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Self-assembled ferrofluid lithography: patterning micro and nanostructures by controlling magnetic nanoparticles

Chih-Hao Chang[1,2,4], **Chee-Wee Tan**[1,3], **Jianmin Miao**[3] and **George Barbastathis**[1,2]

[1] Singapore-MIT Alliance for Research and Technology (SMART) Centre, Singapore
[2] Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, USA
[3] School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore

E-mail: chichang@mit.edu

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Abstract
We have developed an alternative self-assembly process to pattern different geometries with user-defined tunability across the micro and nanoscale. In this approach, field-induced assembly of colloidal magnetic nanoparticles within a microfluidic channel is used as a tunable mask for near-field lithography. We have fabricated dot arrays with controllable spacing and micro-ring patterns with 250 nm feature sizes. The proposed process is versatile, cost-effective, and scalable, presenting itself as a promising nanomanufacturing tool.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years, spontaneous self-assembly of elementary components to form functional geometries has emerged as an exciting new method to pattern nanostructures. For example, self-assembly [1] and templated self-assembly [2–4] of block co-polymers can form structures with feature sizes in the order of 10–100 nm. In nanosphere lithography, the assembly of monodispersed polystyrene spheres in a liquid solution can pattern structures with periods in the range of 100–1000 nm [5, 6]. In these methods the average period is controlled chemically, i.e. by the chemical affinity of the particles, the substrates, and the boundaries. The 'bottom-up' approach to nanofabrication is an attractive cost-effective alternative to 'top-down' lithographic processes.

In this paper we report a novel fabrication process based on the field-induced self-assembly of nanoparticles. A tunable mask is formed by colloidal magnetic nanoparticles in a carrier fluid, commonly known as a ferrofluid [7]. Tuning of the pattern is achieved by controlling the external field. In this two-phase system the nanoparticles are initially randomly dispersed, but aggregate and assemble to form quasi-periodic patterns when an external magnetic field is applied. Depending on the magnitude and direction of the applied field, two-dimensional (2D) hexagonal closed-packed dot arrays [8, 9] and one-dimensional (1D) grating structures can be assembled [10]. The geometry of the assembled structures depends on the magnetization of the nanoparticles, allowing tunable assembly [8–13] in a practical and cost-effective manner.

The proposed process, called self-assembled ferrofluid lithography (SAFLi), is illustrated in figure 1. A polydimethylsiloxane (PDMS) microfluidic channel confines the ferrofluid over the photosensitive resist, as shown in figure 1(a). The photoresist stack contains an antireflection coating (ARC) layer to reduce reflection from the substrate during lithography. An external magnetic field $\boldsymbol{B}$ normal to the substrate is applied to assemble the nanoparticles to a quasi-periodic column array, shown in figure 1(b). The separation of the solid and liquid phases results in sharp optical absorption contrast, spatially modulating the transmission of light through the ferrofluid layer. Ultraviolet (UV) radiation is then used to crosslink the photoresist regions not masked

[4] Author to whom any correspondence should be addressed.

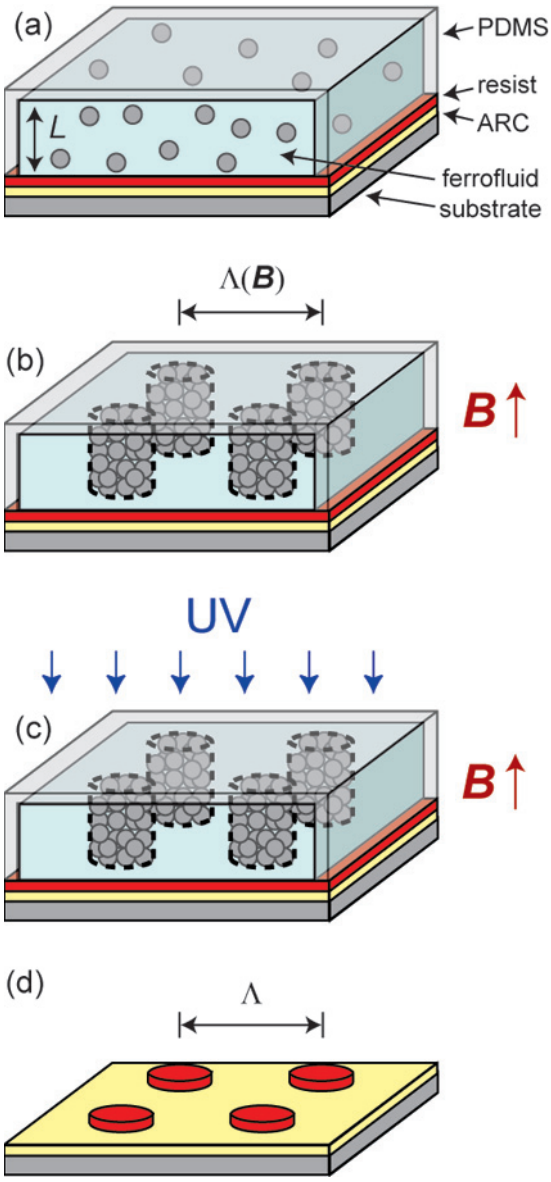

Figure 1. Process diagram for self-assembled ferrofluid lithography. (a) A PDMS channel confines the ferrofluid over a photoresist and ARC stack on a substrate. (b) An external magnetic field is applied to magnetize and assemble the nanoparticles to form a column array. The spacing Λ between the columns is a function of the field magnitude $\boldsymbol{B}$. (c) UV radiation crosslinks the resist region not protected by the nanoparticles, and (d) the assembly pattern is replicated in polymer.

by the nanoparticles, as shown in figure 1(c). After removing the ferrofluid, the developed photoresist replicates the pattern of the assembled structure, as shown in figure 1(d). The spacing Λ between the patterned photoresist is controlled by the magnitude of the applied field.

The main advantage of SAFLi is versatility, as a single assembly system can be actively controlled to pattern different geometries. In addition, the essential components of this system are the ferrofluid, two parallel plates, and a magnetic field source, making the process cost-effective and suitable for manufacturing. Recently, ferrofluid aligning to patterned magnetic material has been proposed for lithography [14]. However in that work pre-patterned substrates are required. The SAFLi process is fundamentally different in that the patterns are self-generated.

2. Materials and methods

The ferrofluid used in our experiment is water-based and contains $2 \pm 1\%$ iron oxide nanoparticles by volume (FerroTec Corporation, EMG707). The surfactant coated particles are a mixture of Fe_3O_4 and γ-Fe_2O_3, and have average diameter of $\sim$10 nm. A silicon substrate coated with 110 nm of ARC (Brewer Science, ARC i-con-11) and 200 nm of photoresist (Sumitomo, PFi-88A2) is used for the exposure. PDMS channels with 3×3 mm^2 area and depths 5 and 10 μm are fabricated using soft lithography, and used to confine the ferrofluid over the photoresist layer. The depths of the PDMS channels determine the confinement gap L of the ferrofluid. The nanoparticles are then assembled using an out-of-plane magnetic field to form a quasi-periodic dot array, induced by an electromagnet underneath the silicon substrate. A broadband UV mercury arc lamp is used to crosslink the resist with an exposure dose of approximately 40 mJ cm^{-2}.

3. Results and discussion

A microscope image of the assembled dot array inside a 10 μm PDMS channel is depicted in figure 2(a). The dots in the figure are solid columns consisting of iron oxide nanoparticles. The applied magnetic field is 30 mT, and the dot spacing is around 3 μm. The assembled pattern is replicated in photoresist using the SAFLi process, and is depicted in figure 2(b). Higher-magnification scanning electron micrographs of another patterned dot array detailing the profile fidelity are depicted in figure 3. The inset diagram illustrates the 2D spatial-frequency spectrum of the pattern, calculated by taking the 2D Fourier Transform of the micrograph. The external magnetic field applied for this sample is 25 mT in a 5 μm channel, and the resulting spacing between dots is $\sim$2 μm. Defects such as connecting and non-circular dots can be seen from the patterned resist. This is because the assembled particles are not perfectly stationary during lithography, and the exposed pattern is averaged over the relatively long exposure time, currently $\sim$3 s. These defects may be removed by using a strong UV source to reduce the exposure time.

While the patterned dot diameter and spacing are consistent, the dot array is randomly oriented and therefore quasi-periodic. This is evident from the spectrum of the same sample shown in the inset diagram of figure 3, where the peak spatial-frequencies resemble concentric circles instead of distinct dots for a periodic lattice. The radius of the inner-most circle represents the fundamental spatial-frequency f_r and can be used to calculate the average spacing between the patterned dots. The distribution of dot spacing can be deduced from the bandwidth of the spectrum, and typically has a standard deviation of 0.3 μm.

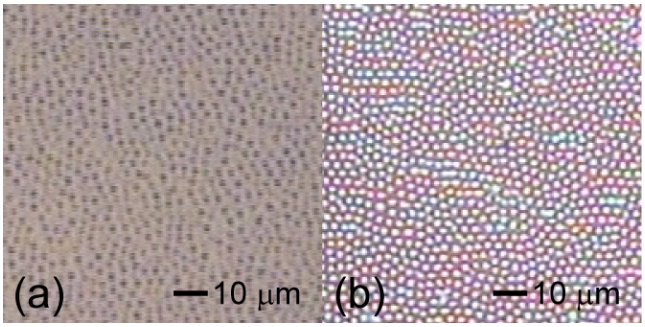

Figure 2. Top-view microscope images of (a) assembled dot array in a PDMS channel with a 10 μm gap induced by an external magnetic field of 30 mT, and (b) patterned photoresist using the SAFLi process.

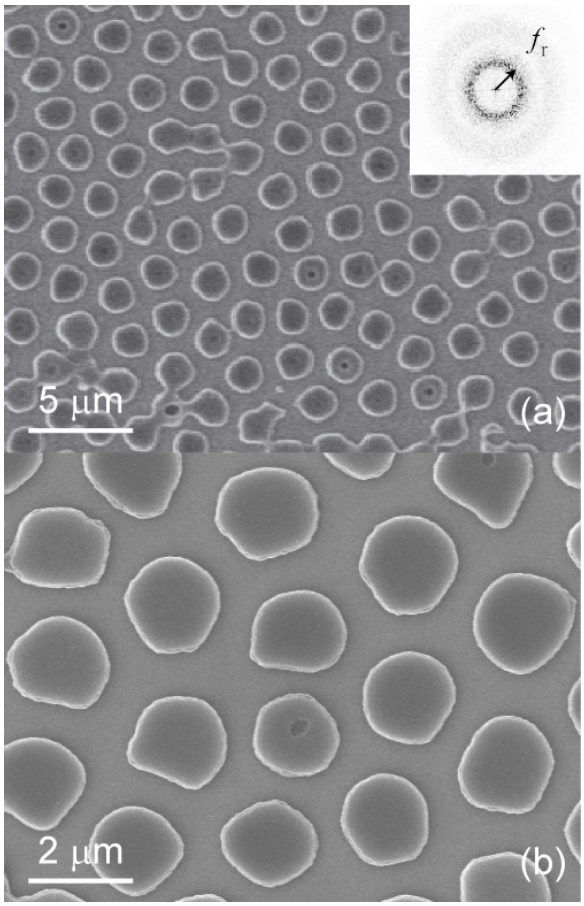

Figure 3. Top-view micrograph of a quasi-periodic dot array in photoresist patterned using SAFLi. A magnetic field of 25 mT was applied parallel to the substrate normal to assemble the particles. Defects such as (a) connecting and (b) non-circular dots can be seen. The inset diagram depicts the 2D spatial-frequency spectrum of the sample.

To demonstrate the active nature of SAFLi, the spacing between the patterned dots was controlled by tuning the external magnetic field during lithography. Figure 4 illustrates the dependence of the average spacing between dots on the magnitude of the applied field for $L = 5$ and 10 μm. The solid curves are power law fits to the experimental data, with residual-squared value over 0.98 for both. The curve fit

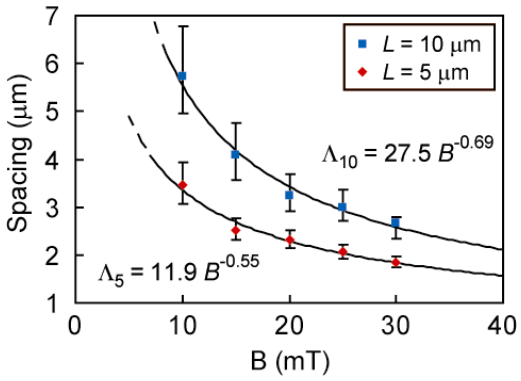

Figure 4. Plot of average dot spacing versus magnitude of the applied magnetic field for confinement gaps of 5 and 10 μm. The solid lines are least-square power law fits.

equations are shown in figure 4, with exponents of -0.55 and -0.69 for $L = 5$ and 10 μm, respectively. As shown in the plot, the dot spacing can be tuned between 5.7 and 2.7 μm for a confinement gap of 10 μm by increasing the field magnitude from 10 to 30 mT. For the channel with $L = 5$ μm, the range of the dot spacing decreases to between 3.5 and 1.9 μm. The confinement gap is therefore critical, as it determines the length scale of the assembly. The trend agrees to physical models describing pattern formation in a confined ferrofluid [11–13]. The curve has no physical significance in the lower field regime, since a minimum field of ∼5 mT is required before any pattern assembly occurs in the system under study.

The smallest spacing between two dots we have patterned is 1.9 μm, but the resolution of SAFLi can theoretically be higher. The physical limit for achieving smaller assembly spacing is when the magnetization of the nanoparticles reaches saturation. This is the case in our experimental system, as the pattern spacing does not decrease when the external field is further increased. To further reduce the assembled pattern spacing in ferrofluids one could reduce the confinement gap. By decreasing the confinement gap to the sub-micrometer range, it may be possible to fabricate structures with spacings in the order of 100 nm [11–13].

In addition to arrays of solid dots, the SAFLi process can also fabricate dots with hollow cores by extending the exposure time. Micro-ring structures patterned in photoresist by ∼30% overexposure in a 5 μm channel are shown in figure 5(a). Some patterns have been completely washed away due to the overexposure, resulting in isolated rings. The structure depicted in figure 5(b) has a diameter of ∼1 μm and ring width of 250 nm. While the exact mechanism is not yet fully understood, we believe the hollow core may be caused by a combination of relatively low absorption of iron oxide at UV wavelength [15] and a partial solid phase volume fraction in the assembled columns [16]. Light might not be fully absorbed over the propagation length, resulting in a low-order mode being guided. This effect can also be readily seen in figure 3, as small holes are starting to form in the center of some patterned dots. These ring array structures might find applications in nanomagnetics, micro-ring optical resonators, and cell confinement.

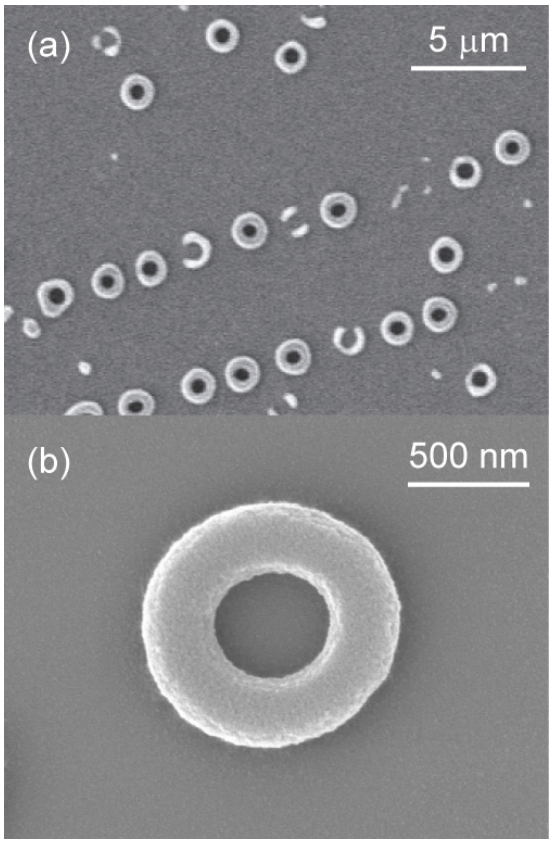

Figure 5. Top-view micrograph of (a) micro-ring structures in photoresist patterned using SAFLi. (b) High-magnification micrograph of a ring structure. The outer diameter of the ring is ∼1 μm and the ring width is ∼250 nm.

4. Conclusion

We have introduced a novel fabrication process to pattern micro/nanostructures with controllable spacing using field-induced self-assembly of magnetic nanoparticles. Future work will focus on reducing the feature size to the 100 nm range, fabricating periodic dot arrays by introducing additional physical constraints, and modeling of transmitted light intensity profile in the photoresist layer to further control the pattern geometry. While our experiments resulted in quasi-periodic dot and ring arrays so far, SAFLi can pattern any particle assembly geometry that can exist in the ferrofluid layer. It may be possible to fabricate 1D grating structures by applying the magnetic field perpendicular to the substrate normal, and more complex periodic geometries with spatially varying parameters by designing the magnetic field profile.

Acknowledgments

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