LETTERS

Fabrication of magnetic force microscopy probes via localized electrochemical deposition of cobalt

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Magnetic force microscopy probes were obtained via the solution phase electrochemical deposition of cobalt nanostructures at the probe apexes. Single tips were fabricated in an atomic force microscope fluid cell. Multiple tips were produced in a single batch with an alternating potential in an electrochemical cell. The probes achieve 50 nm spatial resolution. © *2007 American Vacuum Society.* [DOI: 10.1116/1.2766935]

I. INTRODUCTION

The progressive demand for higher data storage density requires the fabrication of ever smaller magnetic features and more powerful analytical tools for their characterization.[1] Magnetic force microscopy (MFM) is a relatively inexpensive and simple technique for imaging recording media[2] and other magnetic nanostructures.[3–5] The resolution of MFM is strongly dependent on the shape of the probe employed; an ideal tip is not only sharp, but also has a very small ferromagnet positioned precisely at its apex. The presence of any superfluous magnetic material around the tip apex greatly hampers the imaging resolution.[6]

Recently, there have been several advances in the design and fabrication of ideal probes. Ultrasharp, needlelike magnetic tips have been shaped by ion etching,[7,8] direct deposition of cobalt from a gaseous precursor,[9,10] dielectrophoresis of previously synthesized wires,[11] and metal coated carbon nanotubes.[12,13] Magnetic nanodot probes have been demonstrated with metal capped carbon nanotubes,[14] and fabricated with a stencil mask approach.[15] These techniques require serial handling or lengthy and complex fabrication steps not suited for batch production. There is still need for a simple, one step process for parallel fabrication of high resolution MFM probes.

This article presents a facile approach to the production of high resolution MFM tips based on the localized electrochemical reduction of cobalt (II) species in solution.

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II. EXPERIMENT

In situ cobalt deposition was performed on individual probes in the fluid cell of a Digital Instruments Multimode atomic force microscope (AFM) operated in tapping mode. The sample, a heavily doped *p*-type (boron) silicon wafer, and the tip (Tap 300, Veecoprobes) were immersed in a solution of 10 mM cobalt (II) acetate ($Co^{II}Ac_2$) and 100 mM tetrabutylammonium-hexafluorophosphate in dimethylsulfoxide (DMSO). A potential difference (dc) was applied between the tip and the sample using a Nanoscope IIIa controller, while the tip-sample separation was reduced until the cantilever amplitude of oscillation reached 5%–10% of the imaging set point [Fig. 1(a)]. Deposition of Co^0 on multiple probes was also achieved in parallel using an electrochemical cell [Fig. 1(b)] filled with an aqueous solution of $Co^{II}Ac_2$ buffered with 10 mM of *N*-2-hydroxyethylpiperazine-*N*′-2-ethanesulfonic acid. The concentration of the salt ranged from 100 mg/ml (saturation) to 15 mg/ml. An alternating potential was applied between the tips and a Pt counterelectrode (separation ∼10 mm) using a function generator from Stanford Research Systems. Scanning electron microscopy (SEM) investigation of the modified probes was performed either with a Hitachi SEM 5000 or a FEI Sirion XL30 with EDAX electron dispersive x-ray spectroscopy (EDS). Images were acquired at acceleration voltages of 5 kV, while elemental analysis was recorded at 15 or 30 kV. MFM was performed in air at room temperature with the same microscope described above.
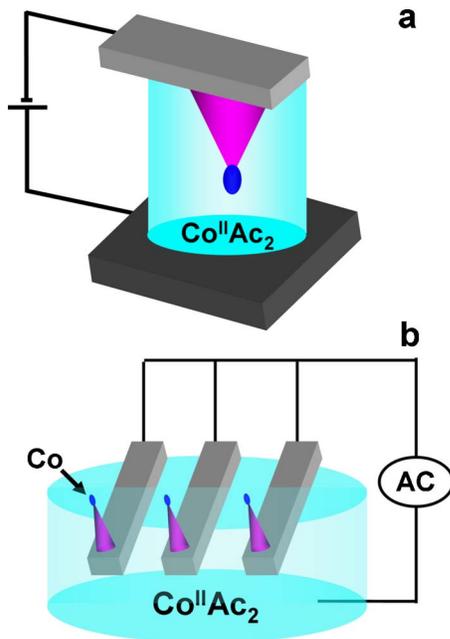
FIG. 1. (a) Cartoon of the biased AFM tip in the fluid cell containing a solution of $Co^{II}Ac_2$ in DMSO for *in situ* metallic cobalt deposition. (b) Schematic of setup in electrochemical cell for batch fabrication of probes with high frequency ac signal.

FIG. 2. Scanning electron micrographs of custom fabricated MFM probes. [(a) and (b)] Tips modified in the AFM fluid cell at −5 V for 15 s and −3.5 V for 0.5 s, respectively. The scale bar in the insert in (b) is 2 μm. [(c) and (d)] AFM probes modified in the same batch the electrochemical cell. Parameters $\nu=300$ kHz, $V=3$ V_{rms}, and $t=30$ s.

III. RESULTS AND DISCUSSION

Typical SEM micrographs of two probes modified in the fluid cell setup are shown in Fig. 2. Figure 2(a) depicts a tip treated at −5 V for 15 s. Although these conditions did not produce an extremely sharp probe, the abundance of metal deposition facilitates SEM investigation. This process positions magnetic material only at the apex of the tip without contaminating the other parts of the pyramid. Figure 2(b) shows a SEM micrograph of a significantly sharper tip modified at −3.5 V for 0.5 s. A 30 nm radius metallic protrusion is present at the very apex; the particle on the side of the picture may be another cluster that was nucleated at an edge. Localization of the deposition can be explained by faster nucleation rates of the metal at the tip apex; this is caused by the higher current density present in the small (~10 nm) tip-sample gap.

The localized deposition of cobalt was extended to parallel production in a macroscopic electrochemical cell. Two probes fabricated in the same batch in a saturated solution of $Co^{II}Ac_2$ are illustrated in Fig. 2(c) and 2(d). A 3 V_{rms} signal at 300 kHz was applied for 30 s and the SEM micrograph shows specific deposition of 50–100 nm of material at the apex; the deposition range is a result of the variability in the radius of curvature of the original tip as purchased. Conditions involving only a dc potential result in extended reduction of the metal on the entire cantilever; when an ac potential was applied, nucleation size and specificity were inversely proportional to the frequency. The alternating signal contributes to the localization of the reaction due to electrophoretic forces driving the metal ions towards the sharp apex of the tip where the rapidly varying field gradient is
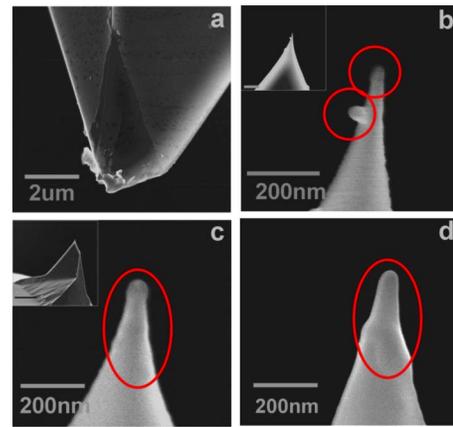
stronger.[16] Several batches comprising either two or three tips each were produced with yield per batch ranging from 33% to 100%. Higher voltages and longer processing times were associated with more extensive metal deposition as already observed in the fluid cell. The probe in Fig. 3(a) was treated at 7 V_{rms} for 2 min in a 50 mg/ml solution and was used for EDS analysis.[17] The growth pattern of the metal is noticeable from the SEM image starting from nucleation at the apex and at the sharp edges of the pyramid and extending to the sides. The shape of the probe suggests a polycrystalline deposition, consistent with previous reports.[18] The x-ray peak at 0.78 keV associated with the presence of cobalt only appears in the spectrum acquired on the pyramid of the tip [Figs. 3(b) and 3(c)]. The iron peak in Fig. 3(c) corresponds to the background from the sample holder. The lack of a distinct oxygen peak (0.52 keV) in Fig. 3(b) indicates that the bulk of the metal is not significantly oxidized, though this does not exclude the presence of a thin oxide on the surface. The two methods differ by the mechanism used to direct the deposition of metal on the tip apex; in the fluid cell localization occurs due to proximity between the tip and the counterelectrode, whereas in the electrochemical cell faster nucleation rates at the apex are obtained by applying an alternating signal. Growth rates are hard to compare for the two techniques because of too many differing parameters. Conditions used to produce the best probes in either setup result in deposition of Co in the fluid cell 60 times faster than in the electrochemical cell.

Functional topographic and MFM probes were successfully fabricated and tested on a commercial longitudinally recorded storage medium (hard drive) with transitions at ~300 nm pitch [Figs. 4(a) and 4(b)]. The magnetic bits are clearly distinguished and features as small as 80 nm are resolved on the tracks [Fig. 4(b)]. This is the minimum size of the written bits and does not represent a limitation in the resolution of the probe itself; ferromagnetic domains as small as 50 nm are also observed on the blank medium [Fig.
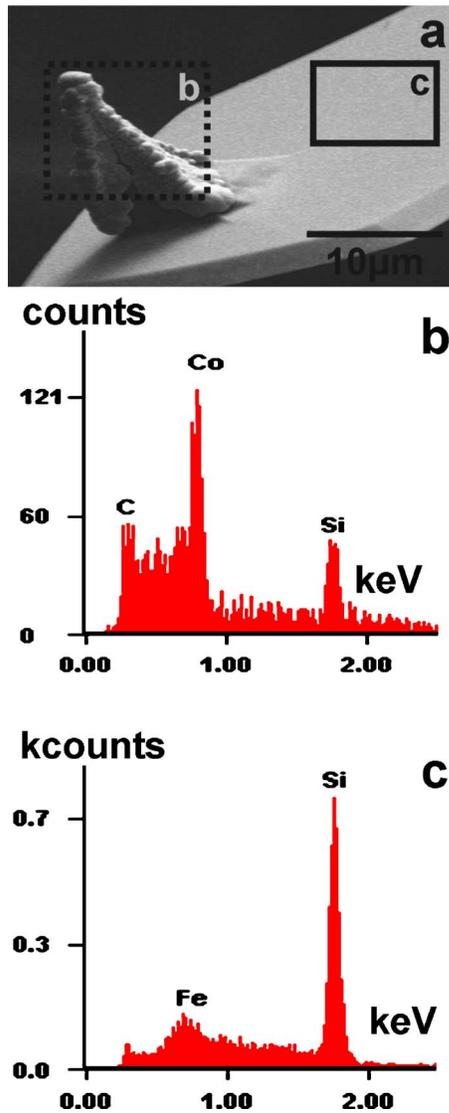
counts

b

kcounts

c

FIG. 3. Scanning electron microscope image (a) and the corresponding electron dispersive x-ray spectroscopy (EDS) spectra [(b) and (c)] of an AFM tip with a substantial amount of electrochemically deposited cobalt. The iron peak in spectrum (c) is due to contaminated background.

4(c)]. Power spectral density analysis of the MFM image [Fig. 4(d)] indicates a cut-off wavelength of 50 nm; the cut-off wavelength is the frequency at which the signal drops below the noise level and can be used to estimate the size of the minimum resolvable feature.[19] The custom tip employed to record this image was modified in the fluid cell setup at −3.5 V for 0.5 s; this probe has more cobalt than the one shown in Fig. 2(b) with a radius of curvature of ∼70 nm. The latter is comparable to the size of the minimum resolvable feature; since in MFM the probe is hovering on the top of the surface, features several times smaller than the tip radius of curvature can be resolved with an optimized tip shape.[13] Probes fabricated in the electrochemical cell showed similar MFM capabilities. Imaging the sample using the sharper fabricated probes did not result in an increase in performance; sharper probes have less magnetic material present at their apexes, thus the signal from the magnetic
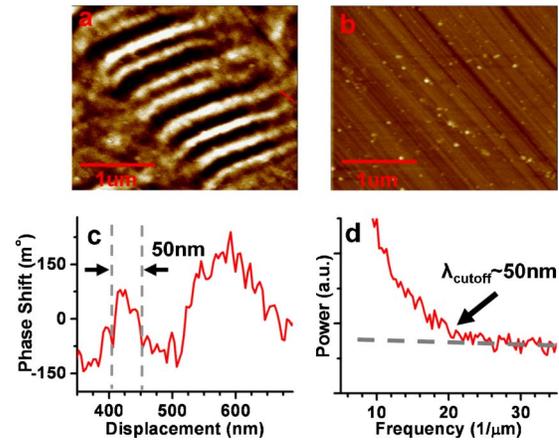

FIG. 4. MFM (a) and AFM (b) image of a commercial hard drive. (a) was acquired in Lift™ mode with the tip oscillating 25 nm from the surface; magnetic features as small as 50 nm are resolved. (b) Topography of same area, height scale is 50 nm. (c) Cross section taken across a 50 nm feature across red line on erased area of top right of (a). (d) Power spectra analysis MFM image (a) in the high frequency range. λ_{cutoff}=50 nm corresponds to a signal to noise ratio of unity.

force is lower and may be embedded in the noise. It is also possible that the metal present in sharper probes suffers a higher degree of oxidation because of a less favorable surface to volume ratio resulting in degradation of its magnetic properties. Measurements with softer cantilevers and more sophisticated microscopes operating in vacuum and at low temperature should overcome these limitations; further improvement in the resolution can also be sought in using the same technique to deposit metals or blends more resistant to oxidation and with a higher magnetic moment. Even smaller magnetic features can be locally deposited on the very end of high aspect ratio structures such as carbon nanotubes[11–13] or ion milled probes.[7,8]

IV. CONCLUSIONS

The facile fabrication of high performance MFM tips via the localized electrodeposition of Co metal at their apexes has been demonstrated serially, and in parallel. In preliminary measurements the tips resolve magnetic features as small as 50 nm. Nanostrucutured metallic probes can also be used for chemical and biological imaging after tip modification with functional molecules preferentially binding to the metal coated apexes. Furthermore, these tips can have applications in near field optical lithography and probe assisted surface enhanced Raman spectroscopy.

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