NMR Spectroscopy for Thin Films by Magnetic Resonance Force Microscopy

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Nuclear magnetic resonance (NMR) is a fundamental research tool that is widely used in many fields. Despite its powerful applications, unfortunately the low sensitivity of conventional NMR makes it difficult to study thin film or nano-sized samples. In this work, we report the first NMR spectrum obtained from general thin films by using magnetic resonance force microscopy (MRFM). To minimize the amount of imaging information inevitably mixed into the signal when a gradient field is used, we adopted a large magnet with a flat end with a diameter of 336 μm that generates a homogeneous field on the sample plane and a field gradient in a direction perpendicular to the plane. Cyclic adiabatic inversion was used in conjunction with periodic phase inversion of the frequency shift to maximize the SNR. In this way, we obtained the 19F NMR spectrum for a 34 nm-thick CaF2 thin film.

NMR is a very powerful research tool used as widely as X-ray in physics, chemistry, biology, medicine and engineering. It may not be an accident that X-ray CT and MRI, which are the two most frequently used fundamental diagnosis tools in hospitals, are based on X-ray and NMR, respectively. The signal obtained from NMR basically contains all information on the local electronic and nuclear states. In physics, mostly the interaction between nuclei and electrons is analyzed to get the state and dynamics of electrons in condensed matters. In chemistry and biology, typically the interaction among nuclei is used to get molecular structure. Since a nuclear spin is adopted as a probe in NMR, measurement hardly disturbs the physical state of a sample under investigation. This noninvasive probing capability is best utilized in imaging. NMR was also the first tool to demonstrate quantum computing. It is difficult to imagine that quantum control of a single quantum state, which is one of the ultimate goals of nanotechnology, can be reached without magnetic resonance. The combination of capabilities to select nuclei, and observe static and dynamic interactions is still generating new applications in various fields.

Nanotechnology has been very successful in showing unprecedented phenomena and developing new quantum devices. Nano-sized devices and thin films often have quite different properties from their bulk forms due to the effect of their reduced dimensions, interfaces, and quantum sizes. It is clear that NMR is an appropriate tool for investigating these systems as well. Unfortunately, however, conventional NMR employing an inductive detection scheme can only obtain signals from bulk samples and not from thin film or nano-sized samples due to its low sensitivity. Exceptions include NMR for magnetic thin films; double resonance experiments; optically, electrically or mechanically detected magnetic resonances; and NMR using the nitrogen vacancy spin in diamond. All of these experiments were carried out on specific samples prepared in special ways.

MRFM was an epoch-making leap that improves the level of detection sensitivity in magnetic resonance. Unlike conventional NMR using coils to pick up induced current, MRFM uses a cantilever, as in an atomic force microscope, to obtain the magnetic resonance spectrum. The first demonstration of MRFM in 1992 was followed by the detection of the spin of a single electron a decade later and NMR spectroscopy of a bulk sample in 2012. In this work, we report the first NMR spectrum obtained from thin films by MRFM. Considering that a thin film sample contains billions of nuclear spins, it may seem to make no sense to report thin film NMR by MRFM when a single electron spin has already been detected. The issue here is that the signal obtained by MRFM is a mixture of the spectrum and image of a sample. MRFM has been mostly developed to obtain images at higher resolutions through continual improvements in the sensitivity. In contrast, here we try to remove the image information from the signal as much as possible to acquire the intrinsic spectrum.
Results

The scheme of our MRFM probe is illustrated in Fig. 1a. Magnetic field \( B(r) \) generated by a magnet and a superconducting coil produces magnetization \( M \) on the sample. If the frequency of the RF electromagnetic wave generated by a coil, \( \omega \), satisfies the resonance condition \( B(r) = \gamma \omega / \gamma \), where \( \gamma \) is the gyromagnetic ratio, the magnetization of the sample at that position changes. Then, the force experienced by the sample on the cantilever, \( F = (M \cdot \nabla)B(r) \), also changes. This force change is detected by a fiber-optic interferometer which is used here to measure the cantilever deflection. Samples are 34 ± 2 and 130 ± 5 nm-thick CaF\(_2\) thin films deposited directly onto a cantilever by e-beam evaporation (Fig. 1b).

MRFM detects the force the sample magnetization experiences in the magnetic field gradient generated by the magnet. The smaller the magnet is, the stronger the gradient is and the higher the force and image resolution are. Therefore, a high field gradient is helpful both to enhance the force and the spatial resolution. In the imaging setup (Fig. 2a), a small magnet on the order of a nanometer generates a high gradient field. The resonance slice, where magnetic resonance occurs, is thin compared to the thickness of the sample. The resulting signal is the superposition of the sample image and the intrinsic spectrum.

In spectroscopy, the spectral shape, including the position and linewidth, should be accurately measured. A homogeneous magnetic field is essential for spectroscopy, while a field gradient is required for imaging and force detection. One way to meet both requirements is to generate a magnetic field that is homogeneous on the plane where a thin film sample is placed and varying in a direction perpendicular to the plane using a large flat magnet, as shown in Fig. 2b. The entire sample then experiences a uniform field and imaging is not involved. The gradient in the perpendicular direction produces force and introduces a little bit of 1-D image across the film thickness onto the spectrum. By making the field homogeneous in 2-D, the gradient along the perpendicular direction also decreases. This inevitably decreases the force on the sample and the SNR of the equipment. It is necessary to find a position where the resonance slice is flattest and the gradient along the perpendicular direction is strongest.

The map of the magnetic field generated by our magnet was measured by an electron spin resonance experiment, which gives a much larger signal than NMR. The sample was a micron-sized DPPH particle with a mass of 20 ng. We chose pure iron as the material for the magnet for two reasons. First, we can avoid the Barkhausen noise hard magnets generate at high fields by adopting a soft iron magnet. Second, iron is predicted to have the largest magnetic moment of 5 \( \mu_B \), as a ferric ion in metallic iron has five unpaired electrons in its \( d \) orbitals. In fact, iron has saturation magnetization of 2.1 T, which is greater than that of the NdFeB magnets frequently used as permanent magnets, for which this value is 1.3 T. The magnet is a cylindrical iron needle cut perpendicularly to the axis.

The ESR spectra obtained for various distances between the sample and the magnet are shown in Fig. 3a. The spectra were taken with the sample placed at the symmetry axis of the magnet. Since the field generated by the magnet decreases as the sample-magnet distance
increases, the external field generated by the solenoid coil increases to make the total field the same. Repeating the experiment with the sample at the off-axis positions, we obtained the field profile shown in Fig. 3b. The figure shows that the equipotential surface is relatively flat near the center and bends approaching the edges as expected. In the NMR experiment, the sample was placed at a distance of 70 μm from the magnet, where the profile is flattest over a wide area. The field gradient of the magnet at this position was 50 G/μm when the total magnetic field was increased to 7.82 T using a superconducting coil for the NMR experiment.

We employed a frequency detection scheme to measure the resonance spectrum. This scheme is superior to amplitude detection when the cantilever response is slow. In our case, we tried to maximize the Q factor of the cantilever to compensate the loss of SNR due to the weakened gradient field. In the amplitude detection scheme, the measurement time gets longer when a high Q factor makes the response time long. In the frequency detection scheme, the measurement time can be flexibly changed by setting the frequency bandwidth irrespective of the cantilever response time. This is handy when studying samples with different relaxation times. Given that the relaxation time of the sample (∼60 s) was much longer than the period of the cantilever vibration, we used a cyclic adiabatic inversion scheme in combination with periodic phase inversion of the frequency shift. In the cyclic adiabatic inversion technique, the direction of the nuclear magnetization is repeatedly inverted in synchronization with the cantilever vibration. Then the frequency shift of the cantilever vibration is maximized in resonance. The periodic phase inversion of the frequency shift is effective in eliminating the noise that oscillates in phase with the cantilever.

The 19F NMR spectra of 34 and 130 nm-thick CaF2 thin films obtained by our MRFM equipment are shown in Fig. 4. In fact, two peaks were detected that are separated by 4,590 G from each other (inset). The peaks on the left- and right-hand sites are the 1H and 19F NMR spectra, respectively. The difference in the gyromagnetic ratios of 1H, 42.6 MHz/T, and 19F, 40.1 MHz/T, is expected to produce 4,590 G at the resonance frequency of ω/2π = 313.3 MHz. Hydrogen gas appears to be adsorbed onto the thin film during or after the evaporation process. A similar observation was reported in earlier work. It is useful to have the 1H spectrum together in the sense that it provides a reference for the exact field.

**Discussion**

The linewidth of the spectrum for the 130 nm sample is 24 ± 6 G, while the natural linewidth is known for the CaF2 bulk to be approximately 10 G. Extra broadening is mainly the imaging effect. A magnetic field gradient of 50 G/μm is expected to produce an image with a width of 6.5 G for a sample thickness of 130 nm. The RF modulation and the field oscillation due to the vibration of the sample in the field gradient broaden the spectrum as well. The amplitude of the RF frequency modulation was 10 kHz, which corresponds to 2.5 G. The RMS amplitude of the cantilever vibration was 25 nm. This motion generates a modulated field with an amplitude value of 1.8 G. The total modulation amplitude of 4.3 G is about one fifth of the observed linewidth. The line broadening due to these modulations is expected to be about 1.6 G. Further broadening should be due to the inhomogeneity of the magnetic field on the film plane. The image width of the 34 nm sample is expected to be 4.8 G thinner than that of the 130 nm sample. The measured linewidth of the 34 nm spectrum is 20 ± 6 G, in good agreement with the prediction.

The spectra of the 34 and 130 nm samples were obtained by averaging 10 and 4 times, respectively. Because the SNR of the 34 nm sample was approximately 3, the minimum thickness of the sample we can study is about 10 nm. Thin films with a thickness of 1 nm or less can be obtained with thousands of averaging steps if the spin-lattice relaxation time is not too long, i.e., less than 1 s. The sample with 34 nm × 40 μm² contains about 10¹² F nuclei. This rather poor looking SNR is due to the weakened gradient. Our magnetic field gradient is hundreds of times weaker than the strongest one used for imaging, 4 × 10¹⁰ T/m². The blurring of the spectrum due to the imaging effect will decrease with a decrease in the sample thickness.

In summary, we adopted MRFM that has much higher sensitivity than the conventional NMR equipment to obtain NMR spectrum from general thin films for the first time. To avoid the imaging effect a sensitive MRFM inevitably produces, the magnetic field that is homogeneous on the plane where a thin film sample is placed and varying in a direction perpendicular to the plane was generated by a large flat magnet with the diameter of 336 μm. The frequency detection scheme was adopted because it is superior to the amplitude detection when the Q-factor of the cantilever is high. The cyclic adiabatic inversion maximizes the SNR for the sample with 1 minute long T2. The periodic phase inversion of the frequency shift eliminates the noises that oscillate in phase with the cantilever motion. The SNR of the resulting 19F NMR spectrum for 34 nm thick CaF2 thin film with was 3. The thickness of the thinnest sample that can be studied by our system could reach below 1 nm with averaging. The result of this study can be applied and expanded to various studies of nano-sized samples and thin films, including fascinating monolayer structures such as graphene.

**Methods**

All parts in Fig. 1a are contained in a high vacuum chamber inside a cryostat equipped with a superconducting coil. The total magnetic field is the sum of the fields generated by the magnet in the figure and the superconducting coil. Iron rod with a diameter of 336 μm was used as the magnet for field gradient. The position of the magnet and the optical fiber was controlled in 3 directions by a nano-positioner (attocube systems AG, Germany, Model: ANPxyz100). The thicknesses of the CaF2 thin film samples were measured by means of spectroscopic reflectometry.

What was actually measured by the interferometer to detect the resonance was not the cantilever deflection but the shift of the cantilever resonance frequency under external force. The details of this measurement scheme are also described in our previous work. The cantilever was driven to vibrate near its mechanical resonance frequency at a constant amplitude level by feedback circuits. A phase-locked loop FM demodulator ensures that the frequency of the driving force always follows the vibration frequency of the cantilever. The force constant of the custom-made cantilevers was obtained by integrating the power spectrum at a given temperature. The quality factor of the cantilever was estimated using the free ring-down method. The vacuum chamber of the sample probe was immersed in liquid helium but the actual sample temperature was about 14 K due to RF heating. At a vacuum pressure of 7.2 × 10⁻⁷ torr, the force constant of the cantilever was 6.2 × 10⁻⁵ N/m and the quality...
factor was about 20,000. The frequency of the RF field was 313.3 MHz, corresponding to 7.82 T for a gyromagnetic ratio of $^{19}$F, $\gamma = 40.1 \text{ MHz/T}$.

The RF frequency modulation is expressed as $\omega = \omega_0 + \Omega \sin(\omega t)$, where $\Omega$ is the RF frequency modulation amplitude and $\omega_0/2\pi$ is the vibration frequency of the cantilever. After the oscillation begins, the magnetization amplitude is attenuated with a time constant similar to the spin-lattice relaxation time in the rotating frame, $T_1$. The signal amplitude increases with the amplitude of the RF frequency modulation $\Phi$, but too strong a modulation amplitude level violates the adiabaticity condition, $\beta < (\gamma B_1)^2/\omega_0 \Omega$. The modulation amplitude was set to $2\pi \times 10$ kHz, leading to $(\gamma B_1)^2/\omega_0 \Omega \approx 8$ with the amplitude of the RF field of $B_1 = 3.3 \text{ G}$ and a cantilever vibration frequency of $\omega_0/2\pi = 2.034 \text{ Hz}$.

Periodical change of the frequency shift of the cantilever is measured by a lock-in amplifier. The inversion cycle of the RF modulation was 0.993 Hz, which corresponds to 2.048 cycles of cantilever vibration. The acquisition time was set to 1.2 seconds to acquire the data during at least one inversion cycle. The lock-in time constant was set to 300 ms for a detection bandwidth of 1.2 Hz. The sweep speed of the external magnetic field was 5 G/s.

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Author contributions

S.W. and S.-B.S. performed all of the experiments. S.G.L. implemented the software to run the equipment, and K.K. and Y.H. were responsible for the hardware. S.L. was involved in all of these processes as a supervisor. All authors reviewed the manuscript.

Additional information

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