Real Time Electrical Detection of Coherent Spin Oscillations

Felix Hoehne,* Christian Huck, and Martin S. Brandt
Walter Schottky Institut, Technische Universität München, Am Coulombwall 4, 85748 Garching, Germany

Hans Huebl
Walther-Meißner-Institut, Bayerische Akademie der Wissenschaften, Walther-Meißner-Str. 8, 85748 Garching, Germany

We demonstrate that the bandwidth of pulsed electrically detected magnetic resonance can be increased to at least 80 MHz using a radio frequency-reflectometry detection scheme. Using this technique, we measure coherent spin oscillations in real time during a resonant microwave pulse. We find that the observed signal is in quantitative agreement with simulations based on rate equations modeling the recombination dynamics of the spin system under study. The increased bandwidth opens the way to electrically study faster spin-dependent recombination processes, e.g., in direct semiconductors which so far have almost exclusively been studied by optically detected magnetic resonance.

Recombination processes are ubiquitous in bipolar semiconductors such as inorganic or organic light emitting diodes and solar cells. Particularly valuable information can be obtained when a recombination process is spin-dependent since this allows for the spectroscopic identification of the participating charge carriers, recombination centers or charge transfer complexes via their spin signatures [1–5] by using methods such as optically or electrically detected magnetic resonance (ODMR and EDMR, resp.) [6, 7]. In addition, by means of coherent spin manipulation and pulsed optical excitation of charge carriers, highly relevant information on charge carrier dynamics can be obtained, allowing to determine, e.g., trapping and recombination times [8, 9]. To this end, complex sequences consisting of microwave (mw) pulses for electron spin manipulation, radiofrequency (rf) pulses for nuclear spin manipulation and light pulses for carrier excitation have been developed [10, 11]. However, in the case of pulsed EDMR the finite bandwidth of conventional preamplifier-based current measurement setups limits the time resolution to some microseconds. For the observation of phenomena faster than that like coherent spin oscillations or fast recombination processes one therefore resorts to an indirect detection technique which allows to reconstruct the state of the different spin ensembles relevant for the recombination by measuring the spin-dependent part of the current transient after the pulse sequence [12]. If, e.g., the coherent driving of a particular spin ensemble in a Rabi oscillation experiment is to be monitored, this requires the time-consuming measurement of a separate transient for each driving pulse length followed by a reconstruction of the Rabi oscillation from an analysis of these transients [13, 14]. Moreover, this method is only applicable to spin systems where at least one of the spin-dependent time constants is sufficiently long to be detected with the available measurement bandwidth. For continuous wave (cw) EDMR, it has been demonstrated [15] that the detection bandwidth can be increased by more than one order of magnitude employing an rf-reflectometry-based detection scheme [16, 17] which simultaneously improves the signal-to-noise ratio by avoiding low-frequency noise. Here, we combine this detection scheme with pulsed spin manipulation and use it to observe coherent spin oscillations in real time during the mw pulse, in contrast to the reconstruction from the photocurrent transient after the pulse. Furthermore, with the help of a quantitative model we show that the signal intensity of real time pulsed EDMR and its time dependence are in very good agreement with the results of the conventional pulsed EDMR, demonstrating that we now have an additional highly versatile method at our hands to characterize fast charge and spin dynamics in semiconductors down to nanosecond time scales.

Before describing the pulsed rf-reflectometry EDMR (rf-EDMR) measurements, we briefly review the principle of pulsed EDMR measurements in a little more detail [12, 13]. Most EDMR signals can be described in terms of weakly coupled spin pairs, where the recombination rate between two paramagnetic localized states depends on the relative orientation of the two spins [red and blue arrow in Fig. 1(a)] [18]. Spin pairs with an antiparallel orientation of the two spins recombine rapidly, while parallel spin pairs are stable on a much longer timescale. Therefore, under above-bandgap illumination a steady-state develops with almost all spin pairs in the parallel state. Resonant excitation of one of the two spins by mw irradiation increases the number of antiparallel spin pairs and consequently also the recombination rate which results in a resonant decrease of the photocconductivity. In the most simple pulsed EDMR experiment illustrated in Fig. 1(a), a resonant mw pulse causes one of the two spins (blue arrow) to coherently oscillate between its eigenstates. This changes the symmetry of the spin pair resulting in an oscillation of the overall recombination rate. The frequency of this oscillation (tens of MHz) is chosen much faster than the typical decoherence rates [19] and, therefore, in many cases larger than the bandwidth of most EDMR current detection setups (usually below
1 MHz) preventing the direct observation of these oscillations. However, the amplitude of the current transient after the mw pulse is proportional to the number of antiparallel spin pairs at the end of the pulse, so that the state of the spin pair can be determined by measuring the current transient [12]. In the following, we demonstrate that the limitations of this indirect detection scheme can be overcome by rf-reflectometry allowing to detect the coherent spin oscillations during the mw pulse.

The samples used in this work were grown by chemical vapor deposition and consist of a nominally 22 nm thick Si layer with a P concentration of $3 \times 10^{16} \text{cm}^{-3}$ on a 2.5 μm thick, undoped Si buffer grown on a (100)-oriented silicon-on-insulator substrate. The doped epilayer leads to a dominant $^{31}\text{P}-\text{P}(\text{m})$ recombination [20], where the P$_{\text{iso}}$ spin partners are defect states at the interface of the doped epilayer and the natural oxide formed on top [21]. All experiments are performed at 5 K under illumination with red light of an LED (photon energy $h\nu = 1.95 \text{ eV}$) in a dielectric mw resonator for pulsed EPR at X-band frequencies. Interdigit Cr/Au electrical contacts with a periodicity of 10 μm are evaporated on an area of 2x2 mm$^2$.

For rf-reflectometry, a chip inductance of L=100 nH is placed between the sample and a 50 Ω coplanar waveguide (CPW), which connects the sample to the room-temperature electronics via a 50 Ω coaxial cable [Fig. 1(b)]. The sample resistance $R$, its stray capacitance $C$ and the inductance $L$ form a resonant LCR tank circuit with a resonance frequency of $f_0 \approx 1/\sqrt{LC}$ whose impedance can be matched to 50 Ω by varying $R$ via the illumination intensity. Measuring the reflected rf power as a function of the radio frequency $f_{\text{rf}}$ using a vector network analyzer, we find a resonance frequency of $f_0=190 \text{ MHz}$ and a bandwidth (FWHM) of $\sim 80 \text{ MHz}$ [Fig. 2(a)]. Note, that we have designed the frequency of the LCR tank circuit to avoid frequencies corresponding to nuclear magnetic resonance transitions in the spin system studied. For rf-EDMR measurements, we use the rf-reflectometry homodyne detection setup shown in Fig. 1(b). It is calibrated for resistance measurements by simultaneously measuring the output voltage $U_{\text{out}}$ at $f_{\text{rf}}=f_0=190 \text{ MHz}$ and the DC sample resistance $R$ as a function of the illumination intensity. From this, we obtain a relation between $U_{\text{out}}$ and $R$ as shown in Fig. 2(c) revealing a linear dependence around the working point at $R=4250 \Omega$ indicated by the arrow. The shape of the resonant dip [Fig. 2(a)] deviates from the expected Lorentzian shape mostly likely due to spurious reflections at the transitions between the coaxial cable and the CPW and between the CPW and the sample. From the resonance frequency and the value of the inductance, we calculate a capacitance of $C = 1/L(2\pi f_0)^2 = 7 \text{ pF}$ in good agreement with the estimated capacitance of the interdigit contact structure of $\sim 14 \text{ pF}$ [22].
In a next step, we use this measurement scheme to detect the change of \( R \) induced by the resonant excitation of \( ^{31}\text{P} \) spin transitions in cw rf-EDMR. For this purpose, the sample is continuously irradiated with microwaves with the frequency of 9.739 GHz chosen such that the spectrally isolated high-field \( ^{31}\text{P} \) hyperfine-split electron spin transitions is resonantly excited at a magnetic field of \( B_0=350.6 \) mT [blue arrow in the spectrum in Fig. 3(b)]. The amplitude of the \( ^{31}\text{P} \) signal shown in Fig. 2(b) as a function of \( f_{RF} \) is maximal for \( f_{RF}=f_0=190 \) MHz and decreases to almost zero for \( f_{RF}>250 \) MHz or \( f_{RF}<100 \) MHz. These results directly reflect the frequency-dependent sensitivity of the rf-reflectometry setup which is maximal when \( f_{RF} \) matches the resonance frequency of the LCR resonator and close to zero for \( f_{RF} \) far away from the resonance [16, 17]. The frequency range over which an EDMR signal is observed [red arrow in Fig. 2(b)] agrees well with the bandwidth of 80 MHz determined in Fig. 2(a) confirming that the rf-reflectometry indeed should allow EDMR measurements with a time resolution of tens of nanoseconds.

In the following, we use the large detection bandwidth of rf-EDMR to observe coherent spin oscillations during the mw excitation pulse as summarized in Fig. 3. To this end, we irradiate the sample with a 2 \( \mu \)s long mw pulse at the fixed frequency of 9.739 GHz and simultaneously measure the time dependence of \( R \) during and after the mw pulse using the calibration of Fig. 2(c). The results in Fig. 3(a) show the relative change of the sample resistance for three different values of \( B_0 \). Two of the values are chosen such that the mw pulse resonantly excites the \( ^{31}\text{P} \) and \( P_{b0} \) transitions (blue and red trace), while the third value is chosen off-resonant for comparison (black trace). The corresponding spectral positions are indicated by the according color-coded arrows in the pulsed rf-EDMR spectrum shown in Fig. 3(b). The resistance first increases during the mw pulse and decreases after the pulse with a time constant of \( \sim 5 \) \( \mu \)s for the two resonant transients, while no variation is observed in the off-resonant transient [Fig. 3(a)]. The maximum value of \( \Delta R/R \approx 7 \cdot 10^{-4} \) is comparable to the maximum change of \( \Delta R/R \approx 10^{-3} \) observed in conventionally detected pulsed EDMR experiments on this sample. During the mw pulse, a weak oscillation is present on the two resonant tracts, which is revealed after subtraction of a second order polynomial background as shown in Fig. 3(d). Oscillations with a period of 500 ns are present in both resonant tracts, while they are not observed for the off-resonant trace. We attribute these oscillations to the changes in the recombination rate caused by coherent spin oscillations during the mw pulse observed in real time [Fig. 1(a)]. For comparison, coherent oscillations measured by conventionally detected pulsed EDMR [13] are shown in Fig. 3(e), exhibiting the same oscillation frequency as those measured by rf-reflectometry. Our interpretation is further confirmed by the linear dependence of the oscillation frequency \( f_{Rabi} \) of the pulsed rf-EDMR on the square-root of the mw power [Fig. 3(c)].

The oscillation amplitude of \( \sim 5 \cdot 10^{-5} \) is much smaller than the overall resonant resistance change of \( \sim 7 \cdot 10^{-4} \). The small amplitude of the oscillation results from two
The first part of Eq. (1) describes the coherent evolution during the mw pulse, while the second part describes the recombination process. Assuming a resonant mw pulse which selectively excites one of the two weakly coupled spins, the rotating frame Hamiltonian is given by

\[ \hat{H} = \frac{\omega_{\text{Rabi}}}{2} \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \]  

with the angular Rabi frequency \( \omega_{\text{Rabi}} \). In Eq. (2), we have taken into account that state \( |3\rangle \) is not paramagnetic and therefore unaffected by the mw pulse.

To simplify the discussion, we further neglect the coherences between states \( |1\rangle \) and \( |3\rangle \) and between \( |2\rangle \) and \( |3\rangle \), since the recombination process is incoherent. Writing the remaining terms of \( \rho \) as a column vector \( \tilde{\rho} = (\rho_{11}, \rho_{12}, \rho_{21}, \rho_{22}, \rho_{33})^T \), the recombination operator \( \tilde{R} \) becomes

\[ \tilde{R} = \begin{pmatrix} -\frac{1}{\tau_p} & 0 & 0 & 0 & \frac{1}{2\tau_p} \\ 0 & -\frac{\tau_p + \tau_{\text{ap}}}{2\tau_p \tau_{\text{ap}}} & 0 & 0 & 0 \\ 0 & 0 & -\frac{\tau_p + \tau_{\text{ap}}}{2\tau_p \tau_{\text{ap}}} & \frac{1}{2\tau_p} & 0 \\ 0 & 0 & 0 & -\frac{1}{\tau_p} & 0 \\ \frac{1}{\tau_p} & 0 & 0 & 0 & -\frac{1}{\tau_p} \end{pmatrix}, \]  

with the recombination time of parallel spin pairs \( \tau_p \), the recombination time of antiparallel spin pairs \( \tau_{\text{ap}} \), and formation time constants of new spin pairs \( \tau_g \) with \( 1/\tau_g = 1/\tau_{\text{ec}} + 1/\tau_{\text{hc}} \), where \( \tau_{\text{ec}} \) and \( \tau_{\text{hc}} \) denote the time constants of an electron and hole capture process, respectively, as defined in Fig. 4(a) and Refs. [9, 11]. We additionally included the dephasing time \( T_d \) to account for the experimentally observed dephasing of the coherent spin oscillations [Fig. 3(d)(e)], which we attribute to inhomogeneities in the driving mw magnetic field.

The operator \( \hat{H} \cdot \tilde{\rho} = \frac{\omega_{\text{Rabi}}}{2} \begin{pmatrix} 0 & 1 & -1 & 0 & 0 \\ -1 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & -1 & 0 \\ 0 & -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \) describing the coherent evolution of \( \tilde{\rho} \) then takes the form

\[ \hat{H} = \frac{\omega_{\text{Rabi}}}{2} \begin{pmatrix} 0 & 1 & -1 & 0 & 0 \\ -1 & 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & -1 & 0 \\ 0 & -1 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix}. \]  

We numerically solve Eq. (1) by calculating

\[ \tilde{\rho}(t) = \begin{cases} e^{(\hat{H} + \tilde{R})t} \cdot \tilde{\rho}(0) \text{ during the mw pulse} \\ e^{\hat{R}t} \cdot \tilde{\rho}(0) \text{ after the mw pulse} \end{cases}, \]  

with \( \tilde{\rho}(0) = (1, 0, 0, 0, 0)^T \) assuming that the spin system is in the parallel state at the beginning of the mw pulse. Finally, we calculate the relative change of the resistance \( \Delta R(t)/R = \Delta n/n \) with \( n \) denoting the electron and hole density in the conduction and valence band. The change of \( n \) due to the spin-dependent recombination is given by \( \Delta n = (n/\tau_g) \cdot n_{\text{ap}} \cdot \Delta \rho_{33} \), with \( \Delta \rho_{33}(t) = \rho_{33}(t) - \rho_{33}(0) \), the carrier lifetime \( \tau_l \) and the total density \( n_{\text{ap}} \) of \( ^{31}\text{P}-^\text{Pb} \) spin pairs. With \( n = G \cdot \tau_l [9] \), the relative change of

FIG. 4. (a) Definition of the time constants of the \(^{31}\text{P}-^\text{Pb} \) recombination process. (b) Simulation of the relative resistance change during and after a 2 \( \mu \)s long mw pulse. (c) First 2 \( \mu \)s of the data shown in panel (a) after subtraction of a second order polynomial background.
resistance is given by

$$\frac{\Delta R(t)}{R} = \frac{n_{sp}}{G \cdot \tau_g} \Delta \rho_{33}(t), \quad (6)$$

where $G$ denotes the excitation rate of carriers by the above-bandgap illumination [9]. The resulting $\Delta R(t)/R$ is plotted in Fig. 4(a), using the parameters $\tau_p=1200 \mu s$, $\tau_{sp}=2 \mu s$, $G = 5 \cdot 10^{20} \text{cm}^{-3}\text{s}^{-1}$ [9], while $\tau_g=2.6 \mu s$, $T_d=210 \text{ns}$ and $n_{sp} = 3 \cdot 10^{12} \text{cm}^{-3}$ are used as fitting parameters to match the experimental data in Fig. 3(a).

The simulated transient reproduces the basic features of the experimental data in Fig. 3(a) with characteristic rise and fall times determined mainly by $\tau_{sp}$ and $\tau_g$, respectively. Again, the coherent oscillations during the mw pulse are revealed after subtraction of a second order polynomial background as shown in Fig. 4(c). The oscillation amplitude of $\sim 2 \cdot 10^{-5}$ is a factor of $\sim 40$ smaller compared to the simulated maximum total change of the resistance in good agreement with the experimentally observed suppression by a factor of $\sim 20$. We therefore conclude that the time constants of the recombination process naturally explain the observed shape of the transient as well as the amplitude of the coherent oscillations. For a more detailed modeling, a distribution of recombination and generation time constants over the spin pair ensemble has to be taken into account [9].

In conclusion, we implemented rf-reflectometry read-out for pulsed EDMR thereby increasing the measurement bandwidth by almost two orders of magnitude compared to current preamplifier-based detection schemes. This opens the way to studying faster charge dynamics, e.g., in direct semiconductors which with very few exceptions [3, 24, 25] so far have almost exclusively been studied by optically detected magnetic resonance because of their shorter carrier life times compared to indirect semiconductors such as silicon. Other systems that might benefit from the increased bandwidth are formation and dissociation processes of spin pairs in organic semiconductors [26, 27] and donor-bound excitons in silicon [28, 29]. Furthermore, when applying rf-reflectometry to device structures like diodes [3, 24] or two-dimensional electron gases [14, 30, 31], where no illumination is needed for EDMR measurements, a significant reduction of the noise level is expected since rf-reflectometry is less sensitive to low-frequency noise [15]. In particular, when spin-dependent scattering processes are detected, the large sensitivity of EDMR and the high time resolution demonstrated here might enable the observation and feedback control of spin fluctuations in small spin ensembles [32, 33].

The work was financially supported by DFG (Grant No. SFB 631, C3).

\[\text{corresponding author, email: hoehne@wsi.tum.de}\]

[1] H. Dersch, L. Schweitzer, and J. Stuke, Phys. Rev. B 28, 4678 (1983).
[2] W. M. Chen, B. Monemar, E. Janzen, and J. L. Lindström, Phys. Rev. Lett. 67, 1914 (1991).
[3] W. E. Carlos, E. R. Glaser, T. A. Kennedy, and S. Nakamura, Appl. Phys. Lett. 67, 2376 (1995).
[4] V. Dyakonov, G. Rössler, M. Schooer, S. Blumstengel, and K. Liuers, J. Appl. Phys. 79, 1556 (1996).
[5] M. Stutzmann, M. S. Brandt, and M. W. Bayerl, J. Non-Cryst. Solids 266-269, 1 (2000).
[6] N. C. Greenham, J. Shinar, J. Partee, P. A. Lane, O. Amir, F. Lu, and R. H. Friend, Phys. Rev. B 53, 13528 (1996).
[7] J.-M. Spaeth and H. Overhof, Point Defects in Semiconductors and Insulators (Springer, Berlin, 2003).
[8] G. W. Morley, D. R. McCallum, H. A. Seipel, L.-C. Brunel, J. van Tol, and C. Boehme, Phys. Rev. Lett. 101, 207602 (2008).
[9] F. Hoehne, L. Dreher, M. Suckert, D. P. Franke, M. Stutzmann, and M. S. Brandt, arXiv:1307.4039 (2013).
[10] L. Childress, M. V. Gurudev Dutt, J. M. Taylor, A. S. Zibrov, F. Jelezko, J. Wrachtrup, P. R. Hemmer, and M. D. Lukin, Science 314, 281 (2006).
[11] L. Dreher, F. Hoehne, M. Stutzmann, and M. S. Brandt, Phys. Rev. Lett. 108, 027602 (2012).
[12] C. Boehme and K. Lips, Phys. Rev. B 68, 245105 (2003).
[13] A. R. Stegner, C. Boehme, H. Huebl, M. Stutzmann, K. Lips, and M. S. Brandt, Nat. Physics 2, 835 (2006).
[14] T. Machida, T. Yamazaki, K. Ikushima, and S. Komiyama, Appl. Phys. Lett. 82, 409 (2003).
[15] H. Huebl, R. P. Starrett, D. R. McCamey, A. J. Ferguson, and L. H. W. van Beveren, Rev. Sci. Instr. 80, 114705 (2009).
[16] R. J. Schoelkopf, P. Wahlgren, A. A. Kozhevinikov, P. Delsing, and D. E. Prober, Science 280, 1238 (1998).
[17] S. J. Angus, A. J. Ferguson, A. S. Dzurak, and R. G. Clark, Appl. Phys. Lett. 92, 112103 (2008).
[18] D. Kaplan, I. Solomon, and N. F. Mott, J. Physique Lett. (Paris) 39, 51 (1978).
[19] H. Huebl, F. Hoehne, B. Grolik, A. R. Stegner, M. Stutzmann, and M. S. Brandt, Phys. Rev. Lett. 100, 177602 (2008).
[20] F. Hoehne, H. Huebl, B. Galler, M. Stutzmann, and M. S. Brandt, Phys. Rev. Lett. 104, 046402 (2010).
[21] A. Stesmans and V. V. Afanas’ev, J. Appl. Phys. 83, 2449 (1998).
[22] H.-E. Endres and S. Drost, Sens. Act. B: Chem. 4, 95 (1991).
[23] F. Hoehne, L. Dreher, J. Behrends, M. Fehr, H. Huebl, K. Lips, A. Schnegg, M. Suckert, M. Stutzmann, and M. S. Brandt, Rev. Sc. Instr. 83, 043907 (2012).
[24] M. W. Bayerl, M. S. Brandt, and M. Stutzmann, phys. stat. sol. (a) 159, R5 (1997).
[25] T. Wimbauer, M. S. Brandt, M. W. Bayerl, N. M. Reinacher, M. Stutzmann, D. M. Hofmann, Y. Mochizuki, and M. Mizuta, Phys. Rev. B 58, 4892 (1998).
[26] F. Grozema, L. Siebbeles, J. Warman, S. Seki, S. Tagawa, and U. Scherf, Adv. Mat. 14, 228 (2002).
[27] T. Virgili, G. Cerullo, L. Lüer, G. Lanzani, C. Gadermaier, and D. D. C. Bradley, Phys. Rev. Lett. 90, 247402 (2003).
[28] W. Schmid, phys. stat. sol. (b) 84, 529 (1977).
[29] M. Steger, K. Saeedi, M. L. W. Thewalt, J. J. L. Morton, H. Riemann, N. V. Abrosimov, P. Becker, and H.-J. Pohl, Science 336, 1280 (2012).
[30] C. F. O. Graeff, M. S. Brandt, M. Stutzmann, M. Holzmann, G. Abstreiter, and F. Schäffler, Phys. Rev. B 59, 13242 (1999).
[31] C. C. Lo, V. Lang, R. E. George, J. J. L. Morton, A. M. Tyryshkin, S. A. Lyon, J. Bokor, and T. Schenkel, Phys. Rev. Lett. 106, 207601 (2011).
[32] R. Budakian, H. J. Mamin, B. W. Chui, and D. Rugar, Science 307, 408 (2005).
[33] S. T. B. Goennenwein, M. W. Bayerl, M. S. Brandt, and M. Stutzmann, Phys. Rev. Lett. 84, 5188 (2000).