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Direct release of synthetic antiferromagnetic nanoparticles fabricated by defect-free thermal imprinting

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We report an improved process, using a defect-free thermal imprinting process that directly releases homogeneously patterned lithographic nanoparticles from a large-area wafer to water. Our method has a substantially larger yield and avoids all the pitfalls that are associated with the sacrificial layers in the traditional imprinting methods. By using an ethylene tetrafluoroethylene mold and a bi-layer resist lift-off, defect-free imprints were achieved in areas larger than 1×1 cm^2. Illustrating the effectiveness of this method, high-quality planar Fe/Ta multi-layered magnetic nanoparticles, 300 nm in diameter, were deposited by ion-beam sputtering and their basic magnetic properties are characterized. These particles prepared by direct release with tunable magnetic properties and good engineering possibilities are ideal for a wide range of applications, including those specifically for biomedicine. © *2012 American Institute of Physics*. [doi:10.1063/1.3673405]

I. INTRODUCTION

Synthetic nanoparticles with unique magnetic, optical or bio-functional properties have been widely exploited in various biological and biomedical applications, such as magnetic resonance imaging, magnetic particle imaging, and drug delivery.[1] These nanoparticles are usually fabricated by "bottom-up" chemical routes that enable mass production, but which also pose difficulties for precisely and independently controlling the particle shape, size, structure, and composition. To overcome these limitations, direct fabrication of synthetic nanoparticles by "top-down" physical routes is promising as an alternative approach. For example, Hu *et al*., recently developed a novel approach that uses nanoimprint lithography, lift-off and release to fabricate water-stable multifunctional magnetic nanoparticles.[2,3] These synthetic antiferromagnetic (SAF) nanoparticles have a number of advantages, such as high moment, monodisperse size, and zero remanence over a wide range of sizes from tens of nanometers[2,3] to micrometers.[4] However, there are still several critical limitations associated with the original fabrication and release procedures, which can be significantly improved. First, functionalization of the particles after release in water always yield poor coating result due to the large size and low solubility of the SAFs. Coating before release (on-wafer) is easier and more desirable. However, the conventional methods use a sacrificial layer, either metal[2] or polymer,[5] to release the SAF nanoparticles from the substrate into aqueous solution. This requires wet etching of the sacrificial layer and other additional steps to transfer the product from etchant to water, which makes it impossible to do functional coating before release, as the etchant (e.g., caustic (pH ~ 12) ammonia-$CuSO_4$ solution used in Ref. 2) will destroy any biological coatings (DNA, protein, etc). Another disadvantage involves the deposition and ion-milling of the Ta protection layer. The long deposition cycles, unstable ion milling rates, and possible release failure makes the process even more complicated. Second, the conventional imprinting process uses Si molds, which normally bring a significant number of defects in the form of pinholes (in micro- and millimeter scale), to the as-imprinted wafer. These defects are quite unfavorable for nanoparticle lift-off where large-area homogeneous fabrication is desired. After deposition and lift-off, good particles (with a narrow size distribution) are mixed with very large or irregular ones in solution. In such a case, an additional particle separation step is required to get reliable products. Finally, due to the defect generation and degradation, a typical Si mold is technically unusable after approximately ten imprinting cycles, which is also quite cost ineffective.

Here we report a much improved process that overcomes both the disadvantages in the conventional imprinting methods. We fabricated disk-shaped SAF nanoparticles with a diameter of ~300 nm directly on Si wafer and released them via a dry etching procedure, which avoided all the related pitfalls associated with the sacrificial layer. This process could potentially enable better functional coating which is done before particle release. The nanoparticles are released directly to water without any etchant transfer. By using an ethylene tetrafluoroethylene (ETFE) mold that is replicated from a master Si mold and a bilayer resist lift-off, defect-free imprints, and subsequently high-quality nanoparticles were achieved over the whole mold size ($> 1 \times 1$ cm^2). The ETFE replicas can be continuously fabricated using one Si mold, and more than 20 times good imprinting can be achieved by one ETFE mold according to our test. Therefore the lifetime of the Si master mold is significantly increased. To demonstrate this process, high moment Fe/Ta multilayer SAF nanoparticles were fabricated and characterized. Metallic Fe was

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chosen for its high saturation magnetization and relatively lower toxicity, as compared to other magnetic metals, such as Co and Ni.

II. EXPERIMENT

Figure 1 illustrates the complete fabrication procedure. The first step is fabrication of the ETFE mold from the Si master mold, Fig. 1(a). A sheet of ETFE (DuPont Tefzel) was first cleaned by sonication in acetone and isopropyl alcohol, respectively, for 5 min, blow-dried, and placed onto a clean Si wafer. The Si master mold (350 nm holes in a hexagonal lattice, from Lightsmyth Technologies) was placed onto the ETFE sheet, which was then embossed using a Nanonex NX-B100 compact thermal nanoimprinter, at 250 °C and 450 psi for 1 min. Detailed embossing recipes can be found elsewhere.[6,7] Next, a bilayer resist, constituting an undercut resist LOR 1 A (MicroChem) and an imprint resist NXR-1025 (Nanonex) were spin-coated on a Si wafer.[8] The coated wafer was then thermally imprinted by the ETFE mold, Fig. 1(b). Demolding was easily achieved by peeling off the embossed ETFE sheets. Flexible ETFE mold (~350 nm pillars in a hexagonal lattice) is obtained with a usable area that is equal to that of the master Si mold. Next, we performed anisotropic oxygen-plasma reactive ion etching (RIE) to remove the imprint resist residue, and then a selective wet-etch on LOR 1 A to develop an undercut profile (Fig. 1(c)). The patterned resist template was then taken into an ion-beam sputtering (IBS) chamber to deposit Fe/Ta multilayers, in the sequence of $Ta_{10nm}/(Fe(t_{Fe})/Ta_{0.6nm})_x/Fe(t_{Fe})/Ta_{10nm}$, followed by the resist stripping (Fig. 1(d)). Series samples with different Fe thickness, t_{Fe}, and repeat cycle, x, are fabricated. Until this step, the disk-shaped SAF nanoparticles were obtained on the wafer. Next, we performed anisotropic SF_6+O_2 mixed gas plasma RIE, with a high etch selectivity to Si, to etch the substrate. Using desired etching parameters, the Si substrate was etched into patterned cone-shaped structures with one SAF loosely attached on each cone, Fig. 1(e), via the van der Waals force. The final step was to release the SAF from the substrate by directly placing the chip into water. The particles were then collected via centrifugation and re-suspension in water. Magnetic properties were measured by a physical property measurement system (PPMS, Quantum Design) using the VSM mode.

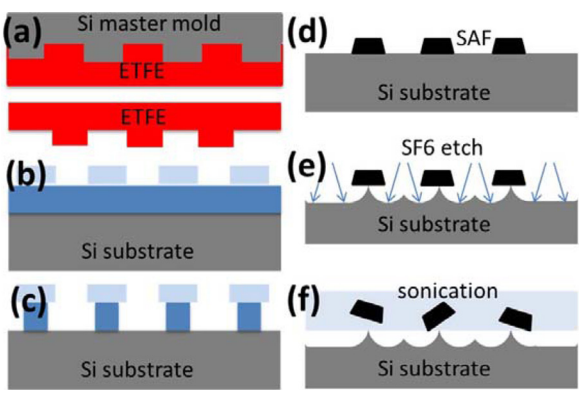

FIG. 1. (Color online) Fabrication steps for the preparation of SAF arrays and nanoparticles.

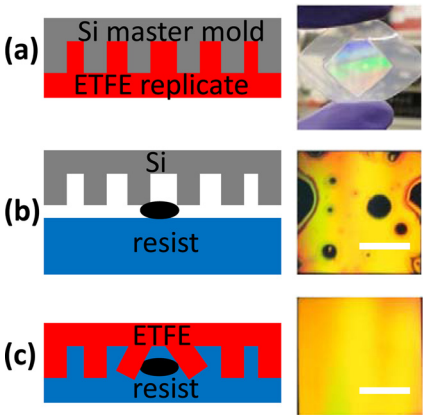

FIG. 2. (Color online) (a) Flexible ETFE replica fabricated by a Si master mold; (b) wafer imprint with a Si mold; (c) wafer imprint with ETFE mold (scale bar: 5 mm).

III. RESULTS AND DISCUSSIONS

A. Defect-free imprint

Figure 2(a) showed the fabrication of the ETFE mold via direct embossing with a Si mold. The ETFE mold is transparent, flexible, and homogeneous, as indicated by the photograph. The use of the ETFE molds makes it possible for large-area fabrication of homogeneous SAFs. As a comparison, we first demonstrated the imprinting result by a traditional Si mold. As shown in Fig. 2(b), even tiny defects in between the mold and wafer will lead to a visibly large unimprintable area because of the rigidness of both wafer and mold. As a result, unpredictable but significant defects in the form of pinholes and thin strips were observed. These defects will be transferred to the final deposition and lift-off, resulting in unwanted magnetic objects (large particles, irregular film pieces, etc.) in solution. Besides, the defects get more substantial with time as the mold is used again and again. These disadvantages cast great limitation on future scaling of the process. However, by using ETFE soft mold, local defects can be tolerated due to the flexibility of the mold and the ambient area will be normally imprinted. After imprinting, the demolding is also much easier for the ETFE mold due to its flexibility. Defect-free imprints can be achieved on the whole mold area (Fig. 2(c)), which is ideal for particle lift-off purpose.

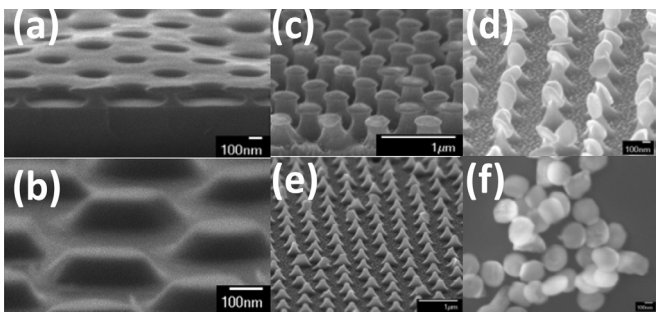

FIG. 3. SEM images showing the steps of SAF fabrication.

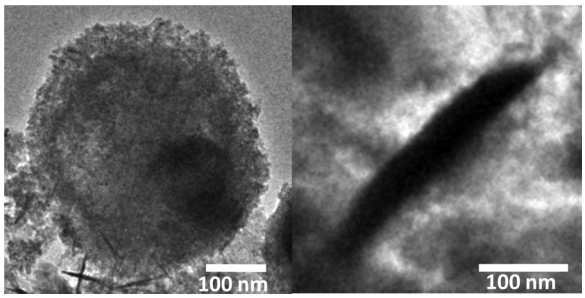

FIG. 4. TEM images of the SAF after release in water (scale bar: 100 nm).

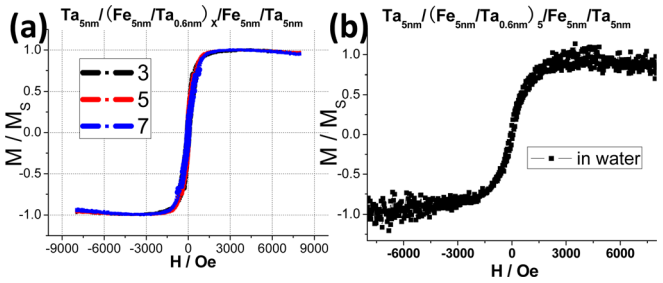

FIG. 5. (Color online) (a) Hysteresis loops of the SAF measured on wafer with different $x = 3, 5, 7$; (b) in-water hysteresis loop measured after release and centrifugation for nanoparticles with $x = 5$.

B. Direct release

Substrate etch has been used to transfer functional nanostructures onto desirable carriers for semiconductor and energy applications.[9,10] Here, we describe our development of a dry etch procedure to directly release the SAF to water *without* using any sacrificial layer. First, the nanostructures are fabricated on substrates using a normal process. Second, a selective chemical reaction with a proper etch process (dry or wet) is used to etch the substrate and set free the nanostructures, making them only loosely attached on wafer. Next, any functional coatings can be easily done after this step because the nanostructures are still in the form of patterned arrays on wafer. Finally, these functionalized nanostructures can be directly released to the target solution, without any additional transfer process. We took SEM images at each step during our fabrication process. Figure 3(a) showed the bilayer resist profile on the Si substrate after the ETFE imprinting and the undercut development. Figure 3(b) showed the as-fabricated SAF on Si substrate after deposition and resist lift-off. The diameter of the disk-shaped SAF is ~300 nm. Next, also the key innovation in our process, is the use of anisotropic SF_6+O_2 mixed gas plasma RIE to etch the Si substrate. The plasma selectively etches the Si substrate and the SAF works as a natural etch mask. Figure 3(c) shows the results of an intermediate etch where the particles are still attached on the Si pillars. Figure 3(d) illustrates the ideal etch result where the particles are loosely attached on cone-shaped Si substrates via weak Van der Waals force. In our experiment, the ideal etch recipe to lift-off the SAF is 30 s and 100 W; over-etch with slight longer etch time (e.g., 50 s) will not affect the SAF. The SAF can be completely released from the original wafer (Fig. 3(e)) to solution (Fig. 3(f)). We took the TEM images of the particles after releasing in water (Fig. 4). The diameter and thickness of the wedge-shaped nanoparticle are ~300 nm and ~50 nm, respectively, as seen from the TEM images. These images also showed that the shape and dimension of the particle remain unchanged during the steps of processing. However, significant over-etch may damage the SAF. Detailed study on the effect of over-etch is being conducted to give a complete evaluation of this process.

C. Magnetic properties

We chose Fe/Ta multilayered SAF to demonstrate the magnetic properties of our SAF. A series of samples in the sequence of $Ta_{10nm}/[Fe(t_{Fe})/Ta_{0.6nm}]_x/Fe(t_{Fe})/Ta_{10nm}$ was deposited by ion-beam sputtering with a deposition rate < 1Å/s. The hysteresis loop of the as-fabricated SAF with $t_{Fe} = 5$ nm and different $x = 3, 5, 7$ are shown in Fig. 5. The particles show a superparamagnet-like behavior with low remanence and coercivity, which are needed for relevant applications. The number of repeats, x, does not change the loop very much but only slightly affects the behavior in the low field region. As an example, we lifted off selectively the nanoparticles with $x = 5$ and measured the hysteresis loop in water, as shown in Fig. 5(b). The saturation field is slightly increased as compared with the on-wafer loop (Fig. 5(a)), which is also consistent with previous reports.[5]

In conclusion, we have developed an improved process to fabricate SAF for biomedical applications. Our innovative process improves the quality of the SAF and could potentially enable better functional coating of the SAF.

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