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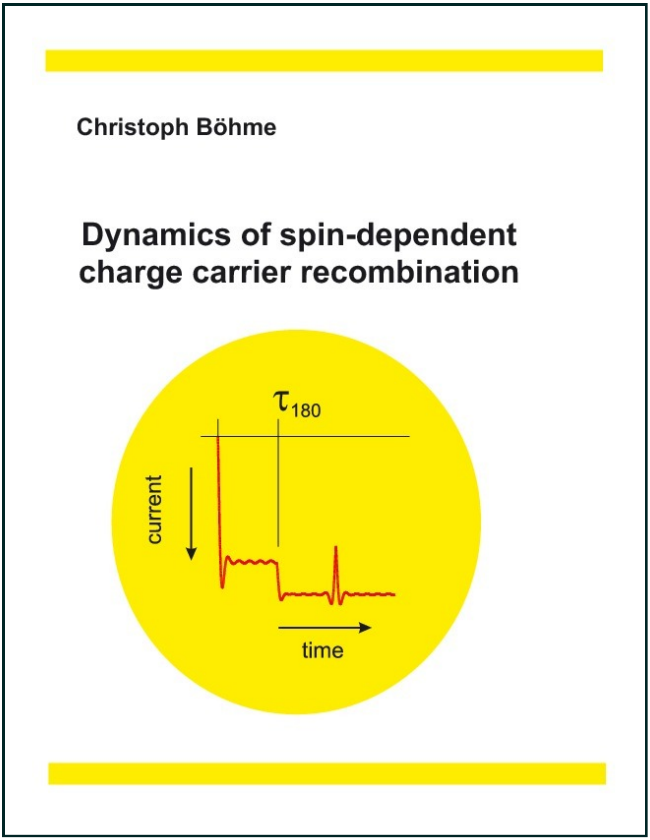
Dynamics of spin-dependent charge carrier recombination



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Chapter 1

Introduction

Recombination in semiconductors are energy loss transitions of electrons and holes that lead to a depletion of excess–charge carrier densities. Since recombination belongs to the determining factors for the electronic properties of semiconductors, the investigation and understanding of recombination has become one of the most important aspects of modern semiconductor research and development. Examples for the relevance of recombination for technological applications can be found in the fields of microelectronics and photovoltaics: The creation of materials with low recombination rates is the crucial task for the further improvement of solar cells since recombination is the most important origin of electronic losses and therefore a major factor for the limitation of solar cell efficiencies [2]. Progress in the field of microelectronics has always been marked by reduced scaling dimensions and an increased speed of thin film transistors [3]. The achievement of these goals depends to a large extend on the reduction of recombination activity at the interface between crystalline silicon and gate dielectric materials.

Obtaining experimental access to the physics of recombination is as difficult as it is important. Recombination can only be observed indirectly through macroscopic observables such as the photoconductivity or luminescence intensity. Moreover, in general, many different recombination paths contribute to a given observable, complicating the identification and characterisation of the different transitions. While standard lifetime measurements such as transient photoconductivity measurements can reveal electronic lifetimes and thus recombination rates, it is hardly possible to attribute the obtained quantitative data to distinct microscopic processes. Thus, other ways to gain a more detailed picture about the defect structure and the densities have been developed such as the capacitance–voltage method [4] or deep level transient spectroscopy [5]. These methods reveal information about different defect centres in a given material, but they still fail to give insight about the microscopic, local structure and most of all, the recombination activity of a certain defect.

Ways to investigate the microscopic environment of point defects are provided by magnetic resonance methods such as electron spin resonance (ESR) or nuclear magnetic resonance (NMR). The foundations of these methods go back mostly to the work of Felix Bloch who developed the theory of resonant nuclear induction [6] and carried out the first NMR experiments [7] in 1946. The first ESR spectrum was recorded by Zavoiski [8]. These first demonstrations were soon proceeded by coherent time–domain NMR experiments, which revealed effects such as coherence decays, coherent dephasing and the existence of the nuclear spin echo, which was detected by Hahn [9] in 1950. After these initial discoveries, the research activity in the NMR field expanded dramatically and led to the development of many applications like different pulse sequences for structural analysis of chemical compounds or the magnetic resonant imaging applied for medical diagnostics. Unlike NMR, the development of time–domain ESR spectroscopy took place at a much slower pace due to the unavailability of fast detection electronics and the necessary strong coherent microwave sources [10]. After these technical challenges had been overcome in the early 1980s, the development of ESR techniques followed those of NMR in many regards, only with a 25 year delay. Time–resolved magnetic resonance spectroscopy is much superior in comparison to the original continuous wave (cw) experiments since it allows a fast high–resolution access to the resonance spectra (Fourier transform spectroscopy), it provides an easy and distinguishable access to the different relaxation and dephasing times and it allows the deconvolution between homogeneous and inhomogeneous line shapes which opens access to information about diffusion related phenomena and many other effects that have an influence on spin motion [10]. Nowadays, NMR experiments are carried out almost only in the time domain. ESR is still practised as cw ESR by many researchers which is due to cost constraints and the higher sensitivity of cw ESR.

While magnetic resonance methods allow access to microscopic information about paramagnetic defects, they still fail to reveal information about the recombination activity of a given defect centre. Because of this limitation, experimental methods have been developed that combine the microscopic sensitivity and selectivity of ESR with other methods such as photoconductivity or photoluminescence measurements. These combined methods take advantage of the spin dependency of many recombination processes in various semiconductor materials. Spin–dependent recombination of charge carriers is recombination through transitions whose probabilities are governed by spin–selection rules. Figure 1.1 illustrates how spin-conservation rules of electronic transitions can prohibit recombination of an electron through a paramagnetic defect. When the electron in the localised state and the defect are in a triplet spin–pair state, the spin of this pair would have to change from a triplet state ($S = 1$) to a singlet state ($S = 0$) during the transition. However, this is impossible when the spin is conserved due to the absence of spin–orbit coupling.

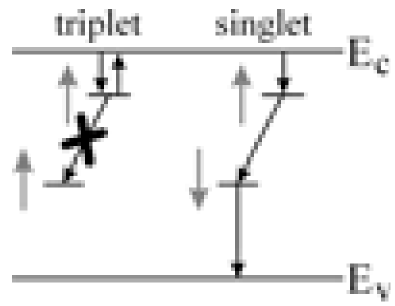

Figure 1.1: Spin–dependent recombination between localised bandgap states. Transitions between paramagnetic states are allowed only when the spin–pair state of the two electrons has singlet content.

The discovery of spin–dependent recombination processes goes back to the first optically detected magnetic resonance (ODMR) experiments carried out by Geschwind et al. in 1959 [11, 12]. In these experiments, spin configurations of excited electronic states were manipulated with ESR, which led to a rate change of recombination processes that could be observed by luminescence measurements. Since ODMR is also applicable to electronic transitions in atomic or molecular systems, it has become a versatile tool for the investigation of chemical reactions and due to the availability of fast and sensitive photo detectors, the development of transient ODMR has kept pace with pulsed-ESR. Many chemical reactions of radicals are spin–dependent electronic transitions similar to the charge carrier recombination in semiconductors. A time–resolved optical detection of the relative coherent spin motion of organic radical ion pairs has already been observed in 1976 by Klein and Voltz [13]. The reaction yield, proportional to the detected fluorescence intensity, oscillated with the Larmor–beat oscillation of the radical pair ensemble that was exposed to a constant magnetic field. Soon after this experiment, transient ODMR became a frequently utilised method for chemical reaction analysis and with the advent of pulsed-ESR in the early 1980s, optically detected electron spin echo techniques [14, 15, 16, 17] and optically detected Rabi–beat oscillations [18] were used for the investigation of atomic and molecular systems.

All of these developments in the ODMR community have had little impact on EDMR and semiconductor research. While cw ODMR has been used also for the investigation of charge carrier recombination, pulsed ODMR on semiconductors is difficult since longer wavelengths (near IR) are difficult to detect on fast time scales and the luminescence is weak in some materials. Moreover, ODMR intensities do not necessarily reflect the charge carrier recombination: Some radiative processes do not contribute to photoconductivity (geminate recombination) while other transitions that do contribute are not radiative.

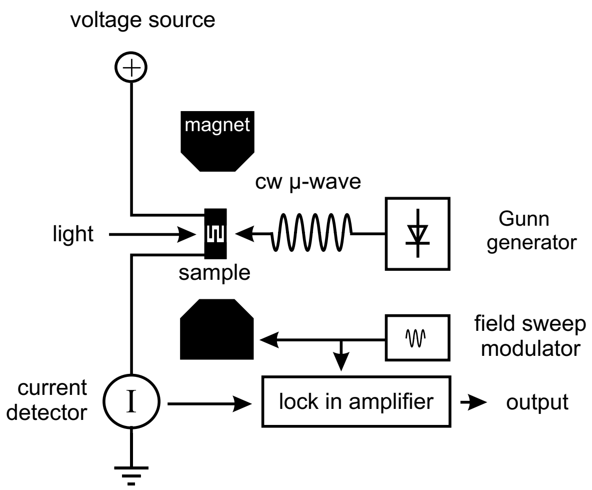

Figure 1.2: Experimental setup for the detection of spin–dependent recombination. Continuous wave EDMR as developed by Honig [19] is performed with continuous microwave radiation which is irradiated onto a semiconductor sample in which a constant current of excess–charge carriers (induced electrically or optically) flows. When the DC magnetic field is swept through an electron spin resonance, the current may be quenched due to an enhancement of recombination.

Alternatively to the detection of ESR by luminescence measurements, spin–dependent recombination of charge carriers in semiconductors can also be detected by resonant changes of the photoconductivity. This method is called electrically detected magnetic resonance (EDMR) or electrically detected electron spin resonance. The standard EDMR experiment, illustrated in fig. 1.2 and explained in greater detail in appendix B.2, is basically a continuous wave ESR experiment where the photoconductivity is measured instead of the radiation intensity in the microwave cavity. Its development followed the closely related ODMR method by about a decade and was started by Maxwell and Honig [19] who investigated the impact of ESR on spin–dependent scattering of charge carriers at impurities in 1966. The first spin–dependent recombination path was discovered by Lepine at the beginning of the 1970s [20, 21]. When Lepine equalised the densities of localised charge–carrier pairs in triplet states and the density of pairs with singlet content, an enhancement of the singlet density and hence of the recombination took place. The latter was detected by photoconductivity measurements. Since these first experiments were carried out, various recombination paths in inorganic [22, 23, 24, 25, 26, 27, 28] and organic [29, 30, 31] semiconductors, semiconductor heterostructures [32, 33] and devices [34, 35, 36, 37], as well as interface systems [38], were investigated with EDMR and much insight into the nature of spin–dependent recombination has been gained.

While the development of time–resolved ESR and ODMR spectroscopy is delayed in comparison to NMR methods, a time–resolved EDMR, which reveals the influence of coherent spin motion on charge carrier recombination, had not even been demonstrated by the turn of the century, when the work presented in the following chapters was begun. The reasons why EDMR has always been limping behind both ESR and ODMR are related to the multiple challenges with regard to a sophisticated coherent ESR experiment that has to be carried out on a conducting (and therefore microwave absorbing) sample and an appropriate detection setup for the subtle current changes which occur on a short time scale. In addition to these technical problems, no theory about the effects and processes which could potentially become visible by "pulsed-EDMR" was existent. A first time–domain approach to standard cw EDMR had been carried out in 1999 by Hiromitsu et al. [30] who recorded the exponential relaxation of a photocurrent through a polymer–fullerene heterojunction during and after a resonant microwave radiation had been imposed on the material. In these experiments the microwave intensities and the time resolution were too low for the detection of coherent phenomena. Applied to other semiconductor systems, a transient measurement of cw EDMR can only reveal spin–relaxation rates — an information that can just as well be obtained by ESR.

The goal of the study presented in the following chapters was therefore to open up the experimental doors of EDMR to the world of coherent spin motion in order to make the wide range of effects utilised for pulsed ODMR and pulsed ESR available for semiconductor characterisation. Point of departure of this work was the theoretical investigation of the dynamics of spin–dependent recombination, a topic which had hardly been treated in the literature before. These theoretical considerations start out with a chapter that deals with the formulation of a general qualitative picture in which the essentials of many models developed in the past 30 years [20, 21, 39, 40, 41, 42, 43, 44, 45] are condensed down into a simple set of properties. The insight obtained from the theoretical descriptions will then lead to an assessment of the experimental feasibility of coherent spin motion measurements with recombination. An experiment, which will be referred to as time–domain measurement of spin–dependent recombination (TSR) is described. In this regard, it is important to point out that the study presented in this book does not deal with the time domain of spin–dependent transport processes, which represent a completely different class of ESR effects on conductivity and photoconductivity. Spin–dependent transport can be due to a variety of qualitatively completely different effects such as spin–dependent tunnelling [22] or spin–dependent scattering [46]. While cw EDMR line shapes due to transport and recombination are usually very similar, the transient behaviour could exhibit quite different features. Thus, all transport related processes have been excluded from the considerations in the following chapters. After the theoretical considerations and an introduction to the experimental foundations are made, first experimental results will be presented for two recombination paths in hydrogenated microcrystalline silicon (μc-Si:H). Based on this model material, the range of experimental data accessible with TSR is demonstrated. It is shown that TSR is able to detect the influence of coherent spin motion on recombination such as the recombination–rate control by coherent dephasing of Rabi–beat oscillations within a spin–pair ensemble and a subsequent rephasing effect, which is referred to as recombination echo. It is then shown that the coherence decay due to incoherent processes such as recombination itself can be detected from these effects. This allows a direct measurement of the recombination dynamics in a distinct recombination path. After the discussion of the experimental observations, a chapter dealing with applications of the TSR method and its results follows. Therein, the data on μc-Si:H is discussed with regard to new insights about the material properties. Then, first experimental data on hydrogenated amorphous silicon (a-Si:H) is presented and potential benefits of TSR measurements in this material are discussed. The final part of this chapter deals with the discovery that coherent spin states can determine recombination processes itself: Based on this effect, a readout concept for spin–based solid–state quantum–computers as proposed by Kane [47, 48] is suggested. Thus, the insight about the dynamics of spin–dependent recombination gained in the study presented may have an impact on quantum computing research and development, which is presently one of the most active areas of physics research.