Effects of the Photoacid Generator Type on the Imaging and Thermal Decomposition Properties of Photodefinable, Thermally Sacrificial Poly(propylene carbonate) Materials

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ABSTRACT: Photosensitive, thermally sacrificial polymer systems consisting of poly(propylene carbonate) (PPC) and a photoacid generator (PAG) were studied for use in the fabrication of buried microchannel systems such as microfluidic devices. Because the fabrication of microchannels was affected by the performance of these materials, changes in the imaging properties were monitored upon the variation of the PAG used in the system. Thin films of PPC loaded with a PAG were spin-cast onto silicon wafers, exposed to UV light to selectively generate acid, and placed on a hotplate to decompose the exposed regions. Properties such as the contrast, sensitivity, and amount of residue remaining after decomposition varied significantly, depending on the PAG used. The use of a metal-free, ionic methide PAG gave the best performance for formulating a chemically amplified, photosensitive, sacrificial polymer system based on PPC. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 266–271, 2006

Key words: catalysis; imaging; photoresists; polycarbonates; thermal properties

INTRODUCTION

A new fabrication technique based on the use of thermally sacrificial polymers has recently been developed that allows the fabrication of microelectromechanical systems (MEMSs) and microfluidic devices containing freestanding and microchannel structures. This new method permits the construction of devices with greater degrees of functionality (i.e., fully integrated, complex, multilevel fluidic systems with functional valves, pumping systems, and other MEMS components) than other fabrication methods because of its compatibility with standard integrated circuit and MEMS fabrication methods.[1] In this new method, a thermally sacrificial polymeric material undergoes a series of processing steps that create a patterned film of the polymer in the shape of the desired channels and devices (Fig. 1). Next, the structures are encapsulated with a permanent structural material such as an inorganic glass or a second polymer. If complex, three-dimensional systems are required, these steps can then be repeated to produce the desired layered structures. Finally, the fully fabricated device is heated to a temperature at which the sacrificial polymer slowly decomposes, thus leaving behind void spaces in the desired areas.

This process was first developed with functionalized polynorbornenes that decompose at temperatures around 425°C, which is not amenable for use with many possible substrates and structural materials that could make high-throughput fabrication more economical. For this reason, polymers with lower decomposition temperatures were desired, and polycarbonates were identified as a class of polymers that decompose at temperatures in one preferred range (200–300°C). A study of commercially available polycarbonates such as poly(propylene carbonate) (PPC) showed promising results for use in the fabrication of microchannels.[2]

As with the original polynorbornenes, however, a major disadvantage of these simple polycarbonates is the complex patterning required to form the microchannel structures (Fig. 1). Also shown in Figure 1, this fabrication process can be greatly simplified with a polymer or polymer system that can be directly patterned with traditional lithographic techniques. Several groups have reported that the thermal decomposition temperature of polycarbonates can be dramatically reduced by the presence of a small amount
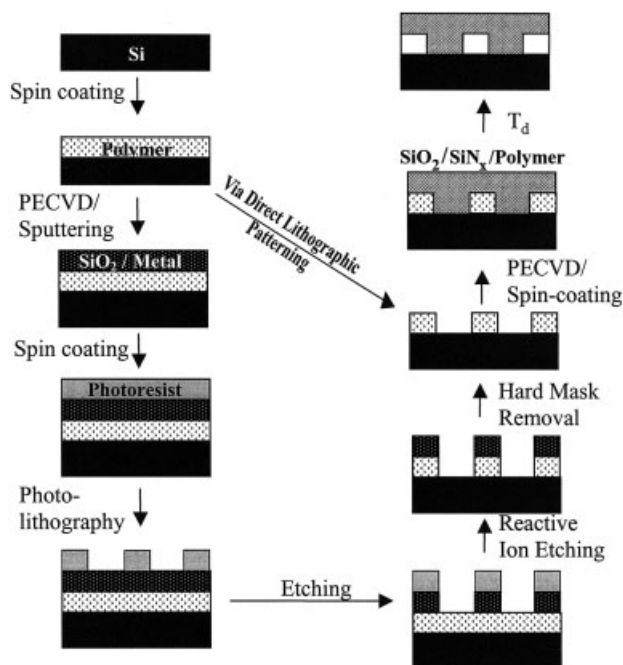
**Figure 1** Fabrication process flow with sacrificial polymeric materials.

of acid[3] and that polycarbonates can be made photosensitive with a photoacid generator (PAG) as the source of this acid.[4–7] With this in mind, one objective of this work has been to develop photodefinable, sacrificial polymer systems based on polycarbonates and other polymers.

There are several key requirements for such sacrificial materials to make them useful in microstructure and microfluidic channel fabrication. Perhaps the most important property is that the materials decompose cleanly to leave little or no residue. When the polymer is patterned with separate masking and etching steps, this only requires the sacrificial polymer itself to decompose cleanly. In the case of photodefinable systems that rely on the use of a PAG, both the polymer and the PAG must decompose cleanly without leaving a residue. Because any residue left after decomposition will define the surface properties of the device walls, one cannot tolerate using PAGs that may leave behind residues that would be unacceptable for a particular application. One example of this would be microfluidic devices for biological systems in which toxic metals or other contaminants left in the residue could interfere with the biological systems. In those cases, metal-free acid generators may be desired.

In addition to thermal decomposition properties, imaging characteristics such as sensitivity and contrast (γ) can be greatly affected by the variation of the PAG used. There are numerous definitions used for sensitivity, and thus a consistent and well-defined measure of sensitivity must be established for compar-

ing the performances of different materials. Lithographically useful sensitivity has been previously defined as the dose per unit area that results in dimensional equality of clear and opaque features that are nominally equal in pattern design.[8] This dose is sometimes also called the dose-to-size. Another common measure of resist sensitivity, the dose-to-clear (E_0), refers to the dose required to completely develop the resist film to the bottom of a pattern or large exposed area. In this work, E_0 is used for reporting material sensitivities. For positive-tone, thermally developed systems such as those studied in this work, the sensitivity in terms of E_0 is represented by the dose required for complete decomposition of the exposed polymer at a given development temperature. The photodefinable materials reported in this work are developed with a dry-develop or thermal-development process in which the polymer film is heated after exposure to a temperature at which photoacid in the films is able to catalyze the local decomposition of the sacrificial polymer. γ, or the resolving power of the resist system, defines how the resist responds to changes in the exposure dose. Both of these properties can be determined by the generation of a plot of the normalized thickness loss as a function of the log dose, also commonly called a contrast curve. The *x* intercept of this curve is E_0, and the slope is γ.

The series of PAGs shown in Figure 2 were studied in this work to determine the effects of the type of PAG used in formulating PPC–PAG systems on the resulting imaging properties and amount of residue left after decomposition for such materials. These four PAGs were chosen on the basis of a previous study in which it was determined that a minimum acid strength is required to decompose PPC.[9]
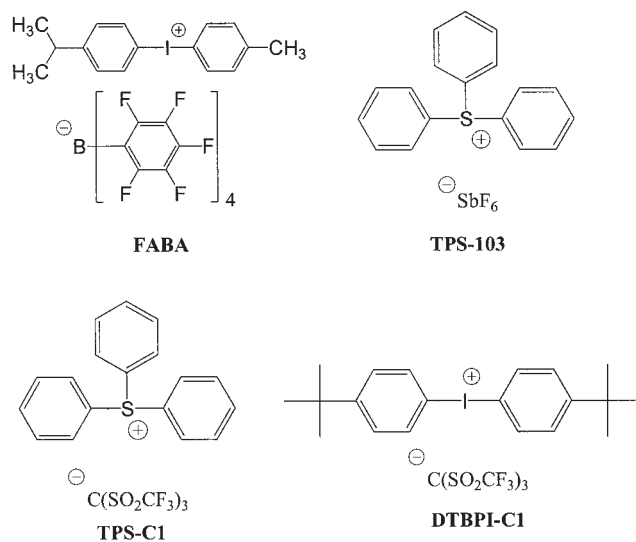
Figure 2 Chemical structures of PAGs used in this study.

EXPERIMENTAL

Materials

All materials were used as received. PPC, propylene glycol methyl ether acetate (PGMEA), and isopropyl alcohol (IPA) were purchased from Aldrich. Triphenylsulfonium hexafluoroantimonate (TPS-103) was purchased from Midori Kagaku Co., Ltd. Rhodorsil photoinitiator 2074 (FABA) was purchased from Rhodia. Triphenylsulfonium tris(perfluoromethanesulfonyl) methide (TPS-C1) and di(p-t-butylphenyl) iodonium tris(perfluoromethanesulfonyl) methide (DTBPI-C1) were donated by 3M Corp. Clean silicon $\langle 100 \rangle$ wafers with native oxide surfaces (Nova Electronic Materials) were used as substrates in these experiments.

Preparation of the PPC/PAG films

Polymer solutions (~10 wt % PPC in solution) were prepared by the dissolution of PPC in PGMEA. A PAG was then added to the PPC solutions (2–3 wt % total solids as PAG). The solutions were filtered with a 0.2-μm Teflon filter. All processing of solutions, casting of films, and exposure and processing of the samples were conducted in a specially filtered, base-free, clean-room environment. This base-free environment is an important condition for properly characterizing the fundamental properties of such materials because trace amounts of basic species in normal room air (amines, etc.) can quickly neutralize the relatively small amounts of acid generated in such films and alter the ability to observe acid-catalyzed phenomena in these materials. Films were spin-cast onto silicon $\langle 100 \rangle$ wafers with a CEE 100 CB spin-coat and bake system (Cost Effective Equipment) at thicknesses of 1–1.5 μm. The spin-coated wafer was immediately soft-baked on a CEE 100 CB hotplate at 90°C for 2 min to remove residual casting solvent. After cooling, the resist film was exposed to 248-nm ultraviolet light at the desired doses with a 6-mm-square aperture plate. The light source used in these experiments was an Oriel 87000 series 500-W Hg–Xe flood exposure tool filtered with a DUV bandpass filter (Newport) with a center wavelength of 248 nm and a full width at half maximum bandwidth of 10 nm. The exposed areas of the sample were then decomposed by the placement of the wafer on a hotplate for a postexposure development bake at 115°C for 3 min. The 115°C temperature was selected on the basis of previous experimental work that showed that at temperatures less than 110°C, the PPC polymer only partially decomposes, leaving behind significant residue. In addition, higher temperatures were avoided to minimize polymer deformation and flow because PPC is well above its glass-transition temperature (T_g; ~20–25°C) under these conditions and to ensure that the polymer did not volatilize too quickly. Decomposing the polymer at high rates can potentially lead to pattern distortion and damage to the channel structure. Thus, although investigating higher decomposition temperatures for PPC may influence the amount and type of residue left from the polymer decomposition, such higher temperature processes would not be useful for practical patterning of these materials. After thermal development, the samples were inspected for residue content with spectroscopic ellipsometry, and the composition of the residue of a representative set of samples was characterized with X-ray photoelectron spectroscopy (XPS). The resulting thermally developed samples were washed with IPA to remove any remaining soluble residues.
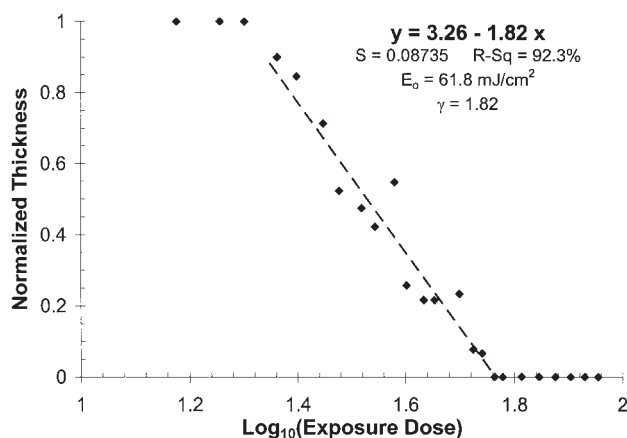
Contrast curve generation

Resist films were prepared as described previously and exposed at doses ranging from 3 to 100 mJ/cm^2 with the Oriel filtered exposure tool in a 5×5 dose array. Contrast curves for each PPC/PAG system were generated in the typical manner by the plotting of the normalized thickness loss (after thermal development and washing) as a function of the log dose.[8] Film thicknesses of each exposed pad were determined with a Tencor Alphastep-500 profilometer and normalized by the original coated film thickness. E_0 and γ were then determined by the performance of a linear regression on the data with Minitab, a statistical analysis software package, and by the recording of the x intercept and slope, respectively.

Residue analysis

Samples for residue analysis were prepared as described previously. The films were exposed at their E_0 value as determined by the contrast curve for each system. Residue thicknesses were measured after decomposition, but before washing with IPA, with a V-VASE variable-angle spectroscopic ellipsometer (J.A. Woollam Co., Inc.). Ellipsometer measurements were made over the spectral range of 400–1100 nm at three different angles (65, 70, and 75° from normal incidence) with a 5-nm sampling interval. All films were modeled with a Cauchy dispersion model to determine the film thickness and optical constants. The Cauchy model is sufficient in this case because the materials used in this work possess no appreciable absorption in the measured wavelength range.

The composition of the residue is an important question depending on the specific application for the microfabricated structures. In this work, XPS with a Physical Electronics (PHI) XPS system was employed to determine the elemental composition of the residues. Monochromatic Al Kα X-rays at 1486.6 eV were used to excite the sample, and a broad survey scan of

Figure 3 Contrast curve generated by the plotting of the normalized film thickness versus $\log_{10}$ of the exposure dose. E_0 and γ were calculated as the x intercept and slope, respectively, of the linear region of this plot. This curve is a representative example of a typical contrast curve generated by all the PPC/PAG systems studied. Only one curve, that of the photosensitive, sacrificial PPC/FABA material, is shown for clarity.

the sample was first measured to determine the binding energies of major constituents in the residue and thus the characteristic elemental makeup of each residue. After the survey scan, high-resolution scans centered at the electron-binding energies of the elements of interest were collected for further quantification of the residue composition.

RESULTS AND DISCUSSION

Contrast curve generation

The effects of PAG selection on the sensitivity and γ were monitored through the generation of contrast curves for each of the PPC–PAG systems used in this work. A typical contrast curve, which in this case is for the PPC–FABA system, is shown in Figure 3, and the results for all the PPC–PAG systems are summarized in Table I.

There is a dramatic difference in the exposure dose (E_0) required to fully decompose the polymer depending on the PAG used in the PPC–PAG formulation. These values range from 151 mJ/cm² for TPS-103 to less than 40 mJ/cm² for TPS-C1. The amount of time required for lithographic device processing will in turn be proportional to the sensitivity of the material; therefore, a small E_0 value will advance the fabrication process toward the desired goal of permitting the high-throughput fabrication of inexpensive and potentially disposable devices. In terms of sensitivity, the TPS-C1 PAG results in the highest photospeed material.

γ also has the potential to greatly enhance the functionality of the proposed processing route by making

it possible to produce microchannels that are shaped in a controlled manner in all three dimensions with gray-scale lithography. This technique was tested previously by Wu et al.[10] with photosensitive polynorbornenes. Channel features on a reticle were designed with an approximately linear gradient in the transmission percentage, creating a gray-scale mask that allowed for the photosensitive, sacrificial material to be exposed to a range of doses across the width of the channel feature with a single lithographic step. Along with a low-γ photosensitive material, this exposure gradient can be used to produce a feature that is shaped in both the lateral and vertical directions with respect to the plane of the substrate. This type of three-dimensionally shaped feature can have numerous benefits. For example, shaped microchannels can be used to help maintain pluglike flow in devices in which curved channels are needed (i.e., chromatographic devices that require long channels).[11] In this work, it has been found that the choice of PAG can also impact γ of the resulting photodefinable PPC system. For use in gray-scale lithography, the TPS-C1 PAG was found to produce the material with the lowest γ value (1.11). Such a relatively low-γ material should be able to be used in conjunction with gray-scale masks to produce three-dimensional microchannel structures, as previously demonstrated with polynorbornenes.[10]

Residue analysis

As mentioned previously, one of the most important characteristics of the photodefinable polymer systems used in the fabrication of microfluidic and other microdevices is that they do not leave a significant amount of residue after decomposition. An earlier study showed that PPC alone leaves no residue upon thermal decomposition.[2] However, for the photosensitive systems explored in this study, the amount of residue may be influenced by the presence of the PAG. In fact, Table II shows that by simply changing the PAG used, we can reduce the amount of residue from approximately 13% of the original film thickness (1300 Å of residue left for PPC combined with the TPS-103 PAG) to essentially no residue (negligible residue re-

TABLE I
E_0, γ, standard error (S), and R^2 Values for Each PPC/PAG Data Set as Determined with Minitab Statistical Analysis Software

PAG	E_0 (mJ/cm²)	γ	S	R^2
TPS-C1	36.3	1.11	0.117	0.888
DTBPI-C1	79.0	1.66	0.092	0.915
FABA	61.8	1.82	0.087	0.923
TPS-103	151.2	1.17	0.079	0.914

TABLE II
Results of Residue Analysis, Including the Original Polymer Film Thickness, Residue Thickness, and Exposure Dose Used in This Set of Experiments

PAG	Dose (mJ/cm^2)	Thickness (Å) Polymer	Thickness (Å) Residue
TPS-C1	37	14,500	Negative
DTBPI-C1	79	13,100	284
FABA	62	13,300	369
TPS-103	152	9,900	1312

maining for PPC combined with the TPS-C1 PAG). The ability of the TPS-C1 PAG, a methide-ion-based PAG, to successfully catalyze the thermal decomposition of PPC while resulting in no measurable residue, coupled with the fact that it is a metal-free PAG, makes it an ideal choice for formulating photodefinable, thermally sacrificial polymers based on PPC. XPS data showed that both the Sb- and B-containing PAG residues contained substantial levels of Sb and B in comparison with the levels that might be expected on the basis of the initial PAG loadings (i.e., as determined by Sb or B concentrations with respect to carbon, oxygen, iodine, and sulfur). These XPS data indicated that the Sb-containing fragment produced from the TPS-103 PAG was abundant in the residue remaining from the TPS-103 PAG. Also, the samples formed from PAGs containing the iodonium cations displayed some residual levels of iodine, which indicated that in these cases the iodonium cations also were not completely removed during the thermal development. Additional experiments with XPS to better quantify the composition of the residues from a larger series of PAGs would be helpful in elucidating additional trends and factors that control the ability for a particular PAG to produce a reside-free photodefinable material. Although it is difficult to draw extensive conclusions concerning the influence of the PAG structure on the residue formation in these materials on the basis of only the data available from the four PAGs tested in this work, the data do suggest that PAGs containing the triphenylsulfonium cation may result in better low-residue performance. This is certainly true, for example, in comparison with the iodonium-based cations, as supported by the performance of the DTPBI-C1 PAG with respect to the TPS-C1 PAG. This may be the result of the fact that triphenyl sulfonium ions are known to further decompose into lower molecular weight species, thus perhaps helping with volatilization, during the PAG photoreaction. It is also clear from the data for the TPS-103 system that the amount of residue left for that PAG was not due solely to the PAG because nearly 13% of the original thickness of the film remained but only 2 wt % PAG with respect to PPC was used in the formulation. Thus,

there appears to be some contribution from the polymer and in certain cases due to some interaction with the PAG or its byproducts during the decomposition. The PAG residue data also suggest that PAGs containing metals and other heavy fragments, such as hexafluoroantimonate-based materials, will also most likely be problematic in terms of residue. If the compounds in the formulation cannot form volatile products during decomposition, then residues will be expected.

There are numerous additional factors that may affect the performance of polycarbonate–PAG systems, particularly with respect to their decomposition and residue properties. For example, the results discussed in this article are for decomposition in an oxygen-rich air environment. Conducting the decomposition process in an inert or different environment may of course affect this process. In addition, the TPS-103 results suggest that there can be an interaction between the PAG and the polymer in some cases that can amplify the amount of residue left after decomposition of the polymer–PAG mixture. Therefore, it is unclear at this point how these results will translate in detail to other polymer systems such as alternative polycarbonate materials.

Figure 4 depicts a test pattern generated with the PPC–TPS-C1 system studied here. The rounded edges and slight loss of proper sizing of the line/space pattern, which should be 200 μm with a 1:1 pitch, occurs because the processing temperature of the system is significantly higher than T_g of PPC; this results in some polymer flow during processing. Therefore, work is currently underway to produce polycarbonates with improved T_g s (i.e., higher T_g materials) and other properties (e.g., semicrystalline phases) that can yield materials with improved patterning performance that can be used as photosensitive, sacrificial materials for the fabrication of microdevices.[7]
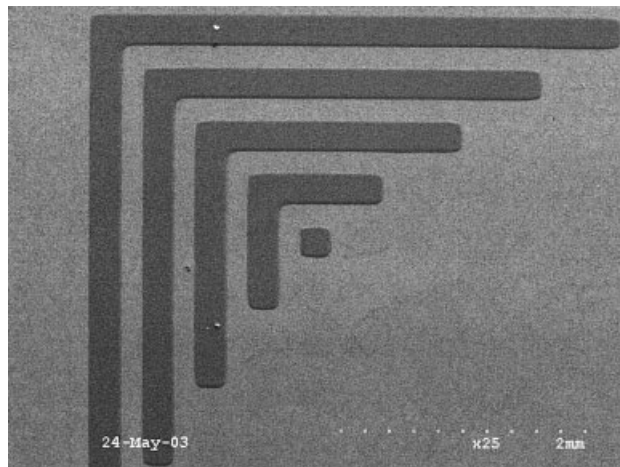
Figure 4 Scanning electron micrograph of patterned PPC with TPS-C1 as the PAG. The L-bar test pattern was a 200-μm line/space pattern with a 1:1 pitch.

One important aspect of the residues produced from PPC–PAG materials that was found in this study and previous works is that they are easily removed by washing with IPA. This property helps to increase the resolution of the system[4,6] and makes the amount of residue left after patterning and thermal development insignificant for these materials. On the other hand, when the full fabrication process is conducted, it is not easy or may even be impossible to wash away any residue left from the PAG-loaded PPC sacrificial polymer after thermal decomposition is completed. This would be particularly true of buried, lengthy microchannel devices or completely enclosed cavities. Further analysis of the residue properties at the uncatalyzed decomposition temperature (or at the thermal acid generation temperature if it is below the uncatalyzed decomposition temperature) will be required to fully understand the impact of PAG selection on the amount of residue remaining during the fabrication of overcoated and buried microstructures. On the basis of the results in this work, however, it is expected that the PPC–TPS-C1 system should perform equally as well in terms of its decomposition in the fabrication of these devices.

CONCLUSIONS

Several properties of photosensitive polymer systems consisting of PPC and a PAG were studied as a function of the PAG structure. PAG selection was found to have a minor effect on γ of the PPC–PAG materials. However, the choice of PAG strongly affected both the sensitivity and the amount of residue remaining after decomposition for such materials. The desired imaging characteristics could be optimized by the choice of a suitable PAG. Of the PAGs studied in this work, the triphenylsulfonium methide based PAG (TPS-C1) gave the best imaging performance and resulted in the least amount of residue after decomposition.

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