Linköping studies in science and technology. Dissertation No.1607

Room-temperature defect-engineered spin functionalities in Ga(In)NAs alloys

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Cover image (front): -schematic representation of a spin polarized defect in a semiconductor.

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ISBN: 978-91-7519-293-2

ISSN: 0345-7524

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Dissertations No. 1607

Printed by LiU-Tryck, Linköping, Sweden, 2014

Abstract

Semiconductor spintronics is one of the most interesting research fields that exploits both charge and spin properties for future photonics and electronic devices. Among many challenges of using spin in semiconductors, efficient generation of electron spin polarization at room temperature (RT) remains difficult. Recently, a new approach using defect-mediated spin filtering effect, employing Ga_i^{2+} -interstitial defects in Ga(In)NAs alloys, has been shown to turn the material into an efficient spin-polarized source capable of generating $> 40\%$ conduction electron spin polarization at RT without an application of external fields. In order to fully explore the defect-engineered spin functionalities, a better understanding and control of the spin filtering effects is required. This thesis work thus aims to advance our understanding, in terms of both physical and material insights, of the recently discovered spin filtering defects in Ga(In)NAs alloys. We have focused on the important issues of optimization and applications of the spin filtering effects.

To improve spin filtering efficiency, important material and defect parameters must be addressed. Therefore, in Papers I–III formation of the Ga_i^{2+} defects in Ga(In)NAs alloys has been examined under different growth and post-growth treatment conditions, as well as in different structures. We found that the Ga_i^{2+} defects were the dominant and important nonradiative recombination centers in Ga(In)NAs epilayers and GaNAs/GaAs multiple quantum wells, independent of growth conditions and post-growth annealing. However, by varying growth and post-growth conditions, up to four configurations of the Ga_i^{2+} defects, exhibiting different hyperfine interaction (HFI) strengths between defect electron and nuclear (e-n) spins, have been found. This difference was attributed to different interstitial sites and/or complexes of Ga_i^{2+} . Further studies focused on the effect of post-growth hydrogen (H) irradiation on the spin filtering effect. Beside the roles of H passivation of N resulting in bandgap reopening of the alloys, H treatment was shown to lead to complete quenching of the spin filtering effect, accompanied by strong suppression in the concentrations of the Ga_i^{2+} defects. We concluded that the observed effect was due to the passivation of the Ga_i^{2+} defects by H, most probably due to the formation of H- Ga_i^{2+} complexes.

Optimizing spin filtering efficiency also requires detailed knowledge of spin interactions at the defect centers. This issue was addressed in Papers IV and V. From both experimental and theoretical studies, we were able to conclude that the HFI between e-n spins at the Ga_i^{2+} defects led to e-n spin mixing, which degraded spin filtering efficiency at zero field. Moreover, we have identified the microscopic origin of electron spin relaxation (τ_1) at the defect centers, that is, hyperfine-induced e-n spin cross-relaxation. Our finding thus provided a guideline to improve

spin filtering efficiency by selectively incorporating the Ga_i^{2+} defects with weak HFI by optimizing growth and post-growth treatment conditions, or by searching for new spin filtering defect centers containing zero nuclear spin.

The implementation of the defect-engineered spin filtering effect has been addressed in Papers VI–VIII. First, we experimentally demonstrated for the first time at RT an efficient electron spin amplifier employing the Ga_i^{2+} defects in Ga(In)NAs alloys, capable of amplifying a weak spin signal up to 27 times with a high cut-off frequency of 1 GHz. We further showed that the defect-mediated spin amplification effect could turn the GaNAs alloy into an efficient RT optical spin detector. This enabled us to reliably conduct in-depth spin injection studies across a semiconductor heterointerface at RT. We found a strong reduction of electron spin polarization after optical spin injection from a GaAs layer into an adjacent GaNAs layer. This observation was attributed to severe spin loss across the heterointerface due to structural inversion asymmetry and probably also interfacial point defects.

Finally, we went beyond the generation of strongly polarized electron spins. In Paper IX we focused on an interesting aspect of using strongly polarized electron spins to induce strong nuclear spin polarization at RT, relevant to solid-state quantum computation using a defect nuclear spin of long spin memory as a quantum bit (qubit). By combining the spin filtering effect and the HFI, we obtained a sizeable nuclear spin polarization of $\sim 15\%$ at RT that could be sensed by conduction electrons. This demonstrated the feasibility of controlling defect nuclear spins via conduction electrons even at RT, the first case ever being demonstrated in a semiconductor.

Populärbeskrivning

Halvledarspintronik är en av de mest intressanta forskningsfält som utnyttjar både laddning och spinnegenskaper för framtida fotonik- och elektronikkomponenter. Effektiv generering av elektronspinnpolariseringen i rumstemperatur (RT) är en av de viktigaste utmaningar med att använda spinn i halvledare. Nyligen har ett nytt tillvägagångssätt med användning av defektmedierad spinnfiltreringseffekt, som använder sig av Ga_i^{2+} -interstitiella defekter i Ga(In)NAs legeringar, visats sig effektiv för att uppnå en spinnpolariserande källa som kan generera > 40% elektronspinnpolarisering i ledningsbandet vid RT och utan externa fält. För att till fullo utforska dessa defekt-genererade spinnfunktioner, krävs en bättre förståelse och kontroll av spinnfiltreffekter. Detta examensarbete syftar således till att öka vår förståelse, både när det gäller fysiska och materiella insikter, av de nyligen upptäckta spinnfiltreringsdefekter i Ga(In)NAs legeringar. Vi har fokuserat på de viktiga frågorna om optimering och tillämpningar av spinnfiltreringseffekterna.

För att förbättra spinn filtreringseffektiviteten, måste viktiga material och defektparametrar tas itu med. I artiklarna I-III har bildandet av Ga_i^{2+} defekter i Ga(In)NAs legeringar undersökts under olika tillväxt- och post- tillväxtbehandlingsförhållanden, såväl som i olika strukturer. Vi fann att Ga_i^{2+} defekter var dominerande och viktiga icke-strålände rekombinationscentra i Ga(In)NAs epilager samt GaNAs/GaAs multipla kvantbrunnar, oberoende av tillväxtförhållanden och post-tillväxt värmebehandling. Genom att variera tillväxt och eftertillväxtförhållanden, har upp till fyra konfigurationer av Ga_i^{2+} defekter hittats. De uppvisar olika hyperfinväxelverkan (HFI) mellan defektelektronen och kärns핀net (e-n). Denna skillnad tillskrevs olika interstitiella platser och/eller komplex av Ga_i^{2+} . Ytterligare studier fokuserade på effekten av posttillväxtvätebestrålning på spinnfiltreringseffekten. Förutom passivering av N, vilket resulterar i en ökning av bandgapet, har H behandling visat sig leda till fullständig utsläckning av spinnfiltreringseffekten, tillsammans med en stark dämpning i bildandet av Ga_i^{2+} defekter. Vi drog slutsatsen att den observerade effekten berodde på passivering av Ga_i^{2+} defekter av H, sannolikt som ett resultat av bildning av H- Ga_i^{2+} komplex.

Optimering av spinn filtreringseffektiviteten kräver också detaljerad kunskap om spinn interaktioner vid defektcentra. Denna fråga togs upp i Artiklarna IV och V. Från både experimentella och teoretiska studier, kunde vi konstatera att HFI mellan e-n spinn på Ga_i^{2+} defekter ledde till e-n spinn mixing, som reducerade spinn filtreringseffektivitet vid 0 Tesla. Dessutom har vi identifierat det mikroskopiska ursprunget till elektronspinnrelaxationstiden (T_1) vid defektcentra: hyperfin-inducerad e-n spin kors-relaxering. Vår slutsats gav därmed en

riktlinje för att förbättra spinn filtreringseffektiviteten genom att selektivt införliva Ga_i^{2+} defekter med svag HFI genom optimering av tillväxt och eftertillväxtbehandlingsförhållanden, eller genom att söka efter nya spin filtrering defektcentra som innehåller noll nukleära spinn.

Implementationen av defekt-tillverkade spinn filtreringseffekten har tagits upp i artiklarna VI-VIII. Först har vi experimentellt visat för första gången vid RT en effektiv elektronspinnförstärkare baserad på Ga_i^{2+} defekter i Ga(In)NAs legeringar, med förmåga att förstärka en svag spinnsignal upp till 27 gånger med en hög gränshfrekvens på 1 GHz. Vi visade vidare att defekt-medierad spinn förstärkningseffekt kunde förvandla GaNAs legeringen till en effektiv RT optisk spinndetektor. Detta gjorde det möjligt att genomföra spinninjektionsstudier över ett halvledarheterogransyta vid RT. Vi fann en kraftig minskning av elektronspinnpolariseringen efter optisk spinninjektion från en GaAs skikt in i ett angränsande GaNAs lager. Denna iakttagelse tillskrevs svår spinn förlust över heterogransytan på grund av strukturell inversionsasymmetri och förmodligen även punktdefekter vid gränssytan.

Slutligen gick vi vidare bortom skapandet av starkt polariserade elektronspinn. I artikeln IX fokuserade vi på en intressant aspekt av att använda starkt polariserade elektronspinn för att framkalla starkt kärnspinnpolarisering vid RT, relevanta för fasta-tillstånds kvantberäkningar med hjälp av ett kärnspinn hos en defekt med ett lång spinminne som en kvantbit. Genom att kombinera spinnfiltreringseffekten och HFI erhöll vi en ganska stor kärnspinnpolarisering av $\sim 15\%$ vid RT som även märks av elektroner i ledningsbandet. Detta demonstrerade möjligheten av att styra defektkärnspinn via elektroner i ledningsbandet även vid RT, för första gången någonsin i en halvledare.

Preface

This thesis is a summary of my research activities during 2009–2014, within my doctoral program in the Functional Electronic Materials Division (FEM) at the Department of Physics, Chemistry and Biology (IFM), Linköping University, Sweden, under the supervision of Professor Weimin Chen and Professor Irina Buyanova. In this thesis, we present the scientific results that aimed at full exploitation of room-temperature defect-engineered spin functionalities in a semiconductor.

The thesis is divided into two parts. To assist the reader, the first part gives a general introduction to the fields, the basis of experimental approaches together with a summary of scientific achievements obtained from the studies. The second part contains research articles, which present the scientific results in detail.

Yuttapoom Puttisong

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List of publications included in the thesis

I. Dominant recombination centers in Ga(In)NAs alloys: Ga interstitials

X. J. Wang, Y. Puttisong, C. W. Tu, Aaron J. Ptak, V. K. Kalevich, A. Yu Egorov, L. Geelhaar, H. Riechart, W. M. Chen and I. A. Buyanova, Appl. Phys. Lett. 95, 241904 (2009).

II. Electron spin filtering by thin GaNAs/GaAs multiquantum wells

Y. Puttisong, X. J. Wang, I. A. Buyanova, H. Carfre, F. Zhao, A. Balocchi, X. Marie, C. W. Tu, W. M. Chen, Appl. Phys. Lett. 96, 52104 (2010).

III. Room temperature spin filtering effect in GaNAs: Role of hydrogen

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IV. Effect of hyperfine-induced spin mixing on the defect-enabled spin blockade and spin filtering in GaNAs

Y. Puttisong, X. J. Wang, I. A. Buyanova and W.M. Chen, Phys. Rev. B 87, 125202 (2013).

V. Limiting factor of defect-engineered spin-filtering effect at room temperature

Y. Puttisong, I. A. Buyanova and W.M. Chen, Phys. Rev. B 89, 195412 (2014).

VI. Room-temperature electron spin amplifier based on Ga(In)NAs alloys

Y. Puttisong, I.A. Buyanova, A. J. Ptak, C.W. Tu, L. Geelhaar, H. Riechart and W. M. Chen, Adv. Mater. 25, 738-742 (2013).

VII. Efficient room-temperature spin detector based on GaNAs

Y. Puttisong, I. A. Buyanova, L. Geelhaar, H. Riechart, C. W. Tu, W. M. Chen, J. Appl. Phys. 111, 07C303 (2012).

VIII. Room-temperature spin injection and spin loss across a GaNAs/GaAs interface

Y. Puttison, X. J. Wang, I. A. Buyanova, C.W. Tu, L. Geelhaar, H. Riechert, W. M. Chen, Appl. Phys. Lett. 98, 12112 (2011).

IX. Efficient room-temperature nuclear spin hyperpolarization of a defect atom in a semiconductor

Y. Puttison, X. J. Wang, I. A. Buyanova, L. Geelhaar, H. Riechert, A. J. Ptak, C. W. Tu and W. M. Chen, Nat. Commun. 4:1751 doi: 10.1038/ncomms2776 (2013).

My contributions

Paper I: I performed part of the spin resonance measurements, data analysis and interpretation together with my co-authors.

Paper II-IX: I performed most of the experimental works, data analysis, theoretical studies and interpretation of the data together with my co-authors. I wrote the first versions of the manuscripts.

Other contributions

I. Temperature dependence of dynamic nuclear polarization and its effect on electron spin relaxation and dephasing in InAs/GaAs quantum dots

J. Beyer, Y. Puttison, I. A. Buyanova, S. Suraprapapich, C.W. Tu, W. M. Chen, Appl. Phys. Lett. 100, 143105 (2012).

II. Extraordinary room-temperature spin functionality in a non-magnetic semiconductor

W. M. Chen, Y. Puttison, X. J. Wang and I. A. Buyanova, Conference paper, Abstract (invited talk), 3rd International Conference on Magnonics, Varberg, Sweden, August 4-8 (2013).

III. Ga interstitials: usual grown-in defects with unusual room-temperature spin functionality in dilute nitrides

W. M. Chen, Y. Puttison, X. J. Wang, I. A. Buyanova, Aaron J. Ptak, C. W. Tu, L. Geelhaar and H. Riechert, Conference paper, Abstract (invited talk), 27th International Conference on Defects in Semiconductors (ICDS 27), Bologna, Italy, July 21-26 (2013).

IV. Spin functional non-magnetic semiconductor for future spintronics

W. M. Chen, Y. Puttison, X. J. Wang, I. A. Buyanova, C. W. Tu, A. J. Ptak, L. Geelhaar and H. Riechert, Conference paper, Abstract (invited talk), 2nd International Congress on Advanced Materials (AM 2013), Zhenjiang, China, May 16-19 (2013).

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XI. First demonstration of room-temperature electron spin amplifier based on Ga(In)NAs alloys

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XII. Optimization of room-temperature defect-engineered spin filtering effect in Ga(In)NAs: rate equation studies

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XIII. Effect of post-growth hydrogen treatment and annealing on spin filtering functionality in Ga(In)NAs alloys

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XIV. Defect-enabled Room-temperature Spin Functionality in Ga(In)NAs

Y. Puttisong, X. J. Wang, I. A. Buyanova, J. Aaron Ptak, C. W. Tu, L. Geelhaar, H. Riechert and W. M. Chen, Conference paper, 31'st International Conference on the Physics of Semiconductors (ICPS 2012), Zurich, Switzerland, July 29-August 3 (2012).

XV. Studies of spin loss during room-temperature spin injection across a GaNAs/GaAs interface

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XVI. Engineering spin-dependent carrier recombination processes in Ga(In)NAs for optoelectronic and photovoltaic applications

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XVIII. Spin-blockade of dominant non-radiative carrier recombination channels via defects in Ga(In)NAs alloys

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XIX. Efficient room temperature spin filter based on GaNAs quantum wells

X. J. Wang, Y. Puttison, I. A. Buyanova, H. Carrere, F. Zhao, A. Balocchi, X. Marie, C. W. Tu and W. M. Chen, Conference paper Abstract, International Conference on Modulated Semiconductor structures (MSS-14), Kobe, Japan, July 19 - 24 (2009).

Acknowledgement

Without realizing, I have already spent five years in the Division of Functional Electronic Materials (FEM), Linköping University. Sometimes, focusing on the academic work makes me forget to express my sincere thanks to many people involved in my studies here. I always feel sorry. Well, now I can use this space for such a purpose.

I would like to thank my supervisors **Prof. Weimin Chen** and **Prof. Irina Buyanova** for your valuable guidance and support. Thanks for always keeping the door open for my “many-times-per-day” discussions. I truly appreciate your patience and kindness. You always have a professional and positive attitude toward research. Working in the research environments that you have provided has shaped me into an individual researcher, in many ways.

I am grateful to **Prof. Xingjun Wang**, my first lab teacher, for the valuable time we have spent in the lab. Your skills and knowledge concerning the lab issues are precious and irreplaceable. It is also a great joy working with **Dr. Sunkyun Lee**. Thanks for all matters concerning the basics of time-resolved photoluminescence measurements.

Our works run smoothly with help in administrative issues from **Lejla Kronbäck** and **Susanne Andersson**. Also, thanks for the technical support from **Arne Eklund** and **Roger Carmesten**.

It is a great joy to get to know my peer colleague **Dr. Shula Chen**. I feel thankful for the time we have spent both inside and outside the lab. Thanks for your valuable discussions that broadened my scientific knowledge.

Many thanks to **Dr. Jan Beyer** for “spinning discussion” during the time you stayed in Linköping. I owe my thanks to **Dr. Vladimir Kalevich** for the help in the Hanle setup. Also, thanks to **Dr. Daniel Dagnelund** for the lab matters concerning the magnetic resonance setup and vacuum systems.

I also owe my thanks to all other group members in FEM. I had a great time in the lab with **Dr. Alexander Dobrovolsky**. Thanks for your positive attitude of living. Thanks to **Stanislav Fillippov** and **Yuqing Huang** for your good company in our quantum dot project. I would like as well to thank **Dr. Jan Stehr**, **Dr. Joseph Cullen**, **Dr. Qinjun Ren**, and **Dr. Deyong Wang** for helping me with all matters and making a friendly working atmosphere. Thanks also for the good company in our Monday meetings.

I truly appreciate the worldwide collaborations from my coauthors. Thank you for the professional work.

It is also a joy for the time we spent inside and outside the university with my **PhD student friends** whom I cannot name all here.

I feel thankful to **Kanya**, **Robbie**, and **Ian McLoed** for your warm welcome to Sweden and your great support for my life outside the university.

Thank you, Mom, for your unconditional support and love.

Well, I keep my last thanks for my wife, **Promptorn Wangwacharakul** (a.k.a. **Prae**) for your unconditional support (with some complaints), your great love, and your patience as a scientist's wife. Life is tough, so we will be together tougher, cheers!

Yuttapoom Puttisong

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Chapter I: Pursuit of room-temperature defect-engineered spin functionalities in a semiconductor

An introduction

Spintronics, which exploits both spin and charge properties of electrons, has been a subject of great interest for future electronics and photonics¹⁻⁸. A new generation of semiconductor devices, made by either adding spin functionality to existing microelectronic structures or using it alone to perform specific operations, shall provide great advantages of nonvolatility, low electrical power consumption, high-speed performance, increased capacities of classical memory units, and eventually, a possibility for building a quantum machine exploiting rules of quantum mechanics—a quantum computer^{6,8-12}.

A primary requirement for spintronic applications is effective and efficient generation of electron spin polarization. This should preferably be completed without external fields and at room temperature (RT), desirable for device applications. Recently, we have demonstrated that this can be accomplished by exploiting an unconventional defect-mediated spin filtering approach using spin-dependent recombination (SDR) via paramagnetic defect centers¹². The introduction of Ga_i^{2+} -interstitial defects in Ga(In)NAs alloys have been shown to transform a nonmagnetic semiconductor into a highly spin-polarized source, where a record-high 43% of conduction electron spin polarization can be achieved at RT without help of an external field¹³⁻¹⁴.

Taking this successful milestone as the starting point, we have further continued our journey aiming at full exploration of spin functionality enabled by the Ga_i^{2+} defects in the Ga(In)NAs alloys. This thesis is devoted to experimental investigations of the defect-engineered spin filtering effect. The word *investigation* may sound elusive to describe the actual aim of the thesis work. To be exact, the strategy of the study can be generally described by the concept of “triple I,” which stands for *improve*, *implement*, and *improvise*.

1.1 Improve

Here we focused on material and defect properties that are important for spin filtering efficiency. We also aimed at identification of the microscopic origin of the spin interactions at the defect centers that control the efficiency of the spin filtering effect. The results obtained from these studies were expected to point towards a possible pathway to improve spin filtering performance.

1.2 Implement

For the second aim of the study, we showed that the Ga_i^{2+} defects can also turn their host material into an efficient RT optical spin detector and spin amplifier with an amplification gain up to 27 times and a fast response up to 1 GHz.

1.3 Improve

For the final aim of the study, we went beyond merely generating strongly spin-polarized electrons. Here we addressed another attractive aspect of manipulating a defect nuclear spin, regarded as a promising candidate as a quantum bit (qubit) thanks to its long spin memory. A key requirement for a spin qubit is our ability to polarize defect nuclear spins. Here we proposed and demonstrated an efficient way to realize this requirement at RT by using electron spins as a polarization source, without applying a magnetic field.

The thesis is organized as follows:

Chapter II gives a brief introduction to material and defect properties, where general properties of GaIn(N)As alloys and the Ga_i^{2+} defects are discussed.

Chapter III introduces several important spin interactions in semiconductors. Here we shall discuss dominant spin relaxation processes that hinder full exploration of spin functionalities. Both conduction and defect electron spin relaxation processes are considered.

Chapter IV is devoted to a central concept governing the defect-engineered RT spin functionality in Ga(In)NAs alloys, SDR. Experimental demonstrations of the effects are supported by theoretical modeling by rate equations and an effective spin Hamiltonian analysis using realistic physical parameters.

Chapters V gives the basics of the experimental approaches. The main emphasis has been placed on optical spin orientation and electron paramagnetic resonance techniques utilizing optical excitation/detection. Manifestations of SDR and dynamic hyperpolarization of defect nuclear spins, which can be observed experimentally, are discussed.

Chapter VI summarizes the results from the published scientific articles included in the thesis.

Chapter II: Ga(In)NAs alloys and Ga-interstitial defects

The material insights

2.1 Introduction to Ga(In)NAs alloys

III–V dilute nitrides have been a topic of research interest owing to their distinct physical properties unseen in conventional semiconductor alloys^{15–16}. In Ga(In)NAs alloys, incorporation of N on a dilute level (<5%) leads to significant modifications of electronic properties due to the difference in atomic sizes and electronegativity between nitrogen and the replaced As anion^{15–17}. Because of a giant bandgap blowing effect, the Ga(In)NAs alloys hold great potential for various device applications. This includes application in near-infrared lasers operating at the telecommunication windows of 1.3 and 1.5 μm and efficient multi-junction solar cells. Moreover, because of the splitting of conduction band (CB) into two subbands by the perturbation of N, dilute nitrides can be used in novel intermediate-band solar cells¹⁸ where CB subbands are utilized for double interband light absorption within a single layer of Ga(In)NAs alloy. This is expected to cover a broader range of the solar spectrum, thus avoiding the technological complications arising from the design and fabrication of multi-junction solar cells.

Unfortunately, the growth of Ga(In)NAs alloys has faced technological challenges. A large local strain, when an N atom is at an As sublattice site, leads to a very low solubility limit of N and a very wide miscibility gap. To overcome this issue, the growth of Ga(In)NAs alloys has been performed under non-equilibrium conditions, that is, at low growth temperatures. This results in incorporation of point defects that deteriorate optical and electronic properties of the alloys. The degradation of optical quality is often associated with the formation of defects acting as nonradiative (NR) recombination centers competing with radiative recombination channels. The NR defects also shorten a minority carrier diffusion length of Ga(In)NAs solar cells, which degrades internal quantum efficiency of these devices.

Despite the harmful roles of NR defects, grown-in paramagnetic defects introduced by the incorporation of N, namely Ga_i^{2+} defects, exhibit astonishing spin properties that can turn the host Ga(In)NAs into an efficient RT spin filter, spin amplifier, and spin detector via the SDR^{13,14,19}. A slight imbalance between spin-up and spin-down conduction electrons can result in a substantially high degree of spin polarization of conduction electrons (P_e) and defect electrons (P_c) when the spin filtering effect is activated (see chapter IV). Spin-filtering defects also modify optical and electronic properties of their host material. It has been shown that upon activation of the spin filtering effect, spin blockade of NR recombination channels leads to a substantial increase (up to 8 times) of the band-to-band photoluminescence (BB-PL) intensity²⁰. This effect

is also expected to improve internal quantum efficiency of solar cell devices, where the NR recombination path is a shunt.

In this chapter, we attempt to provide brief material insights into the Ga(In)NAs alloys and the spin filtering Ga_i^{2+} defects being probed in this thesis study. The nature of the recombination processes is discussed. Basic growth methods and post-growth treatments will also be introduced. At the end of the chapter, properties of the Ga_i^{2+} defects (from a material point of view) will be given.

2.2 Growth and treatments of Ga(In)NAs

2.2.1 Growth methods

Ga(In)NAs alloys are often grown by gas-source and solid-source molecular beam epitaxy (MBE). Be and Si are the common p- and n-type dopants. Ga(In)NAs can also be grown by metal-organic chemical-vapor deposition (MOCVD) using dimethylhydrazine, hydrazine, or t-butylamine as nitrogen sources. The optimum temperature window to incorporate N and to avoid a phase separation is 420°C–600°C. The samples are usually capped with a top GaAs layer. The growth of quantum structures such as Ga(In)NAs/GaAs multiple quantum wells (QWs) and Ga(In)NAs quantum dots (QDs) has successfully been demonstrated¹⁵⁻¹⁶.

2.2.2 Post-growth treatments

To improve crystal quality, both in situ and ex situ thermal annealing have been performed. The in situ thermal annealing was usually done under an arsenic overpressure. The ex situ can be done by placing the sample faced down onto a GaAs substrate to minimize the loss of As atoms. Rapid thermal annealing (RTA) can also be used to remove some point defects.

Post-growth hydrogen (H) ion-beam irradiation has also been studied^{15,16,21-24}. The hydrogen treatment has been shown to passivate N in GaNAs alloys, which leads to bandgap reopening up to the limits of the GaAs bandgap. H treatment has also been shown to restore the GaAs lattice constant. The bandgap reopening effects were tentatively attributed to the formation of N-H complexes. The defect passivation by H in semiconductors is also expected, as being shown by a number of theoretical and experimental studies^{25,26}.

The bandgap reopening by H passivation also allows bandgap engineering by H incorporation. Recently, site-controlled GaNAs QDs made by post-growth hydrogen irradiation of GaNAs QWs with patterning Ti circular masks on top have been successfully implemented²⁷. By this method, the areas that are shaded by the Ti masks (of several nanometers in diameter) are not affected by the H. On contrary, the unmasked areas suffer H passivation and thus restore the bandgap to a level of GaAs, providing lateral confinement of GaNAs QDs. The QD emission of the sample constructed by this method has been confirmed by micro PL measurements and correlation measurements of a single photon source²⁷⁻²⁸.

2.3 Recombination processes in Ga(In)NAs

2.3.1 Radiative recombination

Radiative transitions in Ga(In)NAs epilayers at a cryogenic temperature are shown to be governed by recombination of excitons localized within potential fluctuations in the alloys bandgap due to inhomogeneity of N composition. The PL spectrum exhibits an asymmetric line shape with a sharp cutoff at high emission energy and a long tail at the low-energy side. This lineshape is associated with an exponential density distribution within the potential fluctuations. The direct experimental proof of the emission origin as being due to the localized excitons (LE) recombination has been obtained from near-field scanning optical microscopy (NSOM)^{33,34}. The sharp multi-LE lines have been resolved over the spectrum tail of the macro-PL spectrum.

Temperature dependence of the PL maximum shows the so-called S-shape behavior³⁰⁻³². At low temperatures, a strong red shift of the PL maximum is observed and is associated with thermal depopulation of the localized states. At high temperatures, the emergence of free exciton (FE) emission via the extended band states causes a blue shift of the PL spectrum. A further increase of temperature causes a red shift of the PL maximum due to a temperature-induced reduction of the bandgap. A large Stokes shift between the PL and the photoluminescence excitation (PLE) spectra is shown at low temperatures. This is due to the fact that the transition edge of the PLE spectra is determined by optical absorption via the extended states, whereas the PL emission is from the localized states.

2.3.2 Nonradiative recombination

The optical quality of the Ga(In)NAs alloys is severely degraded at elevated temperatures because of thermal activation of NR recombination via defect centers. The origin of point defects has been determined employing several experimental techniques including nuclear reaction analysis (NRA) with Rutherford backscattering (RBS) channeling technique³⁵⁻³⁷, positron annihilation spectroscopy³⁸, electrical measurements³⁹⁻⁴⁴, and optically detected magnetic resonance (ODMR) measurements^{13,20,45,46}. The results for NRA with RBS channeling suggested incorporation of N interstitials in the alloys that can be suppressed upon thermal annealing. The positron annihilation spectroscopy revealed the presence of vacancy-type defects in Ga(In)NAs alloys. The vacancy-type defects can be suppressed by thermal annealing. Many point defects acting as either carrier trap or recombination centers have been revealed through the deep-level transient spectroscopy (DLTS)³⁹⁻⁴⁴.

For paramagnetic defects such as the spin filtering Ga_i^{2+} defects, the spin resonance spectroscopy is one of the most suitable techniques to probe the microscopic origin and local spin interactions⁴⁷ (see also chapter V). Combined with optical detection, this technique provides reliable identification of spin-dependent NR defects. The dominant paramagnetic defects revealed by ODMR studies are Ga_i^{2+} defects of various configurations acting as efficient SDR centers at RT. Beside the Ga_i^{2+} defects, the paramagnetic defects of unknown chemical origin are also

found in Ga(In)NAs alloys. The latter can be removed by thermal annealing²⁰ and are unlikely to act as spin filtering centers.

2.4 Ga-interstitial defects

Ga_i^{2+} defects have never been found in undoped GaAs. The concentration of the Ga_i^{2+} defects increases with increasing N composition⁴⁶. The defect concentration can be reduced by RTA but is not completely quenched²⁰⁻⁴⁶. Figure 2.1 schematically shows one of possible configurations of an interstitial defect in GaAs - a T_d site surrounded with four nearest Ga neighbors. In Ga(In)NAs alloys, possible involvement and the exact position of an N atom in the vicinity of the Ga_i^{2+} defects is still unknown. Recently, theoretical studies have suggested a possible configuration of the Ga_i defects that has a low formation energy, that is a Ga_i atom surrounded by four Ga atoms with the next nearest As atoms replaced by N⁴⁸.

We reported detailed studies on the formation of the Ga_i^{2+} defects under different growth and post-growth treatments in Paper I. Up to four configurations of the Ga_i^{2+} defects with different hyperfine interaction (HFI) parameters have been founded experimentally²⁰. This suggested the existence of the Ga_i^{2+} defects in different interstitial sites (two T_d sites, surrounded by either group III or group V sublattice, one D_{3d} site of hexagonal symmetry with the nearest neighbors from both sublattices) and/or complex defects involving Ga_i^{2+} . The defect g-factors and HFI parameter A are isotropic^{8,20}. Together with $g \sim 2$ and the rather strong HFI, the defects are concluded to have A_1 symmetry of localized nature. This provided evidence that the Ga_i^{2+} defects found by the ODMR are at the interstitial sites as the antisite defects are predicted to have T_2 symmetry and, therefore, a weak and anisotropic HFI.

Figure 2.1: One of the possible sites of a Ga-interstitial defect in GaAs. Here, the defect has tetrahedral symmetry (T_d) and is surrounded by four Ga atoms.

Chapter III: Spin interactions in semiconductors

And the relevant spin relaxation mechanisms

In this chapter, we describe important spin interactions in bulk semiconductors.

3.1 Spin-orbit interaction

The spin-orbit interaction (SOI) makes a main contribution to carrier spin relaxation in semiconductors. Electrons moving in an atomic potential $V(\vec{r})$ experience an effective magnetic field acting on their spins due to a relativistic effect,

$$H_{so} = \frac{1}{4m_0^2 c^2} \vec{p} \cdot [\vec{\sigma} \times (\nabla V(\vec{r}))].$$

Here, m_0 is the electron mass and c is the speed of light. $\vec{p}$ is canonical momentum and $\vec{\sigma}$ is Pauli spin matrices. In a solid, the potential $V(\vec{r})$ is a periodic lattice potential sensed by electrons. Lack of space inversion symmetry implies that the degeneracy of electron energy states $E_{k\uparrow}$ and $E_{k\downarrow}$ is broken. The SOI term has a form of

$$H_{so} = \frac{1}{2} \Omega(\vec{k}) \cdot \vec{\sigma},$$

where $\Omega(\vec{k})$ is the electron spin precession frequency. Comparing this form of Hamiltonian to a commonly known Zeeman interaction (for example, see chapter V), one can see an action of SOI due to space inversion asymmetry separates electron sublevels into two by the effective magnetic field.

Any type of space inversion asymmetry can cause spin relaxation coupled with SOI. The most common one is a bulk inversion asymmetry in a III–V material that lacks center of inversion⁴⁹. This is typically referred to as the Dresselhaus SO coupling term, which is cubic in $\vec{k}$. An electric field can also break space inversion symmetry. This is important in semiconductor nanostructures and heterostructures in the presence of an electric field at an interface or in the structure with spatial variations of band edge. This effect is known as the Rashba SO coupling^{50,51}. Additional terms of SOI may arise if the interface of a heterostructure does not share common atoms, known as an interface inversion asymmetry⁵².

3.2 Hyperfine interaction

An electron spin interacts with a nuclear spin via a HFI due to a Fermi contact of electron and nuclear wave functions. The reduced form of the HFI term under spherical approximation can be written as

$$H_{HFI} = \sum_n A_n (\vec{S} \cdot \vec{I}_n),$$

where $\vec{S}$ and $\vec{I}_n$ are the electron and nuclear spin, respectively. The subscript n refers to the interaction of n -th nuclei and A is the hyperfine parameter describing the interaction between electron and nuclear spins, involving the overlapping of the electron envelop wave function at nuclear sites. For free electrons, the envelope wave function is a plane wave, thus HFI is weak. However, HFI is greatly enhanced in localized systems such as electrons in a confined potential of QDs or localized electrons bounded to defect centers. The HFI for holes is weaker than that for electrons due to a p-type character of Bloch wave function containing a small wave function overlapping at the nuclear sites. Nevertheless, a long-range dipole-dipole interaction between the hole's angular momentum and nuclear spins can introduce another form of HFI, with its strength approximately one order of magnitude weaker than that of electrons.

3.3 Conduction electron spin relaxation

Here we list important spin relaxation mechanisms known in semiconductors. The majority of the relaxation processes involve SOI.

3.3.1 D'yakonov-Perel mechanism

For III–V semiconductors such as Ga(In)NAs alloys with bulk inversion asymmetry, electrons undergo spin precession along an effective magnetic field $\vec{B}_k$ of the given $\vec{k}$. In the presence of momentum scattering, the electron randomly changes $\vec{k}$ before relaxing to the bottom of the conduction band. This implies the change of spin precession axis along momentum relaxation, which randomizes the phase and relaxes the initial orientation of electron spins^{53,54}. This spin relaxation process thus occurs *between adjacent scattering events*. In a strong scattering regime, fast momentum relaxation leads to a motion narrowing of spin precession and thus long spin relaxation time, i.e.

$$\tau_s \propto \frac{1}{\tau_p},$$

where τ_s is the spin relaxation time and τ_p is the momentum relaxation time.

3.3.2 Elliot-Yafet mechanism

Due to the SOI, the periodic part of electron wave function is no longer a pure spin state but is an admixture between spin up and spin down states. In the presence of spin-mixing,

electrons can flip their spins by impurity or phonon scatterings⁵⁵⁻⁵⁶. Unlike the D'yakonov-Perel mechanism, the Elliot-Yafet mechanism relaxes electron spin *at the event of collision*. The spin relaxation rate is directly proportional to the number of scattering events and, hence,

$$\tau_s \propto \tau_p.$$

3.3.3 Bir-Aronov-Pikus mechanism

This mechanism has a profound effect in p-type semiconductors due to exchange scattering of an electron and a hole⁵⁷. One shall note that even if the mechanism happens at the collision, the dominant effect causing spin relaxation is not by SOI but is from the exchange interaction. This is due to the intrinsic permutative antisymmetry of fermion wave function combined with the Coulomb interaction, which is greatly promoted at the collision when electron and hole wave functions overlap.

3.4 Hole spin relaxation

In semiconductors with a strong SO coupling, the spin of a hole directly couples to the orbital character of the valence band, in which the individual spin and angular momentum are not good quantum numbers, but a total angular momentum $\vec{J} = \vec{L} + \vec{S}$. The effect of this SOI, taking into account band characters together with a lack of inversion symmetry, leads to a strong SOI of holes compared with that of electrons and hence faster spin relaxation.

As a consequence of the aforementioned mechanisms, a conduction electron in GaAs loses its spin orientation very fast at elevated temperatures. This fast spin relaxation restrains many spin-based applications requiring strong electron spin polarization. For a hole, the strong SOI results in extremely fast spin relaxation (~ 100 fs)⁵⁸.

3.5 Defect electron spin relaxation

The spin relaxation processes related to the change of $\vec{k}$, as experienced by conduction electrons and valence band holes as discussed above, are greatly suppressed for an electron bound to a defect center because of the absence of a translational motion. The spin relaxation time of defect electrons is thus usually longer than that of free electrons.

Nevertheless, spin relaxation mechanisms of a defect electron can be governed by several sources. One of these is SOI via phonons, the modulation of the defect's ligand field by lattice vibration⁵⁹. This causes fluctuation of an electrostatic field causing spin relaxation of the defect electron via SO coupling. The rate of such spin relaxation greatly depends on the strength of the SOI that the defect electron experiences, reflected by the extent of the orbital character of the defect electron that mixes its spin states. Roughly speaking, a long spin relaxation time is expected for a defect electron having a g-factor close to 2.0023 for an electron in free space, when SOI is minimized.

There are several types of SO coupling causing spin relaxation of a defect electron at zero field. One is a Raman process that covers a broad phonon spectral band⁶⁰. Interaction of this type involves phonon excitation to a virtual state in which a subsequent phonon emission returns the electron to the ground state with a different spin orientation. The other type is known as the Orbach process⁶¹. This involves direct excitation to a real excited state via phonon absorption. Electron spin flips by either absorbing or emitting a phonon. Both Raman and Orbach processes have characteristic temperature dependences reflecting strong acceleration of spin relaxation at elevated temperature as they involve the interaction via thermally activated phonons.

Another spin relaxation mechanism at a defect center is HFI due to strong localization of electron wave function at nucleus (nuclei) of the defect. This interaction leads to mutual flip-flops between the two spin species that govern the spin relaxation process if HFI is strong. This is further discussed in Chapter IV, where HFI is shown to strongly affect spin filtering efficiency. The HFI with nuclear spins of the lattice atoms surrounding the defect can act as a fluctuating nuclear field, which relaxes electron spin in a random manner. However, the interaction with the lattice nuclear spins is expected to be weaker than that with the defect's core nuclear spin. The spin relaxation process governed by HFI is expected to be insensitive to temperature in zero field as the spin interaction does not require phonon coupling.

Chapter IV: Spin-dependent recombination

Origin of the defect-engineered spin functionality in a semiconductor

4.1 Spin-dependent recombination (SDR): background

SDR relies on efficient carrier recombination via paramagnetic centers. It is governed by a strong connection between conduction and defect electron spins during recombination, transforming paramagnetic defects to efficient spin filtering centers capable of generating conduction electron spin polarization up to $>40\%$ ^{13,14}. Such a property is beneficial for many spin-based applications¹⁻⁸. SDR in III-V semiconductors was discovered in the early 70s, with the first experimental observations in a GaAlAs alloy at 77K, by C. Weisbuch and G. Lampel⁶³. Latter studies of SDR has been done in multilayers of GaAs/GaAlAs and semi-insulating GaAs^{64,65}. All these studies were restricted to low temperatures. Among many experimental and theoretical SDR studies of III-V alloys⁶³⁻⁷⁵, an important step towards defect-engineered RT spin functionality was reported in 2009 by X. J. Wang et al. These authors directly identified the Ga_i^{2+} interstitial defects in Ga(In)NAs alloys as the SDR-active defects and singled out their role as RT spin filtering centers¹³. In this chapter, we shall introduce the principle of the spin filtering effect governed by SDR in more detail.

4.2 Principle of SDR

The defect in a semiconductor that is a good candidate for a spin filtering center needs to satisfy the following requirements:

1. It needs to be a paramagnetic defect that acts as an efficient recombination center.
2. The recombination time via this center must be shorter than spin relaxation times of free and defect electrons.
3. The center must contain only an orbitally non-degenerate ground state within the bandgap to secure spin-selective capture of free electrons by the defect center governed by the Pauli exclusion principle.

4.2.1 Dynamic spin polarization via SDR, spin filtering, and spin amplification

Through the SDR process, conduction electrons with a non-vanishing degree of spin polarization (P_e) can dynamically polarize defect electron spins (leading to P_c) when they undergo efficient recombination via the defect. This is schematically shown in figure 4.1. The simplest example is taken assuming complete spin-polarized conduction electrons. Defect electron spins are unpolarized at thermal equilibrium before the SDR event takes place, and only 50% of the paramagnetic centers can capture conduction electrons to form spin pair-off centers. Releasing one of the electrons at the spin paired-off center by subsequent recombination with unpolarized holes results in 75% of P_c (see figure 4.1(b) and (c)). Consequently, repeating the

process can drive P_C toward 100%. As the centers are all polarized, the conduction electrons that lose spin orientation will be rapidly depleted from the conduction band (CB) by efficient spin-selective capture—the defect-enabled spin filtering process. Such a process maintains P_e as long as the defect electrons keep their spin orientation.

Figure 4.1: Principle of SDR. (a) Spin-selective electron capture by paramagnetic defect centers under completely polarized spin injection. (b) Hole capture by the spin paired-off centers. (c) The outcome of one recombination round, yielding 75% spin-polarized centers. (d) A free electron spin filtering by the spin-polarized defect centers.

The spin filtering concept can be applied to a very weak P_e of injected carriers, where the dynamic spin polarization should further amplify P_e and P_C to a much higher degree. To demonstrate this, we use theoretical studies with the aid of a coupled rate equation analysis employing realistic parameters¹³. The rate equations are

$$\begin{aligned} \frac{dn_{\pm}}{dt} &= G_{\pm} - \gamma_e n_{\pm} N_{\mp} - \frac{(n_{\pm} - n_{\mp})}{2\tau_s}, \\ \frac{dN_{\pm}}{dt} &= -\gamma_e n_{\mp} N_{\pm} + \frac{1}{2} \gamma_h p N_{\uparrow\downarrow} - \frac{(N_{\pm} - N_{\mp})}{2\tau_{SC}}, \\ \frac{dp}{dt} &= G - \gamma_h p N_{\uparrow\downarrow}, \\ N_{SDR} &= N_{+} + N_{-} + N_{\uparrow\downarrow}, \end{aligned}$$

where G is the generation rate of electron (n)-hole (p) pairs. N_{SDR} is the total defect concentration, i.e. the total sum of the concentrations of paramagnetic centers $N_{\pm}$ and spin

paired-off centers $N_{\uparrow\downarrow}$. The subscript $\pm$ refers to spin up and spin down, respectively. γ_e and γ_h are the electron and hole capturing rates by the centers. The spin-selective electron capture term is $\gamma_e n_{\pm} N_{\mp}$. The spin relaxation times of conduction and defect electrons are τ_s and τ_{sc} , respectively. The band-to-band recombination is neglected here because it is known to be much slower than the SDR via the defects, and will thus not affect simulation results. Solving this set of equations yields the values of $n_{\pm}$, $N_{\pm}$, $N_{\uparrow\downarrow}$, and p . The values of P_e and P_C are calculated by

$$P_e = \frac{n_+ - n_-}{n_+ + n_-} \text{ and } P_C = \frac{N_+ - N_-}{N_+ + N_-},$$

and the initial spin polarization of conduction electrons P_e^i is defined by

$$P_e^i = \frac{G_+ - G_-}{G_+ + G_-}.$$

The typical values of defect parameters^{13,14} are $\tau_s = 150$ ps, $\tau_{sc} = 1500$ ps, $\gamma_e = 4\gamma_h$, $N_{SDR} = 2 \times 10^{16} \text{ cm}^{-3}$.

The dynamic processes of P_e and P_C are shown in figure 4.2(a) and 4.2(b). Here we apply a step-like generation of carriers. The SDR process leads to a fast increase of both P_e and P_C with their steady state values approaching 60%, under a merely $P_e^i \sim 5\%$, demonstrating amplification of free electron spin polarization degree by up to 14 times! The origin of spin amplification is in a dynamic spin feedback between P_e and P_C —as P_e is being transferred to P_C via the recombination, the spin-polarized centers improve the value of P_e by the spin filtering effect. The simulation in figure 4.2(a) shows that this process is approaching its steady-state condition within 1 ns after carrier injection.

The efficiency of the spin filtering effect is expected to depend on the relative concentrations of the defect centers and free carriers^{13,69}. The calculated results for P_e and P_C as a function of G (thus carrier concentration) are plotted in figure 4.2(c), taken the values under the steady-state condition. With a low carrier injection level, there is not enough number of free carriers to dynamically polarize the paramagnetic centers so that both P_e and P_C remain low. An increase in the number of injected carriers leads to a better dynamics. As a consequence, an increase of P_e and P_C as the function of G is apparent. On the other hand, a saturation point of the polarization degrees and a further quenching appear at higher G values. This degradation of the spin filtering efficiency can be understood by monitoring the concentration of the spin filtering centers in difference charge states. The transformation of $N_{\pm}$ into $N_{\uparrow\downarrow}$ under strong

carrier injection is clearly seen in figure 4.2(d). The charge transformation is equivalent to a decreasing number of the spin-filtering active centers, which suppresses the spin filtering efficiency. This characteristic power dependence of P_e as shown in figure 4.2(c) is one of the SDR signatures, which can be experimentally observed¹³.

Figure 4.2: (a) and (b) polarization dynamics of conduction and defect electrons upon free carrier injection (c) Calculated P_e and P_c as a function of G . (d) The concentration of the defects in the two different charge states, scaled with N_{SDR} , as a function of G .

4.2.2 Time evolution of SDR under non-equilibrium carrier pumping: a two spin pool model

To demonstrate the dynamics of SDR under the non-equilibrium condition, we perform simulations by applying a strong generation pulse of a Gaussian form to replicate the experimental condition- under strong optical pulse excitation. The simulation results are displayed in figure 4.3(a) and 4.3(b) for the decay of P_e and photoluminescence (PL) intensity arising from the BB radiative recombination, respectively. Two decay characteristics are apparent, which are separated by the shaded and unshaded areas as a guide to the eye. They can be explained within the two spin pool model⁷⁶. The first phase of the decay, marked by the shaded areas, is a rapid capture of electrons/holes by the paramagnetic centers with a characteristic time τ_c , as schematically illustrated in figure 4.3(c). The efficient carrier recombination via the defects results in a rapid PL decay. During the time, the SDR process enhances P_e and P_c . Subsequently, the PL decay slows down due to spin blockade. In the second phase, the spin polarization is maintained as any spin-flipped conduction electrons are rapidly drained out by the spin-polarized centers, see figure 4.3(d). Under the condition of complete spin-

polarization for both conduction and defect electrons, the PL decay due to carrier recombination via the defects is only possible after a free electron flips its spin. Therefore, the PL decay in the second phase is controlled by free electron spin relaxation with a characteristic time τ_S . As a consequence, a proper analysis of the experimental decay curves (time-resolved PL spectra) can be used to estimate the values of τ_C and τ_S .

Figure 4.3: (a) and (b) Dynamics of spin polarization and PL decay under the strong influence of the SDR process. (c) and (d) Schematic illustration of the two spin pool model used to describe the characteristic PL decays.

4.3 Perturbation by an external magnetic field

The simplest way to study the behavior of conduction and defect electron spins under an applied magnetic field $\vec{B}$ is by adopting a classical equation of motion of electron spins in the magnetic field and let free and defect electron spin couple via SDR. The modified rate equations have the following form^{14,67,69}:

$$\begin{aligned}
 \frac{dn}{dt} &= G - \frac{\gamma_e}{2} (nN_1 - 4\vec{S} \cdot \vec{S}_C), \\
 \frac{d\vec{S}}{dt} &= \frac{G}{2} \vec{P}_e^i - \frac{\gamma_e}{2} (\vec{S}N_1 - n\vec{S}_C) - \frac{\vec{S}}{\tau_S} - \vec{S} \times \vec{\Omega}, \\
 \frac{d\vec{S}_C}{dt} &= -\frac{\gamma_e}{2} (n\vec{S}_C - \vec{S}N_1) - \frac{\vec{S}_C}{\tau_{SC}} - \vec{S}_C \times \vec{\Omega}_C, \\
 \frac{dp}{dt} &= G - \gamma_h p N_{\uparrow\downarrow}, \quad N_{SDR} = N_1 + N_{\uparrow\downarrow}.
 \end{aligned}$$

Here, $\vec{S}$ and $\vec{S}_C$ are the spins of free and defect electron, respectively. $N_1 = N_+ + N_-$ is the total concentration of the defect centers in its paramagnetic charge state. $\vec{\Omega} = g\mu_B\vec{B}/\hbar$ and $\vec{\Omega}_C = g_C\mu_B\vec{B}/\hbar$ are the Larmor precession frequencies of free and defect electron spins. μ_B is Bohr's magnetron, g and g_C are the free and defect electron g -factors.

4.3.1 Transverse magnetic field

We first consider the case when $\vec{B}$ is applied perpendicular to $\vec{S}$ and $\vec{S}_C$. The simulated results (the so-called Hanle curves) are displayed in figure 4.4.

Figure 4.4: (a) and (b) simulated P_e and P_C as the function of the transverse magnetic field B_T . (c) and (d) the simulations when a free carrier generation rate has been reduced by 10 times. Solid lines in (a) and (c) are the simulations of free electron spin depolarization governed by SDR process, and the dashed lines are the simulations without taking SDR process into account.

Under the application of the transverse magnetic field B_T , both conduction and defect electron spins are depolarized by the induced Larmor spin precessions. These precession motions are interrupted by events of spin loss, and therefore the magnitude of the B_T field required to completely depolarize electron spins is determined by electron spin lifetime. Because of distinctly different spin lifetimes of defect and free electrons, complete depolarization of these two species is expected to occur in different field ranges, which is distinguishable from depolarization curves.

For a defect electron spin, its long spin lifetime leads to a sharp drop of P_C readily at low B_T , as shown in figures 4.4(b) and 4.4(d). The linewidth of the depolarization curve depends on G . Because the defect spin lifetime is contributed from both spin relaxation time and the lifetime

of the defects in their paramagnetic state, a low value of G implies a longer time that the defect can survive in the paramagnetic state before capturing another free electron. This results in a longer total spin lifetime. As such, P_C is easier to be destroyed by B_T , which implies a narrower width of the depolarization curve. At the extremely low G , the half-width of the Hanle curve is no longer controlled by the lifetime of the paramagnetic centers but by the intrinsic spin relaxation time τ_{SC} ^{69,71}.

Even though spin depolarization of the conduction electrons induced by the spin precession is expected to occur at a different field range, strong quenching of P_e coinciding with that of P_C can also be observed (see figure 4.4(a) and 4.4(c)). The strong depolarization of P_e by the weak B_T (i.e. within the shaded area) is thus not due to the free electron spin precession but rather reflects the deactivation of the defects as the spin filtering centers since their polarization is destroyed. The precession-induced spin depolarization of the free electrons is difficult to be observed within the narrow 0.5 T range because of its short spin lifetime. This effect gives rise to a polarization baseline of $P_e \approx P_e^i = 5\%$ which slowly depolarizes with increasing B_T . This is confirmed by another simulation assuming $P_C=0$. As such, the simulation represents pure free electron spin depolarization, which produces only the baseline component of $P_e \approx P_e^i = 5\%$, shown by the dashed line in figures 4.4(a) and 4.4(c).

The simulation suggests a direct correlation between the width of depolarization curve and spin lifetime. Therefore, Hanle measurements can be used to experimentally deduce electron spin lifetime. Moreover, as the central sharp component of the free electron Hanle curve is determined by the spin properties of the defect electrons, it allows one to probe the defect electron spin by using free electron spin as a mediator which can be easily measured by optical means^{14,69,71} (see also chapter V).

4.3.2 Longitudinal magnetic field

By applying a magnetic field along a spin quantization direction, the Larmor precession no longer destroys electron spins. Instead, an application of the longitudinal magnetic field B_z splits spin quantum states into two Zeeman spin sublevels with $m_s = \pm 1/2$. In other words, the Zeeman interaction leads to a pure projection of electronic spin along B_z . If there are field-independent spin interactions which mix the electron spin states at zero field, the application of B_z shall suppress the spin mixing, which leads to a better spin projection along the magnetic field direction.

4.3.2.1 Spin mixing by hyperfine interaction

For the spin-filtering Ga_i^{2+} defects, the defect electron spin strongly interacts with the nuclear spin of the core Ga_i^{2+} with $I = 3/2$ via a HFI. An effective spin Hamiltonian for the spin filtering center under the application of B_Z is

$$H = g_e \mu_B B_Z S_{CZ} + A S_{CZ} I_Z + \frac{A}{2} (S_{C+} I_- + S_{C-} I_+).$$

S_{CZ} and I_Z are the spin operators of the electron and nuclear spins of the defect along the z-projection, with the corresponding quantum numbers m_S and m_I , respectively. A is the HFI parameter. Because the HFI contains a non-secular term of rising and lowering spin operator (denoted by the subscript + and -), the individual m_S and m_I are not good quantum numbers and the states $|m_S, m_I\rangle$ are not the eigenstates of the Hamiltonian. The new eigenstates are linear combinations of the spin states $|m_S, m_I\rangle$ of the form

$$\psi_n = \sum_{m_I=-I}^{+I} \left[\sqrt{\alpha_{n,m_I}} \left| +\frac{1}{2}, m_I \right\rangle + \sqrt{\beta_{n,m_I}} \left| -\frac{1}{2}, m_I \right\rangle \right], \quad n = 1, 2, 3, \dots, 2(2I+1),$$

where $\sqrt{\alpha_{n,m_I}}$ and $\sqrt{\beta_{n,m_I}}$ are the expansion coefficients of the spin-up and spin-down electron states, respectively, with a given m_I . The expansion coefficient fulfills the normalization condition,

$$\sum_{m_I=-I}^{+I} (\alpha_{n,m_I} + \beta_{n,m_I}) = 1.$$

For the Ga_i^{2+} defects, the spin system is described with $\vec{J} = \vec{S} + \vec{I}$ with $J = 2, 1$. The complete eigenstates $|\vec{J}, m_J\rangle$ at zero field are listed as

$$\begin{aligned}
\psi_1 &= |2,2\rangle = \left| +\frac{1}{2}, +\frac{3}{2} \right\rangle, \\
\psi_2 &= |2,1\rangle = \frac{\sqrt{3}}{2} \left| +\frac{1}{2}, +\frac{1}{2} \right\rangle + \frac{1}{2} \left| -\frac{1}{2}, +\frac{3}{2} \right\rangle, \\
\psi_3 &= |2,0\rangle = \frac{1}{\sqrt{2}} \left| +\frac{1}{2}, -\frac{1}{2} \right\rangle + \frac{1}{\sqrt{2}} \left| -\frac{1}{2}, +\frac{1}{2} \right\rangle, \\
\psi_4 &= |2,-1\rangle = \frac{1}{2} \left| +\frac{1}{2}, -\frac{3}{2} \right\rangle + \frac{\sqrt{3}}{2} \left| -\frac{1}{2}, -\frac{1}{2} \right\rangle, \\
\psi_5 &= |2,-2\rangle = \left| -\frac{1}{2}, -\frac{3}{2} \right\rangle, \\
\psi_6 &= |1,1\rangle = \frac{1}{2} \left| +\frac{1}{2}, +\frac{1}{2} \right\rangle - \frac{\sqrt{3}}{2} \left| -\frac{1}{2}, +\frac{3}{2} \right\rangle, \\
\psi_7 &= |1,0\rangle = \frac{1}{\sqrt{2}} \left| +\frac{1}{2}, -\frac{1}{2} \right\rangle - \frac{1}{\sqrt{2}} \left| -\frac{1}{2}, +\frac{1}{2} \right\rangle, \\
\psi_8 &= |1,-1\rangle = \frac{\sqrt{3}}{2} \left| +\frac{1}{2}, -\frac{3}{2} \right\rangle - \frac{1}{2} \left| -\frac{1}{2}, -\frac{1}{2} \right\rangle.
\end{aligned}$$

As it can clearly be seen, only states $|2,2\rangle$ and $|2,-2\rangle$ are the pure spin states. The other six eigenstates contain linear combinations of the spin up and spin down electron states. Therefore, the pure spin definition of the defect electron used in the rate equations needs to be modified accordingly by taking a time evolution of the spin Hamiltonian containing the HFI. This leads to a numerous set of differential equations. Nevertheless, the basic concept of the spin-filtering mechanism under the application of B_z can simply be understood by analyzing the spin Hamiltonian of the defect electron alone by exact diagonalization of the spin Hamiltonian in a matrix form. This method holds a valid description of the spin filtering system under a low spin injection condition. In this case, the typical lifetime of the defect electron is long enough so that the hyperfine-induced spin mixing is completely evolved and the time-independent spin Hamiltonian is a good representation of the system.

If $\psi_{1,2,3,4}$ and $\psi_{5,6,7,8}$ (new eigenstates in fields) represent electron spin-up and spin-down states at high fields, we can estimate their spin purity toward zero field by calculating an averaged probability of the electron spin-up component of $\psi_{1,2,3,4}$ by

$$\langle \uparrow \rangle = \frac{1}{4} \sum_{n=1}^4 \sum_{m_l=-3/2}^{+3/2} \alpha_{n,m_l}$$

or the electron spin-down component of $\psi_{5,6,7,8}$ by

$$\langle \downarrow \rangle = \frac{1}{4} \sum_{n=5}^8 \sum_{m_I=-3/2}^{+3/2} \beta_{n,m_I}.$$

The percentage of pure electron spin plotted as a function of B_z is shown in figure 4.5(a).

Figure 4.5: (a) The degree of pure electron spin as a function of a longitudinal field. (b) Schematic representation of the effect of the hyperfine-induced spin mixing on the spin filtering and spin blockade efficiency. (c) A perfect condition for SDR when there is no electron spin mixing at high fields.

The simulation is done by using defect parameters of $^{69}\text{Ga}_i^{2+}-\text{C}^{13,20}$. As seen in figure 4.5(a), only 62.5% of states are pure spin states at zero field. The effect of the hyperfine-induced spin mixing can be seen as a “leak” of the spin filtering process at zero field (see figure 4.5(b)), which degrades the spin filtering efficiency. The application of the B_z field, on the other hand, recovers perfect spin filtering conditions and maximum values of P_e and P_C . The recovery curve of P_e is expected to have similarities with that of P_C . For example, the width of the curves for both P_e and P_C should be approximately determined by the strength of HFI. However, we note that field dependences of P_C and P_e are not expected to be identical and are nonlinearly coupled via the recombination and the spin-mixing processes.

4.4 Dynamic hyperpolarization of defect nuclear spin via HFI and SDR processes

The action of electron and nuclear (e-n) spin flip-flop term in the spin Hamiltonian also leads to polarization transfer between electron and nuclear spins. A strong deviation of the defect electron spin from equilibrium causes a redistribution of e-n spins, which affects the nuclear spin distribution. Consequently, a key to polarize the defect nuclear spin is to polarize the nearby

electron spin. For a spin filtering defect, a high value of P_C is obtained as a result of SDR. The combined effect of SDR and HFI can polarize spins of conduction electrons, the defect electron, and the defect nucleus toward the same orientation. The principle of this process is schematically represented in figure 4.6(a)-4.6(d).

Figure 4.6: (a)-(d) Four possible configurations of a electron-nuclear spin system with $S = 1/2$ and $I = 1/2$. The SDR effect combined with HFI drives the spin polarization along the solid line arrows with a final stable state shown in (a).

By taking example of a simple e-n spin system with $S=1/2$ and $I=1/2$, four possible spin configurations are schematically shown in figure 4.6 (a) for $\uparrow\uparrow$, (b) for $\downarrow\uparrow$, (c) for $\uparrow\downarrow$, and (d) for $\downarrow\downarrow$. The thin and thick vertical arrows represent the electron and nuclear spin, respectively. From figure 4.6, we see that by injecting the spin-up conduction electrons, the SDR and HFI will drive this spin system along the path shown by the solid arrows. The SDR polarizes the defect electron spin to the same direction as that of the conduction electrons. If the e and n spins are antiparallel, the simultaneous flip-flops of e-n spins occur. This process governs the transition from the state $\uparrow\downarrow$ into the state $\downarrow\uparrow$. The inverse flip-flop process, which drives e-n spin back to the initial state, is improbable under the condition of strong carrier injection as the state $\downarrow\uparrow$ is predominantly transformed to the state $\uparrow\uparrow$ by SDR. As such, no matter what configuration of e-n spin is, it eventually ends up with polarized electron and nuclear spins of the defect along the spin direction of the injected conduction electrons. The configuration of $\uparrow\uparrow$ is a stable configuration because it is inactive in spin flip-flops, and the SDR process always maintains the parallel spin configuration of the conduction and defect electrons.

The discussed process remains true for a system of higher nuclear spins, for example, the Ga_i^{2+} defects in $\text{Ga}(\text{In})\text{NAs}$. The difference is just an increasing number of steps required to polarize the nuclear spin to the highest quantum number state⁷³. The analytical simulation of this DNP can be done by including all possible e-n defect configurations in the rate equations. The simulation results including e-n spin interaction are shown in figure 4.7(a)-(c).

As clearly seen, dynamic coupling of conduction electrons, electron and nuclear spin of the defect by the SDR and HFI can lead to a substantially high value of defect nuclear spin polarization (P_N), which can reach 70%. Even though the absolute value of spin polarization can be overestimated at low G because of neglecting the spin mixing effect, the common trend of P_e , P_C , and P_N with respect to G indeed reflects a strong coupling among these three spin species. We shall mention that complete polarization of nuclear spins can be reached by properly tuning the concentration of the spin filtering centers and the relevant defect parameters⁷³.

The DNP process of the Ga_i^{2+} defects has been experimentally proven to be faster than microseconds⁷³. Unfortunately, the upper limit of the DNP speed cannot be tested because of instrumental limitations. Nevertheless, theoretical predictions by a rate equation analysis using realistic parameters suggest the response time on the nanosecond scale, providing a promising way for fast initialization of the defect nuclear spins.

Figure 4.7: (a)-(c) Simulated results of P_e , P_C , and P_N as a function of G using rate equations including the e-n spin interaction.

Chapter V: Experimental approaches

5.1 Optical and magneto-optical spectroscopies

5.1.1 Optical orientation of electron spins

Electronic structure

In III–V semiconductors such as Ga(In)NAs alloys, the electronic band structure close to the Γ point can be described by the $k \cdot p$ model. The electronic state of a CB electron has a form of the Bloch function:

$$|\psi_{k,m}^{CB}\rangle = \exp(ik \cdot r) |U_m^{CB}\rangle, \quad m = \pm 1/2,$$

where m represents the spin direction of electrons. Because the CB state near Γ point possesses the same symmetry as the $|S\rangle$ state (s-like nature), the Bloch amplitude could be rewritten as

$$|U_{1/2}^{CB}\rangle = |S \uparrow\rangle \text{ and } |U_{-1/2}^{CB}\rangle = |S \downarrow\rangle.$$

For the valence band of a p-like nature with a sixfold degeneracy including spin in a presence of a strong spin-orbit interaction, the six states of Bloch amplitude ($|U_m^V\rangle$, where V represents a total angular momentum J and m states J_z) have the forms

Heavy hole (HH) states:

$$|U_{3/2}^{3/2}\rangle = |HH \uparrow\rangle = -\frac{1}{\sqrt{2}}(|X \uparrow\rangle + i|Y \uparrow\rangle),$$

$$|U_{-3/2}^{3/2}\rangle = |HH \downarrow\rangle = \frac{1}{\sqrt{2}}(|X \downarrow\rangle - i|Y \downarrow\rangle).$$

Light hole (LH) states:

$$|U_{1/2}^{3/2}\rangle = |LH \uparrow\rangle = -\frac{1}{\sqrt{6}}(|X \downarrow\rangle + i|Y \downarrow\rangle) + \sqrt{\frac{2}{3}}|Z \uparrow\rangle,$$

$$|U_{-1/2}^{3/2}\rangle = |LH \downarrow\rangle = \frac{1}{\sqrt{6}}(|X \uparrow\rangle - i|Y \uparrow\rangle) + \sqrt{\frac{2}{3}}|Z \downarrow\rangle.$$

Spin-orbit split-off (SO) states:

$$\begin{aligned} |U_{1/2}^{1/2}\rangle &= |SO \uparrow\rangle = -\frac{1}{\sqrt{3}} \left(|X \downarrow\rangle + i|Y \downarrow\rangle + |Z \uparrow\rangle \right), \\ |U_{-1/2}^{1/2}\rangle &= |SO \downarrow\rangle = \frac{1}{\sqrt{3}} \left(-|X \uparrow\rangle + i|Y \uparrow\rangle + |Z \downarrow\rangle \right). \end{aligned}$$

The SO states are separated in energy from the HH-LH states by the so-called spin-orbit splitting Δ_{SO} .

Optical interband transitions

Selection rules of electric dipole allowed interband optical transitions are governed by Fermi's golden rule⁷⁸. The dipole transitions of all involved BB optical transitions are determined by dipole matrix elements

$$D_{i \rightarrow f} = \langle f | \hat{D} | i \rangle.$$

The dipole operator changes parity of a p-like state into s-like⁷⁸ and the non-vanishing components of the dipole BB transition are

$$\langle S | D_x | X \rangle = \langle S | D_y | Y \rangle = \langle S | D_z | Z \rangle.$$

The spin part of the Bloch amplitude is normalized and orthogonal.

$$\langle \uparrow | \uparrow \rangle = 1 \text{ and } \langle \uparrow | \downarrow \rangle = 0.$$

Optical orientation

The form of the dipole operator depends on the polarization of the absorbed light. For the excitation light that is linearly polarized along the x-axis (taking the [001] direction as the z-axis), the dipole operator is

$$D_{\sigma^x}^{Linear} = D_x.$$

This operator is spin degenerate; the dipole transition by the action of this operator creates CB electrons with spin up and spin down orientations with equal probability. For example, the transition probability involving the HH-CB electron transition is

$$P_{HH \rightarrow CB} \propto \left| \langle U_{1/2}^{CB} | D_x | U_{3/2}^{3/2} \rangle \right|^2 + \left| \langle U_{-1/2}^{CB} | D_x | U_{-3/2}^{3/2} \rangle \right|^2 \text{ and } \overset{\text{spin up CB electron}}{\left| \langle U_{1/2}^{CB} | D_x | U_{3/2}^{3/2} \rangle \right|^2} = \overset{\text{spin down CB electron}}{\left| \langle U_{-1/2}^{CB} | D_x | U_{-3/2}^{3/2} \rangle \right|^2}.$$

The total angular momentum of the transition is equal to zero as it involves the change of angular momentum of -1 ($J_z = \frac{3}{2} \rightarrow \frac{1}{2}$) and $+1$ ($J_z = -\frac{3}{2} \rightarrow -\frac{1}{2}$) at the same time. This is true as the x-polarized light does not have the quasi-angular momentum along z.

For circularly polarized light, the dipole operator takes the form

$$D_{\sigma^+}^{Cir} = \frac{1}{\sqrt{2}}(D_x + iD_y) \text{ and } D_{\sigma^-}^{Cir} = \frac{1}{\sqrt{2}}(D_x - iD_y).$$

The subscript $\sigma^\pm$ refers to left and right circularly polarized light with the corresponding quasi-angular momentum $J_z = +1$ and -1 in the unit of $\hbar$, respectively. In sharp contrast to the linear excitation, the circular excitation is spin selective. For the BB optical transition under σ^- excitation, the non-vanishing dipole transitions are

$$\left\langle U_{1/2}^{CB} \left| D_{\sigma^-}^{Cir} \right| U_{3/2}^{3/2} \right\rangle_{HH \rightarrow CB}^{\text{spin up CB Electron}}, \left\langle U_{-1/2}^{CB} \left| D_{\sigma^-}^{Cir} \right| U_{1/2}^{3/2} \right\rangle_{LH \rightarrow CB}^{\text{spin down CB Electron}}, \text{ and } \left\langle U_{-1/2}^{CB} \left| D_{\sigma^-}^{Cir} \right| U_{1/2}^{1/2} \right\rangle_{SO \rightarrow CB}^{\text{spin down CB Electron}}.$$

These transitions conserve the angular momentum. We shall note that while the spin-up CB electron is generated under σ^- excitation from the HH valence band, the spin-down CB electron is instead generated for the transition that involves the LH and SO bands. The relative transition strength is

$$\left| \left\langle U_{1/2}^{CB} \left| D_{\sigma^-}^{Cir} \right| U_{3/2}^{3/2} \right\rangle_{HH \rightarrow CB}^{\text{spin up CB Electron}} \right|^2 : \left| \left\langle U_{-1/2}^{CB} \left| D_{\sigma^-}^{Cir} \right| U_{1/2}^{3/2} \right\rangle_{LH \rightarrow CB}^{\text{spin down CB Electron}} \right|^2 : \left| \left\langle U_{-1/2}^{CB} \left| D_{\sigma^-}^{Cir} \right| U_{1/2}^{1/2} \right\rangle_{SO \rightarrow CB}^{\text{spin down CB Electron}} \right|^2 = 3:1:2.$$

Therefore, optical transitions involving three valance bands result in unpolarized CB electron spins. By taking advantage of an energy separation of Δ_{SO} , which separates the SO band rather far away from LH and HH bands, a proper tuning of photon excitation energy where $E_g + \Delta_{SO} > \hbar\omega_{photon} \geq E_g$ can avoid the transition involving the SO band. Under this condition, spin-polarized CB electrons can be optically created. When HH and LH are degenerate in a bulk semiconductor, the maximum CB electron spin polarization achievable by optical orientation is 50%. Removal of the LH-HH degeneracy at the Γ point, either by strained-induced or quantum confinement effects, can be found advantageous for optical spin generation. In this case, the optical transition involving only one of the HH and LH bands can lead to a maximum spin polarization degree of 100%.

5.1.2 Optical spin detection

Optically spin-oriented electrons spend a finite time in CB before they recombine with holes. During this time, P_e could be lost by various types of spin relaxation mechanisms^{78,79}. In

GaAs at RT, merely a few percent of P_e is left. Holes are generally spin unpolarized due to fast spin relaxation induced by SOI⁵⁸. The degree of P_e can be deduced from the circular polarization of the BB PL emission P_{PL} ,

$$P_{PL} = \frac{I_{\sigma^+} - I_{\sigma^-}}{I_{\sigma^+} + I_{\sigma^-}},$$

Here $I_{\sigma^\pm}$ is the intensity of $\sigma^\pm$ -polarized BB-PL emission. Following the optical selection rules described in the previous section, the measured P_{PL} can be converted into P_e as $P_e = -2P_{PL}$. The minus sign states the difference in the direction of the projected quasi-momentum of light and the spin projection of the electron. The pre-factor two takes into account the HH-LH degeneracy, which reduces the spin detection efficiency by half.

5.1.3 Experimental set up for magneto-optical spectroscopies

In this thesis work, the spin studies in Ga(In)NAs alloys rely on PL measurements employing the optical orientation technique. A typical setup is schematically illustrated in figure 5.1.

Figure 5.1: A typical setup for PL and PLE measurements that employed the optical orientation technique. An external magnetic field is applied in two geometries (Voigt and Faraday), which differ in the relative direction between the B-field and an average electron spin direction.

Here, a tunable wavelength Ti-sapphire laser (700–1020 nm) is used as an excitation source. The photon energy obtained from the Ti-sapphire laser needs to fulfill the condition for optical orientation ($E_g + \Delta_{SO} > \hbar\omega_{photon} \geq E_g$) for optical transitions in both GaAs barrier/substrate and Ga(In)NAs alloys with a low indium composition. Circular polarization of the excitation beam is obtained by using a quarter-wave plate in conjunction with a linear polarizer. The quarter-wave plate can be replaced by an electrically controlled polarization modulator. The double lock-in technique has been implemented to improve the signal-to-noise ratio. In typical measurements, a BB-PL signal is recorded as a function of emission wavelength via a spectrometer. The laser beam is modulated by a mechanical chopper with a frequency in the range of 100–200 Hz (referred to as Freq.1 in figure 5.1). The signal, which is registered by synchronizing the detection signal with the frequency of the mechanical chopper, is the BB-PL intensity $I_{total} = I_{\sigma^+} + I_{\sigma^-}$.

The second lock-in amplifier is used to determine P_{PL} . This is done by placing a circular polarization analyzer on the detection side. The conventional way is to use a photoelastic modulator (PEM) in conjunction with a linear polarizer. PEM periodically transforms the incoming circular polarized light into a linearly polarized light of a given direction. A linear polarizer with a fixed direction is thus used to determine whether the incoming light is σ^+ or σ^- polarized. The modulation frequency of the PEM (Freq. 2) is set at 50 kHz to avoid the interference with the signal of Freq. 1. The signal detected by a lock-in amplifier by using this detection protocol is $I_{PEM} = I_{\sigma^+} - I_{\sigma^-}$. Dividing two obtained signals yields a value of P_{PL} monitored as a function of the emission wavelength selected using a spectrometer.

As the studied Ga(In)NAs thin film/QWs structures contain GaAs barriers/substrate/caped layer, studies of spin injection from an adjacent layer into the Ga(In)NAs layer accompanied by energy relaxation is possible. This can be done by tuning the laser wavelength above the GaAs energy gap and detecting the emission from the Ga(In)NAs layer of a lower bandgap, acting as the recombination-active layer. Tuneability of the laser wavelength also provides the possibility of photoluminescence excitation (PLE) spectroscopy. In contrast with the PL measurements where the PL intensity and P_{PL} are measured as a function emission wavelength at a fixed excitation wavelength, the PLE spectroscopy measures the PL intensity and P_{PL} as a function of excitation wavelength at a fixed detection wavelength.

The measurements in magnetic field

Transverse magnetic field

To get further insight into spin properties, spin studies under the application of an external magnetic field (B) are necessary. As can be seen in figure 5.1, two measurement configurations are employed in the studies. The former refers to as the Voigt geometry where the applied B_T field is perpendicular to the averaged electron spin direction (z-direction). As discussed in the

previous chapter, the application of B_T field induces the Larmor spin precession along the direction of the field. This reduces spin projection along the z-axis and thus the total magnitude of the monitored P_{PL} . The field strength required to completely depolarize electron spin is determined by the event of spin loss, that is, spin lifetime, which contains contributions from carrier lifetime and spin relaxation,

$$\frac{1}{T_S} = \frac{1}{\tau} + \frac{1}{\tau_S}.$$

T_S is the spin lifetime, τ is the carrier lifetime, and τ_S is the spin relaxation time.

The evolution of P_{PL} in the field can be expressed by the following equation⁷⁸:

$$P_{PL}(B_T) = P_{PL}(0) \int_0^\infty dt \frac{1}{\tau} \exp\left(-\frac{t}{\tau}\right) \cdot \exp\left(-\frac{t}{\tau_S}\right) \cos \Omega t,$$

where Ω is the Larmor precession frequency and $\hbar\Omega = g_e\mu_B B_T$, g_e is the electron g-factor, μ_B is the Bohr magnetron and $\hbar$ is the Planck's constant. Solving the above integral equation yields

$$P_{PL}(B_T) = \frac{P_{PL}(0)}{1 + (\Omega T_S)^2}.$$

The expression describes a Lorentzian line shape of the monitored P_{PL} vs B_T and is also known as the Hanle curve. Therefore, the effective spin lifetime $g_e T_S$ can be deduced as

$$g_e T_S = \frac{\hbar}{\mu_B B_{1/2}}.$$

$B_{1/2}$ is the half-width of the Hanle curve deduced by a Lorentzian fitting.

The Hanle measurement is a powerful tool to study spin lifetime⁷⁸. For the spin filtering system of coupled conduction-defect electron spins, the above expression is not strictly valid because of dynamic coupling of the two spins, which also involves a spin cascade process. However, because of rather different recombination dynamics and different g-factors of free and defect electrons, the Hanle curve can be decomposed using a double Lorentzian fitting and approximate spin lifetimes can be experimentally deduced. Another way to improve the accuracy of determining the relevant spin lifetimes is by using the rate equation analysis introduced in Chapter III.

Longitudinal magnetic field

In Faraday configuration, the magnetic field (B_z) is applied along the direction of the averaged electron spin, as discussed in the previous chapter. In this case, the precession motion no longer destroys spin projection along the z-axis. In turn, the application of B_z can improve the spin projection by suppressing other spin interactions by the Zeeman interaction.

5.1.4 Time-resolved photoluminescence spectroscopy

The non-equilibrium carrier and spin dynamics can be probed by employing time-resolved photoluminescence (TRPL) spectroscopy. This is done by replacing a continuous-wave Ti-sapphire laser with a mode-locked pulsed Ti-sapphire laser. The pulse width can be 150 fs or 2 ps. The carriers pumped by the pulse laser decay within their recombination lifetime. The two-dimensional temporal profile of the PL emission, i.e. emission wavelength versus decay time, is registered by a streak camera (which replaces a conventional optical detector). The TRPL measurements are capable of measuring the decay of P_{PL} by using a proper combination of polarization optics. For the conventional type of the PL decay, a P_{PL} decay time characterizes an electron spin relaxation time τ_s ⁷⁸. However, under the condition of strong SDR, this conventional method to deduce τ_s cannot be used because the degree of P_{PL} is maintained by the spin-filtering process no matter if free electrons relax their spins or not^{13,67}. A proper analysis for deducing τ_s is to measure a characteristic decay of the PL intensity following the model of two spin pools described in chapter IV.

5.1.5 Manifestations of the SDR process: optical investigations

SDR results in two major effects: spin filtering and spin blockade¹³. The experimental schemes used to investigate these two effects are schematically shown in figures 5.2(a) and 5.2(b). Under linear excitation, conduction electrons are spin unpolarized. Therefore, carrier recombination via paramagnetic defect centers in zero field is spin independent. Efficient recombination process via the defect centers depletes most of the carriers and only few percent of the optically generated carriers can participate in the radiative BB transitions. This results in a weak BB-PL signal with zero P_{PL} , evident from the experimental results shown in figures 5.2(c) and 5.2(d). In sharp contrast, free electron spin polarization is optically generated under circularly polarized optical excitation. Even though only a few percent of P_e is left after the spin loss during momentum relaxation processes, the dynamic coupling of conduction and defect electrons drives their spins toward the same direction resulting in a much higher degree of P_e (thus, the monitored P_{PL}). The high degree of P_{PL} is therefore a manifestation of the spin filtering effect. In our example case shown in figure 5.2(d), P_{PL} reaches up to 25% under σ^+ excitation. A strong spectral variation of the P_{PL} value is due to spectral overlap of the BB PL bands involving the HH and LH bands of opposite circular polarization, split due to a tensile strain in the GaNAs

layer. Moreover, when the conduction and defect electrons have the same spin orientation, the total recombination rate of free carriers is drastically reduced as a result of spin blockade of the recombination channel via the defects. The accumulation of free carriers results in an enhancement of the BB-PL intensity. Let's introduce a measurement parameter:

$$\text{SDR ratio} = \frac{I^{\sigma^{\pm}}}{I^{\sigma^x}},$$

where $I^{\sigma^{\pm}}$ and I^{σ^x} are the total PL intensities under $\sigma^{\pm}$ and σ^x excitation, respectively. The value of the SDR ratio $\frac{I^{\sigma^{\pm}}}{I^{\sigma^x}} > 1$ reflects the PL enhancement by spin blockade. This is shown in figure 5.2(c), where the SDR ratio of 1.8 (80% enhancement of the PL intensity) is obtained by the action of SDR.

Figure 5.2: Schematic representation of the SDR process. (a) Under linearly polarized excitation no electron spin polarization is optically created. The recombination process is dominated by efficient carrier recombination via defects resulting in a weak BB-PL emission. (b) Under circular polarization excitation, the spin filtering and spin blockade processes are activated, yielding a strong degree of P_{PL} and a strong BB-PL intensity. (c) A comparison of the PL spectra measured under circular and linear excitation. (d) P_{PL} spectra under circular and linear excitation. The results in (c) and (d) were obtained from the $\text{GaN}_{0.013}\text{As}_{0.087}$ epilayer grown on a (001) GaAs substrate. All measurements were performed at RT.

Therefore, both the SDR ratio and P_{PL} are spin signals that can be used to probe the efficiency of the spin filtering effect. The interaction between electron spin (both of free and defect electrons) and B fields hence causes a change in both the SDR ratio and P_{PL} . For the

transverse magnetic field (B_T), the Hanle curves obtained by monitoring both the SDR ratio and P_{PL} are plotted in figure 5.3(a) and 5.3(b). The depolarization of P_{PL} consists of two components, the depolarization of the defect electron spin (the sharp component) and depolarization of the free electron spin (the broad component). The Hanle curve of the SDR ratio, however, has only a single component from the defect electron spin. This is beneficial for the study of defect electron spin relaxation because only one spin species is probed. On the other hand, the SDR ratio and P_{PL} as a function of a longitudinal magnetic field (B_Z) is plotted in figure 5.3(c) and 5.3(d). In this case, the application of B_Z and the suppression of hyperfine-induced spin mixing result in better performance of the spin blockade and spin filtering effects. These are evident from the observed increase of the SDR ratio and P_{PL} as a function of B_Z . The saturation at high fields is due to a recovery of pure electron spin states as the Zeeman interaction overcomes HFI. The magnitude of the B_Z field required to overcome HFI is determined by the strength of HFI.

Figure 5.3: (a) and (b) Hanle curves obtained by monitoring the SDR ratio and P_{PL} as a function of B_T field, from the $\text{GaN}_{0.026}\text{As}_{0.074}$ epilayer grown on a (001) GaAs substrate. Optical excitation power is 250 mW with excitation wavelength of 910 nm. The solid lines in (b) are the fitting Lorentzian curves containing two components. (c) and (d) Results from the measurements under the application of the B_Z field obtained from the $\text{GaN}_{0.021}\text{As}_{0.079}$ epilayer on a (001) substrate. The solid curve in (d) is a guide to eyes.

5.1.6 Optical signature of defect nuclear spin polarization

Defect nuclear spin polarization as a result of DNP can be observed experimentally by an optical means. Concerning the polarization recovery curves in figures 5.3(c) and 5.3(d), if nuclear

polarization of the defect center deviates from zero, there is an effective nuclear polarization field (B_N) sensed by the defect electron. The direction of B_N depends on the effective nuclear spin direction, which can be switched by changing the helicity of circularly polarized optical excitation beam. As such, B_N can either add or compensate the external applied field B_Z . This leads to a shift of the overall curve in figure 5.3(c) and 5.3(d). Therefore, the value of B_N can be measured by employing the optical orientation technique under the application of the B_Z field. The results of this type of measurements are shown in figure 5.4. As clearly seen, the minimum points of the curves with opposite helicity of the excitation beam shift towards opposite directions. The difference between the minimum points of these two curves is thus equal to $2 * |B_N|$. If the strengths of the HFI parameters and the relevant defect parameters are known, the values of nuclear spin polarization P_N can be calculated from the measured value of B_N .

Figure 5.4: SDR ratio as a function of B_z under high optical pumping power. The open squares represent the results obtained under σ^+ circular excitation, and open circles represent that under σ^- circular excitation. The results were obtained from the $\text{GaN}_{0.021}\text{As}_{0.079}$ epilayer grown on a (001) GaAs substrate.

5.2 Electron paramagnetic resonance

Electron paramagnetic resonance (EPR) spectroscopy is a powerful tool to study properties of paramagnetic defects in semiconductors and associated local spin interactions⁴⁷. This is thus the most suitable experimental technique for exploring the physical nature of spin filtering defects. EPR monitors transitions between electronic spin sublevels. Let us consider a general example of spin transitions that occur for an electron ($S=1/2$) under application of an external magnetic field due to absorption of a resonance quanta of electromagnetic radiation. Taken the direction of the applied field as z-axis $\vec{B} = [0, 0, B_z]$, the spin Hamiltonian reads

$$H = g_e \mu_B B_z S_z,$$

S_z is a spin operator along z. In addition to a static B_z , let us introduce an electromagnetic field where the magnetic field component of magnitude B_1 ($B_1 \ll B_z$) oscillates in the x-y plane with the resonance frequency ω_0 .

$$B_x = B_1 \cos(\omega_0 t), \quad B_y = -B_1 \sin(\omega_0 t).$$

The time-dependent Hamiltonian can be rewritten in the form

$$H(t) = g_e \mu_B B_z S_z + \frac{g_e \mu_B}{2} (B_+(t) S_- + B_-(t) S_+),$$

where

$$B_+(t) = B_1 \exp(-i\omega_0 t), \quad B_-(t) = B_1 \exp(i\omega_0 t),$$

Even without a solid derivation of the above Hamiltonian, one can clearly see that the action of the perturbation flips the spin of the electron by the action of $S_{\pm}$ operator. The resonance frequency of the oscillating field stimulates the transition between these two Zeeman-split spin sublevels by either emitting or absorbing a photon of the energy $\hbar\omega_0$. We shall note that the spin transition is a pure magnetic-dipole transition where the initial and final states of the transition share the same parity.

The frequency of the perturbation field is usually in the range of microwave frequency, determined by the magnitude of B_z , which is available in a laboratory. The typical resonance microwave frequencies for EPR studies and their associated band's notations are listed in table 5.1.

Table 5.1: Band notations of the microwave frequencies and the position of the spin-resonance line for an electron with $S = 1/2$ and $g = 2.0023$.

Band	Microwave frequency (GHz)	Resonance field (B_0) for $g = 2.0023$ (mT)
L	1–2	35.7–71.4
S	2–4	71.4–142.7
X	9–10	321.2–356.8
K	24	856.4
Q	34	1213.2
W	94	3354.2

A conventional EPR spectroscopy monitors a change of microwave absorption (at a fixed frequency) as a function of B_z . An EPR transition and the corresponding EPR signal of a spin-1/2 electron with $g_e = 2.0023$ under the resonance frequency of 35 GHz are schematically represented in figures 5.5(a) and 5.5(b), respectively.

5.2.1 Defect identification

A strong spin-spin interaction between electron and nuclear spins at a defect renders the possibility to identify the chemical identity of the defect. Let us recall the effective spin Hamiltonian including HFI between electron and nuclear spins:

$$H = g_e \mu_B B_z S_z + \vec{S} \cdot \vec{A} \cdot \vec{I},$$

Here A is the hyperfine tensor (isotropic for the Ga_i^{2+} defects in Ga(In)NAs alloys). The HFI term further splits each electron spin sublevels to $2I+1$ nuclear spin sublevels with a specific m_I for each nuclear spin state. The electron spin transition under the perturbation of the nuclear spin follows the selection rule $\Delta m_S = \pm 1$ and $\Delta m_I = 0$. The total number of the EPR lines is thus $n = 2I + 1$. Let us take the example of the Ga_i^{2+} -C defect in GaNAs^{13,20} for one of its natural abundant isotopes, e.g. ^{69}Ga . The simulated EPR spectrum at a microwave frequency of 35 GHz and the corresponding electron spin transitions are shown in figure 5.5(c) and 5.5(d). From this, preliminary evaluation of defect properties can be done. The appearance of four transition lines of an equivalent distance implies the interaction between $S = 1/2$ and $I = 3/2$. The strength of A can be determined from the distance between the transition lines. Further confirmation of the defect's chemical identity is possible if the defect contains two or more different isotopes. This is done by taking into account differences in nuclear spins, natural abundant ratio, nuclear Bohr's magnetron ratio, and symmetry evaluation from angular dependent measurements of the EPR signal.

Figure 5.5: (a) and (b) Energy diagram and the simulated EPR spectrum of $S = 1/2$ and $g = 2.00232$ at a microwave frequency of 35 GHz. (c) and (d) Energy diagram and the simulated EPR spectrum including $I = 3/2$.

5.2.2 Probing spin mixing by EPR

EPR lines due to resolved HFI splitting have the same intensity and spacing when measured at a high microwave frequency (high B_z). This behavior is kept only if the transitions are from pure electron/nuclear spin states, that is, m_s and m_l are good quantum numbers. Because of a strong HFI, this is no longer the case at low fields. Instead, only the total angular momentum J commutes with the Hamiltonian. A low field energy diagram of the system of $S = 1/2$ and $I = 3/2$ as a function of B_z is represented in figure 5.6(a). At zero field, states are described by $J = 2$ (fivefold degenerate) and $J = 1$ (threefold degenerate). By applying a strong B_z , states become pure m_s and m_l . A deviation from a linear relationship between energy and B_z of a sublevel reflects a degree of spin mixing. Probing the degree of spin mixing can be done by choosing the resonant microwave frequency so that the spin transitions occur at a low field. The simulated EPR spectrum at the microwave frequency of 9.14 GHz is shown in figure 5.6(b). Two signatures of spin mixing are apparent. First, the separation between the lines is not equal. Second, the two inner pairs of the transitions, where the initial and final states of the transition are both spin-mixed, have lower intensity than that of the outer pairs involving one of the pure states. Appropriate fitting of the measured EPR spectrum with the aid of the spin Hamiltonian analysis is thus a powerful tool to determine the degree of spin mixing with respect to B_z .

Figure 5.6: (a) Low field energy diagrams of $S = 1/2$ and $I = 3/2$ under strong HFI. At low fields, only J and m_I are good quantum numbers. The energy level positions strongly deviate from the linear relation governed by Zeeman interaction, indicating spin mixing. At high field, the Zeeman interaction exceeds HFI, and m_s and m_I are good quantum numbers. (b) Simulated EPR spectrum where the resonances involve spin mixed states. The line intensity and the separation from the adjacent peaks are no longer equal because of spin mixing.

5.2.3 Probing nuclear spin polarization by EPR

If defect nuclear spin polarization (P_N) deviates from the equilibrium, P_N can be determined from the measured EPR spectrum. This is due to the fact that the intensity of each EPR line represents the transition probability associated with the nuclear state m_I . Since in equilibrium all m_I states are equally populated, all EPR lines I^{m_I} have the same intensity at a high microwave frequency (see figure 5.5(c)). Nuclear spin polarization means a population difference between nuclear spin states, resulting in different I^{m_I} , which can be observed experimentally. Thus, the relative difference of I^{m_I} is a direct measure of P_N . Figure 5.7(b) shows a simulated EPR signal of the $^{69}\text{Ga}_i^{2+}$ -D defect²⁰, when P_N is negatively polarized to a certain degree. The degree of P_N can be determined by

$$P_N = \frac{\sum_{m_I=-I}^{+I} I^{m_I} m_I}{I \sum_{m_I=-I}^{+I} I^{m_I}},$$

which is general for all nuclear spin numbers I .

Let us recall that the EPR transition needs to fulfill the condition:

$$\hbar\omega_0 = g_e\mu_B B_0 = g_e\mu_B (B_{EPR}^{m_I} + B_N^{m_I}),$$

where B_0 is the resonant field without HFI (marked by the dashed line in figure 5.7(a)), $B_{EPR}^{m_I}$ is the resonant field position of the state m_I , and $B_N^{m_I} = Am_I / g_e \mu_B$ is the effective nuclear field experienced by the electron, that is, an Overhauser field. Here we neglect the non-secular spin flip-flop term that plays a negligible role in high-field resonances. In thermal equilibrium, the total sum of all $B_N^{m_I}$ yields zero averaged field B_N . For any finite P_N , the value of B_N is

$$B_N = \frac{\sum_{m_I=-I}^{+I} I^{m_I} m_I B_N^{m_I}}{\sum_{m_I=-I}^{+I} I^{m_I}}.$$

The value of B_N can also be measured by employing the optical orientation technique under longitudinal magnetic field, as discussed in Chapter IV.

Figure 5.7: (a) The calculated energy levels marked by the resonance transitions at 35.07 GHz. The nuclear fields associated with nuclear spin states m_I are indicated by the horizontal arrows. (b) the EPR signal of a negatively polarized nuclear spin.

5.2.4 Optically detected magnetic resonance spectroscopy

As mentioned earlier, the conventional EPR detects changes of microwave absorption/emission caused by the resonant transitions. This detection protocol faces several limitations. For example, information on a carrier recombination process associated with the monitored defect cannot be acquired. A more severe problem is from poor sensitivity of commercially available microwave detectors, which requires a large number of defect centers per detection volume, preventing the application of EPR in semiconductor thin films and quantum

structures. A further improvement can be done by combining PL spectroscopy with EPR. A general idea is to improve the sensitivity by replacing a microwave detector with a highly sensitive light detector in visible and infrared regions. This is known as the optically detected magnetic resonant spectroscopy. The basic principle of ODMR is schematically represented in figure 5.8(a) and 5.8(b).

Figure 5.8: (a) A schematic illustration of an ODMR signal governed by competing carrier recombination channels (b) Spin resonance under the spin blockade condition.

Here we show possible carrier recombination channels in a semiconductor including recombination via defects, taking the Ga_i^{2+} defect as an example. Because the recombination via different channels shares the same carriers, a change in a recombination rate of one channel will affect all other recombination processes including PL. An ODMR signal is thus a change in the monitored PL signal under the magnetic resonance condition. As shown in the inset in figure 5.8(a), the resonant absorption of microwave radiation transfers population between two Zeeman sublevels. If the two spin sublevels have different recombination rates, PL intensity can be affected under the resonance transition. An example can be taken from the Ga_i^{2+} defect. The carrier recombination via the defect is spin blocked under strong influence of SDR, and a resonant spin flip of the defect electron leads to acceleration of the recombination via the defect as illustrated in figure 5.8(b).

If the BB-PL is monitored, this process leads to quenching of the PL signal upon the resonance, yielding a negative ODMR signal. On the other hand, if the monitor PL is a radiative transition via the defect, the ODMR signal should be positive. The sign of ODMR, therefore, identifies the role of the paramagnetic defect center in recombination processes that can be resolved spectrally because of the difference in the emission energy.

Chapter VI: Summary of the papers

The reflection on “3I-actions concept”

Improve

Paper I

We performed ODMR measurements to study formation of the spin filtering Ga_i^{2+} defects in Ga(In)NAs under different growth and postgrowth conditions. The spin filtering defects were proven to be common grown-in defects in the alloys, independent of the employed growth methods and post-growth annealing treatments. The formation of the defects is thermodynamically favorable in the presence of N.

Paper II

We examined the spin filtering effects in GaNAs/GaAs multiple quantum well (QWs) structures. We found that, in the presence of the Ga_i^{2+} defects in the GaNAs QW layers, the spin filtering effect is rather efficient in the thin QW structures with a thickness of 3–9 nm. The spin filtering efficiency, on the other hand, was shown to scale down as the thickness of the QWs decreases. This finding was attributed to a decrease of the 2-D sheet concentration of the spin filtering defects in thinner QWs, revealed by the detailed time-resolved photoluminescence and ODMR studies.

Paper III

The effect of hydrogen on the Ga_i^{2+} defects in GaNAs epilayers and GaNAs/GaAs multiple QWs was reported. The post-growth H irradiation was shown to lead to complete quenching of the RT spin filtering effect, accompanied by a strong reduction of the concentration of the Ga_i^{2+} defects. This thus provided strong evidence for H passivation of the spin filtering defects, most likely by the formation of H-Ga defect complexes. Our results also suggested that despite the fact that H was a common contaminant during the growth process, it is unlikely a part of the spin filtering defects.

Paper IV

In this work, we examined local spin interactions at the spin filtering centers. The effect of hyperfine interaction between electron and nuclear spins at the Ga_i^{2+} defects in GaNAs alloys was investigated experimentally by magneto-optical and ODMR studies, together with theoretical studies based on a spin Hamiltonian analysis. We provided strong evidence that the HFI causes e-n spin mixing at zero field, thereby degrading the spin filtering efficiency. This could be suppressed by an application of a longitudinal magnetic field as the Zeeman interaction overcame HFI. These findings provided a guideline to improve spin filtering efficiency by selectively

incorporating the Ga_i^{2+} defects with a weak HFI, for example, by optimizing growth and post-growth treatment conditions, known from the studies in Paper I.

Paper V

Here we identified the microscopic origin of electron spin relaxation (T_1) at the spin filtering centers, which was hyperfine-induced cross-relaxation between e-n spins. This conclusion was based on our experimental findings that T_1 was insensitive to temperature and there was a direct correlation between the electron spin relaxation rate and the strength of HFI, following the Fermi-Golden rule. We pointed out that the spin relaxation rate related to a spin-orbit interaction should be strongly quenched for the spin filtering defects. This was due to the fact that the spin blockade effect requires a nonexistence of the orbital excited states of the defect centers, implying strong quenching in the orbital character of the defects. We suggested that the spin filtering defect with weak or no HFI could be a good candidate for a spin qubit. This work thus emphasized the need of search for new spin filtering centers in semiconductors containing zero nuclear spin.

Implement

Paper VI

We experimentally demonstrated for the first time at room temperature an efficient electron spin amplifier exploiting the defect-engineered spin filtering effect in Ga(In)NAs alloys. We obtained a large spin gain at RT (up to 27 times at zero field) for conduction electrons. The spin gain was shown to be very sensitive to a weak transverse magnetic field (B_T) and could be completely suppressed at $B_T \sim 200$ mT, providing a control of the spin gain of the spin amplifier. The purposed spin amplification was shown to have a very fast response, with a cutoff frequency of ~ 1 GHz.

Paper VII and Paper VIII

We showed that the defect-mediated spin amplification effect found in GaNAs alloys could also turn the material into an efficient RT optical spin detector. This provided us a reliable way to gain information concerning the degree of spin loss during spin injection across GaAs/GaNAs heterointerfaces. More than 50% of P_e was found to be lost at the interfaces due to a structural inversion asymmetry and probably interfacial point defects.

Improvise

Paper IX

Here we tackled one of the important aspects in future quantum information processing using defect nuclear spins as qubits: efficient initialization of nuclear spin qubits at RT. We proposed

and demonstrated that the combined effects of spin filtering and HFI could lead to a sizeable RT nuclear spin polarization ($\sim 15\%$) of the Ga_i^{2+} defects, observed in GaNAs alloys. The local nuclear field could be directly sensed by the conduction electrons via SDR, providing a pathway to control nuclear spins by conduction electrons at RT. The nuclear polarization process was shown to be fast and could be completed in less than $5\ \mu\text{s}$.

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