

Photoinduced Mesoporosity of *Tert*-Butoxycarbonyl Acrylic Photosensitive Material with Low Dielectric Constant

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ABSTRACT: We have developed a photosensitive system having low dielectric constant with mesoporous. The photosensitive system we developed is patternable and the mesoporosity is generated through the combination of photo exposure and thermal treatment. The mesopores were formed in a photosensitive material to reduce its dielectric constant. *Tert*-butoxycarbonyl (*t*-BOC) containing acrylic copolymer was activated as a photosensitive material via photochemical reactions. Iodonium salt as a photo acid generator was exposed to ultraviolet light with a wavelength of under 365 nm to form the corresponding Lewis acid. The side chains of *t*-BOC were cleaved by this Lewis acid to yield isobutylene and acrylic acid groups. The small molecules thus formed were further heated in the polymer matrix to generate mesopores. Notably, the *t*-BOC content and heat affect the dimensions and number of mesopores. The dielectric constant decreased as the density of mesopores increases. The formation of mesopores was observed by transmission electron microscope and scanning electron microscopy. We have also studied the mechanisms of formation of mesopores and their effects on the dielectric constant. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: mesopores; low dielectric; photosensitive; chemical amplification

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INTRODUCTION

Generally, materials having low dielectric constants about 3.0 are commonly used as interlayer in many applications. But the new electronic devices may need even lower dielectric constants of 2.5 and below.^{1,2} Furthermore, low dielectric materials are widely adopted as insulating films or cover layers in thin-film transistor liquid crystal displays.³ Recently, a need has also arisen in microelectronics for patternable photosensitive materials with low dielectric constants. It is well known that the mesoporous materials having a low dielectric constant. Many approaches are thus available for preparing low dielectric materials, involving fluorinated polymer^{4–6} and silsesquioxane.^{7,8} A more effective way to take advantage of the very low dielectric constant of air is to introduce voids into the material as in mesoporous material.^{9,10} Recent studies of porous materials have focused on the thermal decomposition of polymer blends^{11–14} and block copolymers.^{15–17} Star-like^{18,19} random copolymers with a low dielectric constant have also been synthesized. These copolymers can be employed to generate mesophase-separated inorganic–organic hybrids by template methylsilsesquioxane and thin films of mesoporous, following after the subsequent thermal degradation of the organic polymer.^{20,21} Walheim et al.²²

developed mesophase-separated polymer films as high-performance antireflection coatings. An approach based on the phase separation of a macromolecular liquid to generate mesoporous polymer films with high optical transmission is developed.²²

The chemical amplification (CA) proposed by IBM researchers has become a major technology in the photolithographic generation of patterned images in polymer films. The original reaction mechanisms of *tert*-butoxycarbonyl (*t*-BOC) chemistry described in 1982 by Ito et al.^{23,24} have been discussed in numerous publications.^{25,26} It was generally assumed the *t*-BOC that contains polymer deprotection loses both CO₂ and isobutylene to form polyhydroxystyrene during simple thermolysis, which thermally activated acid-catalyzed reaction after UV exposure. A more detail study on the reaction mechanisms of *t*-BOC was revealed by Hinsberg et al.²⁷ This study indicated that *t*-BOC deprotection was induced by UV exposure and postexposure bake (PEB). The *t*-BOC deprotection generated numerous small molecules and some of which had been detected in the gas phase. Several new materials have been developed based on *t*-BOC chemistry.^{28–31} The chemically amplified photoresist exhibits low-exposure dosage, high contrast, and high resolution. Polymers that contain the *t*-BOC group are employed

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Table I. Compositions and Molecular Weight of Synthesized *t*-BOC-MA Acrylic Copolymers A, B, C, and D

Copolymer	TBMA (mol %)	MAA (mol %)	BzMA (mol %)	M_w	M_w/M_n	$^1\text{H-NMR}$ (mole ratio) TBMA/BzMA
A	0	25	75	28,000 \pm 2000	2.2 \pm 0.2	0/4.6
B	5	25	70	27,000 \pm 2000	2.2 \pm 0.2	0.5/5
C	25	25	50	29,000 \pm 2000	2.2 \pm 0.2	1.7/3.2
D	40	25	35	31,000 \pm 2000	2.3 \pm 0.2	2.4/2.9

extensively as photosensitive materials, and provide the advantages of high sensitivity, high resolution, excellent film-forming characteristics, and wide processing latitude.^{32,33} These polymers have been used in the integrated circuit industry for many years. Generally, various porous materials have been studied in recent years including photosensitive films that incorporate molecular photo acid generators (PAGs) compartmentalized within a silica-surfactant mesophase have been prepared by an evaporation-induced self-assembly process.³⁴ But few of these films have complied with the stringent low dielectric and photopatternable requirements of photosensitive material.

In this study, a material system of CA photoresist has been designed to have patternable and mesoporosity formable through the combination of photo exposure and thermal treatment. These chemically amplified photosensitive polymers are typically combined with a cationic PAG,^{35,36} such as a polymer that contains a *t*-BOC group with an iodonium salt. Such advanced design of photoresist systems based on CA has attracted much interest because it is highly sensitive to deep UV applications.^{37,38} The PAG undergoes photolysis to produce the Lewis acid, following exposure to ultraviolet light. This strong proton acid then cleaves the side chain of the *t*-BOC-based copolymer to generate mesopores during the hard baking. This process has showed how *t*-BOC content affects the formation of mesopores and dielectric characteristics. Experimental results indicate that the hard-baking temperature influences the pore size and dielectric constant. This *t*-BOC-based copolymer system can also be used in photoelectric devices owing to its high transmittance of light.^{39,40}

EXPERIMENTAL

Synthesis of *t*-BOC Acrylic Copolymer

Radical copolymerization of the *t*-BOC containing acrylate copolymer was carried out at unequal mole ratio monomer of *tert*-butyl methacrylate (TBMA), methacrylic acid (MAA), and benzyl methacrylate (BzMA). The propylene glycol methyl ether acetate (PGMEA) was used as a solvent and 2,2'-azobisisobutyronitrile (AIBN) was used as a radical initiator. The TBMA and MAA monomers and AIBN were purchased from TCI (Tokyo, Japan). The BzMA monomer was purchased from Lancaster Synthesis, Inc. (USA)

A series of *t*-BOC-based copolymers were synthesized by free radical polymerization. Table I summarizes the compositions of synthesized *t*-BOC-containing acrylic copolymers. Additionally, the 0.1–0.3 wt % AIBN initiator and monomers were added with an appropriate amount of PGMEA to form the mixed reaction solution. Meanwhile, 100 mg of PGMEA solvent was

poured in a reaction flask and maintained at 90°C using a heater. The mixed reaction solution was then added dropwise into the reaction flask under nitrogen for 3 h using a feeding pump stirring at constant rate. Stirring was continued following feeding for another 2 h to extinguish AIBN and eliminate radicals.

Characterization of *t*-BOC-Based Copolymer

The molecular weight of the synthesized copolymer was characterized by gel permeation chromatography in THF (GPC, HITACHI, Pump L2130 HTA, and RI-L2490). The acid valued of MAA in copolymer could be confirmed by titration with 0.1N KOH solution. We have characterized the monomer ratio of copolymers by $^1\text{H-NMR}$ with *d*-THF solvent (200 MHz, Varian 200 MHz FT-NMR). The synthesized *t*-BOC acrylic copolymers were dried at 90°C for 2 h in vacuum to remove the PGMEA solvent. The mole ratio of TBMA of copolymers could be calculated by the integration ratio of the *tert*-butyl peak at 1.36 ppm in $^1\text{H-NMR}$. The benzyl peak of BzMA was shown at 7.3 ppm. $^1\text{H-NMR}$: δ 1.36 (s, 9H, CH₃ of *t*-BOC), δ 7.2 (s, 5H, aromatic). Furthermore, the *t*-BOC group could also be identified by Fourier transform infrared spectroscopy at 1371 cm⁻¹ (FTIR, Perkin Elmer, Spectrum one). The thermal properties of copolymers were examined by thermal gravity analyzer (TGA, TA-2050) and differential scanning calorimetry (DSC, TA-10).

Preparation of Photosensitive Material Solution and Formation of Mesoporous Thin Film for Transmission Electron Microscope Observation

Synthesized *t*-BOC acrylic copolymers A–D were initially dissolved separately in a PGMEA solvent to form the photosensitive material solutions a–d. Table II summarizes the solutions a, b, c, and d containing copolymers with 0, 5, 25, and 40 mol% TBMA, respectively. The solid content was adjusted to approximately 30 wt %. Then, 10 wt % of diaryliodonium hexafluoroantimonate as the PAG (purchased from Sartomer Europe, France, CD1012) was added to each solution.

Solution e was prepared from synthesized *t*-BOC acrylic copolymers C without PAG. All of the photosensitive material solutions a–e were filtered through 0.2- μm disk-type filters. Solutions c and e were placed on a copper grid (Agar, 250 meshes) for transmission electron microscope (TEM) observation and heated in an oven at 90°C for 10 min. The treated specimens were flood-exposed from 365 nm ultraviolet light with energy of 150 mJ/cm² using an Oriel instrument 1000 W Hg-Xe short arc lamp. The specimen underwent hard baking in an oven at 150°C for another 10 min and then the formed mesopores were observed using a TEM (JEOL TEM-2000EX).

Table II. Effect of Hard-Baking Temperature on Dielectric Constant and Porosity^a

Solution	Copolymer	PAG (wt %)	Hard baking (°C)	Line pattern	Dielectric constant	Porosity
a	A	10	150	Bad	3.50	X
b	B	10	150	Poor	3.12	Δ
c	C	10	150	Good	2.60	○
d	D	10	150	Poor	3.05	⊙
c	C	10	130	-	-	Δ
e	C	0	130	-	-	X
c	C	10	110	Good	3.33	Δ
c	C	10	130	Good	2.80	Δ
c	C	10	150	Good	2.56	○
c	C	10	180	Good	2.42	⊙

^aX, no nanopore; Δ, few nanopores; ○, more nanopores; ⊙, lots of nanopores.

Line Pattern Formation by Photolithography and Mesopores Observation

The prepared photosensitive material of solutions a–d was spin coated (1000 r.p.m.) on P-type silicon wafer or glass substrate to form 1–2 μm thin films. Figure 1 shows the photolithographic procedure. A quartz mask coated with chromium was used and the line patterns layout were the same as shown in Figure 7. The thin film was initially soft baked in an oven at 90°C for 10 min and then image was exposed with 150 mJ/cm² of 365 nm ultraviolet light. The film was then postbaked in an oven at 110°C for 10 min and the thin film was finally developed in a 0.5 wt % KOH aqueous solution at 25°C for 20–60 s and rinsed with water. The line patterns thus formed were microscopically observed (OLYMPUS-BH2). Moreover, the line patterns were flood exposed again with 150 mJ/cm² and were hard baked at 150°C for 10 min. The mesopores thus generated were studied by scanning electron microscopy (SEM, LEO Instrument, model 1530).

The effect of thermal energy on the formation of mesopores in photosensitive material was characterized as follows. The prepared photosensitive material solution c, containing 25% of *t*-BOC, was spin coated on silicon wafer substrates, to form four thin films, which were separately hard baked at 110, 130, 150, and 180°C for 10 min. Then, the effect of thermal energy on the formation of mesopores in photosensitive material was ana-

lyzed. The sizes and distribution of the mesopores were examined by SEM, and the thermal effect on the dielectric constant of the material was also evaluated.

Measurement of Dielectric Constant

The dielectric constant was used to determine the capacity of an insulator to store electrical energy. The dielectric constant is the ratio of the capacitance induced by two metallic plates with an insulator between them, to the capacitance of the same plates with air or a vacuum between them. The copolymer was coated on a 3 cm × 3 cm square copper substrate to measure the dielectric constant. Then, the same photolithography procedure was repeated without pattern development. The top of circular testing areas of 1 cm in diameter were sputtered with a thin film of gold as electrodes (BIO-RAD SEM coating system). An HP4192A test apparatus with an LF impedance analyzer and an Agilent 16034E test fixture at 1 MHz were used.

RESULTS AND DISCUSSION

Characterization of the Synthesized *t*-BOC Acrylic Copolymers

Table I summarizes the characteristics of the series of synthesized *t*-BOC acrylic copolymers. Figure 2 shows that the molecular weight of copolymers was maintained between 20,000 and 40,000. The polydispersity index was 2.0–2.5 as determined by GPC. Figure 3 shows that the ratios of the ¹H-NMR integrands of all copolymers were about the same as monomer mole ratios

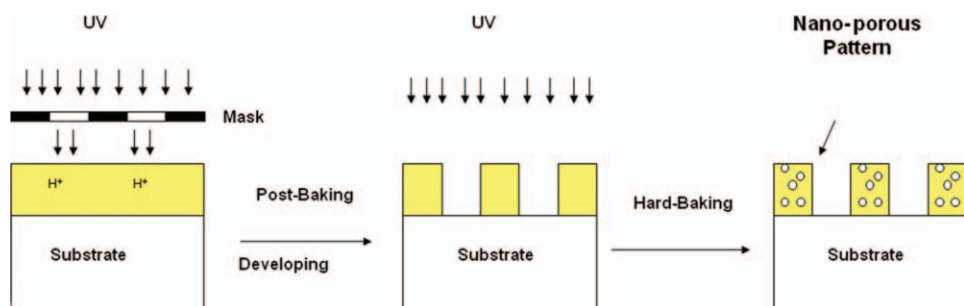


Figure 1. A photosensitive material system of chemically amplified photo resist through two steps of photo lithography process can form line patterns with mesopores which exhibit low dielectric constant. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

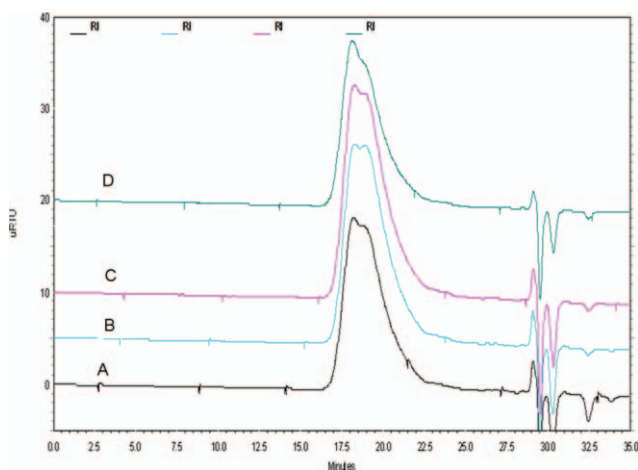


Figure 2. The molecular weight distribution of the series of synthesized *t*-BOC acrylic copolymers by GPC in THF. The monomer mole ratio of TBMA/MAA/BzMA. Polymer A: 0/25/75, B:5/25/70, C:25/25/50, D:40/25/35. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

as listed in Table I. The *t*-BOC group was found at δ 1.36 (s, 9H, *t*-BOC) and benzyl was found at δ 7.2 (s, 5H, aromatic). Figure 4 shows the *t*-BOC group could also be identified at 1371 cm^{-1} by FTIR. The results indicated that the larger amount of *t*-BOC group has the higher 1371 cm^{-1} peak. The MAA monomer of copolymer could be identified by measuring acid value. The acid value of all copolymers was kept around 97–105 mg/KOH. Furthermore, the thermal properties of copolymers were examined by TGA and DSC as shown in Figures 5 and 6. Figure 5 shows that T_g was around 100°C for B copolymer and 130°C

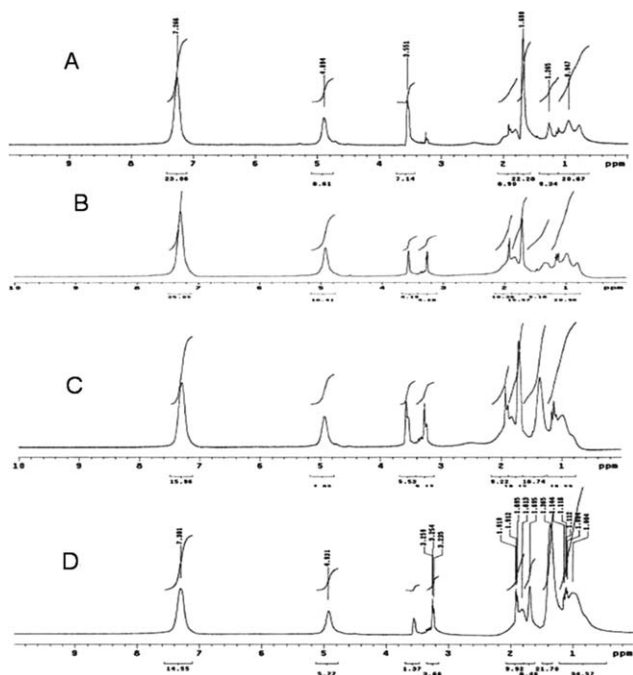


Figure 3. $^1\text{H-NMR}$ spectra of synthesized *t*-BOC acrylic copolymers were dried at 90°C for 2 h in vacuum and then dissolved in *d*-THF.

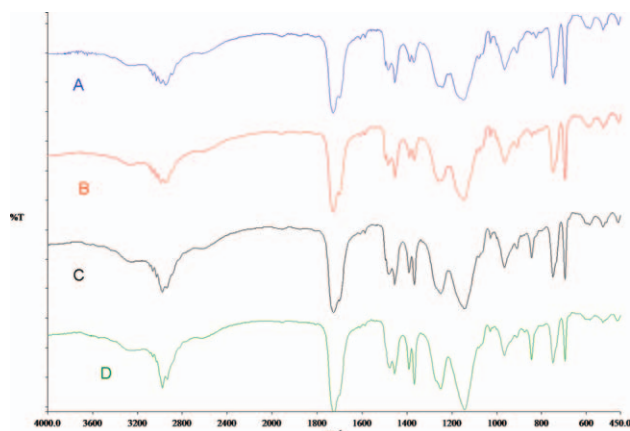


Figure 4. FTIR spectra of synthesized *t*-BOC acrylic copolymers dried film. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

for D copolymer. Thus, the higher content of BzMA gave higher T_g as expected. Figure 6 shows that the decomposition temperature of all the copolymers examined (A–D) was around 200°C by TGA. It indicated that all copolymers we synthesized were thermally stable to 200°C . But the weight loss of the copolymers was found increasing with the increasing of *t*-BOC content (the increase in weight loss: $D > C > B > A$). It also indicated that the *t*-BOC-containing polymer deprotection loses isobutylene during simple thermolysis and thermally activated acid-catalyzed reaction after UV exposure and PEB. A more detail study on the reaction mechanisms of *t*-BOC was revealed by Hinsberg et al.²⁷ The *t*-BOC deprotection generated numerous small molecules, and some of them had been detected in the gas phase by TGA-MASS.²⁷

Examination of the Photosensitivity and Mechanism of Formation of Mesopores

The solid contents of all samples were about 20 wt %. Additionally, the copolymer that contains the *t*-BOC group is regarded as a positive-type photosensitive polymer because the

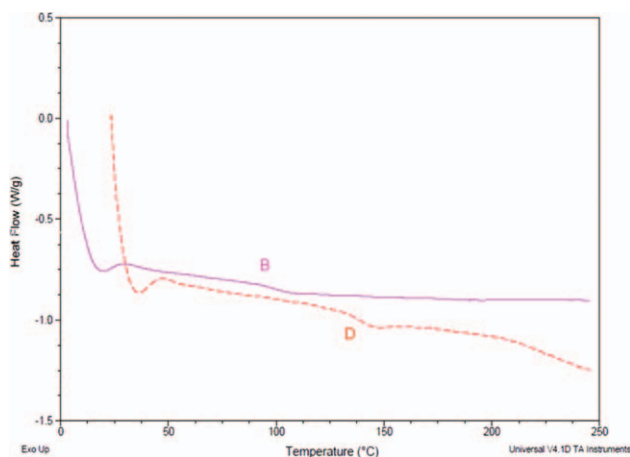


Figure 5. Thermal properties of the polymers B and D dried film measured by DSC. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

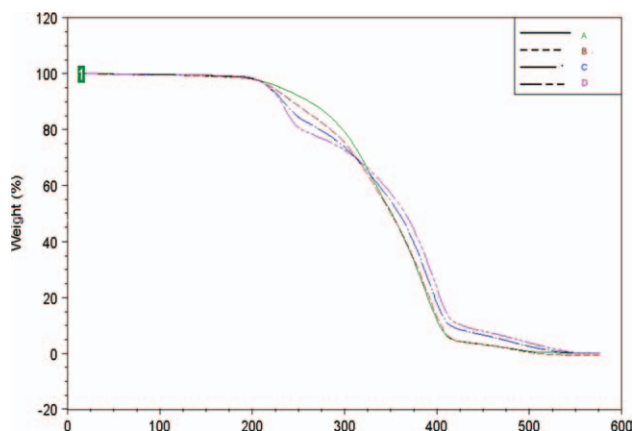


Figure 6. Thermal properties of the polymers A, B, C, and D dried film measured by TGA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

exposed area can be dissolved in an alkaline solution. The *t*-BOC group undergoes photolysis to produce acrylic acid and isobutylene, following exposure to ultraviolet light. These acrylic acids can be easily dissolved in an alkaline solution, the unexposed areas are not easily dissolved; accordingly, the line patterns are formed. The MAA of the copolymers was used to accelerate the dissolving of the exposed areas into an alkaline solution. Figure 2 shows the line pattern. Solution a formed a

poor line pattern following photolithography because it has no *t*-BOC group. Solutions b and c which contain 5 and 25% mole fractions of TBMA monomer, respectively, formed line patterns, whereas solution d with 40 mol % TBMA yields a line pattern with poor resolution. Solution c yields the best-resolved line patterns. The numerals in Figure 7 indicate that the resolution of line patterns is expressed in μm .

Iodonium salt was adopted as a cationic PAG to initiate a photochemical reaction. PAG reportedly forms acid during thermal decomposition.³⁵ The exposure of iodonium salt to light with a wavelength of under 365 nm also generates the Lewis acid. Scheme 1 shows the electronic transfer reaction of diaryliodonium hexafluoroantimate that is exposed to ultraviolet light. Scheme 2 shows the strong proton acid cleaves the side chain of the *t*-BOC-based copolymer to isobutylene and acrylic acid groups.^{27–31} The small molecules of isobutylene thus produced are heated in a polymer matrix to form mesopores, which are critical to the low dielectric constant of the material. Figure 8(A) shows mesopores formed from solution c with 25% *t*-BOC-based copolymer and PAG following photo exposure, but Figure 8(B) shows no mesopore generated from solution e with 25% *t*-BOC-based copolymer but without PAG, following photo exposure. Clearly, PAG can cleave the side chain of *t*-BOC group to produce isobutylene when exposed to ultraviolet light. Isobutylene is then heated in a polymer matrix to form mesopores.

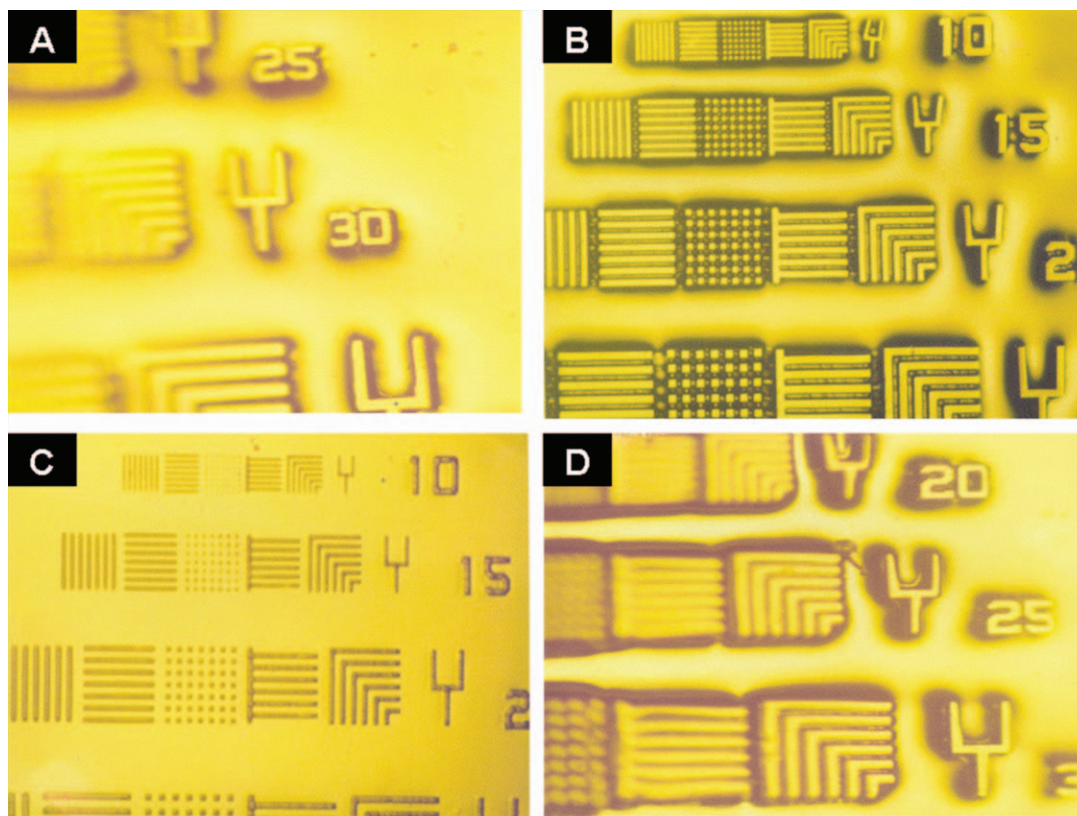
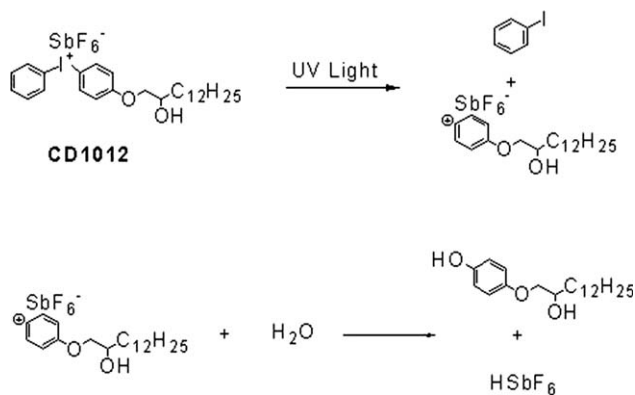


Figure 7. The line pattern's performances of photosensitive copolymer solutions. (A) Solution a, (B) solution b, (C) solution c, and (D) solution d. The numerals in Figure 2 indicate that the resolution of line patterns is expressed in μm . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

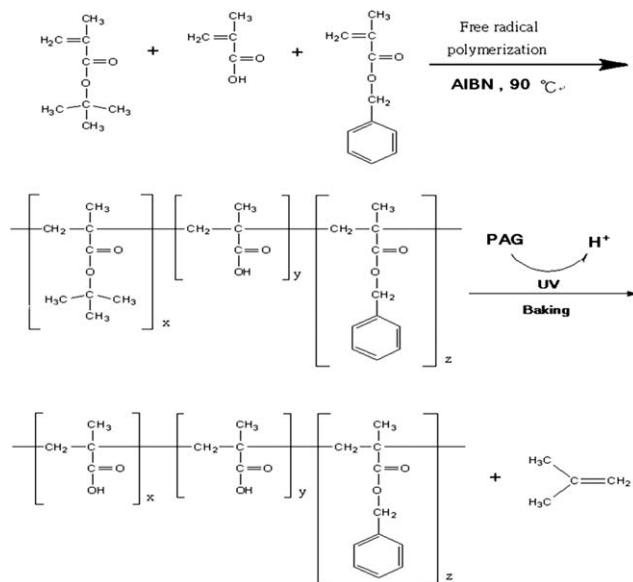


Scheme 1. Electron transfer reaction of diaryliodonium hexafluoroantimonate while exposed with ultraviolet light.

t-BOC content and dielectric constant

The effects of *t*-BOC content on the formation of mesopores and the dielectric constant of the photosensitive material were further studied. SEM was used to observe the dimensions of the mesopores. Figure 9 shows SEM cross-section images of *t*-BOC-based copolymers, following exposure to ultraviolet light. Figure 9(A) shows that the film without *t*-BOC groups does not contain mesopores. Figure 9(B,C,D) shows SEM cross-section images of films with 5, 25, and 40% *t*-BOC contents, respectively. Various amounts of *t*-BOC in the polymer matrix yield various numbers of pores of various sizes. The dimensions of the pores in the film with 5% *t*-BOC content are about 49 nm. The pore sizes and amounts increased with *t*-BOC content. The mesopore increased with the *t*-BOC content because the pores merge during hard baking.

Table II summarizes the relationship between the dielectric constant and the *t*-BOC content in the copolymer matrix. Notably, lower dielectric constants are associated with higher *t*-BOC content, which is responsible for the formation of mesopores. The dielectric constant falls from 3.50 to 2.60 as the *t*-BOC group content increases from 0 to 25%. However, copolymer with 25% *t*-BOC



Scheme 2. The reaction mechanism of the PAG. PAG breaks the side chains of *t*-BOC acrylic copolymer and form acrylic acid and isobutylene.

content does have the lowest dielectric constant because more mesoporous formed as more isobutylene produced by PAG. But the dielectric constant become larger at 40% of *t*-BOC content as there are two competitive mechanisms affecting the dielectric property. Increasing *t*-BOC content will generate more mesopores and reduce the dielectric constant. At the same time, increasing *t*-BOC content will increase the amount of acrylic acid which increases the polarity of the polymer matrix. These polarized elements in the polymer matrix will increase the dielectric constant. Therefore, copolymer with 25% *t*-BOC content exhibits optimal line pattern performance and the lowest dielectric constant.

Hard-baking Temperature, Mesopores, and Dielectric Constant

The TEM images in Figure 8(A) show that mesopores with sizes of about 49 nm were formed, following photo exposure and

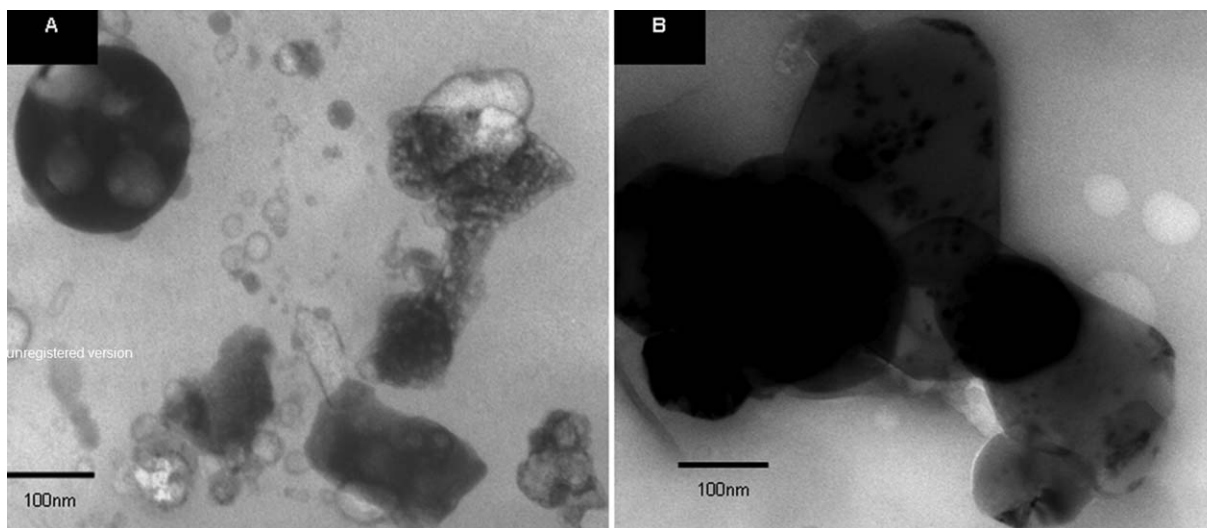


Figure 8. TEM images of copolymer films. (A) Copolymer film of solution c, (B) copolymer film of solution e, hard-baking temperature: 130°C.

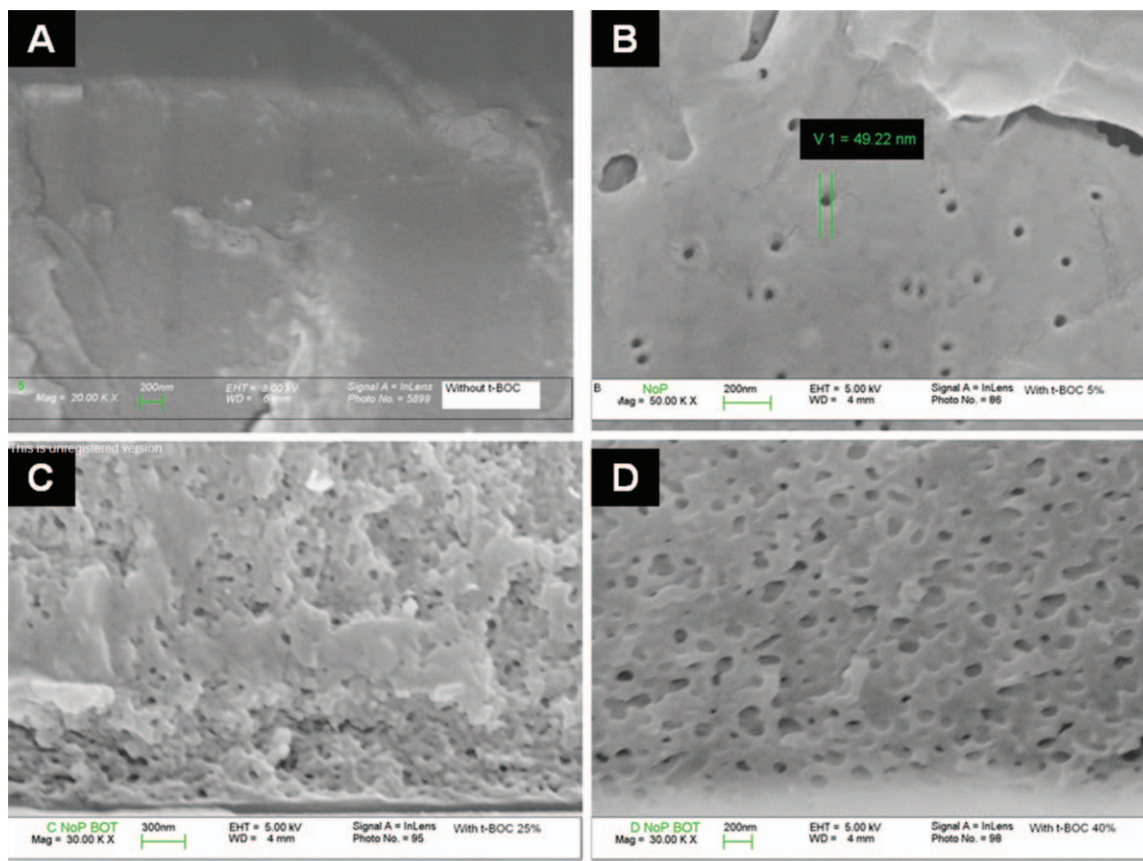


Figure 9. SEM cross-section images of *t*-BOC-based copolymers, following irradiation to ultraviolet light. (A) Copolymer with no *t*-BOC content. (B) Copolymer with 5% mole fraction *t*-BOC content. (C) Copolymer with 25% mole fraction *t*-BOC content. (D) Copolymer with 40% mole fraction *t*-BOC content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

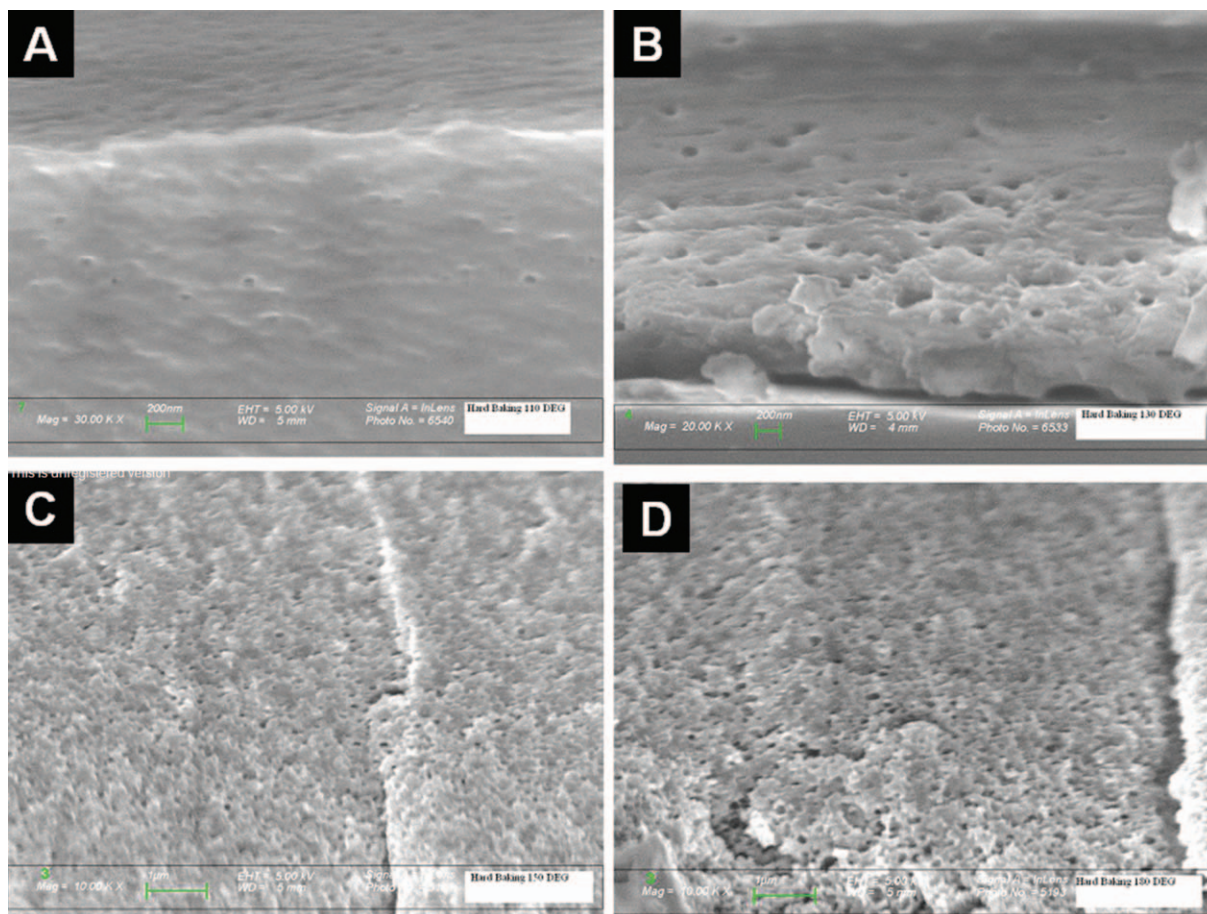


Figure 10. SEM images of the effect of hard-baking temperature on pore formation. (A) 110°C, (B) 130°C, (C) 150°C, (D) 180°C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

heating to 130°C. Figure 9 shows that mesopores with sizes of over 49 nm were formed, following photo exposure and heating to 150°C. Figure 10 also plots the effects of the hard-baking temperature on the pore size and on the amount of pores. In Figure 10(A), the SEM image shows that fewer, smaller pores were formed at a hard-baking temperature of 110°C. Figure 10(B) shows that more, larger mesopores were formed at 130°C. Figure 10(C,D) more clearly indicates that more pores were generated at 150 and 180°C, respectively. It shows that both the amount and the size of porous increase with the increasing baking temperature. Accordingly, lower dielectric constants of such samples are observed, because during hard baking, the polymer chains become soft and small molecules of which merge easily with each other and then vaporize from the polymer matrix, forming mesopores. The size of the mesopores increases with the hard-baking temperature. The results in Table II also summarize that the dielectric constant decreased from 3.33 to 2.42 and the number of mesopores increased as backing temperature increased from 110 to 180°C. The heat treatment might decompose porous structure as we observed that there were more and larger pores generated at higher PEB temperature. This could be owing to the fact that polymer became more flexible at PEB temperature higher than T_g . The small-molecule gas generated would become more mobile and easily merged together to form larger pores. But the film would become puffer, less solid, and more brittle if there were too many large pores.

CONCLUSIONS

In this study, we have synthesized a series of photosensitive acrylic copolymer-containing *t*-BOC. The *t*-BOC copolymer was utilized as a chemically amplified photoresist. We have also studied the effects of the *t*-BOC content on the formation of mesopores and the dielectric characteristic of photosensitive material system. The results show that more mesopores have been formed at higher *t*-BOC content, which leads to a lower dielectric constant. The dielectric constant declines from 3.50 to 2.60 as the *t*-BOC group content increases from 0 to 25%. Furthermore, the hard-baking temperature also affects the pore size and the porosity as well as the dielectric constant. More specifically, we have found that the pore size and porosity also increase with the hard-baking temperature, and have yielded the decrease of dielectric constant. Thus, we have developed new series of low dielectric constant patternable photosensitive materials. We expected that such characteristics will extend the application range of these mesoporous materials in microelectronic and photoelectronic fields.

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REFERENCES

- Shamiryan, D.; Abell, T.; Iacopi, F.; Maex, K. *Mater. Today* **2004**, *7*, 34.
- Homma, T. *Mater. Sci. Eng.* **1998**, *R23*, 243.

- Maier, G. *Prog. Polym. Sci.* **2001**, *26*, 3.
- Mocella, M. T. *J. Fluorine. Chem.* **2003**, *122*, 87.
- Sandrin, L.; Silverstein, M. S.; Sacher, E. *Polymer* **2001**, *42*, 3761.
- Su, Y. C.; Chang, F. C. *Polymer* **2003**, *44*, 7989.
- T. C. Chang, Mor, Y. S.; Liu, P. T.; Tsai, T. M.; Chen, C. W.; Mei, Y. J.; Sze, S. M. *Thin. Solid. Films.* **2001**, *398–399*, 523.
- Kim, J. S.; Kim, H. C.; Lee, B.; Ree, M. *Polymer* **2005**, *46*, 7394.
- Su, Y. C.; Chen, W. C.; Ou, K. L.; Chang, F. C. *Polymer* **2005**, *46*, 3758.
- Kim, K. M.; Adachi, K.; Chujo, Y. *Polymer* **2002**, *43*, 1171.
- Silverstein, M. S.; Caplan, M.S.; Bauer, B. J.; Hedden, R. C.; Lee, H. J.; Landes, B. G. *Macromolecules* **2005**, *38*, 4301.
- Fu, G. D.; Zong, B. Y.; Kang, E. T.; Neoh, K. G.; Lin, C. C.; Liaw, D. J. *Ind. Eng. Chem. Res.* **2004**, *43*, 6723.
- Lee, B.; Yoon, J.; Oh, W.; Hwang, Y.; Heo, K.; Jin, K. S.; Kim, J.; Kim, K. W.; Ree, M. *Macromolecules* **2005**, *38*, 3395.
- Yang, C. C.; Wu, P. T.; Chen, W. C.; Chen, H. L. *Polymer* **2004**, *45*, 5691.
- Yim, J. H.; Jeong, H. D.; Pu, L. S. *Thin. Solid. Films.* **2005**, *476*, 46.
- Yang, S.; Mirau, P.; Sun, J.; Gidley, D. W. *Radiat. Phys. Chem.* **2003**, *68*, 351.
- Lee, Y. J.; Huang, J. M.; Kuo, S. W.; Chang, F. C. *Polymer* **2005**, *46*, 10056.
- Heise, A.; Nguyen, C.; Malek, R.; Hedrick, J. L.; Frank, C. W.; Miller, R. D. *Macromolecules* **2000**, *33*, 2346.
- Oh, W.; Hwang, Y.; Park, Y. H.; Ree, M.; Chu, S. H.; Char, K.; Lee, J. K.; Kim, S. Y. *Polymer* **2003**, *44*, 2519.
- Chen, W. Y.; Wang, Y. Z.; Kuo, S. W.; Huang, C. F.; Tung, P. H.; Chang, F. C. *Polymer* **2004**, *45*, 6897.
- Yang, C. C.; Wu, P. T.; Chen, W. C.; Chen, H. L. *Polymer* **2004**, *45*, 5691.
- Walheim, S.; Schaffer, E.; Mlynek, J.; Steiner, U. *Science* **1999**, *283*, 520.
- Frechet, J. M. J.; Eichler, E.; Ito, H.; Wilson, C. G. *Polymer* **1983**, *24*, 995.
- Ito, H.; Wilson, C. G. Application of photoinitiators to the design of resists for semiconductor manufacturing, *Polymers in Electronics*, ACS Symposium Series 242, **1984**; p 11.
- Wilson, C. G. Introduction to Microlithography, Thomp, L. F., Wilson, C. G., Bowden, M. J., Eds.; ACS Symposium Series 219, ACS: Washington D.C., **1983**; p 153.
- Iwayanagi, T.; Ueno, T.; Nogogaki, S.; Ito, H.; Wilson, C. G. Electronics and Photonic Applications of Polymers, Bowden, M. J., Turner, S. R., Eds.; *Advances in Chemistry Series* 218, ACS: Washington D.C., **1988**; p 109.
- Hinsberg, W. D.; Houle, F. A.; Poliskie, G. M.; Pearson, D.; Sanchez, M. I.; Ito, H. *J. Phys. Chem. A.* **2002**, *106*, 9776.

28. Conley, W.; Breta, C.; Brunsvold, B.; Depietro, R.; Holmes, S.; Ito, H.; Nunes, R.; Fichtl, G. *Proc. SPIE*. **1996**, 2724, 35.
29. Onishi, Y.; Sato, K.; Chiba, K.; Asano, M.; Niki, H.; Hayase, R.; Hayashi, T. *Proc. SPIE*. **1996**, 2724, 70.
30. Allen, R. D.; Wan, I. Y.; Walraff, G. M.; DiPietro, R. A.; Hofer, D. C.; Kunz, R. R. *J. Photopolym. Sci. Technol.* **1995**, 8, 623.
31. Nozaki, K.; Kaimoto, Y.; Takahashi, M.; Takeshi, S.; Abe, N. *Chem. Mater.* **1994**, 6, 1492.
32. Hong, C. S.; Jikei, M.; Kikuchi, R.; Kakimoto, M. A. *Macromolecules* **2003**, 36, 3174.
33. Kudo, K.; Arimitsu, K.; Ohmori, H.; Ito, H.; Ichimura, K. *Chem. Mater.* **1999**, 11, 2119.
34. Doshi, D. A.; Huesing, N. K.; Lu, M.; Fan, H.; Lu, Y.; Potter, K. S.; Potter, B. G. Jr.; Hurd, A. J.; Brinker, C. J. *Science* **2000**, 290, 107.
35. Crevello, J. V. *Adv. Polym. Sci.* **1982**, 62, 1.
36. Itani, T.; Yoshino, H.; Hashimoto, S.; Yamana, M.; Samoto, N.; Kasama, K. *Microelectron. Eng.* **1997**, 35, 149.
37. Maeda, K.; Nakano, K.; Iwasa, S.; Hasegawa, E. *Microelectron. Eng.* **2002**, 61–62, 771.
38. Landis, S.; Pauliac, S.; Hanawa, R.; Suetsugu, M.; Akita, M. *Microelectron. Eng.* **2004**, 73–74, 271.
39. Huang, Y.; Economy, J. *Macromolecules* **2006**, 39, 1850.
40. Penteman, R.; Klink, S. I.; Koning, H. D.; Nisato, G.; Broer, D. J. *Nature* **2002**, 417, 55.