Ferrofluid Masking for Lithographic Applications

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ABSTRACT

A novel self-aligned "soft masking" method that is compatible with traditional photolithographic processes is demonstrated. This method uses a suspension of ultra-fine iron oxide grains (ferrofluid) to protect or de-protect selected areas of a magnetically patterned substrate according to a programmable sequence. Automatic mask formation and registration is controlled by ferromagnetic alignment marks patterned on a substrate. External magnetic field bias applied to the system causes ferrofluid to aggregate only over designated areas on the surface, thereby masking those areas from UV or chemical exposure.

Keywords: ferrofluid, self-assembly, self-aligning, masking

INTRODUCTION

Heterogeneous substrates of the kind used for combinatorial chemistry, drug discovery and genomics, where characteristic features are below a few microns, are difficult to manufacture economically. Most approaches have utilized photolithography to produce these substrates[1], however photolithography is an expensive, chemically intensive, and laborious process typically requiring multiple steps. For the substrate to be functional, many different patterns must be aligned on top of one another with high precision. Ensuring proper geometric relation between the patterns on the surface requires repeating the alignment and registration steps for each new pattern, which becomes increasingly difficult to control when the number of patterns increases and the critical feature size becomes microns or even sub-micron in resolution.

A novel "self-aligned" soft masking method is presented here that overcomes many of the problems of traditional photolithographic masking. The masking methodology uses an array of programmable alignment marks built into the substrate to drive the assembly of sequences of ferrofluid masking patterns. The ferrofluid used in these experiments is composed of ultra-fine iron oxide grains suspended in fluid (ferrofluid). For decades, accumulation of ferrofluid on has been used to detect domain structures in thin films[2]. In this paper, by contrast, the accumulation of ferrofluid is used to mask selected areas of the surface according to a programmable sequence. Controlled photoresist patterns are produced by this methodology for the first time, and the unique advantage of ferrofluid masking is demonstrated in the creation of self-aligned electrical interconnects.

However, the lithographic applications of ferrofluid are not limited to just optical masking. Ferrofluid masking can also be applied as a diffusion mask directly to the surface during solution-based synthesis. This approach is attractive because it does not employ high temperatures, chemical solvents, or UV radiation, while combining mask formation and material deposition into a single step. Potentially, this gentle synthesis approach can be used to pattern multiple layers of delicate biological materials like proteins and cells.

This work represents a departure from previous research, in which micron-sized colloidal particles were programmed to carry various molecules to precise locations on a surface[3]. It was experimentally demonstrated that the number of particles deposited (or not deposited) at each lattice site could be reliably controlled through a combination of magnetic and morphological template features. Regular heterogeneous colloidal patterns were assembled by this technique using only physical forces (i.e. magnetic, hydrodynamic and surface forces). The theoretical process of particle assembly onto magnetic surfaces has also been analyzed previously in order to guide experimental investigations[4-7]. Models indicate that magnetically driven assembly is a plausible patterning approach for a wide range of conditions.

In this paper, by contrast, nanometer sized ferrofluid particles are directed not to deliver molecules but rather to mask particular locations of the surface from the delivery of molecules. A single island by itself attracts ferrofluid to both of its poles. Useful ferrofluid masking, however, occurs only in the presence of a bias field, which causes ferrofluid to prefer specific locations on the alignment marks. Depending on the external field orientation and hence particle magnetization, ferrofluid particles will be preferentially deposited at various locations with respect to the alignment marks, as illustrated in Figure 1.
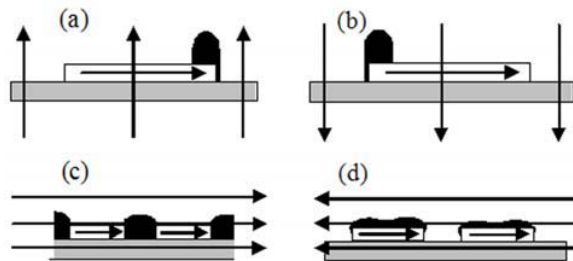

FIG 1. Illustration (a) depicts ferrofluid (black) attracted to the right-side of a ferromagnetic island (white rectangle with arrow denoting island magnetization) by external magnetic field bias applied perpendicularly to the island magnetization. When the external field bias is reversed, the ferrofluid is repelled from the right-hand pole and attracted to the left-hand pole as illustrated in (b). Ferrofluid will deposit in between the islands when external magnetic fields are applied parallel to the island magnetization, as illustrated in (c), and on top of the island when applied field is reversed, as illustrated in (d).

For example, when the external field is applied normal to the plane, ferrofluid particles accumulate over one or the other pole as demonstrated in Figure 1(a,b). Reversing the magnetization of the island rather than the external field bias can also achieve the effect of ferrofluid switching from one end of the island to the other in Figure 1a and 1b. When the external field is applied in the plane with orientation parallel or anti-parallel to the film magnetization, the ferrofluid assembles in between or on top of the film as demonstrated in Figure 1(c,d). Preferential deposition is used to selectively mask certain locations on the surface. After masking and exposure to UV radiation or chemicals, the ferrofluid can be re-suspended by simply reversing or removing the applied magnetic field bias. The ferrofluid can also be easily washed away. Spatial programming of the mask in each step can be accomplished by recording the magnetization direction of individual alignment marks, and thus the desired locations to be masked.

METHODS AND MATERIALS

Experiments were performed using Silicon or Pyrex substrates patterned with 100 nm thick Cobalt alignment marks by conventional photolithographic lift-off process. In the lift-off process, an image is defined by exposing photoresist to ultraviolet radiation through a patterned optical mask. The photoresist pattern is developed, and then Cobalt is evaporated onto the patterned wafer. Finally, the remaining photoresist is stripped to produce a pattern of Cobalt film. While negative or multi-layer resists are frequently utilized to obtain an undercut resist profile, positive Shipley 1813 photoresist yielded satisfactory results.

Individual islands acting as alignment marks in these experiments have planar dimension of 4 μm by 20 μm. Aqueous based ferrofluid domain detection fluid (EMG 807 purchased from Ferrotec) was applied to the substrate in concentrations ranging from 10% to 100% concentration in order to determine optimal masking conditions. When uniform external fields were applied to the system in the range of 10 - 200 G, one of the masking patterns shown in Figure 1 resulted. The assembled ferrofluid masking patterns were used on three different photoresist varieties of both positive and negative tone. The positive tone photoresist was Shipley 1813, and the two negative tone photoresists were NR-7 and SU-8. Ferrofluid masking films were observed as a thin coating of the substrate formed by placing a cover glass slide on top of a drop of ferrofluid.

RESULTS

The masking behavior of ferrofluid in the presence of external magnetic fields applied perpendicularly to the substrate is confirmed in Figure 2. In situations where all islands are magnetized in the same direction, the ferrofluid masks should uniformly assemble on the same side of the

island as shown in Figure 1a. In Figure 2, however, the ferrofluid is not accumulating on the same side for all the islands, because four islands in the left column are magnetized in the opposite direction of the rest of the islands. Hence, it is logical why ferrofluid should accumulate on one end for islands magnetized in one direction, and the other end for islands magnetized in the opposite direction. Effectively, this image demonstrates that the location of ferrofluid accumulation on a surface can be programmed with magnetic alignment marks.
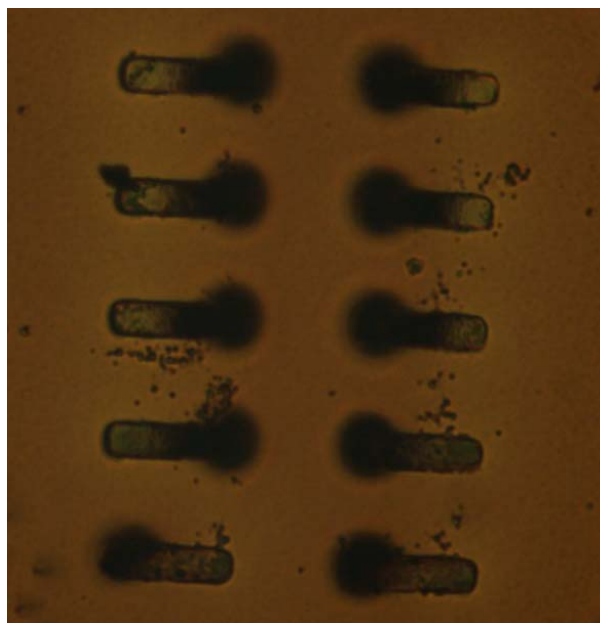

FIG 2. Optical image of ferrofluid accumulation on Cobalt islands. The accumulation is clearly dependent on the island's magnetization, since the 4 islands on the left have ferrofluid accumulating on the opposite side of the island as the 4 islands on the right.

Possible lithographic applications of ferrofluids include optical masking and diffusion masking. To demonstrate the ability of ferrofluid to act as an optical mask, Shipley 1813 photoresist was spun onto a patterned wafer of Cobalt islands, and ferrofluid was dispensed directly on top of the photoresist film. A transparent glass slide was placed on top of the ferrofluid in order to promote the formation of a uniformly thin ferrofluid masking film. When external magnetic fields were applied as shown in Figure 1a, ferrofluid accumulated over one pole of the island while avoiding the other pole. The optical contrast between the two poles was used as a photolithographic mask against flood exposure by UV radiation. A diagram of this process is illustrated in Figure 3. The wafer with ferrofluid mask was exposed to I-line UV radiation ($\lambda \approx 365$nm).

Ferrofluid masking of positive photoresist materials proved to be interesting because of the very nature of ferrofluid masking. For example, the total exposure time was found to depend strongly on the ferrofluid masking

concentration. Highly concentrated ferrofluid masking films required longer exposure times, whereas dilute ferrofluid masking films required shorter exposure times. This discrepancy is due to the discovery that higher ferrofluid concentrations cause the fluid outside the areas of particle aggregation to be less transparent to UV radiation. Typically, 90-120 mJ/cm^2 is sufficient to fully expose Shipley 1813 photoresist film. In these experiments, UV exposure in the range of 150-1500 mJ/cm^2 was needed to expose the photoresist through the various ferrofluid masking film concentrations. Example photoresist patterns produced by this masking methodology on positive photoresist materials are shown in Figure 4. In all experiments, the bake times, spin speeds, and other photoresist processing parameters were kept constant.

The images in Figure 4(a,b) are examples of photoresist patterns produced by concentrated ferrofluid masks. The gray-scale photoresist patterns are the result of highly non-uniform masking of the surface. Photoresist patterns produced by dilute ferrofluid masks, on the other hand like that shown in Figure 4(c,d), were found to create more sharply defined features. The photoresist spot sizes over the poles produced by dilute ferrofluid masks averaged 8-μm in diameter with great uniformity among spots across the wafer. The slope of the photoresist sidewalls was approximately 45° as measured by AFM.
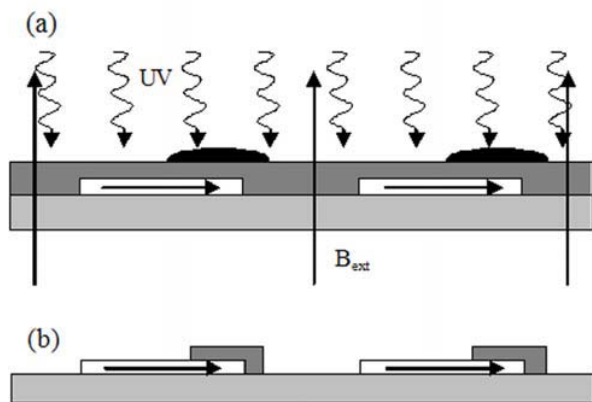

FIG 3. This diagram depicts ferrofluid acting as a photomask. External magnetic fields (B_{ext}) are applied perpendicularly in (a) to the micro-magnet's magnetization, causing the ferrofluid (black) to be attracted to one of the micro-magnet's poles. The accumulation of ferrofluid at the one pole is used to mask exposure of the underlying positive photoresist from ultraviolet (UV) radiation. The resulting positive photoresist structure after development is shown in (b).
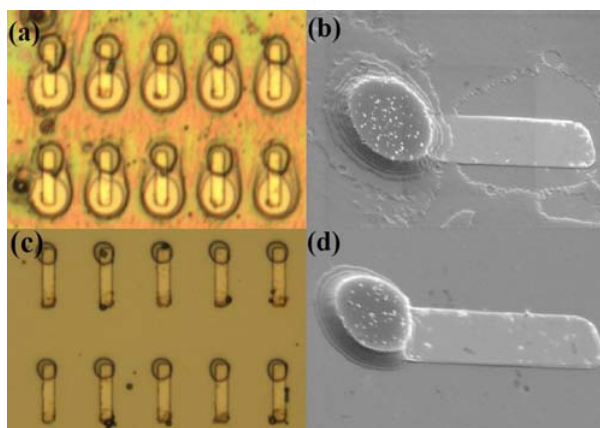

FIG 4. The four images (a-d) depict the results of ferrofluid optical masking of Shipley photoresist. Optical and SEM images of photoresist patterns formed by concentrated ferrofluid masking suspensions are shown in (a) and (b), and by dilute ferrofluid masking suspensions are shown in (c) and (d).

Useful structures, such as arrays of metallic spots and electrical interconnects were fabricated by masking negative tone NR-7 photoresist, which is especially formulated for lift-off. A two-step process was used to produce a self-aligned array of Au spots. First, ferrofluid masks were assembled on the substrate in a configuration like that shown in Figure 1a, and the underlying photoresist was exposed to 400 mJ/cm^2 of radiation through a ferrofluid masking film at 33% concentration. The resulting photoresist patterns were highly regular as shown in Figure 5(a,b). Next, Au metal was evaporated on top of the photoresist pattern and the remaining photoresist stripped, thus producing an array of Au spots. Such an array of may find use in the assembly and fabrication of heterogeneous substrates. Electrical interconnects can be created similarly by applying the masking configuration like that shown in Figure 1c to lift-off photoresist formulation. The photoresist structures produced from this masking configuration are shown in Figure 5(d,e). After Au evaporation and lift-off, the electrically interconnected Co islands are shown in Figure 5f. One of the main problems with self-assembly of useful devices is the question of how to interface with the assembled components. Self-aligned photolithographic patterning may provide one route to electrically connecting self-assembled device.
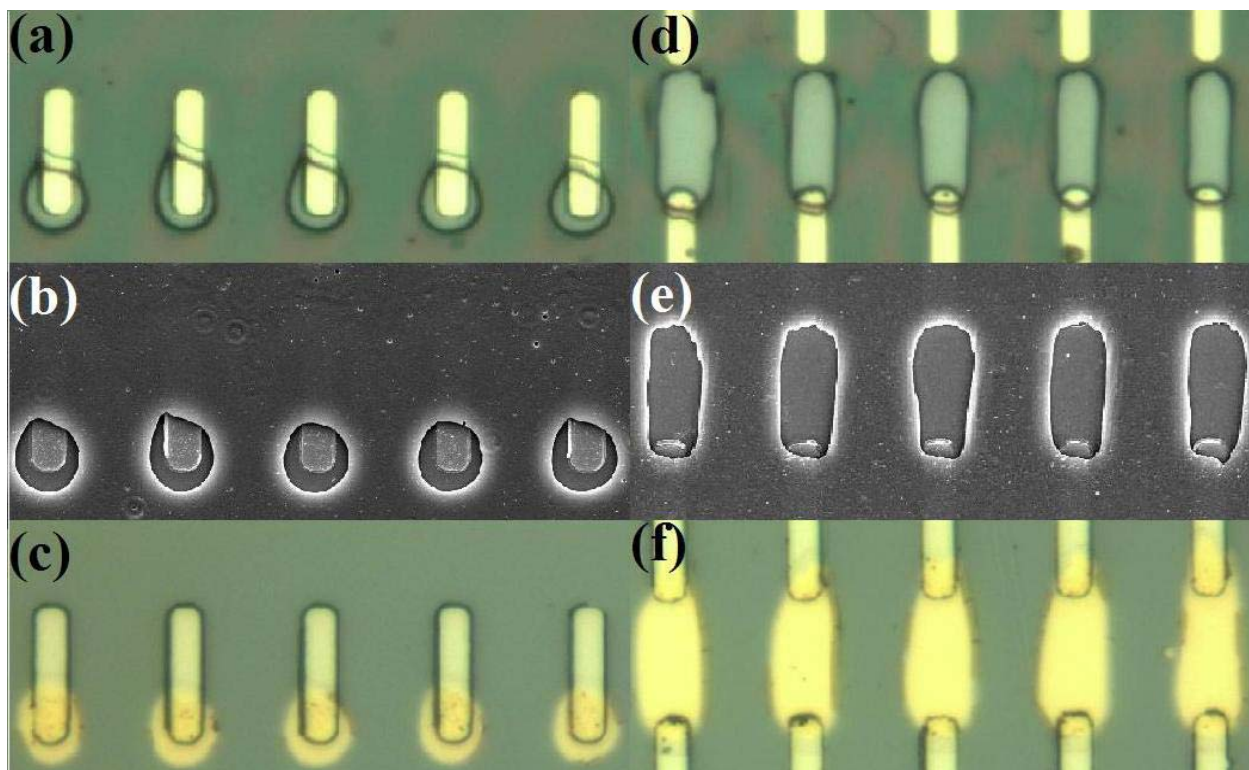
FIG. 6 (a-f) demonstrates some lithographic capabilities of ferrofluid optical masking with negative tone NR-7 photoresist. Photographs (a), (b), (d) and (e) shows the optical and SEM images of photoresist patterns produced by different applied magnetic field bias. Images (c) and (f) are the results after Gold evaporation and lift-off. The sequence of images (a-c) is the resulting pattern due to magnetic fields applied normal to the plane, while the sequence of images (d-f) is the resulting pattern due to magnetic fields applied parallel to the major axis of the islands.

CONCLUSION

In summary, patterning by ferrofluid masking enjoys significant advantages over other masking techniques. It makes resist free lithography possible. Another advantage is automatic alignment of the ferrofluid to the pre-patterned programmable ferromagnetic alignment marks. Single domain magnetic islands have been fabricated as small as 20 nm in width[8]. Such ferromagnetic alignment marks can potentially be used to build heterogeneous patterns with 50 nm resolution or better. Ferrofluid has been shown in this paper to perform consistent optical masking of microscopic features through photoresist micrometers in thickness. The formation of reliable ferrofluid masks at a relatively long range from the alignment features suggests that masking can also be accomplished with alignment marks that are embedded in the substrate or located some distance on top of the substrate. This would allow patterning to be performed on surfaces with homogeneous material characteristics or uniform surface chemistry.

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