ChemComm
www.rsc.org/chemcomm

UV photopatterning of a highly metallized, cluster-containing poly(ferrocenylsilane)

Alison Y. Cheng,[a] Scott B. Clendenning,[a] Guocheng Yang,[b] Zheng-Hong Lu,[c] Christopher M. Yip[b] and Ian Manners*[a]

[a] *Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada M5S 3H6. E-mail: imanners@alchemy.chem.utoronto.ca*

[b] *Department of Chemical Engineering and Applied Chemistry, Institute of Biomaterials and Biomedical Engineering, University of Toronto, Toronto, Ontario, Canada M5S 3G9*

[c] *Department of Materials Science and Applied Chemistry, University of Toronto, Ontario, Canada M5S 3E4*

Received (in Cambridge, UK) 23rd December 2003, Accepted 6th February 2004
First published as an Advance Article on the web 3rd March 2004

Thin films of a cobalt-clusterized poly(ferrocenylsilane) have been shown to behave as a negative-tone resist for UV photolithography, allowing access to feature sizes between 20 and 300 μm. Pyrolysis of the patterned polymer at 900 °C under a N_2 atmosphere afforded patterned ferromagnetic ceramics with excellent shape retention.

Photolithography is the most important manufacturing process in the microelectronics industry. The ever-growing demands for smaller feature size and higher precision have led to the development of sophisticated exposure techniques and resist technologies.[1] The evolution of lithographic techniques has occurred on several fronts. Firstly, a reduction in the exposure wavelength from the near-UV (365–436 nm) to the deep-UV (248 or 193 nm), and then to X-rays and electron beams, was essential for the fabrication of features in the sub-100 nm regime. Secondly, the transition from 1 : 1 contact printing and serial direct writing to projection exposure techniques has allowed for parallel mass production of microelectronics. The development of innovative resist materials which are compatible with these technologies is of considerable interest.[2]

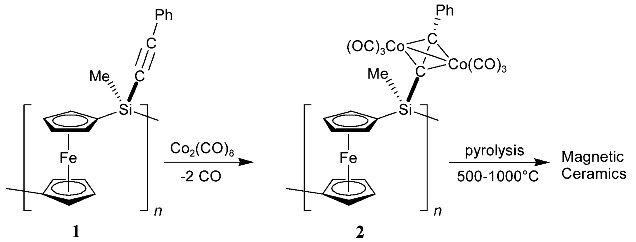
The patterning of surfaces with metal-rich structures is of special interest as it offers the possibility of fabricating functional materials with useful catalytic, optical, sensing, electrical and magnetic properties. For example, a recent report describes the use of an organometallic polymer thin film as a resist for electron beam lithography (EBL). Thin films of $[Ru_6C(CO)_{15}Ph_2PC_2PPh_2]_n$, an organometallic cluster polymer, have been used as a negative-tone EBL resist, allowing the direct writing of conducting wires (*ca.* 100 nm wide) composed of metal clusters.[3] This example illustrates the convenience and utility of combining conventional lithographic techniques with easily processible organometallic polymer resists.

Poly(ferrocenylsilanes) (PFS) are a class of high molecular weight organometallic polymers with interesting properties.[4] These materials are conveniently accessible *via* the thermal, anionic or transition metal-catalyzed ring-opening polymerization of [1]silaferrocenophanes.[5] Furthermore, PFS derivatives that possess acetylenic substituents on Si (**1**; Scheme 1) can be clusterized by treatment with dicobalt octacarbonyl to afford cobalt-clusterized poly(ferrocenylsilane) (Co-PFS, **2**).[6,7] This highly metallized polymer is a precursor to ferromagnetic ceramics containing Co/Fe alloy nanoparticles upon pyrolysis.[7] In this Communication, we report the use of a Co-PFS as a lithographic photoresist and describe the creation of micron size magnetic patterns.

Organic polymers incorporating acetylenic moieties have been shown to be thermally cross-linkable.[8] Upon heating, the acetylene groups from adjacent chains undergo cyclotrimerization and coupling reactions, creating cross-links in the polymer. In addition, photoinduced polymerization of alkyl- and aryl-substituted acetylenes are known to be catalyzed by metal carbonyls such as $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$.[9–11] Recently, Badarau and Wang demonstrated that polyacrylates with pendent acetylenic side groups could be photocross-linked in the presence of $W(CO)_6$ as catalyst.[12] In addition, since **2** inherently contains both acetylenic units and a potential metal carbonyl catalyst, this material is a promising candidate as a resist material for UV photolithography.

Air- and moisture-stable, film-forming Co-PFS **2** was prepared from the acetylenic PFS precursor **1** (M_n = 65 000, PDI = 2.08, GPC in THF, triple detection) and a percentage clusterization of 80–85% was elucidated by ^{1}H NMR spectroscopy. PFS **1** was prepared by transition metal-catalyzed ring-opening polymerization of a [1]silaferrocenophane precursor.[6] Patterning of Co-PFS films was accomplished using a micromachined metal foil shadow mask with features in the size range *ca.* 50–500 μm. A thin film of Co-PFS **2** (*ca.* 200 nm thick, as determined by ellipsometry) on a Si substrate was exposed to UV radiation (λ = 350–400 nm, 450 W) through the mask, which was in direct contact with the polymer film. Fig. 1(a) shows an optical micrograph of a straight line of Co-PFS patterned with the shadow mask. Smaller features (*ca.* 10–20 μm) were obtained using a chrome contact mask [Fig. 1(b)]. In both cases, the unexposed polymer was completely removed during development with THF, leaving behind patterns with well-defined edges.

The negative-tone behavior of Co-PFS resists appears to be consistent with the photoinitiated cross-linking mechanism of acetylenes in the presence of a metal carbonyl catalyst. In addition, thin films of unclusterized PFS **1** remained completely soluble in THF after UV exposure, suggesting that the metal carbonyl is an essential component in the cross-linking mechanism. However, the



Scheme 1 Cobalt clusterization of the acetylenic moieties of poly(ferrocenylsilane) **1** to yield the highly metallized Co-PFS **2**, a precursor to magnetic ceramics.

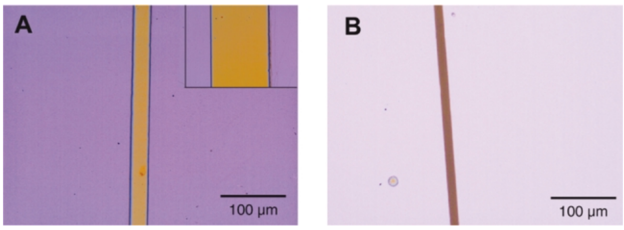


Fig. 1 Optical micrographs of lines of **2** fabricated by UV photolithography using a shadow mask (a) and a chrome contact mask (b). The inset shows the surface morphology of the patterned polymer under higher magnification.

DOI: 10.1039/b316656b

role of the Co clusters as a catalyst in the cross-linking of the polymer is still unclear, as it is also possible for cross-linking to occur as a result of decarbonylation of the Co clusters.

Patterned Co-PFS **2** was pyrolyzed at 900 °C under a N_2 atmosphere for 5 h in order to fabricate magnetic ceramic lines. The resulting ceramic lines show excellent shape retention in the lateral direction with respect to their polymer precursors [Fig. 2(a)]. Inspection of the ceramic lines at higher magnifications revealed a transformation of the surface topologies of the patterned area from a uniform thin film to a collection of small ceramic islands [Fig. 2(b)]. The composition of these ceramic islands is probably comparable with that of the pyrolysis product of Co-PFS **2** in the bulk, which consists of Co/Fe alloy nanoparticles embedded in an amorphous SiC/C matrix.[7] The composition of the patterned ceramic lines was studied by energy dispersive X-ray (EDX) spectroscopy and was found to be consistent with that of the bulk pyrolyzed polymer.[7]

The magnetic behavior of the pyrolyzed lines was studied by magnetic force microscopy (MFM). The surface topology of a 10 μm × 10 μm region of interest was examined by tapping mode atomic force microscopy (AFM), revealing an island morphology similar to that observed by optical microscopy [Fig. 3(a)]. Subsequent section analysis revealed that the islands ranged in height from 5 to 87 nm, with an average value of 30 nm, relative to the supporting silicon substrate. The corresponding MFM image was then acquired by retracing the region of interest using an interleave lift height of 50 nm. This ensures that the MFM image was a result of magnetic forces and not physical tip–sample contact [Fig. 3(b)]. Taking the color of the Si substrate as a non-magnetic internal standard in the MFM image, darker and lighter colors on the image indicate magnetic interactions (either attraction or repulsion) between the probe and the sample. It can be seen in the MFM image that the magnetic dipoles, presumably originating from the Co/Fe alloy nanoparticles, were concentrated in the ceramic islands and nowhere else.

In summary, UV photolithography using Co-PFS as a resist provides a convenient route for the deposition of patterned polymer and magnetic ceramic onto flat substrates. Due to the excellent reqactive ion etching (RIE) resistance of the polymer,[13] Co-PFS patterned by UV photolithography can also potentially be utilized for pattern transfer onto the underlying substrate using conventional plasma etching techniques. Investigations in these areas are under way.

This work is supported by an Accelerator Grant for Exceptional New Opportunities (AGENO) from the National Sciences and Engineering Research Council of Canada (NSERC). I. M. and C. M. Y. thank the Canadian Government for Canada Research Chairs. C. M. Y. acknowledges support from a PREA Award and also funding from NSERC, ORDCF, CFI and OIT. Z. H. L. thanks CFI and OIT for equipment grants. S. B. C. thanks NSERC for a Post-doctoral Fellowship. G. Y. is grateful for support *via* a University of Toronto Open Fellowship. We thank Prof. Eugenia Kumacheva for the use of the ellipsometer, Dr Sijin Han for assistance with UV apparatus and Dr Neil Coombs for useful discussions.

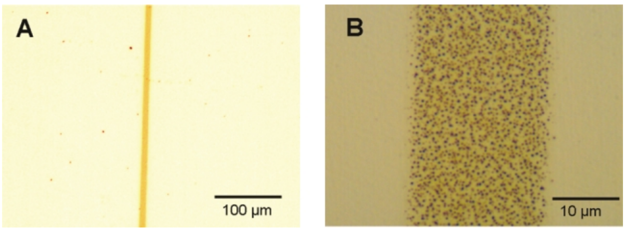


Fig. 2 (a) Optical micrograph of patterns of **2** after pyrolysis (900 °C, 5 h) under N_2. (b) Under higher magnification, the ceramic islands formed after pyrolysis can be clearly observed.

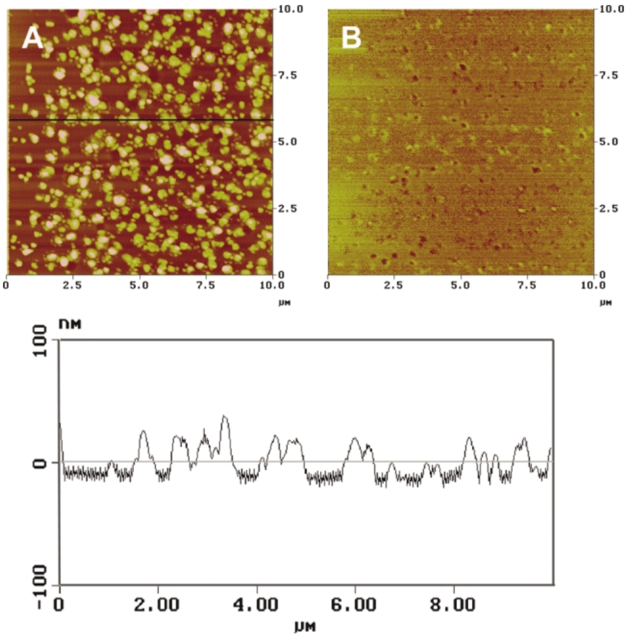


Fig. 3 (a) Tapping mode AFM image of a region on a pyrolyzed pattern of **2** (height scale: 200 nm). A sample cross-section profile showing the height of the ceramic islands is shown below. (b) The corresponding MFM image of the same region. The orientation of the magnetic dipoles appears to be random.

Notes and references

1 G. M. Wallraff and W. D. Hinsberg, *Chem. Rev.*, 1999, **99**, 1801.
2 K. E. Gonsalves, L. Merhari, H. P. Wu and Y. Q. Hu, *Adv. Mater.*, 2001, **13**, 703.
3 B. F. G. Johnson, K. M. Sanderson, D. S. Shephard, D. Ozkaya, W. Z. Zhou, H. Ahmed, M. D. R. Thomas, L. Gladden and M. Mantle, *Chem. Commun.*, 2000, 1317.
4 I. Manners, *Chem. Commun.*, 1999, 857.
5 K. Kulbaba and I. Manners, *Macromol. Rapid Commun.*, 2001, **22**, 711.
6 A. Berenbaum, A. J. Lough and I. Manners, *Organometallics*, 2002, **21**, 4415.
7 A. Berenbaum, M. Ginzburg-Margau, N. Coombs, A. J. Lough, A. Safa-Sefat, J. E. Greedan, G. A. Ozin and I. Manners, *Adv. Mater.*, 2003, **15**, 51.
8 S. A. Swanson, W. W. Fleming and D. C. Hofer, *Macromolecules*, 1992, **25**, 582.
9 T. Masuda, Y. Kuwane, K. Yamamoto and T. Higashimura, *Polym. Bull.*, 1980, **2**, 823.
10 T. Masuda, K. Yamamoto and T. Higashimura, *Polymer*, 1982, **23**, 1663.
11 S. J. Landon, P. M. Shulman and G. L. Geoffroy, *J. Am. Chem. Soc.*, 1985, **107**, 6739.
12 C. Badarau and Z. Y. Wang, *Macromolecules*, 2003, **36**, 6959.
13 S. B. Clendenning, S. Han, N. Coombs, C. Paquet, M. S. Rayat, D. Grozea, P. M. Broderson, R. N. S. Sodhi, C. M. Yip, Z.-H. Lu and I. Manners, *Adv. Mater.*, 2004, **16**, 291.