Surface photovoltage measurements on semiconductors

by

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Chapter 1

Introduction

Surface photovoltage (SPV) measurements allow the determination of the minority carrier diffusion length in semiconductors. However, the interpretation of the SPV data relies on accurately knowing the absorption coefficient of a material. Photoacoustic spectroscopy (PAS) allows the determination of the absorption coefficient.

In this thesis both SPV and PAS measurements are demonstrated using instruments and data acquisition software built at the Science Institute, University of Iceland. Chapter 2 introduces the basic concepts used in the following chapters. The theoretical model describing how the minority carrier diffusion length is determined by SPV measurements is the subject of chapter 3. Chapter 4 exhibits examples of measurements of the minority carrier diffusion length in several silicon (Si) and gallium arsenide (GaAs) samples. Also, it is demonstrated how the iron concentration in boron doped silicon is found by SPV.

In Chapter 5 we discuss how PAS could be used to measure the absorption coefficient in the wavelength region of relevance to SPV measurements. Also, we demonstrate PAS measurements on aluminum gallium arsenide (AlGaAs) epilayers grown on single crystalline GaAs by liquid phase epitaxy (LPE). We demonstrate how PAS can be used to determine the band edge of AlGaAs and we apply PAS to estimate the thickness of the AlGaAs epilayer. In chapter 6 SPV measurements of AlGaAs/GaAs heterostructures are presented. We examine how passivation with hydrogen reveals itself in the SPV spectra and use the results to predict the band structure at the heterojunction.
Chapter 2

Basics of semiconductor theory

This chapter introduces, concepts, symbols and equations to be used later on. The reader is assumed to be familiar with the subject and no attempt is made to derive these basic equations since that is the subject of numerous books on semiconductor- and solid state physics [1, 2, 3, 4].

2.1 Introduction

Let us consider a semiconductor with an energy gap of $E_g = E_c - E_v$, where $E_c$ is the lowest energy level of the conduction band and $E_v$ is the highest energy level of the valence band. When there are no energy levels within the energy gap the Fermi-level, $E_f$, is at its intrinsic value, $E_f = E_i$, close to the middle of the bandgap (see figure 2.1(a)). Also, the number of holes and electrons is the same in the valence and conduction band respectively.

Impurities and defects in the semiconductor may introduce energy levels within the bandgap. These levels are localized, unlike the energy levels of the conduction and valence band which extend through the whole sample. If the charge of an impurity is neutral when it is filled by an electron and positive when it is empty, the impurity-level is termed a donor. An energy level is termed an acceptor if the associated impurity is negatively charged when occupied by an electron, but has neutral charge when empty. An acceptor energy level, $E_a$, close to the valence band ($E_a - E_v \sim k_B T_{RT}$, where $T_{RT} = 300$ K is room temperature and $k_B$ is the Boltzmann constant) is known as a shallow acceptor. Similarly, a donor energy level, $E_d$, close to the conduction band ($E_c - E_d \sim k_B T_{RT}$) is known as a shallow donor.
Figure 2.1: Energy band diagrams of semiconductors. (a) $E_c$ is the bottom of the conduction band, $E_v$ is the top of the valence band and $E_f$ is the Fermi-level. Here, the position of the Fermi-level in the center of the bandgap indicates an intrinsic semiconductor. (b) In an $n$-type semiconductor shallow donor energy levels, $E_d$, contribute their electrons to the conduction band and the Fermi-level is in the upper half of the bandgap. (c) In $p$-type materials, shallow acceptor levels, $E_a$, create holes in the conduction band and the Fermi-level is located in the lower half of the bandgap.

If doping of a semiconductor produces shallow donors within the bandgap then, at room temperature, the donors will donate their electrons to the conduction band. The Fermi-level in this case is in the upper half of the bandgap, closer to the conduction band (see figure 2.1(b)). In a conduction process the negatively charged electrons in the conduction band act as charge carriers and the semiconductor is said to be of $n$-type.

Consider a semiconductor with shallow acceptors. At room temperature, electrons from the valence band will fill the acceptor levels, leaving behind vacancies. These vacancies, or holes, can be treated as mobile particles and since these have a positive charge, the semiconductor is called $p$-type. The Fermi-level of a $p$-type semiconductor will be in the lower half of the energy gap, close to the valence band (see figure 2.1(c)).
2.2 Semiconductors in thermal equilibrium

We now turn to the equations which govern the densities of carriers. In thermal equilibrium, electron and hole densities are given by

\[ n_0 = \int_{E_c}^{\infty} N_c(\epsilon) f(\epsilon) d\epsilon, \]
\[ p_0 = \int_{-\infty}^{E_v} N_v(\epsilon) (1 - f(\epsilon)) d\epsilon, \]

where \( N_c(\epsilon) \) and \( N_v(\epsilon) \) are the densities of states of electrons in the conductance band and the holes in the valence band, respectively. Here \( f(\epsilon) \) is the Fermi-Dirac distribution function given by

\[ f(\epsilon) = \frac{1}{e^{\beta(\epsilon-E_f)} + 1}, \]

where \( \beta = (k_B T)^{-1} \), \( E_f \) is the Fermi-level, \( k_B \) is the Boltzmann constant and \( T \) is the temperature. If the Fermi-level is not too close to the valence or conduction bands, that is \( E_c - E_f \gg k_B T \) and \( E_f - E_v \gg k_B T \), the integrals in equations (2.1) and (2.2) can be evaluated with

\[ n_0 \approx n_i e^{(E_f-E_i)\beta}, \]
\[ p_0 \approx n_i e^{(E_i-E_f)\beta}, \]

where \( E_i \) is the Fermi-level in an intrinsic semiconductor. Here, \( n_i \) is the electron (or hole) concentration in the intrinsic semiconductor given by

\[ n_i^2 = 4 \left( \frac{2\pi k_B T}{h^2} \right)^3 \left( m_n^* m_p^* \right)^{3/2} e^{-\beta E_g}, \]

where \( m_n^* \) and \( m_p^* \) are the effective masses of electrons and holes, respectively, and \( h \) is Planck’s constant. Table 2.1 shows the intrinsic carrier concentrations for silicon and gallium arsenide.

We note that from equations (2.4) and (2.5) we have the useful relation

\[ n_0 p_0 = n_i^2, \]

which reveals that for a \( n \)-type semiconductor \( n \gg p \), and vice versa for a \( p \)-type
semiconductor, where \( p \gg n \). This is the basis for the terminology of majority and minority carriers. In an \( n \)-type semiconductor electrons are majority carriers and holes are minority carriers, and vice versa in \( p \)-type material.

### 2.3 Current flow in semiconductors

An electric field \( \mathcal{E} \) in a semiconductor will accelerate a charge carrier (hole or electron) and this is known as drift. As the carrier drifts, it frequently collides with the lattice and thus slows down. The average velocity at which a hole drifts is

\[
\mathbf{v}_p = \mu_p \mathcal{E},
\]

where \( \mu_p \) is the hole mobility. The average velocity at which an electron drifts is

\[
\mathbf{v}_n = -\mu_n \mathcal{E},
\]

where \( \mu_n \) is the electron mobility.

If both electrons and holes are present, the current density due to drift is

\[
\mathbf{J}_{\text{drift}} = q(\mathbf{v}_p p - \mathbf{v}_n n) = q(\mu_p p + \mu_n n) \mathcal{E} = q\sigma \mathcal{E},
\]

where \( q \) is the absolute value of the electron charge and we define \( \sigma = q(\mu_p p + \mu_n n) \) as the electrical conductivity. We also define the electrical resistivity as \( \rho = \sigma^{-1} \).

The current density of electrons \( \mathbf{J}_n \) is due to both drift and diffusion. This is described by

\[
\mathbf{J}_n = q\mu_n n \mathcal{E} + qD_n \nabla n, \tag{2.8}
\]

where \( D_n \) is the diffusion constant for electrons and \( \nabla n \) is the electron density gradient. For holes we have equivalently

\[
\mathbf{J}_p = q\mu_p p \mathcal{E} - qD_p \nabla p, \tag{2.9}
\]

where \( D_p \) is the diffusion constant for holes. Typical values for the diffusion constants
for silicon and gallium arsenide are given in Table 2.1.

The diffusion constant and the mobility obey the Einstein relation

\[
\frac{D_x}{\mu_x} = \frac{k_B T}{q},
\]

(2.10)

where the subscript \( x \in \{ n, p \} \) indicates holes or electrons.

When carrier concentrations deviate from the thermal equilibrium values, processes of electron-hole recombination attempt to restore the concentrations to their equilibrium values. This can result in photon generation (radiative process) or phonon creation (non-radiative process) or both. The continuity equation for electrons is

\[
\frac{\partial n}{\partial t} = G - R_n + \frac{1}{q} \nabla \cdot \mathbf{J}_n
\]

(2.11)

and for holes we have

\[
\frac{\partial p}{\partial t} = G - R_p - \frac{1}{q} \nabla \cdot \mathbf{J}_p,
\]

(2.12)

where \( G \) is the generation rate and \( R_n \) and \( R_p \) are the recombination rates for

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Si</th>
<th>GaAs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap</td>
<td>( E_g ) (eV)</td>
<td>1.12</td>
<td>1.43</td>
</tr>
<tr>
<td>Intrinsic carrier concentration</td>
<td>( n_i ) (cm(^{-3}))</td>
<td>( 1.45 \times 10^{10} )</td>
<td>( 1.79 \times 10^6 )</td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>( \varepsilon_r )</td>
<td>11.9</td>
<td>13.18</td>
</tr>
<tr>
<td>Electron mobility</td>
<td>( \mu_n ) (cm(^2)/(Vs))</td>
<td>( \sim 1450 )</td>
<td>( \sim 8500 )</td>
</tr>
<tr>
<td>Hole mobility</td>
<td>( \mu_p ) (cm(^2)/(Vs))</td>
<td>( \sim 450 )</td>
<td>( \sim 400 )</td>
</tr>
<tr>
<td>Electron diffusion constant</td>
<td>( D_n ) (cm(^2)/s)</td>
<td>( \sim 37 )</td>
<td>( \sim 219 )</td>
</tr>
<tr>
<td>Hole diffusion constant</td>
<td>( D_p ) (cm(^2)/s)</td>
<td>( \sim 13 )</td>
<td>( \sim 10 )</td>
</tr>
</tbody>
</table>

Table 2.1: Typical material characteristics for silicon and gallium arsenide at room temperature [4]. The mobility and the diffusion constant obey the Einstein relation (equation (2.10)) and their exact values vary from sample to sample.
electrons and holes respectively. The recombination rates are given by

\[ R_n = \frac{\Delta n}{\tau_n}, \]  
\[ R_p = \frac{\Delta p}{\tau_p}, \]  

where \( \Delta n \) and \( \Delta p \) are the excess carrier concentrations and \( \tau_n \) and \( \tau_p \) are the excess carrier lifetimes of electrons and holes. The carrier lifetime is the average time a carrier will exist, from the moment it is created (by light absorption, for example) to the moment it is annihilated by recombination. Note that in our model, recombination rates are governed by carrier lifetimes, which include all possible recombination processes.

If we ignore drift, we may combine equations (2.8), (2.9), (2.11), and (2.12) to form the diffusion equations

\[ \frac{\partial n}{\partial t} = -\frac{n - n_0}{\tau_n} + D_n \nabla^2 n, \]  
\[ \frac{\partial p}{\partial t} = -\frac{p - p_0}{\tau_p} + D_p \nabla^2 p, \]

where \( n = n_0 + \Delta n \) and \( p = p_0 + \Delta p \) are the non-equilibrium electron and hole carrier concentrations, respectively. In the steady state case, time derivatives are zero and the above equations become

\[ \nabla^2 n = \frac{n - n_0}{D_n \tau_n} = \frac{n - n_0}{L_n^2}, \]  
\[ \nabla^2 p = \frac{p - p_0}{D_p \tau_p} = \frac{p - p_0}{L_p^2}, \]

where we have defined the excess carrier diffusion lengths as

\[ L_n = \sqrt{D_n \tau_n} \]  
\[ L_p = \sqrt{D_p \tau_p}. \]

Here \( L_n \) and \( L_p \) are the diffusion lengths of electrons and holes, respectively. The excess carrier diffusion length is the average distance an excess carrier will travel,
from the moment of creation, to the moment it recombines.

Carrier lifetimes and diffusion lengths are very dependent on the purity of the semiconductor. For gallium arsenide the minority carrier diffusion length is often of the order of $L \approx 0.5\, \mu m$ and in silicon it is often of the order of $L \approx 100\, \mu m$.

Let us consider what happens when both excess electrons and excess holes are present and both diffuse down a concentration gradient. This can occur for example when a semiconductor is exposed to a high flux of photons, which energy exceeds the bandgap. Due to the fact that the effective mass of electrons is larger than the effective mass of holes, electrons will diffuse more rapidly than holes. A charge imbalance is developed, resulting in an electric potential drop along the direction of diffusion. This is known as the Dembker potential. If we suppose that one side of the semiconductor is illuminated with photons whose energy exceeds the band gap and that $L_n$, $L_p$, and $\alpha^{-1}$ all are small compared with the sample thickness $d$ (here $\alpha$ is the absorption coefficient) the Dembker potential is given by [3]

$$V \approx G \frac{k_B T}{q} \cdot \frac{\mu_n - \mu_p}{n \mu_n + p \mu_p} \cdot \frac{1}{\sqrt{D_a/\tau_a + S}}, \quad (2.21)$$

where $G$ is the generation rate, $S$ is the recombination velocity of the front or back surface of the semiconductor (assumed to be the same). Here $D_a$ and $\tau_a$ are the ambipolar diffusion coefficient and ambipolar lifetime, respectively, defined as

$$D_a = \frac{(n + p)D_n D_p}{n D_n + p D_p}, \quad (2.22)$$

$$\tau_a = \frac{(n + p)\tau_n \tau_p}{n \tau_n + p \tau_p}. \quad (2.23)$$

We define the ambipolar diffusion length as

$$L_a = \sqrt{D_a \tau_a}. \quad (2.24)$$

### 2.4 The semiconductor surface

The abrupt end of the lattice and the presence of impurities at the surface introduces many new energy levels within the bandgap. As the surface states become filled (or emptied) a surface charge is formed, $Q_{surf}$. This surface charge is exactly balanced by a space charge $Q_{space}$. If the surface charge is negative, the space charge is formed
Figure 2.2: Band structure near the semiconductor surface for (a) depletion, (b) inversion and (c) accumulation. The density of acceptor or donor levels at the surface, \( N_s \), is represented by the curves marked \( A_s \) and \( D_s \), respectively.
2.4 The semiconductor surface

![Graph showing the relationship between $L_1^{\text{max}}$ and $n_0$]

**Figure 2.3:** The upper limit of the depletion region at the surface, $L_1^{\text{max}}$, for an n-type semiconductor (see equation (2.25)) as a function of majority carrier concentration. The solid line shows $L_1^{\text{max}}$ for silicon and the dashed line is for gallium arsenide.

by non-mobile positive ions and thus it extends into the sample. The electric field between the space charge and the surface charge results in band bending at the surface.

Consider the surface of an n-type semiconductor. Depending on the type of surface-defects (acceptors or donors) and the location of their energy levels, three different types of surface band bending are identified:

**A depletion layer** is formed if the surface is governed by acceptors near the middle of the band gap, see figure 2.2(a).

**An inversion layer** is formed if the density of acceptors at the surface is forces the Fermi-level towards the valence band, see figure 2.2(b).

**An accumulation layer** is formed if there are empty donor states at the surface, see figure 2.2(c).

The maximum size of the depletion region at the surface for an n-type semiconductor is given by [1]

$$L_1 = \sqrt{\frac{2\epsilon_0\epsilon_r(V_0 - k_B T/q)}{nq}} < \sqrt{\frac{2\epsilon_0\epsilon_rE_g}{nq^2}},$$

(2.25)
where \( \varepsilon_0 \) is the permittivity of vacuum, \( \varepsilon_r \) is the dielectric constant. This is shown in figure 2.3.

### 2.5 Reaction dynamics

We now consider the simple chemical reaction

\[
A + B \to C. 
\]

(2.26)

If the reaction is obeys first order kinetics, the concentration of \( A \), \( [A] \) is given by

\[
\frac{d [A]}{dt} = -k[A][B],
\]

(2.27)

where \( k \) is the rate constant. It can be shown [5] that the rate constant is given by

\[
k = A e^{-\frac{E_a}{k_B T}}
\]

(2.28)

where \( A \) may sometimes be temperature dependent and \( E_a \) is the activation energy for the reaction in (2.26).

The one-dimensional concentration profile of species \( A \) obeys Fick’s second law

\[
\frac{\partial [A]}{\partial t} = D_A \frac{\partial^2 [A]}{\partial x^2},
\]

(2.29)

where \( D_A \) is the chemical diffusion constant for species \( A \) given by

\[
D_A = D_{A0} e^{-\frac{E_a}{k_B T}}.
\]

(2.30)

We see that the rate constant and diffusion constant are proportional, if \( A \) and \( D_{A0} \) are temperature independent.
Chapter 3

Theory of surface photo-voltage

3.1 Introduction

Surface photo-voltage (SPV) refers to the modulation of the band bending of a semiconductor surface by illumination. SPV is mainly used to determine the minority carrier diffusion length in semiconductors. The minority carrier diffusion length is a strong function of the concentrations of crystal defects and impurities. Thus SPV is extensively used in quality control measurements mostly by detecting iron concentrations in boron doped silicon for integrated circuit manufacturing. Furthermore minority carrier diffusion length has been widely used to characterize the quality of silicon material before it is processed into solar cells, because it provides a prediction of the energy conversion efficiency which may be attained in the final product [6]. The American Society for Testing and Materials has released standards regarding test methods for minority carrier diffusion length measurements in extrinsic semiconductors by measurement of steady-state SPV [7].

SPV has been found to agree with other methods that measure minority carrier diffusion length and minority carrier recombination life time, for example photoconductive decay (PCD) measurements [8]. Another common way to measure minority carrier diffusion lengths is to measure the current response of a Schottky barrier to the electron beam of a scanning electron microscope (SEM) and these are known as electron beam induced current (EBIC) measurements [9]. Not only do EBIC measurements require the formation of a Schottky barrier but they are also destructive and the size of the injection region, which is often of the order of 1 μm, limits the minimum diffusion length that can be measured. SPV measurements
suffer none of these disadvantages.

### 3.1.1 Origins of the surface photo-voltage

Light of wavelength $\lambda < \frac{h}{E_g}$ passing through a semiconductor is absorbed by the material and this is described by the absorption coefficient $\alpha$ which is a function of the photon energy. Absorbed photons produce excess carriers (holes and electrons) inside the semiconductor which drift and diffuse until they recombine. Let us suppose that the semiconductor is $p$-type and that the light intensity is low enough that we can ignore the Dember potential (see section 2.3) and focus our discussion only on minority carrier diffusion. Figure 3.1(a) shows a minority carrier introduced into the conduction band when light is absorbed. One side of the sample is illuminated with photons of energy which exceeds the bandgap. The minority carrier diffusion length $L_n$ is a statistical average of the distance which a minority carrier will travel from the point where it is created to the point where it recombines with a majority carrier as seen in figure 3.1(b). Figure 3.1(c) shows the photon flux $\Phi$ as a function of position $x$ inside the sample. The generation term in the continuity equation (see equations (2.11) and (2.12)) is equal to the negative gradient of the photon flux. The photon flux is given by

$$\Phi(x) = \Phi_{\text{eff}} e^{-\alpha x},$$

(3.1)

where $\alpha$ is the absorption coefficient and $\Phi_{\text{eff}}$ is the effective photon flux into the sample given as

$$\Phi_{\text{eff}} = (1 - \tilde{R}) \eta \Phi_0$$

(3.2)

and $\tilde{R}$ is the reflection coefficient of the semiconductor, $\eta$ is the quantum efficiency and $\Phi_0$ is the photon flux onto the sample.

The surface of the semiconductor has a high density of defects and impurities that introduce energy states within the bandgap. Due to a combination of electrostatics and statistical mechanics a depletion region at the surface is formed. Figure 3.2(a) shows the band structure near the surface of a $p$-type semiconductor in thermal equilibrium. The depletion layer is of width $L_1$ and the potential shift is $V_0$. Some minority carriers that are formed within the semiconductor diffuse into the depletion region and are caught by the electric field. This changes the band bending near the
Figure 3.1: (a) Band structure of a p-type semiconductor. A minority carrier (electron in the conduction band) is formed when light is absorbed. On the average it moves the distance $L_n$ before recombining with a hole. (b) A cross section through a semiconductor sample of thickness $d$. At the surface an electric field forms a depletion region which extends the distance $L_1$ into the sample. The left side of the sample is illuminated with photons with energy above the bandgap of the semiconductor. (c) Photon flux $\Phi(x) = \Phi_0 e^{-\alpha x}$ as a function of $x$ inside the sample.
semiconductor surface. Figure 3.2(b) shows the change in band bending $\Delta V$ that occurs when excess minority carriers reach the surface. This is the origin of the surface photo-voltage (SPV).

### 3.1.2 Detection of SPV

In practice the SPV signal is measured by exposing one side of a semiconductor sample with chopped light thus producing a small time-periodic voltage across the sample. These voltage oscillations are capacitively measured by placing a transparent, conducting electrode very close ($\sim 20 \mu m$) to the illuminated side of the sample and another electrode in contact with the dark side (see figure 3.3). The transparent electrode and the illuminated side of the sample form a parallel plate capacitor. Illumination levels are kept low and the AC-voltage (measured using a lock-in amplifier) across the semiconductor is usually in the range of 1 $\mu V$ to 100 $\mu V$. In figure 3.4 we see a simple circuit diagram of a SPV measurement. The signal originates inside the sample (SPV) and the sample and the transparent conducting electrode act as a parallel plate capacitor $C_1$. Cable capacitance is represented by $C_2$ and a lock-in amplifier (LIA) is used for signal detection.

### 3.2 Goodman’s model of SPV

First we review the original SPV theory of Goodman [10]. It describes how the minority carrier diffusion length in extrinsic semiconductors can be determined by SPV measurements. Suppose that we have a $p$-type semiconductor that is subject to low intensity illumination of wavelength $\lambda$ on one side. We assume that the following statements are true

\[
p \gg n, \quad (3.3)\]
\[
p \gg \Delta n \quad (3.4)\]
\[
d \gg \alpha^{-1} \gg L_1, \quad (3.5)\]
\[
d \gg L_n \gg L_1, \quad (3.6)\]

where $n$ and $p$ are electron and hole concentrations during illumination, $\Delta n$ is the excess electron concentration, $d$ is the sample thickness, $\alpha$ is the absorption coef-
Figure 3.2: (a) Band structure near the surface of a p-type semiconductor in thermal equilibrium. Defects at the surface produce energy states within the bandgap which result in an depletion layer of width \( L_1 \) and potential shift \( V_0 \). (b) When exposed to low illumination, minority carriers are formed within the semiconductor. Some of them diffuse into the depletion region and are caught by the electric field. This changes the charge at the surface and decreases band bending. The change in band bending is the surface photo voltage (SPV) \( \Delta V \).
Figure 3.3: The basic geometry of a SPV experiment. A semiconductor (b) of thickness $d$ is placed between two conducting layers (a) and (c). Light passes through the transparent layer (a) and is absorbed within the sample. The space between the transparent conducting layer and the semiconductor sample is filled with a transparent dielectric of thickness $d_{\text{mica}}$ (not shown). The dielectric of choice is often mica or air.

Figure 3.4: A simple circuit diagram of a SPV measurement. The SPV signal originates inside the sample. The sample and the transparent conducting electrode act as a parallel plate capacitor $C_1$. Cable capacitance is represented by $C_2$ and a lock-in amplifier (LIA) is used for signal detection.
3.2 Goodman’s model of SPV

Sufficient, \( L_1 \) is the depth to which band bending due to surface states extends, and \( L_n \) is the diffusion length of minority carriers. The first inequality (3.3) is only to ensure that we have an extrinsic semiconductor. The inequality (3.4) requires the illumination level be low enough for the majority carrier concentration not to be effected. This allows us to concentrate on minority carriers exclusively. The left inequality in (3.5) guarantees that light never reaches the unilluminated side of the sample. This, along with the left inequality in (3.6), assures that no minority carriers reach the dark side of the sample. The right inequality in (3.5) allows us to ignore carrier generation within the depletion region at the surface.

Inside the sample, the excess minority carrier concentration \( \Delta n(x, t) \) is governed by the diffusion equation

\[
\frac{\partial \Delta n}{\partial t} = G - R + D_n \frac{\partial^2 \Delta n}{\partial x^2},
\]

where \( G \) and \( R \) are the generation and recombination terms respectively given by

\[
G = \Phi_{\text{eff}} \alpha e^{-\alpha x},
\]

\[
R = \frac{\Delta n}{\tau_n},
\]

and \( \Phi_{\text{eff}} \) is the effective photon flux into the sample (see equation (3.2)), \( D_n \) is the minority carrier diffusion coefficient and \( \tau_n \) is the minority carrier lifetime. A time independent solution of equation (3.7) is

\[
\Delta n(x) = \frac{\Phi_{\text{eff}} \alpha^{-1}}{D_n(1 - \frac{\alpha}{\alpha^*})} \left( c_+ e^{x/L_n} + c_- e^{-x/L_n} - e^{-\alpha x} \right),
\]

where \( L_n = \sqrt{D_n \tau_n} \) is the minority carrier diffusion length and \( c_+ \) and \( c_- \) are constants.

Using the left side inequalities in (3.5) and (3.6) we find that \( c_+ = 0 \) and this insures that there are no contributions from the dark surface. By imposing the boundary condition

\[
S \Delta n(0) = D_n \frac{\partial \Delta n}{\partial x}(0),
\]

(3.11)
where \( S \) is the recombination velocity at the surface, we determine \( c_- \) and find that

\[
\Delta n(x) = \frac{\Phi_{\text{eff}}}{D_n(1 - \frac{1}{\alpha^2 L^2})} \left( \frac{L_n}{L_n + D_n/S} \alpha^{-1} + \frac{D_n/S}{L_n + D_n/S} e^{-x/L_n} - \alpha^{-1} e^{-\alpha x} \right).
\]  

(3.12)

At the edge of the depletion zone we have \( x = L_1 \) (see figure 3.2) and using the right side inequalities in (3.5) and (3.6) the above equation becomes

\[
\Delta n(L_1) = \frac{\Phi_{\text{eff}} L_n^2}{(D_n + L_n S)(L_n + \alpha^{-1})}.
\]  

(3.13)

Let \( \Delta V \) be the change in band bending at the surface due to excess minority carriers which reach the surface. We now assume that \( \Delta V \) is a monotonic function \( f \) of \( \Delta n(L_1) \)

\[
\Delta V = f(\Delta n(L_1)).
\]  

(3.14)

There have been many theoretical simulations of the function \( f(\Delta n(L_1)) \) \[11, 12, 13\] and they reveal very complex behavior for different surface conditions, but for low excitation levels small changes in \( \Delta n(L_1) \) will leave \( f(\Delta n(L_1)) \) monotonic. For small enough \( \Delta n(L_1) \) we would expect \( f(\Delta n(L_1)) \) to be linear and that would imply the relation

\[
\frac{\Phi_{\text{eff}}(\lambda)}{\Delta V(\lambda)} \propto L_n + \alpha^{-1}(\lambda).
\]  

(3.15)

Note that the intersection with the abscissa is the negative minority carrier diffusion length, \(-L_n\).

If we relax the assumption of \( f \) being linear to only being monotonic we can invert \( f \) and write equation (3.13) as

\[
\frac{\Phi_{\text{eff}} L_n^2}{(D_n + L_n S)(L_n + \alpha^{-1})} = f^{-1}(\Delta V),
\]  

(3.16)

which, for constant \( \Delta V \), reveals a linear relationship between \( \Phi_{\text{eff}} \) and \( \alpha^{-1} \)

\[
\Phi_{\text{eff}}(\lambda) \propto L_n + \alpha^{-1}(\lambda),
\]  

(3.17)

where the intersection with the abscissa is \(-L_n\).
3.2 Goodman’s model of SPV

3.2.1 Constant flux or constant voltage: Methods A and B

In 1990 the ASTM standard [7] described two methods which apply SPV measurements to determine minority carrier diffusion lengths, methods A and B.

A For varying $\alpha^{-1}(\lambda)$, $\Phi_{\text{eff}}$ is measured for constant $\Delta V$. A plot of $\Phi_{\text{eff}}(\lambda)$, as a function of $\alpha^{-1}(\lambda)$ gives a straight line that intersects the abscissa in $-L_n$, see equation (3.17). Here it is sufficient that $\Delta V$ is a monotonic function of $n(0)$.

B For varying $\alpha^{-1}(\lambda)$, $\Delta V$ is measured for constant $\Phi_{\text{eff}}$. A plot of $\Delta V^{-1}(\lambda)$ as a function of $\alpha^{-1}(\lambda)$ gives a straight line that intersects the abscissa in $-L_n$, see equation (3.15). In order for this method to be valid we require $\Delta V \propto n(0)$.

Theoretical arguments for method A are found in Goodman’s theory but method B had been used for years without rigorous theoretical support until the work of Liu et al. [14, 15]. The practical difference between the two methods resides in that using method B one can design a measuring apparatus that, once calibrated, does not require measuring the light flux. This allows a simpler experimental setup, faster measurements and is more convenient when studying samples with different surface conditions.

Let us assume that $L^*$ is a diffusion length found by SPV measurements using method A or B. For $L^*$ to be a valid measure of the bulk minority carrier diffusion length the following conditions must be met [7, 16].

1. The sample is homogeneous with respect to minority carrier recombination.
2. Minority carrier transport is due to diffusion and not drift.
3. Effects of majority carriers can be neglected.
4. The illuminated surface area is large compared to the cross section of the light beam at the sample surface so the one-dimensional model is plausible.
5. The back side does not contribute to the measured surface photo voltage, see equations (3.5) and (3.6).
6. The relationship between $\Phi_{\text{eff}}$ and $\Delta V$ is linear (method B).
7. The SPV voltage $\Delta V$ is less than $k_B T / e$ [7].
8. The reflection coefficient $\tilde{R}(\lambda)$ is known (or is constant) for the wavelengths of interest.

9. Surface recombination velocity $S$ and the minority carrier diffusion length $L_n$ are constant during the measurement.

10. The absorption coefficient $\alpha$ is known as a function of the wavelength $\lambda$.

### 3.2.2 Extension of Goodman’s model

There have been attempts to extend the standard theory so that SPV measurements can be used to determine the minority carrier diffusion length of “thin” samples, where $d \approx L_n$ [16, 17]. If we allow minority carriers to reach the unlit surface, we can no longer assume that $c_m$ in equation (3.10) is zero. Let $S'$ be the recombination velocity at the back surface, defined in a similar manner as the recombination velocity at the front surface, $S$ (see equation (3.11)). If the SPV voltage is proportional to the density of minority carriers that reach the front surface and we neglect the width of the depletion region we find [17]

$$\frac{\Delta V}{\Phi_{\text{eff}}} \propto \frac{1}{1 - \frac{1}{\alpha^{-1}L_n}} \left(1 - \frac{B}{\alpha^{-1}L_n}\right) \quad (3.18)$$

where

$$B = \frac{D_n S'}{L_n S} \frac{\sinh \frac{d}{L_n} + \cosh \frac{d}{L_n}}{\sinh \frac{d}{L_n} + \frac{D_n}{L_n S} \cosh \frac{d}{L_n}}. \quad (3.19)$$

Equation (3.18) reduces to the classical result of equation (3.15) when $B = 1$, that is when $d \gg L_n$.

### 3.3 SPV in SI-GaAs

In semi-insulating gallium-arsenide (SI-GaAs) little band bending is expected near the surface. This is because the bulk value of the Fermi-level is close to the intrinsic value at the center of the bandgap. In Goodman’s theory, the SPV signal is due to a decrease in band bending at the surface. Thus we expect small a SPV signal where band bending in small. However, in disagreement with conventional SPV
theory, large SPV signals are measured. The strong SPV signal from SI-GaAs is of a different origin than the one found in doped semiconductors. It is attributed to the Dember potential, which in turn is caused by differences in mobility (or effective mass) of electrons and holes.

Following Liu [15] we find that the the SPV signal in SI-GaAs is

$$\Delta V = \frac{k_B T (\mu_n - \mu_p)}{\sigma_0} \cdot \frac{\Phi_{\text{eff}} \alpha L_a}{(S_0 + D_a/L_a)(1 + \alpha L_a)}, \quad (3.20)$$

where $\mu_n$ and $\mu_p$ are the mobilities of electrons and holes respectively, $\sigma_0 = q(\mu_n n_0 + \mu_p p_0)$ is the dark conductivity where, $n_0$ and $p_0$ are the dark carrier concentrations and $S_0$ is the surface recombination velocity defined by

$$D_a \frac{d\Delta n}{dx} = S_0 \Delta n. \quad (3.21)$$

Also, $L_a = \sqrt{D_a \tau_a}$ is the ambipolar diffusion length where $D_a$ and $\tau_a$ are the ambipolar diffusion constant and the ambipolar lifetime, respectively (see section 2.3). In this model the additional assumption to the ones made in section 3.2.1 is that the native surface electrostatic field is negligible.

In a similar manner to Goodman’s model of SPV (equation (3.15)) this model reveals a linear relationship between $\Phi_{\text{eff}}/\Delta V$ and $\alpha^{-1}$

$$\frac{\Phi_{\text{eff}}}{\Delta V} \propto L_a + \alpha^{-1}, \quad (3.22)$$

where the intersection with the abscissa is the negative ambipolar diffusion length $-L_a$.

### 3.4 Iron in boron doped silicon

It is well known that SPV can be used to determine the concentration of iron [Fe] in boron doped silicon, Si:B [18, 17]. Boron is a shallow acceptor ($E_a = E_v + 0.045$ eV) thus leading to $p$-type silicon. Interstitial iron ions $\text{Fe}^+_i$ form FeB pairs with $\text{B}^-$ according to

$$\text{Fe}^+_i + \text{B}^- \rightleftharpoons \text{FeB}^{0/+} \quad (3.23)$$
which is a reversible reaction for temperatures up to 250 °C. Positively charged iron ions are deep donors in silicon with an impurity level at $E_v + 0.4$ eV, but FeB is a rather shallow donor at $E_v + 0.1$ eV. The deep level of Fe$^{+2}_d$ is a ten times more active recombination center than the shallow donor of the FeB complex [18].

At room temperature nearly all iron atoms are bound in FeB pairs. Heating Si:B above 210 °C for five minutes dissociates almost all the FeB pairs, decreasing the minority carrier diffusion length. Using the Shockley-Read recombination model, it can be shown that the iron concentration in silicon is given by

$$[\text{Fe}] = D_n \left( \frac{1}{L_1^2} - \frac{1}{L_0^2} \right) \left( C_n(\text{Fe}_i) - \frac{C_n(\text{FeB})}{\exp[(E_f - 0.1 \text{ eV})/k_BT]} \right)^{-1}, \quad (3.24)$$

where $D_n = 37$ cm$^2$/s is the electron diffusion coefficient at room temperature, $L_0$ is the electron diffusion length before annealing, $L_1$ is the electron diffusion length after annealing and $C(\text{Fe}_i)$ and $C(\text{FeB})$ are the capture coefficients of Fe$^+_i$ and FeB respectively. The capture coefficients have been determined by deep level transient spectroscopy (DLTS) resulting in the convenient equation

$$[\text{Fe}](\text{cm}^{-3}) = 1.05 \times 10^{16} \left( \frac{1}{L_1^2} - \frac{1}{L_0^2} \right), \quad (3.25)$$

where $L_1$ and $L_0$ are given in microns [18].

The detection limit of the SPV method when measuring changes in iron concentration can be estimated by

$$\delta[\text{Fe}] = \frac{2D_n \delta L_n}{C \cdot v L_n^2 L_n}, \quad (3.26)$$

where $C$ is the capture cross section and $v$ is the thermal velocity. Following Lagowski et al. [17] and using $C \cdot v = 6 \times 10^{-7}$ cm$^3$s$^{-1}$, $D_n = 37$ cm$^2$/s, $L_n = 300$ μm and $\frac{\delta L_n}{L_n} = 5\%$, we get $\delta[\text{Fe}] \approx 10^{10}$ cm$^{-3}$. Practical sensitivity limit is reported at $\delta[\text{Fe}] \approx 2 \times 10^{11}$ cm$^{-3}$ while the detection of iron in silicon with ion-beam techniques like secondary-ion-mass spectroscopy (SIMS) or Rutherford backscattering (RBS) is limited to $10^{12}$ cm$^{-3}$ [18].

The iron-boron complex is not the only complex observed by SPV measurements. Annealing at 210 °C can make other metals (nickel, chromium) show effects similar to the iron-boron complex [17]. For the chromium-boron pairs however the diffusion length increases after pair dissociation and the equivalent to equation (3.25)
becomes [19]

$$[\text{Cr}_i](\text{cm}^{-3}) = 10^{16} \times \left( \frac{1}{L_0^2} - \frac{1}{L_1^2} \right).$$

(3.27)

In order to distinguish these metals from iron one must revert to other methods, such as DLTS. SPV measurements observing the formation of copper-boron pairs in Si:B have been reported [6] as well.
Chapter 4

Examples of SPV measurements

4.1 Introduction

Iron is a metal impurity that plays a major role in limiting the yield in integrated circuit fabrication. Surface photo-voltage (SPV) measurements are widely used for wafer-scale diffusion length mapping and micro-contamination studies and it is currently the most convenient technique available to monitor iron in boron doped silicon. SPV is non-destructive, requires little preprocessing of the samples and has been studied extensively [15, 18, 20]. Section 4.2 is a detailed walk-through of SPV measurements of Si:B. In section 4.3 SPV measurements of SI-GaAs and $n$-type GaAs are presented and used to find ambipolar and minority carrier diffusion lengths. The results are compared to known values in the literature to demonstrate the functionality of our SPV system.

4.2 Iron concentration in Si:B

In this section we examine in detail the procedure involved in measuring iron concentrations in boron doped silicon. A sample labeled S1 was a part of an as-grown wafer the properties of which are listed in table 4.1. The wafer was intended for device processing so we expected iron concentrations below $5 \times 10^{12}$ cm$^{-3}$ [18].

One has the option of etching the sample before the SPV measurements, but in this case it was not found to be necessary (for more details on etching see appendix A). We used the ASTM method B [7] to find the minority carrier diffusion length. Thus, the first step was to measure the SPV signal $\Delta V$ as a function of
4.2 Iron concentration in Si:B

<table>
<thead>
<tr>
<th>Property</th>
<th>Symbol</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>$d$</td>
<td>$350 , \mu m$</td>
</tr>
<tr>
<td>Hole concentration</td>
<td>$p_0$</td>
<td>$3 \times 10^{15} , \text{cm}^{-3}$</td>
</tr>
</tbody>
</table>

**Table 4.1:** Properties of the boron doped silicon sample S1 at room temperature.

light flux $\Phi$. In figure 4.1 we see that only for very low light intensity is there a linear relationship between $\Delta V$ and the light-diode current $I(\Phi)$. Judging from the graph we choose to make our measurements with the current from the light-diode $I(\Phi) \approx 5 \, \text{nA}$. The precise value of the current depends on the spectral behavior of the light-diode and the beam splitter, both of which have been determined beforehand (see appendix A). The result is constant photon flux $\Phi_{\text{eff}}$ into the sample for all wavelengths.

An empirical formula for the reflection coefficient $\tilde{R}(\lambda)$ of polished silicon surfaces with native oxide is given by [7]

$$1 - \tilde{R}(\lambda) = 0.6786 + 0.03565 \lambda^{-1} - 0.03149 \lambda^{-2} \quad (4.1)$$

and is shown in figure 4.2. The reflection coefficient varies less than 1% over the wavelength interval of interest and its effect is marginal.

Figure 4.3 shows the light penetration depth $\alpha^{-1}$ as a function wavelength. The absorption coefficient used here is the relation published by Nartowicz and Goodman [21]

$$\alpha^{-1} = (84.732/\lambda - 76.417)^{-2}, \quad (4.2)$$

which is valid in the wavelength region of $\lambda \in [0.7 \, \mu \text{m}, \ 1.04 \, \mu \text{m}]$. For more discussion on the choice of absorption coefficient data, see chapter 5. Figure 4.4 shows typical SPV spectra measured at constant photon flux. The light intensity is kept low enough for $\Delta V$ to be a linear function of the photon flux $\Phi_{\text{eff}}$ ($I(\Phi) \approx 5 \, \text{nA}$) and at the same time $\Phi_{\text{eff}}$ is kept constant within $\pm 1\%$ for all wavelengths.

Expecting the linear relationship predicted by equation (3.17), we combine the data in figures 4.3 and 4.4 and plot $\Phi_{\text{eff}}/\Delta V$ as a function of $\alpha^{-1}$ in figure 4.5. The
Figure 4.1: SPV signal $\Delta V$ as a function of the current from light-diode $I(\Phi)$ for sample S1. Here the wavelength is constant $\lambda = 850$ nm and the modulation frequency is $f = 186$ Hz. The inset shows an enlargement of the region marked by the dotted box.

Figure 4.2: The change in reflection coefficient $\tilde{R}(\lambda)$ can affect SPV measurements. Shown here is $1 - \tilde{R}$ for polished silicon surfaces (see equation (4.1)) but the change is less than 1% over the wavelength interval of interest.
deviation from linearity can in part be attributed to any of the following:

- The light-diode, the beam splitter and the reflection coefficient all have known spectral dependencies. An attempt is made to compensate for all of these during the determination of the incident light intensity (see appendix A for experimental details) but this is a source of uncertainty.

- Goodman’s theory does not apply unless both the light penetration depth and minority carrier diffusion length are (much) less than the sample thickness (equations (3.5) and (3.6)). Based on these assumptions the theory assumes that no carriers reach the back surface.

- Using equation (4.2) is an approximation and ideally one would measure the absorption coefficient (see chapter 5).

The thickness of our particular sample is \( d = 350 \mu m \). We try to fulfill equation (3.5), \( d \gg \alpha^{-1} \), by choosing our maximum light penetration depth to be approximately \( d/4 \approx 87 \mu m \). The thickness of the space charge region at the surface is approximately \( L_1 \approx 1 \mu m \), found using figure 2.3 with a majority carrier concentration of \( p_0 = 3 \times 10^{15} \text{ cm}^{-3} \). Thus we comply to equation (3.5), \( \alpha^{-1} \gg L_1 \), by choosing our minimum light penetration depth larger than \( 10 \times L_1 \approx 10 \mu m \). From figure 4.3 we see that this is fulfilled in wavelength interval \( \lambda \in [880 \text{ nm}, 950 \text{ nm}] \) and this is the interval where we choose to make our linear fit. We find the minority carrier diffusion length to be \( L_n = 112 \mu m \pm 10 \mu m \), as seen in figure 4.5.

Having found the minority carrier diffusion length, equation (3.6) sets restrictions on whether the measurement is valid or not. Indeed we do comply to the right side of equation (3.6), \( L_n \gg L_1 \). The left side of equation (3.6), \( d \gg L_n \), is barely fulfilled. This might explain the gradual deviation from linearity observed in figure (4.5). However using the model described in section 3.2.2 gives a good fit and the same result in \( L_n \).

Sample S1 was annealed at 210 °C for five minutes and then quenched in LN₂. The minority carrier diffusion length \( L_n \) was measured immediately after quenching and then again repeatedly for 10 h. Figure 4.6 shows \( L_n \) as a function of time \( t \). Points at \( t = 0 \) h are measured before annealing and timing starts the moment the sample is brought from 77 K to room temperature. In figure 4.7 interstitial

\(^1\)Here the uncertainty was determined by repeating measurement three times.
Figure 4.3: $\alpha^{-1}$ as a function of $\lambda$ for silicon as described by equation 4.2.

Figure 4.4: SPV signal $\Delta V$ as a function of $\lambda$ for sample S1. Here the photon flux $\Phi$ is constant and $I(\Phi) \approx 5$ nA (compare with figure 4.1). Modulation frequency was $f = 181$ Hz.
Figure 4.5: A graph made from the data in figures 4.3 and 4.4. Equation \((3.17)\) predicts a linear relationship between \(\Phi_{\text{eff}}/\Delta V\) and \(\alpha^{-1}\) and this relation holds rather well. The line was fitted for the crossed points which correspond to \(\lambda \in [880 \text{ nm}, 950 \text{ nm}]\) and the intersection with the abscissa gives the minority carrier diffusion length \(L_n = 112 \, \mu\text{m} \pm 10 \, \mu\text{m}\).

Figure 4.6: Electron diffusion length \(L_n\) as a function of time \(t\) for the Si:B sample S1. The sample was annealed at 210 °C for five minutes and then quenched in LN₂. Points at \(t = 0\) h are measured before annealing and timing starts the moment the sample is brought from 77 K to room temperature. Here \(L_n\) was found using SPV measurements following method B (constant \(\Phi\)) with \(I(\Phi) \approx 5\) nA and \(f = 181\) Hz. The dashed line marks the diffusion length before annealing \(L_n = 112 \, \mu\text{m} \pm 10 \, \mu\text{m}\).
Figure 4.7: Interstitial iron concentration $[\text{Fe}]$ as a function of time $t$ for the Si:B sample Sl. The concentration was found using equation (3.25) and the electron diffusion lengths shown in figure 4.6. The solid line shows a linear regression fit through crossed points and we find the total iron concentration to be $[\text{Fe}] = 6 \times 10^{11} \text{ cm}^{-3}$ and the time constant of FeB pairing $\tau = 6 \text{ h.}$

iron concentration $[\text{Fe}]$ is shown as a function of $t$. As FeB pairs are formed the concentration of interstitial iron $[\text{Fe}]$ decreases exponentially (see section 2.5)

$$[\text{Fe}] = [\text{Fe}]_0 e^{-t/\tau}$$

(4.3)

where $[\text{Fe}]_0$ is the interstitial iron concentration immediately after quenching. For rapid quenching $[\text{Fe}]_0$ equals the total iron concentration [18]. Linear regression through data points measured in the first four hours gives the total iron concentration to be $[\text{Fe}] = 6 \times 10^{11} \text{ cm}^{-3} \pm 2 \times 10^{11} \text{ cm}^{-3}$ and the time constant of FeB pairing $\tau = 6 \text{ h} \pm 2 \text{ h.}$ This is in good agreement to what was to be expected [18].

4.3 SPV measurements in GaAs

In Goodman's 1963 classic paper the semiconductor used for demonstrating SPV measurements to find minority carrier diffusion lengths was GaAs [10]. Using a somewhat different photo-voltage technique Dorantes-Dávila et al. [22] measured the hole diffusion length in $n$-type GaAs with a donor concentration of $n_0 = 2.7 \times 10^{17} \text{ cm}^{-3}$ to be $L_p = 0.23 \mu \text{m}$. In 1991 Castaldini et al. [23] used conventional SPV to find
the diffusion length of minority carriers in Si-doped GaAs. In 1993 Liu et al. [24] were the first to explain the origin of the strong SPV signal measured in SI-GaAs.

Table 4.2 shows the thickness and carrier concentration of the two GaAs samples which we examine below. The first (S2) is n-type (Si doped) and the second (S3) is semi insulating.

### 4.3.1 SPV in n-type GaAs

Sample S2 was studied using SPV method B but before any measurements were made the sample was etched for 30 seconds. Figure 4.8 shows the SPV signal as a function of the photon flux measured at $\lambda = 800$ nm and a modulation frequency of $f = 1087$ Hz. We see a clear and gradual deviation from linear behavior as the photon flux increases and choose to make our SPV measurement at the low intensity corresponding to a current of 17 pA from the light-diode. Figure 4.9 shows the light penetration depth $\alpha^{-1}$ for n-type GaAs with carrier concentration of $1 \times 10^{16}$ cm$^{-3}$ taken from [25, 26]. In figure 4.10 we see the SPV spectrum measured when photon flux is constant within ±1%. The abrupt vanishing of the SPV signal at $\lambda = 870$ nm corresponds to the drop in absorption coefficient at the bandgap of GaAs, $E_g = 1.42$ eV.

In figure 4.11 we see $\Phi/\Delta V_i$ as a function of $\alpha^{-1}$ and a very good linear relationship is found for data points measured in wavelength interval $\lambda \in [650 \text{ nm}, 865 \text{ nm}]$ which corresponds to a light penetration depth $\alpha^{-1} \in [0.41 \mu\text{m}, 1.3 \mu\text{m}]$. This suggests that Goodman’s model is valid (see equation (3.15)). A least squares fit in this interval gives the negative intersection with the abscissa at $L_p = 0.42 \mu\text{m} \pm 0.05 \mu\text{m}$. This is in good agreement with the measurements of Castaldini et al. [23]. The deviation from linearity for $\alpha^{-1} > 1.3 \mu\text{m}$ ($\lambda > 865$ nm) is attributed to the absorption coefficient not being well known for this particular sample in such close proximity.
Figure 4.8: SPV signal $\Delta V_f$ as a function of photon flux $I(\Phi)$ measured for sample S2. The inset shows an enlargement of the area marked by the dotted box. For low light intensities the SPV signal is proportional to the photon flux. Here the wavelength is constant at $\lambda = 800$ nm and the modulation frequency is $f = 1087$ Hz.

to the energy gap. For $\alpha^{-1} < 0.41 \, \mu m$ ($\lambda < 650 \, nm$) the observed deviation may be due to the fact that $\alpha^{-1} \approx L_1$ (see figure 2.3) thus invalidating an assumption of the Goodman model (see equation (3.5)).

4.3.2 SPV in SI-GaAs

We used the SPV method B to study sample S3 which is undoped semi-insulating gallium arsenide (SI-GaAs). Figure 4.12 shows the SPV signal as a function of photon flux. We kept our spectral measurements of the SPV confined to the linear regime in figure 4.12 by selecting a photon flux corresponding to $I(\Phi) \approx 7 \, pA$ from the light diode.

Figure 4.13 shows a the spectral dependence of the SPV signal. We notice that for $\lambda > 650 \, nm$ the signal is essentially flat until reaching the wavelength corresponding to the energy gap of GaAs. The oscillations in the SPV spectrum originate from variations in light intensity due to interference effects in the mica film in front of the sample. They are not faithfully reproduced in the mica film in front of the light detector, which causes errors in photon flux control (see appendix A for details). Figure 4.14 shows $\Phi/\Delta V_f$ as a function of $\alpha^{-1}$. We use the absorption coefficient for $n$-type GaAs with $n_0 \approx 1 \times 10^{16} \, cm^{-3}$ (see figure 4.9). Far above the band gap,
4.3 SPV measurements in GaAs

**Figure 4.9:** The light penetration depth $\alpha^{-1}$ as a function of $\lambda$ for $n$-type GaAs with a carrier concentration $n_0 = 1 \times 10^{16} \text{ cm}^{-3}$. Solid circles are from [25] and pluses are from [26].

**Figure 4.10:** SPV spectra for sample S2. Here $I(\Phi) \approx 17 \text{ nA}$ and the modulation frequency is $f = 1087 \text{ Hz}$. 
Figure 4.11: $\Phi/\Delta V_f$ as a function of light penetration depth $\alpha^{-1}$ for sample S2 using the same data as in figures 4.9 and 4.10. The dashed line is a linear fit to points measured in the wavelength interval $\lambda \in [650 \text{ nm}, 865 \text{ nm}]$ which corresponds to a light penetration depth $\alpha^{-1} \in [0.41 \mu\text{m}, 1.3 \mu\text{m}]$. This predicts a minority carrier diffusion length of $L_p = 0.42 \mu\text{m} \pm 0.05 \mu\text{m}$ which is in good agreement with the measurements of Castaldini et al. [23].

we expect very little dependence of the absorption coefficient on the doping level, but close to the band gap the absorption coefficient is very sensitive to the doping level. With this in mind we make the linear fit to data points measured at the lowest wavelengths. The inset in figure 4.14 shows a linear fit to the data-points measured in the wavelength interval $\lambda \in [580 \text{ nm}, 650 \text{ nm}]$ and we observe a good fit. These data points correspond to a light penetration depth $\alpha^{-1} \in [0.16 \mu\text{m}, 0.25 \mu\text{m}]$. Measurements taken for $\lambda > 650 \text{ nm}$ are far from the fit and are ruled out because the absorption coefficient data is inaccurate. The fact that we do observe linear behavior in figure 4.14 supports the theory reviewed in section 3.3. The fit reveals ambipolar diffusion length of $L_a = 1.1 \mu\text{m} \pm 0.1 \mu\text{m}$. This is in good agreement with the results of Liu et al. [24], where the ambipolar diffusion length was found to be $L_a = 1.4 \mu\text{m}$.

4.4 Reproducibility of SPV measurements

It is evident from figure 4.6 that for minority carrier diffusion length measurements in Si:B there is at least a $\pm 9\%$ uncertainty from one measurement to the next. This
4.4 Reproducibility of SPV measurements

**Figure 4.12:** SPV signal $\Delta V$ as a function of photon flux $I(\Phi)$ measured for sample S3. The modulation frequency is $f = 1086$ Hz.

**Figure 4.13:** SPV signal $\Delta V_f$ as a function of wavelength $\lambda$ measured for sample S3. Here $I(\Phi) \approx 7$ nA and the modulation frequency is $f = 1086$ Hz.
Figure 4.14: The graphs show $\Phi/\Delta V_I$ as a function of $\alpha^{-1}$ for sample S3 using the same data as in figures 4.9 and 4.13. The dashed line is a linear fit to points measured in the wavelength interval $\lambda \in [580 \text{ nm}, 650 \text{ nm}]$ which corresponds to a light penetration depth in the interval $\alpha^{-1} \in [0.16 \ \mu\text{m}, 0.25 \ \mu\text{m}]$. The inset is a close up of the fit marked by the dotted box. The fit reveals a ambipolar diffusion length of $L_a = 1.1 \ \mu\text{m} \pm 0.1 \ \mu\text{m}$ which is in good agreement with the results of Liu et al. [24].

uncertainty is similar to the one found when measuring minority carrier diffusion lengths in extrinsic GaAs, where the absorption coefficient is known. For SI-GaAs the SPV method is limited by the fact that the absorption coefficient is not well known for all wavelengths.

Both methods A and B give the same results when determining minority carrier diffusion lengths, but only if photon flux is low. Higher light intensity will usually result in larger diffusion length.
Chapter 5

Photoacoustic spectroscopy

5.1 Introduction

For accurate determination of minority carrier diffusion lengths in semiconductors by surface photo-voltage (SPV) measurements it is necessary to know the absorption coefficient $\alpha$ as a function of the wavelength $\lambda$ (see chapter 3). Most often the absorption coefficient is cited from tabulated values or empirical formulae from the literature. For example when using SPV to measure minority carrier diffusion lengths in stress-relieved silicon the empirical formula of Nartowitz and Goodman [21] (equation (4.2)) is the most common choice for approximating the absorption coefficient. Saritas et al. [8] have published a different empirical relation for the absorption coefficient of silicon

$$\alpha = (85.015/\lambda - 77.104)^2,$$  \hspace{1cm} (5.1)

which results in at least 10\% higher minority carrier diffusion lengths than when equation (4.2) is used. They support their results by showing that minority carrier diffusion lengths found by photoconductive decay (PCD) measurements on one hand and SPV on the other are in good agreement only when using equation (5.1)$^1$. Still others have published different values of the absorption coefficient [8]. Sometimes the absorption coefficient is not well known. High doping or compensation of a particular sample changes the absorption coefficient, especially close to the bandgap.

$^1$The ASTM standard [7] admits that diffusion lengths measured by SPV are often shorter than ones measured by PCD but it claims that the difference is inherent to the measurement technique and recommends using equation (4.2).
For these samples it becomes a leap of faith to rely on tabulated values.

Photoacoustic spectroscopy (PAS) can be used to determine the absorption coefficient $\alpha$ as a function of $\lambda$ for solids, liquids and gases [27, 28]. The sample is exposed to light, which produces thermal oscillations at the surface which diffuse into the gas (air) adjacent to the surface. Thermal oscillations in the gas result in sound waves that are detected by a microphone. By studying the amplitude and phase of the sound signal as a function of the wavelength of the incident light the absorption coefficient can be calculated provided that the thermal diffusion length of the sample is known.

Section 5.2 is a short description of the theory of PAS in solids. In section 5.3 we discuss whether PAS measurements can be used to supplement SPV measurements in finding the minority carrier diffusion length, by determining the absorption coefficient. We conclude in section 5.4 by demonstrating PAS measurements on AlGaAs/GaAs heterostructures, which allow us to determine the band edge of the AlGaAs and to estimate the thickness of the AlGaAs. These measurements bear witness to the functionality of the PAS system we built.\(^2\)

## 5.2 Theory of PAS measurements in solids

We follow the theory of Rosecwaig and Gersho for PAS in solids [27]. Based on the following material parameters:

\[
\begin{align*}
\alpha & \quad \left( \frac{\text{m}}{\text{m}} \right) \quad \text{absorption coefficient}, \\
c_v & \quad \left( \frac{\text{J}}{\text{kg \cdot K}} \right) \quad \text{specific heat}, \\
\kappa & \quad \left( \frac{\text{J}}{\text{m \cdot K}} \right) \quad \text{thermal conductivity}, \\
\rho & \quad \left( \frac{\text{kg}}{\text{m}^3} \right) \quad \text{density},
\end{align*}
\]

\(^2\)Our PAS setup relies on using an argon ion laser which, during the course of this work, ceased operation. This explains the lack of further PAS measurements.
we define the thermal diffusivity, thermal diffusion length and light penetration depth in the following way:

\[
\sigma_{th} = \frac{K}{c_v \rho_i} \left( \frac{m^2}{s} \right) \text{ thermal diffusivity,} \tag{5.2}
\]

\[
\mu_{th} = \sqrt{\frac{2\sigma_{th}}{\omega \alpha^{-1}}} \text{ (m) thermal diffusion length,} \tag{5.3}
\]

\[
\text{light penetration depth.} \tag{5.4}
\]

The thermal diffusivity is a measure of how quickly a material can carry heat away from a heat source. The thermal diffusion length measures how far temperature oscillations will penetrate a material when a point heat source varies harmonically in time. Light penetration depth was introduced in chapter 3 (see figure 3.1).

In photoacoustic spectroscopy light of wavelength \( \lambda \) is periodically varied in intensity. When the sample absorbs the light, oscillations in temperature are produced within the sample. We assume that the light power density \( I \) is modulated with a frequency \( \omega \) so that

\[
I(t) = \frac{1}{2}(1 + \cos \omega t)I_0, \tag{5.5}
\]

where \( I_0 \) is a constant describing the maximum light power density. Assume a one-dimensional space coordinate as shown in figure 5.1 where the illuminated side of
the sample is placed at \( x = 0 \). For \( x > 0 \), a gas column extends a distance \( l_g \) from the surface of the sample. We suppose that all light absorption takes place inside the sample, and that the sample thickness is \( d \). The equations that describe the temperature in the gas, sample and backing material are, respectively,

\[
\frac{\partial^2 \phi}{\partial x^2} = \sigma_{th,g}^{-1} \frac{\partial \phi}{\partial t} \quad \text{if} \quad 0 \leq x \leq l_g, \tag{5.6}
\]

\[
\frac{\partial^2 \phi}{\partial x^2} = \sigma_{th,s}^{-1} \frac{\partial \phi}{\partial t} - \frac{\alpha I_0}{2\kappa_s} e^{\alpha x} (1 + e^{i\omega t}) \quad \text{if} \quad -d \leq x \leq 0, \tag{5.7}
\]

\[
\frac{\partial^2 \phi}{\partial x^2} = \sigma_{th,b}^{-1} \frac{\partial \phi}{\partial t} \quad \text{if} \quad x \leq -d, \tag{5.8}
\]

where \( \phi \) is the temperature shift from equilibrium and \( g, s, b \) refers to gas, sample and backing material respectively. These equations originate from the one-dimensional heat diffusion equation. The last term in equation (5.7) is the time varying heat source term that describes heat being introduced into the sample by light absorption.

Using that \( \phi \) and its spatial derivative are continuous, equations (5.6) through (5.8) are solved giving

\[
\phi(x,t) = \phi_0 + \phi_{ac}(x,t),
\]

where \( \phi_0 \) is a constant (in time) and the subscript \( ac \) refers to the time dependent part of \( \phi \). For the gas region where \( x > 0 \) we have

\[
\phi_{ac}(x,t) = \theta_{ac0} \exp(-\sigma_{th,g} x + i\omega t), \quad x > 0 \tag{5.9}
\]

and the expression for the complex number \( \theta_{ac0} \) is

\[
\theta_{ac0} = \frac{\alpha I_0}{2\kappa_s (\alpha^2 - \sigma_{th,s}^2)} \times \left\{ \frac{(r-1)(b-1)e^{\sigma_{th,s} d} - (r+1)(b-1)e^{-\sigma_{th,s} d} + 2(b-r)e^{-\alpha d}}{(g+1)(b+1)e^{\sigma_{th,s} d} - (g-1)(b-1)e^{-\sigma_{th,s} d}} \right\}, \tag{5.10}
\]

where

\[
b = \frac{\kappa_b a_b}{\kappa_s a_s}, \tag{5.11}
\]

\[
g = \frac{\kappa_g a_g}{\kappa_s a_s}, \tag{5.12}
\]

\[
r = (1-i)\alpha/2a_s, \tag{5.13}
\]
and \( a = \mu_{th}^{-1} \). We may finally calculate the pressure oscillations in the gas near the surface of the sample finding [27]

\[
\Delta P = \frac{\gamma P_0 \theta g_0}{\sqrt{2l_g\theta g T_0}} \exp[i(\omega t - \pi/4)],
\]

where \( P_0 \) is the ambient pressure, \( T_0 \) is the average gas temperature (room temperature), and \( \gamma = C_P/C_V \) is the ratio between the two heat capacities. For thermally thick samples, that is when \( \mu_{th,s} \ll d \), the amplitude of \( \Delta P \) becomes [28]

\[
|\Delta P| \omega = \frac{A\alpha\mu_{th,s}}{(\alpha\mu_{th,s} + 1)^2 + 1},
\]

where

\[
A = \frac{\gamma P_0 I_0 \sqrt{\sigma_{th,g} \sigma_{th,s}}}{2l_g T_0 \kappa_s},
\]

and the phase is given by

\[
\varphi = -\pi - \arctan(\alpha \mu_{th,s} + 1).
\]

Equations (5.15) and (5.17) can be used to determine the unknowns \( \alpha \cdot \mu_{th} \) and \( A \), and if the thermal diffusion length is known the absorption coefficient can be found.

Figure 5.2 shows \( |\Delta P| \omega \) as a function of \( \alpha \cdot \mu_{th} \). We see that for \( \alpha \cdot \mu_{th} > 10 \) less than 10% change is expected in \( |\Delta P| \omega \) as \( \alpha \cdot \mu_{th} \) is increased further. This is known as the saturation of the PAS signal. The maximum phase change in the photoacoustic signal is \( \Delta \varphi_{max} = \pi/4 \) and in figure 5.3 \((\varphi + \pi)/\pi\) is shown as a function of \( \alpha \cdot \mu_{th} \).

### 5.3 PAS in silicon and gallium arsenide

As seen in equations (5.15) and (5.17) (figures 5.2 and 5.3) for the absorption coefficient to be deductible from PAS, the theory of Rosencwaig and Gersho (RG) [27] requires that \( \mu_{th} \cdot \alpha \leq 10 \). If \( \mu_{th} \cdot \alpha \gg 1 \) the photoacoustic signal becomes independent of the absorption coefficient \( \alpha \) and signal saturation occurs. Stated in terms of light penetration depth, PAS allows measurement of the light penetration depth \( \alpha^{-1} \) as a function of wavelength \( \lambda \) only when the light penetration depth exceeds
\textbf{Figure 5.2:} The graph shows $|\Delta P \omega|/A$ as a function of $\alpha \cdot \mu_{th}$. Here $|\Delta P \omega|$ is given by equation (5.15).

\textbf{Figure 5.3:} The graphs shows $(\varphi + \pi)/\pi$ as a function of $\alpha \cdot \mu_{th}$ where $\varphi$ is given by equation (5.17).
the thermal diffusion length, $\alpha^{-1} \geq \mu_{th}$.

Table 5.1 shows the thermal diffusivity and the thermal diffusion length for silicon and gallium arsenide. We recall the relationship between the two stated in equation (5.3). Using a frequency of $f = 20$ kHz the thermal diffusion length in silicon is $\mu_{th} = 37 \mu m$ and this allows measurements of $\alpha^{-1} > 37 \mu m$ which corresponds to $\lambda > 900$ nm (see figure 4.3). Thus the RG theory predicts that $\alpha$ can be measured for silicon in the wavelength range suitable for SPV. For gallium arsenide however, the thermal diffusion length is $\mu_{th} = 20 \mu m$ at $f = 20$ kHz. Since the above bandgap absorption coefficient is $\alpha^{-1} \leq 1 \mu m$ (see figure 4.9), much higher modulation frequencies are needed if $\alpha$ is to be found by PAS. Furthermore complications would be introduced because the inverse modulation frequency is of the order of the carrier lifetime.

In summary, by using a high modulation frequency PAS it is possible to measure light penetration depths in silicon for $\lambda > 900$ nm, which is the range of wavelengths relevant to SPV measurements. We should not completely abandon PAS measurements in gallium arsenide because knowing the absorption coefficient close to the bandgap may be of interest. For example highly Li compensated GaAs shows strongly distorted energy bands through potential fluctuations [30] which would be worthy of investigation using PAS.

### 5.4 Examples of PAS measurements

Our photoacoustic setup (see appendix A) was limited to light in the wavelength interval $\lambda \in [700 \text{ nm}, 840 \text{ nm}]$ and the maximum modulation frequency of our chopper is $f = 4$ kHz. Thus we were unable to make PAS measurements on silicon but instead we examined a different material in which the absorption coefficient changes
considerably in the interval.

The PAS measurements presented here were made on two Al$_x$Ga$_{1-x}$As epilayer samples, denoted S4 and S5. The samples were grown on single crystalline semi-insulating GaAs by liquid phase epitaxy (LPE). Figure 5.4 shows the bandgap of Al$_x$Ga$_{1-x}$As epilayer as a function of $x$. We note that for $x > 0.4$ the band gap is indirect. For $x < 0.4$ the absorption coefficient for Al$_x$Ga$_{1-x}$As is similar to that of GaAs, with the band edge shifted towards higher energies [26, 31]. Thus the above band gap light penetration depth is less than one micron (see figure 4.9). With the modulation frequency $f = 4$ kHz and the thermal diffusivity from table 5.1 we obtain the thermal diffusion length of $\mu_{th} \approx 60 \mu$m.

Figure 5.5 shows measurements of the samples. In order to demonstrate the level of consistency, two measurements on each sample are presented. Lines (n1, n2) refer to sample S4 and lines (n3, n4) refer to sample S5. Here $\bar{n}$ denotes the measured photon flux from the laser and $\xi_r$ is the raw amplitude of the PAS signal. We know from theory that the PAS amplitude is proportional to the power flux of incident light (see equation 5.15). Hence our normalized PAS signal becomes $\xi_r/(\bar{n} h \nu)$. The phase of the photoacoustic signal is $\xi_\theta$. All variables are measured as a function of incident light energy $h \nu$. The modulation frequency is $f = 4$ kHz.

We see a clear jump in the normalized PAS amplitude $\xi_r/(\bar{n} h \nu)$ and phase $\xi_\theta$ at $E_{S4} = 1.53$ eV and $E_{S5} = 1.72$ eV for samples S4 and S5, respectively. The phase
### 5.4 Examples of PAS measurements

<table>
<thead>
<tr>
<th>$\sigma_{th}$ (cm$^2$/s)</th>
<th>$\mu_{th}$ (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GaAs</td>
<td>0.25</td>
</tr>
<tr>
<td>Al$<em>{0.09}$Ga$</em>{0.91}$As (S4)</td>
<td>0.125</td>
</tr>
<tr>
<td>Al$<em>{0.24}$Ga$</em>{0.76}$As (S5)</td>
<td>0.074</td>
</tr>
</tbody>
</table>

**Table 5.2:** The thermal diffusivities and thermal diffusion lengths for GaAs and Al$_x$Ga$_{1-x}$As epilayer with $x \in \{0.09, 0.24\}$ calculated for the modulation frequency $f = 4$ kHz (thermal diffusivity data from [29]).

jump is $\Delta \xi_{\theta_4} = 44^\circ$ for sample S4 and $\Delta \xi_{\theta_5} = 38^\circ$ for sample S5. Furthermore the amplitude of the normalized photoacoustic signal more than doubles. We interpret $E_{S4}$ and $E_{S5}$ as the bandgap energies of the Al$_x$Ga$_{1-x}$As structures and using figure 5.4 we find $x_{S4} = 0.09$ and $x_{S5} = 0.24$.

For photon energies above the bandgap of the Al$_x$Ga$_{1-x}$As epilayers all absorption takes place in the Al$_x$Ga$_{1-x}$As and for photon energies below the bandgap of Al$_x$Ga$_{1-x}$As all absorption is within the GaAs substrate. The measurements show that both the PAS phase and amplitude are constant in these photon energy regimes and we know that for these energies the light penetration depth, $\alpha^{-1}$, is less than 1 µm (see figure 4.9). We now refer to table 5.2 where the thermal diffusion lengths of gallium arsenide and the two aluminum gallium arsenide samples have been calculated from thermal diffusivity data from the literature [29]. It is evident that for photon energies above and below the bandgap energy of the Al$_x$Ga$_{1-x}$As (where the normalized amplitude and phase are constant), the product $\alpha \cdot \mu_{th}$ will be larger than 20. The theory of section 5.2 indeed predicts very little change in PAS phase and amplitude for such large values of $\alpha \cdot \mu_{th}$ because of PAS saturation (compare to figures 5.2 and 5.3).

The thicknesses of the Al$_x$Ga$_{1-x}$As epilayers, $d_{S4}$ and $d_{S5}$, was not known. Knowing the thermal diffusion lengths, we can use the PAS data to estimate the minimum thickness. By comparing the phase jumps $\Delta \xi_{\theta_4}$ and $\Delta \xi_{\theta_5}$ to figure 5.3 we find that the product $\alpha \cdot \mu_{th}^{\text{eff}}$ must have reached a value less than one. Here $\mu_{th}^{\text{eff}}$ is the effective thermal diffusion length which describes the thermal wave penetration depth through the heterostructure even when absorption occurs within Al$_x$Ga$_{1-x}$As. If we assume that $\mu_{th}^{\text{eff}} > \mu_{th}(\text{Al}_x\text{Ga}_{1-x}\text{As})$, we find

$$\alpha^{-1} > \mu_{th}.$$
This indicates that $d_{s4} > 32 \, \mu m$ and $d_{s5} > 25 \, \mu m$. 
Figure 5.5: PAS measurements on two different Al\textsubscript{x}Ga\textsubscript{1-x}As samples, samples S4 and S5. Lines (n1, n2) refer to sample S4 and lines (n3, n4) refer to sample S5. Here \( \bar{\eta} \) is the average photon flux from the laser and \( \xi_r \) is the raw amplitude of the PAS signal. From theory the PAS amplitude is proportional to the power flux of incident light hence the normalized PAS signal is \( \xi_r / (\bar{\eta} \nu) \). The phase of the photoacoustic signal is \( \xi_\theta \). All variables are measured as a function of incident light energy \( \nu \).
Chapter 6

SPV measurements on hydrogenated AlGaAs/GaAs

6.1 Introduction

It is well known that atomic hydrogen passivates the electrical activity of both shallow acceptor and donor dopants in virtually all semiconductors. This has been the subject of extensive study and the formation of shallow dopant and hydrogen complexes is in most cases well understood [32, 33]. Hydrogen also passivates deep levels and deep level passivation is found to be more stable than shallow level passivation. At the present time, microscopic understanding of many deep levels is not available.

In this chapter we use SPV spectroscopy to examine the AlGaAs/GaAs heterostructure before and after hydrogenation. The samples were grown by LPE on semi-insulating GaAs. The two samples examined, denoted S6 and S6∗, are both from the same growth batch as the sample denoted by S5 in chapter 5. By photoacoustic spectroscopy we found (see chapter 5) that the energy gap was \( E_g = 1.72 \text{ eV} \) and the thickness was at least \( d \approx 25 \text{ μm} \).

Sample S6 was measured as-grown while sample S6∗ was exposed to \( \text{H}_2/\text{Ar} \) plasma in a planar inductive discharge. The details of the inductive discharge used and the plasma properties are given elsewhere [34, 35]. The gas pressure was kept at 20 mTorr with fractional argon pressure of 0.3 and the power applied to the plasma was 400 W for 45 minutes. No external heating was applied to the sample. The electron density was roughly \( 6 \times 10^{16} \text{ cm}^{-3} \) [34] and the mean ion bombarding energy was about 18 eV [35].
6.2 SPV spectral measurements

The majority carrier concentration of the AlGaAs epilayers was determined by Hall measurements. Using square samples in the van der Pauw geometry [36], ohmic contacts were welded on all four corners with tin coated gold wire. The Hall coefficient $R_H$ was estimated from the slope of the Hall voltage versus the magnetic field $B$. The Hall voltage $v_H$ was measured for several values of $B$ between 0 and 0.75 Tesla. An average of four values in each point was calculated, where the two pairs of contacts were interchanged and the current reversed. The AlGaAs epilayer of sample S6 was found to be $n$-type with $n \approx 2 \times 10^{16}$ cm$^{-3}$ and the AlGaAs epilayer of sample S6* was also $n$-type with $n \approx 3 \times 10^{15}$ cm$^{-3}$. In calculating these carrier concentrations we used the thickness of the AlGaAs epilayer estimated from PAS measurements, $d \approx 25$ μm.

6.2 SPV spectral measurements

The SPV measurements on samples S6 and S6* were made at room temperature using the constant photon flux method. Light intensity was kept low so that the SPV signal is proportional to the light intensity. Figure 6.1 shows the amplitude of the SPV signal and figure 6.2 shows the phase of the SPV signal. The light intensity was the same for both samples. The modulation frequency was $f = 1097$ Hz.

In figures 6.1 and 6.2 we see that an abrupt jump in SPV amplitude and phase is present for both samples at $\lambda = 720$ nm. This corresponds to the photon energy of $E = 1.72$ eV which coincides with the energy gap of Al$_{0.24}$Ga$_{0.76}$As found by PAS in chapter 5. Thus for wavelengths $\lambda \in [600 \text{ nm}, 720 \text{ nm}]$ all the light absorption occurs in the Al$_{0.24}$Ga$_{0.76}$As epilayer but for $\lambda \in [720 \text{ nm}, 870 \text{ nm}]$ the light is absorbed within the Si-GaAs substrate. Let us consider the origin of the SPV signal in these two wavelength regions. For $\lambda \in [600 \text{ nm}, 720 \text{ nm}]$ electron-hole pairs are formed close to the surface. Here the oscillating SPV signal is due to alternations in the band bending near the surface. In the wavelength region $\lambda \in [720 \text{ nm}, 870 \text{ nm}]$ electron-hole pairs are formed within the substrate, adjacent to the heterojunction. In this case, carriers diffusing into the heterojunction region will alter the band bending at the junction to produce the SPV signal.

Consider the abrupt change in the SPV phase at $\lambda \approx 720$ nm. The phase jump for sample S6 is $+50^\circ$ while the phase jump for sample S6* is $-140^\circ$. For $\lambda \in [600 \text{ nm}, 710 \text{ nm}]$ and $\lambda \in [730 \text{ nm}, 870 \text{ nm}]$ both samples exhibit constant phase.
Figure 6.1: Normalized SPV amplitude $\Delta V/\Phi$ as a function of the wavelength $\lambda$ for samples S6 (solid line) and S6* (dashed line). Measurements were made at room temperature using the constant flux method. The modulation frequency was $f = 1097 \text{ Hz}$.  

Figure 6.2: Phase of the SPV signal $\theta$ as a function of the wavelength $\lambda$ for samples S6 (solid line) and S6* (dashed line). Measurements were made at room temperature using the constant flux method. The modulation frequency was $f = 1097 \text{ Hz}$.  

- $\lambda$ (nm)
- $\Delta V/\Phi$ (a.u.)
- $\theta$ ($^\circ$)
6.3 Band diagram interpretation

These observations are in accordance with the view that in these two wavelength regions, the SPV signal has different origins.

For \( \lambda \in [870 \text{ nm}, 890 \text{ nm}] \) there is a common feature in the SPV spectra for samples S6 and S6*, both in phase and amplitude. Although more pronounced in sample S6*, both samples show a peak in SPV amplitude and a dip in phase. For these wavelengths, light penetrates the sample, reaching the back side which also has an LPE grown layer\(^1\). Thus, for these wavelengths the back side contributes to the SPV spectra.

For \( \lambda > 890 \text{ nm} \) the SPV signal for sample S6 is almost zero. This is to be expected because the absorption coefficient is very low for photon energies below the bandgap of GaAs. However for sample S6* we see a hump in the SPV amplitude spectra for \( \lambda > 890 \text{ nm} \). This suggests that introducing hydrogen results in below bandgap absorption.

6.3 Band diagram interpretation

SPV measurements on AlGaAs/GaAs heterostructures have been used to distinguish the orientation of dipole moments at the heterojunction in \( p^- \) or \( n^- \)-type AlGaAs epilayers grown on \( n^{++} \) GaAs \([37]\). In this section we use the SPV data described in section 6.2 to predict the band structure in samples S6 and S6* at the heterojunction and near the surface.

Figure 6.3 shows schematic band diagrams for the AlGaAs/GaAs heterostructures in samples S6 and S6*. The right sides of the band diagrams represent the band structure of the GaAs substrate while the left sides show the band structure of the AlGaAs. The solid lines marked \( E_v \) and \( E_c \) represent the top of the valence band or the bottom of the conduction band as a function of position. The dashed line represents the Fermi-level \( E_F \).

Hall measurements of the plain GaAs substrate show that the electron carrier concentration is \( n \approx 3 \times 10^7 \text{ cm}^{-3} \). Thus the substrate is semi-insulating and the Fermi-level will be close to the middle of the bandgap. As stated above the AlGaAs is \( n^- \)-type with \( n \approx 2 \times 10^{16} \text{ cm}^{-3} \) for sample S6 and \( n \approx 3 \times 10^{15} \text{ cm}^{-3} \) for sample S6*. The location of the Fermi-level for these epilayers will thus be close to the conduction band. This is depicted in figure 6.3.

\(^1\)In LPE both sides of the sample are exposed to the same molten Ga and similar heterostructures are formed on either side.
Figure 6.3: Schematic band diagrams for the AlGaAs/GaAs heterostructures in samples S6 (a) and S6* (b). The top of the valence band is marked by $E_v$ and the bottom of the conduction band is marked by $E_c$. The dashed line represents the electro-chemical potential $E_f$ of the electrons, also called the Fermi-level. The short horizontal lines at the surface and the heterojunction represent localized energy levels introduced by impurities and defects.
6.3 Band diagram interpretation

We expect both the heterojunction and the surface to have a high concentration of defects that introduce energy levels within the bandgap. These energy levels are represented in figure 6.3 by short horizontal lines within the bandgap. Thus at the heterojunction and at the surface the Fermi-level is displaced from the bulk or epilayer value, resulting in band bending.

Sample S6* shows a larger SPV signal originating from the heterojunction ($\lambda \in [720 \text{ nm}, 860 \text{ nm}]$) compared to the SPV signal from sample S6. We also see that there is a significant difference in the phase of the SPV signal originating from the heterojunctions of the two samples. We hypothesize that this is due to a difference in band bending at the heterojunction, as seen in figure 6.3. We conclude that this change in band bending is brought on by hydrogen passivation of impurities or defects at the heterojunction, which is at least 25 $\mu$m from the surface.
Chapter 7

Summary and Conclusions

During the course of this work, two measurement systems were built and tested, one for doing surface photovoltage measurements and the other for photoacoustic spectroscopy. The surface photovoltage (SPV) system allows the measurement of the minority carrier diffusion length in extrinsic semiconductors. We demonstrated measurements on both silicon and gallium arsenide. As an example of how SPV can be used to monitor complex formation in semiconductors, the formation of the iron-boron complex in boron doped silicon was examined. This was done by observing changes in the minority carrier diffusion length before and after short annealing. Furthermore we demonstrated SPV measurements on AlGaAs/GaAs heterojunctions and used them to observe changes in bandstructure at the heterojunction before and after hydrogen passivation.

The photoacoustic spectroscopy (PAS) system was utilized to locate the band-edge of AlGaAs and estimate the thickness of the AlGaAs epilayer. We show that it is theoretically possible to use this system to measure the absorption coefficient in silicon in the wavelength region of relevance to SPV measurements. We also find that PAS can not be used to determine the above bandgap absorption coefficient in GaAs.

In the future we would like to use SPV to monitor novel complex formation, for example Au-Li in boron doped silicon or Zn-Li in gallium arsenide. So far our attempts to observe these complexes using SPV have been futile. We would be able to claim better understanding of the SPV spectra from AlGaAs/GaAs samples if theoretical simulations of these spectra were available. However, this is the subject of future research.
Chapter 8

Acknowledgements

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Appendix A

Experimental setup

A.1 SPV experiment

A.1.1 SPV experimental setup

Figure A.1 shows a block diagram of the SPV experimental setup. The light source (A) is a variable powered halogen lamp with $P \in [0 \text{ W}, 100 \text{ W}]$. A monochromator (B) determines the wavelength, $\lambda$, of light that passes through. The monochromator also allows light of wavelength $\lambda/2$ to pass through and we block this light by using a high pass filter (C). The dotted rectangle in figure A.1 represents a light tight box which encloses both the light meter and the SPV sample holder. Light is focused by a convex lens (D) on the blade of the chopper (E) which has an aluminum coating. Thus the chopper serves the function of a beam splitter. When light passes through the chopper, it is focused (F) on to the sample in the SPV sample holder (G). Figure A.2 shows a block diagram of the sample holder. When the chopper blocks light from reaching the sample, reflected light is focused (H) on to the silicon light-diode. Before light reaches the light-diode it passes through glass coated with indium tin oxide and a mica film. This is done to simulate the path the light takes to reach the sample. Figure A.3 shows a photograph of the experimental setup.

In figure A.2 light (A) passes through glass (B) coated with indium tin oxide (ITO) (C). The ITO film is both transparent and it is a good conductor, with sheet resistance less than 10 $\Omega/$. Adjacent to the the ITO coat is a 17 $\mu$m thick, transparent mica film (D). The sample (E) is held in place by a pressure force from a metallic electrode (F) which has indium coating. A metallic electrode with gold coating is in contact with the ITO (G). The electrodes (F) and (G) provide the
Figure A.1: Experimental setup for SPV measurement. The dashed line represents the light path. A: Halogen lamp $P \in [0 \, \text{W}, 100 \, \text{W}]$. B: Monochromator. C: Filter. D: Lens (focal length 100 mm). E: Chopper $f \in [10 \, \text{Hz}, 800 \, \text{Hz}]$. F: Lens (focal length 50 mm). G: SPV Sample holder. H: Lens (focal length 50 mm). I: Photo-diode. The dotted rectangle represents a light tight box and LIA stands for lock-in amplifier.

Figure A.2: SPV Sample holder. A: Light of wavelength $\lambda$ and photon flux $\Phi_0$. B: Glass (thickness 1 cm). C: Thin film of indium tin oxide (ITO). D: Transparent mica film (thickness 17 $\mu$m). E: Semiconductor sample. F: Metallic electrode with indium coating. G: Metallic electrode with gold coating.
Figure A.3: Photograph of the SPV experimental setup. The monochromator is not shown.
ground and reference signals which are fed to the lock-in amplifier.

A.1.2 Tips when measuring SPV

Modulation frequency

The ASTM standard [7] recommends using a modulation frequency of about \( f \approx 13 \) Hz. However some claim that ASTM is in error and recommend using \( f > 500 \) Hz [17, 24]. This is done to avoid minority carrier trapping of deep levels and surface states which will interfere with diffusion length measurements. The time constant of deep levels and surface states in silicon is in the range from minutes to 10 ms [17].

Etching samples

Etching the semiconductor samples can effectively alter band bending at the surface and may often increase weak SPV signals by one or two orders of magnitude. For silicon the ASTM standard [7] recommends using an etching solution consisting of concentrated nitric acid (HNO₃), hydrofluoric acid (HF) and glacial acetic acid (CH₃COOH) in the proportions 5:3:3 (by volume). To further improve the SPV signal, p-type samples may be etched for 1 minute in a mixture of 6 parts NH₄F and 1 part HF. Boiling n-type samples in 30 % unstabilized hydrogen peroxide (H₂O₂) for 15 minutes may prove helpful in increasing the SPV signal.

Etching gallium arsenide has also shown to be very useful in enhancing the SPV signal. We used the etching solution consisting of 1 part water, 1 part hydrogen peroxide (H₂O₂) and and 3 parts sulfuric acid (H₂SO₄).

Interference in the mica film

We placed a thin \( (d_{\text{mica}} = 17 \, \mu\text{m}) \) mica film between the ITO coated glass and the sample (see figures 3.3 and A.2). When the sample is exposed to monochromatic light of wavelength \( \lambda \) interference occurs between light reflected from the front and back side of the mica film. This will result in oscillations in light intensity that reaches the sample \( \Phi \) as a function of \( \lambda \). Interference maxima occur for \( \lambda = \lambda_n \) where \( n \) is an integer such that

\[
2d_{\text{mica}} = n\lambda_n.
\]  
(A.1)
Differentiating this we obtain

\[ 0 = dn \lambda_n + n d\lambda_n \]  \hspace{1cm} (A.2)

and setting \( \Delta n = 1 \) we find the spectral distance between interference maxima

\[ \Delta \lambda_n = \frac{\lambda_n^2}{2d_{\text{mica}}}. \]

An example of interference is clearly seen in the SPV spectra in figure 4.13.

We try to suppress interference by placing a mica film, identical to the one used in the sample holder, in front of the light diode. If the sample holder and the mica film in front of the light diode are carefully adjusted the interference may completely vanish. This is the case in figure 4.10.

### A.1.3 SPV data acquisition software

The data acquisition software for SPV the measurements was written in tcl/tk [38] using the GNU/Linux operating system. It provides the user with a graphics user interface (GUI) but measurement series are easily programmed from a script.

When writing the software, a command library for each device was made thus creating a convenient way to access them from tcl/tk. With the libraries in place, writing other data acquisition software using the same devices is easy and efficient because of code reuse.

### A.2 PAS experiment

#### A.2.1 PAS experimental setup

Figure A.4 shows a block diagram of the PAS experimental setup. An argon ion laser (A) with a maximum output power \( P_{\text{Ar}} \approx 5 \text{ W} \) pumps a titan sapphire laser (B). Using three different mirror sets the titan sapphire laser provides light of wavelength \( \lambda \), where \( \lambda \in [700 \text{ nm}, 850 \text{ nm}] \), \( \lambda \in [850 \text{ nm}, 1000 \text{ nm}] \), or \( \lambda \in [1000 \text{ nm}, 1100 \text{ nm}] \) respectively. The power of the light from the titan sapphire laser varies with wavelength, but we adjusted \( P_{\text{Ar}} \), so that the maximum power was less than \( P_{\text{TS}} < 100 \text{ mW} \). The beam splitter (C) is made of thick glass (1 cm) and the reflection form either the front or back surface was directed to a silicon

photo-diode. When evaluating the current from the photo-diode (I), a digital oscilloscope (J) was used to read the average voltage over a small resistor connected to the photodiode. Light is focused (D) on the chopper blade (E) and then refocused on sample in the PAS cell (G). A voltage signal from the microphones is measured by a lock-in amplifier (H).

The data acquisition software for PAS the measurements was written using TestPoint.

A.2.2 Tips when measuring PAS

For PAS phase information to be reliable we found it very important to focus the the light beam on the chopper blade. If this was not done, the spectral dependence of the PAS phase varied significantly if the chopper rotated clockwise or counterclockwise.
Bibliography


