Fabrication of Oriented Nanoscopic Ceramic Lines from Cylindrical Micelles of an Organometallic Polyferrocene Block Copolymer

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Conventional lithographic techniques become increasingly difficult to use for the formation of periodic and aperiodic features with dimensions smaller than 100 nm. An obvious need exists for alternative approaches which permit fabrication of structures on the nanometer scale.[1] As such, block copolymers offer many opportunities in this area as they can self-assemble into a variety of nanoscale morphologies as a result of the immiscibility between the constituent blocks.[2−7] For example, in a solvent selective for the polystyrene block, previous work has shown that polystyrene-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP) forms spherical micelles with a P2VP core and a corona of PS. Gold can be complexed to the P2VP block and the resulting micellar films display selective plasma etching contrast that allows patterns to be transferred to the underlying inorganic substrate (e.g. GaAs).[3,7] Such spherical micelles have also been templated in lithographically defined holes and grooves and, after plasma etching, ordered but unconnected gold nanodot patterns can be formed.[8] However, connected structures such as lines are inaccessible by this approach.

Living anionic ring-opening polymerization (ROP) of silicon-bridged [1]ferrocenophanes has recently provided access to polyferrocenylsilane block copolymers.[9] These materials possess covalently bound transition metal atoms directly in the main chain of one of the blocks, which avoids the necessity for an additional metallization step. As polyferrocenylsilane homopolymers function as precursors to magnetic ceramics,[10] the phase-separated block copolymers offer opportunities for the generation of nanoscopic patterns via pyrolysis or selective etching procedures.[11] We reported recently that poly(ferrocenyldimethylsilane-*b*-dimethylsiloxane) (PFS_{50}-*b*-$PDMS_{300}$) forms stable cylindrical micelles in *n*-hexane.[12] These well-characterized micelles are continuous and consist of an organometallic core of PFS and a corona of PDMS chains and their dimensions can be varied; for example, the lengths can be controlled from ca. 70 nm to over 10 μm.[12,13] These structures are of interest as etching resists for semiconducting substrates such as GaAs or Si and offer possible access to connected, potentially magnetic nanoscopic ceramic patterns. However, before this idea can be realized, a simple method to create continuous lines of cylindrical micelles is required. Our approach was to attempt to align the cylinders by using capillary forces acting at the edge of prestructured lines on a resist film, which was found to be successful in the case of the spherical PS-P2VP micelle system.[8]

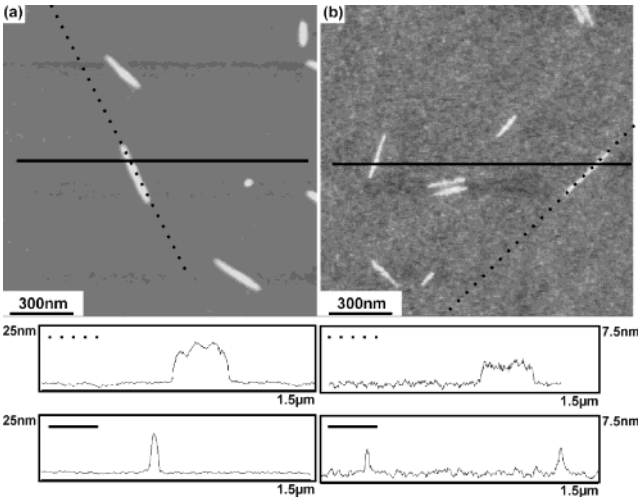
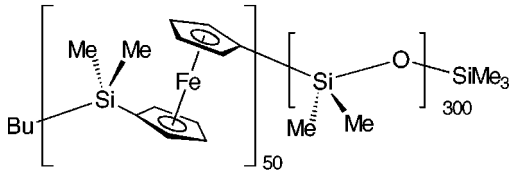


Figure 1. Scanning force micrographs of PFS_{50}-*b*-$PDMS_{300}$ micellar cylinders aerosprayed from hexane onto GaAs (a) before and (b) after hydrogen plasma treatment. The height plots below indicate the topography profiles of the cylindrical structures along the dotted and solid line in the respective images.

The sample of PFS_{50}-*b*-$PDMS_{300}$ (M_n = 35 100 g mol^{-1}, PDI = 1.10) was prepared by a sequential living anionic ROP and was self-assembled into cylindrical micelles by dissolution in *n*-hexane as described previously.[12,13]



To probe the ability of the micelles to function as etching resists, cylinders of average length ca. 500 nm were aerosol sprayed onto an unpatterned GaAs substrate (see scanning force micrograph in Figure 1a). After etching with a hydrogen plasma for 10 min at 100 W and at 1 mbar ceramic structures with a similar shape were formed (Figure 1b). The plots below the

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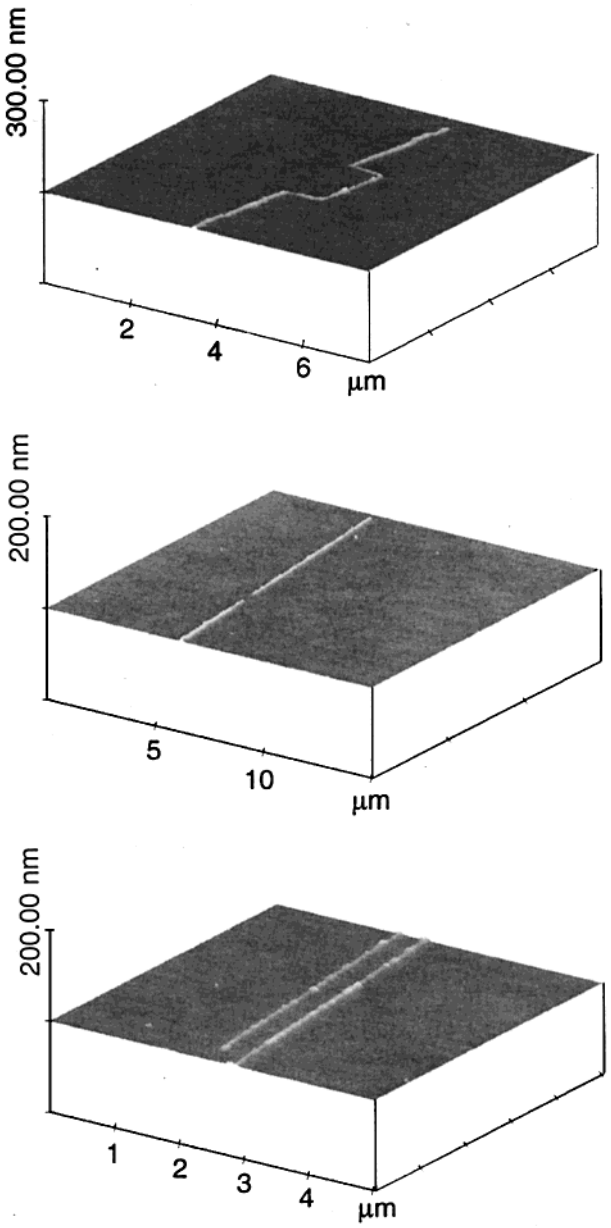

Figure 2. Series of scanning force micrographs of lines on a silicon substrate after the oriented deposition of PFS-*b*-PDMS diblock copolymer cylinders along pre-patterned grooves on a resist film, lift-off with acetone followed by hydrogen plasma treatment.

images show the height profiles of the structures along the solid and dotted lines. The PFS_{50}-*b*-$PDMS_{300}$ cylinders have a height of approximately 20 nm and after the plasma treatment, the height decreases to approximately 4 nm. Etching with hydrogen plasma has previously been shown to predominately remove organic components,[3,7] and a ceramic containing Si, Fe, O, and C is expected to be left on the underlying substrate imaged in Figure 1b.[14] It can also be assumed from the height plot along an individual cylinder in Figure 1b that the cylinder is continuous, i.e., the shape was preserved during etching.

To create oriented nanoscopic lines cylindrical micelles of PFS_{50}-*b*-$PDMS_{300}$ with an average length of ca. 500 nm were then deposited by dipping or spin coating onto a resist structured with grooves created by an e-beam. Figure 2 shows a series of scanning force micrographs in different regions of the silicon substrate after the resist film had been lifted-off by immersion for 30 s in acetone, dried with a N_2 flow, and etched with a hydrogen plasma. The images show aligned nanoscopic lines with a height of approximately 4 nm. From the height of the cylinders and the fact that only one single cylinder is resolved in the images,[15] it can be concluded that the cylindrical clusters of Fe, Si, O, and C result from the alignment of single PFS_{50}-*b*-$PDMS_{300}$ micelles. It is remarkable that alignment of the cylinders using capillary forces occurred irrespective of whether dipping was parallel or perpendicular to the grooves or if the substrate was spin coated.

In summary, we describe our preliminary results which demonstrate that cylindrical organometallic diblock copolymer micelles can be positioned by capillary forces acting along a topographical boundary of a structured resist film. Furthermore, connected ceramic lines of reduced size can be generated by subsequent reactive ion etching. The approach presented here represents a relatively simple method to create lines that have widths which are less than 10 nm and lengths of more than 500 nm through a combined top-down/bottom-up approach. As the dimensions of structures are pushed to smaller and smaller limits, size-dependent material properties are encountered. Thus, the aligned cylinders discussed in this communication are excellent candidates as etching resists to produce 2-D quantum wires in semiconducting substrates with large aspect ratios.

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Supporting Information Available: Experimental details, XPS studies, and figures showing a cross-sectional diagram of the micelles and experiments with higher concentrations of micelles (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) XPS studies of PFS-PDMS cylinders deposited on GaAs after reactive ion etching showed an increase in the Fe:C ratio by a factor of ca. 5 relative to the pristine block copolymer micelles. See Supporting Information for further details.

(15) The dilute solutions used resulted in single micelles located at the groove edge. Experiments with more concentrated solutions resulted in the deposition of multiple micelles. See Supporting Information for further details.