Patterning decomposable polynorbornene with electron beam lithography to create nanochannels

Nicole R. Devlin[a] and Devin K. Brown
Microelectronics Research Center, Georgia Institute of Technology, 791 Atlantic Dr. NW, Atlanta, Georgia 30332-0269

Paul A. Kohl
School of Chemical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0100

(Received 30 June 2009; accepted 26 October 2009; published 1 December 2009)

Unity® 4671E sacrificial material is a decomposable negative tone polymer sensitive to ultraviolet radiation. In this study, it is shown that Unity® 4671E can also be patterned by electron beam lithography. Nanochannels with a width of 65 nm and a pitch of 200 nm have been fabricated. The developed Unity® 4671E patterns can thermally decompose and the products can permeate through the encapsulating material leaving nanocavities. This direct write electron-beam process has fewer processing steps than other published fabrication methods. © *2009 American Vacuum Society.*
[DOI: 10.1116/1.3264658]

I. MOTIVATION

Unity® 4671E sacrificial material [supplied by Promerus LLC (Ref. 1)] is a negative tone decomposable polymer that can be exposed with UV radiation and solvent developed to form freestanding images. The developed images can be encapsulated with a dielectric followed by thermal decomposition of the Unity structures. The thermal decomposition products can diffuse through the overcoat structure to leave hollow nanochannel. Optical lithography has resolution limitations which can be overcome by using electron beam lithography (EBL).

Nanochannels have applications in the areas of fluidics, ring resonators, and various biological areas. DNA sequencing is one potential biological application.[2] In its normal state, DNA has a long, coiled, spherical shape. Flowing DNA through a nanochannel forces it to uncoil into a linear form. Once in its linear form, the DNA can be sequenced more efficiently.

II. PREVIOUS WORK

In a previous report, Dang *et al.* used a decomposable polymer, Unity 200, to improve the speed of electrical interconnect.[3] Their work shows that the sacrificial polymer can be exposed using UV photolithography and can be used to form micrometer-sized channels. In a separate experiment by Harnett *et al.*, 1 μm wide channels were created through a direct write EBL exposure of a positive tone thermally decomposable polycarbonate.[4] The patterned polycarbonate structures could be coated with an overcoat layer and thermally decomposed. Access ports were required on the back side of the wafer for venting polycarbonate products. Since polynorbornene-based Unity can permeate through overcoat dielectrics, venting ports are not required.[5,6] More recently, Lee and Gleason created 70 nm wide nanochannels using a decomposable polymer.[7] In their experiment, the decomposable polymer was spun onto the substrate, followed by spin coating with polymethyl methacralate (PMMA). The PMMA was then patterned with EBL and the pattern was transferred into the sacrificial polymer by etching to create decomposable structures. This method is effective; however, with an EBL-definable sacrificial polymer, such as Unity® 4671E, no pattern transfer step is necessary.

III. MATERIAL CHARACTERISTICS

Unity® 4671E is comprised of a polynorborene backbone with epoxy functionality dissolved in 2-heptanone. When Unity® 4671E is irradiated by an electron beam, a catalyst is activated. Once activated, the catalyst initiates chain cross-linking. An unstable carbocation from the open epoxy ring forms a covalent bond to a separate polynorbornene chain cross-linking the two chains together (Fig. 1).

After the Unity structures have been cross-linked by EBL, Unity® 4671E can be thermally decomposed at ~400 °C. It was found that a fast ramp rate (15 °C/min) resulted in cavities with lower residue.

IV. RESULTS AND ANALYSIS

In this investigation, the exposure and development processes were optimized. Unity® 4671E was diluted, 1:1 by volume, with 2-heptanone spun coated at 2000 rpm for 60 s on a silicon wafer resulting in a 100 nm thick film. The wafer was soft baked at 100 °C for 5 min to evaporate the solvent. The Unity® 4671E was exposed by EBL using a JEOL JBX-9300FS tool at 100 kV acceleration voltage and 50 pA beam current. It was found that this Unity is very sensitive to e-beam radiation and a latent image was formed at doses as low as 5 μC/cm^2. After exposure, the wafer was postexposure baked at 90 °C for 30 s and developed in toluene for 45 s followed by a 1 min rinse in isopropanol. A range of development times were tested, and a 45 s development time resulted in the sharpest features with no residue from underdeveloping resist (Fig. 2). Four developers were

[a]Electronic mail: nicole@gatech.edu

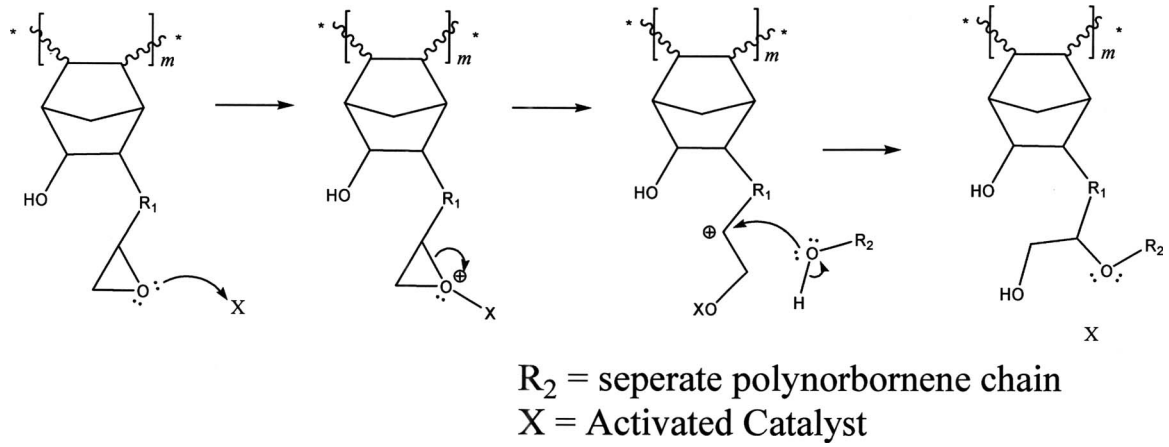

FIG. 1. Unity® 4671E thickness measured over a dose range with different development times.

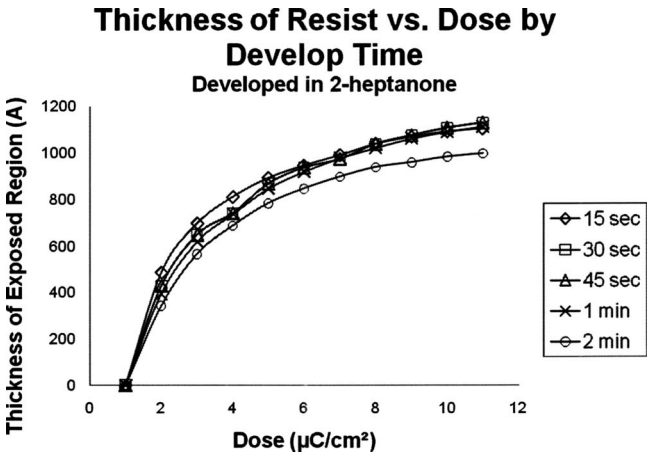

FIG. 2. Unity® 4671E thickness measured over a dose range with four different developers.

tested with no observable difference in results (Fig. 3). In addition, it was found that the temperature of developer did not adversely affect the contrast of pattern features (Fig. 4). Using this optimized process, the minimum feature size of 90 nm was achieved (Fig. 5).

The purpose of using Unity® 4671E sacrificial material was to create a template for forming hollow nanochannels. Complete thermal decomposition of the Unity® 4671E is desirable to avoid residue in the nanochannels. A series of Unity® 4671E test structures was formed to investigate the residue after thermal decomposition. The test lines were 5 mm long and 400 nm tall, and had widths of 2 μm, 500 nm, and 100 nm. These samples were developed in toluene and then coated with 200 nm of plasma enhanced chemical vapor deposited (PECVD) silicon oxide. To create the hollow channels, the sample was heated to 430 °C in a nitrogen-filled furnace for 2 h to decompose the Unity. The decomposed sample and a control sample (where the Unity was not decomposed) were cross sectioned and imaged. The control sample (with Unity intact) clearly showed the Unity® 4671E present within the encapsulated PECVD oxide (Fig. 6). The thermally treated sample was hollow with no appar-

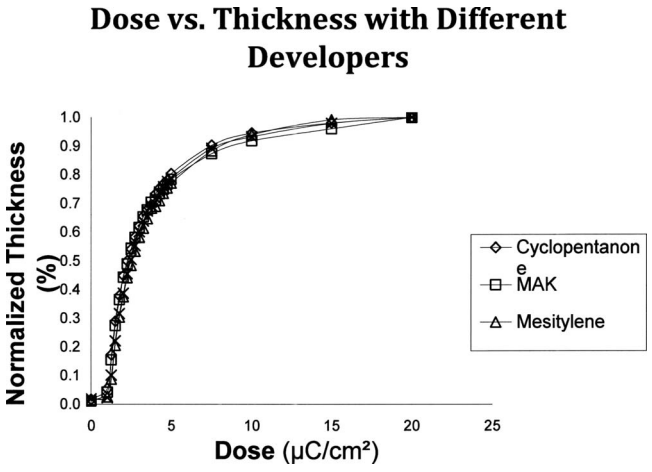

FIG. 3. Unity® 4671E thickness measured over a dose range with different development temperatures.

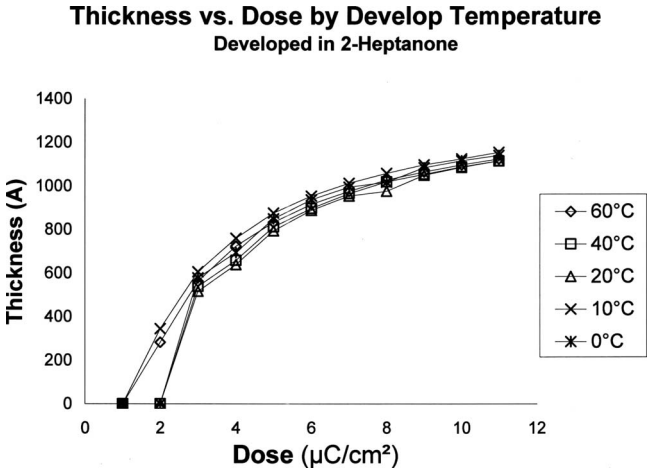

FIG. 4. 90 nm wide line of Unity® 4671E on silicon.

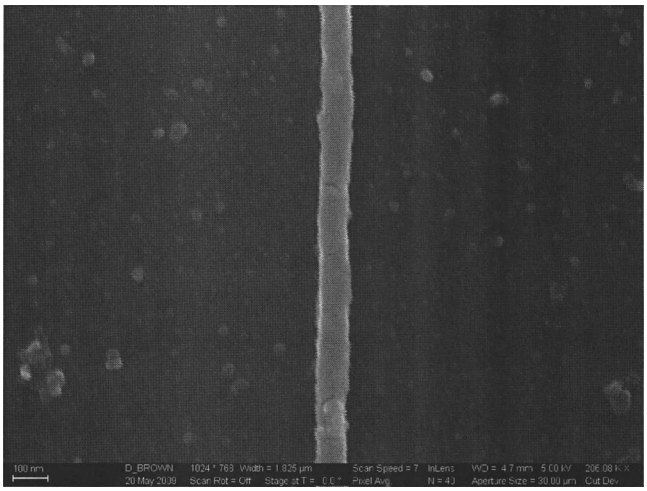

FIG. 5. PECVD oxide coating of a 500 nm line of Unity with no decomposition.

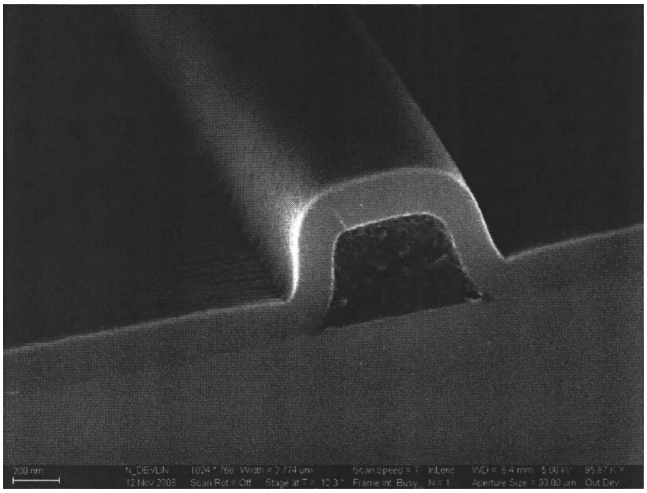

FIG. 6. PECVD oxide coating after Unity decomposed by furnace creating 500 nm channels.

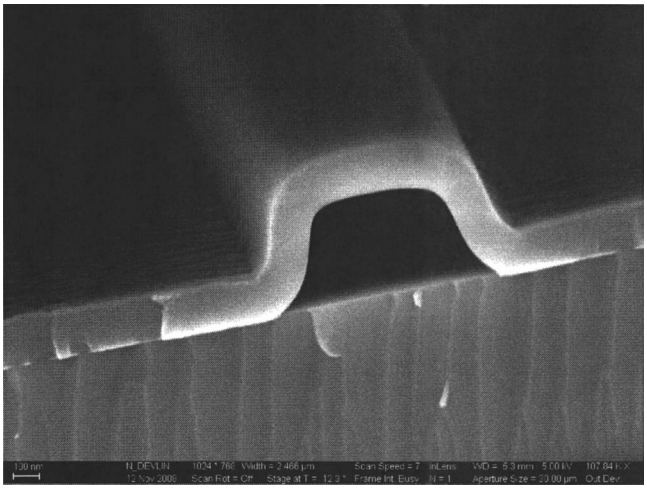

FIG. 7. Cross-linking mechanism of polynorbornene chains in Unity® 4671E.

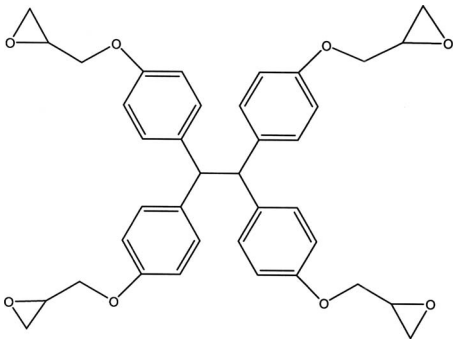

FIG. 8. 4EP molecule.

ent residue (Fig. 7). Using the same procedure, channels were successfully created using a 200 nm thick overcoat of titanium in place of the oxide layer. The titanium overcoat was deposited by dc sputtering. Thus, Unity® 4671E can thermally decompose and the products can diffuse through either a titanium or silicon dioxide overcoat.

Feature sizes smaller than 90 nm can be readily produced by EBL. To resolve smaller features, the polymer structure, including molecular weight, needs to be tailored for high resolution. The contrast can be improved through higher cross-link density which can be achieved by adding additional cross-link sites. Additional cross-linking was achieved by adding tetraphenylolethane glycidyl ether (4EP) (Fig. 8) to the Unity mixture. The resulting contrast pattern was improved, as shown in Fig. 9, on a 50 μm square pattern. 4EP has been used in other photosensitive negative tone to improve the cross-link density of the polymer.[8] With 4EP the minimum exposure dose to create the latent image increased to 7 $\mu C/cm^2$ and the developer was changed to 2-heptanone (the solvent in Unity® 4671E) to avoid potential solubility problems of 4EP in toluene. With a 3 wt % 4EP in Unity, the minimum feature size decreased to 65 nm.

To test the thermal decomposition of Unity® 4671E at the nanometer scale with 3 wt % of 4EP added, 3 mm long lines with a thickness of 130 nm and widths of 65 and 130 nm were fabricated using an electron-beam dose of 15 $\mu C/cm^2$. The substrates were postexposure baked at 90 °C for 30 s

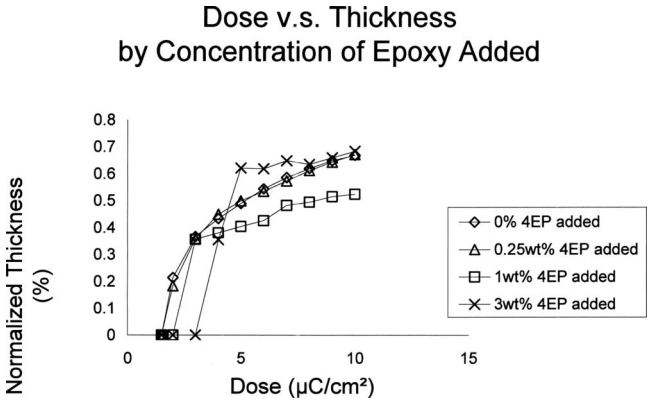

FIG. 9. Unity® 4671E thickness measured over a dose range with different concentrations of 4EP added.

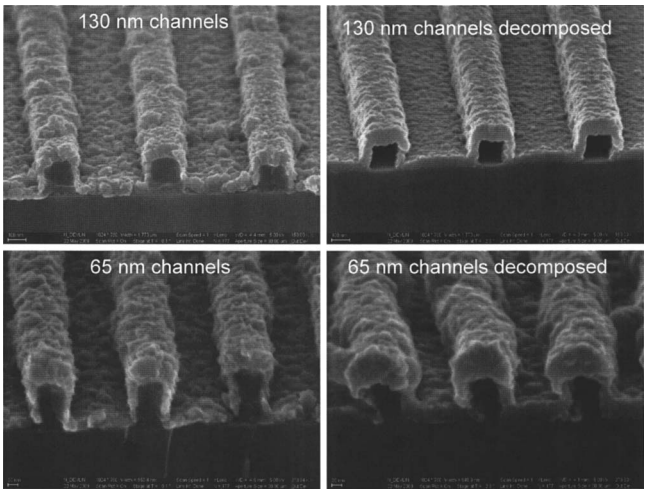

FIG. 10. 65 and 130 nm nanochannels before and after decomposition.

and were developed for 45 s in 2-heptanone with an isopropanol rinse. The lines were then sputter coated with 60 nm of titanium. The Unity was decomposed in a nitrogen purged furnace at 430 °C for 2 h. The sample and control (no thermal exposure) were cross sectioned and imaged, as shown in Fig. 10. The decomposed lines had no residue or the overcoat was intact without collapse resulting in well-shaped nanochannels.

V. DISCUSSION

The minimum spatial resolution found with 3 wt % of 4EP added to Unity® 4671E was 65 nm. In addition to improved resolution, the line edge roughness also improved by adding 4EP, as shown in Table I. The line edge roughness values are three sigma, calculated by the method given by Leunissen *et al.*[9] Additional improvements in line edge roughness and minimum feature size are likely possible through new Unity® 4671E formulations. The average molecular weight of the polynorbornene backbone in Unity® 4671E is ~65 000 g/mole yielding an average molecular size of 90 nm[3]. Reducing the molecular weight of Unity® 4671E would likely improve the spatial resolution. Additionally, there are only three molecules of 4EP for each norbornene chain. The optimum cross-linking to produce the highest resolution and contrast was not investigated and may be the subject of future reports.

TABLE I. Three sigma line edge roughness of 200 nm wide lines of Unity® 4671E with different concentrations of 4EP; magnification of images is 200 000×.

Epoxy concentration (wt %)	Line edge roughness (nm)
0	37.7
0.25	24.4
1.0	21.9
3.0	9.0

VI. SUMMARY

Unity® 4671E sacrificial polymer can be patterned by electron beam lithography and solvent developed to give high resolution freestanding patterns. In addition, the steps to create nanochannels from overcoated Unity are straightforward and include spin-coated Unity® 4671E, exposed via electron beam lithography, developed, and overcoated with silicon dioxide or metal, and thermally decomposed the Unity® 4671E at 430 °C. Nanochannels with a 65 nm width, 200 nm pitch have been achieved. This fabrication method can be used to form microfluidic devices, ring resonators, and other components.

ACKNOWLEDGMENTS

The authors would gratefully acknowledge the technical contributions of Ed Elce (Promerus LLC) and Mehrsa Raeiszadeh (Georgia Institute of Technology).

[1]Promerus LLC, 9921 Brecksville Rd., Brecksville, OH 44141-3201.
[2]Michael Zwolak and Massimiliano Di Ventra, Rev. Mod. Phys. **80**, 141 (2008).
[3]Bing Dang, Muhannad S. Bakir, Chirang S. Patel, Hiren D. Thacker, and James D. Meindl, J. Microelectromech. Syst. **15**, 523 (2006).
[4]C. K. Harnett, G. W. Goates, and H. G. Craighead, J. Vac. Sci. Technol. B **19**, 2842 (2001).
[5]Xiaoqun Wu *et al.*, J. Electrochem. Soc. **150**, H205 (2003).
[6]Paul J. Joseph, Hollie A. Kellenher, Sue Ann B. Allen, and Paul A. Kohl, J. Micromech. Microeng. **15**, 35 (2005).
[7]Long Hua Lee and Karen K. Gleason, J. Electrochem. Soc. **155**, G78 (2008).
[8]Richard A. Lawson, Cheng-Tsung Lee, Wang Yueh, Laren Tolbert, and Clifford L. Henderson, Microelectron. Eng. **85**, 959 (2008).
[9]L. H. A. Leunissen, W. G. Lawrence, and M. Ercken, Microelectron. Eng. **73–74**, 256 (2004).