive copolymer film with 25 μm thickness on a quartz plate. The transmittance of the copolymer is greater than 90% at the wavelength range of 300–800 nm as shown in Fig. 1 and Table 1. This copolymer shows acceptable transmittance.

photosensitive copolymer

Scheme 1. Chemical structures of chemicals studied.

Table 1
Characterizations of the photosensitive copolymer

MMA/MAA/styrene/2-EHA/GMA loading (in copolymer; wt%)	M_w	PDI	T_g (°C)	Transmittance* (%)
18.9/32.9/18.0/22.1/8.1 (19.0/34.8/12.5/24.6/9.1)	75,600	2.32	128.6	98.2

* Transmittance was observed at 365 nm wavelength.

Fig. 2 gives the UV/vis spectra of various unexposed dry photoresist films on quartz plates. The film of photoresist 1, free of MI-POSS, has high transmittance (99%) in the wavelength region from 425 to 800 nm, but low transmittance at 300–425 nm due to the strong UV
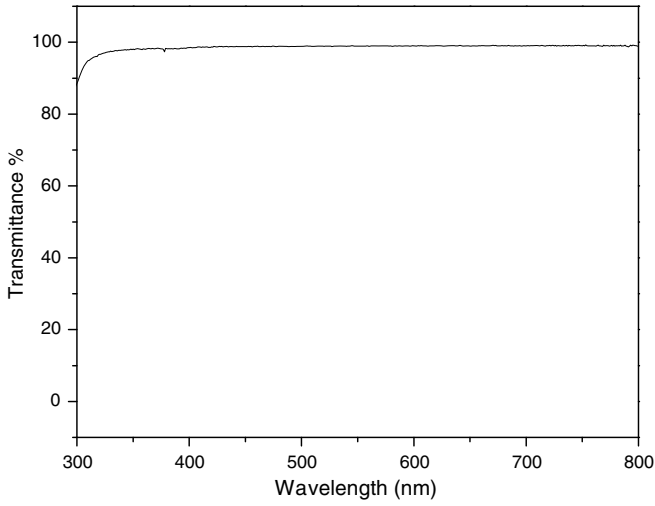
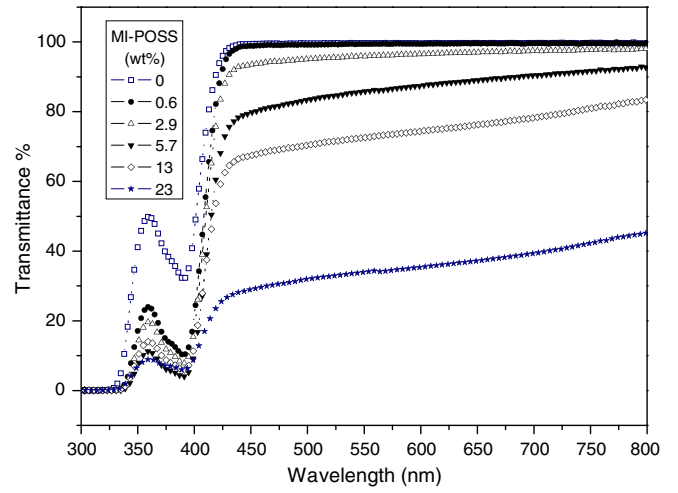**Fig. 1.** UV/vis spectrum of the photosensitive copolymer.

Fig. 2. UV/vis spectra of the unexpose photoresist films.

(a) photoresist 1 (0 wt% MI-POSS)　　　　　(b) photoresist 2 (0.6 wt% MI-POSS)

(c) photoresist 3 (2.9 wt% MI-POSS)　　　　　(d) photoresist 4 (5.7 wt% MI-POSS)

(e) photoresist 5 (13 wt% MI-POSS)　　　　　(f) photoresist 6 (23 wt% MI-POSS)
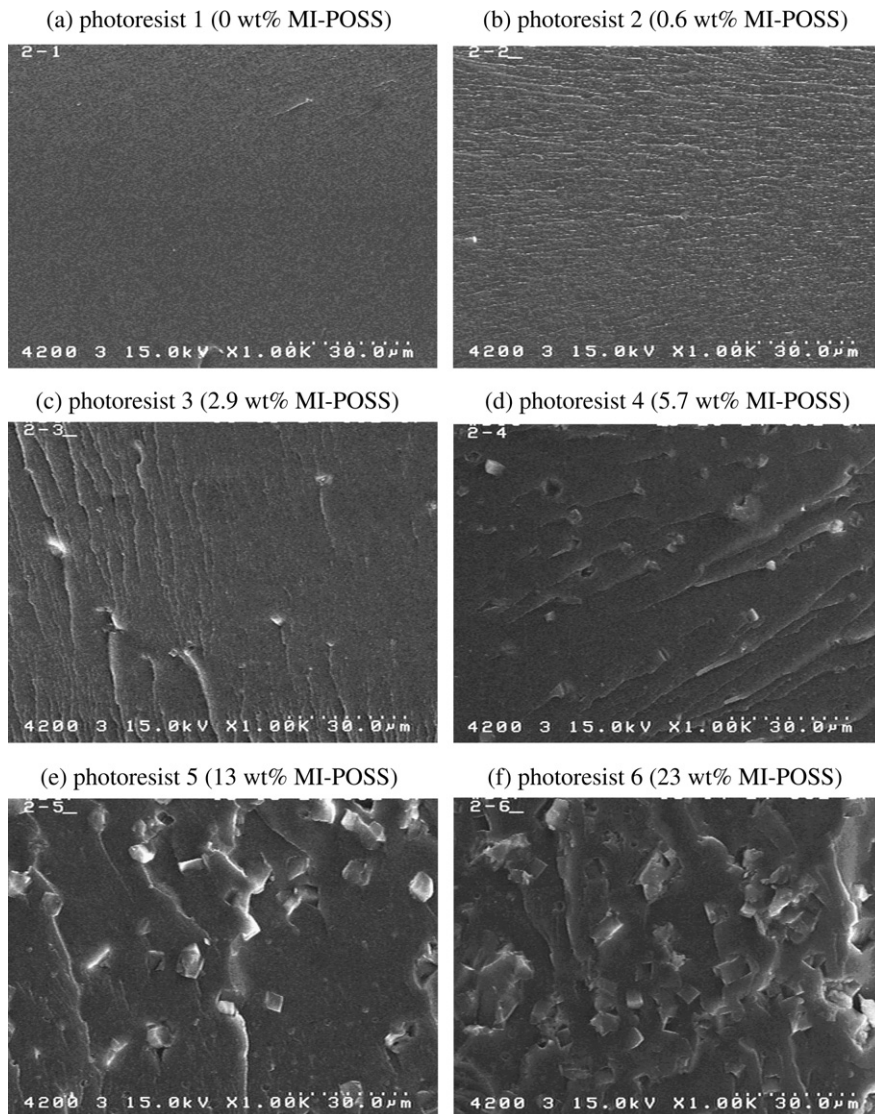
Fig. 3. SEM images of the photoresist sample sections with variant MI-POSS contents.

absorption of photoinitiators (Irgacure 907 and ITX). As the MI-POSS loading is increased, the photoresist film gradually becomes opaque because the MI-POSS tends to aggregate or crystallize [24,25] to form its own domain in the photoresist before exposure.

Fig. 3 displays SEM images of the exposed photoresist sample sections containing 0–23 wt% MI-POSS. The photoresist 1 did not contain MI-POSS, showing a smooth surface while the surface of photoresist 2 (0.6 wt% MI-POSS) becomes rough. Micron-sized particles appear in the SEM images of photoresists 3–6. As the MI-POSS content is increased, the size and number of particles also increase. The methacrylate functional group of MI-POSS can react with photosensitive copolymer and TMPTA monomer. The organic–inorganic compatibility is enhanced by the i-butyl substituents of the MI-POSS, or the hydrogen bonding between MI-POSS and photosensitive copolymers. Nevertheless, MI-POSS molecules prefer to crystallize or aggregate to form their own domain particles [25] in this series of organic–inorganic hybrid photoresists.

The characteristic curves of the photoresists for exposure doses ranging from 2 to 100 mJ cm^{-2} are shown in Fig. 4. 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 summarized in Table 2. The sensitivity ($D_n^{0.5}$) of the photoresist is defined as the minimum energy dose required to form resist pattern to retain 50% of the original film thickness after development [26,27]. The sensitivity is inversely proportional to $D_n^{0.5}$ ($1/D_n^{0.5}$) in the strict sense of notation [28]. The sensitivity for the POSS-free photoresist 1 is 71.5 mJ cm^{-2} while sensitivities of the POSS-containing photoresists, photoresists 2–6, are significantly lower ranging from 32.0 to 24.9 mJ cm^{-2}. It implies that the photoresist becomes more sensitive to radiation energy and a lower dose is needed to get pattern formation by incorporating the MI-POSS macromer. The contrast (γ) is obtained as the slope of the initial tangent of the characteristic curve with logarithmic abscissa [28,29]. The contrast for photoresist 1 is 23.1 and photoresists 2–6 are ranging from 35.1 to 17.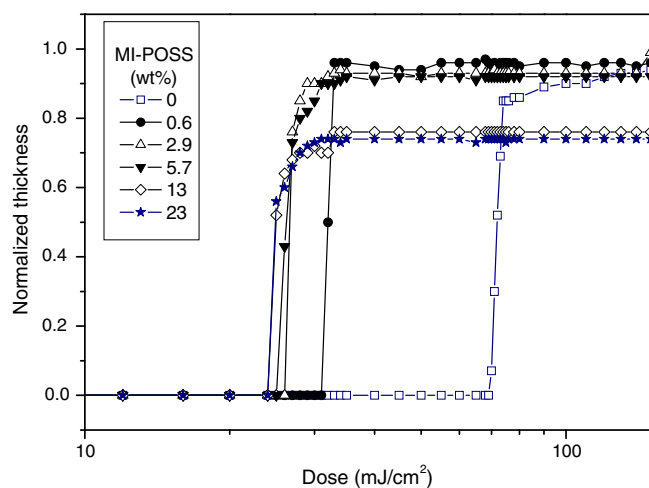3. These results imply that the presence of MI-POSS unit does play an important role in improving the negative type photoresist properties. The bulky MI-POSS structure and the hydrogen bonding between MI-POSS particles and the photosensitive copolymer tend to restrict polymer chain motion and result in changing the characteristics of photoresists [30–33]. Table 2 shows that sensitivities ($D_n^{0.5}$) for photoresists 5 and 6 are nearly constant at 25 mJ cm^{-2}, implying that the photoresist 5 (13 wt% MI-POSS) has already reached its minimum induction energy for this series of POSS-containing photoresists. In Fig. 4, the normalized thickness of photoresists 5 and 6 are less than 0.8 even at higher exposure doses. This MI-POSS macromer has a large molecular structure (M_w = 943.64 g mol^{-1}) with only one methacrylate functional group, increasing MI-POSS content in a blend leads to a decrease in the crosslinking density of the photoresist and results in reduction of normalized thickness after development.

The influence of physically cross-linked MI-POSS structure on photopolymerization of photoresists was studied by photo-DSC. Fig. 5 shows the exothermal curves of photo-polymerizations for these photoresists. It has been reported [34] that the heat flux is related to the rate and extent of photopolymerization. According to the photo-DSC results, the induction time and the peak maximum of heat flux shift to shorter time (Table 3) with the increase of MI-POSS content, implying that the photo-polymerization rate of the photoresist is accelerated by the increase of the MI-POSS content. Competitive hydrogen bonding interactions are present in these MI-POSS-containing blends in terms of hydroxyl–siloxane and carboxylic acid-siloxane. However, the hydrogen bonding interaction of hydroxyl–siloxane is dominant as a major contributor to influence the methacrylate double density. Therefore, it is reasonable to explain that higher photo-polymerization rate achieved from these MI-POSS-containing photoresists is come from the strong hydroxyl–siloxane hydrogen bonding interaction between the MI-POSS particles and hydroxyl groups in the photosensitive copolymer. The strong hydrogen bond interaction tends to attract
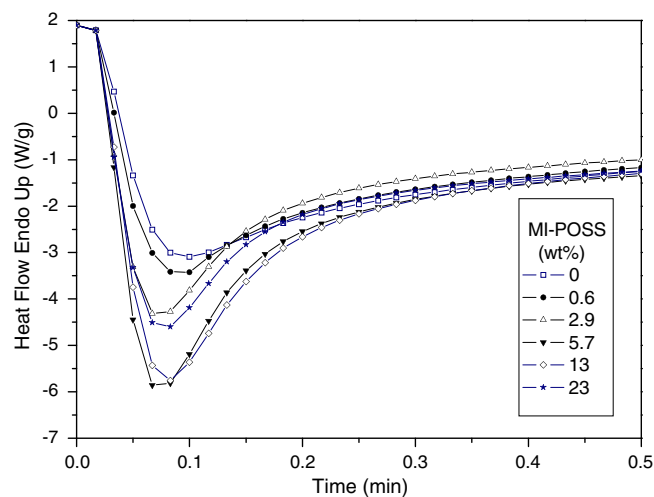

Fig. 4. Characteristic curves of photoresists.

Fig. 5. Photo-DSC exothermal curves for the photo-polymerization of photoresists.

Table 2
Characterizations of photoresists

Photoresist number	MI-POSS (wt%)	Sensitivity ($D_n^{0.5}$; mJ cm^{-2})	Contrast (γ)
1	0	71.5	23.1
2	0.6	32.0	35.4
3	2.9	26.7	26.4
4	5.7	26.2	21.8
5	13	25.0	18.4
6	23	24.9	17.3

Table 3
Exothermal results for the photopolymerization of photoresists 1–6

Photoresist number	MI-POSS (wt%)	Induction time (min)	Peak maximum (min)	ΔH (J g^{-1})
1	0	0.021	0.100	133.4
2	0.6	0.020	0.100	145.0
3	2.9	0.016	0.067	159.4
4	5.7	0.017	0.067	212.1
5	13	0.019	0.083	201.9
6	23	0.018	0.083	185.6
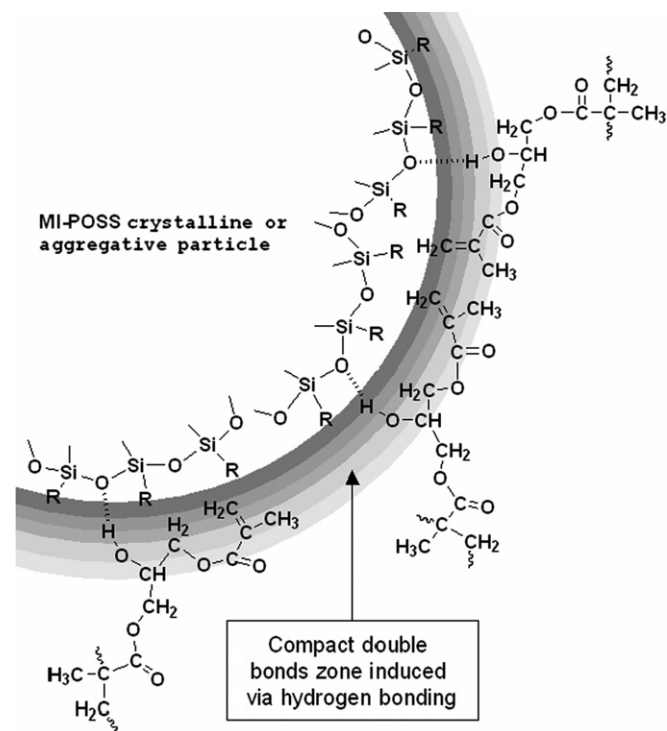
Scheme 2. The proposed microstructure via hydrogen bonding interaction between a MI-POSS particle and photosensitive copolymers.
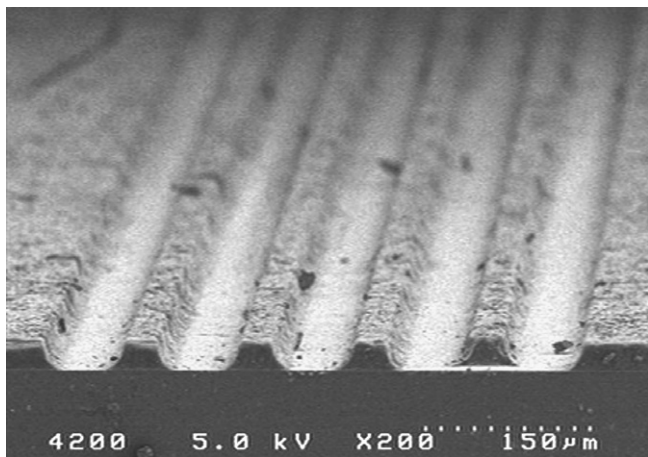

Fig. 6. SEM image (line pattern) for photoresist 3 at a dose of 60 mJ cm^{-2}.

and dense these methacrylate double bonds in the vicinity of MI-POSS particles, resulting in a higher concentration of methacrylate double bonds surrounding MI-POSS particles, thus enhancing the rate of photo-polymerization. The proposed schematic microstructure via hydrogen bonding interaction between MI-POSS particles and hydroxyl groups resulting in locally higher concentration of double bond segments is shown in Scheme 2. However, the C=C group density of photoresists is diluted by adding excessive amount of MI-POSS. As a result, photoresists 5 and 6 have smaller heat flux and peak area than photoresist 4 as shown in Fig. 5 and Table 3.

Fig. 6 shows the negative pattern of photoresist 3 used in UV-lithography. One concern about the usage of MI-POSS is that it may cause a sensitivity decrease of the photoresist due to its inorganic nature. The result shown in Fig. 6 indicates that this is not a problem in our system, giving a nice line pattern (50 μm) with a thickness of 25 μm after a dose of 60 mJ cm^{-2}. According to the above pattern result, the POSS-containing negative-type photore-

sists are suitable applying in the circuit patterning process of manufacturing printed circuit boards. After modification, these photoresists can also be used in the production of displays, flexible electronics, optoelectronics, etc. Besides, these photoresists are considered stable with shelf lives greater than 6 months.

4. Conclusions

A series of negative-type photoresists with various polyhedral oligomeric silsesquioxane (MI-POSS) methacrylate contents were prepared and characterized. The sensitivity and photo-polymerization rate were significantly enhanced by the presence of the MI-POSS moiety. Hydrogen bonding interaction between the MI-POSS particles and the hydroxyl groups of the photosensitive copolymer forms a physical crosslinkage structure and increases the density of methacrylate double bonds surrounding MI-POSS particles and thus enhances the photopolymerization rate. Results of lithographic properties of photoresists under collimated exposure show that better photoresist sensitivity can be achieved by this method, which has potential utility for ultraviolet lithography. This blending type photoresists with monomethacrylate group POSS has similar photoresist characteristics as the copolymer type [23] with slightly less efficiency but better processibility.

References

[1] R. Balaji, D. Grande, S. Nanjundan, Polymer 45 (2004) 1089.
[2] P. Jalonen, Microelectron. J. 34 (2003) 99.
[3] S. Trakhtenberg, J.C. Warner, R. Nagarajan, F.F. Bruno, L.A. Samuelson, J. Kumar, Chem. Mater. 18 (2006) 2873.
[4] K.-H. Kim, S. Jang, F.W. Harris, Macromolecules 34 (2001) 8925.
[5] Y. Wang, M. Bachman, C.E. Sims, G.P. Li, N.L. Allbritton, Langmuir 22 (2006) 2719.
[6] M. Wissen, H. Schulz, N. Bogdanski, H.-C. Scheer, Y. Hirai, H. Kikuta, G. Ahrens, F. Reuther, K. Pfeiffer, Microelectron. Eng. 73–74 (2004) 184.
[7] M.D. Vittorio, M.T. Todaro, T. Stomeo, R. Cingolani, D. Cojoc, E.D. Fabrizio, Microelectron. Eng. 73–74 (2004) 388.
[8] T. Ogoshi, Y. Chujo, Macromolecules 37 (2004) 5916.
[9] Y. Ni, S. Zheng, K. Nie, Polymer 45 (2004) 5557.
[10] J.-C. Huang, C.-B. He, Y. Xiao, K.Y. Mya, J. Dai, Y.P. Siow, Polymer 44 (2003) 4491.
[11] M.J. Abad, L. Barral, D.P. Fasce, R.J.J. Williams, Macromolecules 36 (2003) 3128.
[12] W.-Y. Chen, Y.-Z. Wang, S.-W. Kuo, C.-F. Huang, P.-H. Tung, F.-C. Chang, Polymer 45 (2004) 6897.
[13] H. Wu, Y. Hu, K.E. Gonsalves, M.J. Yacaman, J. Vac. Sci. Technol. B 19 (2001) 851.
[14] H. Wu, K.E. Gonsalves, Adv. Mater. 13 (2001) 670.
[15] M.A. Ali, K.E. Gonsalves, V. Golovkina, F. Cerrina, Microelectron. Eng. 65 (2003) 454.
[16] E. Tegou, V. Bellas, E. Gogolides, P. Argitis, D. Eon, G. Cartry, C. Cardinaud, Chem. Mater. 16 (2004) 2567.
[17] A.M. Douvas, F.V. Roey, M. Goethals, K.G. Papadokostaki, K. Yannakopoulou, D. Niakoula, E. Gogolides, P. Argitis, Chem. Mater. 18 (2006) 4040.
[18] Y. Ni, S. Zheng, Chem. Mater. 16 (2004) 5141.
[19] A. Sellinger, R.M. Laine, Macromolecules 29 (1996) 2327.
[20] M. Fujiwara, K. Shiokawa, N. Kawasaki, Y. Tanaka, Adv. Funct. Mater. 13 (2003) 371.
[21] B. Pan, T. Clark, C.E. Hoyle, J.D. Lichtenhan, Polym. Prepr. 45 (2004) 170.
[22] A. Schmidt, S. Babin, K. Böhmer, H.W.P. Koops, Microelectron. Eng. 35 (1997) 129.
[23] H.-M. Lin, S.-Y. Wu, P.-Y. Huang, C.-F. Huang, S.-W. Kuo, F.-C. Chang, Macromol. Rapid Commun. 27 (2006) 1550.
[24] Y.J. Lee, S.W. Kuo, Y.C. Su, J.K. Chen, C.W. Tu, F.C. Chang, Polymer 45 (2004) 6321.
[25] Y. Zhang, S. Lee, M. Yoonessi, K. Liang, C.U. Pittman, Polymer 47 (2006) 2984.
[26] W.Y. Chiang, H.T. Kuo, Eur. Polym. J. 38 (2002) 1761.
[27] V. Kudryashov, X.-C. Yuan, W.-C. Cheong, K. Radhakrishnan, Microelectron. Eng. 67–68 (2003) 306.
[28] S. Nonogaki, T. Ueno, T. Ito, Microlithography Fundamentals in Semiconductor Devices and Fabrication Technology, Marcel Dekker, New York, 1998. p. 6.
[29] A. Reiser, Photoreactive Polymers – the Science and Technology of Resists, John Wiley and Sons, New York, 1989. p. 228.
[30] Y.J. Lee, S.W. Kuo, W.J. Huang, H.Y. Lee, F.C. Chang, J. Polym. Sci. Polym. Phys. 42 (2004) 1127.
[31] H. Xu, S.W. Kuo, J.S. Lee, F.C. Chang, Polymer 43 (2002) 5117.
[32] C.F. Huang, S.W. Kuo, F.J. Lin, W.J. Huang, C.F. Wang, W.Y. Chen, F.C. Chang, Macromolecules 39 (2006) 300.
[33] H.C. Lin, S.W. Kuo, C.F. Huang, F.C. Chang, Macromol. Rapid Commun. 27 (2006) 537.
[34] K.S. Anseth, C.M. Wang, C.N. Bowman, Macromolecules 27 (1994) 650.