Distribution of frequencies of a single precessing spin detected by scanning tunneling microscope

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We have measured high frequency signals in the tunneling current of scanning tunneling microscopy for a submonolayer oxide thin film on the Si(111)-7×7 surface. We demonstrate that the signal is related to the Larmor precession of the electron spin associated with a dangling bond. The detected precession frequency possesses a broad distribution (linewidth is comparable to that observed by conventional electron spin resonance) and a split near the maxima, both of which are attributed to the inhomogeneity of the *g* factor of a single spin. © *2008 American Institute of Physics*.
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The detection of a single spin is demanded for variety of applications, e.g., for chemical characterization of a single molecule, reading and manipulation of isolated spins for spintronics and quantum computation. Various techniques have been examined including optical spectroscopy,[1] magnetic resonance force microscopy,[2] and spin noise spectroscopy.[3] A method that detects the Larmor precession by monitoring a variation of tunneling current has attracted much attention due to its compatibility with solid devices and atom-scale spatial resolution. Experiments have been performed using scanning tunneling microscope (STM) on various systems[4–6] and several theoretical works were published.[7–10] Although sharp peaks have been detected in the current versus frequency plot, fluctuations in the position of such peaks have been observed and currently lack a satisfactory explanation.

In this letter, we describe an electron spin resonance (ESR)-STM study of an initial stage of oxidation for the Si(111)-7×7 surface. We have examined the origin of the fluctuations of the detected precession frequency of a single spin. We plot a histogram for the distribution of the detected frequencies and have found that the distribution width is similar to that of the spectra of a conventional ESR measurement on the same surface with a splitting in the middle. This behavior might be similar to a phenomenon called *spectral diffusion* which is observed in the optical absorption for isolated molecules. We will discuss an inhomogeneous distribution of the *g* values as representing the origin of the broadening and the splitting of the histograms.

The experimental setup is shown in Fig. 1(a), which is similar to the one used in a previous paper.[6] As it has been discussed previously, the impedance matching is critical to prevent loss of the signal containing the high frequency component.[11] We have used a dynamic impedance matching circuit containing a field effect transistor device.[12]

The behavior of ESR signals at an initial stage of oxidation of Si(111)-7×7 surface has been investigated.[13] The dangling bonds of the Si(111)-7×7 surface can be spin centers.[14] Umeda *et al.* have observed ESR signal from the dangling bond (P_{s0}), whose intensity shows its maximum with a small exposure of oxygen molecules.[13] In this experiment, we intended to measure the behavior of P_{s0} on the Si(111)-7×7 surface after an exposure to 1 L of oxygen gas (1 L$=10^{-6}$ torr s).

Figures 1(b) and 1(c) show plots of the signal intensity of the lock-in amplifier output versus frequency.[12] We have established criteria for assigning a signal feature as being derived from a spin related feature.[12] The feature with a marker in Fig. 1(b) satisfies conditions by exhibiting a derivative shape.

Another example that we assign as a spin related feature is shown in Fig. 1(c). The derivativelike peak shape is identical with the one shown in Fig. 1(b). A puzzling issue, however, is that the frequencies of the detected features of Figs. 1(b) and 1(c) are not identical. In order to strengthen the reliability of our observation, we have accumulated sufficient data on the spin precession features and performed statistical analysis with an automated peak-search algorithm.[12]

In Figure 2, we show a histogram plot of the number of the detected signal (yield) versus frequency out of the stored

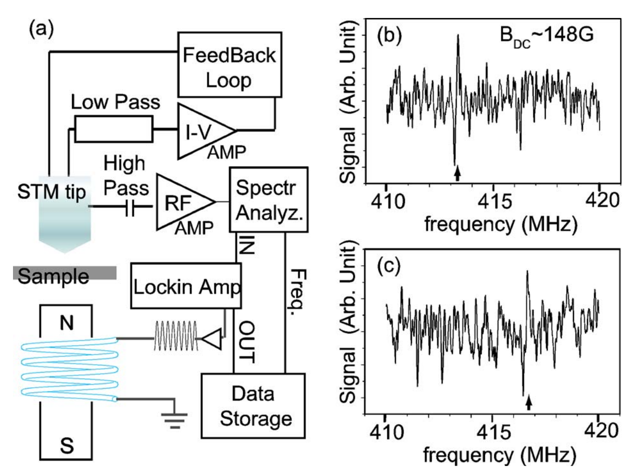

FIG. 1. (Color online) (a) Schematics of ESR-STM measurement setup. (b) Observed ESR-STM spectrum and the detected spin signal are marked at 413.3 MHz (experimental detail in Ref. 12). (c) Same as (b) but the marked position shifted to 416.7 MHz.

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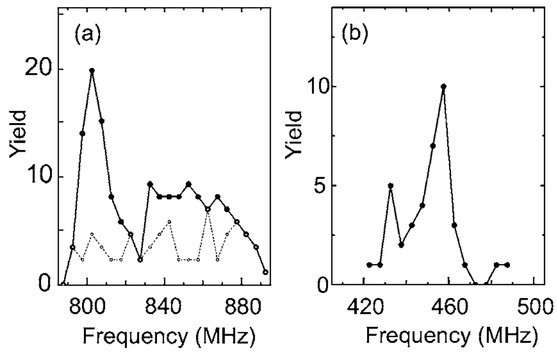

FIG. 2. (a) Histogram of the number of detected signal vs frequency. Totally, 1.5×10^3 spectra were scanned. The bin size of frequency is 5 MHz. The thick (thin) line corresponds to $B=288$ G (160 G). (b) Histogram obtained with $B=160$ G. $I_{tunnel}=1.0$ nA and $V_{bias}=2.0$ V.

data. In total, 3.3×10^3 scans have been executed, resulting in the detection of ~140 signals. The measurements were performed with two different magnetic field strengths, which were measured as 288 and 160 G by a Hall device.

The histogram corresponding to $B=288$ G (806 MHz) is depicted by a thick line in Fig. 2(a). The distribution is centered at ~800 MHz and the width is ~15 MHz at its half maximum. The plot should be compared to the case in which a weaker magnetic field of 160 G (~448 MHz) was used. The results are shown as thin lines in Fig. 2(a) from almost the same number attempts with the above case. As expected the plot shows no characteristic feature other than white noise features.

The measurement for the frequency range of 420–490 MHz is shown in Fig. 2(b) with the use of the same magnetic field strength of 160 G. In total, 1.5×10^3 scans were examined, resulting in the detection of 60 signals. Moreover, the center of the frequency distribution at ~455 MHz is close to the expected Larmor frequency of 448 MHz. The width of the distribution is ~10 MHz and is narrower than that observed for case with $B=288$ G.

The main observation from the plot of Fig. 2 is that the signals assigned to spin related features are distributed in a broad manner. Moreover, the center frequency is close to the expected Larmor frequency. To examine further the latter feature, we constructed histograms such as Fig. 2 with various static magnetic field strengths and the results are presented in Fig. 3. The error bars in the vertical direction correspond to the peak width of the histogram plot. The lateral

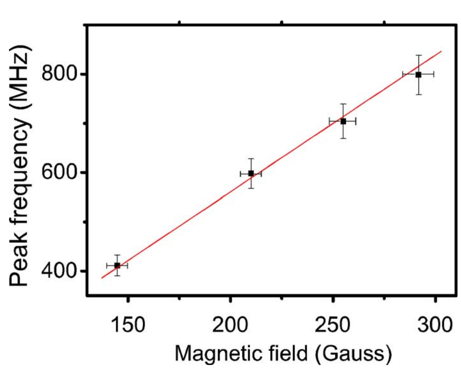

FIG. 3. (Color online) Plot of magnetic field (B) vs frequency of the detected peak. The vertical error bars correspond to the fluctuation of the frequency, as shown in Fig. 1. The line is calculated for the expected Larmor frequency assuming $g=2$.

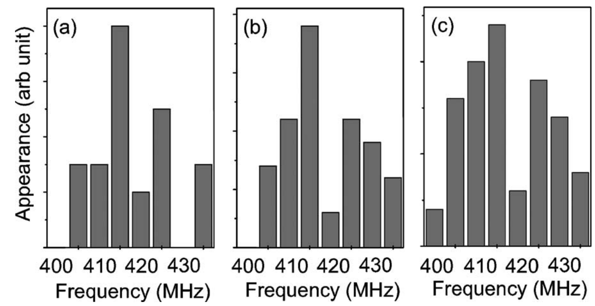

FIG. 4. Histogram of the number of detected signal vs frequency. The magnetic field ~148 G and the bin size is 5 MHz. The (a)–(c) spectra were obtained with tunneling current of $I_t=1$, 2, and 4 nA, respectively.

error bar corresponds to the uncertainty of the field strength measured with the Hall device. The magnetic field itself is stable over time and fluctuations contribute negligibly to the error.

The center frequency can be compared to a line possessing a slope of 2.8 MHz/G, which is the conversion ratio between the magnetic field and the Larmor frequency. This notable observation is consistent with the idea that the detected frequency is related to the Larmor frequency of $\mu_B B$. Thus, it is very likely that signals such as those shown in Fig. 1 originate from the spin center of P_{s0}. In addition, it is apparent that the width of the histogram (the vertical error bars in Fig. 3) is also proportional to the magnetic field. This indicates that the width is a result of an inhomogeneous distribution of the g values.

The combination of individual sharp peaks concomitant with a wide distribution of their center frequency is similar to the phenomenon called spectral diffusion, which is studied in single molecule spectroscopy (SMS). The mechanism has been explained by the spatial inhomogeneity and time-dependent dynamics of a single molecule. In particular, chemical reactions[15] and conformational changes[14] have been extensively studied.[16] The spectral broadening results from variations in the chemical environment and is similar to the spectrum measured for an ensemble of molecules.

Consequently, as SMS can be compared to the spectrum measured for an ensemble of molecules, we likewise compare the spectra shown here to the results obtained for an ensemble of spins. To enable such comparison, we refer to the conventional ESR result. This study reported a 5 mT linewidth after a 0.4 L exposed surface with X-band ESR at 340 mT. The linewidth corresponds to ~1.5% of the Larmor frequency,[13] which is comparable to the frequency distribution of Fig. 2 (~2%). We suggest that the relation of the apparent sharp peak shown in Fig. 1 and the broad distribution of the center frequency (the latter being similar to the spectrum of the conventional ESR) is analogous to the relation of a SMS measurement and a spectrum obtained for an ensemble of molecules. In a similar vein, the center frequency represented by a snapshot, such as shown in Fig. 1, is expected to fluctuate in frequency owing to environmental effects in a manner similar to that of spectral diffusion in SMS. In this scenario, the frequency of single spin, as measured with our STM probe, appears to fluctuate.

In addition to the broadening, we often observe a gap in the histogram near the center frequency. The results that are shown in Figs. 4(a)–4(c) are obtained with different tip-sample distances. We further note that the shape of the distribution varies with the tip-to-sample distance, although the center frequency and the split reproduce well in Figs. 4(a)–4(c).

We consider that both the broadened distribution of peaks and its split can be explained with inhomogeneous distribution of the g values. The first scenario is that there exists a minimal variation in chemical environment. One possibility is the contribution from spin centers different from P_{s0}. It was reported that there appear P_{s1} and P_b spin centers at different stages of oxidation,[13] and such additional centers can be a source of broadening. Second, there is a dynamic change in chemical environment of a single spin. Here, we consider an effect of strain caused by the STM tip. Strain broadening, that gives an inhomogeneous distribution of the g values, is well known in the ESR spectroscopy and was observed in Pb centers many years ago.[17] Since the broadening of the histogram increases when the field is higher (Fig. 2), we suggest the possibility that strain broadening is the cause of the increase in both the linewidth and splitting. In an unstrained spin center, the anisotropy of the g tensor is $\Delta g = 0.01$. When the spin center is strained in such a way that the angle between the dangling bond and the other Si–Si bonds is smaller, this will cause an increase in Δg.

During tunneling, it was observed previously that significant forces are applied between the tip and the sample.[18] As a result, significant deformation of the surface is possible and is of the order of ~ 1 Å for this surface.[19] Since the spin centers in the 7×7 surface are not equivalent according to the dimer-adatom-stacking fault (DAS) model and the dangling bonds are not perpendicular to the surface,[12] they will have a larger Δg. This explanation is in agreement with the fact that the splitting and the width become clearer when the tip-to-sample distance is reduced (Fig. 4). In addition, this is supported by the observation that the shift in frequency is dependent on the position of the tip, as reported previously.[5] Although the interaction between the spin and the tunneling electrons would also be an origin of the broadening of the peak width,[8] it seems that the behavior is a result of several competing effects.

In summary, we have studied the ESR-STM spectroscopy of the Si$(111\text{-}7 \times 7)$ surface with submonolayer coverage of oxygen. High frequency components in the tunneling current derived from the P_{s0} spin center have been detected in the plot of current versus frequency. They have a sharp peak width but the distribution of the detected center frequencies shows a broad peak and a split near the maxima. The frequency distribution is comparable to the peak width of the conventional ESR data. The broadening and split are derived from inhomogeneity of the g values of spins, which might be originated from a fluctuation of chemical environment of spins and/or surface stress induced by STM tips.

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