

## Drying Mediated Pattern Formation in a Capillary-Held Organometallic Polymer Solution

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Poly(ferrocenylsilanes) (PFS) are a novel class of transition metal-containing polymers with a main chain that consists of alternating organosilane and ferrocene units.<sup>1–17</sup> They possess intriguing physical properties that have potential applications in magnetic data storage,<sup>1,2,4–7,10,12,13</sup> photonic device,<sup>1,9</sup> and redox-active materials.<sup>2,5</sup> In addition, they are ideal precursors for producing magnetoceramics whose magnetic properties can be tuned by pyrolysis temperature.<sup>1,2,4–8,10–13</sup> For example, pyrolysis of poly(ferrocenyl-dimethylsilane) at 1000 °C turns it into ferromagnetic  $\alpha$ -iron ( $\alpha$ -Fe) nanoparticles embedded in an amorphous silicon carbide/carbon (SiC/C) matrix.<sup>1,7</sup> It has been demonstrated that the patterned, micron-scale PFS bars, circles, and lines exhibit a significant increase in coercivity in magnetic properties measurements.<sup>12</sup> Furthermore, these patterned PFS

can also serve as etch barriers in nano- and microlithographic applications, for example, transferring the patterns into silicon substrate.<sup>11,15–17</sup> PFS is stable in reactive ion etching process compared to common organic polymers due to the presence of iron and silicon in the polymer backbone.<sup>17</sup> However, the creation of these micrometer size patterns involves the preparation and use of either a mask in UV-lithography<sup>11,14</sup> or a stamp in capillary force lithography,<sup>16,17</sup> or requires the use of expensive electron-beam lithography that is not cost-effective and operated under high vacuum chamber.<sup>11,12</sup> Moreover, a subsequent step of removal of unexposed PFS is required.<sup>11,12,14</sup>

Self-assembly via irreversible solvent evaporation of a droplet containing nonvolatile elements (dyes, nanoparticles, or polymers) represents an extremely versatile way for one-step creation of complex large-scale<sup>18–34</sup> or long-range ordered structures.<sup>35,36</sup> However, the flow instabilities within the evaporating droplet often result in irregular dissipative structures (e.g., convection patterns and fingering instabilities). Therefore, to fully utilize the evaporation as a simple, non-lithography route to produce well-ordered structures that have numerous technological applications, it requires delicately controlling the evaporative flux, the solution concentration, and the interfacial interactions among the solvent, solute, and substrate. To date, a few attempts have been made to control the droplet evaporation in a confined geometry in which self-organized mesoscale patterns are readily obtained.<sup>37–39</sup> Recently, patterns of remarkably high fidelity and regularity have been reported.<sup>37</sup> They are formed simply by allowing a drop to evaporate in a confined geometry

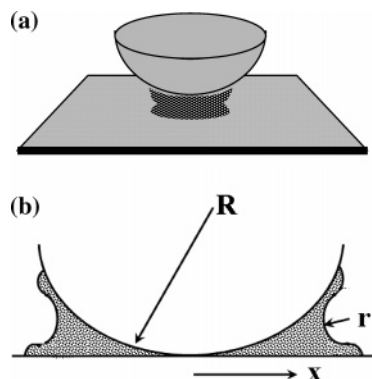
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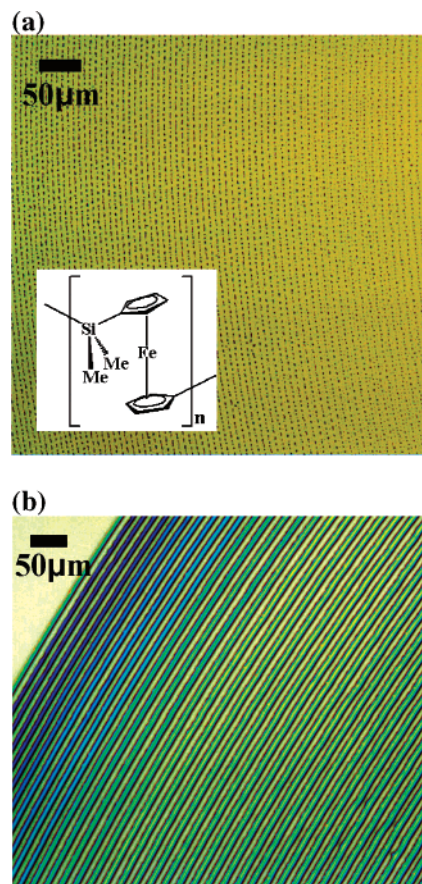


**Figure 1.** Schematic representation of a droplet of PFDMS toluene solution (a) placed in a confined geometry consisting of a spherical lens on a silicon substrate separated by a few hundred micrometers apart. Then (b) the upper sphere was brought into contact with the lower silicon surface such that a capillary bridge forms with evaporation rate highest at the extremity. This leads to unstable stick-slip motion of the contact line, which moves toward the center of the sphere/Si contact during the course of solvent evaporation.

composed of two cylindrical mica surfaces placed at right angle to one another.<sup>37</sup>

Here we show that, by constructing a much simpler confined geometry consisting of a spherical lens on a silicon (Si) surface (sphere-on-Si), patterns of periodic concentric rings of poly(ferrocenyldimethylsilane) (PFDMS) can be formed in one step in a precisely controllable manner without the need of lithographic techniques and external fields. Subsequent pyrolysis of the patterned PFDMS rings yielded ferromagnetic ceramics containing  $\alpha$ -Fe nanoparticles. The use of a sphere-on-Si geometry carries advantages over the case in which two crossed cylindrical mica surfaces were employed.<sup>37</sup> It eliminates the need of mica cleaving to prepare step-free mica thin films, the sputtering of silver on the backside of mica thin film for optical imaging in the reflection mode, and the gluing of mica thin films onto cylindrical lenses.<sup>40,41</sup> The present much simpler yet general geometry affords a means to produce and organize surface patterns in a concentric fashion with unprecedented regularity.

Poly(ferrocenyldimethylsilane) (PFDMS) (Polymer Source Inc.) having molecular weight ( $M_n$ ) of  $1.61 \times 10^5$  and polydispersity index (PDI) of 2.3 was used in the studies. Solutions of PFDMS in toluene (1.25 and 0.0625 mg/mL) were prepared and purified with  $0.2 \mu\text{m}$  filter. To construct a sphere on a flat surface geometry, a spherical lens made from fused silica with a diameter of  $\sim 1$  cm and a Si wafer were used. Both sphere and Si were cleaned by a mixture of sulfuric acid and Nochromix and then firmly fixed at the top and the bottom of sample holders, respectively. To implement a confined geometry, an inch-worm motor with a step motion of a few micrometers was used to place the upper sphere into contact with the lower stationary Si substrate. Before they contacted (i.e., separated by approximately a few hundred micrometers apart), a small amount of PFDMS toluene solution was loaded ( $\sim 25 \mu\text{L}$ ) and trapped within the gap between the sphere and Si due to the capillary force as schematically illustrated in Figure 1a. The sphere was finally brought into contact with Si



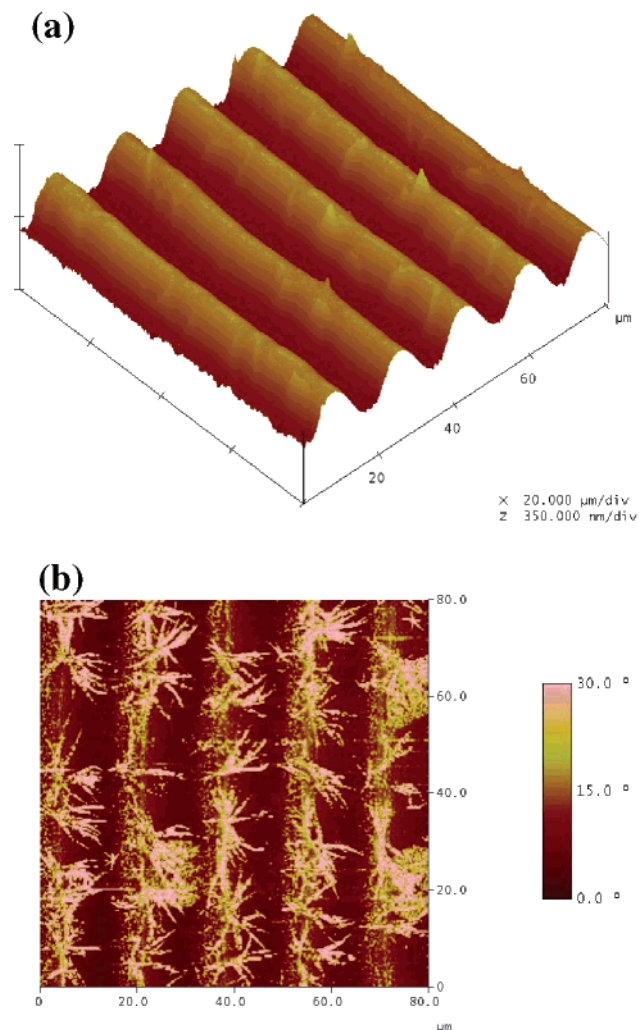
**Figure 2.** Optical micrographs of the periodic concentric ring patterns on Si substrate formed by the deposition of PFDMS in the geometry shown in Figure 1b. The concentrations of PFDMS toluene are 0.0625 mg/mL in (a) and 1.25 mg/mL in (b). The scale bars are  $50 \mu\text{m}$  in both images. Inset: the chemical structure of PFDMS.

substrate by the inch-worm motor such that a capillary-held PFDMS solution forms with evaporation rate highest at the extremity (Figure 1b). This leads to unstable stick-slip motion of the three-phase contact line, which moves toward the center of the sphere/Si contact during the course of solvent evaporation.

The evaporation, in general, took 1 h to complete. Afterward, the two surfaces were separated. A periodic family of microscopic concentric rings was formed on both sphere and Si surfaces. An optical microscope (OM; Olympus BX51) in the reflection mode was used to examine the deposited patterns without delay since crystallization was observed after leaving rings at the ambient conditions for a few days. Instead of performing characterizations on the spherical lens, including atomic force microscope (AFM; DI Dimension 3100 in tapping mode) and scanning electron microscopy (SEM; Jeol 6060LV) as will be shown later, the patterns formed on Si substrate were investigated. This is because the surface of the spherical lens is curved, which makes it hard to take images without the curving effect from the lens. Shown in Figure 2 are the optical micrographs of the concentric ring patterns over a lateral distance of several hundred micrometers obtained by the deposition of PFDMS from 0.0625 and 1.25 mg/mL PFDMS toluene solutions in the geometry shown in Figure 1b. It should be noted that only a small region of the entire ring patterns is shown in the images. In both cases, a definite spacing between

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**Figure 3.** AFM images of PFDMS stripes on Si substrate produced from the solution with  $c = 1.25$  mg/mL. (a) 3D height image; (b) 2D phase image. The crystallization of PFDMS is clearly evident in 2D phase image. The image size is  $80 \times 80 \mu\text{m}^2$ .

microscopic rings was seen. The average center to center distance of the rings ( $\lambda_{C-C}$ ) for the 0.0625 mg/mL solution is  $6.3 \mu\text{m}$  as determined by both AFM and fast Fourier transfer of the optical micrograph. The average height ( $h$ ) and width ( $w$ ) of the ring are 96 nm and  $2.5 \mu\text{m}$ , respectively, as measured by AFM. For 1.25 mg/mL solution  $\lambda_{C-C} = 16.7 \mu\text{m}$ ,  $h = 182$  nm, and  $w = 14 \mu\text{m}$ . From the result of 0.0625 mg/mL solution each individual ring broken into dots was observed (i.e., forming dotted rings), indicating, as would be expected, a surface tension driven Rayleigh instability at the three-phase contact line since the concentration is twenty times dilute than 1.25 mg/mL solution. For both solutions the surfaces of PFDMS rings appeared uniform, suggesting that PFDMS was in amorphous state and has not yet crystallized. This is presumably due to the presence of trapped solvent. It should be noted that these unique concentric rings patterns described here were highly reproducible.

After a few day of leaving sample in ambient condition, the surface of PFDMS patterns were checked by AFM. Shown in Figure 3 are the 3D height and 2D phase images of a PFDMS surface pattern made from 1.25 mg/mL solution. In 3D height image (Figure 3a), ridge-like rings were

observed. Locally, they appeared as stripes in  $80 \mu\text{m} \times 80 \mu\text{m}$  scan area. A close examination of AFM phase image revealed that the crystallization of PFDMS occurred. Brighter thin curved lines covered at the surface of each stripe can be seen, which indicates that higher, curve-like features were formed over a few day period. The fibril-like crystals are clearly evident and subsequently branch out to cover the bare Si wafer surface between two PFDMS stripes. Moreover, PFDMS crystals were even seen to grow and connect two adjacent stripes, for instance, in the lower left of the image (Figure 3b). The symmetric chain structure of PFDMS (shown in the inset in Figure 2a), which allows close packing of PFDMS molecules into crystalline lamellae, favors the crystallization. For a PFDMS with molecular weight (MW) of  $3.4 \times 10^5$  the glass transition temperature ( $T_g$ ) and melting point ( $T_m$ ) of PFDMS with two substituent methyl groups are 33 and 122–145 °C, respectively.<sup>42,43</sup> These contrast with asymmetrically substituted PFS that possesses a significantly lower  $T_g$  and is amorphous.<sup>44,45</sup> The residual amount of solvent trapped in the rings, acting as plasticizer, causes a reduction in  $T_g$  of PFDMS used in our study. In addition, the MW of PFDMS is  $1.6 \times 10^5$ , lower than  $3.4 \times 10^5$ , suggesting a  $T_g$  lower than 33 °C.<sup>42</sup> Taken together,  $T_g$  of PFDMS rings much lower than 33 °C is expected. This provides a sufficient mobility for PFDMS chains to fold and form crystals at room temperature ( $\sim 25$  °C).

The concentric PFDMS rings were further pyrolyzed at 1000 °C in a quartz tube under vacuum in a pyrolysis furnace for a few hours to obtain the  $\alpha$ -Fe crystallites embedded in the SiC matrix.<sup>1,7</sup> Shown in Figure 4 are SEM images of PFDMS before and after pyrolysis. The integrity of originally formed ring patterns (Figure 4a) was retained after pyrolysis (Figure 4b). As a consequence, very low-cost magnetic ceramic rings in a circumferential fashion were produced in a precisely controllable manner and that have promising applications in magnetic data storage, especially the rotating-disk medium.<sup>1,7,12</sup>

The formation of periodic concentric rings can be understood as a direct consequence of *controlled*, repetitive “stick-slip” motion of contact line resulted from the competition between friction force (pinning force,  $F_p$ ) and capillary force,  $F_c$  (depining force) during the course of irreversible solvent evaporation.<sup>30,32–34</sup>  $F_p$  reflects the interaction between the deposit and the solution.<sup>30,46,47</sup> The counter force ( $F_c$ ) is a function of the surface tension of the solvent and the interfacial area of capillary formed between spherical lens and Si surfaces. In the present study, a capillary-held PFDMS toluene solution bridges between sphere and Si surfaces with certain contact angle governed by the surface tension of toluene and interfacial interactions between the surface (both

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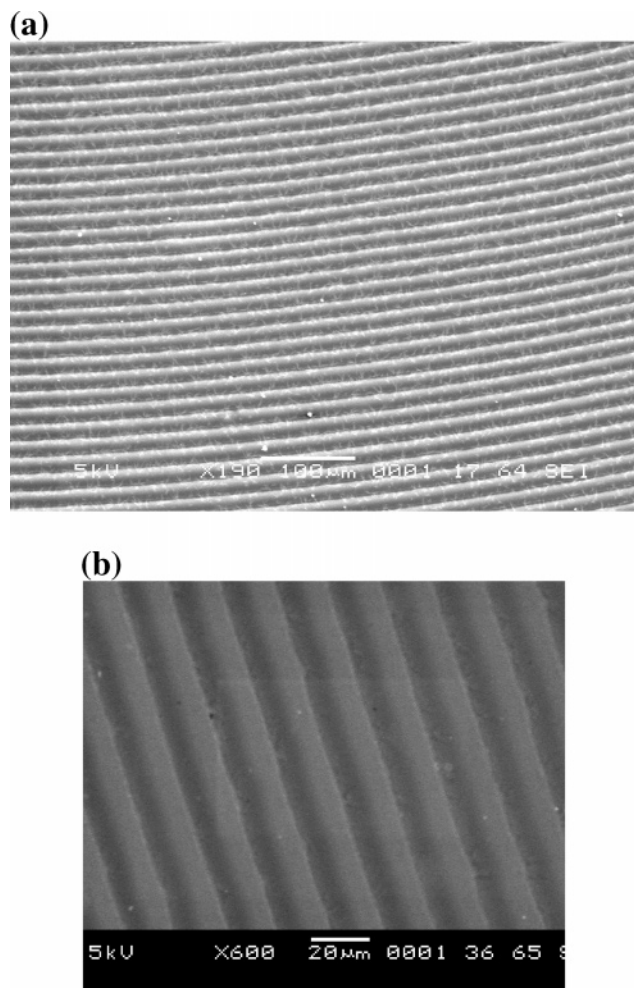
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**Figure 4.** SEM images of PFDMS rings (a) as formed and (b) after pyrolysis at 1000 °C. The pyrolysis resulted in the formation of ferromagnetic ceramic rings containing  $\alpha$ -iron ( $\alpha$ -Fe) crystallites in a silicon carbide/carbon (SiC/C) matrix. The integrity of originally formed patterns in (a) was maintained. The white scale bars are 100  $\mu\text{m}$  in (a) and 20  $\mu\text{m}$  in (b).

sphere and Si) and the solution. A line of polymer<sup>18–20</sup> is then formed as toluene evaporates, ensuring that toluene evaporating from the edge of the capillary is replenished by toluene from the interior, so that outward flow carries the nonvolatile PFDMS to the edge. The deposition of PFDMS exerts a  $F_P$  against the movement of the contact line.<sup>48,49</sup> During the evaporation of toluene the contact angle decreases and the interfacial area of the capillary increases. This causes an increase in  $F_C$ . When  $F_C$  reaches a value greater than  $F_P$ , the contact line becomes unstable and hops to a new position. Thus a new ring develops.<sup>46,47</sup> This process repeats over and

over until it reaches the sphere/Si contact area. The present confined geometry facilitates the suppression of hydrodynamic instabilities and convections due to the facts that the experiments were performed inside a chamber and evaporation was constrained to occur at the capillary edge. As a result it provides a better control over the solvent evaporation. Thus, rather than a stochastic stick-slip motion that was responsible for the formation of irregular rings,<sup>34</sup> the periodic ring patterns of PFDMS were deposited on both sphere and Si surfaces. In contrast to cases in which gradient concentric rings were seen in confined geometries either consisting of two crossed cylindrical mica surfaces<sup>37</sup> or a sphere on a Si surface,<sup>50</sup> the lack of gradient (i.e., a constant  $\lambda_{C-C}$  observed in the present study) may be due to a delicate interplay of the geometrical constraint, the friction force, and the capillary force. It merits a detailed study that is currently being pursued.

In conclusion, we have developed a simple route to produce highly regular concentric ring patterns in an easily controllable, cost-effective, and reproducible manner simply by allowing a drop to evaporate in a confined geometry consisting of a sphere on a Si surface. The confined geometry provides unique environment for controlling the flow within the evaporating droplet, which, in turn, regulates the pattern formation. The organometallic polymer (PFDMS) was chosen as a model system. By employing PFDMS toluene solution with an appropriate concentration, either dotted (at low concentration) or continuous (at high concentration) concentric ring patterns can be produced. The symmetrically substituted PFDMS rings crystallized over a period of a few days at ambient condition. Thermal treatment of PFDMS transforms it, with the retention of concentric ring patterns, into magnetic ceramic rings containing  $\alpha$ -Fe embedded within SiC/C matrix that have applications in magnetic data storage and photonic materials etc. We envision that the formed PFDMS ring patterns can be used as etching barriers for preparing features with high aspect ratio by transferring patterns into various substrates using reactive ion etching. This work is currently under investigation.

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(50) Recently, we have successfully produced gradient concentric rings made of other polymers such as poly(2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) and poly(methyl methacrylate) (PMMA) using the sphere-on-Si geometry.