Patterned polymer growth on silicon surfaces using microcontact printing and surface-initiated polymerization

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Patterned polymer films were grown on SiO_2/Si surfaces by a process starting with microcontact printing (μCP) of octadecyltrichlorosilane (OTS), formation of a monolayer derived from norbornenyl trichlorosilane (Nbn–$SiCl_3$) in areas not protected by OTS, activation of the surfaces derived from Nbn–$SiCl_3$ with a ruthenium catalyst, and surface-initiated ring-opening metathesis polymerization of derivatives of norbornene by the catalytically active ruthenium species. These patterned polymer films were successfully used as reactive ion etching resists. The combination of μCP and surface-initiated polymerization makes possible molecular-level control of polymer composition and thickness in both lateral and vertical directions: the smallest patterned lateral features were 2 μm lines; this width was determined by the features of the stamp used in μCP and is not the intrinsic limit of the method. The thickness of the polymer film was, typically, 5–100 nm and could be controlled by monomer concentration and reaction time. © *1999 American Institute of Physics.* [S0003-6951(99)01052-9]

This letter describes the combination of microcontact printing (μCP)[1,2] and surface-initiated ring-opening metathesis polymerization (ROMP)[3] to generate patterned polymers on surfaces, and the use of these patterns as reactive ion etching (RIE) resists. The objective of this work is to identify a reliable, flexible process that can be used to generate patterned polymer films on technologically important surfaces such as SiO_2/Si, and to explore the use of additively patterned polymer thin films in the fabrication of simple microelectronic and optoelectronic devices. We believe that additive deposition of thin film based on μCP has the potential to be a practical strategy for the fabrication of features for microelectronic systems having smallest lateral dimensions on the order of microns.

Microcontact printing of thiols (RSH)[1,2,4] has been explored as a lithographic technique to transfer patterns into the surface of gold and silver thin films. The patterned thiol monolayers selectively protect these metals from wet etchants, and allow reproducible generation of metallic features as small as 500 nm. The methods used for μCP of RSH on Au and Ag cannot be used directly with SiO_2/Si, and it has proved more difficult to pattern octadecyltrichlorosilane (OTS) on SiO_2/Si surfaces (by μCP) than to pattern RSH on Au.[5–8] Patterned SAMs of OTS on SiO_2/Si (Ref. 9) do not protect the surface against etching in aqueous $HF/NH_4^+F^-$ or KOH solutions.[10] SAMs (on both SiO_2/Si and Au) perform poorly as RIE resists because they are too thin to provide useful protection.[5–8]

The patterned polymer films described here have two attractive features not offered by SAMs for lithographic applications: (i) They are thicker and more robust (chemically, thermally, and mechanically) than these SAMs, and thus can be used as RIE resists. (ii) Substantial control of the chemical composition of the film perpendicular to the surface is possible: for example, the composition of polymers and block copolymers can be formed.[11]

We have formed a variety of patterned polymer films using the ROMP catalyst developed by Schwab *et al.*[12] [$(Cy_3P)_2Cl_2Ru$=CHPh, Cy=cyclohexyl] with appropriate monomers [norbornene or 5-bicycloheptene (Nbn), 5-(bicycloheptenyl) trichlorosilane (Nbn–$SiCl_3$), and 5-(bicycloheptenyl) triethoxysilane (Nbn–$Si(OEt)_3$). We have used Nbn–$SiCl_3$ to form the initial SAMs to which the catalyst attaches: it has the requisite norbornene (Nbn) terminal group.[3,13] The use of Nbn–$SiCl_3$ and ROMP thus make it possible to apply μCP to SiO_2/Si and other metal oxide surfaces.

First, the surface of the substrate was patterned with OTS (2–3 nm) by μCP following published procedures [Fig. 1(a)].[9,10,14] Second, the OTS-patterned sample was placed in a solution of Nbn–$SiCl_3$ (60 mM in toluene) for 6–12 h. This step formed a Nbn-terminated SAM in areas not patterned with OTS [Fig. 1(b)]. The attachment of the ruthenium catalyst to the surface was carried out by immersing the substrate in a CH_2Cl_2 solution (17 mM) of the ruthenium catalyst for 30 min [Fig. 1(c)].[15] Third, the polymer films were formed by placing the substrates in a solution of monomer (0.01–0.4 M in CH_2Cl_2) for 5–30 min [Fig. 1(d)]. The

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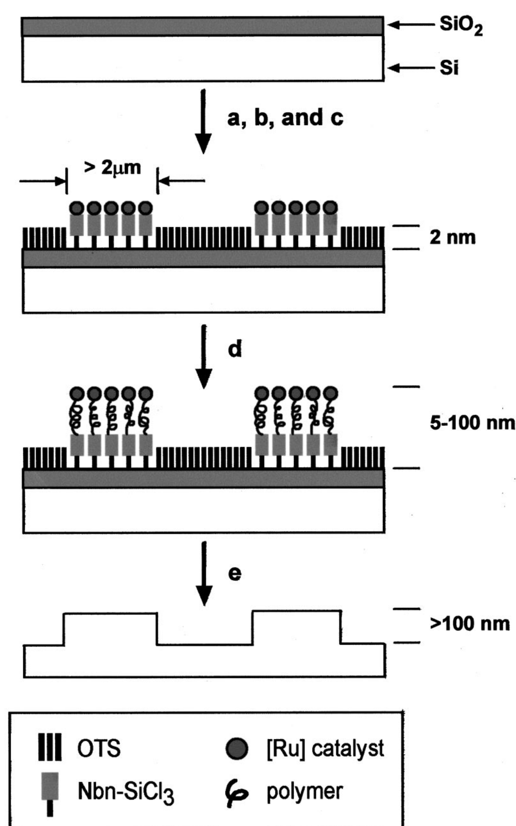
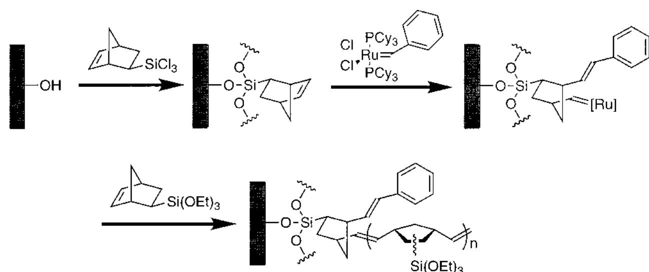


FIG. 1. Schematic representation of patterned polymer formation by μCP, activation, and ring-opening metathesis polymerization on the surface of SiO_2/Si. No order or structure is implied by the representation of the OTS (octadecyltrichlorosilane), norbornene-terminated SAM, [Ru] catalyst $[(Cy_3P)_2Cl_2Ru{=}CHPh$, Cy=cyclohexyl], and polymer.

sample was placed in a RIE chamber and the polymer pattern was transferred into the substrate [Fig. 1(e)].

Figure 2(a) shows an optical micrograph of a patterned, 50-nm-thick poly[Nbn–$Si(OEt)_3$] film. In this sample, the polymer film (light) formed outside the $10\times 10\ \mu$m square (dark) that had been printed with OTS. Scheme 1 shows the reaction steps, including detailed chemical structures of the



Scheme 1.

monomer, catalyst, and the resulting polymer. Profilometry, ellipsometry, and AFM showed uniform polymer film thickness across the sample. Polymer films with thicknesses from 5 to 100 nm were grown reproducibly. The thickness of the polymer films varied with polymerization time and monomer concentration.[11]

Higher-magnification SEM [Fig. 2(b)] showed that the polymer film has a well-defined pattern with distinct boundaries between the polymer (dark) and OTS (light). The edge resolution of the polymer thin-film pattern (~300 nm) is

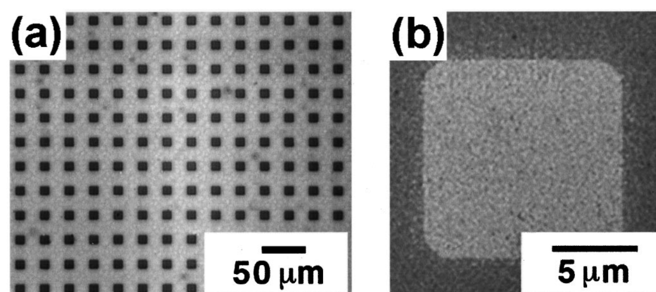


FIG. 2. (a) Optical micrograph of the patterned poly[Nbn–$(OEt)_3$] film (50 nm) on the surface of SiO_2/Si. A uniform polymer film covers the surface except inside the $10\ \mu m\times 10\ \mu$m squares, where OTS had been printed by μCP. (b) Scanning electron microscopy shows well-defined boundary (with edge roughness <300 nm) between the polymer (dark region) and the area modified with OTS (the lighter square).

lower (that is, the roughness of the edge is greater) than that observed for RSH on gold[16] (~50 nm) and OTS on SiO_2/Si (~200 nm).[10] This increase in the value of edge roughness is expected, considering that the thickness of the polymer film (50–100 nm) is greater than that of the typical SAM (2–3 nm). At present, the smallest feature that can be generated using this procedure is ~2 μm, a size that is limited by the resolution of the μCP step used to pattern OTS.

These patterned polymers act as RIE resists in etching Si substrates. Figure 3 shows optical (a) and SEM (c) micrographs of a patterned poly[Nbn–$Si(OEt)_3$] on SiO_2/Si surface before RIE. The dark lines in Figs. 3(a) and 3(c) correspond to the 2-μm-wide polymer film (10 nm thick). Figures 3(b) and 3(d) show corresponding optical and SEM micrographs, respectively, after the sample had been etched for 3 min in a parallel-plate RIE reactor (30 W, 25 mTorr) using SF_6.

Figure 4(a) shows a contact-mode AFM image of a patterned poly(Nbn–$SiCl_3$) on SiO_2/Si surface.[17] Line analysis indicated that the thickness of the polymer was ~15 nm. Figure 4(b) shows a corresponding AFM image after the sample had been etched for 2 min. The unprotected areas

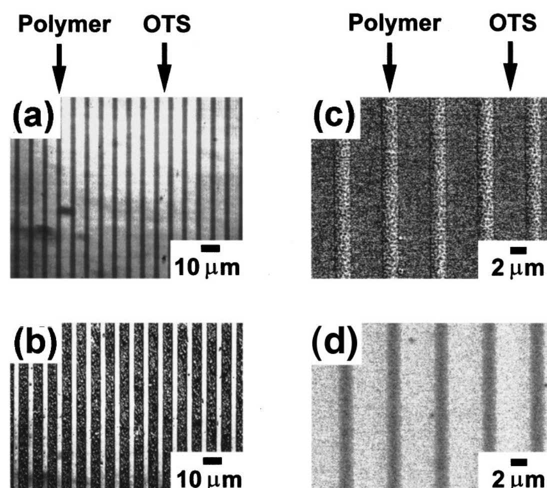


FIG. 3. (a) Optical micrograph of 2-μm-wide lines of patterned poly [Nbn–$Si(OEt)_3$] film generated by polymerization from surface before RIE (thickness ~10 nm). (c) Optical micrograph of the sample after RIE with SF_6 for 3 min at 30 W in a parallel-plate etcher. (b) SEM micrograph of the sample before RIE [same sample as shown in (a)]. (d) SEM micrograph of the sample after RIE.

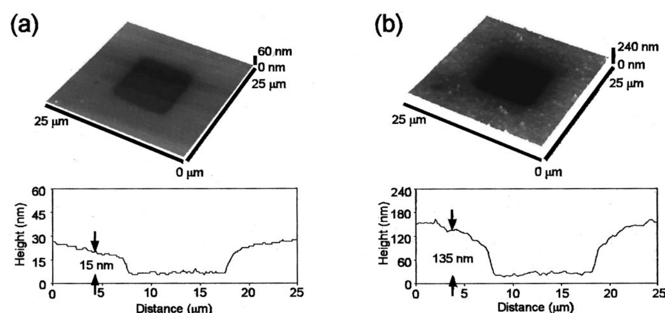


FIG. 4. (a) Contact-mode AFM of patterned poly(Nbn–$SiCl_3$) film generated by polymerization from surface before RIE (thickness ~15 nm). (b) The surface after RIE with SF_6 for 2 min at 30 W in a parallel-plate etcher. The polymer films were completely removed after RIE and before measuring surface profiles. The dark square in the image is the area on which no polymer was present. The height difference between the square and the area around it was ~135 nm after RIE.

without poly(Nbn–$SiCl_3$) were etched more rapidly in RIE (~135 nm height difference) than areas with poly(Nbn–$SiCl_3$). Under the same RIE conditions (SF_6, 30 W), the etch rate for the SiO_2/Si substrate was ~100 nm/min, compared to ~20 nm/min for the poly(Nbn–$SiCl_3$) film. The etched surface is quite rough, as is commonly observed in RIE.[18]

This letter demonstrates a strategy for forming patterned polymer films, and using them as RIE resists in etching SiO_2/Si. A possible advantage of this approach is its ability to control the composition (by sequencial addition of monomers) and dimension of polymer thin films both laterally (by μCP) and vertically (by the time of polymerization in ROMP and monomer concentration)[11] on surfaces. In addition with appropriate monomers, the approach described in this letter can be used to grow active polymer films (i.e., films that are electrically conductive or light emitting).[19–22] Although the procedure involves several steps that occur in solution and an indirect method for attaching the ruthenium catalyst, it is operationally straightforward. Methods for generating thick (~100 nm) films that combine μCP with either polymerization[11,23] (and extendable, in principle, to other polymerization systems[24]) or polymer adsorption[25,26] will make it possible to use μCP and other soft lithographic techniques in conjunction with rigorous processes useful in microfabrication, and to reduce the level of pinhole defects produced in these techniques.

The additive growth of patterned polymer films by surface-initiated ROMP is complementary to the additive deposition of metal and ceramic thin films. We believe that the additive formation of patterned thin films based on μCP has the simplicity and performance required for applications in relatively low-resolution (feature sizes of several microns) microfabrication.

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[1] A. Kumar and G. M. Whitesides, Appl. Phys. Lett. **63**, 2002 (1993).
[2] Y. Xia and G. M. Whitesides, Angew. Chem. Int. Ed. Engl. **37**, 550 (1998).
[3] W. A. Hermann, A. W. Stumpf, S. Bogdanovic, V. Dufaud, and J.-M. Basset, Angew. Chem. Int. Ed. Engl. **35**, 2803 (1996).
[4] L. Libioulle, A. Bietsch, H. Schmid, B. Michel, and E. Delamarche, Langmuir **15**, 300 (1999).
[5] P. M. St. John and H. G. Craighead, Appl. Phys. Lett. **68**, 1022 (1996).
[6] M. J. Lercel, H. G. Craighead, A. N. Parikh, K. Sechadri, and D. L. Allara, Appl. Phys. Lett. **68**, 1504 (1996).
[7] T. K. Whidden, D. K. Ferry, M. N. Kozicki, E. Kim, A. Kumar, J. Wilbur, and G. M. Whitesides, Nanotechnology **7**, 447 (1996).
[8] E. Delamarche, H. Schmid, A. Bietsch, N. B. Larsen, H. Rothuizen, B. Michel, and H. A. Biebuyck, J. Phys. Chem. B **102**, 3324 (1998).
[9] N. L. Jeon, K. Finnie, K. Branshaw, and R. G. Nuzzo, Langmuir **13**, 3382 (1997).
[10] Y. Xia, M. Mrksich, E. Kim, and G. M. Whitesides, J. Am. Chem. Soc. **117**, 7576 (1995).
[11] N. Y. Kim, N. L. Jeon, I. S. Choi, S. Takami, Y. Harada, K. R. Finnie, G. S. Girolami, R. G. Nuzzo, G. M. Whitesides, and P. E. Laibinis (unpublished).
[12] P. Schwab, R. H. Grubbs, and J. W. Ziller, J. Am. Chem. Soc. **118**, 100 (1996).
[13] E. L. Dias, S. T. Nguyen, and R. H. Grubbs, J. Am. Chem. Soc. **119**, 3887 (1997).
[14] N. L. Jeon, R. G. Nuzzo, Y. Xia, M. Mrksich, and G. M. Whitesides, Langmuir **11**, 2024 (1995).
[15] Initial attempts to use μCP to pattern Nbn–$SiCl_3$ directly on SiO_2/Si, or to pattern the ruthenium catalyst on Nbn-terminated SAM, both led to unsatisfactory results.
[16] H. Biebuyck and G. M. Whitesides, Langmuir **10**, 4581 (1994).
[17] Polymerization of Nbn was too fast to control; we were not able to control the thickness of this polymer film. We used Nbn–$SiCl_3$ both for the formation of SAM and as the polymerized monomer.
[18] J. L. Vossen and W. Kern, *Thin Film Processes* (Academic, New York, 1978).
[19] S. Tasch, W. Grapner, G. Leising, L. Pu, P. Wagaman, and R. H. Grubbs, Adv. Mater. **8**, 125 (1996).
[20] L. Pu, M. P. Wagaman, and R. H. Grubbs, Macromolecules **29**, 1138 (1996).
[21] V. P. Conticello, D. L. Gin, and R. H. Grubbs, J. Am. Chem. Soc. **114**, 9708 (1992).
[22] U. H. F. Bunz, D. Song, and L. Kloppenburg, J. Am. Chem. Soc. **120**, 7973 (1998).
[23] M. Husemann, D. Mecerreyes, C. J. Hawker, J. L. Hedrick, R. Shah, and N. L. Abbott, Angew. Chem. Int. Ed. Engl. **38**, 647 (1999).
[24] M. Weck, J. J. Jackiw, R. R. Rossi, P. S. Weiss, and R. H. Grubbs, J. Am. Chem. Soc. **121**, 4088 (1999).
[25] W. T. S. Huck, L. Yan, A. Stroock, R. Haag, and G. M. Whitesides, Langmuir **15**, 6862 (1999).
[26] M. L. Bruening, Y. Zhou, G. Aguilar, R. Agee, D. E. Bergbreiter, and R. M. Crooks, Langmuir **13**, 770 (1997).