

Focused electron beam induced deposition of high resolution magnetic scanning probe tips

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ABSTRACT

Apexes of commercial pyramidal silicon scanning microscopy tips were magnetically functionalized by means of local focused electron beam induced deposition. High aspect ratio supertips and local tip coatings with varying apex diameters can be produced by varying exposure time, beam current, and scan mode. The carbonyl precursor $\text{Co}_2(\text{CO})_8$ was used as source of magnetic metal. Tip performance was tested with magnetic force microscopy (tapping / lift-retrace mode) and magnetically actuated cantilever atomic force microscopy. The deposit contains 34 ± 2 at.% Co, dispersed as 2-5 nm metal nanocrystals in a carbonaceous matrix. Specific surface reactions and Boudouard reactions are proposed to explain the resulting deposit composition measured by Auger spectroscopy. The electrical resistivity is 10^4 higher than bulk Co resistivity.

INTRODUCTION

In view of future's magnetic data storage single-grain addressing at ultrahigh densities becomes a challenge. Self-assembly of regular 4 nm iron-platinum dot patterns (4 Tbit/cm^2) was recently achieved [1]. To be able to characterize such grains there is need for magnetic force microscopy (MFM) of very high resolution. Furthermore, some designs of ultrahigh-density magnetic readout systems rely on magnetic force tips to perform the actual data access. Today's commercially produced magnetic tips are fabricated by physical or chemical vapor deposition of a magnetic thin film onto Si or Si_3N_4 tips on cantilevers for scanning probe microscopy systems having relatively large apex diameters of about 80-100 nm. Furthermore, oxidation protective coatings of several nm-thickness on top of magnetic films are often applied.

Focused Electron Beam (FEB) induced deposition is a local chemical vapor deposition technique, which can produce high aspect ratio tips and other more complex 3D nanostructures [2]. The first single-step production of magnetic FEB tips was carried out in our group [3]. In this paper we report on further characterization of these magnetic deposits and their use in wet cell magnetically actuated cantilever setups for atomic force microscopy of biological samples.

EXPERIMENTAL DETAILS

Our FEB-system is based on a Cambridge S100 Scanning Electron Microscope (SEM) with tungsten thermionic emitter. With an oil-free turbomolecular pump backed by a membrane pump a chamber background pressure of 1×10^{-6} mbar is achieved. The volatile precursor

$\text{Co}_2(\text{CO})_8$ (CAS 10210-68-1) is supplied by an internal syringe reservoir. Commercial Si cantilevers with pyramidal tips were used for supertip deposition without any prior cleaning procedure. The cantilever is moved by an x-y-z stage close to the nozzle (distance $< 300\mu\text{m}$) of an internal reservoir of the solid precursor. FEB was carried out at electron acceleration voltage of 25kV. The tip length is controlled by the deposition time and the diameter by the beam current, i.e. the beam diameter.

The FEB tip geometry was determined with a SEM Jeol 6400 (LaB₆ emitter). The deposit composition was measured on $5\times 5\mu\text{m}^2$ large deposits of approximately 100nm thickness on Si substrates by Auger electron spectroscopy using a PHI 660 Perkin Elmer system. Bulk deposit composition values were obtained after consecutive sputtering-AES cycles. High-resolution TEM dark/bright field and diffraction images were taken with a Philips EM 430 ST using thin FEB deposits on carbon TEM grids, to determine the nano-composite structure. Our FEB deposited tips were tested in a hard disk inspection atomic force microscope under ambient conditions using the MFM lift-retrace tapping mode (Digital Instruments). Magnetic tracks on a hard disk with varying magnetic bit densities were scanned. The bit period is known from the track circumference and the write frequency. The magnetic resolution can be determined from the magnetic bit contrast loss of the MFM image (= bit period/2). Magnetically actuated liquid cell AFM with our tips was carried out with a Molecular Imaging Pico MS300 at an excitation frequency of 18kHz on latex particles in a liquid cell. Electric point probe resistivity measurements were performed with Co lines deposited between photo-lithographically pre-patterned gold electrodes. The voltage was swept between $\pm 100\text{mV}$ and the current detected with a HP semiconductor analyzer HP 4155A.

DISCUSSION

Deposition

Both high-aspect-ratio tip and local apex coatings were deposited on top of commercial, as received, pyramidal Si tips (Nanosensors). The electron beam is focused on top of the tip apex at the start of deposition. No refocusing is required during the deposition process due to the large depth of field of the electron beam. The length of the tips is controlled by the exposure time. Average deposition rates were about 15 nm/s. For high-aspect-ratio tips the exposure time was

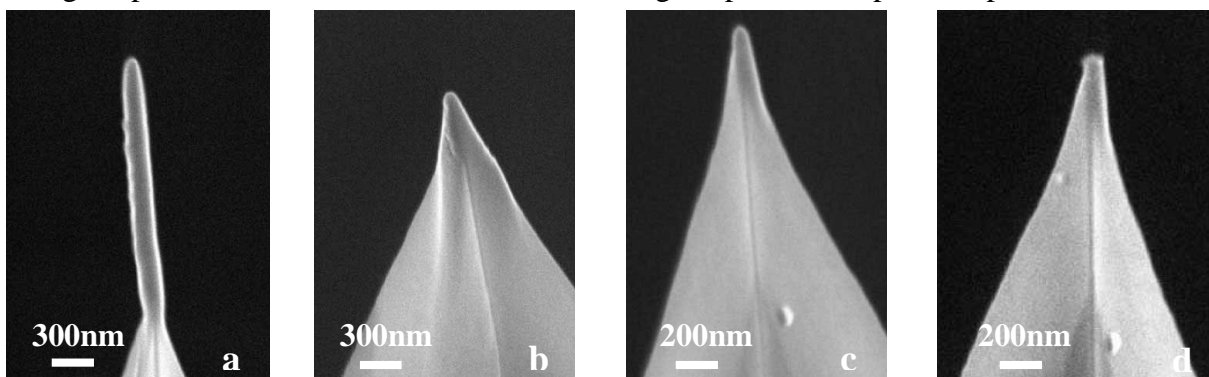


Figure 1: SEM images of a) a high-aspect-ratio tip grown with 100 pA at 25 kV during 85 s; apex diameter 72 nm and length 1.7 μm . b) tip apex coating deposited with a 400 nm^2 scan during 1 min at 25 kV and 100 pA, apex diameter 59 nm. c) low-aspect-ratio tip of 54nm diameter after 2 s at 100 pA at 25kV and same tip after MFM measurement d).

about 2 min and the tip apex diameter corresponds to the electron beam size, see figure 1a. Our SEM with bad signal to noise ratio below 100 pA and a comparatively large beam diameter of 70-80 nm at 25 kV limits the minimum diameter of our deposited high-resolution high-aspect-ratio tips. However, short exposures of about 2s or scans at high magnification (field of view: 400 nm²) result in thin, adherent local tip apex coatings, the diameter of which is determined by the initial pyramidal tip geometry (sharpness) and the coating thickness, see figure 1b. The deposits show both good adhesion and sufficient wear resistance during MFM measurements in the lift-retrace tapping mode, although they undergo a small deformation as shown in figure 1c-d for a low aspect ratio tip. The deformation is more pronounced for high aspect ratio tips, however, tip fraction was only observed under crash-like conditions where the underlying pyramidal tip also was fractured. We attribute this fact to the hard embedding carbon matrix. The quantitative mechanical stability of our magnetic FEB deposits is still under investigation.

Deposit characterization: Auger electron spectroscopy, TEM, electrical resistivity

Cobaltcarbonyl Co₂(CO)₈ was used as precursor. The FEB-deposit composition was determined by Auger Electron Spectroscopy: 32-36 at.% Co, 47-55 at.% C, and 13-17 at.% O. With regard to the precursor stoichiometry (11 at.% Co and about 44 at.% for C and O), the metal and carbon content in the deposit is increased by factors of about 3 for Co and 1.2 for C, whereas the oxygen content is lower (factor 0.3).

Decomposition of surface adsorbed precursor molecules is mainly attributed to secondary electrons SE (<50eV) due to the two orders of magnitude higher interaction cross section compared to primary beam electrons (25 keV). Thermal effects can be excluded [4]. The precursor bond dissociation energies are well positioned in the SE-energy range with Co-C bonds having dissociation energies of around 2 eV [5] and C-O bonds having dissociation energy of about 11 eV [6].

Specific surface reactions and Boudouard reactions are proposed to account for the change from precursor stoichiometry to deposit composition during electron beam irradiation. Co₂(CO)₈ undergoes chemical changes in vacuum on silica surfaces at 25°C. Loss of carbon monoxide (CO) results in clustered carbonyls like Co₄(CO)₁₂ or even Co₆(CO)₁₆ [7]. Putting all facts in a simplified reaction scheme:



we obtain :



with n the (unspecified) number of electrons. A fraction of carbonyl groups (CO) from the surface adsorbed precursor is dissociated under electron beam exposure producing highly reactive oxygen. This in its turn can directly oxidize further adsorbed CO groups to volatile CO₂, which accounts for the low oxygen content found in our deposits.

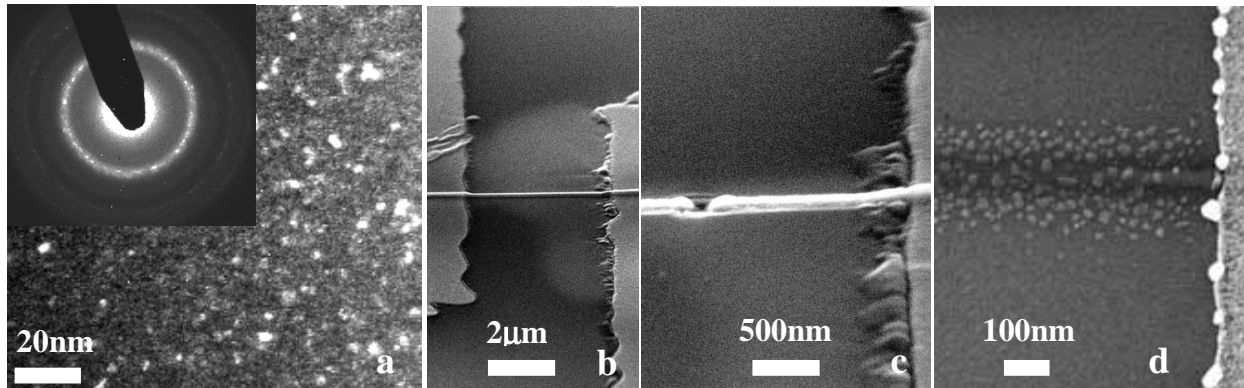


Figure 2. a) Dark field TEM image with diffraction pattern (inset) showing the nano-composite structure of a thin deposit on a carbon TEM grid. The cubic Co nanocrystals are 2-5 nm in size dispersed in an amorphous carbonaceous matrix. b) SEM tilt view of line deposit obtained with 84 pA at 25 kV from the same precursor between pre-patterned gold electrodes on SiO₂/Si substrate. c) SEM tilt view of same line after electrical break down. d) SEM top view of line after annealing in air at 350°C . Same FEB deposition parameters as in b).

An alternative explanation for the increased carbon content in the deposit might be the Co-catalyzed Boudouard equilibrium reaction generally taking place at temperatures > 445°C [8]:



The energy input of electrons is then supposed to produce similar conditions as for the optically induced plasma Boudouard reaction taking place at *low* temperature as discussed in [9].

The deposit nanostructure revealed by transmission electron microscopy consists of cobalt nanocrystals with 2-5nm in diameter dispersed in an amorphous carbonaceous matrix. The diffraction pattern obtained from this deposit can be identified as the ferromagnetic cubic Co phase Fm3m, see figure 2a.

Line deposition experiments were performed on Si substrates covered with a 100 nm thick SiO₂ film and pre-patterned gold electrodes see figure 2b. The electron beam (84 pA at 25 kV) was scanned with a point-to-point distance of 10nm and a dwell of 1s resulting in a 100nm thick and 165nm wide line deposit between the electrodes spaced at distances of 5, 10, and 20 μm. The resistance of a 10μm line was measured to be 6.8 kΩ, i.e. the resistivity is about 50 mΩcm. Compared to the bulk resistivity of 6.2 μΩcm of pure Co, a ratio of approximately 8000 is obtained at room temperature. It can be seen from table I, that the resistivity ratio and composition of our deposits obtained from the Co₂(CO)₈ precursor fit into the range of other metal carbonyl FEB depositions, except for the cases where subsequent deposit annealing or low energy electron beams were applied.

Applying a 5 V potential causes the line resistance to decrease with each sweep cycle. With two sweep cycles the resistivity could be improved by a factor of about 3, i.e. the resistivity ratio is decreased down to 3000. This might be due to the fact that local ohmic heating at bad contact sites leads to carbon oxidation and release, and consequently to a compaction of the nano-composite structure, i.e. the metallic nanocrystals percolation increases. Alternatively, electro-migration effects could be the cause of the resistivity change.

Table I. Comparison of FEB deposits obtained from different carbonyl precursors.

Precursor	Deposit Composition	Resistivity Ratio	Remarks	Reference
Co ₂ (CO) ₈	34 at.% Co, 51 at.% C, 15 at.% O	10 ⁴		This work
W(CO) ₆	55 at.% W, 30 at.% C, 15 at.% O	10 ⁴		[10]
W(CO) ₆	–	10 ² 10 ⁵	Low energy electrons: 250 eV	[11, 12]
Mo(CO) ₆	10 at.% Mo, 50 at.% C, 40 at.% O	400		[13]
Fe(CO) ₅ Cr(CO) ₆	pure Fe low C content	10 6-12	Substrate 140°C Substrate 280, 330°C	[14]
Os ₃ (CO) ₁₂ Ru ₃ (CO) ₁₂	Nanocrystals in carbonaceous matrix	-		[15]
W(CO) ₆ Cr(CO) ₆ Re ₂ (CO) ₆	Nanocrystals < 20 nm in amorphous matrix (not specified)	-	TEM 100kV In-situ anneal 600-800°C	[16]

However, when a temperature limit is reached the exothermic oxidation of carbon and cobalt locally reaches the melting temperature of the cobalt-percolated structure presented in figure 2c.

Ex-situ annealing of identical line deposits at 300°C in air atmosphere resulted in non-conductive lines due to separated cobalt grains of up to 30 nm in size, which coalesced from the small nanocrystals stabilized in its former carbonaceous matrix, see figure 2d. We assume that the strong and localized heat source for resistively heated small line cross section results in melting, whereas the heating in air results in smooth oxidation of the carbonaceous matrix, followed by a slow cobalt grain oxidation.

MFM and liquid cell magnetically actuated cantilever AFM

Prior to testing, the FEB tips were magnetized. Magnetic tracks written with increasing

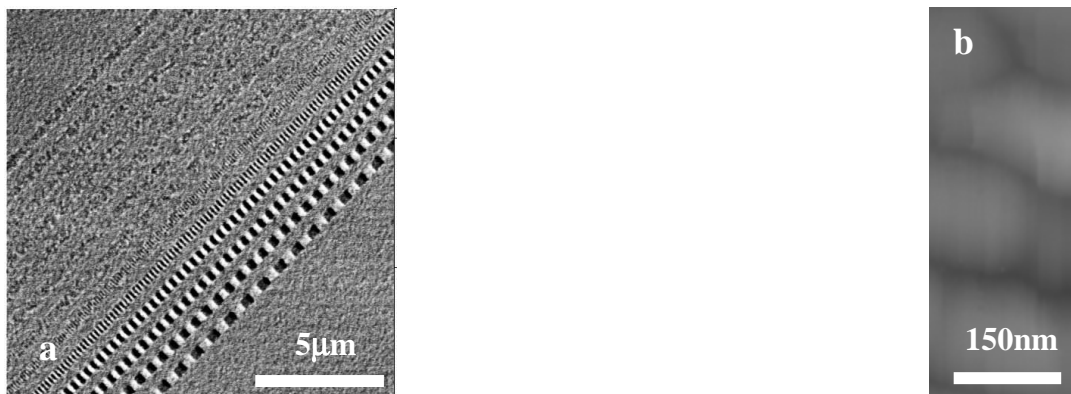


Figure 3. a) MFM image of magnetic tracks with resolved bit periods of 950 nm, 640 nm, 500 nm, 380 nm, 195 nm, and 125 nm (from right to left) b) Magnetically actuated cantilever AFM with FEB-deposited, high-aspect ratio magnetic tip of latex particles. Grey scale of contrast corresponds to 160 nm.

bit density allow determining the resolution of our FEB deposited tips with MFM. The magnetic resolution is then given by half the magnetic bit period, which can still be resolved as a periodic pattern peak above the noise ratio in a spectral Fourier analysis. In figure 3a, the loss of visible track information is seen between bit periods of 125 and 91nm, i.e. the magnetic resolution is 52 ± 10 nm. This image was taken with a tip having an apex diameter of 60 nm. In general, we found that the magnetic resolution scales almost linearly with the tip or coating apex diameter (for more details see [3]). Figure 3b shows that magnetically actuated cantilever AFM, preferably used in liquid cell measurements of biological samples, can be performed with our tips without any additional deposition steps. The FEB deposits show no aging or loss of MFM functionality with storage time (>12 months).

CONCLUSIONS

We have shown high resolution MFM imaging and AFM using single step FEB-produced magnetic tips and coatings. The deposits consist of about 34at.% Co, dispersed as nanocrystals of 2-5nm in size in an embedding carbonaceous matrix. The electrical resistivity is about 10^4 times larger than pure cobalt. In the future we will decrease the beam size of the deposition system, to obtain tips of smaller diameter and thus further increase the magnetic and topographic resolution.

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