Lithographic Applications of Highly Metallized Polyferrocenylsilanes

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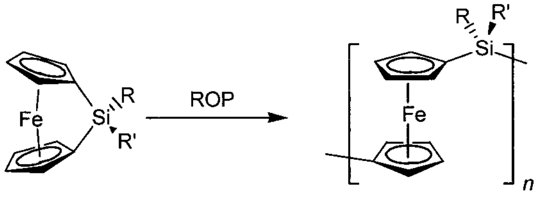
Summary: Organometallic polymers are excellent candidates for the introduction of metals into nanostructures using lithographic techniques due to their inherently high and uniform metal loadings and processibility. Soluble, high molecular weight polyferrocenylsilanes possess unique physical properties and function as excellent ceramic precusors. Recent advances in the use of lithographic techniques with a highly metallized PFS resist to form new nanopatterned materials will be presented.

Keywords: lithography; nanopatterned materials; organometallic polymers; polyferrocenylsilanes; resists

Introduction

The patterning of surfaces on the nanometer scale with metals offers the possibility of fabricating materials with novel catalytic, optical, sensing, electrical and magnetic properties. Patterning methods can vary from soft lithography, scanning probe lithography, electron beam lithography and photolithography. Recent reports include the use of microcontact printing (μ-CP) to order monodisperse nanoparticles of iron oxide[1] and nanotransfer printing (nTP) to transfer a gold pattern with 75 nm feature sizes from a gold coated GaAs stamp to an appropriately primed PDMS substrate.[2] Scanning probe techniques also offer precise control of patterning. An AFM tip has been used to pen 35 nm wide lines of MoO_3 through local oxidation of a Mo film[3] while Pt lines 30 nm wide have been drawn *via* the reduction of H_2PtCl_6 at an AFM tip using electrochemical AFM dip-pen lithography.[4] It is also possible to employ a film of an organometallic polymer as a resist for electron-beam lithography. Johnson and co-workers have used thin films of the organometallic cluster polymer $[Ru_6C(CO)_{15}Ph_2PC_2PPh_2]_n$ as negative electron-beam resists to direct write conducting wires 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. The ring-opening polymerization of sila[1]ferrocenophanes (**1**) by thermal,[6] anionic[7] and transition metal-catalyzed[8] routes yields high molecular weight, soluble polyferrocenylsilanes (**2**, PFS) containing 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 shielding.[9] Furthermore, the low plasma etch rates of polymers containing organometallic moities in comparison to their purely organic counterparts[10] suggest their use as etch masks which can also deposit interesting materials. The introduction of additional metals into the PFS chain can increase metal loadings and allow access to binary or higher metallic species.



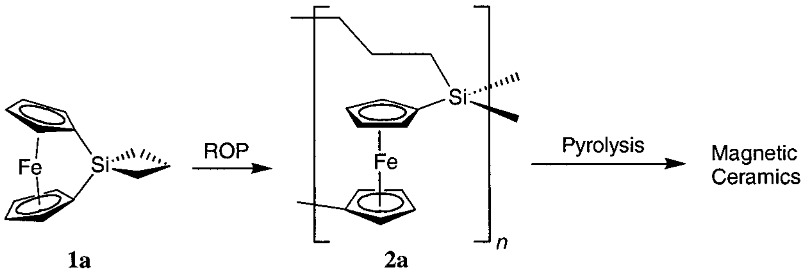
1 **2**

Scheme 1. Ring-opening polymerization of a sila[1]ferrocenophane (**1**) to afford a polyferrocenylsilane (**2**).

Polyferrocenylsilanes as Ceramic Precursors

The synthesis of shaped ceramics from processible polymer precursors is currently receiving much attention. For example, Sneddon and co-workers have prepared BN[11] and SiBNC[12] ceramic fibers from polymer precursors. The primary obstacle to this process is the scarcity of high ceramic yield polymers with interesting chemical compositions. One promising avenue of research is the incorporation of transition metals into the polymer precusor. In collaboration with Ozin, we have found that a highly cross-linked PFS (**2a**) network can be formed through the thermal ROP of the spirocyclic sila[1]ferrocenophane **1a** (Scheme 2).[9,13] Furthermore, pyrolysis of the cross-linked polymer network under a nitrogen atmosphere affords

$Fe/SiC/C/Si_3N_4$ ceramics in greater than 90% ceramic yield with good shape retention and approximately 10% reduction in dimensions. Most interestingly, these ceramics contain α-Fe nanoparticles ranging in size from 1.5 to 70 nm in diameter with smaller superparamagnetic particles formed at temperatures below 900 °C and larger ferromagnetic particles resulting from pyrolysis at 1000 °C. On the road to nano-patterned magnetic materials, the soft lithographic technique of micromolding has been used to create micron scale patterned polymer channels housed inside silicon wafers and their derived magnetic ceramics.[13] It has also proved possible to control the size of the α-Fe nanoclusters through the thermal ROP and subsequent pyrolysis of **1a** within the hexagonal *ca.* 3-4 nm channels of mesoporous silica (MCM-41).[14] In this case only superparamagnetic clusters calculated to have diameters between 5.0-6.4 nm coated with a 0.4-0.6 nm Fe_3O_4 layer were present. Similarly, a templating process has been employed to fabricate inverse opal magnetic ceramics.[15] Crosslinked PFS microspheres formed by precipitation polymerization may be oxidized and electrostatically self-assembled with silica spheres to form core-shell particles. Their pyrolysis affords ceramic microspheres which can be magnetically arranged.[16] Finally, we have reported that pyrolysis of a thin film of self-assembled PS-*b*-PFS block copolymer affords an array of ceramic dots *ca.* 20-25 nm in diameter on a silicon substrate.[17] Such an array may find applications in magnetic data storage or as an etch resist for the formation of high aspect ratio features. This work illustrates the potential of organometallic polymers to function as metal sources for the growth of metallic nanoclusters within a larger patterned structure.



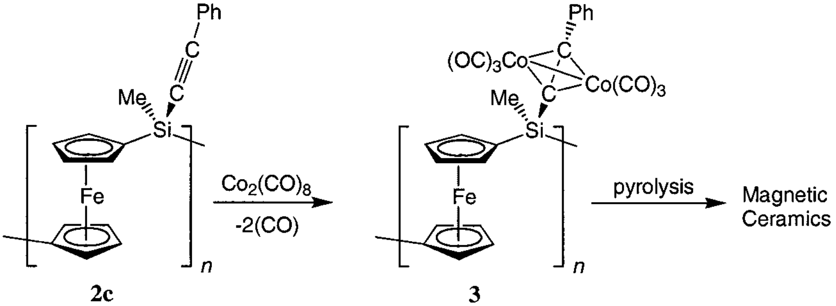
1a **2a**

Scheme 2. Thermal ROP of a spirocyclic sila[1]ferrocenophane (**1a**) to yield a cross-linked preceramic polyferrocenylsilane network (**2a**).

Polyferrocenylsilanes as Plasma Etch Resists

The ability of block copolymers containing immiscible blocks to self-assemble into regular morphologies on the nanometer scale in both solution and the solid state is of great interest for block copolymer lithography when a difference in etch rates between the two blocks exists. It is know that the plasma etch rate of polymers can be greatly reduced through the incorporation of metals which tend to form an involatile refractory layer.[10] In the past this has been achieved by selective reaction of a metal reagent with one block. For example, Möller and co-workers selectively vaporized Ti onto the self-assembled PS clusters protruding from a thin films of polystyrene-*b*-poly(2-vinylpyridine) to form a high contrast mask for ion etching.[18] The direct incorporation of metal into the polymer chain ensures a high and uniform loading and avoids post-resist fabrication metallization steps. We were able to exploit both the solution self-assembly and plasma chemistry of inorganic polymers to form nanowires on a semiconducting substrate.[19] Living anionic polymerization was employed to prepare a poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) block copolymer with suitable block ratios for self-assembly into cylinderical micelles with an iron-rich PFS core in *n*-hexane. The micelles are *ca.* 20 nm in diameter and their length can be controlled from between 70 nm to 10 μm. It proved possible to align the micelles using capillary forces on an electron-beam patterned silicon substrate. Subsequent treatment with a hydrogen plasma stripped away the hydrocarbon component leaving behind iron-silicon-carbon-oxide ceramic lines approximately 4 nm high. Thus self-assembled block copolymers containing PFS have great potential as etch resists for nanopatterning metal-containing structures through plasma RIE.

Polyferrocenylsilanes would be expected to have low plasma etch rates due to the formation of a protective layer of involatile iron and silicon compounds upon reaction with the plasma.[20] X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopic (AES) depth profiling have shown that polyferrocenyldimethylsilane (**2b**) reacts with an oxygen plasma to form a *ca.* 10 nm thick carbon-depleted layer rich in iron and silicon oxides.[21] In addition, by varying etching conditions it was possible to obtain a remarkably high etch ratio of almost 50:1 between PI and PFS (**2b**).[22] The same study demonstrated that PFS (**2b**) is an effective etch barrier in CF_4/O_2-RIE used to etch silicon wafers. Thus a self-assembled organic-PFS block copolymer film is an ideal candidate for the patterning of large aspect ratio nanometer-sized features in an underlying substrate using plasma RIE.[20] This process was illustrated using a poly(isoprene-*b*-ferrocenyldimethylsilane) block copolymer which phase segregated into a monolayer of PFS spheres in a PI matrix with a domain spacing of 30 nm.[21] Under the oxygen plasma conditions employed the etch rate of the PFS domains was 40 times less than that of the PI matrix. Following O_2-RIE, an AFM height image revealed 7 nm high organometallic regions with short-range hexagonal order and the same domain spaces as found in the initial resist. The ordering of the organometallic domains can be greatly improved using graphoepitaxy in which film growth is ordered by artificial topographic patterning of the substrate.[23] Near perfect alignment of the self-assembled 20 nm spherical PFS domains in a PS matrix in an annealed thin film of PS-*b*-PFS was achieved in 240 nm wide grooves made in an oxidized silicon wafer using interference lithography.[24] Reactive ion etching of the film with a CHF_3 plasma led to the formation of ordered silica posts 20 nm wide with aspect ratios of three or greater. This process has the potential to be generalized to the patterning of many substrate materials.



Scheme 3. Cobalt clusterization of the acetylenic substituent of a polyferrocenylsilane (**2c**) to yield the highly metallized Co-PFS (**3**), a precursor to magnetic ceramics.

The incorporation of additional metals into the PFS chain is particularly attractive for the metal patterning of surfaces using standard lithographic processes. We have found that polyferrocenylsilanes with acetylenic substituents at silicon (**2c**)[25] can be clusterized by treatment with dicobalt octacarbonyl to yield the highly metallized, soluble, air stable cobalt-clusterized polyferrocenylsilane (Co-PFS) (**3**) (Scheme 3).[26] We have also shown that the pyrolysis of Co-PFS affords ceramics containing magnetic Co/Fe alloy nanoparticles in high yield. Thin films of Co-PFS are readily accessible *via* spin coating. Results on the lithographic patterning of this novel highly metallized organometallic resist will be presented.

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