Lithographic Characteristics and Thermal Processing of Photosensitive Sacrificial Materials

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Previously, a novel method for fabricating microfluidic and microelectromechanical devices with buried microchannel structures using thermally sacrificial polymers was reported. These previous methods required separate lithographic and etching sequences to pattern the sacrificial polymer. In this work, a more advanced approach in which the sacrificial material is radiation sensitive and can be patterned directly using standard lithographic techniques is explored. The lithographic performance of a new class of photosensitive polynorbornene (PNB) sacrificial materials has been characterized. The effect of soft bake and postexposure bake (PEB) on the cross-linking of photodefinable PNB has also been investigated. It was found that significant cross-linking of PNB occurs after exposure during the subsequent postexposure bake. However, this phenomenon is strongly dependent on the soft bake conditions used in preparing the sample, presumably due to varying levels of residual solvent content. This may be due to the high mass transport of the reactive species because of evaporation of residual solvent and shrinking of polymer matrix during the PEB process. No noticeable influence of residual solvent on cross-linking has been found during exposure.
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Interest in microfluidic and microelectromechanical system (MEMS) devices has risen dramatically in recent years. A number of papers including Koch *et al.*[1] and Bhusari *et al.*[2] have recently reviewed the applications and features of such microfluidic devices in particular. A common issue in more advanced microfluidic devices is fabrication of the complex 3D network of interconnected microchannels that is required to perform independent transport of various fluids in the device. The structure, cost, quality, and complexity of these devices depends on the manufacturing method, yield, and characteristics of the microchannels that are produced.

In particular, the microfluidic devices used in the combinatorial synthesis of drug compounds, biomedical diagnostics, microchemical analysis and sensing, and ink-jet printing typically deal with a variety of fluids. These applications demand that the microchannel components display particular geometries and surface properties (*e.g.*, hydrophobicity). The most prevalent commercial method for obtaining 3D microchannel systems involves the bonding of layers of ultraflat glass that already contain patterned channels to a second planar substrate surface (*e.g.*, glass, silicon) that also may contain predefined channel structures. In this manner, a complex network of microchannels is formed.[3] This method presents some drawbacks including (*i*) difficulties in manufacturing and the issues with defects leading to low yields and (*ii*) the general difficulty of integrating other materials and devices, such as electronic capability, into the microfluidic device to produce more functional structures.[3-5]

In order to allow for fabrication of microfluidic devices with higher levels of functionality, a novel method was recently proposed to use conventional lithography and silicon fabrication technologies to build microfluidic devices that can be directly integrated with integrated circuit (IC) components.[2] Also, polycarbonates have been used as sacrificial placeholders for microfluidic devices.[6,7] A schematic of the processing steps used in this approach is depicted in Fig. 1. The basic premise in this method is the use of thermally sacrificial polymers that can be used to act as placeholders and fabricate microchannels during the buildup of complex devices on silicon, glass, and other substrates. After fabrication of the device layers, the polymer can be heated and cleanly decomposed to leave behind the desired open channel structures. In principal, the new approach avoids the majority of flaws raised in the glass-bonding method. However, currently the processing is somewhat complex due to the need for separate deposition, photolithography, and reactive ion etching steps required to pattern the sacrificial polymer materials. Also, with this approach it is hard to form channels with varying depth. Thus, the goal of this work was to develop simplified and more flexible processing methods based on this concept of microchannel fabrication using sacrificial polymers.

In this work, a simple and flexible method is proposed (see Fig. 2) for the direct patterning of the sacrificial material. The new concept here is to make photosensitive versions of the sacrificial polymers that can be used in an analogous fashion to conventional photosensitive polymers. This has two distinct advantages: (*i*) the number of processing steps required to produce the patterned polymer structures is significantly reduced and (*ii*) the photosensitive polymers open up the opportunity to use "gray scale" lithographic masks and methods to produce channels that have structure in the direction normal to the substrate (*i.e.*, nonuniform channel heights). This second advantage unlocks the possibility of building arbitrarily complex, truly 3D patterned structures in a straightforward manner. In this work, alkenyl-addition polymerized polynorbornenes (PNB) have been selected as the polymer platform since they can be easily functionalized with reactive groups that enable photodefinition; nonphotosensitive PNB materials have been previously shown to decompose cleanly to produce microchannels.[2] PNB polymers can also be functionalized to control the surface properties (*e.g.*, hydrophobic nature), using appropriate reactive functional groups.[8] PNB materials are also well suited for IC-compatible fabrication methods since they are known to retain their shape (due to their high glass transition temperature) and remain thermally stable until their decomposition temperature ($\geqslant 350°C$). This work is aimed at exploring the influence of formulation and processing on the lithographic performance of such photodefinable PNB sacrificial materials. Photosensitive materials have been obtained by synthesizing PNB polymers containing cross-linkable functional groups and formulating these polymers with photosensitive radical initiators. The effect of polymer structure, photoinitiator loading, and thermal processing on the lithographic performance of these materials has been investigated.

Experimental

Copolymers of butyl norbornene (BuNB) and pendant alkenyl-substituted norbornene (ANB), shown in Fig. 3, were synthesized and supplied by Promerus LLC (Brecksville, OH). The characteristics of the copolymers used are shown in Table I. The alkenyl side group enables free radical induced cross-linking, thus allowing for photopatterning of the material.

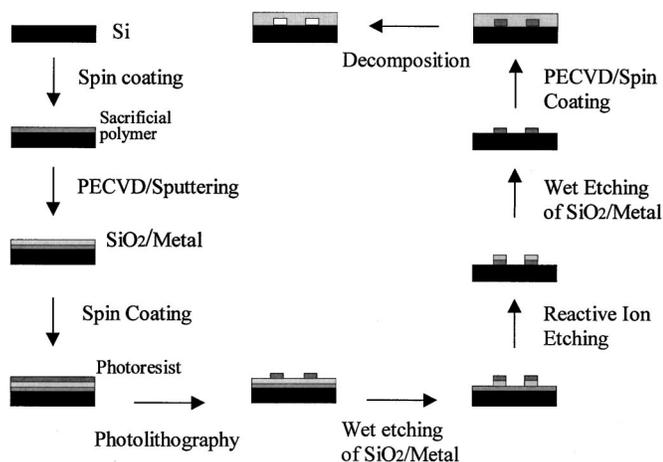**Figure 1.** Schematic of processing steps involved in the fabrication of microchannel structures using thermally sacrificial PNB materials.[2]

R_1: butyl group, R_2: alkenyl group

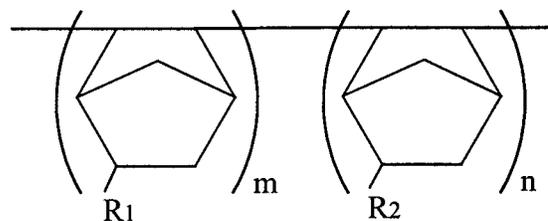**Figure 3.** Generic structure of the PNB copolymers used in this work.

The solvents, mesitylene (97%, Aldrich) and xylene (98.5+%, Aldrich), and the photoinitiator, benzoin ethyl ether (BEE, 99%, Aldrich), were used as received. A series of photosensitive PNB/BEE solutions were prepared as shown in the recipes listed in Table II. The prepared solutions were stored in amber-glass bottles. All experiments were performed under UV-filtered yellow light conditions to prevent undesired exposure during handling. The thermal characteristics of BEE were investigated with a Seiko Instruments, Inc., differential scanning calorimeter, DSC220C system.

The solutions were spin-coated onto 4 in. silicon wafers and soft baked using a Brewer Science CEE 100 spin-coating system. Film thicknesses, as measured using a Veeco Dektak profilometer, of 3-4 μm were acquired at spin speeds of 2400-3200 rpm.

UV exposures were performed on an OAI mask aligner with an *i*-line filtered UV irradiation source (365 nm wavelength). Exposure doses were calculated based on multiplying the exposure time for each sample with the exposure intensity as measured using an OAI model 356 exposure analyzer with a 365 nm probe. Wafers were postexposure baked (PEB) using the same Brewer Science CEE 100 hot plate. After PEB, the samples were spray developed with xylene using a continuous spray while the wafer was spun at 500 rpm.

Results and Discussion

Exposure characteristics.—The first task in this work was to understand the influence of formulation and processing on the lithographic performance of this class of photosensitive PNB materials. In order to do this, contrast curves, which plot normalized film thickness remaining after development (the ratio of remaining film thickness after development to the film thickness before development) as a function of the log of the exposure dose, were measured. The contrast data was generated by (*i*) polymer films were spin coated at 2400 rpm to achieve a nominal thickness of 4 μm, (*ii*) soft

baked at 110°C for 60 s, (*iii*) initial film thickness was measured using profilometry, (*iv*) the samples were exposed to varying doses, (*v*) where appropriate the films were post-baked at 120°C for 30 min, and (*vi*) films were spray developed using xylene and the final film thickness was again measured using profilometry. Results for the various formulations described in Table II are shown in Fig. 4. Two important lithographic characteristics for these materials, the lithographic sensitivity and contrast, can be evaluated from this data.

For negative tone materials, such as those studied in this work, the sensitivity (S) can be defined as the exposure dose required to obtain a standard normalized thickness after development. This use of a standard remaining thickness after development allows for a comparison of materials at approximately the same degree of cross-linking, even though they may have been formulated in slightly different manners or processed at different exposure and bake conditions. In this study, the sensitivity is defined as the dose needed so that the film thickness after development is 50% of the original thickness. A smaller value of S implies that the photodefineable system is more sensitive to UV irradiation. The contrast factor (γ), which is a measure of how sharp the change in remaining film thickness is as a function of change in exposure dose, is usually defined by

$$\gamma = \frac{1}{\log\left(\dfrac{D^0}{D^i}\right)} \qquad [1]$$

Here D^i is referred to as the interface gel dose and corresponds to the dose at which the first amount of photosensitive polymer film remains after development and D^0 is the dose required to produce no decrease in remaining film thickness after development (normally determined by extrapolating the linear portion of the curve to a value of 1.0 normalized thickness). The contrast gives a measure of the ability of a photosensitive material to reproduce sharp relief profiles with vertical sidewalls when exposed and developed. Depending on the contrast of a material, it may act to reproduce patterns with heights more or less proportional to exposure intensity
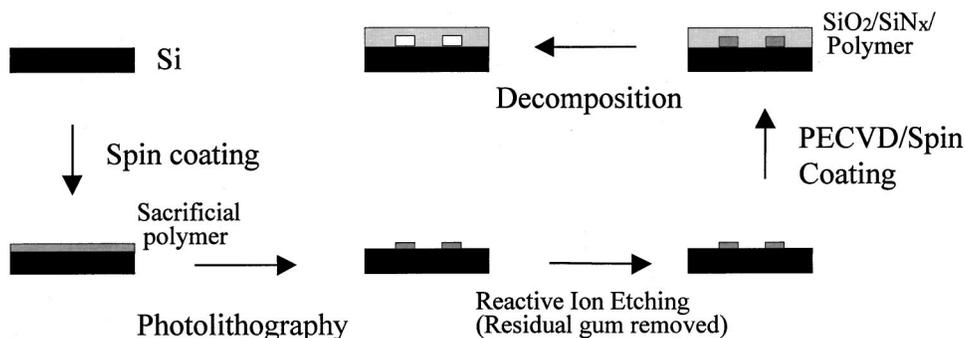

Figure 2. Schematic of processing steps in the proposed microchannel fabrication method using photopatternable polymer sacrificial materials.

Table I. Characteristics of PNB.

Property	Copolymer 1	Copolymer 2	Copolymer 3
BuNB/ANB (mol/mol)	90/10	83/17	77/23
Weight-average molecular weight	328,900	247,600	315,400
Polydispersity index	6.44	4.22	4.63

(low contrast) or it may produce "digital" patterns with feature edges defined at some nominal "threshold" dose (see Fig. 5). The contrast of a photosensitive polymer is calculated from the slope of the contrast curve. In this work the slope of a linear fitting function to the contrast curve data over the range of 0.2-0.8 remaining thickness was used. The values of S and γ for each sample are given in Table II.

The content of reactive or cross-linkable groups in the copolymer is expected to play an important role in the performance of a negative tone photosensitive polymer system. In order to study this relationship, three PNB copolymers with ANB contents of 10, 17, and 23 mol % were formulated and evaluated in experiments ER1-ER3 (see Table II). The sensitivity and contrast as a function of ANB content in the PNB are shown in Fig. 6. It is seen that increasing the amount of reactive groups (*i.e.*, alkenyl group) in the polymer decreases S and increases γ of the material. In particular, the sensitivity and contrast are sharply changed by increasing the amount of reactive groups over the low-end range (10-17 mol %).

It is also clear from the data in Table II that a (PEB) dramatically improves the sensitivity of these materials, presumably by aiding in propagating the cross-linking reactions initiated by radical generation during the exposure step. The influence of the PEB on the contrast of the materials is somewhat more complex. For the polymer containing only 10 mol % of the alkenyl group, the contrast was degraded by performing the PEB. For the polymer containing 23 mol % of the alkenyl group, both sensitivity and contrast were enhanced by the use of a PEB.

The effect of initiator content on the exposure characteristics of this class of materials was also investigated by formulating the same PNB copolymer and varying levels of BEE photoinitiator (experiments ER3-ER5 in Table II). The contrast curves for these samples are shown in Fig. 7. The sensitivity and contrast as a function of initiator level are plotted in Fig. 8. As anticipated, higher initiator loadings result in enhanced sensitivities and higher contrasts. At low initiator loadings (between 0.55 and 1.55 wt %), increasing the initiator content results in a sharp change in the sensitivity of the material, with a reduction of over 300% in required dose, and only a slight increase of approximately 1% in contrast. Thus, over this low initiator content range, the sensitivity of the material can be tuned without affecting contrast.

It is clear that both initiator loading and ANB content in the photosensitive PNB formulations influence exposure sensitivity and contrast. Increasing the initiator loading is the most direct and
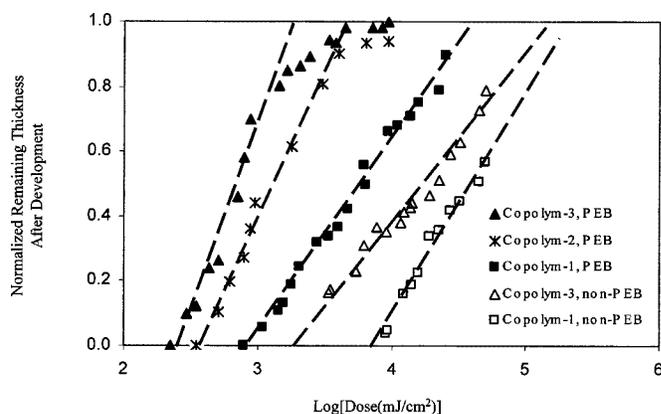

Figure 4. Contrast curves for photosensitive PNB formulations both with and without PEB. $(- - -)$ The linear trend for each curve in the range 0.2-0.8 normalized thickness.

straightforward way to improve the sensitivity and also generally results in an increase in the contrast of the material. Improving the sensitivity aids in reducing the required exposure times and thus increases the throughput of fabrication processes using these methods. In addition, increases in contrast produce more vertical sidewalls on features, which may be useful for the fabrication of certain device structures.

However, in many cases, it may be desired to perform gray scale imaging to obtain patterned features with different heights and shapes in the vertical direction (*i.e.*, along the direction normal to the substrate). In this way, truly 3D structured patterns could be generated. In these cases, materials with lower contrast values are desired. In order to illustrate this point, a comparison of the shape of a feature obtained using a linearly graded gray scale mask was simulated. The contrast data for the 10 and 23 mol % PNB formulations was used for the comparison. A linearly graded mask function (0-100% transmission) was used to simulate the exposure of both materials, with the nominal dose in the 100% transmission areas set to the minimum dose required to achieve a 1.0 value of normalized remaining thickness after development. In this case, the nominal doses for the 10 and 23 mol % PNB formulation was 18 and 2 J/cm² , respectively. The results are shown in Fig. 9. It is clear from these figures that the materials explored in this work have reasonably high contrast since they produce relatively steep-walled images from an exposure profile that is smooth and continuous. Materials with lower contrast values would be valuable for additional gray scale imaging work and could most likely be achieved by lowering the reactive functional group content in the polymer.

Thermal processing effects.—In order to better understand the influence of thermal processing on the lithographic performance of

Table II. Conditions and results for UV exposure response experiments with varying alkenyl group content and BEE loading.[a]

Exposure response experiment	Recipe of PNB/BEE solution Copolymer/BEE/mesitylene (wt %)	PEB	Sensitivity (S) (mJ/cm²)	Contrast (γ)
ER1n	Copolymer 1: 16/4/80	No	12,023	0.63
ER1	Copolymer 1: 16/4/80	Yes	1820	0.58
ER2	Copolymer 2: 16/4/80	Yes	407	0.86
ER3n	Copolymer 3: 16/4/80	No	5623	0.51
ER3	Copolymer 3: 16/4/80	Yes	229	1.18
ER4	Copolymer 3: 16/1.55/82.45	Yes	603	0.91
ER5	Copolymer 3: 16/0.55/83.45	Yes	1995	0.90

[a] Processing conditions: spin-coating 2400 rpm, soft bake 110°C, 1 min, PEB 120°C, 30 min, Developer xylene. The compositions for copolymer 1, 2, and 3 are given in Table I. For comparison purposes, the sensitivity and contrast of Shipley S1813, a typical positive photoresist, are given as 48.5 mJ/cm² and 2.30, respectively.[14]
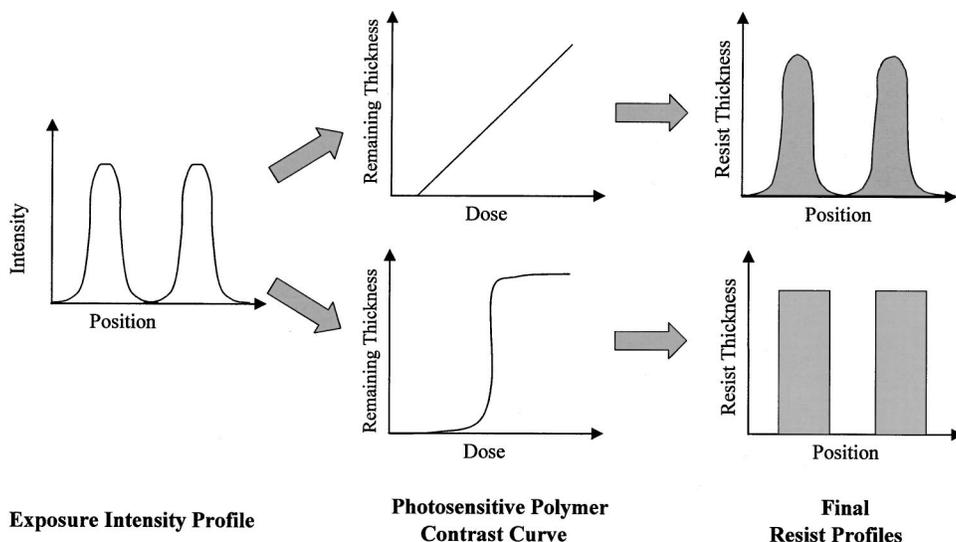
Figure 5. Influence of photosensitive polymer contrast on imaging performance.

these PNB materials, a series of experiments was conducted whose goal was to investigate factors such as the influence of residual casting solvent and postexposure delay on imaging performance.

First, in order to estimate the amount of casting solvent remaining in the film after soft bake, a calibration curve of solvent content *vs.* soft bake time was made for a 110°C bake. A wafer was spin-coated with PNB/BEE solution (copolymer-1/BEE/mesitylene: 16/4/80 wt %) at 2400 rpm rotation speed, and softbaked on a hot plate at 110°C for varying lengths of time. The changes in thickness and the weight of film (dry film + solvent) as the soft bake progressed were measured. The relative thickness of the film at a given time was calculated as the ratio of the thickness of film at that time to the thickness of a nominally "fully dried film." The fully dried film was prepared by baking a sample for an extended period of time at 130°C for 60 min. The residual solvent content was calculated as the ratio of the solvent weight in the film to the weight of the fully dried film. Thus, the profile of residual solvent content as a function of relative thickness is shown in Fig. 10.

The effect of soft bake conditions on the lithographic performance of this class of PNB materials was investigated using this previous data as a guide. It was expected that the residual solvent content in the polymer film after soft bake could strongly affect imaging performance of these materials. Three sets of samples were prepared with PNB/BEE solution (copolymer-1/BEE/mesitylene:16/4/80 wt %) at 2400 rpm rotation speed to investigate this effect. Their residual solvent contents were controlled by varying the soft

bake time and residual solvent levels of 23.3 wt % (soft bake condition: 110°C, 20 s), 13.9 wt % (110°C, 90 s) and 4.5 wt % (110°C, 330 s) were obtained. The thicknesses of the films are 4.45, 4.21, and 3.92 μm, respectively. The coated wafer was exposed to 365 nm UV light at a dose of 6000 mJ/cm^2. After exposure, the wafer was cut into several pieces. Immediately the samples were baked on a hotplate for different times (*e.g.*, 1, 2, 4, and 8 min) at 120°C. The samples were then developed with xylene for 60 s. The final film thickness was then measured, and the normalized remaining thickness after development was calculated. The resulting data is shown in Fig. 11. The figure illustrates, for the PEB time of 50 min, the normalized remaining thicknesses are 0.84, 0.78, and 0.57, respectively, for the films with three different soft bake conditions and therefore three with residual solvent levels (23.3, 13.9, and 4.5 wt %). The normalized remaining thickness of developed films without PEB for three soft bake conditions are very close, varying from 0.35 to 0.37. These nearly identical results in the absence of a PEB would imply that the soft bake conditions had little effect on the extent of cross-linking that occurred during the exposure step itself. The effect of soft bake conditions on imaging performance in the presence of a PEB was dramatic. Lower soft bake time, resulting in higher residual solvent content, led to slower dissolution and presumably higher extent of cross-linking at identical exposure and PEB conditions. This decrease in development rate is somewhat counterintuitive, since higher residual solvent content typically leads to faster development in many photosensitive polymers. It is postulated that
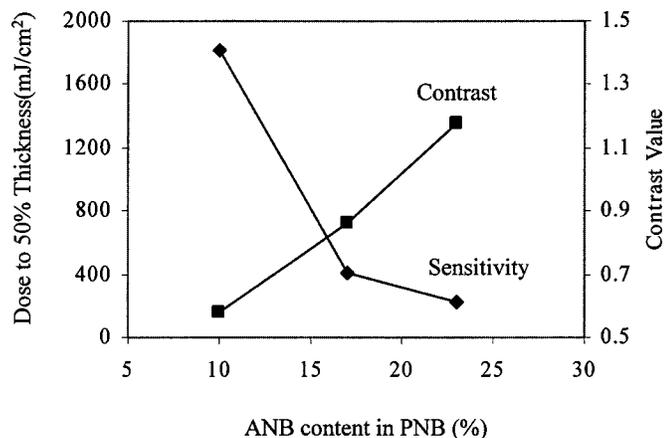

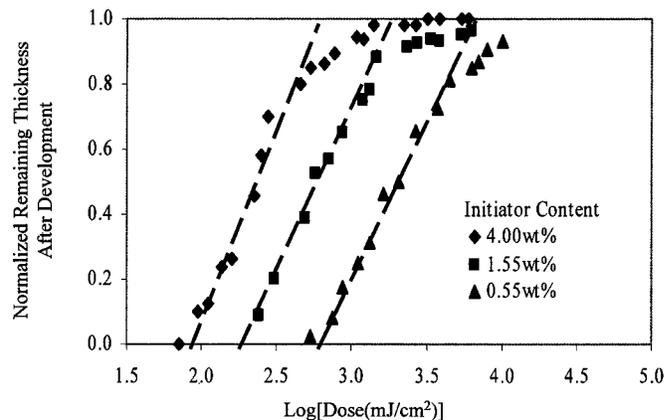**Figure 6.** Sensitivity and contrast as functions of ANB content in the PNB.

Figure 7. Contrast curves for photosensitive PNB formulations with varying initiator loading. (— — —) The linear trend for each curve in the range 0.2-0.8 normalized thickness.
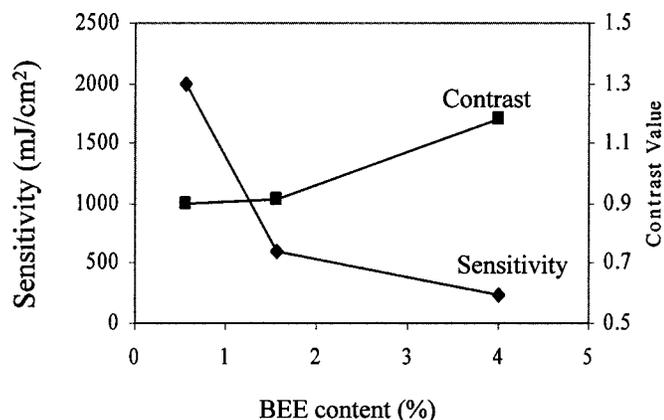
Figure 8. Contrast and sensitivity as functions of initiator loading. The composition of PNB used in the experiment was BuNB/ANB 77/23 mol/mol.

Figure 10. Film weight and residual solvent content change with relative thickness of film. (− − −) Linear fittings.

higher residual solvent content enhances the radical cross-linking during postexposure bake.

In order to better understand over what period of time the PEB affects the imaging performance, the effect of PEB time on residual film thickness after development was studied. Wafers were spin-coated with the same PNB/BEE solution (copolymer-1/BEE/mesitylene: 16/4/80 wt %) at 2400 rpm, and soft baked on a hot plate for 90 s at 110°C. The coated wafer was exposed at a dose of 6000 mJ/cm^2. After exposure, the wafer was cut into several pieces. Immediately the samples were baked on a hot plate for different times (*e.g.*, 1, 2, 4, and 8 min) at 120°C. The samples were then developed with xylene. In the process of development, the samples were dried and tested to obtain the thickness in every 5 s interval. Thus, the relationship between normalized remaining thickness after development as a function of development time and PEB time was obtained and is shown in Fig. 12. The figure shows (with the exception of the blank sample) that the thickness decreases quickly with development time then levels off after approximately 15 s of development. The decrease in film thickness with development time is greater for samples with short postexposure bake times. The complete removal of the fully baked film without exposure (blank sample) shows that thermally initiated cross-linking was insignificant.
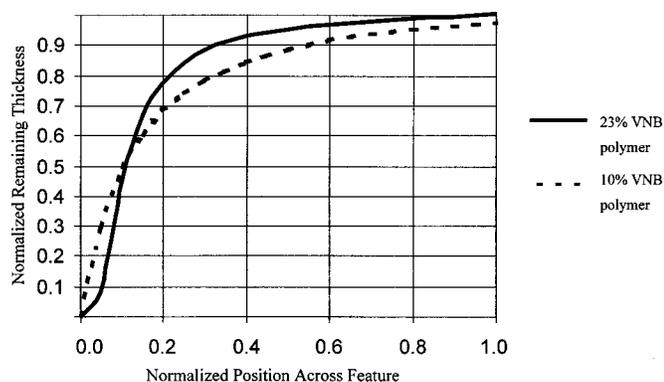
The fact that the cross-linking continues to occur throughout the PEB process for times up to at least 50 min in the absence of UV irradiation implies there still exists a considerable amount of radicals that persist after the UV light is switched off. In order to make an indirect observation on the lifetime or decay of radicals after the exposure is halted, an experiment with delayed PEB was carried out. A wafer sample was spin-coated and soft baked (PNB/BEE solution: copolymer-1/BEE/mesitylene:16/4/80 wt %, spin speed: 2400 rpm, and soft bake: 90 s at 110°C) to contain 14 wt % residual solvent. Upon finishing exposure with dose of 6000 mJ/cm^2, the wafer was immediately cut into several pieces, and the samples were then post-baked for 50 min after different delay times under normal room conditions. After development in xylene for 60 s, the normalized remaining thickness of the films was obtained and plotted against the delay time as shown in Fig. 13. The figure shows that the normalized remaining thickness decreases gradually with the delay time, and for comparison the remaining thickness of a sample without PEB is shown on Fig. 13 as the dashed line. It appears that the PEB samples have higher remaining thickness values for delay times up to and possibly exceeding 1 h. This result implies that radicals in these films are terminated gradually, and that radicals may still exist in the sample after long delay times or during long PEB cycles.

Extended lifetimes of radicals after exposure in photopolymerization systems was observed by Shen *et al.*[9,10] and Kurdikar and Peppas[11] in bulk radical polymerization systems. In these cases, they suggested that the reactivities of radicals in such systems are not equal and that radicals surrounded by polymer chains can be "protected" or trapped and experience lower reactivities. Such protected

Figure 9. Simulated photosensitive polymer profiles for a linear exposure dose gradient using the contrast data obtained in this work for two different PNB copolymers. The shape of channel pattern was simulated on the basis of the fitting equation of contrast curve and the feature property of the gray scale mask by using $d = f[\log(dose \cdot TP)]$, where d is the normalized remaining thickness of the film (after development) at a position across feature, f is the fitting function of contrast curve, TP is the transparency of the feature on a linearly graded gray scale mask.
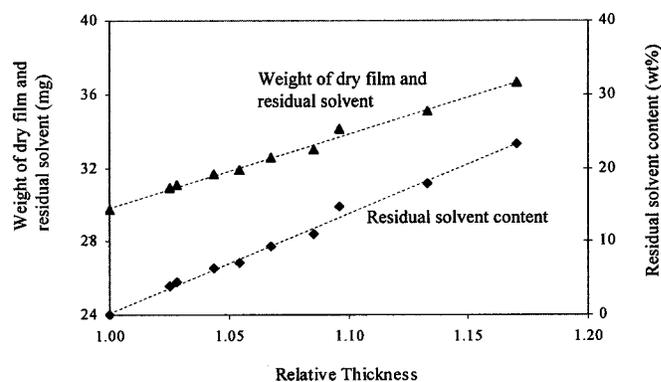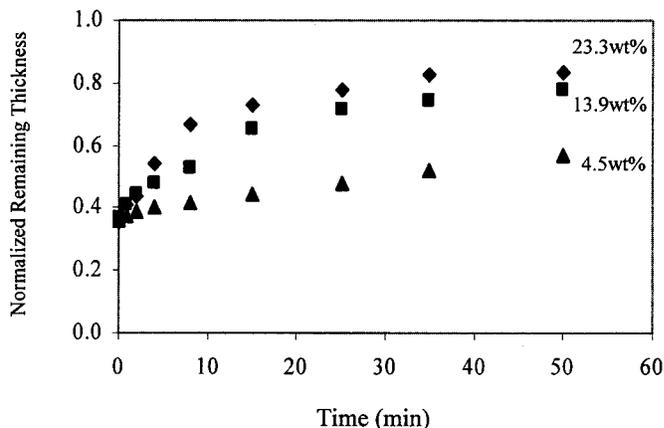

Figure 11. Normalized remaining thickness after development *vs.* PEB time curves for samples with 23.3, 13.9, and 4.5 wt % residual solvent content.
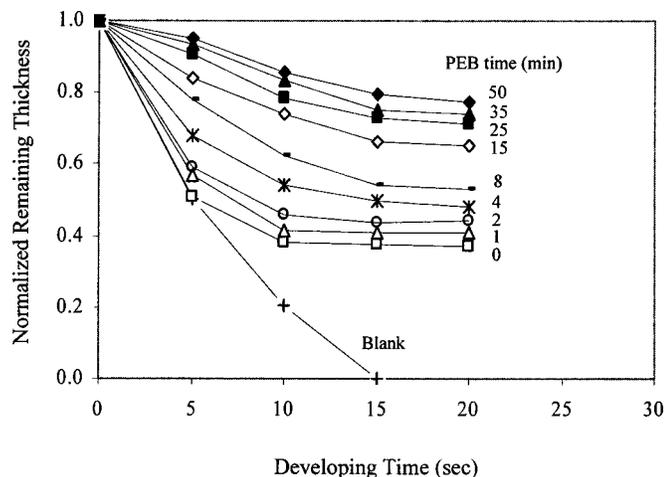
Figure 12. Normalized remaining thickness *vs.* development time curves for the samples with 13.9 wt % residual solvent content. The blank sample was unexposed and baked at 130°C for 1 h. Other samples were exposed with a dose of 6000 mJ/cm^2, then baked at 120°C for 0-50 min.

radicals are terminated more slowly, and hence have longer lifetimes. In the case of the thin-film materials investigated here, the "protection" of radicals in the polymer matrix may in part account for the long observed lifetimes. Radicals embedded in the polymer matrix may have limited access to or encounters with other reactive groups in the film. However, it is also possible that a variety of secondary radicals with a spectrum of stabilities and lifetimes are formed from the primary radicals generated photochemically. For example, oxygen absorbed in the film may play a role in the inhibition and long lifetimes observed in the cross-linking process. Oxygen can react with radicals formed from initiator dissociation (primary radicals) to produce peroxy radicals of lower reactivity or higher stability than the primary radicals.[11-13] The peroxy radicals tend to have long lifetimes and may live much longer than the primary radicals. Due to their thermal instability, however, peroxy radicals may decompose to generate new radicals that result in cross-link formation during the PEB process.

The effect of residual solvent in the polymer film can be attributed to the improvement in the diffusion of reactive species. After exposure to UV light, the samples immediately undergo a postexposure bake. As soon as the PEB process begins on the hot plate, solvent diffuses to the free surface of the film and the polymer matrix shrinks. This provides an opportunity for radicals to come
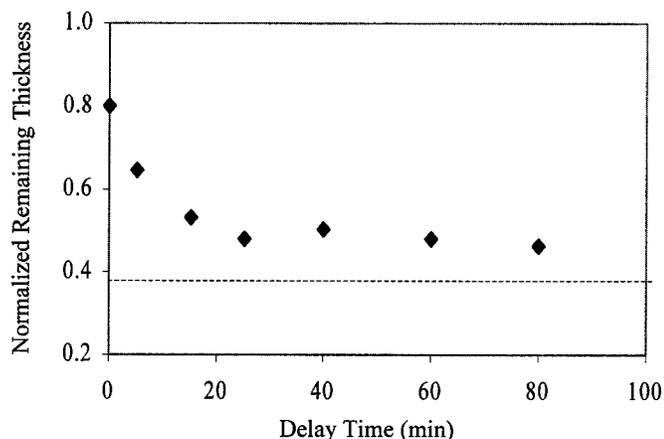

Figure 13. Normalized remaining thickness after development changes *vs.* delay PEB time.
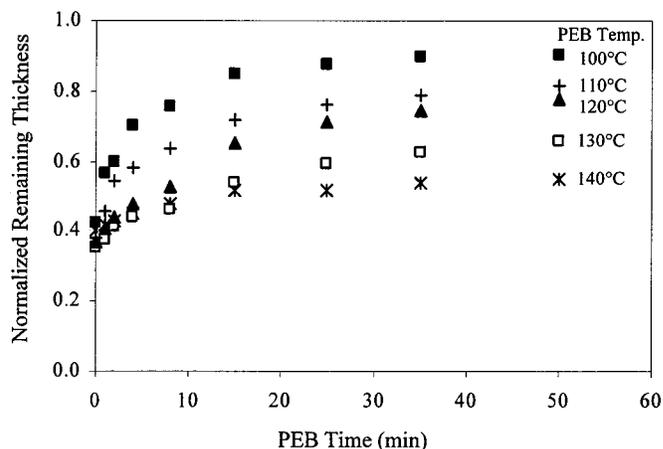

Figure 14. Normalized remaining thickness after development *vs.* PEB time curves for the samples treated with different PEB temperature.

into contact with new alkenyl groups and promotes further cross-linking. This effect would be expected to be more significant in films with higher residual solvent contents, and the data shows that films with higher residual solvent cross-link to a greater degree under otherwise identical processing conditions.

Finally, the effect of PEB temperature on the imaging performance for these PNB materials was investigated. Five wafers were prepared (copolymer-1/BEE/mesitylene: 16/4/80 wt %, spin speed: 2400 rpm, and softbake: 90 s at 110°C) to contain 14.0 wt % residual solvent content in the films. The thickness of the coated films was approximately 4.20 μm. The prepared wafers were exposed to the UV light at a dose of 6000 mJ/cm^2. After exposure, the wafers were cut into small pieces and postbaked at different temperatures for varying lengths of time (*e.g.*, 1, 2, 4, and 8 min). The samples were then developed with xylene. The resulting curves of normalized remaining thickness after development *vs.* PEB temperature and time are shown in Fig. 14. As expected, PEB temperature has an obvious effect on the cross-linking process. Increasing PEB temperature can lead to improvements in the diffusion of reactive species and the rate constants for cross-linking reactions. At low temperatures, due to relatively low cross-linking reaction rates, a large amount of the radicals appear to be quenched before they generate cross-links. This effect is clearly seen in the relatively small increase in remaining polymer film thickness after PEB for the sample baked at 100°C as compared to both the initially exposed film and those films baked at higher temperatures. As the PEB temperature is raised (see 100-130°C PEB data), the quenching of radicals during the PEB appears to no longer be the dominant factor at temperatures in the range of 130°C. At these higher temperatures, it appears that the extent of cross-linking is controlled by the initial number of radicals generated in the exposure step. This conclusion is supported by the near identical normalized remaining thickness after development for the 120 and 130°C PEB trials, even though the 130°C curve shows a much faster initial rate of cross-linking. However, when the PEB temperature is increased to 140°C, an abrupt acceleration of cross-linking could be seen. It was suspected that thermally generated radicals were responsible for additional cross-linking at this temperature. The thermal decomposition of BEE was investigated with differential scanning calorimetry (DSC, see Fig. 15). In Fig. 15, the DSC peak around 59°C indicates the melting point of BEE, and appreciable thermal decomposition appears as the temperature increases above 125-130°C. In addition, experiments with unexposed films baked at temperatures in the range of 140-150°C show some residual film thickness after development, thus supporting the idea of thermally induced cross-linking. This data therefore suggests that the PEB temperature for these materials be set in range of 120-130°C in order to promote the maximum degree of cross-linking
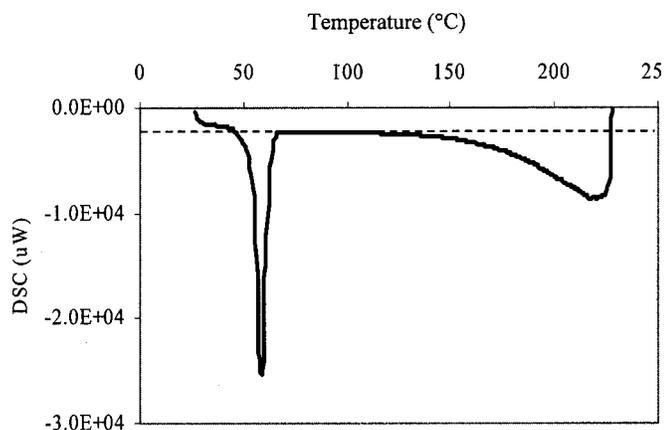
Figure 15. DSC spectrum for BEE with heating rate 5°C/min.

possible due to radicals generated during exposure while preventing undesired thermal cross-linking in unexposed areas of the material.

Conclusions

The lithographic characteristics and the effect of thermal processing on imaging performance of a novel class of photodefinable PNB sacrificial materials has been studied. The lithographic studies indicate that the sensitivity and contrast of these materials can be controlled by adjusting both the loading of photoinitiator used and the relative content of photodefinable groups in the polymer. Specifically, increases in the alkenyl group content of the polymer lead to consistent improvement in both exposure sensitivity and contrast. The results of thermal processing studies indicate that cross-linking can continuously occur throughout the PEB process for PEB times approaching 1 h. This fact implies that there still exist a large number of radicals after UV exposure, which was verified by postexposure delay experiments. It has been shown that the PEB process can significantly affect the cross-linking of PNB; however, this effect is strongly subject to the residual solvent content in the film as dictated by the soft bake conditions used in preparation of the film. This phenomenon can probably be ascribed to an improvement in diffusion of reactive species occurring along with the evaporation of residual solvent and shrinking of the polymer matrix during the PEB process. The influence of residual solvent on cross-linking has been found to be less meaningful for samples that are not subjected to PEB.

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