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



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ABSTRACT

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#### 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  $f_L$ . A peak at  $f_L$  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.

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© 2013 Elsevier B.V. All rights reserved. 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 directly modifies the tunneling current *I*. Alternatively, the 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)

The Si(111)7  $\times$  7 surface exposed to 0.1 L of O<sub>2</sub> 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  $\times$  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  $A \cong 9$  MHz for vacancies in SiC interacting

with next-nearest neighbor <sup>29</sup>Si. 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.

[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 tunneled 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



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done for Co atoms on Pt(111) [30]. An analysis of the resulting singleatom 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  $\mu$ eV 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 influenced by the substrate [35]. Probing LDOS changes after adsorption [32–34] is not chemically specific and the chemical contrast observed, e.g., on a PtNi alloy, resulting from different bonding between the last tip atom and the surface atoms is rather restricted to alloys [36].

#### 2. Experimental setup

The ESR-STM experiments are performed using a home-made STM based on a well-known design [55] and operated in ultrahigh vacuum (UHV) with a commercial control unit (APE research, Trieste, Italy). Two bar magnets induce a static magnetic field of about 200 G parallel to the sample surface. The field is measured at the sample center by a Gaussmeter prior to each experimental run. The *B* field uncertainty is dominated by different tip positions within the inhomogeneous field during different experiments resulting in an error of several Gauss. An additional coil around a ferrite bar is used to apply an additional alternating *B* field with an amplitude of 22 mG parallel to the surface for lock-in detection. This coil is also used for *B*-field sweeps.

The detection of the frequency spectrum of the tunneling current *I* is performed using a bias-T to separate DC and AC currents, an *rf* amplifier (MITEQ) and a HP spectrum analyzer operated at a band width of 30 kHz. A broad band impedance matching circuit is used to reduce

the resistance mismatch between the tunneling junction and the detection system [37]. In order to improve the signal-to noise ratio further, the *B*-field is modulated by a sinus and the resulting spectral change (output of the spectrum analyzer) is detected via a Stanford lock-in amplifier [13]. A sketch of a similar detection scheme has been shown in Fig. 1a of [20]. The resulting derivative signal from the lockin amplifier is afterwards integrated numerically in order to ease comparison with macroscopic ESR spectra. Notice that the value of zero intensity is arbitrary in this procedure, since the integration offset is not known. We fix it to the value at the initial frequency of each spectrum. Correspondingly, negative values indicate a reduced noise with respect to this value, while positive values indicate an increased noise level. About 100 spectra, each lasting either 30 s or 100 s, are taken subsequently in the same sample region and are summed after the integration. We made sure before each spectrum that the tip achieves atomic resolution without obvious double tips. Due to thermal drift in the experiment, each of the ~100 spectra belongs to different surface atoms such that the presented spectra are averaged over various defect configurations resembling ensemble measurements. Typically also a single spectrum is recorded on a number of atoms due to the thermal drift during 30 s, such that it does not contain the information on a particular defect configuration.

## 3. Sample preparation

The Si(111)7 × 7 surface was prepared by annealing for 30 min at a temperature of 950 °C and 30 subsequent short flashes to 1200 °C. This thermal cycling was repeated for 3 times leading to the (7 × 7) reconstruction in STM images as shown in Fig. 1(a) and to a (7 × 7) diffraction pattern in LEED (low energy electron diffraction). During all heating processes, the pressure remained below  $1.5 \times 10^{-10}$  Torr. Afterwards, the sample was exposed to 0.1 L of molecular oxygen at room temperature. Initial experiments were performed on samples cleaned by an established degreasing procedure (rinsing with trichloro-ethylene, acetone, ethanol and deionized water – in an ultrasonic bath). Later experiments, which aimed at a higher carbon contamination, skipped the degreasing step leading to a disordered ( $\sqrt{3} \times \sqrt{3}$ ) structure in STM images (Fig. 2(b)) after the thermal cycling. This sample is called C-rich Si(111).

### 4. Results

Fig. 1(b) shows the STM image of Si(111) after oxygen exposure. The image looks more disordered than before exposure. It exhibits bright bumps and protrusions on the atomic scale. These structures have previously been attributed to different oxidation states of the Si adatoms [21]. After obtaining stable imaging conditions, individual ESR-STM spectra were recorded. While the clean Si(111) surface shows a rather featureless averaged frequency spectrum of the tunneling current 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 O<sub>2</sub> 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  $g \approx 2$  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 in SiC in ensemble measurements. For example, macroscopic ESR spectra of vacancies

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