Analyzing multiple encounter as a possible origin of electron spin resonance signals in scanning tunneling microscopy on Si(111) featuring C and O defects

Y. Manassen a,⁎, M. Averbukh a, M. Morgenstern b

a Department of Physics and the Bas-Katz Center of Science and Technology in the nm Scale, Ben-Gurion University of the Negev, P.O. Box 653, Beersheva 84104, Israel
b II. Institute of Physics and JARA-FIT, RWTH Aachen University, D-52074 Aachen, Germany

A R T I C L E   I N F O

Article history:
Received 25 August 2013
Accepted 17 December 2013
Available online 28 December 2013

Keywords:
ESR-STM
Hyperfine coupling
Single spin detection

A B S T R A C T

The Si(111)7 × 7 surface exposed to 0.1 L of O2 and the carbonized Si(111) surface are investigated by electron spin resonance scanning tunneling microscopy (ESR-STM) using frequency sweeps and magnetic field sweeps. Only after oxidizing the clean Si(111)7 × 7 or by using the carbonized Si(111), spatially averaged ESR-STM spectra exhibit several peaks and dips around the frequencies corresponding to g = 2. The energy difference between these features is close to the known hyperfine splitting of A ≅ 9 MHz for vacancies in SiC interacting with next-nearest neighbor 28Si. Such spectra with peaks and dips can be qualitatively reproduced by introducing a primary encounter of the lead electrons with the localized spin correlating the two spins which afterwards evolve in different local hyperfine fields, thus, developing a relative spin angle prior to tunneling.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The attempt to detect and manipulate a single spin is a fundamental challenge in nanoscience and nanotechnology [1–5]. For that purpose, several scanning tunneling microscopy (STM) techniques providing unprecedented spatial resolution have been developed, e.g., inelastic spin flip spectroscopy below 1 K [6,7], spin polarized scanning tunneling spectroscopy, again below 1 K [8], detection of the Kondo peak below 10 K [9,10] and ESR-STM at room temperature [11–21].

The technique of ESR-STM detects single spins on surfaces in magnetic field B by their Larmor frequency fL. A peak at fL appears within the frequency spectrum of the tunneling current I driven by a DC voltage V. Evidence for such a peak has been found for several spin systems, including dangling bonds [11–13], metal impurities in silicon [14], and adsorbed molecules as BDPA [15], TEMPO [16], DPPH [17], nitronyl nitroxide [18] and TTM [19] radicals. A recent breakthrough in ESR-STM detection was the assembling of all frequencies with signal strength above a certain threshold for many spectra, which were plotted as a frequency histogram [20,21]. For Si(111)7 × 7 exposed to oxygen at room temperature, two peaks at 403 MHz and 407 MHz are obtained at B = 14.4 mT within the histogram. Subsequently, these peaks could be spatially correlated to two defect types appearing differently in the STM images [21]. This implies that ESR-STM can provide spectroscopic information down to the atomic level.

However, the mechanism of ESR-STM is still under debate, i.e. several different explanations with different drawbacks are offered in the literature [22–29]. One explanation assumes a periodic change of the local density of states (LDOS) of the sample due to the precessing localized spin. The LDOS change is induced by the interplay of the exchange interaction between the precessing spin and conduction electrons of the sample surface and the Rashba-type spin–orbit interaction of these conduction electrons [22]. The resulting, oscillating LDOS around the localized spin leads to an oscillating electric dipole moment [23], which couples capacitively to the tunneling junction. However, both mechanisms require a strong spin–orbit (SO) interaction with a Rashba parameter of the order 0.1 eV nm at the substrate surface, which is hardly available in the experiments on Si(111) [11–14,20,21] or HOPG [15,16], but exists as 3.3 eV nm [53] in the experiments on Au(111) [17–19].

Another explanation relies on the fact that the spin-dependent tunneling barrier is periodically modulated by the exchange interaction of the tunneling electrons with the precessing spin [24]. If the about 10–100 electrons, which are tunnelled during a single period of the precession, exhibit a 1/f type noise in spin polarization, one obtains an increased noise component of I at the Larmor frequency. This model, thus, requires a time correlation of the tunneling electron spins which has been related to a fluctuating magnetic moment with multiple relaxation times at the apex of the tip [25]. Reasonable agreement with experimental signal strength is found, if the exchange interaction between tip and localized spin is assumed to be 0.1 eV. Such an exchange interaction can be detected, in principle, using spin polarized scanning tunneling microscopy in varying magnetic field as has been...
done for Co atoms on Pt(111) [30]. An analysis of the resulting single-atom magnetization curves shows an oscillating exchange splitting between neighboring Co atoms decaying with increasing Co-Co distance. The oscillations could be measured down to an amplitude of 50 μeV giving an upper bound for the exchange interaction between tip electrons and the probed spin level for this particular system at tunneling currents of about 1 nA [30]. It is unlikely, but not impossible, that spins from an unpolarized W tip interact with the systems studied in [11–21] stronger by more than three orders of magnitude. Since the exchange interaction between tunneling electrons and a localized spin also guides the strength of the inelastic spin–flip channel [26], it can be deduced, in principle, from inelastic scanning tunneling spectroscopy results performed at larger B [6] rather directly.

Further explanations require a spin polarization of the leads, i.e. of the tip and of the sample area, which are coupled to the local spin. This spin polarization must have a perpendicular component to the external magnetic field [26,28,29]. Then, a signal-to-noise ratio of 4 for the peak at the Larmor frequency with respect to shot noise is predicted assuming full spin polarization of both leads perpendicular to B and a spin life time of the probed spin dominated by the interaction with the tunneling current [26]. However, it is not clear, how the required spin polarization of the leads could be achieved within the published experiments, where the B-field induced spin splitting is about four orders of magnitude lower than temperature.

Here, we propose dynamic spin polarization by the radical pair mechanism, well known for ESR experiments in solutions [31], as the mechanism which induces the required spin polarization of the leads. The mechanism is usually based on a double encounter between the probed localized spin and an electron of the probing electrodes. It relies on a combination of mutual exchange and different hyperfine fields between an electron of the electrodes and the localized spin. We present ESR-STM data obtained on the oxidized and the carbonized Si(111) surface to be qualitatively consistent with such a model. Peaks and dips around the frequencies expected for g = 2 could be naturally explained by the model, which are thereby attributed to multiplets caused by hyperfine splitting, i.e. different relative orientation of probed electron spin and a nearby nuclear spin. A first ESR-STM spectrum attributed to hyperfine splitting was reported earlier on TEMPO molecules, however, without detailed explanation [16].

Sincerely, the local detection of hyperfine splitting could impose a novel, reliable method for chemical sensitivity of STM [32–36]. Inelastic scanning tunneling spectroscopy is also chemically sensitive by detecting vibrational and rotational modes of adsorbed molecules and atoms, but the spectra can be strongly inhomogeneous within the inhomogeneous field around the Larmor frequency (blue line in Fig. 1(c)), a broad peak with full width at half maximum (FWHM) of about 8 MHz appears after O2 exposure (Fig. 1(d) and (e)) or after three days of waiting in UHV (black curve in Fig. 1(c)). The center of this peak varies by about 1% between subsequent measurement runs in accordance with the estimated uncertainty of B. Similar peaks corresponding to g ≈ 2 with a width of ~10 MHz have been observed previously by ESR-STM data of oxidized Si(111) at slightly lower B [20,21].

While the spectral peak of the naturally contaminated sample is featureless (black curve in Fig. 1(c)), a small fine structure consisting of several peaks and a high energy dip appears in the spectra of the intentionally oxidized sample (Fig. 1(d),(e)). A similar combination of peaks and dips was observed repeatedly also on the carbonized surface as described below.

The distances between the peaks and dips (~10 MHz) are similar to distances expected from hyperfine splitting on SiC in ensemble measurements. For example, macroscopic ESR spectra of vacancies...
in SiC induced by electron bombardment exhibit three lines with a separation of the two outer peaks of $A = 8.7 \text{ MHz}$ [38 (Fig. 4 - in that paper), 39 (Fig. 6) 40 (Fig. 7)]. They are attributed to the hyperfine splitting between the radical of the vacancy and a next-nearest neighbor $^{29}\text{Si}$ nucleus with nuclear spin $I = 1/2$, which is separated from the probed spin by a C atom (see Fig. 2(c)). The central peak corresponds to a vacancy which has only $^{28}\text{Si}$ as next-nearest neighbors, while the outer peaks are caused by dangling bonds with a $^{29}\text{Si}$ next-nearest neighbor.

Of course, the hyperfine spectrum of the surface could be different from the bulk. For example, the experimentally observed hyperfine field for Si dangling bonds increases at the interface between Si and SiO$_2$ with respect to the bulk [56]. Thus, an exact quantitative agreement of ESR-STM data to bulk ESR data is not to be expected, but they should be of the same order of magnitude.

A triplet of blue arrows with total energy distance of $8.7 \text{ MHz}$ is, however, used to mark the peaks and dips in Fig. 1(d) and (e). The small shift in frequencies of this triplet with respect to $g = 2$ (red arrow) is compatible with the $B$ field uncertainty. Thus, it is likely that the observed substructure is related to the hyperfine splitting of the spin flip signals [38–40]. Notice that a similar hyperfine splitting is expected for other Si radicals with next-nearest neighbor $^{29}\text{Si}$ atoms, e.g., separated by an oxygen atom. Notice further that the probability of finding one $^{28}\text{Si}$ at a next-nearest neighbor position is significant albeit the small natural abundance of $^{28}\text{Si}$ (4.7%). Of course, spectra recorded on a single position would either exhibit a single central line indicating no $^{29}\text{Si}$ in the surrounding or either a double line separated by $A$ if the close-by nuclear spin flips faster than the acquisition time of a spectrum or a single line shifted by $\pm A/2$ with sign depending on the nuclear spin direction with respect to $B$. Partly, we, indeed, observe single spectra with single lines, but since the position of the tip is not sufficiently confined to the atomic scale during the acquisition, we postpone the corresponding analysis to future measurements at low temperature.

In order to substantiate the relation of the spectra to vacancies in SiC, we increased the disorder of our sample surface by C contamination, i.e., we repeated the experiments with samples that were not cleaned with the degreasing method prior to annealing and flashing. Auger electron spectroscopy (AES) shown in Fig. 2(a) revealed a strong C contamination of these samples of about 40%. If one takes the sensitivity ratio between the Si(90 eV) peak and the C(270 eV) peak of about 3 into account, thus, the surface has a similar stoichiometry as SiC. The samples show a hexagonal LEED pattern (inset of Fig. 2(b)). STM images (Fig. 2(b)) exhibit an irregular hexagonal atomic structure with nearest neighbor distances of 0.54 nm on average. This distance is identical to the atomic distances measured by STM on SiC(111) [41]. $3 \times 3$ reconstruction with hexagonal atomic appearance in STM was also observed on C-rich Si(111) prepared by acetylene adsorption [42].

A cross section of the T4 site structural model of SiC(111) [43] is depicted in Fig. 2(c) including a subsurface Si vacancy and a next-
known. It might be due to dangling bonds in amorphous silicon carbide spectrum after oxidizing the sample by 0.1 L of O\textsubscript{2} at a different magnetic added. It obviously does not show the dip-like feature. A zoom into the ESR-STM spectrum of Au(111) recorded with the same equipment is spurious responses of the matching circuit or the STM circuitry, an fi

The ESR-STM spectra in Figs. 1(d), (e), 2(e), (f) and 3(a) consistently exhibit a dip at the high frequency (low field) side of the spectrum, while the low frequency (high field) components are peaks at positive sample bias. This is reminiscent of macroscopic ESR spectra observed after so-called chemically induced dynamic electron polarization (CIDEP) via the radical pair mechanism (RPM) [31,44]. Motivated by this reminiscence, we developed a model which qualitatively explains the multiple peak and dip structure of the spectra. A sketch of this model is shown in Fig. 4(a)-(e). The process requires localized states at the tip and within the sample, between which a hopping transport occurs (Fig. 4(a)). A first encounter of the probing spin from the tip with a localized one in the sample leads via an exchange interaction J to a preferential relative orientation of the two spins (Fig. 4(b) top). Afterwards, the two spins are separated again (Fig. 4(b) bottom) and precess in an effective local B-field, which is different for the localized spin and the probing one, e.g., due to a different hyperfine interaction with the nuclear bath (Fig. 4(d)). This leads to a relative angle between the two spins. The same must happen between two localized spins within the sample (Fig. 4(c)-(d)) with one becoming the drain contact of the probed impurity. Finally, the probing spin tunnels through the localized level in the central impurity into the drain and from there into the substrate (Fig. 4(e)). According to [28] the corresponding tunneling probability oscillates with the Larmor frequency which gives rise to a peak or a dip in the noise spectrum depending on the relative

nearest neighbor \(^{29}\text{Si}\) atom, which mimics the structure proposed for a hyperfine splitting of \(A = 8.7\) MHz [38–40]. Fig. 2(d) shows a large scale ESR-STM sweep of the surface which indicates the noise level within the spectra far away from the Larmor frequency (475–560 MHz). It exhibits a strong dip approximately 60 MHz wide close to the Larmor frequency at \(g = 2\). The dip appears reproducibly, but its origin is not known. It might be due to dangling bonds in amorphous silicon carbide adsorbed on the tip [57]. In order to exclude that the dip is caused by spurious responses of the matching circuit or the STM circuitry, an ESR-STM spectrum of Au(111) recorded with the same equipment is added. It obviously does not show the dip-like feature. A zoom into the spectrum after oxidizing the sample by 0.1 L of \(\text{O}_2\) at a different magnetic field uncertainty. We performed an additional experiment on oxidized C-rich Si(111) where the frequency is fixed to 513 MHz and the B field is swept (Fig. 2(f)). In order to compare this spatially averaged spectrum with the spatially averaged frequency spectrum of Fig. 2(e) directly, the B field was swept from higher values to lower ones around 183 G. The probed field range of 6 G corresponds to the frequency range of 17 MHz (around 513 MHz) probed in Fig. 2(e). Indeed, the two spectra exhibit a similar fine structure albeit slightly shifted with respect to each other.

Finally, we discuss ESR-STM spectra recorded at different voltage polarities in the same sample area. The results obtained on the C-rich Si(111) surface without oxidation are shown in Fig. 3(a)-(b). At positive sample bias \(U = +3\) V, again peaks and one dip at high energy are visible. The central peak, however, becomes a prominent dip after reversing the sample bias to \(U = -3\) V. In contrast, no significant dependence of the spectra on tunneling current is found (not shown).

5. Discussion

The ESR-STM spectra in Figs. 1(d), (e), 2(e), (f) and 3(a) consistently exhibit a dip at the high frequency (low field) side of the spectrum, while the low frequency (high field) components are peaks at positive sample bias. This is reminiscent of macroscopic ESR spectra observed after so-called chemically induced dynamic electron polarization (CIDEP) via the radical pair mechanism (RPM) [31,44–48]. Motivated by this reminiscence, we developed a model which qualitatively explains the multiple peak and dip structure of the spectra. A sketch of this model is shown in Fig. 4(a)-(e). The process requires localized states at the tip and within the sample, between which a hopping transport occurs (Fig. 4(a)). A first encounter of the probing spin from the tip with a localized one in the sample leads via an exchange interaction \(J\) to a preferential relative orientation of the two spins (Fig. 4(b) top). Afterwards, the two spins are separated again (Fig. 4(b) bottom) and precess in an effective local B-field, which is different for the localized spin and the probing one, e.g., due to a different hyperfine interaction with the nuclear bath (Fig. 4(d)). This leads to a relative angle between the two spins. The same must happen between two localized spins within the sample (Fig. 4(c)-(d)) with one becoming the drain contact of the probed impurity. Finally, the probing spin tunnels through the localized level in the central impurity into the drain and from there into the substrate (Fig. 4(e)). According to [28] the corresponding tunneling probability oscillates with the Larmor frequency which gives rise to a peak or a dip in the noise spectrum depending on the relative

Fig. 2. (a) Auger electron spectrum of undegreased Si(111) after three cycles of annealing and flashing as described in Section 3, peaks C(270 eV) and Si(90 eV) are marked, primary beam energy: 3 keV; (b) STM image of the same surface, area: 25 × 20 nm\(^2\); \(U = 3\) V, \(I = 0.1\) nA, some hexagonal structures are highlighted by white circles; inset: corresponding LEED pattern, beam energy 100 eV; (c) cross section of the Ta substrate structural model of SiC(111) according to [44], additional subsurface vacancies are included, atoms are colored in black (C) and white (Si) and dangling bonds (db) in red, the \(^{29}\text{Si}\) position required for a hyperfine splitting of \(A = 8.7\) MHz is indicated; (d) blue: ESR-STM spectrum on the surface from (a) and (b), average of 40 spectra, sweep time: 300 s for each spectrum, \(U = 3\) V, \(I = 0.1\) nA, \(B = 212\) G, the two spectra are scaled such that they represent the same counts/s, Larmor frequency for \(g = 2\) is marked by a red arrow; (e) ESR-STM spectrum of C rich Si(111) + 0.1 L \(\text{O}_2\), average of 105 spectra, sweep time: 30 s for each spectrum, \(I = 0.2\) nA, \(U = 2\) V, \(B = 183\) G. The expected Larmor frequency for \(g = 2\) is marked by a red arrow. Blue arrows mark the hyperfine-split triplet shifted by about 9 MHz as indicated; (f) B field sweep of ESR-STM signal at \(f = 513\) MHz of C rich Si(111) + 0.1 L \(\text{O}_2\), \(I = 0.2\) nA, \(U = 2\) V, average of 30 spectra (100 s each), red arrow corresponds to expected \(g = 2\) line and blue arrows mark the hyperfine-split triplet.
importance, the $x$ axis is the relative spin polarization $S_{1z} - S_{2z}$ along $B$, and the $y$ axis describes the difference in the non-diagonal terms of the density matrix, i.e. the relative angle of the two spins. When the spins collide for the first time, the exchange interaction ($J$) leads to differences in the occupation of singlet and triplet states as indicated by $\mu(0)$. After separation, the two radicals are prone to their different Zeeman fields with difference $2Q = \Delta gB = \Delta A_{1y}m_{1y} - \Delta A_{2y}m_{2y}$ for hyperfine couplings of spin 1, 2; $m_{1y}, m_{2y}$ nuclear magnetic moments) for time $\tau_0$. Formally, this leads to a difference in the non-diagonal terms in the density matrix of the singlet–triplet basis [31]. Thus, the two spin state is rotated towards the $y$ axis of the Bloch sphere by an angle $\Phi$ (Fig. 4(g)). The reencounter with the reappearance of $J$ finally leads to rotation around the $y$ axis ending up in spin polarization $(S_{1z} - S_{2z} \neq 0)$ of the two spins along the external $B$ field.

$Q$ and $J$ can also act simultaneously, but to get a significant spin polarization, one needs $J \approx Q$ for at least $Q^{-1}$ s [31]. Transferring this model to a localized spin and a second electron from the tip or from the sample is appealing, since it can lead to a significant relative spin polarization of the localized spins and the lead electrons even at 300 K, which is possibly the central requirement for the observation of ESR-STM peaks. In contrast, the thermal spin imbalance of the localized spin in $B$ field at 300 K is only about $10^{-4}$ at 180 G.

Importantly, the first encounter and the subsequent different development of the two spins leads to a relative spin angle, which is the requirement of our second model [28] explaining the ESR-STM signal. The angle is already induced by $Q$ only acting for time $\tau_0$ after the primary encounter. This leads to $|1\uparrow\uparrow\uparrow > + e^{i\theta}1\downarrow\downarrow\uparrow > $ with $\Phi = 2Q/h \cdot \tau_0$, which is identical to the projection of two spins with a mutual angle $\Phi$ to the singlet–triplet ($m = 0$) basis. The secondary encounter is, thus, not required in our model except for probing. The projection can be seen explicitly by writing the two spins within a basis perpendicular to the spin in the impurity, i.e. $|1 + |1 - > + e^{i\phi}\uparrow\downarrow >$ (constants are omitted), respectively, and using the $m = 0$ components of the triplet only.

The other part of the model is given in Ref. [28], which we adapt, or rather similarly in Ref. [29]. The model describes transport between two spin polarized leads via a central magnetic impurity and is depicted in Fig. 4(h). In our experiment, we identify the magnetic impurity with a defect of the carbonized Si surface. The two leads are identified with the tip and a sample region having developed a relative angle to the defect spin by a primary encounter of its electrons or holes with the defect. The electrons in the leads are, thus, spin polarized into directions with angle $\theta_i$ and $\theta_q$ with respect to the external $B$-field. The electron, consequently, tunnels into a superposition of Zeeman states within the impurity and accordingly oscillates. Spin flip transitions towards the collector mix the two components, which leads to an oscillating tunneling current at the Larmor frequency. The model is quantified in terms of rate equations for the density matrix of the localized Zeeman levels [28]. We have repeated this calculation for the case where double population of the impurity is forbidden (Coulomb blockade) with $\theta_i = \theta_q = \pi/2$, i.e. parallel magnetization of the leads, and for $\theta_i = -\theta_q = \pi/2$, i.e. antiparallel magnetization of the leads. The tunneling couplings were $R_1 = 1$ and $R_2 = 0.1$ for the left and right lead, respectively, given in units of the Zeeman splitting of the impurity. The Fano factors $F$ shown in Fig. 4(i) and (j) reveal a peak close to the Larmor frequency, if the lead spins are parallel, and a dip at this frequency if the lead spins are antiparallel, in accordance with [28,29]. Thus, different relative angles of the spins of the two probing leads and the probed spin can turn peaks into dips and vice versa offering a natural explanation for the appearance of both, peaks and dips, in the measured spectra. Semiclassically, the origin of the peaks or dips is explained in [29] in terms of the minimum dwell time of the electron in the dot, before it can tunnel out of a superposition state. If the spins of both leads are parallel, the tunneling out can happen immediately, while for antiparallel leads, a minimum dwell time of half the Larmor period is required (Fig. 4(g)). Thus, the exponential decay of
the dot occupancy after occupation is modulated by the Larmor period. The modulation is either cosine-like or sine-like leading to enhancement or suppression of the current component at the Larmor frequency, i.e., 

\[ \frac{\Delta q}{2} \text{ or } \sin{q} \]

The required polarization of the leads canted with respect to the localized Zeeman level is suggested to be provided by RPM. Firstly, the impurity spin creates a partial singlet or triplet with nearby electrons. The subsequent precession corresponds to hyperfine splitting of the impurity spin. We calculate \( \theta_{\text{hyper}} \) for three different \( Q \) according to the three anticipated hyperfine lines of the impurity. We use a hyperfine splitting of 10 MHz and assume \( \Delta B = 1.5 \text{ MHz} \) for both electrodes, i.e., \( Q_1 = 6.5 \text{ MHz}, Q_2 = 1.5 \text{ MHz}, Q_3 = -3.5 \text{ MHz} \), corresponding to the hyperfine fields at the three different nuclear environments. Then, the Fano factor spectrum is calculated again for \( \Gamma_L = 0.025 \) and \( \Gamma_R = 0.0025 \) for each \( Q \). The reduced tunneling rates with respect to Fig. 4(c) and (d) are required to obtain sharper peaks within the spectrum. The three resulting curves are multiplied by the probabilities to find zero or one 29Si nuclear spin with the corresponding orientation at a next-nearest neighbor position in bulk SiC. Finally, the three curves representing different hyperfine environments

---

**Fig. 4.** (a)-(e) Schematic representation of the leading to Larmor precession of the tunneling current (see text); (f) Bloch sphere representation of the central spin level (related to the angle between the polarizations of the leads) which is Zeeman split by \( B_{\text{ext}} \), the green dot is the starting point of the spin evolution, if the injecting lead is perpendicular to \( B_{\text{ext}} \). Green and blue dots symbolize the position of the oscillating spin for a maximum in the tunneling probability to the detecting lead for parallel and antiparallel leads, respectively; (g) Bloch sphere states (dashed lines) according to [28]; vectors of electron spin polarization in the left lead, the dot and the right lead are indicated as blue arrows, external fields. Green and blue dots symbolize the position of the oscillating spin for a maximum in the tunneling probability to the detecting lead for parallel and antiparallel leads, respectively; (h) schematic representation of the leading to Larmor precession of the tunneling current (see text); (i) calculated Fano factor according to [28] for the case \( \Gamma_L = 0.025 \) and \( \Gamma_R = 1.0 \), in units of \( s \); (j) calculated Fano factor for the case \( \Gamma_L = 0.025 \) and \( \Gamma_R = 1.0 \), in units of \( \mu s \); (k) calculated Fano factor using the relative angles between a lead spin and a localized spin resulting from [31], \( \theta_{\text{L}} \) and \( \theta_{\text{R}} \) are angles of spin polarization of the lead electrons with respect to the impurity spin. We calculate \( \theta_{\text{L}} \) for three different \( Q \) according to the three anticipated hyperfine lines of the impurity. We use a hyperfine splitting of 10 MHz and assume \( \Delta q = 1.5 \text{ MHz} \) for both electrodes, i.e., \( Q_1 = 6.5 \text{ MHz}, Q_2 = 1.5 \text{ MHz}, Q_3 = -3.5 \text{ MHz} \), corresponding to the hyperfine fields at the three different nuclear environments. Then, the Fano factor spectrum is calculated again for \( \Gamma_L = 0.025 \) and \( \Gamma_R = 0.0025 \) for each \( Q \). The reduced tunneling rates with respect to Fig. 4(c) and (d) are required to obtain sharper peaks within the spectrum. The three resulting curves are multiplied by the probabilities to find zero or one 29Si nuclear spin with the corresponding orientation at a next-nearest neighbor position in bulk SiC. Finally, the three curves representing different hyperfine environments.
are added in order to mimic our experimental situation averaging over several atomic configurations. The results for two different evolution times $\tau_q$ after the first encounter are shown in Fig. 4(k) and (l). The following similarities to the measured spectra are observed. In Fig. 4(k) ($\tau_q = 5 \mu s$) we see a peak at low frequency (mostly $F > 1$), a dip at high frequency (mostly $F < 1$) and a derivative-like feature in between close to $g = 2$. A similar appearance of the spectra is visible in Fig. 1(d) and (e), in Fig. 2(e) and (f) and in Fig. 3(a) with the distance between peak and dip close to $A = 9$ MHz. Using a different $\tau_q = 17.5 \mu s$ and exchanging $g$, we find a broad peak with a double peak fine structure at low frequency and a double dip at higher frequency. This resembles the spectrum in Fig. 3(b) except of the double peak fine structure. Thus, the model using previous encounter and different precession frequencies after the encounter qualitatively reproduces the observed spectra including their change with voltage polarity. Similar line shapes consisting of peaks and dips appear in the calculations for a broad range of parameters. The intensities of the peaks and dips are a few percent of the shot noise. The intensity scales linearly with the width of the peaks, i.e. they get larger and wider with stronger coupling to the leads.

However, in order to get a sufficient spectral weight at the experimentally observed linewidth, the evolution time $(5 \mu s, 17.5 \mu s)$ has to be much larger than the typical time period between two tunneling events $(\sim 2$ ns). A possible explanation would be that the electron spin is stored coherently for a few $\mu s$ after the first encounter prior to tunneling. Since the spin relaxation time of Si conduction band electrons at room temperature is about $10$ ns [50], this is only possible within another local defect. There, the Larmor precession can evolve with larger spin relaxation and coherence times. Recent spin coherence measurements of defects in SiC have revealed room temperature coherence times up to $50 \mu s$ [54] and even up to $100$ ms have been found for P impurities in Si without nuclear purification at low temperature [51]. Of course, the exact coherence times depend on unknown details of the local impurities and the confining potential [52], but it is possible that they exceed $10 \mu s$. Thus, we propose that the disorder at the surface introduced by carbon or oxygen leads to a hopping type transport, which stores the spin coherently after the primary encounter close to the vacuum gap, as a decisive step for the observation of ESR-STM signals at $300$ K. This requires, hence, that the tip is made out of disordered silicon, too, which is a reasonable assumption due to the regular structure of the W tip with the Si surface. The model naturally implies that changing the polarity couples the lead electrons differently to the contact of the W tip with the Si surface. This requires, hence, that the tip is made out of disordered silicon, too, which is a reasonable assumption due to the regular structure of the W tip with the Si surface.

The coherence times exceed $10^2 \mu s$, thus leading to a different peak shape at high frequency (mostly $F > 1$) and a derivative-like feature in between close to $g = 2$. A similar appearance of the spectra is visible in Fig. 1(d) and (e), in Fig. 2(e) and (f) and in Fig. 3(a) with the distance between peak and dip close to $A = 9$ MHz. Using a different $\tau_q = 17.5 \mu s$ and exchanging $g$, we find a broad peak with a double peak fine structure at low frequency and a double dip at higher frequency. This resembles the spectrum in Fig. 3(b) except of the double peak fine structure. Thus, the model using previous encounter and different precession frequencies after the encounter qualitatively reproduces the observed spectra including their change with voltage polarity. Similar line shapes consisting of peaks and dips appear in the calculations for a broad range of parameters. The intensities of the peaks and dips are a few percent of the shot noise. The intensity scales linearly with the width of the peaks, i.e. they get larger and wider with stronger coupling to the leads.

Secondly, one of the lead spins tunnels via the probed localized spin to the other lead leading to the oscillating tunneling current peaked at the Larmor frequency or the Larmor frequency additionally influenced by close-by $^{28}$Si nuclear spins. This scenario shows striking qualitative similarities to the measured ESR STM spectra and is supported by the change in line shape with bias voltage polarity. However, the similarity in terms of signal strength and the required complicated electron hopping and storage close to the tunneling gap implying a rather disordered surface are less satisfactory. We believe that this novel model would contribute to the still missing quantitative understanding of ESR-STM.

Note added to proofs

Two papers discussing the mechanism of ESR-STM were recently published: Phys Rev B 88, (2013) 15423 and cond-mat arxiv 1306.0363v1.

Acknowledgment

This work was funded by the European project FP7-people 2011 IAPP ENSSTM grant agreement #286196 and the German Science Foundation via Mo 858/8-2. Additional support was given by a grant from the USA Israel Binational Science Foundation (BSF) and the Israel Ministry of Science (Taiwan–Israel program), the International Collaborative Research Grant by the National Institute of Information and Communications Technology of Japan (NICT) and the Israel Science Foundation. We acknowledge helpful discussions with V. Meden, B. Horovitz, D. Schuricht, H. Bluhm, and M. Pratzer. Moreover, we appreciate the helpful measurements on the impedance matching circuit by C. Saumus and M. Morgenweg and the assistance of H. Reale with the AES.

References