ENHANCEMENT OF NMR SENSITIVITY IN NANOLITER SAMPLES BY DYNAMIC NUCLEAR POLARIZATION AND MICROCOILS FABRICATED ON CAPILLARIES BY SHADOW MASK LITHOGRAPHY

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ABSTRACT

Modern dynamic nuclear polarization (DNP) systems produce a high nuclear magnetic resonance (NMR) signal enhancement but distort the static magnetic field in an NMR system. As a result the obtained spectrum has a resolution not suitable for most NMR applications. Localizing the detection region only to the part of the resonator where the magnetic field component of microwave (MW) is the highest and highest static magnetic field homogeneity should increase the resolution without compromising enhancement. Here we present a novel method of manufacturing a microcoil on a capillary, enabling localized in-situ NMR detection inside a MW cavity.

KEYWORDS: Dynamic Nuclear Polarization, Nuclear Magnetic Resonance, Microcoil

INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy is a very valuable technique for identification of molecules, but because of poor sensitivity requires a large quantity of molecules to collect signal in a reasonable amount of time. This is a major drawback when considering mass limited liquid samples. Dynamic nuclear polarization (DNP) in the liquid state is a technique that may help to overcome that problem. The mechanism behind the DNP enhancement in liquids is described by the Overhauser effect [1] by which the much larger electron spin polarization can be transferred to nuclear spins through a (partial) saturation of electron paramagnetic resonance (EPR) transitions. The enhancement ε of the signal is given by:

$$\varepsilon = -\xi \mathrm{fs} \frac{\gamma_e}{\gamma_n},$$

where γ_e is the electron gyromagnetic ratio, γ_n is the nuclear gyromagnetic ratio, ξ is the coupling factor, f is the leakage factor and s is the saturation factor. The coupling factor ξ depends on the dynamics of the electron-nuclear spin system. In liquids, for pure dipolar coupling it takes the maximum value of 0.5 at low fields. This means that the maximum theoretical enhancement with respect to the thermal equilibrium is -330, which in theory reduces measurement times by a factor of ca. 10^5. Although theory predicts that this value of enhancement is achievable only at low magnetic fields, recent studies have shown that significant enhancement is also possible at much higher magnetic fields.

To measure the DNP efficiency we use an experimental setup based on the concept of the non-radiative (NR) dielectric microwave (MW) resonator [2]. The resonator assembly is shown in Figure 1. The quartz cylinder placed between two copper plates forms a MW cavity. The NR cavity operates in cylindrical TE_{011} mode where the magnetic flux MW B_1 is concentrated along the axis of the structure.

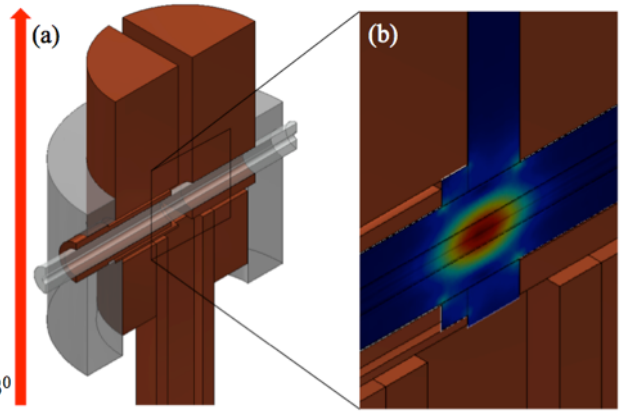

Figure 1. a) Schematic representation of the NR resonance structure. The red arrow illustrates the direction of the static magnetic field. b) The microwave field profile of the TE_{011} mode of the resonator is characterized by the magnetic field distribution concentrated along the axis of the resonator.

In previous studies with this structure [3,4] the NMR coil was hand made out of small gauge copper wire, creating a single loop with wires oriented parallel to the axis of the structure. The length of this coil was much larger than the size of the MW cavity. In this configuration the acquired signal originates from the sample placed both inside and outside of the resonator cavity. The structure of the probe placed inside the large magnetic field, due to the magnetization produces

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a small magnetic field that changes the resulting magnetic field experienced by molecules in the sample. The effect of this aggravates the results as the sample placed outside the resonator has larger volume. This means that the sample has to be probed only inside the resonator, were the MW magnetic field is the strongest. This can be achieved by an altered NMR coil design, the operation of which is based on the rule of reciprocity. The rule states that the sensitivity of the NMR coil as a detector is proportional to the efficiency as a transmitter. This implies that the sample has to be placed in the part of the coil generating the strongest magnetic field in the transverse plane.

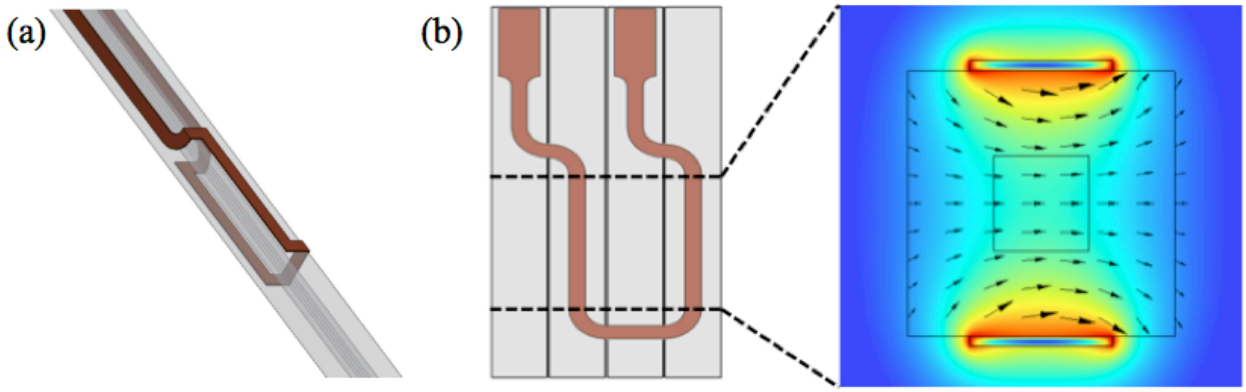

Figure 2. a) 3D rendering of a designed microcoil. b) Layout of the four sides of the microcoil with RF B_1 field profile across the sensitive region.

MANUFACTURING

The presented method uses a shadow mask to selectively deposit a Cr/Cu seed layer on four sides of the rectangular capillary. Figure 3 illustrates the multistep fabrication process. The whole coil requires deposition of four distinctive patterns in four steps. After each deposition the capillary had to be rotated and aligned inside the shadow mask. Accurate alignment between every side was kept using alignment markers deposited in previous steps. Paths on adjacent sides are electrically connected to create a cathode for electroplating of a thicker copper layer to reduce coil resistance.

This new coil manufacturing process starts with the fabrication of a silicon shadow mask. The capillaries for the microcoils were 280 µm x 280 µm x 50 mm therefore the channels to guide capillaries inside the shadow mask had to be of similar dimensions. Employing 100 mm silicon wafers and leaving excess space for handling of the capillary during metal deposition allowed placing of 16 shadow masks on a single wafer. A single microcoil requires four patterns, one for each side. The shadow masks were produced by deep reactive ion etching of a 525 µm thick silicon wafer. First the side with deep channels was etched approx. 475 µm. The side with the pattern was opened in the following step creating an approx. 50 µm thick stencil.

A square capillary (Polymicro technologies, WWP100375) was cut into 52 mm long pieces. The polyimide coating was stripped in concentrated sulfuric acid at 130 °C. In the following step the capillaries were placed in a polymer frame and etched in 50% HF solution to reach a length of the side of 280 µm. During etching, the frame with capillaries was floating in the etching solution providing uniform etching from all sides. Capillaries etched this way kept their resistance to bending despite the lack of polyimide coating.

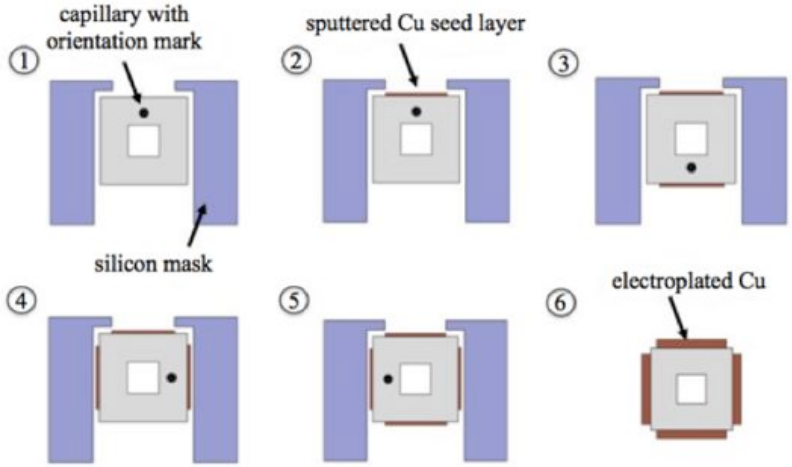

Figure 3. An overview of the microcoil manufacturing process. The orientation marker has been added to indicate rotation of the capillary. The fused silica capillary is placed inside the silicon micromachined shadow mask in step 1. In steps 2-5 seed layer is deposited on four sides of the capillary. Finally (step 6) Cu is electroplated on the seed layer.

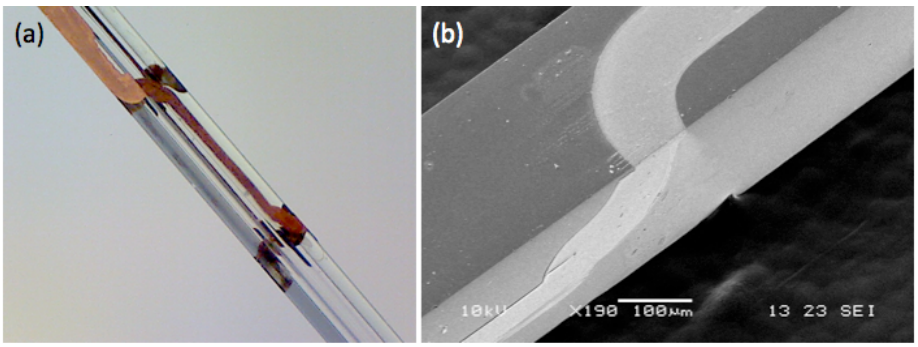

Figure 4. a) Loop microcoil on a 280 µm fused silica capillary. b) SEM image of the sputtered Cr/Cu multilayer.

RESULTS

The designed microcoil was successfully manufactured and tested inside the MW resonator at a field of 3.4 T (144 MHz ^{1}H). The loaded quality factor of the resonance with aqueous sample was Q_L=900 with corresponding unloaded Q_0=2100. The sample used to evaluate the system was 10 mM and 20 mM TEMPO in water and ethanol-water solutions. Preliminary DNP results are shown in Figure 5. The ^{1}H signal line-width of a ca. 10 nL sample is 0.2 ppm. This value of spectral resolution allows identifying peaks of the ethanol and also allows tracking of temperature changes due to dissipation of the applied MW power.

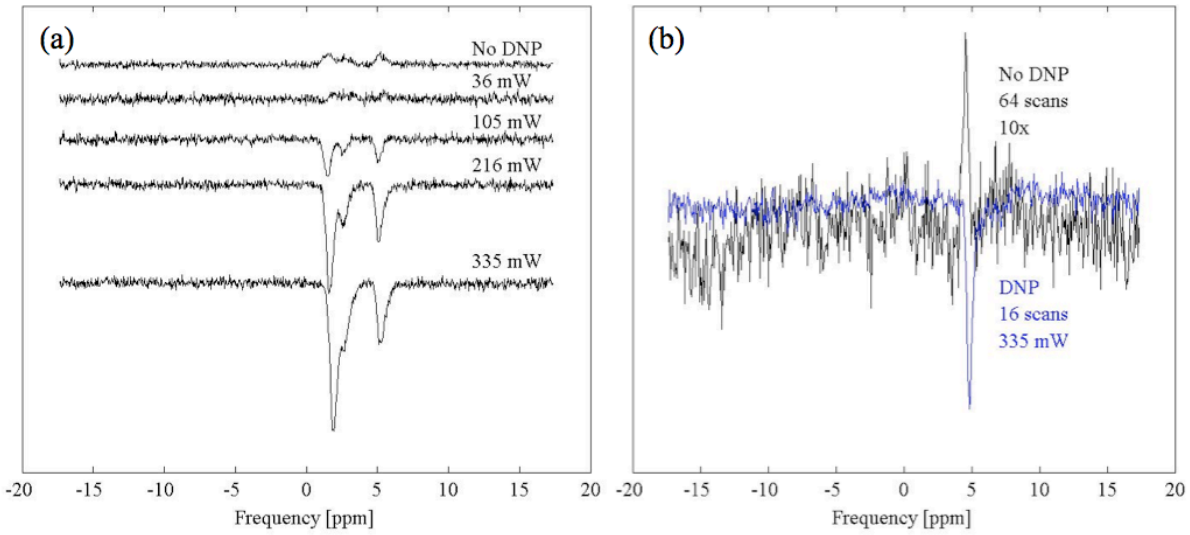

Figure 5. a) ^{1}H NMR spectra of 20 mM TEMPO solution in ethanol-water solution with different MW irradiation power collected using microcoil with localized detection. b) ^{1}H NMR spectra of 10 mM TEMPO solution in water with increased MW irradiation power collected by the microcoil with localized detection. The achieved enhancement is 20.

CONCLUSIONS

The shadow mask manufacturing technique allowed us to create the microcoil on the surface of the fused silica capillary. The created microcoil was successfully tested inside the microwave resonator. The spectra recorded by the spectrometer show no peaks that were not enhanced by the DNP. It means that all of the recorded response belongs to the sample placed inside the resonator. This solution can allow for stopped flow experiments and might find application in small sample screening.

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