# Synthesis and Lithographic Applications of Highly Metallized Cluster-Based Polyferrocenylsilanes

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**Summary:** We report the use of a cobalt-clusterized polyferrocenylsilane (Co-PFS) as a precursor to patterned ferromagnetic ceramics. Co-PFS was synthesized. Functioning as a negative resist, Co-PFS lines with widths of 10–300 μm were patterned using UV-photolithography, while features as small as 500 nm were afforded by electron-beam lithography. Subsequent pyrolytic treatment of the lithographically patterned Co-PFS yielded ferromagnetic ceramics containing Fe/Co nanoparticles. Due to its high metal-loading, Co-PFS is a good etch resist for oxygen and hydrogen plasma reactive ion etching. Reactive ion etching of a thin film of Co-PFS in a secondary magnetic field allowed direct access to ferromagnetic ceramic films, providing a viable alternative to pyrolysis.

**Keywords:** ferromagnetic nanoparticles; lithography; metal clusters; polyferrocenylsilanes; ring-opening polymerization

## Introduction

Patterning of surfaces on the nanometer scale with metals offers the possibility of fabricating materials with useful catalytic, optical, sensing, electrical and magnetic properties. Available patterning methods range from soft lithography, scanning probe lithography, electron-beam (e-beam) lithography (EBL) and photolithography. Recent reports include the use of microcontact printing to order monodisperse nanoparticles of iron oxide,[1] and nanotransfer printing to transfer a gold pattern with 75 nm feature sizes from a gold-coated GaAs stamp to an appropriately primed polydimethylsiloxane substrate.[2] Alternatively, scanning probe techniques also offer precise control of patterning. An atomic force microscope (AFM) tip has been used to pen 35 nm-wide lines of $MoO_3$ through local oxidation of a Mo film,[3] while 30 nm-wide Pt lines have been drawn via the reduction of $H_2PtCl_6$ at an AFM tip using electrochemical AFM dip-pen

DOI: 10.1002/masy.200450511

lithography.[4] In EBL, a film of an organometallic polymer can be used as a resist. Johnson and co-workers have used thin films of the organometallic cluster polymer $[Ru_6C(CO)_{15}Ph_2PC_2PPh_2]_n$ as a negative resist in EBL to direct write conducting wires (*ca.* 100 nm wide) composed of metal nanoparticles.[5] This example illustrates the convenience and utility of combining conventional lithographic techniques with easily processible organometallic polymer resists. Moreover, post-development treatments of the patterned organometallic resist such as pyrolysis or reactive ion etching (RIE) offer additional control over the chemical and physical properties of the surface.

While polymers containing metal clusters are attractive as lithographic resists, their synthesis remains a poorly developed area. Nevertheless, three examples are worth mentioning. The previously mentioned organometallic polymer with ruthenium carbonyl clusters in the backbone $[Ru_6C(CO)_{15}Ph_2PC_2PPh_2]_n$,[5] was prepared by reacting $[Ru_6(CO)_{17}]$ with $[Ph_2PC_2PPh_2]$ in tetrahydrofuran under reflux to give the dark brown polymer. Its degree of polymerization was estimated to be 1 000–1 020 by electron microscopy. In the second example, Humphrey *et al.* used a step-growth polycondensation approach to synthesize oligourethanes containing bimetallic $Mo_2Ir_2$ clusters in the backbone (Figure 1).[6] In the presence of catalytic amounts of dibutyltin diacetate (DBTA), the bimetallic cluster diol $[Mo_2Ir_2(CO)_{10}\{\eta\text{-}C_5H_4(CH_2)_2OH\}_2]$ was reacted with 1,ω-alkyl- or aryldiisocyanates to give red powders or waxy solids. The degree of polymerization was estimated using gel permeation chromatography and $^1H$ NMR spectroscopy; this ranged from 5–30, depending on the length of the spacer. While the diisocyanate alkyl group chain length had little effect on the extent of polymerization, increasing the spacer length between the cyclopentadienyl and hydroxyl groups led to a significant increase in $M_n$.

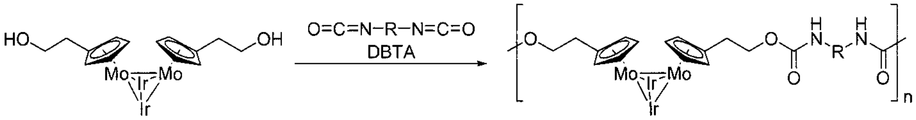


Figure 1. Synthesis of bimetallic cluster polymers ($Mo_2Ir_2$ = $Mo_2Ir_2(CO)_{10}$, R = alkyl or aryl spacer). (Adapted from [6])

In the third approach, Brook *et al.* synthesized oligomers and polymers containing alkynylsilane and arylsilane groups; they were complexed with either dicobalt octacarbonyl at the alkyne, or chromium hexacarbonyl at the aryl group to give metallized oligomers or polymers.[7] Using the same routes, a highly metallized oligomer containing both chromium and cobalt was prepared via sequential clusterization of both aryl- and alkynylsilane groups (Figure 2).

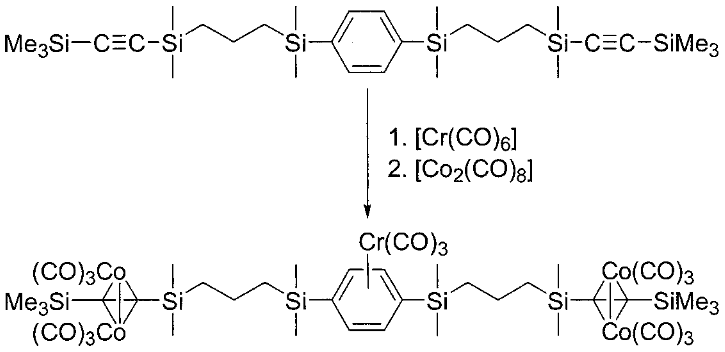
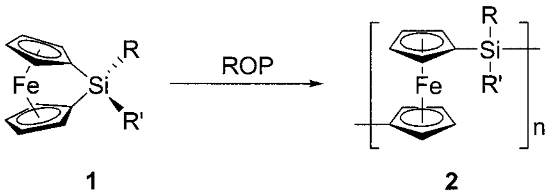


Figure 2. Structure of an oligosilane containing chromium and cobalt carbonyl clusters. (Adapted from [7])

One focus of our current research is the incorporation of metal clusters into a well-defined organometallic polymer that can be lithographically patterned. Thermal,[8] anionic[9] and transition metal-catalyzed[10] ring-opening polymerization (ROP) of sila[1]ferrocenophanes (**1**) are well-established routes to high molecular weight, soluble polyferrocenylsilanes (**2**, PFS) that contain covalently bonded iron atoms in the main chain (Scheme 1). The incorporation of PFS into patterned surfaces has already yielded materials with tunable magnetic properties that may find applications as protective coatings, magnetic recording media and anti-static shields.[11] Furthermore, polymers containing organometallic moieties exhibit low plasma etch rates compared to their purely organic counterparts,[12] suggesting they can be used as etch masks to deposit interesting materials.

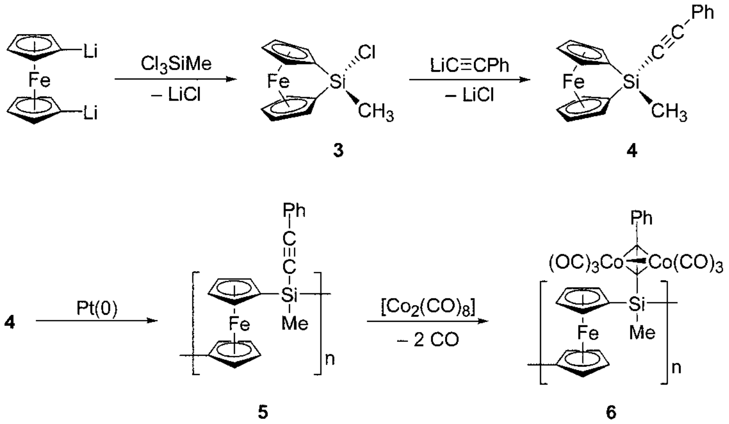


Scheme 1. ROP of a sila[1]ferrocenophane (**1**) to afford a polyferrocenylsilane (**2**).

## Results and Discussion

### *Synthesis of Highly Metallized PFS and Precursors to Metal-Containing Ceramics*

The introduction of additional metals into the PFS chain can increase metal loadings and allow access to binary or higher metallic alloy species. This can be accomplished by adding an acetylenic substituent at silicon that can be further transformed via reaction with an appropriate metal carbonyl. The synthesis of an acetylide-substituted sila[1]ferrocenophane and the corresponding highly metallized PFS is shown in Scheme 2. 1,1'-Dilithioferrocene was reacted with trichloromethylsilane to form the chloro-substituted sila[1]ferrocenophane **3**. Lithium phenylacetylide was then used to substitute the chloride group of **3** to yield **4**. Monomer **4** was ring-opened with a platinum(0) catalyst to give high molecular weight polymer **5**.[13] The acetylenic substituent in **5** was clusterized with dicobalt octacarbonyl to yield the highly metallized PFS (Co-PFS) (**6**) with three metal atoms per repeat unit.[14]



Scheme 2. Synthesis of highly metallized Co-PFS (**6**).

We tested the utility of Co-PFS as a magnetic ceramic precursor.[14] Pyrolysis of **6** under a nitrogen atmosphere at either 600 °C or 900 °C afforded black magnetic ceramics in relatively high yields (72% and 59%, respectively). Powder X-ray diffraction studies revealed that the ceramic residue contained Fe/Co alloy particles embedded in an amorphous C/SiC matrix. Figure 3 shows the cross-sectional transmission electron microscopy (TEM) images of the ceramics prepared at 600 °C and 900 °C. Electron-rich metal nanoparticles can clearly be seen, and their chemical compositions were determined by electron energy-loss spectroscopic (EELS) elemental mapping experiments. The results indicated that both iron and cobalt were localized in the same nanoparticles, thereby suggesting a homogeneous alloy. Superconducting quantum interference device (SQUID) magnetometry showed that ceramics formed at 900 °C were ferromagnetic with no blocking temperature up to 355 K.

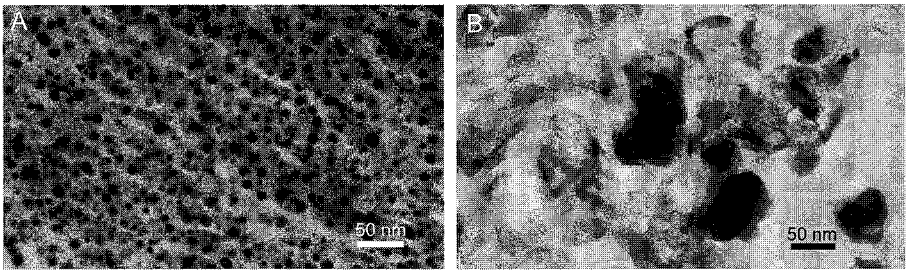
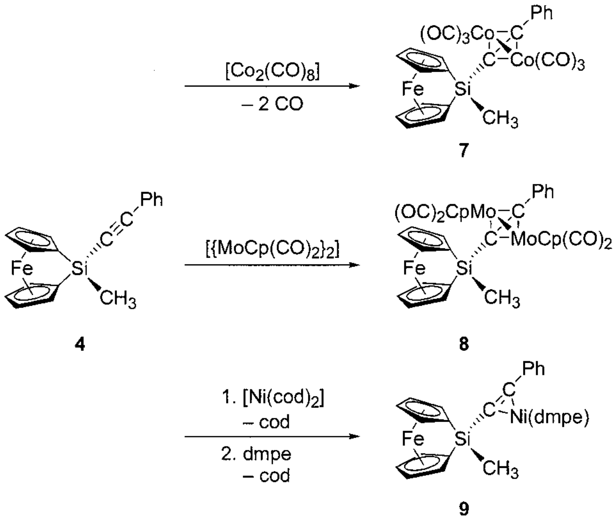


Figure 3. Cross-sectional TEM images of ceramics resulting from pyrolysis of Co-PFS **6** at (a) 600 °C and (b) 900 °C

*Highly Metallized Sila[1]ferrocenophanes as Polymer Precursors*

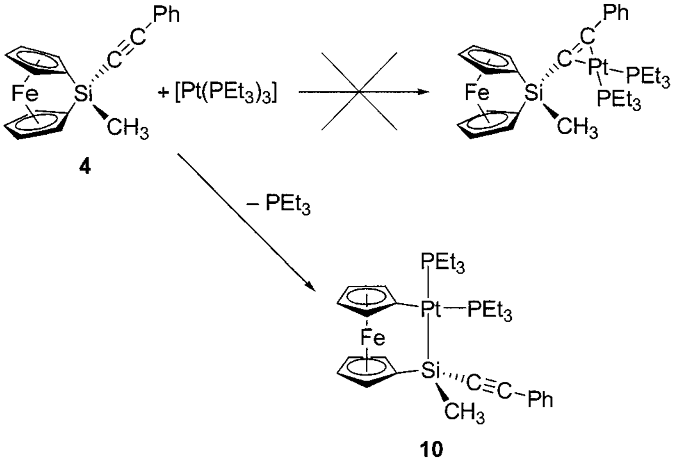
Although highly metallized PFS can be obtained via functionalization of the polymer, this reaction is often incomplete as the core of the polymer may be well shielded from reagents. To circumvent this problem, the monomer could be functionalized and then ring-opened to give a fully functionalized polymer. We have investigated the reactions between acetylide-substituted monomer **4** and metal complexes containing cobalt, molybdenum and nickel (Scheme 3).[15]



Scheme 3. Synthesis of sila[1]ferrocenophanes containing pendent cobalt, molybdenum, or nickel units.

As in the synthesis of Co-PFS **6**, the triple bond in monomer **4** reacted smoothly with dicobalt octacarbonyl to give the cobalt-clusterized product **7**. Molybdenum clusters were introduced via molybdenum cyclopentadienyl dicarbonyl dimer; this reaction was sluggish at room temperature and required heating to 75 °C to form **8**. Bis(1,5-cyclooctadiene)nickel(0) also reacted with the triple bond in **4** to add a nickel unit; however, all attempts to separate the desired product from unidentified side-products were unsuccessful, possibly due to subsequent dissociation of the labile cod ligand. When 1,2-bis(dimethylphosphino)ethane (dmpe) was added to the above product, substitution of the cod ligand occurred to give nickel-containing sila[1]ferrocenophane **9**. Investigations into the ROP behaviour of these highly-metallized sila[1]ferrocenophanes are underway.

Having demonstrated that different metal complexes could be incorporated into the acetylenic substituent of **4**, we turned our attention to the synthesis of a platinum-containing sila[1]ferrocenophane. After ring-opening polymerization, the Pt-PFS formed may be used as a magnetic ceramic precursor to FePt nanocrystals. FePt nanoparticles are currently under investigation for ultrahigh-density magnetic recording media applications due to their large uniaxial magnetocrystalline anisotropy.[16] We attempted the reaction of acetylide-substituted monomer **4** with tris(triethylphosphine)platinum(0).[15] Instead of reacting with the triple bond, [Pt($PEt_3$)$_3$] inserted into the *ipso*-cyclopentadienyl carbon–silicon bond to form platinasila[2]ferrocenophane **10** (Scheme 4). The tendency of platinum(0) fragments to undergo oxidative insertion has so far prevented the synthesis of a sila[1]ferrocenophane with a pendent platinum unit.



Scheme 4. Attempted synthesis of a platinum-containing sila[1]ferrocenophane; formation of platinasila[2]ferrocenophane **10**.

### *Lithography*

The use of Co-PFS **6** as a lithographic resist offers several advantages: high metal content, ease of processibility, atomic level mixing and stoichiometric control over composition. We have recently demonstrated the use of this metallopolymer as a resist in electron-beam lithography (EBL),[17] UV-photolithography,[18] as well as $O_2$- and $H_2$-RIE (RIE = reactive ion etching).[19]

### *Cluster-Based Polyferrocenylsilanes as EBL Resists*

In order to determine whether Co-PFS **6** could function as an e-beam resist, uniform thin films (*ca.* 200 nm thick) of **6** were spin-coated onto silicon substrates and EBL was carried out at various doses and currents in a modified scanning electron microscope. The treated films were then developed in THF and characterized. Co-PFS was found to be a negative e-beam resist, with best results obtained at a dose of 25 mC/cm$^2$. Shapes including dots and bars were successfully fabricated (Figure 4).

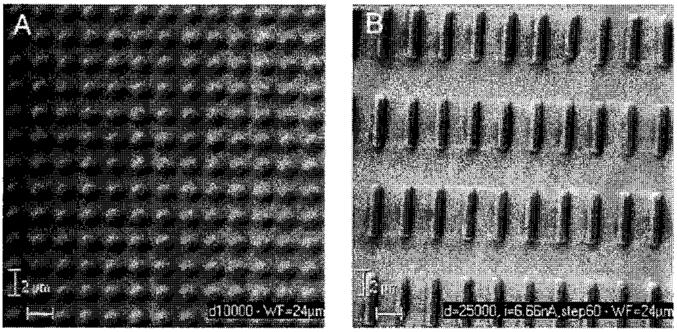


Figure 4. SEM images of (a) dots and (b) bars fabricated by EBL using a Co-PFS **6** resist

The elemental composition of these patterns was investigated using time-of-flight secondary ion mass spectrometry (TOF SIMS) and X-ray photoelectron spectroscopy (XPS). Elemental maps of iron and cobalt for the array of bars on the silicon substrate were obtained using TOF SIMS. The mapping clearly revealed that iron and cobalt were concentrated within the bars. Information regarding the chemical environment and distribution of iron and cobalt throughout the bars was obtained via XPS and compared to data from an untreated film of Co-PFS. The atomic ratio of Fe:Co for the bars was in agreement with the theoretical value of 1:2. Detailed scans for iron and cobalt revealed no change in binding energy for the elements at 3 nm and 12 nm depths, indicating uniformity in the average chemical environment. Overall, XPS revealed little change in the chemical composition of the polymer resist after EBL. Finally, magnetic force microscopy (MFM) indicated no appreciable magnetic field gradient above the bars following EBL.

In order to enhance the magnetism of the patterned bars, the were pyrolyzed at 900 °C under a nitrogen atmosphere to promote the formation of metallic nanoclusters.[14,20] The same array of bars was characterized before and after pyrolysis by tapping mode AFM. Comparison of the images and cross-sectional profiles suggested there is excellent shape retention, accompanied by a decrease in the dimensions of the bars. MFM studies of the bars indicated that they contained heterogeneous ferromagnetic clusters whose magnetic dipoles appeared to be randomly oriented. The ferromagnetism of the pyrolyzed array of ceramic bars was independently confirmed by magneto-optic Kerr effect (MOKE) measurements.

Although the aforementioned proof-of-concept experiments dealt with the formation of micron-scale objects,[17] EBL can be used to routinely fabricate structures down to 30–50 nm.[21] Indeed, this process has already been extended to the patterning of sub-500 nm bars and dots from Co-PFS (**6**).

*Cluster-Based Polyferrocenylsilanes as UV Photoresists*

Organic polymers incorporating acetylenic moieties have been shown to crosslink under thermal conditions. Upon heating, the acetylene groups from adjacent chains undergo cyclotrimerization and coupling reactions, creating crosslinks in the polymer.[22] In addition, photo-induced polymerization of alkyl- and aryl-substituted acetylenes are known to be catalyzed by metal carbonyls such as $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$.[23–25] Recently, Bardarau *et al.* demonstrated that polyacrylates with pendent acetylenic side groups could be photocrosslinked with $W(CO)_6$ as catalyst.[26] We believe that Co-PFS **6** is a promising candidate as a resist for UV-photolithography, as it contains both the acetylenic unit and the metal carbonyl catalyst.[14]

To study this possibility, a thin film (*ca.* 200 nm) of Co-PFS **6** on a silicon substrate was exposed to near-UV radiation ($\lambda$=350–400 nm, 450 W) for 5 minutes. The exposed film was developed in tetrahydrofuran before characterization. Co-PFS was found to be a negative-tone photoresist; the exposed area is presumably crosslinked and less soluble. This would be consistent with the photo-initiated crosslinking mechanism of acetylenes in the presence of metal carbonyls. However, it is also possible to form crosslinks in Co-PFS through decarbonylation of the cobalt clusters. The thickness of the film before and after UV treatment was determined by ellipsometry. A 200 nm-thick film of Co-PFS had a thickness of *ca.* 170 nm after exposure to UV radiation and solvent development. The decrease in thickness is probably a reflection of the decreased volume of the crosslinked polymer.

Patterning of Co-PFS **6** films was accomplished using a metal foil shadow mask with *ca.* 50-

300 μm features fabricated by micromachining. Figure 5a is an optical micrograph of a straight line of Co-PFS patterned using the shadow mask. Smaller features (*ca.* 10-20 μm) were obtained using a chrome contact mask (Figure 5b). In both cases the unexposed polymer was completely removed during development with THF, leaving behind patterns with well-defined edges.

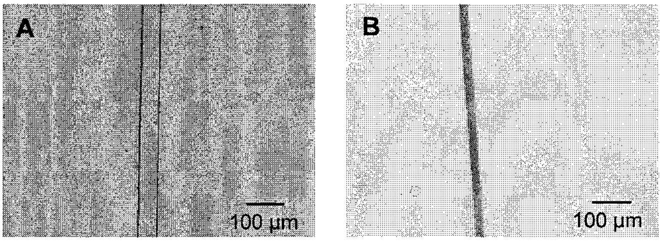


Figure 5. Optical micrographs of Co-PFS **6** lines fabricated by UV photolithography using (a) a shadow mask and (b) a chrome contact mask

A patterned Co-PFS **6** film was pyrolyzed at 900 °C under a nitrogen atmosphere in an attempt to fabricate magnetic ceramic lines. The resulting ceramic lines have the same dimensions as the polymer precursor and show excellent shape retention in the lateral directions. Inspection of the ceramic line at higher magnifications revealed the formation of what appeared to be Co/Fe nanoparticles throughout the line.

UV photolithography using Co-PFS **6** as a resist provides a convenient route to deposit patterned polymer and magnetic ceramic onto flat substrates over large areas. Due to the excellent RIE resistance of the polymer, Co-PFS patterned by UV photolithography can potentially be used for pattern transfer onto the underlying substrate using conventional plasma etching techniques. Investigations are underway to improve the resolution of this resist.

### *Cluster-Based Polyferrocenylsilanes as Reactive Ion Etch Resists*

It has been demonstrated that polyferrocenylsilanes exhibit low plasma etch rates, which can be attributed to the formation of a protective layer of involatile iron and silicon compounds.[27] This property has been exploited with PFS block copolymers that self-assembled into micelles or phase-separated thin films for the deposition of patterned ceramics and pattern transfer onto the substrate. [28–30] In our research, we are interested in the direct formation of high metal content magnetic ceramic films by plasma RIE treatment of Co-PFS.[19]

To test the feasibility of this approach, thin films of Co-PFS **6** on a silicon substrate were treated with either a hydrogen or an oxygen plasma. Effects of the plasmas on the chemical composition of the treated films were studied by TOF SIMS depth profiling. In both cases, plots of the intensity of the $Si^+$, $Fe^+$, $FeO^+$, $Co^+$ and $CoO^+$ signals as a function of depth showed that the plasma affected only the top 10 nm of the films, leaving the underlying polymer relatively untouched. The chemical composition of the modified films was analyzed by XPS. In both cases, a Co:Fe ratio of approximately 1:1 was found at 3 nm depth, rather than the stoichiometric 2:1 ratio found in the untreated polymer. This deficiency of Co on the film surface is most likely due to the volatilization of cobalt carbonyl clusters during the high vacuum processing required for RIE. Formation of iron oxides (FeO and $Fe_2O_3$) as well as cobalt oxides (CoO and $Co_3O_4$) were observed at 3 nm depth in the oxygen plasma treated films. In the case of $H_2$-RIE, small amounts of oxides were also observed at 3 nm depth, presumably due to the oxidation of reduced metal upon exposure to atmospheric oxygen.

Morphological changes in the surface of Co-PFS films following RIE were investigated by TEM and AFM. Thin films of the polymer (*ca.* 50 nm thick) on a carbon-coated copper TEM grid were exposed to either an oxygen or a hydrogen plasma. In both cases, analysis by TEM revealed the presence of electron rich nanoworms with widths ranging from 4–12 nm on the supporting carbon film. Untreated samples were featureless, supporting plasma-induced nanoworm formation. Electron energy-loss spectroscopic (EELS) elemental mapping and energy-dispersive X-ray (EDX) analysis indicated that there was a high concentration of iron, cobalt and silicon in the nanoworms. In contrast to the essentially flat and featureless surface of the untreated film, AFM images of both plasma treated films exhibited a pervasive interconnected reticulated structure, which would appear as nanoworms in a projection normal to the plane of the sample. These features are reminiscent of surface reticulations observed by Thomas *et al.* in AFM images of organosilicon polymers following ambient temperature $O_2$-RIE.[31] We hypothesize that these features resulted from dewetting caused by a polarity difference between the overlying inorganic layer and the native polymer, or spinodal decomposition of the strained inorganic layer.

In order to access films with useful magnetic properties, plasma-induced crystallization of metallic nanoclusters was attempted on a thin film of Co-PFS **6** in a secondary magnetic field. The Co-PFS films (*ca.* 200 nm thick) on silicon substrates were placed between two samarium-cobalt (SmCo) magnets, aligned with opposite magnetic poles facing each other during $H_2$- or $O_2$-RIE. The magnets caused the formation of an intense plasma plume around the sample, which in turn resulted in intense etching conditions. Nanostructures obtained under these conditions were shown to be ferromagnetic by MFM. A tapping mode AFM image and the corresponding MFM image of a hydrogen plasma treated film are shown in Figure 6. These reticulations were much larger than those found for samples treated under similar plasma conditions without the SmCo magnets. We postulate that the secondary magnetic field concentrated the plasma and accelerated nanoworm formation through more efficient removal of carbonaceous material and silicon, while the additional thermal energy present in the plasma plume promoted metal crystallization. To the best of our knowledge, this is the first example of the formation of a ferromagnetic film directly from the plasma treatment of a metallopolymer. A standard lithographic technique such as soft lithography, EBL or UV-photolithography used in conjunction with RIE in a secondary magnetic field should offer access to ordered arrays of ferromagnetic ceramics. These arrays may find applications in spintronics as an isolating, magnetic layer in a nano-granular in-gap structure[32] or the formation of logic circuits using magnetic quantum cellular automata.[33]

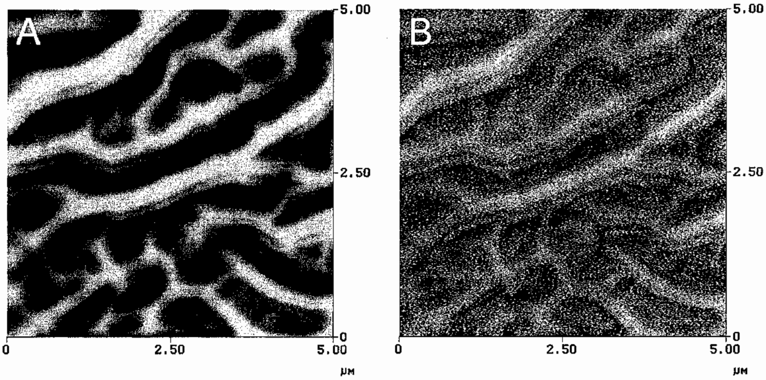


Figure 6. (a) Tapping mode AFM image of a thin film of Co-PFS **6** following $H_2$-RIE in a secondary magnetic field and (b) the corresponding lift mode MFM image (5×5 $\mu m^2$)

## Conclusions

We have developed synthetic routes to highly metallized sila[1]ferrocenophanes and the corresponding high molecular weight polymer Co-PFS **6**. This polymer is readily accessible via transition metal-catalyzed ROP of sila[1]ferrocenophane **4**, followed by clusterization of the acetylenic substituents with dicobalt octacarbonyl. The intrinsic high metal content, air-stability and solution processibility of Co-PFS make it an excellent precursor to lithographically patterned ceramics. Fabrication of patterned arrays of polymer and magnetic ceramics on the sub-micron scale was achieved by EBL and pyrolysis of thin films.[17] We also demonstrated that Co-PFS can function as a negative-tone UV-photoresist.[18] The crosslinking mechanism in this system is still under investigation. Finally, we showed the utility of this highly metallized polymer as a RIE resist; treatment of the Co-PFS films with either a hydrogen or an oxygen plasma in the presence of a secondary magnetic field afforded ferromagnetic ceramics.[19]

## Acknowledgements

I.M. would like to thank the Canadian Government for a Canadian Research Chair. W.Y.C. acknowledges an NSERC postgraduate scholarship. A.Y.C. thanks the University of Toronto for a Graduate Fellowship in Chemistry. S.B.C. is grateful to NSERC for a PDF. The authors would also like to acknowledge the excellent work of our collaborators: EBL: Prof. Harry E. Ruda; Dr. Stephane Aouba (Center of Advanced Nanotechnology, University of Toronto); AFM/ MFM: Prof. Christopher M. Yip, Mandeep S. Rayat, Guocheng Yang (Department of Chemical Engineering and Applied Chemistry, University of Toronto); TEM: Dr. Neil Coombs, Ellipsometry: Chantal Paquet (Department of Chemistry, University of Toronto); RIE, UV Photolithography, XPS: Prof. Zheng-Hong Lu, Dr. Sijin Han, Dr. Dan Grozea (Department of Materials Science and Engineering, University of Toronto); TOF SIMS: Dr. Rana N. S. Sodhi, Dr. Peter M. Brodersen, (Surface Interface Ontario, Department of Chemical Engineering and Applied Chemistry, University of Toronto); MOKE: Prof. Mark R. Freeman, Jason B. Sorge (Department of Physics, University of Alberta).

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