Repeatability of magnetic-field driven self-assembly of magnetic nanoparticles

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We demonstrate 27 ± 11 nm precision using stray magnetic fields from hard disk drive media to assemble 13 nm Fe3O4 magnetic nanoparticles in de-ionized water. By aligning the substrate polishing striations found in atomic force microscopy (AFM) images of the media topography, we determine the variance of multiple nanoparticle coatings. The widths of the assembled features are ~200 nm, and features are always distinct when separated by a median distance of 500 nm. As these nanoparticles predictably follow the field gradient, trapped nanoparticles offer a nanoscale precision metrology for mapping the stray magnetic fields of high density media using AFM. Thus our approach offers a means to verify magnetic force microscopy images, as well as a method for nanomanufacturing complex nanoparticle assemblies. © 2011 American Institute of Physics. [doi:10.1063/1.3556770]

I. INTRODUCTION

Ferrofluid (FF), in the form of Fe3O4 nanoparticles (NPs), has been utilized for detecting domain structures because the particles follow the gradient of magnetic fields emanating from surfaces. Crystal defects,1 permalloy domains,2 and disk drive media3 have been visualized using magnetic particles in this way. Recently, NPs have been employed for producing deliberate patterns using the stray fields as nanoassemblers.4 These applications require the NPs to reliably self-assemble. Here we take advantage of longitudinal recording media’s narrow bit transitions to quantify the viability of these techniques for both nanomanufacturing and nanovisualization.

II. PREPARATION

Prerecorded disk drive media are cut into 1.5 cm circular coupons, and then sonicated in Fomblin Perflorosolv (PFS-1 flushing fluid, Solvay Solexis). Once the flushing fluid removes the hydrocarbon lubricant, numbered copper frames,5 70 μm across, are sputter-deposited onto patterned photoresist generated via optical lithography. The coupons are mechanically cleaned first with acetone and then with isopropyl alcohol using a foam-tipped swab that removes any previous coatings of NPs. After cleaning, the coupons are placed in an open-top fluid cell and covered with FF. The commercial FF used (Ferrotec, Nashua, NH, EMG-707) has an average size of 13 nm immersed in de-ionized (DI) water. We dilute the FF to 0.05% by volume before applying it to the coupon surface.

III. APPLICATION

The fluid cell, with the coupon inside, is filled to 2.8 mm using a pipette. After allowing the particles to self-assemble on the surface for 3 min, we introduce a few drops of phosphate buffer (pH 7.2, VWR, Inc.) as a fixing agent. The remaining particles in suspension are rinsed away with DI water using a peristaltic pump and the coupon is set aside to dry.

IV. MEASUREMENT

Atomic force microscopy (AFM) images are obtained with an Agilent PicoPlus scanning probe microscope, equipped with a 100 μm closed loop scanning stage, operating in noncontact (AC) mode. We utilize BudgetSensors Tap300 300 kHz tips having 40 N/m force constants and <10 nm tip radius to extract topography data of the assembled NPs on top of the disk media. Through a series of magnifications, specific features of the assembled nanoparticles can be singled out because of their particular merit. The feature we describe here contains two bit transitions close enough together to cause apparent particle bridging between them. To understand if the particles assemble this way repeatedly or randomly because of the transition proximity, the particles are cleaned off the disk, the coupon is recoated, and the same feature is reimaged several times.

Magnetic force microscopy (MFM) images of the coupon’s surface are acquired with 75 kHz HR MFM tips (Team Nanotec GmbH) with <25 nm radius, coated with Co alloy at the tip and Al on the cantilever back-side. Because the phase contrast of the magnetic field gradient is rendered during a retrace of the coupon topography, we have a one-to-one relationship between MFM signal and the polishing striations on the coupon surface (Fig. 1). By comparing striations on the clean disk to those in the background of the same disk after coating, we have a direct correlation between particle placement and the magnetic interaction of the surface and the MFM tip. We conduct the same imaging scheme after rotating the coupon 180° with the same MFM tip and parameters. With AFM and MFM scans ranging from 50
down to 3 μm, we compare both global structuring along with subfeature clustering.

V. ANALYSIS

Topography images are initially flattened using second-order polynomial background removal in GWYDDION. They are then passed to Apple KEYNOTE and layered atop each other according to scan sizes. Robust algorithms for alignment, such as point pattern matching, presented by Chang et al.,6 work well for this type of problem, but establishing the necessary registration parameters for the disk striations proved problematic in our case. Instead, manual transformations were performed and yielded an error of 24 nm from image resolution obtained via AFM and the interpolation functions within KEYNOTE. Each image is aligned by setting the top layer at various levels of transparency and then rotating and translating accordingly; scaling is directly derived from the AFM. Perfect alignment is achieved only when zero variation is observed between full transparency of the top layer (thus viewing the lower layer), and a completely opaque top layer [Fig. 1(a)]. All alignments are conducted at 400% magnification for subpixel level comparisons. As shown in Figs. 1(b) and 1(c), each MFM image is directly positioned relative to the appropriate AFM images. Individual snapshots are then generated by sequentially sending the topmost layer to the rear and exporting the whole KEYNOTE canvas as a TIFF image file. These new images are imported into IMAGEJ and IGOR PRO for analysis.

To test the reliability of the alignment, we cross-correlate two profiles along identical data points from different coatings. The path was chosen to cover as much of the surface as possible without intersecting any NPs in either image. Figure 2(a) presents the individual line scans, which were 981 nm long and taken at an angle of about −10° from horizontal. Figure 2(b) plots the un-normalized cross covariance of the profiles indicating they are ideally overlapped. To determine a quantitative error in the alignment, the profiles were linearly interpolated and then intentionally shifted by various amounts relative to each other. The cross correlation was able to correctly resolve a 0.98 nm shift out of alignment in either direction, which is 1/5 the pixel width of the original AFM images. Having verified that the striations are correctly aligned, we now determine the variance across multiple coating procedures.

According to methods described in Ref. 7, IMAGEJ converts a binary threshold image matrix into a skeletonized image. By definition, skeletal lines found in this way, after adaptive thresholding, are the centerlines of our particle assemblies. Taking into account all of the separate NP coatings, the skeletonized images are then combined into a single image matrix where the centerlines are distinguishable by indices.

From the placement of multiple centerlines in the composite image, a new reference line is drawn orthogonal to the innermost centerline in that region. Points of intersection with the reference line and the indexed centerlines are then related only to each other and not the background topography, i.e., particles’ preferred placement is unknown. The average differences between centerlines for multiple coatings are found through

\[
\frac{1}{N} \sum_{i \neq j} |j - i| \quad i < j.
\]

Traversing the reference line throughout the skeletonized image, while maintaining orthogonality, an average of 27 nm precision is obtained with a 1σ standard deviation of 11 nm. In addition to finding the centerline of each feature, we normalize the threshold images and sum them to produce a
repeatability map as in Fig. 3(a). After converting to gray scale, the map expresses (at each pixel) how often a particle is attached at that position, ranging from never, in white, to always, in black, and sometimes, in gray. Furthermore, Fig. 3(b) gives the cross section of two of these bit transitions comprising three particle coatings assembled 800 nm apart.

With 27 nm repeatability of NP self-assembly established, we compare the MFM and AFM images of the same region as shown in Figs. 3(c)–3(e). The MFM data presented here are interpreted as the magnetic force between the media and the tip, where dark contrast is attractive and light contrast is repulsive. However, the cantilever is mounted at an angle of 9° relative to the z direction, and therefore feels nonperpendicular forces. Even after accounting for this effect by dividing the image matrix in Fourier space by its lever canting function,8 we do not directly see a clear relationship between the clustered NPs and the MFM image or its rotated counterpart [Figs. 3(c)–3(e)]. This may be attributed to the fact that superparamagnetic NPs are not assembled by an attractive force along any one particular axis, and thus respond to forces in all three dimensions. The assembly process itself is also nonlinear in that the particles themselves produce stray fields attracting or repelling each other.9 Independent of why the bridging in Fig. 3(c) occurs, it occurs consistently and has potential to either provide new information about stray fields not detectable by MFM, or introduce challenges and opportunities in designing patterns for future self-assembled nanoarchitectures.

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