Electron spin resonance microscopic surface imaging using a microwave scanning probe

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We report on a scanning electron-spin-resonance microscopy based on a microwave near-field probe. The probe consists of an open dielectric resonator with a thin-slit aperture. The spatial resolution in one direction is determined by the slit width and can be varied between 1 and 100 μm, while the spatial resolution in the perpendicular direction is ~10 times larger. We demonstrate spatially-resolved measurements on diphenyl-picryl-hydrazil samples on a substrate. A sensitivity of 10^{11} spins could be achieved using a 4-μm-wide slit operating at 8.5 GHz and in a contact mode.
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The electron-spin-resonance (ESR) technique is a powerful analytical tool in chemistry, biology, and physics. In conventional ESR spectrometers, the sample is mounted inside a microwave resonator and is strongly coupled to the microwave magnetic field. Such a setup provides high sensitivity (10^{12} spins at ambient temperature), but imposes severe geometrical restrictions on the sample size. This limits the use of standard ESR spectrometers to small samples with a minimum amount of water. Three-dimensional imaging of such samples inside the cavity can be achieved using a field-gradient technique.[1] It is highly desirable to develop scanning ESR probes for spatially-resolved, two-dimensional measurements of spin distribution in biological tissues, and for large samples that cannot be mounted inside the cavity. In the past, this was done using a low-frequency, surface-scanning coil.[2] The spatial resolution of this technique is limited by the coil size and amounts to few millimeters. The microcoil probes[3–5] allow detection of the ferromagnetic resonance with better spatial resolution, although their sensitivity is not high enough for ESR detection. Magnetic resonance can also be measured locally using a microwave cavity with a small hole.[6–9] In this case, the sample should be mounted outside the cavity in close vicinity to the hole. Here, the coupling of the sample to the microwave magnetic field is weak due to the cutoff effect in a circular hole of a subwavelength size, hence the spatial resolution is limited to 1–3 mm. Microwave scanning probes based on a sharp conducting tip[3,4,10] have an excellent spatial resolution, but their high impedance renders them less suitable for ESR-imaging.

Recently, there have appeared several very sensitive non-inductive ESR detection methods, such as magnetic resonance force microscopy (MRFM),[11–13] scanning tunneling microcopy,[14,15] optically detected magnetic resonance (ODMR),[16] and the Hall bar technique.[17] The ultimate goal of these techniques is the single-spin sensitivity (motivated by quantum computing. Therefore, these techniques have a very limited field of view and usually operate at low temperatures and under vacuum. In this letter, we report on a scanning aperture ESR probe developed with quite a different goal: surface scanning of large-area samples with the highest possible spatial resolution. This requires high sensitivity, which may be achieved using a two-dimensional (2D) resonator (already suggested by Wingfield *et al.*,[18] who used a superconducting coplanar resonator for this purpose).

We developed (i) an *X*-band probe operating at 8.4 GHz and based on sapphire, and (ii) a *C*-band probe operating at 4.5 GHz and based on low-loss microwave ceramics, with $\epsilon=50$. The probe is based on a cylindrical dielectric resonator. The back surface of the resonator is flat, while the front surface is concave (or conical), and is silver-coated, leaving a long, narrow slit at the probe apex.[19] The slit length is $l \sim \lambda/\epsilon^{1/2}$, and its width w, can vary between 1 and 100 μm. Such a slit is a resonant element by its own virtue. The lengths of the slit and of the dielectric resonator are chosen in such a way that they resonate at one common frequency, whereby most of the microwave energy is concentrated in the near field of the slit.[20] This is an open resonator with a Q-factor of 100–1000. The microwave energy is coupled to the resonator through the specially designed coax-to-waveguide adaptor, a dielectrically-filled, cylindrical waveguide (transducer), and a variable air-gap [Fig. 1(a)]. The overall size of the probe is very small [Fig. 1(b)], being determined by the diameter of the dielectric resonator $D \sim 0.7\lambda/\epsilon^{1/2}$. The probe is placed between the poles of an electromagnet (Fig. 2) in such a way that the dc magnetic field is perpendicular to the slit. For the sample mounted in the close proximity to the probe apex, the ESR signal arises only from the component of the microwave magnetic field parallel to the slit. Our estimates yield that the spatial resolution in this direction is equal to the slit width w, while in the direction parallel to the slit, the resolution amounts to $\sim 2\lambda/\pi\epsilon^{1/2}$ for the flat slit and $\sim(2wR)^{1/2}$ for the curved slit.[20] Here, R is the curvature radius of the front surface of the resonator. Unequal spatial resolution of our probe in two perpendicular directions may be partially amended by sample rotation.[21]

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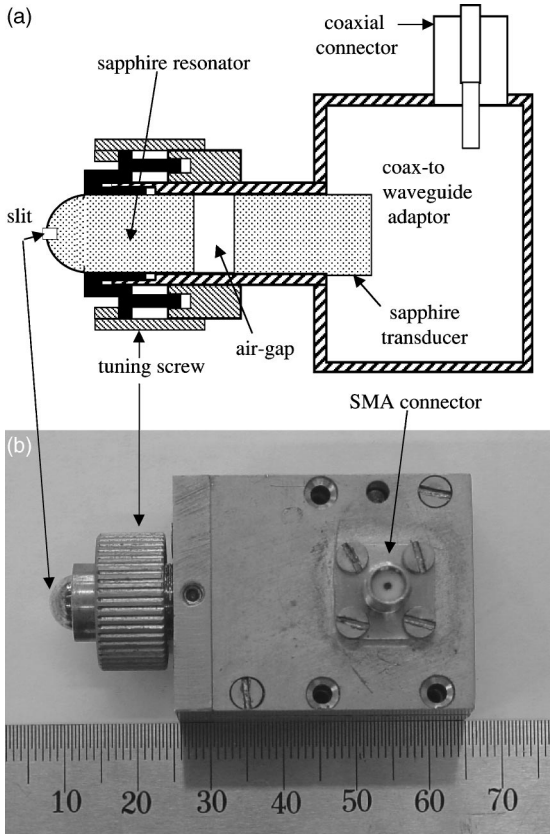

FIG. 1. (a) Design of an *X*-band sapphire probe. (b) Actual probe. $Q=100-1000$; radius of the probe $R=4$ mm, slit width $w=1-100$ μm. Design of the *C*-band probe is quite similar, although the probe radius is 1.8 mm.

ESR detection is performed as follows: The sample is mounted on the *XYZ* positioning stage as close as possible to the slit. This is crucial, since the spatial resolution quickly deteriorates when the probe–sample distance increases. The measurements are done in a contact mode or by mechanically scanning the sample at constant probe–sample separation. We vary the frequency and the coupling to the resonator to achieve the best possible matching, whereupon the reflected signal from the resonator is minimal. We then sweep the dc magnetic field and observe the field-dependent change in the microwave reflectivity (ESR signal). The detection is done directly by an HP-8510C vector network analyzer, or by using magnetic-field modulation, a square-law microwave detector, and the lock-in amplifier.

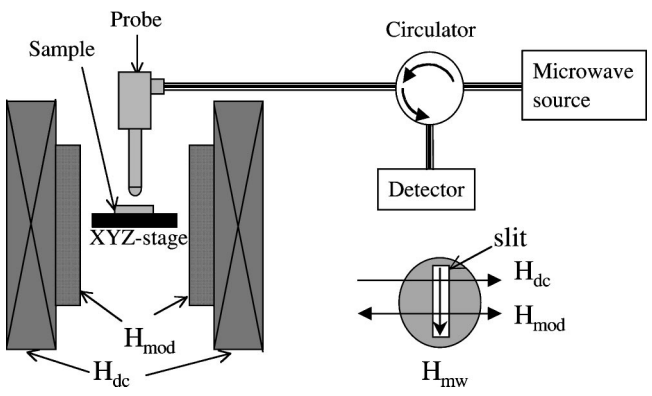

FIG. 2. Measurement setup.

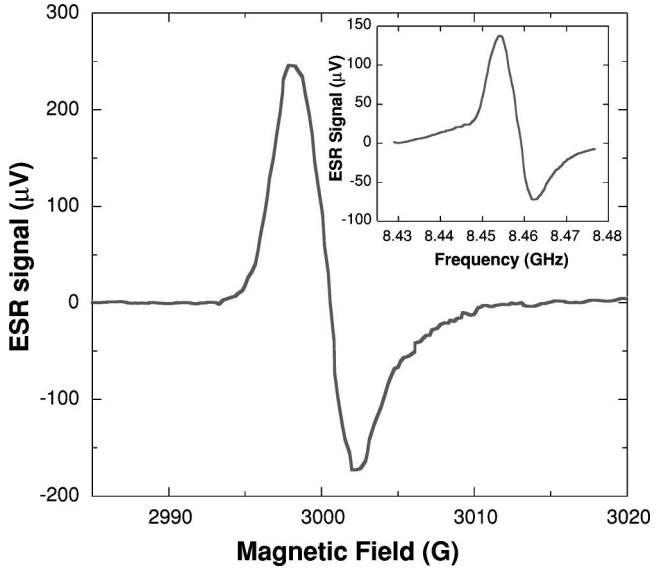

FIG. 3. Local ESR signal from a 120-μm-thick DPPH layer measured by a sapphire probe. Slit width is $w=4$ μm, microwave frequency is 8.45 GHz, modulation frequency is 1 kHz, modulation field is 3 G. The inset shows the ESR signal (using a different DPPH sample and a different probe) obtained via a frequency sweep and a field modulation.

Similar to other studies,[12,13,17] we have used diphenyl-picril-hydrazyl (DPPH) samples to characterize the spatial resolution and sensitivity of our system. Figure 3 shows an ESR signal from a 120-μm-thick DPPH layer measured using a 4-μm-wide slit on sapphire. In contact mode, the knowledge of the size of the illuminated spot and of the sample thickness yields the number of spins exposed to microwave radiation to be $N\sim10^{14}$. Based on this number, and on the signal-to-noise ratio in this experiment (the ESR signal is 250 μV, the noise is 50 nV, microwave power is 200 mW, integration time is 1 s, modulation frequency is 4 kHz), we estimate the minimal number of spins that we can measure with our present method as $\sim10^{11}$. In another experiment, the sensitivity was determined using a relatively wide slit ($w=115$ μm) and a $50\times50\times20$ μm^3 DPPH grain ($\sim10^{14}$ spins) attached directly to the slit. In this case, the whole sample was within the illuminated area. The ESR signal was 4 μV, yielding $N_{\min}\sim10^{12}$ spins for this wider slit. Instead of sweeping the dc magnetic field, we can sweep the frequency. The inset in Fig. 3 shows an ESR signal from a different sample measured via frequency sweep.

Figure 4 shows our ability to scan a relatively large area and to perform spatially-resolved measurements. Here, we made an *XY*-scan, at fixed field and at fixed frequency, over a flat glass substrate on which four small grains of DPPH were attached. The magnetic field H satisfies the resonance condition: $\hbar\omega=g\mu_B H$, where g is the g-factor of the DPPH, μ_B is the Bohr magneton, and $\omega/2\pi=8.45$ GHz is the resonant frequency of the probe. We observe four clearly defined ''hills,'' corresponding to the four DPPH grains. Since the grains were of irregular shape, the probe–substrate distance was rather large ($z\sim1$ mm), hence the spatial resolution in Fig. 4 is determined by the probe–sample distance rather than by the slit width.

We compare the sensitivity of our 2D resonator to the sensitivity of a conventional ESR cavity. For the latter, the absorption signal at the condition of critical coupling is *S*

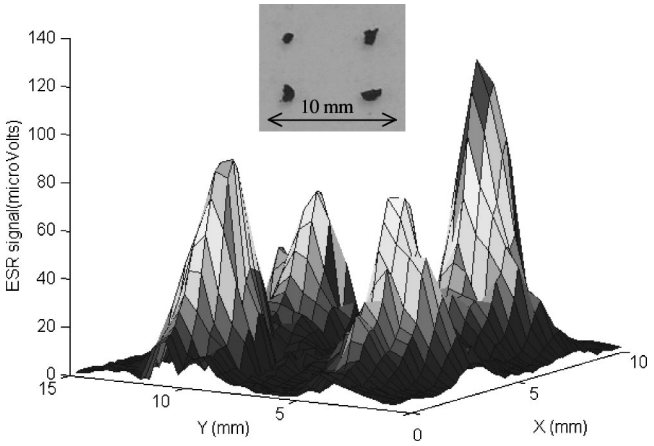

FIG. 4. Spatially-resolved ESR signal from four DPPH grains on glass. Slit width $w=100$ μm, integration time is 0.1 s. The inset shows the optical image of the sample.

$\sim\chi''\eta Q$, where χ'' is the lossy part of the magnetic susceptibility of the sample, Q is the unloaded quality factor of the resonator, and η is the filling factor.[22,23] For a three-dimensional cavity and a small sample in the maximum of microwave magnetic field, $\eta\sim V_s/V_r$, where V_s and V_r are the volumes of the sample and the resonator, respectively (usually $\eta\sim 10^{-4}$). For the sample mounted directly on the 2D resonator, the filling factor is $\eta\sim A_s d_s/A_r d_r$, where A_r is the area of the resonator, d_r is the decay length of the rf magnetic field in the direction perpendicular to the resonator (for a thin resonant slit $d_r\sim w$), A_s is the area of the illuminated spot, and d_s is the penetration depth of the rf magnetic field into the sample (for thin samples it is equal to the layer thickness). For a thick, flat sample on a flat, 2D resonator, the effective filling factor may be close to unity. However, to achieve satisfactory spatial resolution in two directions, the resonator should be curved; hence the area of the illuminated spot is $A_s\sim w\times(2wR)^{1/2}$.[20] This yields an effective filling factor $\eta\sim w^{1/2}\epsilon^{1/4}\lambda^{-1/2}$, which can reach $\eta\sim 1\%$ even for very thin slits ($w=10$ μm) operating in the X-band. The sensitivity of the resonator is determined by the figure of merit ηQ, which for a conventional ESR cavity is ~ 1,[22] while for our probe it is more than 10. This means that the minimal number of spins detected by our technique may be at least the same as, or even smaller than, conventional ESR spectrometers operating at the same frequency. This sensitivity may be increased by increasing the dielectric constant of the probe, similar to Refs. 24 and 25.

Our future plans include the development of a miniature, a ''pocket'' ESR spectrometer that can be used, in particular, for human skin examination in a contact mode. Moreover, the requirement of the dc-magnetic-field homogeneity for our setup is less stringent than that in a conventional ESR spectrometer, due to the small probing area. This will allow replacing the split-coil electromagnet with a small permanent magnet encircling the probe. The detection will be carried out by frequency scanning. We also envision the possibility to conduct optical and microwave measurements with one integrated probe, which can be used, for example, for local ODMR.

In summary, our ESR spectrometer allows us to scan large samples and to probe very small, micron-sized samples. The sensitivity of our present probe is already somewhat better than the sensitivity of a conventional ESR spectrometer. It exceeds the sensitivity of the recently discussed Hall bar technique[17] and approaches that of the MRFM[11] at ambient temperature. Our preliminary studies with the slit widths ranging from 100 to 4 μm suggest that the sensitivity increases when decreasing the slit width (this is probably due to the enhanced Q-factor in very narrow slits). This very interesting feature will be examined in more detail in the future. Our present near-field scanning system is far from being optimized. Eventually we expect to achieve a sensitivity of at least 10^{10} spins.

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