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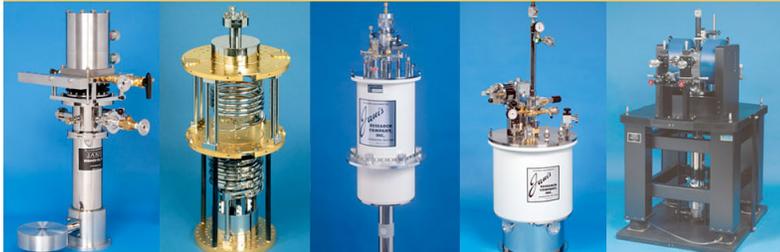
Note: High sensitivity pulsed electron spin resonance spectroscopy with induction detection

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Commercial electron spin resonance spectroscopy and imaging systems make use of the so-called "induction" or "Faraday" detection, which is based on a radio frequency coil or a microwave resonator. The sensitivity of induction detection does not exceed $\sim 3 \times 10^8$ spins/$\sqrt{Hz}$. Here we show that through the use of a new type of surface loop-gap microresonators (inner size of 20 μm), operating at cryogenic temperatures at a field of 0.5 T, one can improve upon this sensitivity barrier by more than 2 orders of magnitude and reach spin sensitivities of $\sim 1.5 \times 10^6$ spins/$\sqrt{Hz}$ or $\sim 2.5 \times 10^4$ spins for 1 h. © *2011 American Institute of Physics*. [doi:10.1063/1.3611003]

Electron spin resonance (ESR) is a well-established technique with many applications in a wide variety of scientific fields ranging from chemistry, biology, and materials science, through to physics. One significant drawback of *conventional* ESR, however, is its relatively low sensitivity of $\sim 10^7$–10^9 spins (for ~ 1 h),[1,2] compared to other spectroscopic techniques. This sensitivity limitation also affects the available imaging resolution of heterogeneous samples, reaching only recently the micrometer and sub-micrometer range.[1,3]

Recently, we have engaged in the development of a unique type of efficient surface loop-gap microresonators that make possible a considerable reduction of the resonator effective volume, V_c (down to a few nanoliters operating at ~ 12.7 GHz), but with a rather low quality factor of ~ 15.[4] These new structures allow us to obtain a measured spin sensitivity of $\sim 3.1 \times 10^8$ spins/$\sqrt{Hz}$ at room temperature for a sample of E$'$ centers in SiO$_2$, which has a relatively broad signal (and is, therefore, not optimal in terms of sensitivity considerations). We present here an improved and much smaller design of these types of surface microresonators that were operated at temperatures ranging from room temperature down to 5 K and showed improved measured spin sensitivity, down to 1.5×10^6 spins/$\sqrt{Hz}$ for a sample of phosphorus doped ^{28}Si (^{28}Si:P). This spin sensitivity corresponds to $\sim 2.5 \times 10^4$ spins for a reasonable one hour of average time, which constitutes an improvement of over 2 orders of magnitude compared to previous "state-of-the-art" induction detection ESR.

Our pulsed ESR experimental setup is described in details in Ref. 3. Briefly, it is a wideband, homemade, 6 to 18 GHz pulsed ESR imaging spectrometer (but in this work we did not make use of its imaging capabilities). In the present setup we employed an improved version of the loop-gap surface microresonators,[4] as presented in Fig. 1 The resonators are produced by photolithography and are made of a thin (1 μm) layer of gold deposited on a TiO$_2$ single-crystal substrate (from MTI Corporation, USA). The coupling to the

microwave (MW) transmission line is achieved using a microstrip line.[4] The geometry of the current version of the surface resonator enabled much better coupling even with a loop inner diameter of 20 μm (whereas in our previous work we could couple well only to a relatively large 150-μm loop[4]). The magnetic and electric fields' distributions in the surface of the resonator are shown in Fig. 2 (calculated by CST Microwave Studio). The calculated fields reveal a small effective resonator volume of only $V_c = 0.62$ nl. Another new feature of the probe is its combination with a cryogenic system (based on the Janis Research, USA, cryostat model STVP-200) that provides an operating temperature range of ~ 3–300 K. Our probe design maintains a variable coupling capability of the microstrip feed line's mechanical movement with respect to the resonator even under cryogenic temperatures through the use of special two-axis piezo positioners (model ANPx101 from Atocube, Germany). The resonator's quality factor was measured with a MW vector network analyzer (Agilent E8361A) and was found to be ~ 15 at room temperature and ~ 200 at 5 K, respectively. The resonance frequencies of the empty resonator were measured as 16.048 and 14.248 GHz at room temperature and 5 K, respectively (due to the increased relative permittivity of the TiO$_2$ substrate from ~ 165 at room temperature to ~ 245 at 5 K.[5])

The experimental tests of the spin sensitivity of our setup were carried out with three types of test samples. The first is a 1-mM partially de-oxygenated water solution of a stable organic radical (deuterated trityl[6]). The relaxation times of this sample at room temperature were found to be $T_1 = 2.5$ μs (measured by saturation recovery), $T_2 = 910$ ns (by two-pulse Hahn echo), and $T_2^* = 230$ ns (by the inverse of the echo spectral width $T_2^* = 1/\pi \, \Delta \nu$). A second type of sample was made of thin, 150-μm fused quartz slide, which was placed in a solution of N@C$_{60}$ (Ref. 7) and C$_{60}$ mixture in CS$_2$ with a N@C$_{60}$:C$_{60}$ ratio of $\sim 2 \times 10^{-4}$. The solution was left overnight in a fume hood, resulting in the evaporation of the CS$_2$ and crystallization of the solid N@C$_{60}$:C$_{60}$ on the slide's surface, creating a thin layer of solids on one side of the glass (~ 10–20 μm thick, based on optical microscopy).

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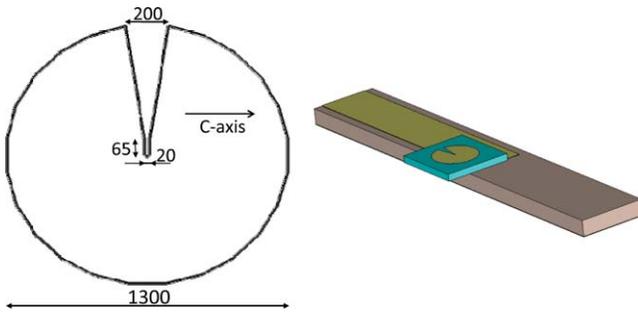
FIG. 1. (Color online) Mechanical drawing of the resonator setup employed in this work, showing the dimensions (in μm) of the gold print on the TiO_2 single crystal (left) and the coupling method to the microstrip line (right). The crystal C-axis is in the resonator plane as marked on the left drawing.

The sample was measured in a conventional Bruker ESR spectrometer (EMX) and its signal was compared to a reference 1-μM deuterated trityl radical water solution. The results gave us the spin concentration of the $N@C_{60}:C_{60}$ sample to be 4.7×10^4 spins per μm^2. The relaxation times of this sample were measured to be $T_1 = 6.8$ ms, $T_2 = 3.1$ μs, and $T_2^* = 127$ ns, at 10 K, which was the most useful temperature for our sensitivity experiments (see below). The third sample was made of a thin 10-μm layer of ^{28}Si:P ($\sim 10^{16}$ P cm^{-3}) with ^{28}Si purity of more than 99.9%, placed on a high-resistivity p-type silicon substrate.[8] At a temperature of 10 K we measured for it T_1 of 1 ms, T_2 of 260 μs (assuming simple exponential decay) and T_2^* of 0.8 μs.

Following this introductory work we went ahead and measured the spin sensitivity of our system with the above-mentioned test samples. Representative results for the trityl sample, obtained by a simple one-pulse free-induction decay (pulse length 30 ns, MW power 1.5 W), are provided in Fig. 3(a) The measurements were carried out at room temperature with the de-oxygenated solution placed on the resonator and then sealed from above to maintain some
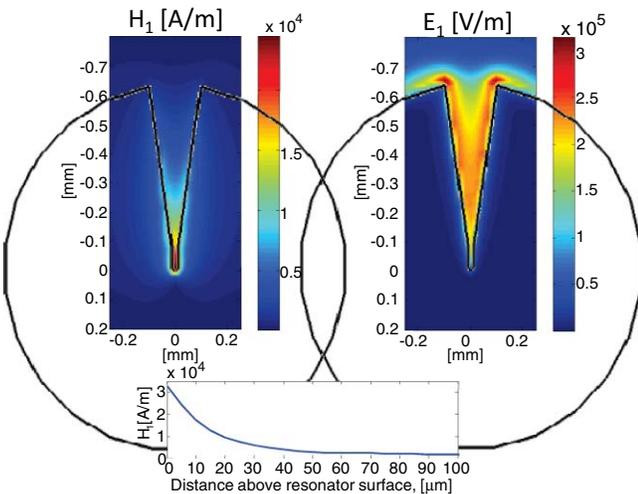

FIG. 2. (Color online) The calculated H_1 (left) and E_1 (right) MW fields for the resonator in a surface located 5 μm above the gold print. The input power in the microstrip feed is 1 W in these calculations. The bottom plot shows the H_1 field in the center of the resonator, as a function of the distance from the resonator's surface.
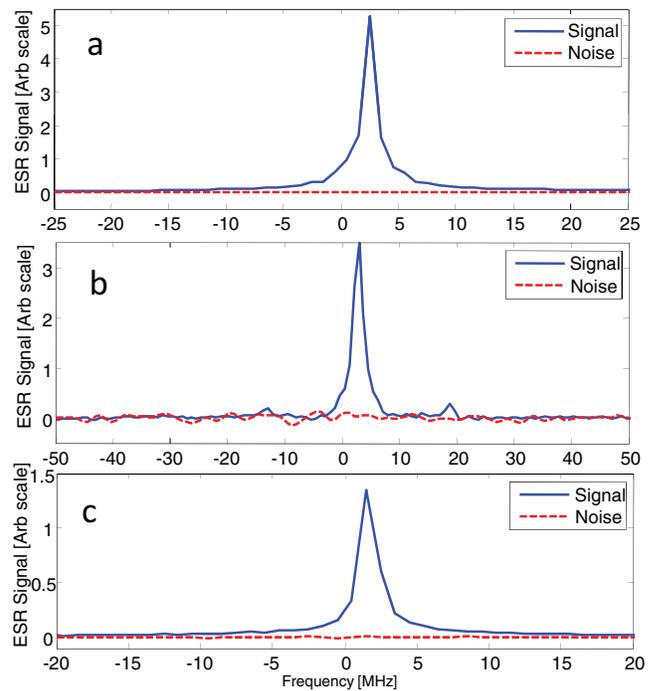

FIG. 3. (Color online) (a) ESR signal (solid line) and noise (dashed line) in the frequency domain for the 1-mM trityl solution sample. Frequency: 16.037 GHz, repetition rate: 70 kHz. Averaging time 9 s. (b) The same as (a) but for the $C_{60}:N@C_{60}$ sample. Frequency: 14.248 GHz, repetition rate: 150 Hz. Averaging time 21 s. (c) The same as (a) but for the ^{28}Si:P sample. Frequency: 13.736 GHz, repetition rate: 1000 Hz. Averaging time 8 s.

de-oxygenation (in a glove box, under Ar atmosphere). The signal-to-noise ratio (SNR) in Fig. 3(a) is $\sim 10\,192$, which for 1 s of acquisition is $\sim 10\,192/\sqrt{9} \sim 3397$. The volumetric analysis of the 3D calculated magnetic fields' distribution of the resonator reveals that $\sim 1\%$ of the signal originates from the most sensitive region at its center, in a volume of 3000 μm^3. (This analysis assumes that the signal in each part of the resonator is proportional to the local $|H_1|^2$.[9]) On the basis of the trityl solution concentration one can calculate that this volume holds $\sim 6 \times 10^5 \times 3000 = 1.8 \times 10^9$ spins, which means that the spin sensitivity of this measurement is $\sim 1.8 \times 10^9/(3397/100) \sim 5.3 \times 10^7$ spins/$\sqrt{Hz}$.

The measurements with the $N@C_{60}:C_{60}$ sample were carried out both at room temperature and cryogenic temperatures (in the 5–18 K range). The most favorable conditions, in terms of spin sensitivity, were found to be at 10 K. Typical results for this temperature obtained by a simple two-pulse Hahn echo sequence (pulse lengths 30 and 70 ns, pulse separation 500 ns, MW power 5 mW) are given in Fig. 3(b) In this measurement the SNR is ~ 60, which for 1 s of acquisition is $\sim 60/\sqrt{21} \sim 13.1$. The analysis of the resonator surface fields' distribution (Fig. 2, left) reveals that $\sim 10\%$ of the signal originates from a surface of 750 μm^2 at the center of the resonator, which is most sensitive. Based on our sample calibration (see above) this surface holds $\sim 4.7 \times 10^4 \times 750 \sim 3.5 \times 10^7$ spins, which means that the spin sensitivity of this measurement is $\sim 3.5 \times 10^7/(13.1/10) \sim 2.7 \times 10^7$ spins/$\sqrt{Hz}$.

Experiments with the ^{28}Si:P sample were conducted only at cryogenic temperatures. Optimal sensitivity for this type of sample was obtained at the lowest temperature in which

$T_1 \approx T_2$ (found to be $\sim$10 K). Going to lower temperatures increases the net magnetization but greatly limits the signal averaging capability due to rapid increase of T_1. The results in Fig. 3(c) were obtained at 10 K with a Carr-Purcell-Meiboom-Gill (CPMG) sequence of 100 echoes (since $T_2 \gg T_2^*$), $\pi/2$ and π pulse lengths of 30 and 70 ns, respectively, $\pi/2 - \pi$ pulse separation of 2 μs and MW power of 0.5 mW. The SNR in Fig. 3(c) is $\sim$1349, which for 1 s of acquisition is $\sim$1349/$\sqrt{8}\sim$477. As before, $\sim$10% of the signal originates from a surface of 750 μm^2 at the center of the resonator. On the basis of the known P concentration this "surface" holds $\sim$750$\times$10$^5 \sim$ 7.5$\times$10^7 spins (we consider the entire 10-μm thickness of the sample as "surface"), which means that the spin sensitivity of this measurement is $\sim$7.5$\times$10^7/(477/10)$\sim$1.5$\times$10^6 spins/$\sqrt{}$Hz.

The experimental results can be compared to the theoretical prediction by Eq. (1) in Ref. 1 The results of this calculation are found to be 8×10^7, 4.8×10^6, and 7.4×10^4 spins/$\sqrt{}$Hz, for the trityl, N@C$_{60}$ and ^{28}Si:P samples, respectively (taking into consideration the sample parameters, under the conditions of the experiments). The value for T_1 used in these calculations was the inverse of the repetition rate, except for the ^{28}Si:P sample, where we considered an actual "signal averaging" repetition rate of 100 kHz (100 echoes in the CPMG train, every 1 ms). The experimental results are in good agreement with the theory for the trityl sample. For the N@C$_{60}$ sample one must include also a factor of 3 "missing" in the signal, due to hyperfine splitting, and also it is speculated that the attachment of this "grained" sample to the surface was not optimal (see below). As for the ^{28}Si:P sample, again there is a factor of 2 due to the consideration of only one of the hyperfine lines, while the other "missing" signal factor is the averaging over the CPMG train (which is summed to only $\sim$1/3 of the maximum signal due to signal decay along the train and other pulse imperfections). Furthermore, additional signal is "lost" because of the relatively thick size of this sample (10 μm), where the resonator's H$_1$ field already decays considerably at such distance (see Fig. 2).

The calculated conversion factor at the resonator's most sensitive point reaches $\sim$207 G/$\sqrt{}$W (see Fig. 2). This implies that the 30-ns $\pi/2$ pulses require a nominal power of only $\sim$0.21 mW. In the trityl sample the experimentally required power is much higher since the volume of the sample is large and extends well above the resonator surface, where the MW field decays rapidly (see also discussion in Ref. 4). The other two samples are much more "surface-like" and indeed here we see a good agreement between theory and experiment, especially for the ^{28}Si:P sample. The requirement for higher-than-nominal power for the N@C$_{60}$ sample may be an indication of an attachment problem.

The results presented in this work can be utilized in a variety of applications that require ultra high spin sensitivity. For example, spectroscopic ESR and electron nuclear double resonance measurements of samples that are hard to obtain in large quantities or hard to crystallize[10] (providing increased spectral resolution in the latter case); observation of defects and impurities in semiconductors and semiconductor-based devices, such as polycrystalline silicon for solar-cell applications;[11,12] measurements of paramag-

netic monolayers;[13] and measurements of fixed small biological samples with stable free radicals.[14] Furthermore, high sensitivity is a prerequisite for high resolution imaging. Future work can reduce V_c by a factor of at least 10, increase the resonator quality factor, Q_u by a factor of $\sim$100 (by the use of copper or even superconducting substrate[15]) at low temperatures, and increase field to $\sim$1.2 T ($\sim$35 GHz (Ref. 1)). Another possible improvement can come from placing the MW system's circulator and low noise amplifier in the cryostat, which may add another factor of $\sim$3 to the SNR. The collective effect of these improvements can add up to sensitivity increased by up to a factor of $\sim$400, which, when accompanied by longer acquisition times of several days, may make it possible to approach single spin sensitivity in some unique samples. If this boundary is actually reached, it can open a whole new range of applications that combine high resolution ESR imaging with single spin sensitivity, such as direct mapping of the distance between two spin labels in macromolecules,[16] and quantum computing applications.[17–19]

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