Luminescent Properties of Transition Metal Impurities in Silicon

Diplomarbeit
von
Matthias Knopf

Januar 1998

Lehrstuhl Prof. Dr. G. Maret
Universität Konstanz, Fakultät für Physik
78434 Konstanz, Universitätsstr. 10
# Contents

1 Introduction 1

2 Experimental Methods 3
   2.1 Photoluminescence Spectroscopy 3
      2.1.1 Excitation and Recombination 3
      2.1.2 PL Spectrum of Si:Au+Pt 5
   2.2 Experimental Details 9
      2.2.1 Experimental Set-up 9
      2.2.2 Bandpass and Response Function of the Spectrometer 10
   2.3 Sample Preparation 11
      2.3.1 Investigated Si Material 11
      2.3.2 Implantation 12
      2.3.3 Annealing Procedure 13

3 Experimental Results 15
   3.1 Si:Au and Si:Pt - Implantations with Stable Isotopes 15
      3.1.1 Evidence for Au-Related PL Signals in Si
            Dependence of the Signals on the Implantation Dose 15
      3.1.2 Evidence for Pt-Related PL Signals in Si
            Dependence of the Signals on the Implantation Dose 18
      3.1.3 Conclusion 20
   3.2 Optimisation of the PL Signals 21
      3.2.1 Anneal Procedure 21
      3.2.2 Excitation Density 23
      3.2.3 Measurement Temperature 24
   3.3 Si:Hg - Implantations with Radioactive Isotopes 26
      3.3.1 Choice of Isotopes 26
      3.3.2 PL Measurements of Si:^{193}Hg 28
      3.3.3 Comparison with Reference Sample Si:Au (stable) 36
      3.3.4 Comparison with DLTS Measurements 38
      3.3.5 PL Measurements of Si:^{191}Hg 39
   3.4 Quantitative Approach to the Interpretation of PL Intensities 40
   3.5 Miscellaneous Results 44
      3.5.1 Si(Freiberg, n-type, 125 Ωcm):Au+Li 44
      3.5.2 Si(SEH, n-type, 1-10 Ωcm):Pt+Fe 45

4 Conclusions and Outlook 47
### List of Figures

2.1 Excitation and recombination Processes in Si. For details see text ........ 4
2.2 Typical lengths in Si .................................................. 5
2.3 PL spectrum of Si containing Au and Pt impurities ...................... 6
2.4 Configuration diagram illustrating the origin of a typical PL band due to transition metal impurities. For details refer to text .................. 8
2.5 Standard PL set-up .................................................... 9
2.6 Spectrometer response for a black-body spectrum ...................... 11
3.1 PL spectra of Si:Au .................................................. 17
3.2 PL spectra of Si:Pt .................................................. 19
3.3 PL signals of the 735-meV and the 777-meV centres as a function of anneal temperature .................................................. 22
3.4 Different PL intensities as a function of laser power .................. 23
3.5 “AuFe” centre at 1687 nm (735 meV) at different measurement temperatures 25
3.6 “Pt3” centre at 1594 nm (777 meV) .................................. 25
3.7 Decay scheme of $^{193}$Hg ........................................... 27
3.8 Population of the isotopes occurring in the decay of $^{193}$Hg .......... 27
3.9 PL spectra of Si(SEH):$^{193}$Hg at different times after implantation ... 28
3.10 Si(SEH):$^{193}$Hg, PL intensities as a function of time after implantation 30
3.11 PL spectra of Si(Freiberg, p-type, 10 Ωcm):$^{193}$Hg at different times after implantation .............................................. 31
3.12 Si(Freiberg, p-type):$^{193}$Hg, PL intensities as a function of time after implantation .............................................. 33
3.13 PL spectra of Si(Freiberg, n-type):$^{193}$Hg at different times after implantation .............................................. 34
3.14 Si(Freiberg, n-type):$^{193}$Hg, PL intensities as a function of time after implantation .............................................. 35
3.15 Normalised PL intensities as a function of time for both stable and radioactive impurities .............................................. 37
3.16 Typical DLTS spectra for Si(Freiberg, n-type):$^{193}$Hg .............. 39
3.17 Illustration of the two-layer model after Magerle ....................... 41
3.18 Si(Freiberg, n-type) spectra after Au implantation and Li diffusion .. 44
3.19 Si(SEH, n-type, 125 Ωcm) spectra after Pt+Fe implantation and Fe diffusion 46
List of Tables

2.1 PL bands between 1050 and 1800 nm appearing in Si: Au+Pt ............. 7
2.2 Si materials used for PL experiments. ........................................ 12
2.3 Projected range and standard deviations for different implantations in Si. 13

3.1 Compilation of the fitted lifetimes in hours of PL features in different
Si: $^{193}$Hg samples ................................................................. 36
Chapter 1

Introduction

Exactly 50 years ago, Bardeen, Brattain and Shockley invented the transistor. As it is known today, this discovery marks the beginning of the information age. Whereas the first experiments were performed on Ge crystals, this material was soon replaced by Si providing faster performance and cheaper availability. This invention led to an enormous development in solid state physics, in particular semiconductor physics. These days, a number of compound semiconductors play a major role in device fabrication. However, the elementary semiconductor Si is still the most used material in device fabrication.

Transition metal impurities in Si introduce deep levels in the band-gap, at least 0.1 eV from the nearest band edge, which provide effective recombination centres [Mil73]. On one hand, this can be exploited to control carrier lifetimes in device technology, e.g. to reduce switching times for transistors. On the other hand, unintentional contamination with these impurities can give rise to unwanted reduction of carrier lifetimes and its corresponding parameter, the diffusion length. For photovoltaic devices, for example, long diffusion lengths are essential for the extraction of free carriers and thus for good efficiency [Sze81]. Furthermore, as devices get smaller and the level of integration increases, requirements on chemical purity of materials become more stringent. Therefore, a fundamental understanding of the impurity metal properties is essential, not only from the point of view of basic research.

Whereas the case of isolated substitutional Au impurities in Si is well established [Mil73], this is not the case for Pt. Moreover, many centres exist whose nature is not yet understood, both for Au and Pt impurities. Techniques such as Photoluminescence (PL) Spectroscopy, Deep Level Transient Spectroscopy (DLTS) and Electronic Paramagnetic Resonance (EPR) have been widely exploited to investigate the properties of such centres [Pan86].

The experiments presented in this work were focused on the luminescent properties of Au and Pt in Si. This project has been part of a collaboration with other groups, comprising the techniques quoted above. The main attention has been given to the similarities between the neighbouring elements Au and Pt. Their availability as radioactive isotopes at the online separator ISOLDE at CERN, Geneva [Rav89], has been exploited in order to measure the changes in DLTS signals due to the chemical transformation Au → Pt [Pet90].

The use of radioactive isotopes in nuclear hyperfine interactions techniques such as Mössbauer spectroscopy or Perturbed Angular Correlation (PAC) spectroscopy is well established [Sch95]. However, the application of radioactive isotopes is not restricted to such techniques. Any technique requiring some element-specific fingerprint can make use of the
Introduction

half-life of radioactive isotopes. Hitherto, only a few examples for this application exist in semiconductor defect identification. Petersen et al. [Pet90] performed the first DLTS experiment using radioactive isotopes. They implanted Si with radioactive Hg decaying via Au and Pt to Ir. A recent example for DLTS using radioactive isotopes focuses on Ti, V, Cr and Co in Si [Ach96]. In the case of PL, some results have been reported. The first successful performance of PL using radioactive isotopes was done by Broser et al. [Bro65] over 30 years ago. In their experiment, ZnS was homogeneously doped with radioactive $^{65}$Zn by neutron irradiation. PL spectroscopy using direct implantation of radioactive isotopes was first done independently by two groups. Firstly, Daly et al. [Dal94] implanted the radioactive isotope $^{111}$In into Si and recorded PL spectra thereafter, PL bands related to the decay $^{111}$In $\rightarrow$ $^{111}$Cd. Secondly, Magerle et al. [Mag95b] used the same isotope, applying ion implantation, to investigate the corresponding PL features in GaAs. In a further experiment, the same group produced Ga$_{As}$ antisites in GaAs by implanting $^{71}$As in GaAs [Mag97]. The transmutation via the decay chain $^{71}$As$_{As}$ $\rightarrow$ $^{71}$Ge$_{As}$ $\rightarrow$ $^{71}$Ga$_{As}$ was observed with PL spectroscopy. Preliminary experiments using implantation of radioactive Au and Pt into Si were undertaken by Henry et al. [Hen96].

The first objective of this work was to confirm provisional PL results for Au and Pt in Si [Hen96, Alv97a]. This was to be performed using both stable and radioactive isotopes. The use of stable isotopes was designed to establish optimum conditions for the experiments using radioactive isotopes. Furthermore, the results for the radioactive isotopes in PL experiments were to be analysed in a more quantitative way. Additionally, a bigger variety of Si materials was to be investigated. Finally, it was considered desirable to establish a connection to other techniques in conjunction with other groups.

In this report, the experimental methods are described first. Then, the results are presented, comprising PL experiments on Si implanted with stable Au and Pt isotopes, the optimisation of experimental conditions and finally the results for the PL experiments making use of radioactive isotopes. A brief cross-reference to corresponding DLTS-results is made and a way of approaching the obtained results quantitatively is illustrated. Last, conclusions are drawn and possible future experiments are mentioned.
Chapter 2

Experimental Methods

2.1 Photoluminescence Spectroscopy

Photoluminescence spectroscopy (PL) has become a standard method for the characterisation of semiconductors properties. It combines the advantages of an optical method, namely being non-destructive and not requiring electrical contacts, with very high sensitivity. PL can be used to determine energy levels and concentrations of impurities and defects in semiconductors [Lig90, Col87, Taj78]. Particularly in the case of indirect band-gap semiconductors such as silicon, PL reveals information on vibrational properties, too. PL is usually combined with Zeeman or piezospectroscopic measurements in order to obtain information on the defect symmetry [Dav88, Dav88, Lig90].

A brief introduction to PL spectroscopy can be found in [Sch90] and [Lig90], a more detailed treatise in [Per93]. A theoretical approach is illustrated in [Beb72]. The properties of deep luminescent centres in silicon were reviewed by Davies [Dav89].

2.1.1 Excitation and Recombination

When photons with an energy $h \nu > E_g$ interact with a semiconductor surface, they can undergo different processes. They can be transmitted, reflected, scattered or absorbed. The case of absorption results in the formation of electron-hole-pairs. This process is shown schematically on the very left of figure 2.1.

The free electrons and holes then diffuse in the crystal and relax to states at the band edge of the conduction band before they recombine, either directly or after exciton formation. Typical diffusion lengths at low temperatures lie in the order of several hundred $\mu$m in high purity Si [Sar88]. A number of possibilities of radiative processes exist, all of which result in the emission of a photon of the corresponding energy:

- **Direct band-to-band recombination:** This process is only observed at room temperature [Sch90]. As PL spectroscopy has mainly been performed at very low temperatures in this work, this process is not shown in the figure.

- **Free exciton formation and recombination (FE):** A free exciton is a hydrogen-like system of an electron bound to a hole [Dea79]. The energy of the emitted photon is

$$h \nu = E_g - E_x$$  \hspace{1cm} (2.1)
Figure 2.1: Excitation and recombination Processes in Si. For details see text.

where $E_g$ is the bandgap energy of the semiconductor and $E_x$ the Coulomb energy of the exciton.

- **Bound exciton formation and annihilation (BE):** One speaks of a bound exciton (BE) when a defect binds at least one hole or electron. For instance, bound exciton formation occurs when a free exciton is captured by a defect. A bound exciton may also be formed by the sequential trapping of two particles. As the binding energy is lowered by this trapping process, a photon being emitted following a bound exciton annihilation has the energy

$$h\nu = E_g - E_x - E_b$$

(2.2)

where $E_b$ is the binding energy of the exciton to the defect. Apart from binding one exciton, a defect can bind several excitons leading to a more cumbersome system of states, called bound multi-exciton [Lig90].

- **Transitions between excited bound-exciton states (BE(PD)):** The pseudodonor (PD) model [Mon87] describes an isoelectronic bound exciton. The starting point is a neutral ground state binding a positive hole tightly with typical binding energies of a few hundred meV. The resulting positively-charged centre then binds an electron with binding energies of at most 0.1 eV. This feature is very common for deep isoelectronic bound excitons in silicon [Sin95] and will be discussed later on. Similarly, pseudoacceptors can be formed [Wag82]. Such complexes can be quantum-mechanically treated in a similar way as an atom. Hence, electronic transitions between the different energy states can take place, resulting in photon emission or non-radiative processes, e.g. the Auger effect.

As a result of Si being a semiconductor with an indirect bandgap the transitions mentioned above are often accompanied by phonon emission or absorption. In fact, these processes are predominant for all transitions except internal de-excitations between bound-exciton
states. The production or absorption of phonons results in an alteration of the photon energy which can be observed in PL spectra as so-called phonon replica [Dav89].

Apart from radiative recombination, non-radiative recombination plays an important role. These processes are mainly due to surface states and crystal imperfections including implantation damage, but also the Auger effect is of some importance [Dea79].

In order to get a feeling for the region of a semiconductor one investigates with PL spectroscopy, typical lengths are shown in figure 2.2. Because of the weak absorption coefficient $\alpha$ of Si even for photons with energies above the band gap, the optical absorption length $1/\alpha$ is very large. For the 514.5 nm line of an Ar ion laser, for example, the absorption length amounts to 1 $\mu$m [Dav89]. This is very large compared to typical values for direct bandgap semiconductors like GaAs where photons of such energies only reach depths up to 100 nm [EMI90]. Additionally, the free carriers produced by illumination can diffuse hundreds of microns [Sar88] so that relevant recombination can take place well below the surface. As the energies of luminescence photons lie below the bandgap energy, the absorption coefficient drops by several orders of magnitude with respect to the corresponding value of the incident laser light [Jel82]. However, as there are electronic states present in the band gap, self-absorption of the luminescence photons may occur, thus reducing the mean free path of such photons. Nevertheless, luminescence may originate from regions well below the surface and PL is not a pure near-surface technique in the case of silicon. Figure 2.2 shows a typical implantation profile, too. It is obvious that the laser light reaches the implanted regions so that features due to implanted impurities should occur in the PL spectra.

2.1.2 PL Spectrum of Si: Au+Pt

In order to get familiar with the PL features this work has been focused on, a typical PL spectrum of Si is plotted in figure 2.3.

This spectrum shows both impurities mentioned in the literature (marked with \("\star\") and
Figure 2.3: PL spectrum of Si at $T_m = 20$ K containing Au ($\approx 6 \times 10^{11}$ cm$^{-2}$) and Pt ($\approx 4 \times 10^{11}$ cm$^{-2}$) impurities produced by implantation of radioactive $^{193}$Hg ions ($\approx 10^{12}$ cm$^{-2}$ at 60 keV). The sample was annealed at $T_a = 1323$ K. The PL lines reported in the literature are marked with "*". Refer to the text for further details.
2.1 Photoluminescence Spectroscopy

<table>
<thead>
<tr>
<th>label</th>
<th>wavelength (nm)</th>
<th>energy (meV)</th>
<th>temperature (K)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>FE(TA)</td>
<td>1090</td>
<td>1136</td>
<td>2 - 26</td>
<td>[Vou77, Dea67]</td>
</tr>
<tr>
<td>FE(TO)</td>
<td>1129</td>
<td>1097</td>
<td>2 - 26</td>
<td>[Vou77, Dea67]</td>
</tr>
<tr>
<td>BE(P)</td>
<td>1135</td>
<td>1092</td>
<td>2 - 19</td>
<td>[Lig77]</td>
</tr>
<tr>
<td>FeB</td>
<td>1161</td>
<td>1066</td>
<td>4.2 - 70</td>
<td>[Moh84]</td>
</tr>
<tr>
<td>Pt1</td>
<td>1207</td>
<td>1027</td>
<td>7.6 - 40</td>
<td>[Alv97a]</td>
</tr>
<tr>
<td>Pt2</td>
<td>1402</td>
<td>884</td>
<td>7.6 - 35</td>
<td>[Alv97a]</td>
</tr>
<tr>
<td>Au1</td>
<td>1583</td>
<td>782</td>
<td>2 - 15</td>
<td>[Car89]</td>
</tr>
<tr>
<td>Pt3</td>
<td>1594</td>
<td>777</td>
<td>7.6 - 25.3</td>
<td>[Alv97a]</td>
</tr>
<tr>
<td>AuFe</td>
<td>1687</td>
<td>735</td>
<td>4 - 40</td>
<td>[Cal88, Hen96]</td>
</tr>
</tbody>
</table>

Table 2.1: PL bands between 1050 and 1800 nm appearing in Si:Au+Pt

PL bands having been observed in this work or by other groups being involved in this collaboration [Alv97a]. The thick line at 1158 nm (1170 meV) labelled \( E_g \) represents the lower edge of the conduction band below 20 K. The band labelled “AuFe” has been assigned to Fe but not to Au in the literature. However, there exist several reasons why it could be Au related, too. The corresponding results will be discussed in further detail below.

The near-band-gap luminescence features to the left of the spectrum in figure 2.3 are the phonon replica of the free exciton. The sharp line - BE(P) - close to the broad free exciton peak - FE(TO) - is assumed to stem from the recombination of an exciton bound to a P donor, accompanied by the emission of a transverse optical (TO) lattice phonon [Lig77]. The sharp lines marked with arrows in figure 2.3 are the principal no-phonon lines (NPL), sometimes consisting of two or more closely located peaks. On the low-energy side of the NPL, a number of broader peaks, the phonon replica, are present. This is a typical property of PL bands related to transition metal impurities [Con87] and can be explained with the help of a configuration diagram [Fit68] like in figure 2.4. All the prominent features in the experimentally accessible energy range are listed in table 2.1. The measurement temperatures in the table are the values quoted in the references. This does not necessarily mean that the corresponding PL bands can not be observed at higher temperatures.

In figure 2.4 the potential marked with \( V_g \) describes the ground state of an impurity in the host lattice. \( Q \) is the displacement parameter. When the electronic system at a defect is put into an excited state, the Coulomb forces are changed and the result is a new equilibrium displacement parameter \( Q_0 \). In general, the corresponding potential of the excited state, \( V_e \) differs from the ground state. In this simple picture, only one vibrational mode is considered, for example a localised phonon [Kle68], thus the eigenstates are equal to those of a harmonic oscillator. The corresponding quantum numbers are \( n \) and \( m \), respectively. When an electronic transition between the excited state and the ground state takes place, this can be a process not involving any phonon annihilation or creation. This case is illustrated by an arrow in the diagram, connecting two states for which \( n = m \). If there are phonons involved in the transition, i.e. \( n \neq m \), the energy of the emitted photon is increased or decreased by the phonon energy, resulting in a number of broadened peaks on the low energy side of the NPL in the case of phonon generation at low temperatures.
At higher temperatures, the phonon replica appear on the high energy side of the NPL, too, due to phonon absorption.

This sideband system of a PL line reflects the *vibronic* properties of the corresponding centre, i.e. the relation between the electronic and the vibrational states. At low temperatures \((kT \ll \hbar \omega)\), only the \(m = 0\) vibrational state of the excited state is occupied, hence only transitions from this state to all the vibrational levels of the ground state \((n = 0, 1, 2, \ldots)\) can occur. The relative intensity \(I_{0n}\) of the sideband due to the \(n^{th}\) localised mode with respect to the intensity of the NPL, \(I_{00}\) can be expressed in terms of the *Huang-Rhys-Parameter* \(S\) being a measure for the coupling strength between the electronic and the vibronic states \([Fit68]\).

\[
\frac{I_{0n}}{I_{00}} = \frac{S^n}{n!} \tag{2.3}
\]

In general, there are additional normal modes present, either localised phonons or crystal lattice phonons. Then, the considerations made above can be adopted for each mode separately and the total coupling strength \(S\) is the sum of the individual coupling strengths \(S_i\); \(S = \sum_i S_i\). This holds only for discrete states; in the case of continuous modes like the lattice modes, the sum becomes an integral.

Typical Huang-Rhys factors for transition metal impurity PL bands in Si range from 1 to 5, whereas typical local-mode phonon energies are 5 to 10 meV \([Con87]\). If the energy of the local-mode phonon lies within the range of the corresponding values for lattice phonons, it is referred to as an *in-band phonon.* If its energy lies within the energy gap for crystal lattice phonons, one speaks of a *gap phonon,* if the energy is greater than the biggest lattice phonon energy, one speaks of a *local-mode phonon* \([Sri90]\).
2.2 Experimental Details

2.2.1 Experimental Set-up

In this work a conventional PL set-up [Sch90] has been used. The set-up and its components are thoroughly described in [Mag95a]. The schematic figure 2.5 shows the experiment.

The sample can be mounted in two different cryostats. First a CryoVac liquid He-flow cryostat allowing temperatures as low as 4 K was available. In order to avoid any adsorption or condensation on the sample surface, the chamber is flushed with He gas before the cooling process. He gas at a partial pressure of 200 mbar (at room temperature) is used to provide sufficient heat contact between the sample and the flowing liquid He. The sample holder is equipped with a heating facility to provide higher measurements temperatures.

A second possibility of mounting the sample consists in using a CTI Cryogenics closed cycle cryostat. The lowest temperature possible with this cryostat is approximately 11 K. However, the effective cooling power for the sample is not as high as in the case of the He-flow cryostat. This is due to the character of the heat contact of the sample, not using He contact gas but a low temperature varnish with which the sample is glued onto the Cu coldfinger of the closed cycle cryostat. At typical excitation powers of the Ar ion laser PL spectra can still be clearly detected, even though the temperature rises slightly. In order to estimate the temperature of the sample, the thermalisation of the double peak of the Fe-related PL band at 735 meV was used [Cal88]. The temperature of the coldfinger itself can be controlled by an external control unit including a heating facility.

Luminescence is excited by an Ar ion laser at a wavelength of 514.5 nm (2.5 eV).

Figure 2.5: Standard PL set-up. For details refer to text.
The output power was typically 100 mW. In order to make illumination of a bigger area possible, lens L1 slightly defocuses the laser beam so that the laser spot covers a bigger area on the sample, which is estimated to be around 0.01 cm$^2$. Hence the typical excitation power density is approximately 10 W cm$^{-2}$. This power density can be varied either by the power control of the laser power supply or by introducing neutral density filters into the laser beam. The actual power of the laser can be measured by a photodiode being placed right before the cryostat chamber containing the sample.

In order to control the position of the laser spot on the sample, a projection set-up has been used. This set-up is not shown in the sketch, but it is described in [Mag95a].

The emitted luminescence light is bundled onto the entrance slit of the monochromator by lens L2. The focal length of the monochromator was 750 mm and a grating with 600 lines per millimeter was used. Note that the optical path of the light within the monochromator is only shown schematically. The light was then detected using a North Coast high resistivity Ge diode, cooled to 77 K with liquid nitrogen. The outgoing signal was fed into a lock-in amplifier using the reference frequency of the chopper which chops the laser light with a frequency of approximately 30 Hz. The spectra were recorded using a conventional PC equipped with an I/O card controlled with the aid of the instrumentation package LabView$^\text{TM}$. In order to reduce the number of spikes due to cosmic rays in the spectra, a removal algorithm [Dun87] was implemented in the software.

### 2.2.2 Bandpass and Response Function of the Spectrometer

The Spex monochromator uses the standard Cerny-Turner-configuration [Jam69] fitted with a dispersive grating. For a focal length of 750 mm and the given grating of 600 lines/mm, the linear dispersion $d_l$ is 2.1 nm/mm. In the case of a big slitwidth, the bandpass $BP$ is mainly determined by the slitwidth $\Delta_s$ and can be calculated as [Jam69]

$$BP = \Delta_s \times d_l.$$  

Due to the weak luminescence signal of silicon, the slitwidth was chosen to be 600 $\mu$m in order to provide sufficient transmission. Thus the bandpass was 1.28 nm. Higher resolution was not used as it has been found to make the recording of PL spectra time-consuming. This is clearly not desirable, particularly during experiments using radioactive isotopes.

The response of the light detecting system is not constant for all wavelengths. This effect is due to both the detection efficiency of the Ge-diode for photons of different energies and the non-constant response of the monochromator to different wavelengths. The response function can be investigated experimentally. In order to do so, a halogen lamp (Xenophot HLX, 12 V, 50 W) was positioned in front of the entrance slit of the monochromator. Using these parameters, the lamp temperature accounts to 3100 K [For45].

The spectrum is shown in figure 2.6 along with a black-body spectrum at a lamp temperature of 3100 K [Sto97]. The spectrum was then divided by the black-body spectrum yielding the corresponding efficiency, plotted in the lower part of figure 2.6. However, in this work no quantitative cross-reference to PL spectra recorded with different set-ups were made. Thus, all spectra in this report have not been corrected with the response function.
Figure 2.6: Spectrometer response for a black-body spectrum. Top: Black-body spectrum and corresponding detector signal in the wavelength window used. Bottom: Resulting spectrometer efficiency for a 600 lines/mm grating.

2.3 Sample Preparation

2.3.1 Investigated Si Material

In this work, different Si wafers were tested using implantation with stable Au and Pt isotopes. As one of the objectives of this work was to establish a connection between PL spectroscopy and DLTS, experimental conditions suitable for both techniques had to be developed. Thus, as the different techniques require different background doping of the Si material, the wafers listed in table 2.2 were used for tests.

All crystals have been grown by a Czochralski (CZ) process. Apart from the Freiberg p-type material, the crystals have been subsequently cleaned using the float zone technique [Sze81]. The values in table 2.2 are either quoted by the manufacturer or measured by J. Bollman, Humboldt University Berlin [Bol97]. The corresponding parameters are taken from tabulated data [EMI88].
### Table 2.2: Si materials used for PL experiments.

<table>
<thead>
<tr>
<th>dopant, concentration (cm(^{-3}))</th>
<th>type</th>
<th>resistivity (Ωcm) at RT</th>
<th>manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>P, 4x10(^{14})</td>
<td>n-type</td>
<td>1-10</td>
<td>Shin-Etsu</td>
</tr>
<tr>
<td>P, 1.5x10(^{13})</td>
<td>n-type</td>
<td>125</td>
<td>ex-GDR Si-manuf., Freiberg</td>
</tr>
<tr>
<td>B, 10(^{15})</td>
<td>p-type</td>
<td>10</td>
<td>ex-GDR Si-manuf., Freiberg</td>
</tr>
<tr>
<td>P, 10(^{15})</td>
<td>n-type</td>
<td>0.1-1</td>
<td>ex-GDR Si-manuf., Freiberg</td>
</tr>
</tbody>
</table>

#### 2.3.2 Implantation

In order to introduce impurities into the crystal, transition metal ions were implanted into the Si samples. Hitherto, most of the PL spectra reported in the literature have been produced by high-temperature diffusion rather than implantation. Obviously, implantation requires more sophisticated facilities. However, it has some advantages over diffusion, the most important of which is the fact that it is a mass-separated process and thus provides higher purity doping. For diffusion, the purity of the metal used is essential as the different vapour pressures and diffusion coefficients of the contaminants can lead to significant unwanted contamination [Sze81]. For ion implantation, the vapour pressures of contaminants are a problem, too, but this is minimised by mass selection. One further strength of ion implantation is the fact that by using current integrators the implantation dose can be determined with high accuracy.

The implantations have taken place at different facilities. Stable isotopes have been implanted at the University of Bonn, the Humboldt University Berlin and the University of Lisbon. The radioactive isotopes have been implanted at the on-line separator ISOLDE, CERN, Geneva [Rav89].

One objective of the implantations with stable isotopes was to establish a relation between implantation dose and PL intensity. However, the main purpose was the optimisation of the PL signals in order to obtain strong signals in the samples implanted with radioactive isotopes. Hence, most of the implantations with stable isotopes were carried out at 60 keV, which is the standard implantation energy at ISOLDE. Typical implantation doses were ranging from 10\(^{11}\) to 10\(^{14}\) ions per cm\(^2\). The implantation profile has been assumed to be Gaussian [Mul86], so that the maximum impurity concentrations have reached values between approximately 10\(^{17}\) and 10\(^{19}\) cm\(^{-3}\). The projected range \(R_p\) and the standard deviation \(\Delta R_p\) have been computed using the program TRIM [Bie80], based on Monte-Carlo simulations. The calculated values for the different isotopes are shown in table 2.3.

The Fe implantation at 90 keV was done in addition to the Pt implantation at 200 keV. As one can see from the table, the corresponding implantation profiles show a strong overlap. The Fe dose was varied in order to study its influence on the Pt-related PL lines. However, as the diffusion coefficient of Fe exceeds the corresponding value of Pt by some orders of magnitude at annealing temperatures above 1200 K [EMI88], no effect has been observed.
Table 2.3: Projected range and standard deviations for different implantations in Si.

<table>
<thead>
<tr>
<th>element</th>
<th>impl. energy</th>
<th>$R_p$</th>
<th>$\Delta R_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au, Pt, Hg</td>
<td>60 keV</td>
<td>33.5 nm</td>
<td>7.3 nm</td>
</tr>
<tr>
<td>Pt</td>
<td>200 keV</td>
<td>75.0 nm</td>
<td>17.5 nm</td>
</tr>
<tr>
<td>Fe</td>
<td>90 keV</td>
<td>77.0 nm</td>
<td>28.5 nm</td>
</tr>
</tbody>
</table>

It has been concluded that most of the Fe atoms leave the Pt implanted layer during the high-temperature anneal.

### 2.3.3 Annealing Procedure

In order to remove implantation damage and produce the defects leading to prominent PL bands, the implanted samples were annealed at temperatures between 1123 and 1373 K. Before this procedure, the samples were cleaved into small pieces, the typical size being $3 \times 3 \text{ mm}^2$. Before the high-temperature anneal, the pieces were submerged in HF in order to remove both the SiO$_2$ layer and any possible metal contamination due to sample handling [EMI88]. The samples were then sealed in quartz ampoules containing He gas at a pressure of 0.5 bar at room temperature. The ampoules were heated in a furnace for typically 10 minutes and rapidly submerged in water at room temperature. At high anneal temperatures, standard contaminants such as Cu, Fe or Li can be readily introduced into the crystal due to their high diffusion coefficients [EMI88]. Thus, their involvement in all observed PL signals could not be fully prevented. In fact, many of the recorded spectra reveal the well-investigated PL band at 1014 meV due to an exciton bound to a Cu pair [Web82].

There exist a number of alternative ways of annealing, one of which is the so-called Rapid Thermal Anneal (RTA). In this method, the samples are heated by several halogen lamps for a few seconds. This procedure prevents significant out-diffusion of implanted impurities. However, preliminary experiments, kindly undertaken by M. Fanciulli at Aarhus, have revealed that RTA can lead to enormous dislocations in the crystal. Furthermore, in some cases the complexes involving transition metal atoms have not been formed. Nevertheless, a thorough study of RTA is highly desirable as it might lead to enhanced s/n ratios.

Apart from removing implantation damage, the high temperature anneal is intended to enable the formation of the complexes leading to PL spectra. In order to prevent the metal impurities from forming precipitates, which is very likely at concentrations close to the solid solubility, a rapid quench as described above is necessary.
Chapter 3

Experimental Results

As the main objective of this work was the identification of the PL lines due to transition metal impurities, it was intended to use the samples implanted with stable Au and Pt isotopes in order to optimise the corresponding PL signals. The radioactive implants would then provide an isotope-specific fingerprint, namely the characteristic half-lives with which the PL signals should disappear or appear, respectively. However, the stable isotopes provide information on the origin of particular PL lines and give evidence for the elements involved, too.

In the first part of this chapter, PL results for Si implanted with stable Au and Pt isotopes are presented. The influence of experimental parameters such as implantation dose, anneal temperature, anneal time, measurement temperature and laser power are discussed in the second part. The implantation with radioactive Hg, decaying to Au, Pt and Ir is qualitatively discussed in the third part of this chapter. A brief possibility of a quantitative explanation is developed. Last, miscellaneous results are presented. They include experiments giving rise to possible future directions of research.

Almost all the PL bands described hereafter show the typical behaviour of bound-exciton luminescence interpreted in terms of the pseudodonor model briefly described in section 2.1. The wavelengths and energies of the peaks given are the values for the principal no-phonon lines of the PL band.

3.1 Si:Au and Si:Pt - Implantations with Stable Isotopes

3.1.1 Evidence for Au-Related PL Signals in Si

Dependence of the Signals on the Implantation Dose

A simple method for providing evidence for the identification of a PL band is the intensity variation with implantation dose of the corresponding element. In this case, different Au doses were implanted into n-type Si (resistivity at room temperature 125 Ωcm). These implantations were kindly carried out by J. Bollmann, Humboldt-Universität zu Berlin. All samples were annealed at 1173 K for 10 minutes at standard conditions. The PL spectra are shown in the upper part of figure 3.1. Furthermore, the Shin-Etsu wafers (SEH, n-type, 1-10 Ωcm) were implanted with stable Au both in Berlin by J. Bollmann and in Bonn by K. Freitag. Again, the anneal temperature was 1173 K and the anneal time 10 minutes.
The spectra can be seen in the bottom half of figure 3.1. For clarity a logarithmic scale is used and all spectra have been shifted by the same distance against each other. Note that the strength of the PL band labelled “AuFe” does not depend linearly on the implantation dose.

The bottom spectrum in the top half of figure 3.1 shows the features of unimplanted Si (Freiberg, n-type, 125 Ωcm). The broad peak centred at 1129 nm (1097 meV) is the TO replica of the free exciton peak. The corresponding TA replica can be seen as a smaller peak centered at 1090 nm (1136 meV). The rest of the spectrum is very flat being a characteristic of high purity material. The peak at 1538 nm (807 meV) labelled “D1” in the spectra above has been identified as the D1 line [Sau85] due to a dislocation in the crystal.

The three remaining spectra in the top half show the effect of increasing implantation dose. The PL band at 1687 nm (735 meV), labelled “AuFe” grows sub-linearly with increasing Au dose. Even though an involvement of Au in this PL band has been considered unlikely [Sin95, Cal88], these results and earlier radioactive PL studies [Hen96] give rise to the conclusion that this feature is related to a defect containing Au. It is important to note that this does not contradict the interpretation that this complex contains an interstitial Fe atom [Sin95].

A second PL feature has been consistently observed in these spectra. The identification of the system of peaks labelled “Au1” has been reported by do Carmo et al. [Car89] and has been related to Au impurities. These lines are interpreted to be caused by internal radiative transitions at the defect. However, as the PL spectra in figure 3.1 are dominated by the luminescence due to the “AuFe” defect at 1687 nm (735 meV), the “Au1” system appears weak.

Another PL feature widely attributed to an FeB-complex appears at 1161 nm (1066 meV). This system has been interpreted to stem from excitons bound to an iso-electronic trap associated with boron and iron [Moh84], but not being due to a Fe,Bs (interstitial iron atom, substitutional boron atom) pair [Klu88]. The latter authors already suggested the involvement of additional impurities. It is noteworthy that this feature grows with increasing Au implantation dose, up to $10^{12}$ cm$^{-2}$. This has led to the suspicion that Au might be involved in this complex, too. This suspicion will become even stronger when the results for the implantations with radioactive isotopes are presented.

The two peaks marked with a question mark have not yet been identified.

In the bottom half of figure 3.1, spectra from samples prepared from Si(SEH, n-type, 1-10 Ωcm) are shown. In addition to the PL features having occurred in Si(Freiberg, n-type, 125 Ωcm) implanted with Au, these samples produce near-bandgap luminescence due to phosphorus donors. The sharp no-phonon line at 1077 nm (1150 meV) has been associated with a P bound-exciton [The77], its TO phonon replica is located at 1136 nm (1092 meV) [Lig77].

One important fact regarding the identification of Au-related PL bands is that they occur in different Si materials and are not related to impurities already present in a certain material. Furthermore, their incorporation has been shown to be independent of the laboratory where the implantations have taken place.
Figure 3.1: PL spectra of Si implanted with Au, measured at 7.5 K. All samples were annealed at 1173 K for 10 minutes. Top: PL spectra of Si(Freiberg, n-type, 125 Ωcm):Au, various implantation doses. Bottom: PL spectra of Si(SEH):Au, various laboratories. For clarity a logarithmic scale is used and all spectra have been shifted by the same distance against each other.
3.1.2 Evidence for Pt-Related PL Signals in Si

Dependence of the Signals on the Implantation Dose

The same procedure as in the case of Si:Au was undertaken for Si:Pt, using stable Pt isotopes. The implantations with varying doses appearing in the top half of figure 3.2 were performed by E. Alves (Lisbon). The Si material was manufactured by Shin-Etsu (SEH, n-type, 1-10 Ωcm). All samples were annealed at 1173 K for 10 minutes under standard conditions. The near-bandgap luminescence is essentially the same as in the case of Si(SEH):Au, described in the previous section. The broad band on the low-energy side of the BE(P) peak, arising in the spectrum of the unimplanted SEH wafer (fourth from the top) is an electron-hole-droplet caused by strong excitation density [Lig90].

The bottom half of figure 3.2 illustrates the results of Pt implantation into a different Si material (Freiberg n-type, 0.1-1 Ωcm) carried out by J. Bollmann (Berlin). Again, the samples were annealed under standard conditions at 1173 K for 10 minutes. In this case, the measurement temperature was 20 K. In this figure, a logarithmic scale is used and all spectra have been shifted by the same distance against each other.

The most striking feature in the spectra of the top half of figure 3.2 is the growing intensity of the PL system at 1594 nm (777 meV), labelled “Pt3”, with increasing Pt implantation dose. Note that this centre is different from the 780-meV centre observed in Si:Ag by several authors [Son94, Iqb94]. The PL band at 1402 nm (884 meV), which has been related to Pt, too [Alv97a], reveals similar behaviour. The third Pt-related spectrum having been reported in [Alv97a] does not occur. However, this feature has been found to be very sensitive to background doping and anneal temperature [Hen97].

The group of four lines having the NPL at 1221 nm (1014 meV) is the well-investigated Cu-spectrum [Web82] due to unintentionally incorporated isoelectronic Cu pairs binding an exciton. A similar system appearing at 1312 nm (943 meV) in this spectrum has been observed after Cu diffusion [McGui89].

An interesting feature appearing in the spectrum of unimplanted Si(Freiberg, n-type, 0.1-1 Ωcm) in the bottom half of figure 3.2 is the FeB band at 1161 nm (1066 meV) [Sau85]. This seems to indicate that there is already an amount of impurities present in this particular wafer before implantation, giving rise to this centre.

In the implanted Si (Freiberg, n-type, 0.1-1 Ωcm), the well-known Pt related PL bands appear, yet not as strong as in the SEH wafer. In this case, even the “Pt1” band at 1207 nm (1027 meV) is present. As mentioned before, the presence and intensity of this band strongly depend on the background doping and annealing procedures and has not yet been thoroughly investigated.

In this sample, again, Cu contamination can be observed with the aid of the two groups of peaks at 1221 nm (1014 meV) and 1312 nm (943 meV) [Web82, McGui89].
Figure 3.2: PL spectra of Si implanted with Pt. All samples were annealed at 1173 K for 10 minutes. Top: PL spectra of Si:Pt(SEH) at $T_m = 7.5$ K implanted at Lisbon with various implantation doses. Bottom: PL spectra of Si(Freiberg, n-type, 0-1 $\Omega$cm):Pt implanted at Berlin and measured at 20 K. For clarity a logarithmic scale is used and all spectra have been shifted by the same distance against each other.
3.1.3 Conclusion

So far, the presented results have given strong evidence for the correctness of the assumed involvement of Au in the PL feature at 1687 nm (735 meV), which had been assigned to Fe, but not to Au. At 1583 nm (782 meV), a band so far observed after Au diffusion has been produced by implantation of stable Au, too. The centre assigned to a FeB pair at 1161 nm (1066 meV) appears to contain Au.

In the case of Pt, all the features reported in [Alv97a] have been observed after implantation of stable Pt.

Contamination with Cu, and possibly with Fe, occurs in some samples, probably incorporated during the high-temperature annealing process if not already present in the samples before implantation.

Even though the results presented so far confirm the involvement of both Au and Pt in the observed PL lines, experiments using radioactive Au and Pt isotopes should provide undoubted insights in the origin of the observed luminescence bands.
3.2 Optimisation of the PL Signals

As Si is a semiconductor possessing an indirect band gap, radiative band-to-band processes always require a momentum-conserving phonon [Sap95]. This three-body process is less likely than a two-body process, thus radiative transitions in a semiconductor with an indirect band gap are not as strong as in semiconductors having a direct band gap, e.g. GaAs. Furthermore, as the impurity concentrations observed with PL can be very small, signals due to internal transition at a pseudodonor or pseudoacceptor defect can be very weak, too. Hence, observing luminescence features in Si can be very difficult due to poor signal to noise ratio.

Additionally, effects such as saturation of PL lines with increasing implantation dose or increasing excitation density have to be considered in order to optimise the experimental conditions for PL with radioactive isotopes.

During this work, a number of experiments have been undertaken in order to optimise experimental parameters. In these experiments, Si samples implanted with stable isotopes were used in order to provide situations comparable with the case of radioactive isotopes having been incorporated.

3.2.1 Anneal Procedure

As mentioned before, the main purposes of the anneal step are the removal of the implantation damage and the formation of the complexes giving rise to luminescent centres. The technique of sealing the sample in a quartz ampoule before annealing is one of the standard techniques and has been used from the early stages of research of Au in Si [Col57] on. The free parameters of this anneal are the anneal temperature, anneal time, atmosphere and cooling rate during quench.

As the half-lives of the radioactive isotopes of interest can be as low as a few hours, the anneal time is clearly limited. Additionally, an anneal time of 10 minutes has been found to be sufficient to remove implantation damage. The intensity of the free-exciton related PL bands are clearly a means to monitor the quality of the crystal lattice.

In order to provide high cooling rates during the rapid quench, the quartz ampoules have been filled with He gas at a partial pressure of 0.5 bar at room temperature providing sufficient heat contact between the quartz tube and the sample. Without this gas ambient, the formation of complexes during the quench is suppressed to some extent and precipitates of metal atoms might be formed instead.

The anneal temperature not only dominates the removal of implantation damage, it also determines the solid solubility of the impurities in the crystal. Even though high anneal temperatures would be desirable in terms of a high solid solubility of Au and Pt, both the diffusion coefficient and the solid solubility of contaminants become very high for temperatures above 1200 K [EMI88] so that the likelihood of incorporating unwanted impurities, which might be present in the quartz ampoule or the furnace, is unacceptably high. In addition to that, the anneal temperature has been limited by the unavailability of furnaces providing reproducible temperatures above 1400 K. Furthermore, anneal temperatures below 1123 K have not been found to lead to the production of PL centres at concentrations to be readily detected. Hence, mainly temperatures between 1173 and 1373 K have been used for annealing. Unfortunately, the number of implanted samples did not allow a thorough study of the dependence of PL intensities on the anneal tem-
Experimental Results

Figure 3.3: PL signals of the 735-meV and the 777-meV centres as a function of anneal temperature. The Pt signals were measured at 7.5 K in Si(SEH, n-type, 1-10 Ωcm) implanted with $10^{12}$ cm$^{-2}$ Pt ions at 60 keV, the “AuFe” signals at 7.5 K in Si(Freiberg, n-type, 125 Ωcm) implanted with $10^{12}$ cm$^{-2}$ Au ions at 60 keV. In both cases, the samples were annealed for 10 minutes under standard conditions.

Temperature. However, in order to obtain information on this behaviour, the PL intensities of the two PL lines of main interest, namely the “AuFe” centre at 1687 nm (735 meV) and the “Pt3” centre at 1594 nm (777 meV) have been recorded at three different anneal temperatures, using pieces of the same implanted sample. The implantation dose for each sample was $10^{12}$ cm$^{-2}$. The Au ions were implanted into the Freiberg n-type (125 Ωcm) material whereas the SEH wafer (n-type, 1-10 Ωcm) was used for the Pt implantations. All the spectra were recorded at 7.5 K. The results are displayed in figure 3.3.

The s/n ratio of the Au-related centre at 1687 nm (735 meV) is relatively poor for all anneal temperatures but rises approximately by a factor of 5 between 1173 K and 1373 K. This behaviour can be explained by the increase of the solid solubility for Au in Si with increasing temperature [EMI88, Sze81].

In the case of Pt, no data for its solid solubility at those high temperatures are available. However, an increase of the solubility within the temperature window investigated would be expected. Surprisingly, the intensity of the “Pt3” band at 1594 nm (777 meV) decreases with increasing anneal temperature. This behaviour is believed to be due to out-diffusion of Pt atoms, which has been confirmed by RBS measurements [Alv97b].

Considering the results above, high annealing temperatures ($T_a > 1250$ K) would be preferable for PL experiments using implantation of radioactive isotopes. This has been done, as for most of the samples implanted with radioactive isotopes, the anneal temperature was 1323 K. However, in one case, it was chosen to be 1173 K as a direct comparison between DLTS and PL results was to be established, and for DLTS under the given circumstances, lower anneal temperatures have been considered advantageous [Bol97].
3.2.2 Excitation Density

In order to make use of all centres forming one particular recombination channel for luminescence, high excitation densities are required. In this case, the PL signal saturates and thus becomes independent of the excitation density. This saturation effect can be easily understood with the aid of a very simple consideration. At low excitation densities, the recombination rate of electron-hole-pairs (ehp) is much bigger than the corresponding generation rate. Thus, a generated ehp can easily recombine through the considered channel. The luminescence will be dominated by the excitation density. In first order, this will result in linear dependence of the PL signal on the excitation density. At high excitation density, when the generation rate is much greater than the recombination rate, there are not enough centres available for the ehp to be captured and recombine instantly. Thus, the PL signal intensity will be determined by the density of impurity centres and therefore independent of the excitation density. This is a typical saturation effect.

Figure 3.4 reveals the behaviour of several PL signals as a function of laser power.

![Figure 3.4: Different PL intensities as a function of laser power. Top: PL signals of the “AuFe” band and the FE(TO) phonon-assisted free-exciton band in Si(Freiberg, n-type, 125 Ωcm) implanted with Au. In both cases standard annealing procedures were performed at 1173 K for 10 minutes and the spectra were recorded at 7.5 K. Bottom: PL signals of the “Pt2” centre, the “Pt3” centre and the FE(TO) phonon-assisted free-exciton band in Si(SEH, n-type, 1-10 Ωcm) implanted with Pt.](image-url)
and hence excitation density. The output power of the Ar ion laser on the 514.5 nm line was confined to 120 mW, measured with a conventional power meter right before the laser beam enters the cryostat chamber and illuminates the sample. The samples used for these measurement were Si(Freiberg, n-type, 125 Ωcm) implanted with $10^{12}$ cm$^{-2}$ Au and Si(SEH, n-type, 1-10 Ωcm) implanted with $10^{12}$ cm$^{-2}$ Pt. The annealing was performed at 1173 K for 10 minutes under standard conditions. The PL spectra were recorded at 7.5 K. As one can see from the plots, the signals could not be saturated. Thus, it was decided to carry on with the highest possible laser power in order to approach the ideal situation as closely as possible. In a quantitative analysis of PL intensities, the fact that the signals are not saturated might be taken into account (see section 3.4).

Additionally, the TO phonon-assisted free-exciton band intensity as a function of laser power is displayed in figure 3.4. According to several authors [Ham81, Nak80], this intensity depends linearly on laser power at low excitation density. This result has been confirmed within the experimental accuracy.

### 3.2.3 Measurement Temperature

The choice of the measurement temperature in PL experiments is on one hand of practical interest. On the other hand, it is interesting from a spectroscopic point of view and provides insight in the electronic structure of defects. However, these two points can not be disentangled.

In order to minimise effects in the sample like diffusion, which might result in the disintegration of unstable defect complexes, the sample should be kept at very low temperatures during the observation of the PL signals as a function of time in experiments involving radioactive impurities. This has been realised using a liquid He-flow cryostat, making temperatures as low as 7.5 K possible. However, in order to minimise intervention during the experiment, such a low temperature is not feasible, as the liquid He reservoir is not infinite. Thus, measurements at temperatures up to 20 K have been made using samples implanted with stable Au and Pt isotopes. This leads to a significant decrease in liquid He consumption. Furthermore, as the feasibility of PL experiments at around 20 K has been concluded, the use of a closed cycle cryostat has been considered, too, resulting in even less intervention during experiments.

Apart from these practical considerations, the behaviour of the peak ratios within one particular PL band is of fundamental interest and has been widely exploited [Alv97a, Cal88], not only in the case of Au and Pt in Si [Sau85, Web82].

As the thermalisation of double no-phonon lines is a useful means of temperature measurement of the sample while recording spectra, this behaviour has been studied. In all cases, the liquid He-flow cryostat was used and the temperature was regulated by additional heating of the sample holder.

In the top part of figure 3.5, PL spectra of Si (Freiberg, n-type, 125 Ωcm) implanted with stable Au are shown. The dashed line is the recording at 7.5 K, the solid line at 20 K. In the inset, the corresponding level scheme is plotted. The peaks labelled “a” and “b” clearly thermalise and thus can be interpreted as a two-fold excited state of a bound exciton having a single ground state [Cal88]. The bottom part of figure 3.5 displays the peak ratio $R_p$ as a function of temperature. The dashed line is a fit to the experimental peak ratio $PR$, using a Boltzmann function.
3.2 Optimisation of the PL Signals

Figure 3.5: “AuFe” centre at 1687 nm (735 meV). Top: Spectra at different measurement temperatures. Bottom: Boltzmann function fitted to the experimental peak ratio of “a” and “b”.

Figure 3.6: “Pt3” centre at 1594 nm (777 meV) Top: Spectra at different measurement temperatures. Bottom: Boltzmann function fitted to the experimental peak ratio of “a” and “b”.

\[ PR = A e^{-\frac{\Delta E}{kT}}, \]  

where \( A \) denotes the fitting parameter, \( \Delta E \) the energy difference between the two excited states and \( kT \) the thermal energy. In the case of the Au-related double peak at 1687 nm (735 meV), the fit yielded \( A=7.3(4) \). This function can be used to determine the actual measurement temperature of any spectrum containing this centre.

The peak system of the Pt-related feature at 1594 nm (777 meV) is very similar to the 735-meV band. Again, the dashed line in the top part of figure 3.6 shows a spectrum recorded at 7.5 K, the solid line at 20 K. Here, the excited state consists of two levels, too. In the bottom part of figure 3.6, the data points are fitted with a Boltzmann function yielding 2.5(2) for the pre-exponential factor.

As mentioned above, the temperature-dependent behaviour of manifold states can give a useful means of temperature measurement. Furthermore, the vibrational properties can be explored through changes in the phonon system with changing crystal temperature. However, the result of main interest to this work is that at temperatures as high as 20 K, luminescence of the centres of interest can still be conveniently detected.
3.3 Si:Hg - Implantations with Radioactive Isotopes

3.3.1 Choice of Isotopes

At ISOLDE, different radioactive Hg isotopes are available. In the choice of the suitable isotopes, some considerations had to be made.

- **Half-life**: As the samples had to be transported from Geneva to Konstanz in order to carry out the PL measurements, the half-lives of the interesting isotopes, namely Au and Pt, in the decay should not be too short.

- **Recoil energy**: The recoil energies should be less than typical displacement energies in semiconductors (20-30 eV), i.e., $E_r \ll E_d$. This prevents the displacement of implanted isotopes during decay processes. Then, no processes other than the chemical transformation of one element into the other should take place in the sample, provided it is kept at low temperature.

- **Activity**: Not only for the purpose of observing safety regulations, but also for the health of the people carrying out the experiments, the implantation dose and the nature of the decay had to be carefully considered in order to keep the risk of exposure to radiation as low as possible.

The first experiments using PL for radioactive Hg isotopes were made with $^{195}$Hg and $^{191}$Hg [Hen96]. However, the half-life of the decay $^{195}$Hg $\rightarrow$ $^{195}$Hg amounts to 183 days [Led78]. This is clearly too long to prevent experimental parameters and sample properties from changing. Thus, the two isotopes $^{191}$Hg and $^{193}$Hg were chosen for the implantations at ISOLDE. The relevant characteristics of the decays and the resulting PL spectra will be described hereafter. The PL experiments for Si:$^{191}$Hg were done at Dublin City University and shall not be described in detail in this report.

The decay scheme of $^{193}$Hg taken from [Led78] is displayed in figure 3.7. The calculated populations are plotted in figure 3.8. In these calculations, only the production of the $^{193}$Hg ground-state is assumed. This holds true as the gamma spectra taken after the implantations revealed that more than 90% of the $^{193}$Hg isotopes were in the ground state.

As the PL measurements could not be performed at CERN, the observed time window comprises $t > 20$ h. This means that merely the transformation of $^{193}$Au to $^{193}$Pt was observed in the PL spectra.

The decay chain $^{193}$Hg $\rightarrow$ $^{193}$Au $\rightarrow$ $^{193}$Pt involves only electron captures, so the whole decay energy (mass difference $Q_{EC}$) is transferred to the emitted neutrino resulting in a unique recoil momentum of the created nucleus [Smi65]. Hence, the recoil energy $E_r$ absorbed by the nucleus reads

$$E_r = \frac{Q_{EC}^2}{2Mc^2},$$  \hspace{1cm} (3.2)

where $M$ is the rest-mass of the created nucleus and $c$ the vacuum velocity of light. Thus, the recoil energy of the beta decay from $^{193}$Hg into $^{193}$Au is $E_r = 15.1$ eV, for the decay from $^{193}$Au into $^{193}$Pt $E_r = 3.1$ eV. Both values are below 20 eV, the typical displacement energy for semiconductors [Bie80].
3.3 Si: Hg - Implantations with Radioactive Isotopes

Figure 3.7: Decay scheme of $^{193}$Hg [Led78].

Figure 3.8: Population of the isotopes occurring in the decay of $^{193}$Hg.
3.3.2 PL Measurements of Si:\(^{193}\)Hg

The PL measurements were performed for three different Si materials. The implantation doses were approximately \(10^{12}\) cm\(^{-2}\) and the implantation energy was 60 keV for each sample.

Si(SEH):\(^{193}\)Hg

This sample was annealed for 10 minutes at 1323 K approximately 10 hours after implantation, i.e. when the Au population reaches its maximum value. This anneal was performed under standard conditions. All the spectra were recorded at \(T_m = 20\) K using a liquid He-flow cryostat. In figure 3.9, regions of interest are displayed at different times after implantation. The intensity of the free-exciton-related peak at 1129 nm (1097 meV) appeared to be stable for the different spectra, therefore reproducibility was provided for the measurements. In the graphs, peaks labelled “LP” are local-mode phonon replica.

In the graph on the left hand side of figure 3.9, one can clearly observe that the “AuFe”-labelled PL band at 1687 nm (735 meV) \[\text{Cal88}\] vanishes within approximately three half-lives of the decay \(^{193}\)Au \(\to\) \(^{193}\)Pt (the y-axes in these plots are linear scale). The two other PL bands, the Au–related system at 1583 nm (782 meV) and the “Pt3” PL band at 1594 nm (777 meV), have an inconvenient overlap. However, it is obvious to see that

![Figure 3.9: PL spectra of Si(SEH):\(^{193}\)Hg measured at \(T_m = 20\) K at different times after implantation. Peaks labelled “LP” are local-mode phonon replica. Left: “Au1”, “Pt3” and “AuFe” centres. Right: “FeB” centre. The spectra are shifted against each other by the same distance.](image-url)
some of the peaks in this energy window have disappeared after three half-lives of the corresponding decay. These peaks have been observed after Au diffusion [Car89]. The remaining lines, i.e. the strong double line at 1590/1594 nm and the broad side-band at approximately 1615 nm stem from the “Pt3” band [Alv97a]. As one can see from the graph the “Pt3”-related peaks stay essentially constant with time. This is probably due to either some stable $^{193}$Pt contamination in the ion beam or saturation of the signal at low Pt concentrations. Additionally, phonon replica belonging to the Au-related system starting at 1583 nm (782 meV) are located at the same wavelength in the spectra. As these replica decay with time and the “Pt3”-related NPLs grow with time, their sum stays constant within experimental accuracy.

The right hand side of figure 3.9 illustrates the behaviour of the “FeB” band at 1161 nm (1066 meV). It clearly disappears, roughly in accordance with the $^{193}$Au half-life. This provides strong evidence for the involvement of Au in this centre. At room temperature, the intensity of the “FeB” band is known to decrease with time due to instability of the corresponding complex. However, reference measurements, where the samples containing stable Au were kept at below 20 K over several days, have revealed that these complexes are stable below 20 K within this period of time (see figure 3.15). Hence, the observed disintegration of the PL signals has been assumed to be related to the chemical transformation of $^{193}$Au into $^{193}$Pt.

The PL intensities as a function of time after implantation are presented in figure 3.10. For clarity, the curves have been normalised and error bars have been omitted. With the aid of measurements on samples implanted with stable isotopes, the relative error has been estimated to account to 20%.

The values are peak areas of the principal NPLs; in the case of double lines, the sum of them has been taken. The problem of the overlap of the two PL bands in the region around 1590 nm has been worked around by considering the double line at 1590/1594 nm for the “Pt3” signals and the broad phonon side-band at 1600 nm for the Au-related band with its double NPL at 782 nm (1583 meV). However, the “Pt3” NPL and the “Au1” line at $\sim$1590 nm can not be readily distinguished.

The times quoted are the fitted lifetimes of the PL lines. They were obtained by fitting the population functions of figure 3.8 to the experimental data, using the nuclear lifetime $\tau_{Au} = 25.3$ hours [Led78] of $^{193}$Au as the fitting parameter. In addition to a scaling factor $B$, an offset $A$ for the signals was allowed, taking possible contamination with stable Au or Pt into account, which could be incorporated into the crystal either before or during implantation. Thus, the fitting function for Au-related signals reads

$$PL_{Au}(t) = A + B(-1.3e^{-t/\tau_{Hg}} + 1.3e^{-t/\tau_{Au}}).$$

Similarly, the fitting function for the Pt-related signals is

$$PL_{Pt}(t) = A + B(0.3e^{-t/\tau_{Hg}} - 1.3e^{-t/\tau_{Au}} + 1).$$

In these equations, $\tau_{Hg} = 5.8$ h is the nuclear lifetime of $^{193}$Hg [Led78] which has not been varied during the fitting procedure. This value holds only for $^{193}$Hg in the ground state after implantation. Gamma spectra have revealed that this assumption is true for the implantations made. In this procedure the full population functions have been used. Thus, it has been assumed that non-radiative recombination centres involving $^{193}$Hg were formed during the quench. If there are no Hg atoms involved in such centres, a simple exponential decay function $\sim \exp(-t/\tau_{Au})$ would have to be used for the Au population.
Figure 3.10: Si(SEH):$^{193}\text{Hg}$. PL intensities measured at $T_m = 20$ K at different times after implantation. For clarity the estimated relative error $\Delta_{PL} = 20\%$ is not displayed. The curves are normalised and shifted against each other by a constant factor. Top: Decaying features. Bottom: Features related to Pt.

It is important to note that this fitting procedure assumes linear dependence of the PL intensities on the impurity concentrations. In general, this is not true, which will become obvious when interpreting the experimental results. The fitted functions are plotted as solid lines. As the Pt-related intensities are constant, horizontal lines were inserted at the mean values.

In the top diagram, all decaying features are plotted. Remarkably, the “FeB” signal at 1161 nm (1066 meV) [Sau85], disintegrates in a similar way as the Au-caused PL line labelled “Au1”. Also, the curve representing the “AuFe” signal at 1687 nm (735 meV) follows the Au-caused PL line at 1600 nm, which has been identified to be part of a band having its double NPL at 1583 nm (782 meV) first reported by do Carmo et al. [Car89].

Even though these results strongly indicate the involvement of Au atoms in the complexes causing the luminescence, they have not exactly matched the nuclear lifetime of the
transformation of $^{193}$Au into $^{193}$Pt. This discrepancy has been observed since the first experiments using radioactive isotopes for the identification of PL lines [Mag95b, Dal94]. With the aid of a two-layer model, a solution has been suggested by Magerle et al. [Mag95b]. In section 3.4, this model will be adopted to the given situation in Si.

The lower part of figure 3.10 focuses on the behaviour of the Pt-related PL signals as a function of time. All three signals stay constant over the observed period of time. The explanation for this, provided the signals labelled “Pt1”, “Pt2” and “Pt3” stem from complexes involving Pt atoms, might be saturation of the signals due to $^{193}$Pt contamination during implantation. The “Pt3” NPLs are compensated in the spectra by a growing peak being part of the Au-related 782-meV band. Reference measurements on samples implanted with stable Au could reveal the relative intensity of this particular peak with respect to other “Au1”-related peaks which do not overlap with “Pt3” related peaks. Hence, the growth of the “Pt3” NPLs may be evaluated after subtraction of the intensity of the underlying “Au1”-related peak.

Si(Freiberg, p-type): $^{193}$Hg

The procedure described above was done for different Si materials. The main difference to the experiments described hitherto is that this material is p-type, thus the carrier concen-
Experimental Results

32

tration and therefore the electronic properties could be significantly different. This sample was annealed approximately 10 hours after implantation, i.e. when the Au population reaches its maximum value. The anneal was carried out under standard conditions at 1323 K for 10 minutes. All the spectra were recorded at $T_m = 20$ K using a liquid He-flow cryostat. In figure 3.11, regions of interest are displayed at different times after implantation. The intensity of the free-exciton-related peak at 1129 nm (1097 meV) appeared to be stable for the different spectra, therefore reproducibility was provided for these measurements, too.

The region around 1600 nm, displayed on the left-hand side of figure 3.11, looks different from the corresponding spectra for n-type Si (see figure 3.9). The Au-related band at 1600 nm (part of the system with a double NPL at 1583 nm (782 meV)) is only very weakly present. In order to account for the absence of the “AuFe” centre in p-type material, the following argument has been proposed [Hen97]. In n-type material with the Fermi-level close to the conduction band edge, the Au atoms in substitutional sites exist in the negative charge state, and they provide an attractive potential for the positively charged Fe ions which are mobile at temperatures close to room temperature. This results in the efficient production of neutral Au-Fe pair centres in n-type material. For p-type material with the Fermi-level close to the valence band edge, the Au atoms are likely to be in either neutral or positive charge states so that the formation of the Au-Fe pair centres is strongly inhibited. The absence of this centre in p-type material has been observed by other groups, too [Hen97].

The spectrum labelled “Pt3” at 1594 nm (777 meV) is clearly detectable. As one will see in the quantitative analysis, the intensity is growing in accordance with the nuclear lifetime of the chemical transformation from $^{193}$Au to $^{193}$Pt.

In this sample, too, the FeB luminescence feature decays roughly in accordance with the lifetime of the decay $^{193}$Au $\rightarrow$ $^{193}$Pt, as one can see from the graph on the right-hand side of figure 3.11.

The measurement temperature does not appear to be the same for the different spectra. This can be concluded from the changing peak ratio of the double line at 1590 nm and 1594 nm, respectively. However, the change in temperature does not exceed 2 K. In this range, the major change due to temperature changes in the sample is the peak ratio. This problem can be eliminated in the quantitative analysis by considering the sum of the two peaks.

The extraction of the peak areas and the fitting procedure for the spectra of this material was done in the same way as for the SEH samples. The decaying features are plotted in the top part of figure 3.12. The intensity of the “FeB” peak decreases roughly in accordance to the intensity of the Au-related line at 1600 nm, which is part of the system beginning at 1583 nm (782 meV).

The bottom half of figure 3.12 illustrates the Pt-related signals as a function of time after implantation. Whereas the “Pt1” and “Pt2” lines are constant, the “Pt3” line grows with a lifetime of 30.5(3.6) hours. In this case, unlike in the case of the SEH sample described above, the underlying “Au1”-related peak is very weak so that the growth of the “Pt3” NPL can be clearly observed. Unlike in n-type material, the “Pt3” signal is not present right after the quench, i.e. when the first spectrum was recorded. This behaviour is likely to be due to thermal instability of the corresponding complexes in p-type material at room temperature which has been observed in this sample.

In order to summarise the results for Si(Freiberg, p-type):$^{193}$Hg, the main point to be
Figure 3.12: Si(Freiberg, p-type):$^{193}$Hg. PL intensities measured at $T_m = 20$ K at different times after implantation. For clarity the estimated relative error $\Delta_{PL} = 20\%$ is not displayed. The curves are normalised and shifted against each other by a constant factor. Top: Decaying features. Bottom: Features related to Pt.

stated is that the behaviour of the PL bands as a function of time are very similar to the corresponding data of the SEH material. However, the same discrepancy regarding the lifetimes is observed. Additionally, the altered position of the Fermi-level causes the “AuFe” centre at 1687 nm (735 meV) to disappear from the spectra. The question whether this complex is formed in p-type material would have to be answered by using a technique different from conventional PL.

Si(Freiberg, n-type):$^{193}$Hg

For this Si material, the main difference to the experiments described above is the use of a closed cycle cryostat instead of the liquid He-flow cryostat for the measurements. Again, the sample was annealed approximately 10 hours after implantation, i.e. when the Au
population peaks. The anneal was carried out under standard conditions, yet this time the sample was heated at 1173 K for 10 minutes. This was done in order to be able to establish a relationship between PL and DLTS measurements which were carried out using the same sample preparation procedure. All the spectra were recorded at $T_m = 20$ K. Due to poor heat contact between the sample and the coldfinger of the cryostat, the sample temperature was estimated to have risen by approximately 3 K. However, the peak ratios of the two double peaks investigated in section 3.2.3 indicate a reasonably stable measurement temperature.

In figure 3.13, the regions of interest are displayed at different times after implantation. The intensity of the free-exciton-related peak at 1129 nm (1097 meV) was found to be stable for the different spectra, therefore reproducibility was provided for these measurements, too.

A problem occurring for this Si material have been the poor PL intensities of the prominent spectra (see e.g. figure 3.2). This makes a proper observation of the intensities as a function of time difficult. However, the spectra show the expected tendencies, as one can see in figure 3.13. In the left plot, the Pt double line at 1590/1594 nm ($\sim 777$ meV) appears to grow. On the other hand, the spectra assigned to Au are significantly decreased after approximately three half-lives of the corresponding decay $^{193}$Au $\rightarrow ^{193}$Pt. The same applies to the FeB signal at 1161 nm (1066 meV), plotted on the right hand side of figure 3.13.
Figure 3.14: Si(Freiberg, n-type):$^{193}$Hg. PL intensities measured at $T_m = 20$ K at different times after implantation. For clarity the estimated relative error $\Delta_{PL} = 20\%$ is not displayed. The curves are normalised and shifted against each other by a constant factor. Top: Decaying features. Bottom: Features related to the growth in Pt population.

Once again, the presence of Au in the sample before the implantation would provide an explanation for the presence of Au-related signals even after several half-lives of $^{193}$Au. Like in Si(SEH, n-type, 1-10 $\Omega$cm), it is difficult to distinguish Pt-related from Au-related features at $\sim$1590 nm.

The graphs in figure 3.14 reflect the behaviour of the prominent PL spectra as a function of time, the symbols are the same as in the corresponding graphs in the previous two sections. In the top plot, the decaying features are displayed along with the fitted half-lives. The reference feature, the “Au1” band beginning at 1583 nm (782 meV), however, is very weak. The decay can be observed anyway. The reasonably strong “FeB” and “AuFe” intensities, respectively, clearly decay in a similar way as in the samples discussed in the two preceding sections.

In the lower part of figure 3.14 the three Pt-related PL intensities are shown as a
function of time. In this case the experimental data regarding the “Pt1” band at 1207 nm (1027 meV) and the “Pt2” band at 1402 nm (884 meV), respectively, have been fitted with equation 3.4 describing the Pt population. However, the biggest changes in Pt population take place in the first 15 hours after implantation. This time window has not been accessible for PL spectroscopy as the samples could not be measured on-site at ISOLDE. Hence, the presented data do not reflect the corresponding Pt population accurately. The intensity of the “Pt3” band at 1594 nm (884 meV) shows the trend to grow with time, yet not exactly with the lifetime of the corresponding transformation from $^{193}\text{Au}$ to $^{193}\text{Pt}$. As mentioned before, this is partly due to the overlap with a Au-related feature in the spectrum.

Summary of PL results for Si:$^{193}\text{Hg}$

In order to obtain a thorough picture of the results obtained with PL spectroscopy for Si:$^{193}\text{Hg}$, all the fitted lifetimes (in hours) of the PL signals are compiled in table 3.1. The nuclear lifetime of $^{193}\text{Au}$ is 25.3 hours [Led78]. The relative error of 20% in intensity leads to big errors in the fitted lifetimes of the peaks in the case of intensities. For Pt related PL bands, the errors in the fitted lifetimes are smaller. This is due to the fact that the corresponding intensities stay constant for $t > 30$ h and a great number of data points have been sampled in this time window.

<table>
<thead>
<tr>
<th></th>
<th>FeB</th>
<th>Au1</th>
<th>AuFe</th>
<th>Pt1</th>
<th>Pt2</th>
<th>Pt3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEH</td>
<td>18.4(2.8)</td>
<td>13.9(4.0)</td>
<td>20.6(4.0)</td>
<td>n/f</td>
<td>n/f</td>
<td>n/f</td>
</tr>
<tr>
<td>Freib. p-type</td>
<td>25.6(13.2)</td>
<td>15.1(1.8)</td>
<td>-</td>
<td>n/f</td>
<td>n/f</td>
<td>30.5(3.6)</td>
</tr>
<tr>
<td>Freib. n-type</td>
<td>15.6(1.4)</td>
<td>19.0(2.9)</td>
<td>21.0(3.8)</td>
<td>9.5(1.4)</td>
<td>8.5(0.5)</td>
<td>11.3(0.8)</td>
</tr>
</tbody>
</table>

Table 3.1: Compilation of the fitted lifetimes of PL features in different Si:$^{193}\text{Hg}$ samples. The lifetime of $^{193}\text{Au}$ is 25.3 hours. In this table, “-” means that the centre has not been observed in the sample, “n/f” means that the signal was not fitted as a function of time, see figures 3.10 and 3.12.

3.3.3 Comparison with Reference Sample Si:Au (stable)

As mentioned before, complexes giving rise to PL bands are often not stable at room temperature. In order to distinguish these effects from the disintegration of PL signals due to chemical transformation of the radioactive isotopes, a reference experiment with Si(Freiberg, n-type), implanted with $10^{12}$ cm$^{-2}$ Au atoms at 60 keV, was performed at Dublin City University. The sample was annealed under standard conditions and then permanently kept at 12 K in a closed cycle cryostat using He gas for heat contact. During the recording of the PL spectra the temperature slightly rose due to the creation of phonons following laser irradiation. PL spectra were taken over a period of 4 days, comparable to the time window used for the measurements of the samples implanted with radioactive isotopes. In order to compare the intensities, all curves in figure 3.15 were normalised to their starting value.

It is obvious to see that the PL bands stemming from the reference sample do not vanish with increasing time. As described above, the Au associated PL bands in the Si:$^{193}\text{Hg}$ sample disappear with time, roughly in accordance with the half-life of $^{193}\text{Au}$. A similar study for the Pt related signals is yet to be made.
3.3 Si:Hg - Implantations with Radioactive Isotopes

Figure 3.15: PL intensities as a function of time. The reference data were obtained from Si(Freiberg, n-type) implanted with stable Au, the decaying curves illustrate the behaviour of corresponding lines in different Si samples implanted with radioactive ions. (a) Behaviour of the “FeB” line (1161 nm/1066 meV) in different implanted wafers as a function of time. (b) Behaviour of the “Au1” line (1600 nm/782-meV-band) in different implanted wafers as a function of time. (c) Behaviour of the “AuFe” line (1686 nm/735 meV) in different implanted wafers as a function of time.
3.3.4 Comparison with DLTS Measurements

Deep level transient spectroscopy (DLTS) was first performed by Lang et al. [Lan74] and has become a well-established technique for the detection of energy levels of deep impurities in semiconductors [Sch90, Pan86]. These levels lie in the bandgap, more than 0.1 eV away from the closest band edge.

There exist a number of advantages of DLTS over PL. The main advantage comprises the fact that DLTS signals are directly proportional to the defect concentration in the depletion layer of the metal-semiconductor junction which has to be established in order to perform DLTS. Hence, the absolute concentration of deep levels can be determined, provided the set-up has been calibrated. Another strength of DLTS is that there exist no competing processes such as non-radiative recombination in PL spectroscopy leading to deteriorated signal intensities.

However, DLTS has some disadvantages, too. A mainly practical one is the fact that for DLTS, being an electrical method, metal-semiconductor contacts have to be made which is not always straightforward. Secondly, if one wants to compare PL and DLTS data, this is made difficult by the fact that DLTS only detects ground states of defect levels whereas in the case of deep impurity related PL, mainly internal transitions at defect complexes are observed. Hence, the assignment between PL lines and DLTS peaks is often a puzzle.

The first DLTS measurement using radioactive Au and Pt in Si was performed at ISOLDE, too [Pet90]. There, the well-known donor and acceptor levels of substitutional Au and Pt [Mil73] were found.

In DLTS, one measures the capacitance of a Schottky contact as a function of time after a reverse bias pulse, which causes an increase of the width of the space charge region and thus of its capacitance. The capacitance as a function of time reads [Sch90]

\[ C(t) = C_0 \left(1 - \frac{n_T(0)}{N_T} e^{-t/\tau_e}\right), \]  

where \( C_0 \) is the capacitance under constant reverse bias, i.e. when the pulse is switched off. \( N_T \) is the total concentration of trap centres present in the interesting region, \( n_T(0) \) the number of electrons emitted from the traps into the conduction band at the point of time when the bias pulse was just switched off. The parameter carrying information on the energy level of the corresponding impurity is the characteristic emission time constant [Sch90]

\[ \tau_e = \frac{e^{(E_c-E_T)/kT}}{\gamma_n \sigma_n T^2}. \]  

Here, \( E_c \) and \( E_T \) denote the energy levels of the bottom edge of the conduction band and the trap, respectively. \( \gamma_n \) is a material-specific constant being a function of thermal carrier velocity, effective density of states in the conduction band and the absolute temperature \( T \). In the equation above, \( k \) is the Boltzmann constant. Measuring \( C(t) \) as a function of temperature yields a maximum at a certain temperature with which the corresponding emission time and hence the energy level of the trap can be evaluated.

There exist a number of variations of DLTS, the most important of which are briefly described in [Sch90].

The DLTS measurements in the joint experimental survey which this work has been part of have been carried out by J. Bollmann, HU Berlin, who has kindly given me permission
to quote from his results. Typical DLTS spectra, in this case for Si(Freiberg, n-type):$^{193}$Hg at different times after implantation, are shown in figure 3.16. Each spectrum is slightly shifted with respect to the preceding one in order to display all spectra. The sample was annealed at 1323 K for 10 minutes under standard conditions before the Au contacts were made to the sample.

The identification of the peaks has been undertaken by J. Bollmann and feature some interesting details [Bol97]. The peak labelled “E13” corresponds to a level at $E_c - 0.16$ eV; its increase follows the population of $^{193}$Pt (see figure 3.8). The peak labelled “E11” stays stable with time. The corresponding energy level is $E_c - 0.22$ eV, close to that assigned to Pt [Pet90, Bro80]. Contamination of the ion beam with stable $^{193}$Pt could be the reason for the behaviour of this peak. Another peak growing with Pt population belongs to the trap level $E_c - 0.25$ eV and is labelled “E9”; thus, the responsible complex is believed to contain Pt. The peaks “E6” and “E7” have not yet been identified. As they roughly follow the Pt and Ir concentrations, respectively, they might be related to these elements. The energy level connected to “E7” is $E_c - 0.31$ eV. The origin of the peak labelled “E3” is not yet understood, the peak labelled “E1” might be Au related.

These results are in good agreement with the presented PL results mainly sensing levels different from the substitutional impurities. To date, connections between levels observed by DLTS and PL have not yet been established.

### 3.3.5 PL Measurements of Si:$^{191}$Hg

As mentioned before, measurements of Si implanted with $^{191}$Hg were made at Dublin City University in addition to the presented results. The decay chain $^{191}$Hg → $^{191}$Au → $^{191}$Pt →
191\textsuperscript{Ir} was exploited to monitor the change in PL signals due to the isotopes involved. As the half-lives of both 191\textsuperscript{Hg} (49 min) and 191\textsuperscript{Au} (3.2 h) are quite short, mainly the transition 191\textsuperscript{Pt} (2.9 d) \rightarrow 191\textsuperscript{Ir} was observed using PL spectroscopy. Apart from the different mass of the implanted isotope, the measurements were carried out at the same experimental conditions as for Si (Freiberg, n-type, 125 \textOmega cm). Amongst other features, the signals labelled “Pt1”, “Pt2” and “Pt3” in this work appeared in this sample. The corresponding intensities decreased with half-lives between 2.4 and 2.8 days [Hen97]. This is close to the half-life of 191\textsuperscript{Pt}, 2.9 days [Led78]. Therefore, the PL measurements of Si:191\textsuperscript{Hg} have corroborated the conclusion that the PL bands labelled “Pt1”, “Pt2” and “Pt3” in this work are in fact due to complexes containing Pt atoms.

### 3.4 Quantitative Approach to the Interpretation of PL Intensities

As mentioned in the preceding chapters, a significant discrepancy between the expected lifetime of PL signals connected to radioactive isotopes and the measured lifetime exists. This problem has been solved by Magerle [Mag95a, Mag95b] using a simple two-layer-model resulting in a non-linear relation between PL intensities and defect concentrations. This model shall be briefly described and adopted to the given situation hereafter. However, this action is not intended to yield exact results, only a possible direction of analysis is pointed out with the aid of an example.

Consider the implanted sample as two layers (see figure 2.2). The top layer contains, in this simplified picture, a homogeneous concentration of impurity atoms, in this case a mixture of Hg, Au and Pt. Additionally, non-radiative recombination centres due to implantation damage and surface states are present. The bulk only contains residual impurities and defects.

When laser light is shone onto the surface of the material, a non-equilibrium situation will result. However, after a short time, a complicated dynamic equilibrium of generation, diffusion and recombination will occur. In Magerle’s situation two AlGaAs barriers were introduced during the growth of the GaAs samples. Thus, free carriers generated in the implanted layer were unable to diffuse to the surface or the bulk. Whereas both surface recombination and diffusion of free carriers between the implanted layer and the bulk could be neglected in that situation, they have to be taken into account here.

Figure 3.17 illustrates the situation. The incoming photons produce excess carriers in the form of electron-hole-pairs. \( G \) denotes the total generation rate per unit area, \( f_L \) the fraction of light absorbed in the layer, \( f_B \) the fraction of light absorbed in the bulk. Thus, \( f_L G \) excess carriers are generated (per unit area per unit time) in the layer. Similarly, \( f_B G \) excess carriers are produced in the bulk. Additionally, an amount \( D \) of excess carriers diffuse between the layer and the bulk. \( D > 0 \) describes diffusion from the implanted layer to the bulk, \( D < 0 \) from the bulk to the implanted layer.

At all times, \( \Delta n_L \) excess carriers (note that \( n \) may denote either electrons or holes, depending on the type of semiconductor) are present in the layer and \( \Delta n_B \) are present in the bulk. They give rise to recombination through the different channels with the corresponding carrier lifetimes (not to be mistaken with nuclear lifetimes). Here, the reciprocal total excess carrier lifetime in each layer, \( 1/\tau_B \) for the bulk and \( 1/\tau_L \) for the layer, is the sum of the reciprocal lifetimes for the different channels [Sze81], indexed \( i \).
3.4 Quantitative Approach to the Interpretation of PL Intensities

Figure 3.17: Illustration of the dynamic equilibrium comprising excitation, recombination and diffusion of excess carriers in both the implanted (layer) and unimplanted (bulk) areas of the sample [Mag95b].

\[
\frac{1}{\tau_{L/B}} = \sum_i \frac{1}{\tau_i} \quad (3.7)
\]

The equilibrium conditions for the layer and the bulk, read

\[
f_{L}G - D = \frac{\Delta n_{L}}{\tau_{L}} \quad (3.8)
\]

and

\[
f_{B}G + D = \frac{\Delta n_{B}}{\tau_{B}} \quad (3.9)
\]

respectively.

Whereas Magerle et al. used a carbon related PL line due to background doping for normalisation, this cannot be done for Si. Here, the only feature present in every spectrum is the free-exciton related luminescence. In the works undertaken in quantitative PL in Si [Taj78, Col87], the ratio of TO phonon-assisted bound-exciton bands and the TO phonon-assisted free-exciton band were used for establishing the concentration of impurities binding excitons. Similarly, the TO phonon-assisted free-exciton band at 1129 nm (1097 meV) can be used to normalise PL intensities due to deep level impurities. This exciton-related band varies linearly with excitation power [Ham81, Nak80]. Thus, linear dependence of the corresponding intensities on the excess carrier density has been assumed.

For small signals, the total recombination in the implanted layer is a linear superposition of the recombination without implantation and the additional recombination due to implantation [Ort90]. The first is equivalent to the recombination in the bulk as it does not contain any defects due to implantation. In PL spectra of Si:193Hg spectra there are a big number of radiative recombination centres present. Thus, the calculations have been simplified. All the non-changing features, e.g. the PL bands labelled “Pt1” and “Pt2”, and the non-radiative recombination channels including surface recombination are described by one term, \(1/\tau_{\text{rest}}\). In the Si(Freiberg, n-type, 125 Ωcm):193Hg sample, for example,
the changing features are the ones labelled “FeB”, “Au1” and “AuFe”. Hence the total recombination rate in the layer reads

$$\frac{\Delta n_L^{(FRn)}}{\tau_L} = \frac{\Delta n_L}{\tau_B} + \frac{\Delta n_L}{\tau_S} + \Delta n_L N_{Hg}(t = 0) + \Delta n_L (B_{FeB} + B_{Au1} + B_{AuFe}) N_{Au} + \Delta n_L B_{Pt3} N_{Pt}.$$  

(3.10)

In this equation, \(\tau_S\) and \(\tau_{\text{const}}\) denote the lifetimes of excess carriers recombining through the surface channel and the channels producing constant luminescence, respectively. The first term in the second line describes the different Au-related channels decaying with time, the remaining term in the second line the “Pt3” channel. \(B_{FeB}\) is the transition coefficient for the “FeB” channel, the remaining transition coefficients are labelled correspondingly. It should be noted that the transition coefficients include the ratios of the different defect complexes being responsible for the corresponding PL bands. \(N_{Au}\) and \(N_{Pt}\) denote the Au and Pt concentration in the implanted layer, respectively. The last term in the first line of the equation describes the non-radiative recombination channels due to implantation damage by the initial Hg implantation. Hence, it is proportional to the initial Hg concentration \(N_{Hg}(t = 0)\). In first order, there is no change of implantation damage during the decay of \(^{193}\text{Hg}\) so that this term can be considered constant. As the first three terms in the first line of equation 3.11 are constant, too, they can all be written in one expression, along with the recombination due to non-radiative processes. Thus, equation 3.11 can be written as

$$\frac{\Delta n_L^{(FRn)}}{\tau_L} = \frac{\Delta n_L}{\tau_{\text{rest}}} + \Delta n_L (B_{FeB} + B_{Au1} + B_{AuFe}) N_{Au} + \Delta n_L B_{Pt3} N_{Pt}.$$  

(3.11)

As mentioned before, the free-exciton (FE) related peak at 1129 nm (1097 meV) will be used for normalisation. The intensity varies linearly with excitation density [Nak80]. Since the luminescence can originate both from the layer and from the bulk, the total intensity will be proportional to the sum of these two contributions.

$$I_{FE} \propto \frac{\Delta n_L}{\tau_{FE,L}} + \frac{\gamma \Delta n_B}{\tau_{FE,B}}$$  

(3.12)

Here, \(\gamma' = \gamma (\tau_{FE,L}/\tau_{FE,B})\) and \(\gamma\) is a measure for the fraction of FE-related luminescence stemming from the bulk. \(\tau_{FE,L}\) and \(\tau_{FE,B}\) are the effective lifetimes of the carriers forming a free exciton in the layer and bulk, respectively. They are actually products of the corresponding lifetimes for holes and electrons.

An example is used to illustrate this model. For this reason, the ratio of the PL band labelled “Au1” and the intensity of the TO phonon-assisted free exciton band are considered. With the help of the equation above, this ratio reads

$$\frac{I_{Au1}}{I_{FE}} = \frac{\Delta n_L B_{Au1} N_{Au1}}{(\Delta n_L + \gamma' \Delta n_B)/\tau_{FE,L}}$$  

(3.13)
3.4 Quantitative Approach to the Interpretation of PL Intensities

Using the equilibrium conditions 3.8 and 3.9, this ratio may be written as

\[
\frac{I_{\text{Au}}}{I_{\text{FE}}} = \frac{B_{\text{Au}1}N_{\text{Au}1}\tau_{\text{FE},L}}{1 + \gamma'\tau_B(f_BG + D)/\tau_L(f_LG - D)}
\]

\[
= \frac{B_{\text{Au}1}N_{\text{Au}1}\tau_{\text{FE},L}}{1 + \gamma''/\tau_L}
\]

with \(\gamma'' = \gamma'\tau_B(f_BG + d)/(f_LG - D)\). With the help of the rate equation 3.11, this equation can be brought to the form

\[
\frac{I_{\text{Au}}}{I_{\text{FE}}} = \left[ \frac{a + b + cN_{\text{Pt}}}{N_{\text{Au}}} \right]^{-1}
\]

The coefficients \(a\), \(b\) and \(c\) can be used as fitting parameters and are defined as follows:

\[
a = \frac{1}{\tau_{\text{FE},L}} + \frac{1}{B_{\text{Au}1}} + \frac{\gamma''}{\tau_{\text{rest}}\tau_{\text{FE},L}B_{\text{Au}1}}
\]

\[
b = \frac{\gamma''}{\tau_{\text{FE},L}} \left( 1 + \frac{B_{\text{Fe}B} + B_{\text{AuFe}}}{B_{\text{Au}1}} \right)
\]

\[
c = \frac{\gamma''}{\tau_{\text{FE},L}} \frac{B_{\text{PG}}}{B_{\text{Au}1}}
\]

In all equations, \(N_{\text{Au}}\) and \(N_{\text{Pt}}\) are the Au and Pt concentrations, respectively. In the case of stable isotopes giving rise to luminescence, \(N_{\text{Au}} = \text{const.}\) and \(N_{\text{Pt}} = \text{const.}\). If radioactive decay is considered, \(N_{\text{Au}} \approx N_{\text{Hg}}(t = 0) \exp(-t/\tau)\) and \(N_{\text{Au}} \approx N_{\text{Hg}}(t = 0)(1 - \exp(-t/\tau))\), which is an approximation for the case of \(t > 15\) hours in the decay of \(^{193}\text{Hg}\).

In order to fit equation 3.15 to the experimental data, the number of fit parameters has to be reduced. Standard software packages (e.g. ORIGIN\textsuperscript{TM}) have consistently failed to perform their built-in least-square error reduction data analysis in a reproducible manner.

The simple model used so far is clearly only one way of describing the obtained results quantitatively. Some effects have not even been taken into account. For example, the capture cross section of a defect for an electron-hole-pair was assumed to be independent of the concentration of the remaining defects which lacks experimental or theoretical justification. Furthermore, during the radioactive decay, the complexes might change their charge states which could result in a change of the corresponding capture cross section, too.

This chapter has made clear that a quantitative analysis of the PL data of the samples implanted with radioactive isotopes is, due to the number of changing features, not straightforward. Further actions have to be taken. A more sophisticated model in conjunction with experiments where the transformation \(^{193}\text{Au}\) to \(^{193}\text{Pt}\) is simulated by implantation of stable isotopes, similarly done in [Mag95b] might have to be considered. These experiments using co-doping of different transition metal impurities, however, are not always straightforward in terms of simulation of the radioactive decay. Due to different diffusivities of the elements involved, the implantation doses and the anneal parameters would have to be carefully chosen.

Alternatively, uniform impurity doping, which could be achieved by using long annealing times, might make quantitative conclusions easier.
3.5 Miscellaneous Results

In this section two results are quoted which have been obtained during the work on the experiments presented so far. The possible directions of research they could comprise have not yet been followed. They both indicate the possible involvement of Li and Fe, respectively, in complexes leading to PL bands.

3.5.1 Si(Freiberg, n-type, 125 Ωcm):Au+Li

Figure 3.18 illustrates the different steps the observed sample underwent. All PL spectra were recorded at 7.5 K and the excitation density was 10 W cm\(^{-2}\). In the graph, they are shifted against each other by the same distance. After implantation with stable Au isotopes, the implantation energy having been 60 keV and the dose \(10^{12}\) cm\(^{-2}\), the sample was annealed under standard conditions at 1173 K for 10 minutes. The second spectrum from the bottom was recorded right after this anneal. A further high-temperature step was undertaken after this. This time, a small amount of Li was inserted into the quartz ampoule in addition to He gas before sealing. Again, the ampoule containing the sample under Li- and He-atmosphere was heated to 1173 K for 10 minutes and rapidly immersed in water at room temperature. After this procedure, the third spectrum from the bottom of figure 3.18 was recorded. The increased intensity of the AuFe centre at 1687 nm (735 meV)

![Figure 3.18: Si(Freiberg, n-type, 125 Ωcm) spectra after Au implantation and Li diffusion. From bottom to top, PL spectra recorded after additional processing steps, shifted against each other by the same distance. Refer to text for details.](image-url)
is not necessarily due to higher Li concentration but could be a result of the second anneal providing a more uniform distribution of the impurities. However, two features in the spectrum are clearly due to Li being incorporated in the sample during the anneal under Li atmosphere. The peak at the low energy side of the free-exciton TO phonon-assisted band is centred at 1133 nm (1094 meV) and has been interpreted as the TO phonon replica of a Li-bound-exciton [The78]. Similarly, the line at 1094 nm (1133 meV) has been assigned to a TA phonon replica of a Li-bound-exciton [Hen80]. The exact locations of these peaks have been confirmed using high-resolution fourier transform photoluminescence spectroscopy (FTPL) [Per93] by the Dublin group [Hen97]. The top spectrum was recorded after a further annealing procedure. In this case, the sample was exposed to 473 K for 10 minutes in an open quartz ampoule. The appearance of the AuFe centre changed significantly. Several new lines occurred, the highest energy peak, probably consisting of more than one line, appearing at 1619 nm (766 meV). As Li atoms are mobile at these low temperatures in Si [EMI88], the observed effect might be interpreted in a very simple way. During the low temperature anneal, Li atoms are either incorporated in the complex or leave the complex, thus changing the binding energy of the complex which would result in a change in photon energy of the luminescence. To date, the most significant result reported regarding complexes containing Au and Li is the accidental trace Li contamination leading to hitherto unidentified defects observed by EPR [Alt95]. However, as mentioned at the beginning of this chapter, this direction, namely investigating the binding partners of the transition metal atoms in luminescent centres, has not yet been followed in further detail. In particular, at this stage, a connection to the relevant EPR results can not yet be established.

3.5.2 Si(SEH, n-type, 1-10 \( \Omega \text{cm})\):Pt+Fe

For the stable implantations, one set of Pt implanted samples containing co-implanted Fe in various doses, was prepared. However, due to the high diffusivity of Fe in Si at typical anneal temperatures [EMI88], the Fe concentrations in the implanted region were found to be several orders of magnitudes lower than the Au concentration. Thus, no dependence of the AuFe centre at 1687 nm (735 meV) or the Pt related bands on the Fe concentration could be observed. The problem of low Fe concentrations has been attempted to be solved by Fe diffusion. For this purpose a layer (thickness 100(10) nm) of high-purity Fe metal (total metallic contamination < 10 ppm) was evaporated onto the back side of samples implanted with Au or Pt. The subsequent diffusion was performed at 1273 K for 10 minutes under He ambient, as in the standard annealing process. After the Fe diffusion, the quartz ampoule was rapidly submerged in water at room temperature.

The most surprising result of the experiments using diffusion for Fe co-doping appeared in a Si(SEH, n-type, 1-10 \( \Omega \text{cm})\) sample which had been implanted with Pt (10^{12} \text{ cm}^{-2}) and Fe (2\times10^{11} \text{ cm}^{-2}). The corresponding spectra, recorded at 7.5 K using an excitation density of 10 Wcm\(^{-2}\), are displayed in figure 3.19. Note that the spectra are shifted against each other by the same distance. Whereas the bottom spectrum belongs to the unimplanted sample, the middle one is typical for Si implanted with Pt. Besides the Cu contamination resulting in PL bands at 1221 nm (1014 meV) [Web82] and 1312 nm (943 meV) [McGui89], the three prominent bands associated to Pt [Alv97a] are present. The subsequent Fe diffusion produces a Fe concentration in the implanted layer which is comparable to the Pt concentration [EMI88, Mul86]. Surprisingly, the spectrum recorded
after this step (top in figure 3.19) reveals the well-known 735-meV luminescence. One might argue that this is not surprising as this band has been observed after Fe diffusion \cite{Cal88, Sin95, Car89} without any involvement of Au. This seems to be a contradiction to the results presented in the previous chapters indicating an involvement of Au in the corresponding complex. However, taking possible Au contamination before or, even more likely due to similar masses, during Pt implantation into account, this dilemma can be solved. If one assumes that before Fe diffusion, mainly the Pt atoms bind the Fe atoms, the relatively weak Au related luminescence does not appear. When the concentration of Fe atoms in the implanted layer increases, the Au atoms capture Fe atoms, too, and the corresponding complexes giving rise to Au-related luminescence bands are formed. One of these bands, the “FeB” band at 1161 nm (1066 meV) is present in the spectrum, too. Fe is a well known trace contaminant so that it is no surprise that these defects occur in nominally Fe-free Si, too.

Again, one should note that this experiment had only preliminary character and yielded interesting results giving rise to future research. The conclusions drawn are only qualitative, sometimes even speculative.
Chapter 4

Conclusions and Outlook

In the presented work, the luminescent properties of transition metal impurities, in particular of Au and Pt, in Si were studied. The main objective was the identification of prominent photoluminescence bands. The technique of ion implantation, which was used for doping the Si materials with both stable and radioactive Au and Pt isotopes, appeared to provide a clean method of deliberately incorporating impurities into Si.

In the case of Pt, significant progress towards the confirmation of earlier results [Alv97a, Hen96] has been made. In an earlier publication, two Pt related centers have been reported, one of which is assigned to interstitial Pt, the other one to substitutional Pt [Arm86]. These centers were not detected. Nevertheless, three other centers could be produced. The centers having principal no-phonon lines at 1207 nm (1026 meV) and at 1402 nm (884 meV) have not yet been thoroughly investigated. However, in PL experiments with radioactive $^{191}$Hg performed at Dublin City University the corresponding intensities followed the population of $^{191}$Hg. The experiments performed have yielded strong evidence that the center at 1594 nm (777 meV) is Pt related. Firstly, its PL intensity has shown the tendency to grow with increasing implant doses, yet not linearly correlated. Secondly, in experiments detecting luminescence due to radioactive $^{191}$Pt and $^{193}$Pt being part of complex centers, this center has roughly followed the changes in Pt population. In p-type material this centre has been found to be highly unstable at room temperature. This property of the centre has not yet been studied systematically. Further investigation of the behaviour of the center due to different background doping should provide deeper insight into the possibility of lighter atoms such as Fe or Li being involved in the complex.

The investigation of Au related luminescence, particularly in the case of the radioactive isotope $^{193}$Au, revealed a number of results. First, Au-related luminescence centre with the principal two no-phonon lines at 1583 nm (782 meV) [Car89] appeared to be readily formed in the samples used. In radioactive experiments, its intensity varied qualitatively in accordance with the nuclear lifetime of $^{193}$Au. The PL band possessing a principal no-phonon line at 1161 nm (1066 meV), which has so far been assigned to a FeB pair [Sau85], has revealed evidence to be Au related, too. Firstly, whereas it has not appeared in lightly doped Si samples, it has shown to become stronger for increasing Au implantation doses. Furthermore, its intensity followed roughly the population of radioactive $^{193}$Au in the case of radioactive isotopes having been implanted. It should be noted that the involvement of further atoms in this center has been proposed before [Klu88]. Regarding Au involvement, the center known as the 735-meV band (principal no-phonon line at 1687 nm), has shown similar behaviour. So far, this band has been assigned to Fe by various
authors, e.g. \cite{Cal88, Sin95}, but not to Au. However, the results obtained in this work strongly indicate the involvement of Au in this center, too. These indications consist of its increasing intensity with growing Au implantation dose and its behaviour in terms of following the concentration of radioactive $^{193}$Au.

All the results obtained have only been interpreted qualitatively. Even though a quantitative interpretation similar to Magerle’s work \cite{Mag95b} has been attempted, no success has been obtained in this matter. Further experiments and more sophisticated modelling will be required. These experiments probably include uniform transition metal doping and the simulation of radioactive decay by implanting stable isotopes, despite the difficulties mentioned, which would accompany these experiments.

As regards the pairing of transition metal atoms with trace contaminants such as Li or Fe, some experiments have given hope to be helpful for obtaining deeper insights in this matter in future. Experiments helping to identify these complex partners might include deliberate co-doping of either stable or radioactive Li or Fe isotopes. In the case of light partners, a further possibility would comprise the detection of isotope shifts using high resolution FTPL.

Last, the combination of different techniques including DLTS and EPR, which has already been started, should be continued as additional information on the defects will be obtained. In this context, on-site PL measurements at ISOLDE would be advantageous so that changes over the full radioactive decay chain could be monitored.
Zusammenfassung


Bei der Identifizierung der durch Pt verursachten Energieniveaus konnten drei bekannte Rekombinationszentren beobachtet werden.

Die Intensität des PL-Bandes bei 1594 nm (777 meV) zeigte eine qualitative Abhängigkeit von der Pt-Dosis. Weiter trat ein Anwachsen der Intensität mit der charakteristischen Halbwertszeit des Mutterisotops $^{193}$Au im Falle von dem durch $^{193}$Pt verursachten Störstellenkomplex auf.

Dieses Anwachsen wurde für die beiden Rekombinationszentren mit Nullphononenlinien bei 1207 nm (1026 meV) bzw. 1402 nm (884 meV) nicht beobachtet. Jedoch zeigten beide Linien eine starke Abhängigkeit von der Implantationsdosis von stabilen Pt-Ionen. Auch nach Implantation von radioaktivem $^{191}$Hg nahmen die Linienintensitäten der entsprechenden Rekombinationskanäle mit der Halbwertszeit von $^{191}$Pt ab.


Bei der Untersuchung von Au-verursachten Störstellen wurden mehrere Ergebnisse erzielt.

Nach Implantation von stabilem Au und nachfolgendem Ausheilen des Implantations schadens konnte ein PL-Band bei 1583 nm (782 meV) beobachtet werden. Dieses Rekombinationszentrum wurde an anderer Stelle bereits nach Eindiffusion von Au beobachtet [Car89]. Nach Implantation von radioaktivem $^{193}$Hg nahm die Linienintensität mit der Halbwertszeit von $^{193}$Au ab.

Das PL-Band bei 1161 nm (1066 meV), welches bisher einem Fe-B Paar zugeschrieben wurde [Sau85], konnte auch in mit stabilen Au implantierten Proben beobachtet werden. Die Intensität wuchs mit steigender Au Dosis an. Die Linienintensität nahm nach Implantation von radioaktivem $^{193}$Hg mit der Halbwertszeit von $^{193}$Au ab. Die Beteiligung von weiteren Atomen außer Fe und B an diesem Komplex wurde bereits von anderen Autoren vorgeschlagen [Klu88].

zu dem Schluß, daß der entsprechende Komplex außer Fe- auch Au-Atome enthält. Dies wurde durch Experimente mit radioaktivem $^{193}\text{Au}$, das durch Implantation des Mutterisotops $^{193}\text{Hg}$ produziert wurde, bekräftigt. Die Intensität dieser PL-Linie nahm mit der Halbwertszeit von $^{193}\text{Au}$ ab.

Die Halbwertszeiten, die sich aus der Intensitätsänderung der jeweiligen PL-Linien ermitteln lassen, unterscheiden sich um bis zu einen Faktor 2 von den Halbwertszeiten der entsprechenden radioaktiven Isotope. Um diese Diskrepanz zu begründen, wurde ein von Magerle et al. [Mag95b] entwickeltes Zweischichtmodell des Fließgleichgewichts auf die hier vorliegende Situation angewandt. Die numerische Anpassung der bisher vorhergesagten PL-Intensitäten an die experimentellen Daten gelang aufgrund der großen Zahl freier Parameter nicht.

Bibliography


[Hen97] M. O. Henry, private communication.


