Direct Observation of the Precession of Individual Paramagnetic Spins on Oxidized Silicon Surfaces

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The precession of individual spins on partially oxidized Si(111) surfaces has been detected using a scanning tunneling microscope. The spin precession in a constant magnetic field induces a modulation in the tunneling current at the Larmor frequency. This radio-frequency signal is shown to be localized over distances less than 10 Å and follows the expected magnetic field dependence.

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The characteristic precession frequencies of paramagnetic atoms and defects can provide unique information about their physical and chemical environments. The most commonly used technique for detection of paramagnetic spin centers, electron-spin resonance (ESR), measures the precession of an induced macroscopic magnetization (which is a result of the alignment of many electron spins) around an external magnetic field.[1] In many cases, valuable spectroscopic information about the properties of individual spins is lost as a result of inhomogeneous line broadening. In addition, ESR measurements typically require a minimum of about 10^{10} spins in order to be detectable.

The presence of small quantities of magnetic impurities or other localized spin centers in bulk tunnel junctions has been shown to significantly affect tunneling characteristics.[2-5] Thus, one may expect that it should be possible to observe this and other spin-related tunneling effects with the scanning tunneling microscope (STM). The STM[6] is unique because it can provide truly local information with atomic resolution about the measured sample and should therefore be sensitive to any local perturbation which is close enough to the tunneling region to affect the tunneling probability. Such a perturbation could be caused, for example, by the magnetic moment of an electron-spin center at a surface interacting with the tunneling electrons via dipolar or exchange interactions. In a constant magnetic field, this magnetic moment will precess around the field direction at the classical Larmor frequency. If the magnetic moment affects the tunneling probability in surrounding regions, then we expect that the precession of the spin around the magnetic field will induce a modulation in the tunneling current at the same frequency, providing a way of detecting and studying individual spin centers using the STM.

It is shown here that the rf component of the tunneling current indeed contains information about the paramagnetic centers located at the surface. Moreover, with the atomic resolution we have obtained with the STM, we believe that we have detected the precession of individual spins.

The experiments were performed using an STM on which two parallel bar magnets were mounted to establish a magnetic field perpendicular to the surface. The strength of the field could be varied by changing the separation between the magnets. The tip was a polycrystalline tungsten wire etched to a sharp point and thermally annealed in vacuum for cleaning. The surfaces were partially oxidized Si(111) which were prepared by first outgassing and annealing a commercial Si(111) wafer (Sb-doped, 5 mΩ cm) at 1000 °C to produce well-ordered regions of Si(111)-(7×7) as observed in the STM. After the 1000 °C anneal the sample was cooled to 800 °C and the vacuum chamber was backfilled with dry oxygen to expose the sample to 10^{-8} Torr O_2 for 300 s. The samples were then cooled to room temperature for the STM measurements. Other experiments, where the surfaces were not oxidized at all or where much more oxygen was backfilled into the chamber, did not show any rf signals. The exact nature of the spin centers formed in this manner has not been determined. However, previous ESR experiments have established that several types of spin centers are typically formed.[7-10]

For these measurements the magnetic field was chosen to be around 180 G, implying a precession frequency around 500 MHz, assuming a g value of 2. These values are much smaller than those normally used in ESR, and allow us to avoid the use of waveguides, which would be difficult to incorporate into our STM without deterioration of the vibrational isolation system.

Another experimental consideration is whether it is possible (using conventional rf equipment) to detect less than 1 nA rf current from the tip of a STM without significantly affecting its operation. Standard signal-to-noise (S/N) ratio calculations[11,12] predict that using a spectrum analyzer with a bandwidth of 100 Hz combined with an rf amplifier should give a S/N ratio of 16 dB. In our experiments, a network was constructed to separate the rf current from the dc tunneling current and to provide impedance matching, consisting of a UHV-compatible low-pass filter for the dc tunneling current and a high-pass filter for the rf current. This network degraded the system S/N ratio by 3 dB, providing a final system S/N ratio of 13 dB. Upon testing system sensitivity, it was found that the measured S/N ratio agreed with that calculated within 1 dB. Our setup thereby allows us to detect a 0.25 nA rf current at 500 MHz, and we have incorporated this system into an atomic-resolution STM with no noticeable image degradation.

In order to firmly establish our identification of individual precessing spins, we have performed several types of measurements which show that (1) each spin center gives rise to a well-defined signal at a frequency which is (within experimental error) at the Larmor frequency, (2) the frequency of this signal is proportional to the magnetic field as predicted for Larmor precession, and (3) the signal is correlated with the lateral position of the tip above the surface and is restricted to regions of approximately 10 Å diam.

Before any tunneling current was established, a careful examination for any background signals was performed and any external signals not related to tunneling were identified. An example is seen as the left peak in the rf power spectrum shown in Fig. 1(a) at a frequency of 483.2 MHz. These background rf signals were found to be very narrow in frequency and stable in time. Most importantly, such spurious signals do not depend on the location of the tip above the surface. Spin centers were identified by slowly scanning the tip from point to point, and measuring the rf power spectrum of the tunneling current at each point with the tip position fixed. The average tunneling current was typically set at 1 nA.

The signals observed for typical spin centers can be seen in Figs. 1(a) and 1(b). These figures show the rf power (within a 1-kHz bandpass) as a function of frequency, measured at spatial locations ≃3 Å apart. In Fig. 1(a), at 483.8 MHz, the signal from a typical spin center is observed. The magnitude of the signal is very small when the tip is far away from the spin center, increases in magnitude as the center is approached, and finally decreases in magnitude as the tip moves past the center. This behavior is typical of the spin centers and, as shown later, the rf signals are strongly correlated with the position of the tip and are quite reproducible. The signal from another spin center is shown in Fig. 1(b). This peak more clearly shows that the peak has a nearly Gaussian line shape; the full width at half maximum is approximately 100 kHz.

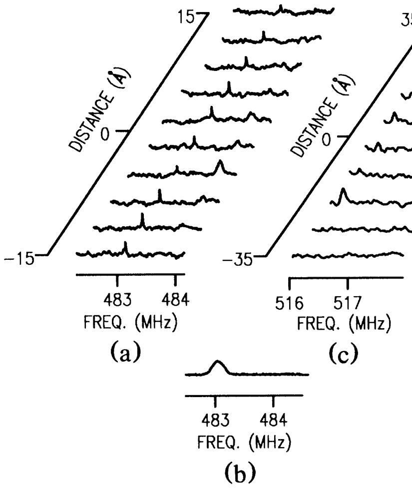

FIG. 1. (a) Consecutive rf power spectra of the tunneling current, measured at different lateral separations of the tip from a spin center in a field of 172 G. Each spectrum was taken at a point separated by 3 Å from the previous one. (b) A power spectrum near another spin center in a 172-G field, showing the nearly Gaussian line shape. (c) Same as (a), except for a field of 185 G; separation between scans = 7 Å.

The signals observed in Figs. 1(a) and 1(b) were both acquired using an applied magnetic field of 172 G; the expected precession frequency is then approximately 481.6 MHz, for $g=2$. Our measurements of these and other spin centers consistently show that their frequency spectra are restricted to the 483–484 MHz region, while no spatially dependent signals are observed in other frequency regions. The difference between the predicted and experimental frequencies as well as the day-to-day variations in the frequency can have several sources.

One possibility is simply an error of ≃0.7 G in the magnetic field (which is within the error limits of our gaussmeter). These day-to-day variations in the observed frequencies can arise from a slight variation in the location of the tunnel junction with respect to the magnets, since the magnetic field is not homogeneous over macroscopic distances. Part of this range in frequency can also arise from variations in the frequency of different spin centers in which case the observed frequency can also provide important information about the identity of the spin center. For example, other ESR studies of oxidized silicon have detected a number of centers with different g values resulting from their different physical environments.[7-10]

Finally, small shifts (on the order of the linewidth) can result from the electric field at the tunnel junction. Previous studies have shown that high electric fields can, in some cases, produce small changes (usually 1% or less) in effective g values.[13] In the STM, the local electric field depends on the shape of the tip and the local, atomic-scale topography of the sample. This in turn could produce small shifts in the precession frequency which depend both on the lateral separation of the tip from the spin center as well as on the local sample-tip geometry.

The Larmor precession frequency is proportional to the magnetic field strength. In order to test the field dependence of our rf signals, experiments were performed at different magnetic fields. Increasing the magnetic field to 185 G leads to the disappearance of the signals near 483 MHz and, as shown in Fig. 1(c), it leads to the appearance of *new* signals at 516.2 MHz, close to the Larmor frequency of 518 MHz expected for this increased field.

Final evidence for the detection of spin centers is provided by directly imaging the two-dimensional spatial extent of the rf signal. This is achieved by first identifying the precession frequency from the frequency scans discussed in Fig. 1, and then adjusting the spectrum analyzer to measure the total rf signal in a narrow bandpass centered at the observed Larmor frequency. The total rf power within this bandpass is then measured as a function of the x-y location of the tip in a two-dimensional raster scan over the surface.

Figure 2(a) shows an image of the rf power as a function of the x and y coordinates of the tip in a gray-scale representation, with regions of high rf power appearing white and regions of low rf power appearing black. This image clearly shows that the rf signal from the precessing spins is localized to a region of $\simeq 10$ Å spatial extent. Since the image is acquired in a raster-scan fashion and the rf signal appears in more than ten sequential raster lines, it confirms that the observed rf modulations result from a localized perturbation at the *surface.*

The corresponding conventional STM topographic image acquired simultaneously during this scan is shown in Fig. 2(b). Atomic resolution on the oxidized surface is not achieved due to the disordered nature of such oxygen-covered surfaces and local charging effects, as has been noted in previous STM studies of oxidized silicon.[14,15] The surface appears quite flat, except for a channel approximately 4 Å deep extending through the image. The spin center observed in Fig. 1(a) originates from within this channel. The spatial extent of this rf signal also appears to be greater in directions parallel to the channel than perpendicular to it. Additionally, a "node" is observed in the magnitude of the signal. This shape may arise from two nearby spins or, more likely, it may represent a nodal character of the signal directly above a single source located within the channel. We see evidence for such nodal character in scans of other centers as well. However, this spatial distribution of the rf power around the paramagnetic center (when measured in this way) cannot be predicted without knowing the mechanism of the interaction between the precessing spin and the tunneling electrons.

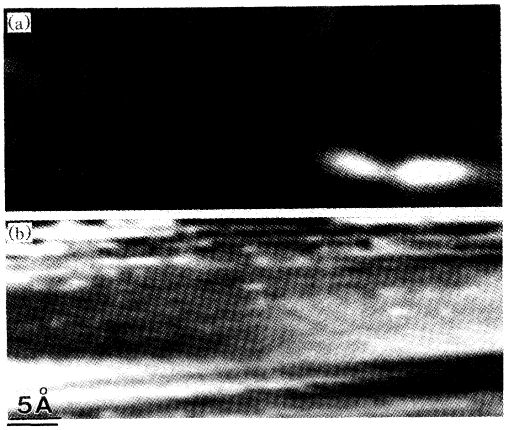

FIG. 2. (a) Gray-scale image showing the rf signal at a fixed frequency (483.8 MHz) as a function of the tip location. (b) The corresponding topographic image recorded simultaneously with (a).

The rf signal levels we observe correspond to at least a modulation in the tunneling length or tunneling barrier of 0.1 Å or 50 meV, respectively. Such modulations can arise from several processes. At small distances from a spin center we expect strong interactions. Suppose the spin carries a magnetic moment of 1 Bohr magneton (μ_B) (corresponding to $S=\frac{1}{2}$ and $g=2$). Associated with this spin is a magnetic dipole field B which has a magnitude of approximately μ_B/r^3. At a distance of 1 Å this field is roughly 10000 G. In the presence of a constant external magnetic field the spin and its associated magnetic dipole field pattern precess at the Larmor frequency. As a result, close to the spin, both the direction *and magnitude* of this magnetic dipole field B are modulated at ω_L. At such small separations from the spin center, it is possible that the strong magnetic fields directly influence the tunneling probability.

Another explanation might be that the precessing spin induces a strong modulation (at ω_L) in the density of states of the conduction electrons in the neighborhood of the spin. This explanation is based on the fact that the presence of a magnetic impurity in a conductor is known to induce strong Friedel-type oscillations in the electron density of states[16] near the impurity. This phenomenon (which was proposed as an explanation of the Kondo effect)[16] arises from exchange interactions between the impurity and the conduction electrons. If these density of states changes are dependent on the spin orientation, then we expect that the spin precession leads to a modulation of the tunneling current—at ω_L.

The possibility of assisted tunneling through spin flips or any other mechanism which requires exchange interactions between the tunneling electrons and the localized spin is not plausible because of the expected nearly random spin orientation of the tunneling electrons.

It is also possible that several interactions can be important and that their individual contributions depend on the lateral separation of the tip from the paramagnetic center. Whatever the interaction mechanism is, it must be dependent on the orientation of the spin of the paramagnetic center relative to the tunneling current. Since this orientation is periodic at ω_L, the interaction will also contain a component at this frequency. Further experimental and theoretical efforts are required in order to discriminate between these mechanisms.

An additional interesting question is how the random thermal motions of the spin change the signal. It is clear that spin-spin relaxation processes, which randomize the phase of the spin, should broaden the observed signal. Spin-lattice relaxation processes might have a different effect. Close to the dipole such processes induce magnetic field changes only in a direction parallel to the "trajectory" of the tunneling electrons. The effects of these processes pose interesting questions for future experiments with different spin systems and at different temperatures.

We have shown that the rf signals characteristic of local spin precession can be detected with the STM with atomic-scale resolution. Although the mechanism of interaction between the precessing spins and the tunneling electrons is not fully understood, the potential of this technique is clear. The new ability to observe spin precession with atomic spatial resolution provides the scanning tunneling microscope with an additional powerful capability—to identify different paramagnetic atoms and defects at surfaces based on their spin precession.

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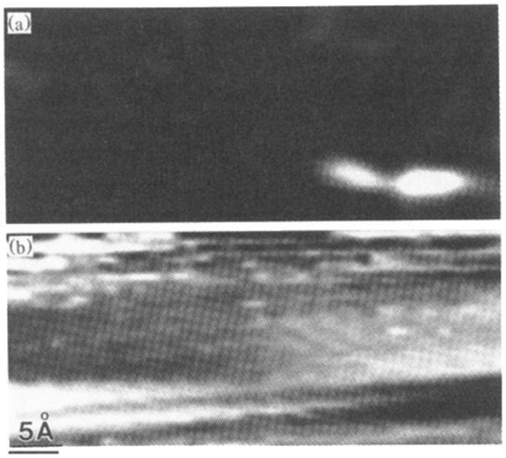

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