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Executive Summary of the Thesis

Optical Properties of Germanium-Vacancy Centers in Diamonds Produced by Ion Implantation and Annealing Treatment

Laurea Magistrale in Engineering Physics - Ingegneria Fisica

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Introduction

The scope of this thesis is to study the optical properties of Germanium-Vacancy (GeV) color centers in diamond, produced by ion implantation and annealing. These defects represent an appealing solid-state system for quantum communication and computing purposes [1]. The present Executive Summary covers the most important aspects of this work. First, a theoretical introduction to the fabrication strategies and properties of GeV defects in diamond is provided. Then, an overview of the investigated diamond samples as well as the utilized experimental methods is given. Finally, optical spectroscopy of GeV color centers is presented and the impact of annealing conditions (i.e., temperature and duration of the treatment) and ion implantation parameters on the optical properties of the formed centers is discussed.

1. Theoretical background

Diamond is a metastable allotrope of carbon. In diamond, the crystal structure is a Face-Centered Cubic and the carbon atoms have sp^3 hybridized orbits which build strong tetrahedral bonds, resulting in the highest hardness among known materials. The large electrical bandgap of 5.5 eV at room temperature [2] makes it transparent for a broad range of radiation. However, in most diamonds, optical properties, such as absorption, are determined by the dominating defects and impurities contained in the lattice. Color centers in diamond are optically active impurities, i.e., they show fluorescence when excited by light. As a host matrix, diamond has beneficial properties, such as transparency in a broad spectral range, chemical inertness and high thermal conductivity.

The properties of natural diamonds depend on the environment and the growth conditions, which results in uncontrollable concentration of color centers. Control can be achieved in synthetic diamonds. Color centers are most commonly produced through either impurity incorporation during synthesis or via targeted ion implantation and subsequent annealing treatment. In ion implantation, the diamond is exposed to an ion beam, which can consist of ions of different elements [3]. A great benefit of the implantation technique is the possibility to incorporate impurities in specific regions of the sample. However, the production of high quality color centers from implanted ions requires subsequent

annealing [3]. The annealing process activates the vacancies and increases the probability that they reach the impurity atoms. The vacancies might bind to the impurity atoms and form the desired defects [3]. At the same time, annealing reduces the damage produced in the diamond lattice by the implantation process.

Optical excitation of color centers leads to fluorescence. The typical fluorescence spectrum consists in two main components: the Zero Phonon Line (ZPL) and the Phonon Sideband (PSB). Both features result from transitions between an excited state and the ground state of the center. The ZPL frequency is determined by the energy difference of ground and excited state. The shape of ZPL can be described by a Lorentzian profile [4]. At absolute zero temperature the (homogeneous) line width of the ZPL is determined by the excited state lifetime T_1. Above absolute zero temperature, thermal motions will introduce a temperature-dependent broadening of the line width. The PSB arises due to electron-phonon interactions and is shifted to higher frequencies in absorption and to lower frequencies in fluorescence. The line shape of the PSB can be described by a Poisson distribution. At high temperatures, or in the case of strong interaction of the color centers with the lattice, the PSB can be approximated by a Gaussian distribution. At cryogenic temperatures, the ZPL is very prominent while the PSB is strongly suppressed due to lack of phonon-mediated transitions [4]. In the case of a large number of defects, each of them can contribute to the absorption and emission spectra. The spectra are therefore called inhomogeneously broadened due to different local environments for the centers, which results in shifts of the energy levels. Inhomogeneous broadening leads to an increase in the line width, since the total fluorescence spectrum is averaged over differently emitting centers [4].

Group-IV Vacancy color centers are point defects in diamond in which a group-IV atom is located in an interstitial lattice position between two adjacent vacancies, as shown in Fig. 1. Group-IV centers possess D_{3d} symmetry. The inherent inversion symmetry results in absence of static electric dipole moment, leading to first-order insensitivity to electric fields and, therefore, to stable optical transitions [5]. Eleven

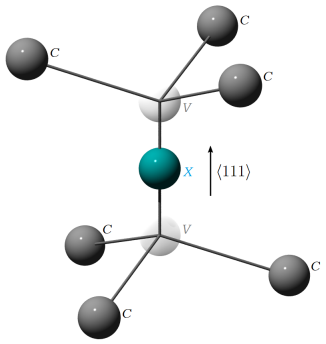

Figure 1: Group-IV defect inside the diamond lattice. The carbon atoms are depicted by dark-gray spheres, the X impurity atom by a blue sphere and the vacancies by light-gray spheres.

electrons in total are bound to the defects, leading to a negative charge state. The spin-orbit interaction lifts the degeneracy of the ground ^2E_g and excited ^2E_u states, which are therefore split into two levels each. The splittings of the ground and excited state sub-levels are different due to the different spin-orbit interactions. All four transitions (named A to D) between the ground and excited states are optically allowed. This results in a four fold fine structure of the ZPL, which can be observed at low temperatures [1]. As an example, the level scheme and PL spectra of GeV centers is shown in Fig. 2. With increasing temperature, the spectral lines broaden and merge together at room temperature.

In the experiments, the photoluminescence (PL) spectra can be recorded by off-resonant excitation into the E states. Radiative decay processes from the ^2E_u excited state to the ^2E_g ground state result in the characteristic ZPL emissions. The group-IV defects have similar spectral features, but the absolute position of the ZPL and the ground and excited state splittings differ. In addition, group-IV centers are susceptible to both axial (along the ⟨111⟩ direction) and transverse strain within the diamond lattice. That shifts the energy levels, thus shifting the ZPL or changing the ground and excited state splittings, respectively. Strain in diamond containing group-IV defects is commonly introduced as a result of the lattice damage produced by ion implantation.

In this work, GeV defects in diamond are relevant. The emission in the GeV ZPL, peaked at 602 nm, is a significant amount of the overall

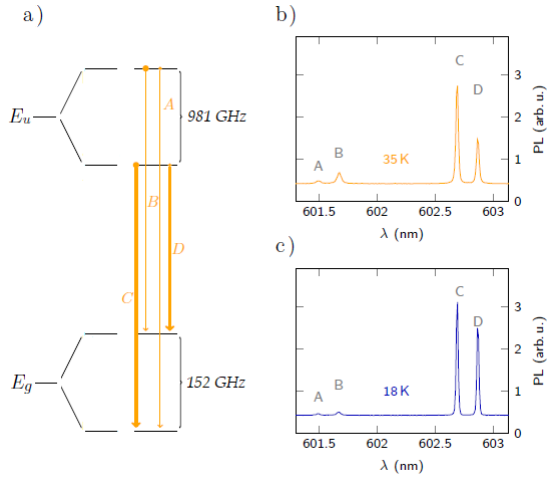

Figure 2: Low temperature spectra of a single GeV center [1]. (a) Level scheme and optically active transitions. (b) Temperature of 35 K. All four ZPL transitions can be clearly observed. (c) Temperature of 18 K. The A and B lines are suppressed in intensity.

fluorescence. The spin-orbit splitting ΔSO_g of the GeV is 152 GHz (Fig. 2(a)). Excited state lifetimes T_1 of 1.4-5.5 ns [5] and ZPL line widths of transition C as narrow as 42 MHz [1] are reported for GeV. These near lifetime-limited line widths promote the GeV as a source of indistinguishable single photons. The indistinguishability $\xi \in [0, 1]$ of a single-photon source can be measured by quantifying the extent to which the full width at half maximum line width $\Delta\nu$ of an emitter is lifetime-limited

$$\xi = (2\pi T_1 \Delta\nu)^{-1} .$$

The lifetime-limited line width for GeV centers equals 26 MHz [1]. That leads to the opportunity to obtain GeV centers with transition line widths narrower than 42 MHz, which is beneficial for single-photon sources.

2. Experimental methods

Six 1×1 mm diamond samples were investigated. All the samples are commercially available elementsix™ type-IIa electronic grade single crystal diamonds, grown by CVD synthesis. They were grouped in two sets, called UU601 and UU602, respectively. Each set consists in three samples cut from the same substrate. ^{74}Ge ions were implanted into the samples. Ahead of each experiment and annealing step, the samples were cleaned in a boiling acid mixture consisting in equal parts of nitric, perchloric and sulfuric acid to remove surface contaminants. The samples were subjected to different annealing processes in high-vacuum (pressure of 10^{-8} mbar). An overview of the implantation and annealing parameters is given in table 1.

Sample	E_i (keV)	d_i (nm)	T_a (°C)	τ (h)
UU601-1	95	38	850	1+3
UU601-2	95	38	1200	1+1
UU601-3	95	38	1500	1
UU602-1	350	131	850	1+3
UU602-2	350	131	1200	1+1
UU602-3	350	131	1500	1

Table 1: Overview of samples and applied treatments. E_i is implantation energy, d_i is implantation depth, T_a is annealing temperature and τ is annealing time. The implantation dose equals 10^{10} ions/cm^2 for all the samples.

The experiments were performed in the Institute for Quantum Optics of the University of Ulm, Germany. As a standard technique, confocal fluorescence microscopy was used to perform experiments on GeV centers in diamonds. In a confocal microscope the excitation light is focused to the diffraction limited spot, whereas the luminescence signal is filtered from out-of-focus background by the pinhole. This enhances the sensitivity of confocal microscopes in comparison to conventional ones. In the context of the present work, two home-built confocal microscopes have been utilized: one for all spectroscopy experiments performed at room temperature (RT) and one for the low temperature (LT) investigations. Cryogenic experiments were performed at the temperature of 4 K utilizing a continuous flow cryostat. For the photoluminescence spectroscopy, a 532 nm continuous wave laser was used. The Photoluminescence Excitation spectroscopy was performed utilizing a dye laser operating with Rhodamine B in Ethylenglycol. The wavelength of the dye laser was tuned to 602 nm. For the lifetime measurements, a femtosecond optical parametric oscillator system tuned to 532 nm was used.

3. Results and discussion

3.1. Room temperature spectroscopy

Samples UU601-1 and UU602-1. After the first annealing step, i.e., 850 °C for 1 hour, no indication of formation of GeV centers was observed. The recorded spectra show a relatively strong background. To clarify the feasibility of the annealing temperature of 850 °C to form GeV centers, the same samples were annealed for additional 3 hours. After the treatment, the confocal scannings reveal distinguishable sites. The corresponding PL spectra show the presence of GeV features. However, the obtained spectra contain a strong background, only slightly mitigated by the additional annealing treatment.

Samples UU601-2 and UU602-2. The presence of GeV centers was observed directly after the first annealing. In comparison to the samples annealed at 850 °C, the background was suppressed, whereas the density and brightness of GeV sites increased. Similar results were obtained after the second annealing step at 1200 °C. Nevertheless, the second treatment led to slightly improved optical properties.

Samples UU601-3 and UU602-3. The annealing treatment at 1500 °C for 1 hour led to increased density and brightness of the color centers. The ZPL peak is generally sharper and more intense in comparison to the other cases. The background level is strongly reduced.

In order to extract relevant information, i.e., ZPL peak positions and line widths, an analysis of the RT photoluminescence spectra was performed. The acquired spectra were analyzed and fitted by means of a function which allows to replicate the overall shapes of the spectra. For the ZPL, a Pseudo-Voigt profile was used to represent inhomogeneous and homogeneous broadening components. The PBS profile can be approximated by an asymmetric Gaussian line shape at RT. A skewed Gaussian line shape (skew-normal distribution) was used. The resulting fit function was used to analyze the GeV spectra collected from each sample after completing all the annealing steps. An example of fit is shown in Fig. 3. From the statistical analysis, the average peak positions λ_0 and line widths $\Delta\lambda$ of the ZPLs were retrieved.

For the low temperature annealing (850 °C) case, the annealing time of 4 hours leads to formation of centers. However, significant background contribution to the GeV emission indicates strong radiation damage. The properties of the formed GeVs are strongly affected by their surroundings, e.g., local strain. High strain results in broad line widths due to inhomogeneous broadening, as revealed by the fit. Increasing the annealing temperature leads to more efficient GeV formation. After 1 hour of annealing at 1200 °C, clear evidence of GeV color centers formation is observed. The situation is only slightly improved when increasing the annealing time. However, the average values of $\Delta\lambda$ still indicate a high local strain. The samples annealed at 1500 °C show a large number of bright GeVs and narrower inhomogeneous distributions as well as line widths of the ZPL. This indicates reduced strain, i.e., better recovery of the diamond lattice from the implantation damage.

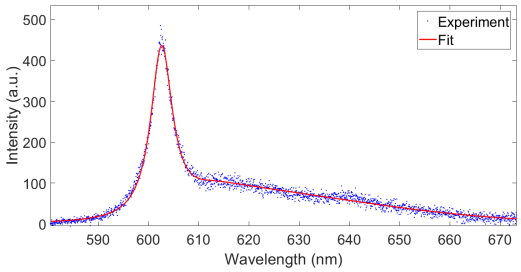

Figure 3: RT GeV spectrum and corresponding fit for sample UU602-3, showing the typical RT PL features of GeV.

3.2. Low temperature spectroscopy

Samples UU601-1 and UU602-1. The PL spectra show characteristic spectral features of GeV color centers, i.e., lines relatively close to 602 nm corresponding to C and D transitions. However, the strong background, related to the lattice damage, contributes to the spectra. Moreover, the peak positions are strongly shifted from the expected 602 nm.

Samples UU601-2 and UU602-2. The acquired spectra show clear signatures of GeV. In comparison to the samples annealed at 850 °C, the background reduces, similarly to the RT observations. In addition, the GeV ZPL peak positions appear to be closer to the expected 602 nm and the peak centers are less separated.

Samples UU601-3 and UU602-3. The collected spectra generally show no damage-related

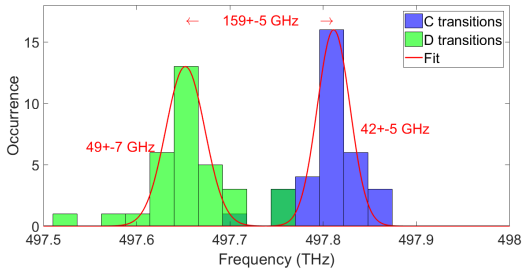

Figure 4: Histogram of C and D transition frequencies and corresponding fit for GeV centers in sample UU602-3.

background and ZPL peaks very close to 602 nm. The peak positions are close to each other for different centers.

The low temperature PL spectra allow to obtain the frequency difference of C and D transitions, i.e., the ground state splitting ΔSO_g. The C and D peak positions of the probed emitters were extracted from the acquired spectra. Based on the data, the histograms were built and analysed. The widths of the distributions provide information on similarity of the defects. An example of histogram is shown in Fig. 4. In the case of the samples annealed at 850 °C and 1200 °C, the obtained transition frequency distributions have widths above 100 GHz independently of the annealing time. This indicates strong differences in the properties of the created GeV centers. The strong shift of ZPL peak positions for different centers indicates high longitudinal strain. Moreover, the ground state splittings ΔSO_g, related to transversal strain, are almost a factor of 2 larger than the reported splitting of non-strained GeV centers. In contrast, samples UU601-3 and UU602-3 revealed narrow distributions of transition frequencies. Based on Gaussian fits, the obtained histograms show widths around 40 GHz. Moreover, the calculated values of ΔSO_g are close to the low-strain reference splitting of 152 GHz, indicating a reduction of strain in samples annealed at high temperatures.

3.3. Photoluminescence Excitation

Photoluminescence Excitation was performed at T = 4 K. The excitation wavelength was tuned in each case to the wavelength of the C transition of the GeV center. The laser wavelength was then scanned around the transition, whereas fluorescence in the PSB was recorded. The line widths of the measured PLE spectra were fitted with Lorentzian functions. In order to stabilize the charge state of the color centers, each experiment was first performed with additional off-resonant 532 nm light. The same measurements were then repeated with resonant excitation only to probe spectral stability. Powers of ≈ 1 nW of resonant excitation were used to avoid power broadening of the line widths [1].

Samples UU601-1 and UU602-1. No PLE spectra could be recorded in the case of sample UU601-1, probably due to severe spectral instability. In the case of sample UU602-1, one center was spectrally stable. A line width of 285 ± 24 MHz was recorded. However, the center showed strong blinking behaviour.

Samples UU601-2 and UU602-2. For 1 hour annealing, the probed emitters showed strong blinking and/or bleaching behaviour. Only one center for sample UU601-2 and three emitters for sample UU602-2 were spectrally stable. In comparison to the previous samples, resonant excitation of several centers at approximately the same excitation wavelength indicates similarity of the created emitters. The measurements were repeated after the additional annealing step. No significant effects on the spectral properties were observed. However, the number of stable emitters increased for both samples. The narrowest recorded PLE line widths are $\Delta\nu_{\text{min}} = 68 \pm 6$ MHz and $\Delta\nu_{\text{min}} = 70 \pm 5$ MHz for samples UU601-2 and UU602-2, respectively.

Samples UU601-3 and UU602-3. Blinking, bleaching and spectral diffusion were strongly suppressed. A larger number of spectrally stable centers and significantly narrower PLE line widths were observed. An example of PLE spectrum is shown in Fig. 5. An increase in the number of fluorescing centers was also visible in resonant confocal scans at fixed resonant excitation wavelength, see Fig. 5. For both samples, narrowest PLE line widths down to $\Delta\nu_{\text{min}} = 38$ MHz were observed. Moreover, repetitive scans over the resonances show spectral stability for up to 10 minutes (see Fig. 5). Blinking during the scans can be attributed to changes in the charge state of GeVs. The usage of resonant excitation only is sufficient to recover the charge state and, consequently, fluorescence. The results of the PLE measurements follow the same trend as for the photoluminescence studies.

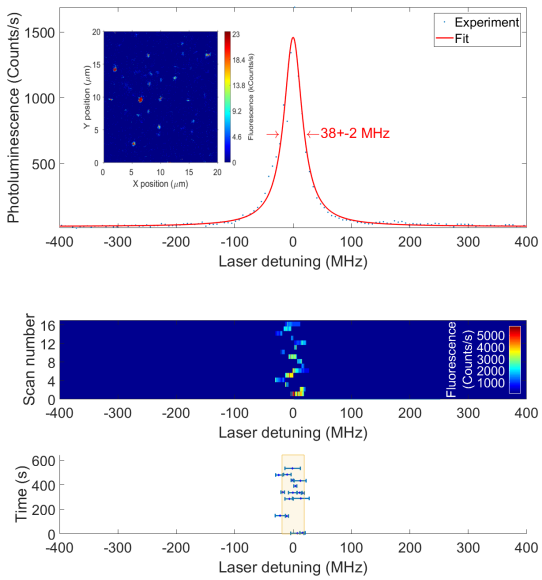

Figure 5: Repetitive PLE scans of GeV C transition in sample UU602-3. In the inset: confocal microscope image of the region where the center was found. The transition is stable in frequency for ≈ 10 minutes. The absolute drift of the transition frequency is less than the natural line width (orange shaded area).

The higher spectral stability and the reduction of the PLE line widths clearly indicate improvement in the local surroundings of the probed GeV centers with increasing annealing temperature. Higher temperature results in lower residual implantation damage in the diamond samples, which is beneficial for the optical properties of the created emitters. Moreover, several spectrally stable centers with identical transition frequencies can be created. This opens up an opportunity to address centers several times and on-demand. The narrowest line widths observed for centers in samples annealed at 1500 °C are close to the lifetime-limited value of 26 MHz [1]. The difference can be attributed either to remaining implantation damage or residual laser power broadening of the line widths.

3.4. Lifetime measurements

The excited state lifetime measurements were performed on 40 GeV emitters for every samples after completing all the annealing treatments. The measurements were performed at the temperature of 4 K. The recorded signals were fitted by a single exponential decay model, resulting in excited state T_1 lifetimes. The average values of T_1 increase with annealing temperature. From the values of T_1, the expected lifetime-limited line widths $\Delta\nu$ were calculated. The resulting average values of $\Delta\nu$ are all broader than the intrinsic value of 26 MHz [1], which is expected since the investigated samples are not strain-free. The corresponding expected average values of lifetime-limited line width $\Delta\nu$ are close to 30 MHz for the samples annealed at 1500 °C and in good agreement with the narrowest line widths of $\Delta\nu_{\text{min}} = 38$ MHz, measured by PLE. This indicates high quality of GeV centers formed at 1500 °C. The results of the lifetime measurements support the spectroscopic investigations, confirming the increase in the quality of the emitters for high temperature annealing.

Conclusions and future developments

The impact of annealing on the optical properties of GeV centers in diamonds was systematically studied. The experimental investigations were performed by means of PL spectroscopy, PLE and lifetime measurements at room and cryogenic temperatures. The obtained results show a strong dependence of formation and properties of GeV on the annealing treatments. An increase in annealing temperature leads to enhancement in the quality of the emitters. No significant impact of the different implantation energies is observed, which indicates the robustness of the GeV with respect to depth. The obtained results show that GeV emitters can be reliably created by ion implantation and subsequent annealing at high temperature for quantum communication purposes.
The studies presented in this work can be extended to produce high quality GeV centers. The impact of additional and intermediate annealing steps on the properties of the created GeVs might be investigated. Implantation of Ge ions at higher energies (μm depth range) into the diamond samples could be investigated as well. Finally, the role of implantation dose may be studied. Similar studies can be extended to the heavier group-IV elements, Sn and Pb. The following step is integration of color centers, via deterministic ion implantation, with nanophotonic devices, which can be used for different quantum applications.

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