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14. ABSTRACT

Nanometer-scale magnetic resonance imaging (Nano-MRI) has the potential to be a powerful tool to investigate and characterize materials. The goal of the proposed research program is to develop fundamentally new approaches in force-detected magnetic resonance techniques and achieve nanometer-scale nuclear spin imaging by: (1) achieving sub-attonewton force sensitivity using ultra-sensitive rf nanowire mechanical resonators, (2) generating intense pulsed field gradients greater than 10^6 T/m on the nanometer scale, (3) developing efficient spin imaging

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Nanometer-Scale Force Detected Nuclear Magnetic Resonance Imaging

ABSTRACT

Nanometer-scale magnetic resonance imaging (Nano-MRI) has the potential to be a powerful tool to investigate and characterize materials. The goal of the proposed research program is to develop fundamentally new approaches in force-detected magnetic resonance techniques and achieve nanometer-scale nuclear spin imaging by: (1) achieving sub-attonewton force sensitivity using ultra-sensitive rf nanowire mechanical resonators, (2) generating intense pulsed field gradients greater than 10^6 T/m on the nanometer scale, (3) developing efficient spin imaging protocols using time-dependent B_0 and B_1 gradients, compatible with imaging statistical polarization. During the first year of the ARO grant, we developed a new method for nanometer-scale pulsed nuclear magnetic resonance imaging and spectroscopy. In the first proof-of-concept experiments, we demonstrated two-dimensional Fourier transform images of proton spins in a polystyrene sample with 10 nm spatial resolution. This new paradigm in force-detected NMR allows well-established spectroscopic and imaging pulsed NMR techniques to be applied to the nanometer scale. In the coming year, our goal is to extend the spatial resolution to be between 1-3-nm, obtain three-dimensional tomographic images, and perform high-resolution NMR spectroscopy on the nanometer scale.

In previous work, we demonstrated that high frequency silicon nanowire (SiNW) mechanical resonators significantly enhance force detection sensitivity by substantially reducing surface-induced force noise. Thus, they have the potential to enhance the sensitivity of force-detected MRI, and extend the spatial resolution to biologically relevant length scales of order 1 nm. To couple nuclear spins to the mechanical resonance of SiNW oscillators, we developed the MAGGIC spin detection protocol, which enables ensembles of nuclear spins within a several hundred cubic nanometer volume to be detected with near thermal limited force sensitivity [1]. In the MAGGIC protocol, an oscillating electric current through a nanometer scale metal constriction generates a strong magnetic field gradient that alternates at the SiNW resonance frequency. The force of interaction between the spins in the sample and the alternating inhomogeneous magnetic field induces Ångstrom-scale vibrations of the SiNW, which is measured using an optical interferometer.

During the first year of the grant, we developed a new method, which allows the spins within the detected volume to be imaged with nanometer resolution. Unlike previous MRFM techniques that rely on a static magnetic field gradient, the MAGGIC protocol uses time-dependent magnetic fields generated by flowing current through a nanometer scale metal constriction (Fig. 1a). Current densities of order 10^9 A/cm^2 can be sustained through the constriction for long periods of time. Such locally intense current densities generate (1) large time-dependent magnetic field gradients that couple nuclear spins in the sample to the resonant displacement of the SiNW, (2) rf magnetic fields to excite magnetic resonance in the sample, and (3) pulsed gradients for imaging. Furthermore, the ability to control the time dependence of the applied fields permits the use of pulsed NMR techniques for imaging and spectroscopy on the nanometer scale. This capability in force-detected NMR creates new opportunities for nano-MRI, which previously could not be realized.

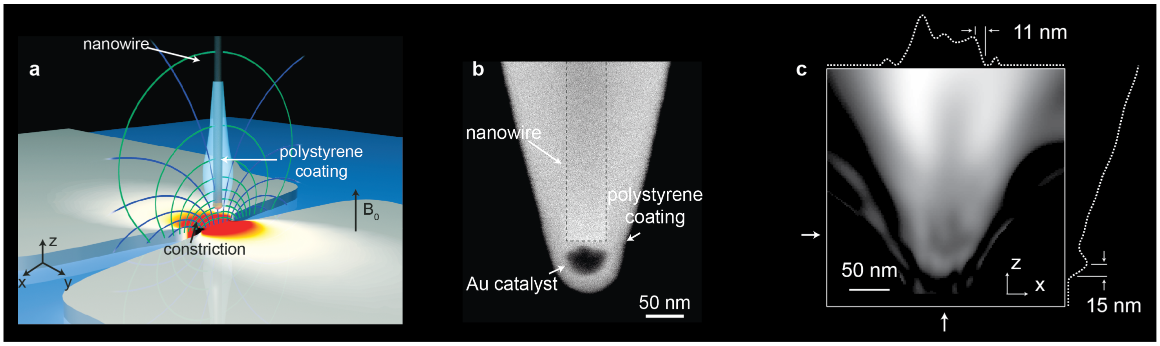

Figure 1. (a) Schematic of the experimental setup. A silicon nanowire coated with polystyrene is positioned near the constriction in a Ag current-carrying wire. The locally high current density through the constriction generates intense fields and gradients used for readout, spin manipulation, and spatial encoding. During imaging, the spin density was encoded along contours of constant Larmor and Rabi frequency, which are illustrated as blue and green lines, respectively. (b) Scanning electron micrograph of a representative nanowire and polystyrene coating prepared in the same manner as the nanowire and sample used in the study. (c) Real-space reconstruction of the projected spin density. The nanowire and gold catalyst are clearly visible through the polystyrene in the image as a reduction in the spin density. The cross-sections above and to the right of the image are taken along the lines indicated by the arrows.

In the first proof-of-concept work, we demonstrated Fourier-transform spectroscopy and imaging with nanoscale resolution by periodically applying rf pulses to create correlations in the statistical polarization, or spin noise, of a polystyrene coating applied to the tip of a SiNW [2]. Gradient pulses for imaging are generated using ultrahigh current densities in a nanoscale metal constriction, and the spin noise correlations are recorded for a set of pulse configurations and Fourier transformed to give the two-dimensional spin density. The reconstructed image shown in

Fig. 1c shows the spin density in the polystyrene with about 10-nm spatial resolution. In reciprocal space imaging schemes, such as Fourier-transform imaging, all components of the sample spectrum are averaged for the entire acquisition period. When detector noise is the limiting factor, these techniques significantly increase signal-to-noise ratio in what is known as the multiplex advantage over methods that acquire each element of the spectrum sequentially.

This first set of imaging experiments were performed in a low field setting. The static field of 0.18 T used for magnetic resonance was produced using a small hand-wound solenoid placed near the sample. To minimize imaging artifacts, the magnitude of the fields produced by the pulsed fields from the constriction must be much smaller than the static field. We therefore had to operate with rather small amplitude pulses, which in turn limited our spatial resolution. Through the support provided by the ARO grant, we have since purchased a cryogenic system with a 6 T superconducting magnet. In the coming year, we plan to repeat the imaging experiments at 2 T, which will allow us to apply substantially larger encoding pulses, and achieve higher spatial resolution. In addition to being able to operate in high field, we have made a number of other technical improvements, which we expect will allow us to achieve spatial resolution significantly below 10 nm within the next year. These improvements include construction of a shot-noise-limited optical interferometer that can detect the SiNW displacement with sensitivity below 1 pm/rtHz with low optical power. We have tested this setup, and realized nanowire heating below 1 K. This level of heating is nearly a four-fold reduction in heating compared to imaging experiments reported here. The reduced heating is expected to improve the detection signal-to-noise ratio by a factor of two. We are also in the process of integrating high frequency arbitrary waveform generators and rf synthesizers for the upcoming high frequency (84 MHz) NMR studies.

One of the major challenges to sensitive force detection is to control the force fluctuations experience near the surface. As mentioned, the high frequency surface-induced fluctuations responsible for decreasing the force sensitivity are significantly reduced with rf nanowire oscillators. The low frequency fluctuations however, which cause the resonant frequency to fluctuate, can also be detrimental. Our studies suggest that these low frequency fluctuations are caused by charges located within approximately 50-100 nm from the tip coupling to stray electric field gradients generated by patch potentials emanating from the surface. We are pursuing two paths to minimizing these low frequency fluctuations. The first is to minimize the number of fluctuators near the surface by fabricating a thin scaffold on the SiNW tip, onto which the sample being imaged

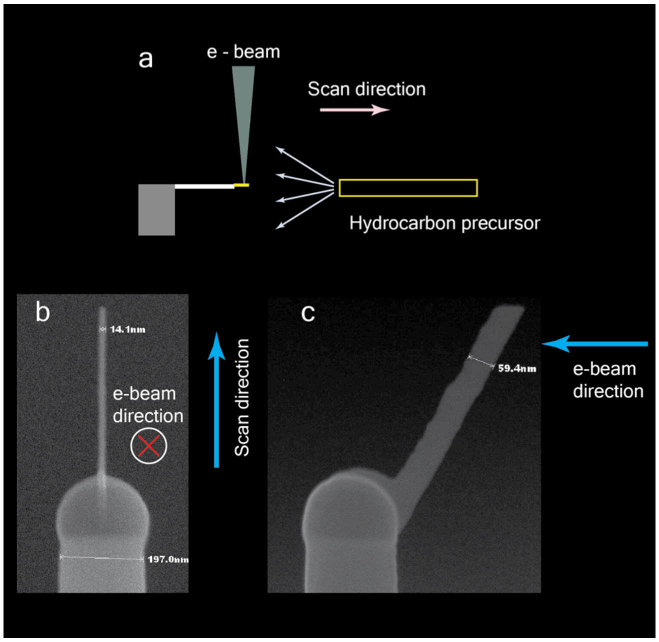

Figure 2: (a) Schematic of the EBID setup. A naphthalene precursor is used to deposit 200-500 nm long hydrocarbon scaffolds on the tip of the SiNW. (b) and (c) Top and side views of the EBID scaffold, respectively.

will be attached. Our goal is to minimize the number of charge traps near the tip by making the lateral dimensions of the scaffold much smaller than the SiNW resonator. Figure 2 shows a hydrocarbon scaffold grown on the tip of a SiNW using electron beam induced deposition (EBID). Our first set of low temperature measurements using the EBID tips indicate that they are effective in minimizing low frequency fluctuations. The second route to minimizing charge fluctuations is to fabricate constrictions from epitaxial Ag films, rather than polycrystalline Ag films. It is thought that grain boundaries in polycrystalline metal films give rise to stray electric fields near the surface of the film. The electric fields are produced as a consequence of the work function difference between grains of different crystallographic orientation. Single crystal thin films should thus minimize the stray electric fields by reducing the number of grain boundaries. We have recently completed construction of a Ag sputtering system capable of growing epitaxial Ag films on MgO. To achieve epitaxial growth, the system incorporates an *in situ* substrate heater capable of heating the MgO substrate to 850 °C prior to Ag deposition. We expect the combination of the EBID scaffolds on the SiNW, and constrictions fabricated using epitaxial Ag films to significantly reduce the low frequency charge fluctuations.

Our main goal for next year is to incorporate the above-mentioned changes and repeat the proton imaging measurements with a resolution substantially below 10 nm. In addition, we will also be pursuing high-resolution spectroscopic detection. Nanometer scale imaging with spectroscopic resolution would be new capability that could provide valuable information about the local chemical environment of the spins within the sample. Our goal is to measure the chemical shift in a statistically polarized ensemble of proton spins in a solid organic sample using the same encoding protocol we developed for Fourier transform imaging. To do this, we will need to apply a homonuclear decoupling pulse sequence, such as magic echo, in order to remove the dipole-dipole interactions that broaden the proton spectra. The composite pulses will be applied using a small coil capable of producing a uniform B_1 field within the nanometer detection volume. We are currently designing the pulse coil and electronics, and we expect to incorporate this feature within the next year. We will then be able to apply the full suite of composite pulse sequences developed for high resolution NMR to nano-MRI.

[1] J.M. Nichol, E.R. Hemesath, L.J. Lauhon, and R. Budakian, “Nanomechanical detection of nuclear magnetic resonance using a silicon nanowire oscillator” *Phys. Rev. B* **85**, 0554414-1-6 (2012).

[2] J.M. Nichol, T.R. Naibert, E.R. Hemesath, L.J. Lauhon, and R. Budakian, “Nanoscale Fourier-transform MRI” arXiv: 1302.2977, accepted for publication in *Phys. Rev. X.*