A Thin Film Transfer Sample Preparation Technique for Single-Electron Magnetic Resonance Imaging

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Primary CNF Tools Used: SC 4500 combination thermal/e-gun evaporation system

Abstract:

Magnetic resonance force microscopy (MRFM) is a type of scanning probe microscopy that uses the excellent force sensitivity of a silicon micro-cantilever in combination with spatially-resolved magnetic resonance made possible by the large local field gradient of the nanomagnet tip to image magnetic spins with theoretical sub-nanometer resolution. The primary goal of this research project is to advance the use of MRFM as a tool for imaging biomolecules and biomolecular complexes such as membrane proteins, whose structure is difficult to obtain by other means. Here we discuss recent developments in measurement sensitivity made possible through cantilever and waveguide fabrication performed at the Cornell NanoScale Science and Technology Facility (CNF) as well as new sample preparation techniques that will enable advances including electron paramagnetic resonance (EPR) detection of individual electron radical spin labels.

Summary of Research:

By employing nanomagnet-tipped attonewton-sensitivity cantilevers developed at the CNF in a magnetic resonance force microscopy (MRFM) measurement, the Marohn group has demonstrated the detection of 500 proton magnetic moments in a 1 mHz bandwidth [1]. In concert with a modified version of the spin modulation protocol first developed by Moore, et al. [2], these cantilevers should have the sensitivity required to image individual nitroxide spin labels on a single biomolecule or biomolecular complex with nanometer resolution.

A major challenge in performing such an experiment is mitigating cantilever frequency noise. One method that has proven effective in reducing this noise is applying a 10-20 nm thick metallic coating to the sample via electron-beam deposition to shield the cantilever from dielectric fluctuations in the sample. Proof-of-concept MRFM-EPR experiments performed on metal coated, tempamine-doped polystyrene samples, have demonstrated noise which is sufficiently low for imaging, however, have demonstrated significantly smaller signal than expected. Numerical simulations suggest the decreased spin signal is due to a 0.20 nm thick "dead layer" at the sample surface in which EPR active radicals are absent (Figure 1). Due to force-sensitivity limitations, this dead layer poses a significant challenge to MRFM detection of single electron spins.

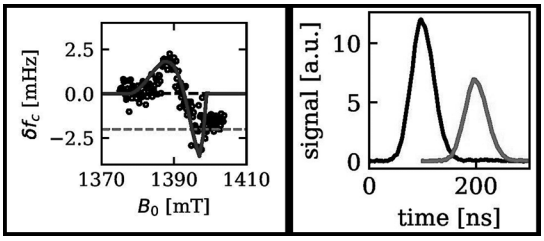

Figure 1, left: Electron spin resonance signal vs. applied magnetic field. The detection protocol developed by Moore, et al. detects the magnetic field gradient produced by sample spins as a modulated shift in the cantilever resonance frequency. Experimental results (black circles) from 30 seconds of signal acquisition, simulated signal of ~50 spins with a 20 nm dead layer (blue line) and expected frequency shift from a single electron near the sample surface (red dashed line).

Figure 2, right: Representative conventional pulsed-EPR measurement demonstrating a reduction in magnetic resonance signal from nitroxide spin probes which had been exposed to gold vapor deposition. Peaks are offset for clarity.

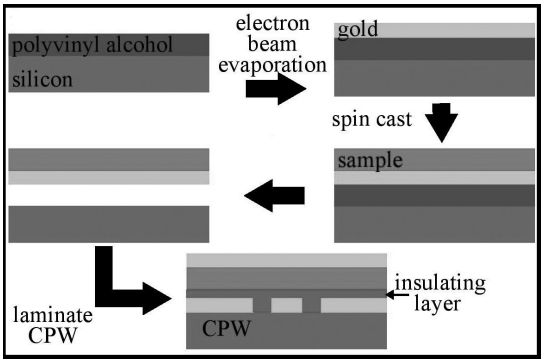

Figure 3: An outline of the sample/top contact transfer process that allows samples to be produced without exposing sensitive nitroxide electron radicals to physical deposition of the gold top contact.

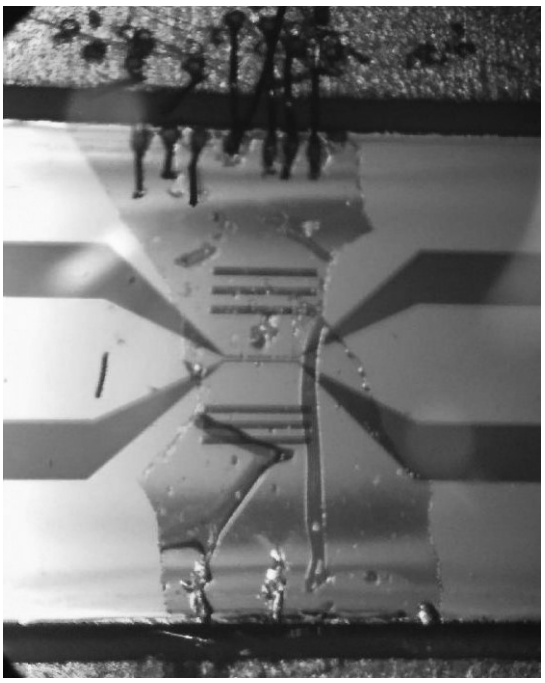

Figure 4: Optical image of a prepared sample/top contact over the tapered microwire region of the waveguide.

Using instrumentation at the National Biomedical Center for Advanced Electron Spin Resonance Technology to perform conventional EPR measurements on prepared 40 nm thick films using identical techniques, we have shown that the total EPR signal is reduced by about 50% after electron-beam vapor deposition of a 10 nm gold top layer — supporting our simulated estimations and suggesting that the process of gold deposition damages the spin probes in the uppermost layers of the sample (Figure 2).

To protect sample spins from direct exposure to the physical vapor deposition of the gold top contact, we developed a new sample preparation protocol. Figure 3 is a schematic of this protocol. A thin layer of polyvinyl alcohol is spin-coated onto a silicon substrate. A 10 nm thick layer of gold is then e-beam deposited on top of the PVA using the SC 4500 combination thermal/e-gun evaporation system at the CNF. The sample in this case, polystyrene doped with 40 mM tempamine, is then spin-coated on top of the gold layer. The Si/Au/polystyrene stack is then placed in a dish containing nanopure water that dissolves the PVA, allowing the Au/polystyrene layers to be transferred directly onto the waveguide to be used to deliver microwaves in the magnetic resonance experiment. Before the transfer, a thin layer of poly(methyl methacrylate) is spin-coated onto the waveguide to prevent shorting through the gold layer. We have found it necessary to transfer only a narrow strip of gold-coated sample because gold contact over the un-tapered region of the waveguide significantly reduces power transmitted through the waveguide. Recent room temperature measurements of the noise over these transferred sample top contacts have demonstrated frequency noise comparable to directly deposited samples.

Application of these newly prepared samples to detection/imaging experiments is currently underway.

References:

[1] Longenecker, et al. ACS Nano 2012, 6 (11), 9637-9645.

[2] Moore, et al. PNAS 2009, 106 (52), 22251-22256.