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Diffusion of impurities and vacancies in compound semiconductors

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ABSTRACT

Compound semiconductors have been the focus of numerous studies in the last few decades. Their direct and wide band gap make them especially suitable for optoelectronic devices, such as laser diodes. Knowledge of their material, structural and electronic properties is therefore of importance.

In this thesis diffusion processes in compound semiconductors have been investigated. The diffusion of impurity atoms, their location in the host lattice and the formation and migration of vacancies have been studied by the use of ion beam techniques and positron spectroscopy. A novel analysis procedure has been developed for the determination of depth profiles with Rutherford backscattering spectrometry from samples with rough surfaces. This procedure is utilized for the determination of diffusion profiles for gold in ZnSe.

Gold and platinum diffusion in ZnSe were found to be concentration independent with the activation energies 1.6 and 1.7 eV, respectively. The diffusion velocity of gold in ZnSe was found to depend on the crystalline quality. Silicon was found to diffuse in GaAs through a combination of the interstitial and vacancy mechanism. The activation energy for interstitial diffusion is 1.72 eV and for the vacancy mechanisms 2.2 - 2.8 eV, depending on the vacancy involved.

The formation and migration of the P vacancy in InP was studied by combining the exponential dependency of the vacancy concentration on the formation energy with a probability model for the formation of V_P-Zn complexes. The energy of migration was found to be 0.4 eV and the formation energy was found to be 1.0 - 1.2 eV depending on the position of the Fermi level.
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1 INTRODUCTION

Diffusion can be defined as thermally stimulated random motion of atoms or molecules in liquids and solids. This type of motion was first observed by Robert Brown in 1827 [1]. The mathematical formulation of Brownian motion was done by Albert Einstein in 1905 and 1906 [2, 3]. Understanding diffusion phenomena in compound semiconductors is of fundamental interest, since the electrical properties of a semiconductor device can depend on the thermal stability of a p-n junction or an ohmic contact. Diffusion can also be used as a means to incorporate dopant atoms into a semiconductor.

Traditionally the semiconductor industry has been based on silicon and the knowledge of the material and electrical properties of silicon is therefore extensive. However, silicon has disadvantages, when compared to compound semiconductor materials, such as GaAs and InP. For example, silicon cannot be used in optoelectronic devices, since it has an indirect bandgap. The use of compound semiconductors in electronic devices has taken a huge step forward in the last two decades. Much of everyday electronics, from CD-players to laser pointers, rely on compound semiconductor structures. However, with the rapidly decreasing size of the active components, more and more knowledge of the electronic and material properties of the semiconductors used in the fabrication of devices is required.

A compound semiconductor device needs a power supply to operate. The integrated circuits are connected to a power source and to other electronic devices by thin charge transmitting metal wires. These ohmic contacts should be thermally stable to maintain as good electronic properties as possible. That is, there should be no mixing of contact and device material through diffusion, no deformation and no loss of adhesion. The ohmic contacts are often heterostructures of many materials, such as Pt, Au, Ni and Ti. Platinum and gold are both used in ohmic contacts to ZnSe devices [4–6] and the understanding of the thermal properties of these materials are thus important.

Silicon is used as an n-type dopant in GaAs and the dopant is often incorporated into GaAs by ion implantation or by diffusion from an external source. Since silicon is a group IV element it can show
amphoteric behavior in compound semiconductors, i.e., it can act both as a donor and as an acceptor depending on its position in the host lattice. Previous studies have explained Si diffusion in GaAs by considering Si as an amphoteric impurity, diffusing via pairing with Ga and As vacancies [7]. However, it has been shown experimentally that a large amount of Si occupies interstitial sites [8]. These interstitial Si atoms must be taken into account in order to fully be able to explain the diffusion of Si in GaAs. The charge state of the interstitial Si atom is also of interest, since it will influence the position of the Fermi level.

Point defects, such as vacancies, can influence the electrical properties of semiconductors by introducing energy levels in the forbidden band gap, which can act as compensators and charge carrier traps [9]. Much work has been focused on the identification of vacancies and vacancy complexes in Zn doped InP [10–12], also the diffusion of Zn in InP and its effect on the electrical properties has been extensively studied [13–15]. Very little experimental data, however, is found in the literature about the formation of vacancies in semiconductors. Positron spectroscopy is an ideal analysis method for studying vacancy type defects. It is thus, not only of importance for the understanding of the material properties of InP to be able to determine the formation mechanism of a vacancy type defect, but also of general scientific interest to the community of positron physicists.

Rutherford backscattering spectrometry (RBS) is probably the most common depth profiling tool in physics and chemistry. A problem with RBS is that it can be sensitive to inhomogenities on the sample surfaces, such as grains, which can make the interpretation of RBS spectra difficult [16]. The development of a reliable method for the extraction of the influence of surface properties from the RBS spectrum is therefore of great importance. We have shown that by combining RBS with atomic force microscopy it is possible to determine the influence of the surface properties on backscattering spectrum and thus, obtain correct depth profiles.

The aim of this thesis is to focus on the problems above, to gather information about the diffusion of impurities and vacancies in compound semiconductors and to develop new experimental methods.
2 STRUCTURE OF THE THESIS

This thesis is divided into sections as follows. In section 1, the introduction, the background and purpose of the thesis are presented. In section 2, the articles of the thesis are briefly summarized. Section 3 describes basic diffusion theory and diffusion mechanism and section 4 deals with the experimental methods used in the thesis. The major results of the thesis are discussed in section 5 and the thesis is summarized in section 6.

The experimental part of this thesis has been conducted at the Accelerator Laboratory of the University of Helsinki, at the Laboratory of Physics of the Helsinki University of Technology and at the Technical Research Centre of Finland. The author has been involved in the experiments done at the Accelerator Laboratory and at the Laboratory of Physics, done most of the theoretical and numerical work related to the calculation of the diffusion and been the corresponding author, responsible for the writing of the manuscripts, in most of the articles.

The original articles of this thesis are included at the end of this work. They will be referred to by Roman numbers.


A method for determining correct depth profiles from samples with rough surfaces is presented. The method combines Rutherford backscattering spectrometry with atomic force microscopy. The topographical information obtained by atomic force microscopy is used to calculate the effect of the surface roughness on the backscattering spectrum. As an example annealed Au/ZnSe heterostructures are studied. Gold grains were observed on the surfaces of the annealed samples. The annealing also caused diffusion of gold into the ZnSe. Backscattering spectra of the samples were measured with a 2 MeV $^4\text{He}^+$ ion beam. A scanning nuclear microprobe was used to verify the results by measuring backscattering from grains and from areas of the samples where no grains had been formed during annealing.

Diffusion of gold in zinc selenide has been studied by using $^{12}$C and $^{4}$He ion backscattering technique. The samples were thin films grown by molecular beam epitaxy on bulk GaAs (100) substrates and on GaAs (100) epitaxial layers followed by evaporation of gold and annealing in the temperature range 400 - 800°C. The surface properties of the samples were studied with scanning electron microscopy and atomic force microscopy. The crystal quality of the samples was studied with $^{4}$He ion channeling. The gold diffusion was found to depend significantly on the crystal quality of the ZnSe. An empirical model for calculating the diffusion coefficient for different crystal quality ZnSe is presented.


Diffusion of platinum in zinc selenide has been studied by the use of $^{4}$He and $^{12}$C ion backscattering technique. The samples were thin films grown by molecular beam epitaxy on GaAs (100) epitaxial layers followed by evaporation of platinum and annealing in the temperature range 550 - 800°C. The diffusion coefficients were determined by the fitting of a concentration independent solution of the diffusion equation to the experimental depth profiles. The activation energy and the pre-exponential factor of the diffusion process were found to be 1.7 eV and $6.4 \times 10^{-6}$ cm$^2$/s, respectively.


The lattice location of diffused gold and platinum in ZnSe epitaxial layers was studied using Rutherford backscattering channeling technique. Thin Au and Pt films were evaporated onto ZnSe samples. The Au/ZnSe samples were annealed at 525°C and the residual Au film was removed by etching. Channeling angular scan measurements showed that about 30% of Au atoms were close to substitutional sites. In the case of the Pt/ZnSe samples annealing temperatures ranged from 600 to 800°C. The Pt minimum yields along the $<100>$ direction were close to the random value, varying from 80 to 90 %. The measured Pt angular scans along the $<100>$ and $<110>$ directions indicated a random location.


The diffusion of silicon in ion implanted GaAs has been studied in the temperature range 650 -
850°C. A combination of concentration dependent and concentration independent diffusion theory is applied to depth profiles obtained by secondary ion mass spectrometry. The results indicate that silicon atoms diffuse by the vacancy mechanism in the Ga and As sublattices and by interstitial diffusion. The activation energies were 1.72 eV for the interstitial diffusion and 2.2 - 2.8 eV for the vacancy mechanism depending on the vacancy species and its charge state. An empirical description of the solubility of silicon in GaAs as a function of temperature is also given.


Positron spectroscopy has been used to study the formation and migration of P vacancies in heavily Zn-doped InP. The spontaneous formation of V\textsubscript{P}-Zn complexes is observed by annealing at temperatures around 600 K. We infer that this vacancy-impurity complex is formed when a diffusing P vacancy gets trapped at a Zn atom. The Fermi-level-dependent formation energy of 1.0 - 1.2 eV and the migration energy of 0.4 eV are determined for the P vacancy. A large lattice relaxation is observed, when the V\textsubscript{P}-Zn complex changes from neutral to negative charge state.

Articles I-III deal with metal/semiconductor heterostructures and their thermal stability. In article I a novel analysis method is developed for the determination of correct diffusion profiles by Rutherford backscattering spectrometry from samples with rough surfaces. This method is then used in article II to determine diffusion profiles of gold in ZnSe. Gold and platinum are both promising contact materials to ZnSe, and in articles II and III it is shown that the diffusion of gold and platinum in ZnSe is negligible at the fabrication and working temperatures of ZnSe devices. In article IV the lattice site of diffused gold and platinum in ZnSe is studied. Platinum is found to be randomly oriented in the ZnSe lattice, whereas a significant part of the gold atoms are found to occupy lattice sites. In articles V and VI impurity atom and defect diffusion in III-V compound semiconductors is studied. We show in article V that the diffusion of silicon in GaAs is a complex phenomenon involving interstitial and substitutional silicon and host lattice vacancies. Article VI considers the formation and migration of phosphorus vacancies in InP. The formation of phosphorus vacancies in InP, as well as the diffusion of silicon in GaAs, are found to depend on the position of the Fermi level.
3 DIFFUSION EQUATIONS AND MECHANISMS

The redistribution of particles due to their thermal energies is called diffusion. Usually the net flow of particles is from lower concentration to higher concentration, but the opposite case is also possible if a driving force, for example an electric field, is present in a system. In gases and liquids, where the particles can move more freely, diffusion can generally be considered as a macroscopic process. In crystalline solids, where the movement of atoms is confined to a lattice, a microscopic description is often needed and the diffusion velocity can depend heavily on the diffusion mechanism.

3.1 Diffusion equations

The mathematical formulation of macroscopic diffusion was done by Albert Fick in the middle of the 19th century. He extended the theory of heat conduction, developed by Fourier a few decades earlier, to the redistribution of matter. The basis for macroscopic diffusion is the rate equation,

\[ F = -D \frac{\partial C}{\partial x}, \tag{1} \]

which gives the relation between the flow \(F\) of diffusing substance through a unit area of a section and the concentration \(C\) gradient measured normal to the section. The constant of proportionality \(D\) [cm\(^2\)/s] is called the diffusion coefficient. Eq. (1) is known as Fick’s first law [17]. This mathematical description of diffusion is macroscopic, nothing is said about the microscopic nature of the diffusion. Eq. (1) can also be derived microscopically by considering the flow of particles between two atomic planes in a crystalline solid [18].

The time dependence of the diffusion is described by Fick’s second law [17]

\[ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right), \tag{2} \]
If $D$ can be considered constant, as in articles II and III, Eq. (2) simplifies to

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}.$$  \hfill (3)

If the diffusion coefficient is a function of time or concentration, Fick’s second law must usually be solved numerically. The concentration dependence of the diffusion coefficient can be studied with the so-called Boltzmann-Matano method [19, 20]. By substituting $\eta = x/2\sqrt{t}$ into Eq. (2) and by integrating over $\eta$, $D$ can be derived as a function of the concentration

$$D_{C=C_1} = -\frac{1}{2t} \frac{dx}{dC} \int_0^{C_1} x \, dC.$$  \hfill (4)

Eq. (4) was used in articles II, III and V to check the concentration dependence of the diffusion coefficient.

### 3.2 Solutions to the diffusion equation for concentration independent diffusion

Analytical solutions to the diffusion equations can be obtained for different initial and boundary conditions. It is easy to check that

$$C(x,t) = \frac{1}{\sqrt{4Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$$  \hfill (5)

is a solution of Eq. (3). The initial one-dimensional distribution of a diffusing substance is in this case a delta function. Eq. (5) is the Green function or the fundamental solution of the diffusion equation with constant $D$. The solution of the diffusion equation with initial delta function distribution can be used to describe the probability density for a one-dimensional Brownian particle. Wiener used this approach in the development of the path integral [21], which was later reinvented by Feynman in his "third formulation of quantum mechanics" [22]. This shows that diffusion theory is not only restricted to materials science.
Figure 1: Solutions of the diffusion equation for an infinite source and an infinite medium for $D_t$ equal to 500, 800 and 1000 nm$^2$. The concentration of the diffusing substance is increasing in time where the second derivative is positive and decreasing where it is negative.

Solutions for arbitrary initial conditions can be obtained from the Green function by integration:

$$C(x,t) = \int_{-\infty}^{\infty} G(x-y,t)p(y) \, dy,$$

where $p(y)$ is the initial distribution at $t = 0$ and $G$ the Green function. If the initial distribution is a step function, the solution will describe diffusion from an infinite diffusion source to an infinite medium:

$$C(x,t) = C_0 \text{erfc} \left( \frac{x}{\sqrt{4Dt}} \right),$$

where erfc is the complementary error function and $C_0$ the concentration at $x = 0$. In Fig. 1 the solution of the diffusion equation, Eq. (7), is plotted along with its derivatives. Eq. (7) was fitted to the experimental depth profiles in articles II and III.
Figure 2: Solutions of the diffusion equation for an infinite diffusion source and an infinite medium with different concentration dependencies for the diffusion coefficient. The diffusion time is 10 s.

3.3 Solution of the diffusion equation for concentration dependent diffusion

As mentioned earlier, the diffusion equation, Eq. (2), must be solved numerically if the diffusion coefficient is a function of the concentration. The usual way of solving the diffusion equation numerically is the flux method, where Eq. (2) is written as a difference equation

$$\frac{\Delta C}{\Delta t} = \frac{\Delta}{\Delta x} \left( D \frac{\Delta C}{\Delta x} \right).$$

From this equation the concentration at the next time step is solved, yielding

$$C_{i}^{t+\Delta t} = C_{i}^{t} + \frac{\Delta t}{(\Delta x)^2} \left( \frac{D_{i} + D_{i+1}}{2} [C_{i+1}^{t} - C_{i}^{t}] - \frac{D_{i} + D_{i-1}}{2} [C_{i}^{t} - C_{i-1}^{t}] \right).$$
Figure 3: Examples of diffusion mechanisms: a) interstitial diffusion, b) vacancy mechanism and c) substitutional or kick-out mechanism.

In Fig. 2 solutions of Eq. (8) for diffusion coefficients with different concentration dependencies are shown. The concentration profile at $t = 0$ in this example is a step function with height 1. In order to keep the solution stable when the concentration is changing rapidly the time and space steps have to be small. However, this increases computation time, which can make the fitting of a solution of Eq. (8) to an experimental diffusion profile very time consuming. In article V a faster method of solution is developed, which uses the Boltzmann-Matano transformation, mentioned earlier.

3.4 Diffusion mechanisms

The diffusion of impurities in semiconductors often involves several different diffusion mechanisms, which depend on the chemical properties of the impurity atoms and the lattice atoms. For example the charge and size of the impurity atoms, the concentration of defects in the semiconductor, the position of the Fermi level, and the crystalline structure of the host lattice are all factors that can influence diffusion. The most common diffusion mechanisms are schematically illustrated in Fig. 3.

Interstitial diffusion (Fig. 3a), where the diffusing atom jumps from one interstitial site to a neighboring interstitial site, is often involved when the diffusing atom is small. This is due to the fact that a diffusion jump from an interstitial site to another interstitial site disturbs the surrounding lattice, the smaller the impurity atom, the smaller the disturbance. In article V we suggest that the broadening of
the initial silicon distribution in the annealed GaAs samples is due to slow interstitial silicon diffusion. This suggestion was later confirmed [23].

In the vacancy mechanism (Fig. 3b) the impurity atom diffuses by jumping from a substitutional site to a vacant neighboring lattice site. This can also be interpreted as vacancy diffusion proceeding in the opposite direction. This mechanism is considered in article VI, where the migration of P vacancies in InP is studied. The diffusion through the vacancy mechanism will depend on the concentration of vacancies [24], which on the other hand can depend on many factors, such as the position of the Fermi level. This is the case in article V where the diffusion of silicon in GaAs is explained partly by diffusion through gallium and arsenic vacancies and partly by interstitial diffusion.

Diffusion through the substitutional or kick-out mechanism (Fig. 3c) is especially probable when the diffusing impurity and host atoms are approximately of the same size. In this diffusion mechanism the impurity atom jumps from an interstitial site to a substitutional site and at the same time pushes a lattice atom to an interstitial site. An example of substitutional diffusion is the Frank-Turnbull-mechanism, which has been used to describe the diffusion of copper in germanium [25]. In this substitutional diffusion mechanism it is assumed that the diffusion coefficient of the substitutional atoms is negligible compared to the interstitial diffusion coefficient. The diffusion of gold in silicon is also described by the kick-out mechanism, see for example refs. [26, 27]. This fact along with the RBS/channeling angular scans presented in article IV could indicate that gold diffuses by the kick-out mechanism in ZnSe.
4 EXPERIMENTAL METHODS

4.1 Ion beam techniques

The invention of the particle accelerator in the beginning of the 20th century [28] did not only revolu-
tionize nuclear and particle physics, it also laid the basis for a whole new world of analysis methods in 
materials science. Abbreviations like RBS (Rutherford backscattering spectrometry), NRA (nuclear 
reaction analysis), PIXE (particle induced x-ray emission), PIGE (particle induced γ-ray emission) 
are now being used in many materials science publications and these methods are only a few of the 
ion beam analysis techniques made available by particle accelerators.

4.1.1 Rutherford backscattering spectrometry

Since its development in the first half of the 20th century backscattering spectrometry (RBS) has 
become the most commonly used ion beam technique in materials science. Its power lies in the 
speed of the analysis and its versatility in the non-destructiveness and in the ability to simultaneously 
determine the depth distribution of several atomic species below the surface. Combined with ion 
channeling, RBS becomes a powerful tool to detect crystalline defects in single-crystal materials, 
such as semiconductors. RBS is especially suitable for the determination of depth distributions of 
heavy elements in lighter substrates, where other analysis methods fail.

RBS is based on Coulomb interaction between the target atom and the incident ion. The mass resolu-
tion of RBS is determined by the kinematic factor, which is the ratio of the incident ion energy after 
and before the elastic scattering event. The kinematic factor depends on the masses of the incident 
ion and target atom and on the geometry of the experiment. Isotopic resolution can be achieved for 
light target atoms with proper choice of ion, beam energy and experimental geometry.

The depth scale of a RBS measurement is related to the energy of the detected backscattered ion and 
its energy loss in the analysed material. Typically the depth scale ranges from a few nm’s up to several
μm’s. The depth resolution is usually greater than 5 - 10 nm.

The detection limit depends on the scattering cross section, which has a $Z^2$ (atomic number) dependency [16]. In ideal conditions ppm (parts per million) concentrations can be measured.

A problem with RBS measurements is that often smooth sample surfaces are required in order to make the interpretation of the spectrum straightforward. Surface roughness, such as grains, can cause diffusion-like broadening of the spectrum and render the interpretation of the result difficult.

### 4.1.2 Ion channeling

Ion channeling is an analysis method for studying the structure of crystalline materials. Mainly two features of the lattice can be studied, lattice disorder and the lattice site of impurity atoms. The lattice disorder is studied by aligning the ion beam along axial or planar crystalline directions. The yield in the aligned backscattering spectrum of the studied sample is then compared to the yields taken in random and aligned directions of a presumably defect free reference sample.

The lattice site of impurity atoms can be studied by scanning over a crystalline direction and by comparing the yield from the impurity atoms to the yield from the lattice atoms. In this type of study it is not necessary to record backscattered ions, other ion beam analysis methods, such as nuclear resonance broadening and particle induced x-ray emission, are also suitable for angular scan measurements. To fully exploit the potential of the method, the measured angular scans can be compared to simulated angular scans. Computer programs have been developed for this purpose [29].

### 4.1.3 Nuclear resonance broadening

In article V nuclear resonance broadening (NRB) is used to determine depth profiles of silicon atoms in GaAs. NRB analysis is based on the resonance reaction of the incident and target atom. The width of the resonance should be narrow enough to enable good depth resolution. Narrow resonances are
usually found in the excitation curves of light isotopes. For an example of resonance reactions and their strengths see ref. [30].

In an NRB measurement the gamma yield from the chosen resonance reaction is measured as a function of the incident ion energy. The absolute concentration of an isotope is deduced by measuring the gamma yield from a reference sample with a known isotope concentration. The depth scale is determined by the stopping of the incident ion, similarly to RBS. The detection limit will depend on the resonance cross section and the depth resolution on the energy straggling of the incident ion and on the energy width of the resonance. Typically concentrations of approximately 0.1 at. % can be measured and the depth resolution is of the order of a few nm’s. Computer programs have been developed to convert measurements of gamma yield versus beam energy to depth profiles [31–35].

4.1.4 Secondary ion mass spectrometry

In article V secondary ion mass spectrometry (SIMS) is applied for the depth profiling of the diffusing silicon atoms. In typical SIMS measurements a primary ion beam is raster scanned over an area ranging from $100 \times 100 \mu m^2$ to $500 \times 500 \mu m^2$. Primary ions $O_2^+$, $Cs^+$, $Ar^+$, $Kr^+$ and $Xe^+$ with energies of 1 keV to 50 keV are used. Collisions between the primary ions and the target result in the release of atoms and molecules from the target into vacuum. A small fraction of the released atoms and molecules are ionized. These ions are extracted with an electric field and analyzed with a mass spectrometer. The depth scale of the SIMS spectrum is determined by measuring the depth of the induced crater with a profilometer. The sputtering rate can then be calculated when the elapsed measurement time is known. The mass resolution of SIMS is good enough to distinguish isotopes of an element from each other and, depending on the studied impurity, concentrations of $10^{13}$ to $10^{15}$ at./cm$^3$ can be detected [24].
4.2 Positron spectroscopy

Positron spectroscopy as an analysis method for defect detection has been used since the 1970’s and the application to semiconductors started in the beginning of the 1980’s. Positron spectroscopy is thus a rather new analysis method.

The strength of positron spectroscopy lies in its ability to detect vacancy type defects. Since the positron has positive charge it will be attracted by negative and neutral vacancies in the semiconductor lattice. In semiconductors, where the electrical properties play a significant role, it is also important to be able to study and determine the charge state of vacancy type defects. This can also be done with positron spectroscopy, by studying the annihilation of positrons as a function of temperature.

When a positron annihilates with an electron two gamma quanta with the energy 511 keV are emitted. The photons carry with them information about the momentum of the annihilating electron-positron pair. This information can be used to determine the chemical environment of the vacancy.

A $\beta^+$ active isotope is used as a positron source. The most common source is $^{22}$Na, where the emitted positron is accompanied by a 1.28 MeV photon. Three different methods of positron spectroscopy are used in this thesis, positron lifetime spectroscopy, Doppler broadening spectroscopy and core annihilation spectroscopy.

4.2.1 Positron lifetime spectroscopy

With positron lifetime experiments the different positron states, their annihilation rates and their relative intensities can be studied. In bulk studies the positron source is sandwiched between two identical sample pieces. For the measurement of the lifetime of the positron, the 1.28 MeV photon from the $^{22}$Na source is used as a start signal and the 511 keV annihilation photon is used as a stop signal. The lifetime of positrons in semiconductors is usually of the order of 200 - 300 ps. For the measurement of positron lifetimes in thin layers, pulsed positron beams have been constructed.
In order to be able to determine defect concentrations, the lifetime of a free positron in a defect free lattice must be known. A p-type semiconductor is usually a good reference sample, since all vacancies are in their most positive charge state and thus the positron trapping is minimized. The free positron lifetime or bulk lifetime $\tau_B$ stays practically constant as a function of temperature.

If negative or neutral vacancies are present in a sample the average lifetime will increase. Thus, a measurement resulting in a higher average lifetime than the bulk lifetime confirms that vacancy-type defects are present in the sample. The average lifetime is a superposition of all positron states \[ \tau_{av} = \eta_B \tau_B + \sum_i \eta_D_i \tau_D_i. \] \[ (10) \]

In Eq. (10), the subscripts $B$ and $D$ refer to bulk and defect, respectively and $\eta$ is the probability of annihilation in state $i$. If a single type of defect is present in a sample, as in article VI the trapping rate $\kappa_D$ and thus the vacancy concentration can be determined from \[ \kappa_D = \mu_D c_D = \frac{\lambda_B \tau_{av} - \tau_B}{\tau_D - \tau_{av}} \] \[ (11) \]

In the above equation $c_D$ is the concentration of vacancies. $\mu_D$ is called the trapping coefficient and it depends on the defect and the host lattice. $\lambda_B$ is the bulk annihilation rate. For positive vacancies the trapping coefficient is so small that trapping of positrons do not occur. For neutral vacancies typical values of the trapping coefficient are $10^{14} - 10^{15}$ at./s. Thus vacancy concentrations of $10^{16}$ cm$^{-3}$ or more are observed. $\mu_D$ is independent of the temperature for neutral vacancies. For negative vacancies $\mu_D$ increases with decreasing temperature. At room temperature the trapping coefficient is $10^{15} - 10^{16}$ at./s and vacancy concentrations of $10^{15}$ cm$^{-3}$ or more can be measured.

### 4.2.2 Doppler broadening spectroscopy

When a positron annihilates with an electron in a semiconductor the two emitted gamma quanta will carry with them information about the momentum of the annihilating electron-positron pair. This is
seen as Doppler broadening of the 511 keV annihilation peak.

The Doppler broadening is often measured as a function of the positron beam energy, with a Ge gamma detector. The resolution of such a detector is approximately 1 keV at 500 keV, which can be compared to the total width of the annihilation peak (2 - 3 keV). This means that the measurement is strongly influenced by the detector resolution. Various shape parameters have therefore been introduced to characterize the annihilation line.

The S, or low-momentum parameter, is defined as the ratio of counts in the central region of the annihilation peak to the total counts in the peak. Similarly the W, or high momentum parameter, is defined as the ratio of counts in the wing regions of the annihilation peak to the total counts. The regions in the annihilation peak of the line shape parameters S and W are shown in Fig. 4. Since core electrons have higher momentum than valence electrons, mainly core electron annihilation contribute to the W parameter and valence electrons to the S parameter. The absolute values of the S and W parameters will depend on the choice of energy windows, therefore it is customary to report relative values. Free annihilation in the lattice is used as reference.

When a positron is trapped in a vacancy-type defect the S parameter will increase and the W parameter will decrease. The increase of the S parameter is due to the fact that in the vacancy the density of valence electrons is reduced, which leads to the narrowing of the momentum distribution. The decrease of the W parameter is easily understood, since the overlap of positrons with core electrons naturally decreases in a vacancy.

The S and W parameters can be expressed as superpositions of the parameters of a specific defect and the bulk values:

\[
S = (1 - \eta_D)S_B + \eta_D S_D, \quad (12)
\]
\[
W = (1 - \eta_D)W_B + \eta_D W_D, \quad (13)
\]
Figure 4: Doppler broadening of the annihilation peak of a Si implanted GaAs sample. The shape parameters S and W are calculated by dividing the indicated areas with the total area of the peak. The energy per channel ratio is approximately 0.13 keV/chl.

where the subscripts D and B refer to defect and bulk, respectively. Examples of S and W parameter curves are shown in the results section, Fig. 11. We can see from Eqs. (12) and (13) that they define a segment of a line in the (S,W) plane. Thus, if there is only one defect present in a sample, the (S,W) point for the sample should be somewhere on the line from \((S_B, W_B)\) to \((S_D, W_D)\). An example of a \((S,W)\) plot is also shown in the results section, Fig. 12.

### 4.2.3 Core annihilation spectroscopy

Even though Doppler broadening and positron lifetime studies can give information about the defect species in a sample, a much more effective way of identifying defects is by studying the annihilation of positrons with core electrons surrounding the vacancy-type defect. The tighter an electron is bounded to its host atom, the higher will the momentum of the annihilating electron-positron pair be. This can
be seen as a broadening of the annihilation peak. In this way the atoms surrounding a vacancy can be identified. This technique is applied in article VI where the detected vacancy-type defect is identified as a P vacancy-Zn atom complex in InP. The 3d electrons of Zn have a higher momentum than the In 4d electrons and this results in a broader annihilation peak.

This type of measurements cannot be done with conventional Doppler broadening instrumentation described in the previous section, since the high background level in the measurements prevents an effective study of core electron annihilation above approximately 515 keV. The high background level is due to Compton scattering of the 1.28 MeV start photon and incomplete charge collection. Therefore core annihilation spectroscopy must be done as a coincidence measurement.

### 4.3 Surface study techniques

#### 4.3.1 Atomic force microscopy

The atomic force microscope (AFM) is designed for surface studies and especially for topographical studies. In an AFM measurement a measuring needle is scanned over the surface of the sample. The needle is interacting with the sample surface and the movement of the needle is registered with the aid of a laser. The light from the laser is mirrored from the measuring needle and detected by a photodiode. Under ideal conditions even atomic resolutions can be achieved with an AFM. The benefits of AFM compared to other microscopes is that it is easy to use. Samples need not be pre-treated, a fact that speeds up the measurement and enables studies of the true sample surface. Measurements can also be done in different measuring environments and different pressures, a vacuum is not required.

In this thesis AFM is used to determine the surface topography of annealed metal/semiconductor samples. It is shown that by combining AFM with RBS, the influence of surface properties on RBS profiles can be eliminated.
4.3.2 Scanning electron microscopy

The scanning electron microscope (SEM) is a versatile surface study tool, which is used in various fields of science, from materials science to medicine and biology. The SEM image is produced by scanning an electron beam over a sample and detecting either secondary electrons, backscattered electrons or characteristic x-rays. Since the SEM image is produced by the use of an electron beam, the sample must be in vacuum in order to avoid collision between electrons and gas molecules. The lateral resolution of a SEM is typically 4 - 6 nm.

In this work SEM is utilized to study grain formation on metal/semiconductor heterostructures.
5 RESULTS

5.1 Backscattering from samples with rough surfaces

In article I a novel method is presented, which combines RBS with AFM, in order to obtain correct depth profiles of diffusing atoms from samples with rough surfaces. A few previous studies on this subject can be found in the literature. Early works by Campisano et al. showed that RBS profiles from samples with rough surfaces can be wrongly interpreted as diffusion [37]. Other studies have focused on the impact of the experimental geometry. Tilting of the sample and the use of glancing angles will have an effect on the resulting spectra, see for example Bird et al. [38], Campisano et al. [39] and Andersen et al. [40]. RBS has also been used to study the surface topography [41–43], recently Metzner et al. have proposed a model which extracts height distributions of the surface roughness from RBS spectra [44, 45]. None of these studies, however, have focused on the essential problem of obtaining correct depth profiles from samples with rough surfaces.

To fully understand the necessity of such a method, this section will briefly consider backscattering from rough surfaces. The problem related to the backscattering from samples with rough surfaces is schematically shown in Fig. 5a. For an ion beam with normal incidence the energy of the detected backscattered ion is given by [16]

\[ E_B = K_M \left( E_0 - N \int_0^t \varepsilon \, dx \right) - N \int_0^{t/\cos \theta} \varepsilon \, dx, \]  

(14)

where \( E_0 \) is the initial energy, \( K_M \) the kinematic factor, \( t \) the scattering depth, \( \theta \) the scattering angle, \( \varepsilon \) the stopping cross section and \( N \) the atom density. Since the kinematic factor is a function of the mass of the scattering atom, Eq. (14) enables us to distinguish backscattering events from different atoms from each other. The depth scale of the backscattering spectrum is given by the stopping integral in Eq. (14) and the concentration of a specific atom species within a target is related to the backscattering
Figure 5:  
a) Schematic figure of how surface roughness will affect RBS with normal incidence. Backscattering from grains will cause diffusion-like effects on the spectrum. 
b) Schematics of the tilting effect on the RBS spectrum. With increasing tilt angle, $\alpha$, less free substrate will be visible for the ion beam and the RBS spectrum will start to show resemblance with the spectrum from a homogeneous film, see also Fig. 6.

cross section. With this knowledge together with information about the experimental setup, an RBS spectrum from a smooth sample can be interpreted correctly.

As an example, let us consider a sample initially consisting of a thin layer of a heavy element on a lighter substrate. After annealing, small islands of the heavy element are formed on the sample surface. If this annealed sample is measured with an ion beam with normal incidence and large scattering angle ($\theta > 150^\circ$) the resulting spectra can easily be misinterpreted as a diffusion profile. This error occurs mainly because of two reasons: First the signal height from the heavy element will decrease at the surface, since large portions of underlying substrate are now free and can be directly seen by the beam. This can be interpreted as diffusion of the heavy element from the surface layer into the substrate.
Figure 6: Example of the effect of sample tilting on the RBS spectrum. The Au(80nm)/ZnSe sample was annealed at 575°C for 5 h. Gold grains were observed on the sample with a scanning electron microscope. The spectra were measured with a 2 MeV $^4\text{He}^+$ beam and a scattering angle of 170°.

Secondly, since the stopping cross section is higher in the islands than in the substrate a diffusion-like tail in the signal of the heavy element will be formed. The length and shape of the tail will depend on the topography of the islands. If this tail is interpreted as diffusion, an incorrect concentration profile will be deduced from the RBS spectrum. This effect can be reduced by tilting the sample, as shown schematically in Fig. 5b. With increasing tilt angle, less free substrate will be visible for the ion beam and thus the surface signal from the heavy element will increase, as seen in Fig. 6 where spectra of an annealed Au/ZnSe heterostructure measured at different tilt angles are shown. In this case, diffusion has also occurred. This can be seen in the spectrum of the most tilted sample (tilt angle 60°) as the low energy tail after the sharp edge in the gold signal.
5.2 Obtaining correct depth profiles from samples with rough surfaces

The study of diffusion from thin metal films into, for example, compound semiconductors can be awkward if metal grains are formed on the surfaces of annealed samples. This will cause overlapping of the diffusion signal and the signal from the grains and render the interpretation of the RBS spectra difficult. This problem can be solved by measuring the height distribution of the grains with an atomic force microscope and thus deduce the effect of the grains on the RBS spectra.

From the topographical information of the AFM images, we can calculate the area a certain grain thickness covers, an example of such a height histogram is shown in Fig. 7 along with the corresponding AFM image. By calculating theoretical RBS spectra with the same step interval as the height histogram and by summing these spectra according to

$$Y_i(n) = \sum_i p_i Y_i(n),$$  \hspace{1cm} (15)

the effect of the surface properties can be eliminated from the measured spectrum. In Eq. (15) $p_i$ is the relative area covered by a certain grain height, $n$ is the channel number and $Y_i(n)$ is the calculated yield for channel $n$. For the calculation of the theoretical RBS spectra a computer program, such as Gisa [46] and Rump [47, 48] can be used. An example of such a calculation is shown in Fig. 8 along...
Figure 8: Experimental and calculated spectra of the sample considered in Fig. 7. The energy per channel ratio in this measurement was 3.42 keV/chl.

with the measured spectra. The calculated spectrum corresponds to the height histogram shown in Fig. 7.

5.3 Channeling results for Au/ZnSe and Pt/ZnSe heterostructures

A comparison between aligned spectra for two samples of different ZnSe crystal quality used in article II is shown in Fig. 9. Sample series I was grown directly on bulk GaAs and sample series II was grown on a GaAs epitaxial buffer layer. We see that the minimum yield in the $\langle 100 \rangle$ channel varies between different sample series, indicating increasing disorder with increasing minimum yield. It has been shown that the use of a GaAs epitaxial buffer layer in the preparation of ZnSe results in a reduction of dislocations and stacking faults [49].

The lattice site of diffused gold has been studied in article IV. Channeling angular scans along the
Figure 9: Comparison between aligned $<100>$ spectra of two of the ZnSe sample series studied in article II. Sample series I was molecular beam epitaxy grown on bulk GaAs and sample series II was grown on a GaAs epitaxial layer.

$<100>$, $<110>$ and $<111>$ directions were measured. Fig. 10 shows the angular scan for an annealed Au/ZnSe sample. In order to avoid dechanneling in the gold layer, the layer was removed prior to channeling measurements by etching the samples in a potassium-iodine (KI) and iodine ($I_2$) solution. We can see from the figure that the yield from the gold atoms decrease in the channeled direction indicating that some of the gold atoms occupy lattice sites. Monte Carlo simulations with the Flux program [29] show that 30% of the Au atoms are close to the lattice site (displaced 0.2 Å).

This could be an indication of the diffusion mechanism for gold diffusion in ZnSe. As mentioned earlier, gold diffuses through the kick-out mechanism in silicon and since gold can act as an acceptor in ZnSe, while on a Zn lattice site [50] this mechanism could also explain gold diffusion in ZnSe.

A similar study for platinum in ZnSe was also conducted in article IV. This study did, however, not reveal any preferential lattice site location of platinum in ZnSe, since random location for the platinum
Figure 10: Angular scan along the $<100>$ channel of an annealed Au(10 nm)/ZnSe sample. The dip in the gold yield indicates that a fraction of the gold atoms are located on lattice sites. The lines in the figure are guides to the eye.

was obtained.

## 5.4 Positron spectroscopy study of Si implanted GaAs

In addition to the results presented in the articles we also present some new positron spectroscopy analysis of Si implanted GaAs. The aim of the study was to investigate if the vacancy concentration beneath the implanted Si distribution will change as Si impurity atoms diffuse into the sample.

A set of GaAs samples implanted with a dose of $10^{16}/\text{cm}^2$ 40 keV Si atoms were prepared for this study. One of the samples was annealed in steps of 100°C from 500 to 700°C, all these annealings lasted for 1 hour. This annealing procedure was done in order to study the recovery process without Si
Figure 11: Valence (S) and core (W) parameter curves for Si implanted GaAs samples. The curves marked with 500°C, 500°C+600°C and 500°C+600°C+700°C are from the same sample annealed in steps for 1 hour. No significant Si diffusion has occurred in this sample. A Si diffusion profile of 0.5 - 1 μm has been formed in the sample annealed at 800°C for 1.5 hours.
diffusion. A second sample was annealed at 800°C for 1.5 hours, which would produce a Si diffusion profile with a depth of 0.5 - 1 µm. All the annealings were done in a quartz-tube furnace, in an argon atmosphere with a pressure of approximately 660 Torr.

The valence and core annihilation parameters, S and W, were measured as a function of the positron energy. In Fig. 11 examples of S and W parameter curves are shown for different annealings. The maximum of the implanted Si profile is at a depth of approximately 50 nm. As can be seen from the figure the S and W parameters gradually approach the bulk values as the annealing temperature is increased. All the detectable implantation induced vacancies have disappeared at 700°C. No significant Si diffusion has occurred in the samples annealed up to 700°C. The sample annealed only at 800°C show approximately the same behaviour as the sample annealed in steps up to 700°C. The decrease in the core annihilation parameter near the sample surface for this sample is probably due to surface

Figure 12: S-W plot of a Si implanted GaAs sample annealed at different temperatures. As can be seen the slope of the S-W plot decreases with annealing, indicating that the dominant defect species changes.
effects, *e. g.* Si clustering, and can therefore not be attributed to vacancies.

In Fig. 12 a S-W plot of the same measurement is shown. As can be seen from the figure the slope of the S-W curve changes as the sample is annealed. This is an indication of the change of defect species. The probable explanation of Fig. 12 is that after implantation there is a mixture of monovacancies and divacancies (or vacancy clusters) in the sample. After annealing in 500°C the monovacancies disappear and only the divacancies remain. The surroundings of a divacancy will be a mixture of Ga and As atoms, whereas the monovacancy is surrounded by either Ga or As atoms. This difference will result in a different slope for the S-W curve [51]. Since the monovacancies are not seen in the annealed samples this is a clear indication that they are mobile at the temperatures considered, which is a requirement for Si diffusion through the vacancy mechanism.

Even though vacancy-type defects are seen beneath the implanted Si in the as implanted and the samples annealed up to 600°C, no vacancies are detected at higher temperatures were diffusion occurs. This is probably due to the fact that the measurements are done at room temperature (RT) and the defect concentrations are too small in thermal equilibrium at RT to be detected with positron spectroscopy. On the other hand, it is also clear that all implantation induced point defects have disappeared at the temperatures required for Si diffusion (*T*> 700°C). In order to study the true diffusion phenomena *in situ* annealings should be done. This is, however, impossible due to the material properties of GaAs, which do not allow annealing in vacuum at the high temperatures required in such an experiment.

### 5.5 Diffusion results

In articles II and III the diffusion coefficients for gold and platinum diffusion in ZnSe are determined. The concentration dependence of the diffusion is studied by applying the *Boltzmann-Matano* method, Eq. (4), and the diffusion coefficient is then calculated by applying a concentration independent diffusion model. The activation energies for gold and platinum diffusion in ZnSe are found to be 1.6 and
1.7 eV, respectively. In addition we find that the gold diffusion depends on the crystal quality of the ZnSe.

In article V silicon diffusion in GaAs is investigated. We show that the diffusion process is a combination of two different diffusion mechanism, interstitial and vacancy mechanism. The activation energy for the interstitial mechanism is found to be 1.7 eV and the activation energies for diffusion in the two sublattices (Ga and As) by the vacancy mechanism are found to be between 2.2 and 2.8 eV depending on the vacancy species and its charge state.

In article VI the migration energy for the P vacancy in InP is determined to be 0.4 eV. From the results obtained it is also possible to deduce the activation energy for the self-diffusion of P atoms through the vacancy mechanism. By combining the result for the migration energy with the formation energy of the P vacancy, which is 1.0 - 1.2 eV depending on the background doping, a value of approximately 1.5 eV is obtained for the activation energy.
In this thesis the properties of three compound semiconductors, ZnSe, GaAs and InP, are investigated. All these compounds are used in optoelectronic devices, such as light emitting diodes and semiconductor laser structures. GaAs and InP are also used in the fabrication of solar cells. They all have superior features compared to conventional semiconductors, such as silicon. For example, they all have direct band gap (silicon has indirect band gap) and they all have higher electron mobility than silicon. While the development of better features for silicon is becoming more and more difficult, the features of compound semiconductors are just being discovered.

In article I a novel analysis method is developed for determining depth profiles by ion backscattering from samples with rough surfaces. The development of this technique makes it possible to obtain correct diffusion profiles from samples with surface roughness, that yield anomalous spectra with conventional RBS. This method is used in article II for the determination of depth profiles in annealed Au/ZnSe heterostructures. The method is also usable in other ion beam techniques, such as elastic recoil detection analysis and in some NRA measurements, especially when emitted particles are detected.

In articles II and III new insight on the thermal stability of metal contacts on ZnSe is given as the diffusion of gold and platinum is studied. Gold diffusion in ZnSe is found to be concentration independent, but to depend on the crystalline structure of the ZnSe. The activation energy for the diffusion is 1.6 eV. The diffusion of platinum in ZnSe is studied similarly. Platinum diffusion in ZnSe is also concentration independent with an activation energy of 1.7 eV.

Article IV deals with the lattice location of diffused gold and platinum atoms in ZnSe. A large amount of the gold atoms is found to be close to lattice sites. For platinum a random location is obtained.

The subject of article V is silicon diffusion in GaAs. Silicon is found to diffuse through a combination of a vacancy mechanism and interstitial diffusion. This is in good agreement with previous
experimental studies of silicon implanted GaAs, which show that large amounts of the silicon atoms occupy interstitial sites.

The formation and migration of P vacancies in InP is studied in article VI. The migration energy of the P vacancy is determined by applying a probability model for the pairing of vacancies and Zn dopant atoms. The formation energy is deduced by applying the commonly known Arrhenius behaviour to the $V_P$-Zn complex concentrations determined from positron lifetime experiments. The formation energy is found to depend on the position of the Fermi level.

In addition to the results presented in the articles, some new results on positron spectroscopy studies of Si implanted GaAs are given in the thesis. The aim of this study was to investigate if the vacancy distribution in the samples changes when the silicon is diffusing. No such behaviour could, however, be observed, since no vacancies were detected in the samples for annealing temperatures over 700°C, which is the temperature required to diffuse enough silicon into the bulk. The recovery mechanism for the GaAs lattice could be determined. It was found that monovacancies disappear already at 500°C, whereas divacancies require annealing temperatures higher than 600°C.

In the future, the diffusion studies in this work can be extended to other impurity atoms and compound semiconductors. The diffusion model and computer programs developed in article V can easily be modified to describe diffusion processes in, for example, II-VI semiconductors. It would also be interesting to study diffusion processes in GaN, which is a very hot topic at the moment. In an ongoing project the P vacancy diffusion in InP is studied in more detail. Exciting new results for vacancy formation on InP surfaces [52–54] are the base for this project. A study were the vacancies diffuse from the surface into the bulk would give more accurate information on the diffusion of the P vacancy in InP. A more detailed study of the grain formation mechanism on Au/ZnSe samples is also planned.
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