Diffusion of Be, Co and Mn impurities in compound semiconductors and glassy carbon studied by the modified radiotracer technique

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ACADEMIC DISSERTATION

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**Abstract**

The main method of modifying properties of semiconductors is to introduce small amount of impurities inside the material. This is used to control magnetic and optical properties of materials and to realize $p$- and $n$-type semiconductors out of intrinsic material in order to manufacture fundamental components such as diodes. As diffusion can be described as random mixing of material due to thermal movement of atoms, it is essential to know the diffusion behavior of the impurities in order to manufacture working components.

In modified radiotracer technique diffusion is studied using radioactive isotopes of elements as tracers. The technique is called modified as atoms are deployed inside the material by ion beam implantation. With ion implantation, a distinct distribution of impurities can be deployed inside the sample surface with good control over the amount of implanted atoms. As electromagnetic radiation and other nuclear decay products emitted by radioactive materials can be easily detected, only very low amount of impurities can be used. This makes it possible to study diffusion in pure materials without essentially modifying the initial properties by doping.

In this thesis a modified radiotracer technique is used to study the diffusion of beryllium in GaN, ZnO, SiGe and glassy carbon. GaN, ZnO and SiGe are of great interest to the semiconductor industry and beryllium as a small and possibly rapid dopant hasn’t been studied previously using the technique. Glassy carbon has been added to demonstrate the feasibility of the technique. In addition, the diffusion of magnetic impurities, Mn and Co, has been studied in GaAs and ZnO (respectively) with spintronic applications in mind.
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1 Purpose and structure of this study

The purpose of this study is to expand the use of the modified radiotracer technique as a tool for studying diffusion in semiconductors and other materials. The previous studies have shown the feasibility of the technique in thoroughly examined self- and impurity diffusion in silicon germanium (SiGe) materials [1, 2]. In the present study, the modified radiotracer technique is applied to examine diffusion in a broader selection of materials, namely gallium nitride (GaN), zinc oxide (ZnO), gallium arsenide (GaAs) and glassy carbon as well as SiGe alloys. Of these, all but glassy carbon are of great interest to the semiconductor industry looking for new materials of the future. The glassy carbon, with dissimilar structure as well as applications, has been added in the thesis to demonstrate the flexibility of the technique.

Beryllium has been chosen for the main impurity for the study as the technique hasn’t been previously applied to study the diffusion of a small, and most likely rapid, dopant element. The diffusion of beryllium is studied in GaN, ZnO, SiGe and glassy carbon. Another focus of the study is on diffusion of magnetic impurities
for spintronic applications. For this, diffusion of manganese in GaAs and cobalt in ZnO has been studied.

The structure of this study is the following: first, an introduction is provided for motivation and background for the study. Second, the theory of diffusion is explained briefly. The governing laws and most common solutions to corresponding equations are presented. Also the diffusion mechanisms in solid materials are discussed. Third, the modified radiotracer technique is explained in detail. Everything from fabrication of samples by ion implantation to construction of the diffusion profiles by ion beam sputtering and measurement of activity is covered. Next, the materials used in this study are discussed. General properties as well as previous knowledge of diffusion properties found in the literature are cited. Finally, there are some concluding remarks about the technique and it’s feasibility as shown by the studies presented in the thesis.

Below, indicated by roman numerals, are listed the publications included in the thesis. The abstracts have also been included for a brief description of the contents of each individual study. Later in this thesis, these publications are cited using the respective roman numerals.

I Migration kinetics of ion-implanted beryllium in GaN and ZnO
submitted to Phys. Status Solidi B

Migration kinetics of ion-implanted beryllium in ZnO and GaN has been studied using the modified radiotracer technique utilizing \(^{7}\text{Be}\) tracers. For ZnO the studies were carried out in the temperature range of 650 - 750°C. Clear Be diffusion following Arrhenius type behavior with low solubility was noted. An activation energy of \(E_A = (2.9 \pm 0.3)\) eV and pre-exponential factor of \(D_0 = 4 \times 10^{-3}\) m\(^2\)/s were deduced for Be diffusion in ZnO. In the case of GaN two annealing temperatures were employed, 850 and 950°C. Distinct trapping of Be in defects induced via implantation was noted.

II Diffusion of cobalt in ion-implanted ZnO
O. Koskelo, J. Räsänen, F. Tuomisto, D. Eversheim, K. Grasza and A.
Diffusion of implanted $^{57}$Co in ZnO has been determined in the temperature range 660 - 950 °C using the modified radiotracer technique. The diffusion was found to follow the Arrhenius type relation with an activation enthalpy of $(2.9 \pm 0.3)$ eV and a pre-exponential factor of $3 \times 10^4$ m$^2$/s. Supported by diffusion data and conclusions provided in the literature, it is proposed that cobalt diffuses substitutionally in ZnO.

III The effect of a material growth technique on ion-implanted Mn diffusion in GaAs
O. Koskelo, J. Räisänen, F. Tuomisto and J. Sadowski
*Semicond Sci Technol* 24 (2009) 045011

Diffusion of ion-implanted Mn in semi-insulating (SI) and liquid encapsulated Czochralski (LEC)-grown GaAs has been determined employing the modified radiotracer technique. The effect of the growth technique and conditions on Mn diffusion in low temperature molecular beam epitaxy (LT-MBE)-grown GaAs has also been studied. Two distinct diffusion components appear in ion-implanted Mn diffusion in GaAs: slow and fast. As the diffusivity for the SI material is slightly higher than that for the LT-grown material, it is observed that the diffusivity of the fast component retards with increasing initial concentrations of Ga sublattice defects. At the same time the Mn concentration in the tail part of the diffusion profile is higher in the LT-grown material. Ga vacancy-assisted clustering of Mn is proposed as a likely reason for the observed effects.

IV Migration kinetics of ion-implanted beryllium in glassy carbon
O. Koskelo, U. Köster, I. Riihimäki and J. Räisänen

Migration kinetics of low-concentration implanted $^7$Be in glassy carbon has been studied by the modified radiotracer technique at temperatures 1285 °C and 1340 °C. The annealed sample concentration profiles show two distinctive components: (i) Main profile broadening assigned to beryllium trap-
ping in defects during annealing. (ii) Tail parts on both sides of the profile maximum related to faster migration. Of the latter the profile representing bulk diffusion lies on the region free of defect influence and is well described by concentration-independent diffusivity. The features of the concentration profile broadening towards the sample surface indicate partial Be trapping in defects upon annealing. Diffusion coefficients for Be migration in the damaged and defect-free material are provided. It is concluded that light impurity atom diffusion in glassy carbon is of the same order of magnitude as diffusion in diamond.

V Diffusion of beryllium in Ge and Si-Ge alloys

O. Koskelo, P. Pusa, J. Räisänen, U. Köster, and I. Riihimäki


Diffusion of implanted $^7\text{Be}$ in Si$_{1-x}$Ge$_x$ ($x=0.20, 0.65, 1.00$) systems has been studied under intrinsic conditions in the temperature range of 460 - 720°C by the modified radiotracer technique. Arrhenius-type behavior with activation enthalpies of 2.0 eV for Ge and 2.5 eV for the SiGe alloys was noted. Unexpectedly, the diffusivity of beryllium is higher in the Si$_{0.80}$Ge$_{0.20}$ material than in Si$_{0.35}$Ge$_{0.65}$ which is discussed in terms of possible prevailing diffusion mechanisms. It is proposed that Be diffusion in Si$_{1-x}$Ge$_x$ systems is dissociative mechanism dominated for germanium rich materials and the kick-out (or interstitialcy) mechanism dominates in silicon rich materials.

1.1 Authors contribution

The author has been responsible for all experimental work in publications I - III and most of the experimental work in publications IV and V. The author has also participated in implantation of samples in publication III. The author has developed computational methods for the analysis and extraction of the diffusion coefficient throughout all the publications. The author has been a main writer in publications I and II, and contributed in writing publications III - V.
2 Introduction

Diffusion is a phenomenon that exists everywhere in nature. It is a result of random movement of matter which tends to even out differences in concentration. A classic example of diffusion is mixing of two fluids of different color. When a dark fluid is poured in to a clear fluid it forms a distinct shape with sharp edges. However, after some time, the dark fluid is spreading and the edges are less distinct. Eventually one ends up with a homogenous mixture of the two with no variation of different concentrations.

Due to intuitive nature of the process above, it is understandable that the mathematical treatment of diffusion was clear before the actual atomic nature of the phenomena. Inspired by the work of Thomas Graham (1805-1869), Adolf Fick (1829-1901) formulated his famous laws in 1855 [3] and they are still valid as long as concentrations are large enough so that small scale fluctuations can be neglected. The first step towards understanding the microscopic nature of the process was taken by no other than Albert Einstein (1879-1955) by his interpretation of the Brownian motion. It had been known for a long time that small particles embedded
in a fluid experience rapid random movement called Brownian motion but no one was able to explain the cause of this jittery movement. It was Einstein, in his miraculous year 1905, who interpreted Brownian motion to be caused by thermal motion of atoms and molecules [4]. The same outcome was also reached independently by Marian Smoluchowski (1872-1917) who published his results a year later [5].

Initially it was thought that diffusion took place only in gases and liquids - even when diffusion of carbon in iron had been used for centuries to harden tools and weaponry by dipping them in a fire. However, the experimental evidence of the crystal structure of solid materials by Max von Laue (1879-1960) and the concept of atomic defects introduced by Yakov Frenkel (1894-1952) and Walter Schottky (1886-1976) laid a ground for a deeper understanding of atomic migration in solid materials. The idea of using radioactive isotopes as tracers in solids was first introduced by Georg Karl von Hevesy (1885-1966). Radioactive isotopes are an effective way to study self-diffusion, i.e., mixing of atoms among themselves, as they are chemically equivalent with the stable isotopes but yet emit electromagnetic radiation which can be easily detected. After a successful measurement of self-diffusion of lead by von Hevesy in 1921 [6], the concept has been (and still is!) used in numerous diffusion experiments.

The birth of solid state electronics with the invention of the transistor in 1947 [7] has led to a remarkable technical evolution in the last decades. From the first commercial transistor radios in the 50’s to the large scale integrated circuits of 80’s and modern computers of 2010. Most of the success of the recent development of computing power is due to downscaling of the components. According to the famous prediction called Moore’s law the number of transistor placed on a microchip will double every two years. The prediction was originally made in 1965 [8] and remarkably it still holds after 45 years! At the same time the success of the technology has grown the semiconductor industry into a huge business with worldwide sales of $226 billion in 2009 and a workforce of 200 000 in United States alone [9]. It is estimated that in 2010 the industry is making 1 billion transistors for every man, woman and child on Earth [10].

Downscaling, however, has its natural limits. When, for example, the thickness of the oxide gate in FET reduces down to a few atomic layers, quantum-mechanical
tunneling of electrons introduces a sharp increase in the leakage current [11]. With smaller scale and higher frequencies, the heat created becomes an increasing problem as well and components must be constantly cooled down in order to prevent the chip from burning. For these reasons, the search for new materials with better properties is a topic of constant research and silicon is in no means the only choice these days. For example, LED televisions recently introduced to larger audiences are based on the gallium nitride technology.

The main method for modifying the properties of semiconductor materials, in order to manufacture basic building blocks such as \( p-n \) junctions, is to introduce a controlled amount of impurities inside the material. As heating the materials is often a part of the procedure during the growth in order to remove some of the unwanted defects, it is necessary to know how do different impurities behave in the material during the annealing. Increased temperature is also used to control the concentration and distribution of the impurities in a preferred manner. As diffusion is accelerated by temperature, the knowledge of diffusion behavior of different impurities in different materials is essential for successful fabrication of working materials.

To understand diffusion in solids, one must do a lot of measuring. Different elements and materials give different, and sometimes conflicting, results. But all of them are needed in order to fully understand the fundamental mechanisms. In science you can never tell what piece of information afterwards might turn out to be crucial. And of course, if one would know beforehand which method provides the best results and knowledge for the future, one might argue why was research needed in the first place! I’m modestly hoping that this thesis would end up as a part of the bigger picture that someone could use in future for making the world a better place. The history of science is also full of life changing results gained from experiments designed to deliver something else in the first place. It is always motivational to return back to the birth of the transistor in 1947 and wonder whether Bardeen and Brattain ever though Internet as one of the outcomes of their invention.
3 Theory of diffusion

3.1 Fick’s laws

Macroscopic diffusion can be described by Fick’s laws [12]. If we assume a macroscopic concentration of particles $c(x,t)$ embedded in some matrix, it can be assumed that in the case of a concentration gradient $\frac{\partial c}{\partial x}$, a flux of particles $J$ is created towards the lower concentration and this flux is proportional to the gradient. The flux $J$ can therefore be expressed by

$$J = -D \frac{\partial c}{\partial x}, \quad (1)$$

where $D$ is conveniently called the diffusion coefficient. This is Fick’s first law and it can easily be generalised in three dimensions.

In a steady state the flux $J$ does not depend on time. In order to describe a time-dependent case one must also include the conservation of matter. It can be easily derived that, if no particles are created nor annihilated, the net flux of particles out from an infinitesimal space at given time is equal to the negative
change in concentration over infinitesimal period of time in that given space. This gives us the following equation of continuity

\[ \frac{\partial J}{\partial x} = -\frac{\partial c}{\partial t}. \]  

Combining (1) with (2) gives

\[ \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial c}{\partial x} \right). \]  

If \( D \) is assumed independent of concentration and therefore \( x \), this simplifies to

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}. \]  

This is Fick’s second law and is often referred as the diffusion equation. Whenever \( D \) cannot be approximated to be independent of concentration, other methods, such as the Boltzmann-Matano analysis [12–14], must be applied in order to solve the diffusion equation.

Diffusion is isotropic in cubic crystals and amorphic materials. However, with non-cubic crystals, such as wurtzite, experiments can usually be designed in such a way that the flow can be considered as one dimensional. Diffusion is one dimensional if a concentration gradient exists only in one direction (\( x \)) and it, as well as the concentration, is the independent of the perpendicular coordinates (\( y, z \)) [12, chapter 2.3].

### 3.2 Solutions to diffusion equation

One wants to use the diffusion equation (4) to solve the concentration \( c(x,t) \) at given time and location. The diffusion equation is a partial differential equation and some boundary, as well as initial, conditions are needed. As comprehensive mathematical treatment to obtain the solution is tedious, we just briefly refer here to the solutions of the equation used in this thesis. For a more comprehensive analysis one should look in to the literature [12, 15–17].
3.2.1 Constant surface concentration

In many practical applications the diffusing particles are let to diffuse inside the material so that the concentration on the surface of the material is kept constant. This is the case, for example, when the material is embedded in a gas or a liquid containing the diffusing particles. If one assumes the constant surface concentration of $c_0$ on top of the semi-infinite material ($0 < x < \infty$), the solution of equation (4) is

$$c(x, t) = c_0 \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right),$$

where erfc is the *complementary error function*\(^1\), $D$ is the diffusion coefficient and $t$ is the elapsed time. In addition, this solution is to be used when diffusion is limited by the solubility of the diffusing particles in material. If the concentration at source, even if not constant, is kept above the solubility limit, the particles diffuse inside the material as if the concentration at the source would be constant at the solubility limit.

3.2.2 More general solution

As a common practice, the distribution of an implanted species is often assumed Gaussian. As a result, the shape of the profile retains it’s Gaussian form. One extreme of this is the so called *thin film solution* where the initial distribution of atoms is assumed to be set on a plane of infinitesimal thickness. The concentration $c(x, t)$ at $t = t_0$ is therefore described by

$$c(x, t_0) = M \delta(x),$$

where $M$ is a number of diffusing particles per unit area and $\delta(x)$ is Dirac’s delta function\(^2\). If this plane is inside an infinite material ($-\infty < x < \infty$) at a point $x_0$ on the $x$ axis and $t_0 = 0$, the solution of equation (4) is

$$c(x, t) = \frac{M}{2\sqrt{\pi Dt}} \exp \left( -\frac{(x - x_0)^2}{4Dt} \right).$$

\(^1\text{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}} \int_0^x \exp(-\eta^2) d\eta\)

\(^2\text{Dirac’s delta function is actually a distribution with } \delta(x) = 0 \text{ for } x \neq 0 \text{ and } \int_{-\infty}^{\infty} \delta(x) dx = 1\)
As $t_0$ can be arbitrary chosen, this solution can be used with any normally distributed initial profiles.

Sometimes, if the Gaussian approximation of the initial distribution of the diffusing material is insufficient, a more general solution is required. If one assumes an arbitrary, but physically sensible, distribution of particles $c(x, t_0) = c_0(x)$ in an infinite material, the solution can be obtained by using Fourier integrals [18]. Then the solution of equation (4) is

$$c(x, t) = \frac{1}{2\sqrt{\pi Dt}} \int_{-\infty}^{\infty} c_0(\nu) e^{-\frac{(x-\nu)^2}{4Dt}} \, d\nu.$$ (8)

It can be easily seen, that in a case of the thin film source (6), the above solution simplifies to equation (7) according to definition of $\delta(x)$. If the surface of the sample is assumed to be at $x = 0$ and it is too close to be ignored, the above solution can be used to obtain the following result [19, 20]

$$c(x, t) = \frac{1}{2\sqrt{\pi Dt}} \int_0^{\infty} c_0(\nu) \left[ e^{-\frac{(x-\nu)^2}{4Dt}} + \alpha e^{-\frac{(x+\nu)^2}{4Dt}} \right] \, d\nu,$$ (9)

where $\alpha \in [-1, 1]$ can be used to describe the “reflectivity” of the surface. When $\alpha = 1$, it’s referring to situation where all the particles diffusing to the surface, remain inside the material, i.e., they don’t vaporise. This is obtained by imposing the boundary condition $\frac{\partial C}{\partial x} |_{x=0} = 0$. The other opposite, $\alpha = -1$, is obtained using boundary condition $C(0, t) = 0$. This refers to situation where all of the atoms diffusing to the surface escape from the material. The effect of $\alpha$ is illustrated in Fig. 1.

The above solution (9) has been used in all of the publications I-V. In addition, the solution for the constant surface concentration has been used in publication I due to solubility issues explained more in detail in the paper.

### 3.3 Dependence on temperature

It has been found empirically that the diffusion coefficient $D$ can be described by [14]

$$D = D_0 e^{-\frac{E}{RT}},$$ (10)
where $D_0$ is a pre-exponential factor, $E_A$ activation energy, $T$ absolute temperature and $k$ Boltzmann constant. This equation describing the temperature dependence of the diffusion coefficient is called an Arrhenius equation.

The temperature independent constants $E_A$ and $D_0$, often cited in literature, can be determined experimentally by measuring the diffusion coefficient in varying temperatures. When the logarithm of the measured values is plotted against the inverse of temperature, $E_A$ and $D_0$ can be obtained by fitting a straight line. $E_A$ is then the slope of the line and $D_0$ is the point where the line crosses the y-axis.

### 3.4 Diffusion in solids

At atomic level diffusion in solids is considered as consecutive jumps of atoms from discrete positions to another. It is clear that the mechanisms available for atoms to diffuse depend on the surroundings of the atom, i.e., the structure of the material. Therefore, before moving on to the diffusion mechanisms, the structure of solid materials as well as defects are discussed. As the structure of the material
is mainly dictated by chemistry and is more or less unchangeable, the focus is on
defects, which play a major role in atomic diffusion in solids.

3.4.1 Point defects

A material is called a solid when its atoms cannot move freely around. They
are localized in their specific positions that form the atomic structure of the solid
material. In most cases atoms are arranged in a repetitive three dimensional
structure that can be mathematically described by a lattice. In this case atoms
form a crystal. The structure of the crystal depends on the material but it might
also depend on the temperature, the pressure or even the previous state of the
solid as in the case of ice [21]. If the atoms are distributed randomly without any
repetitive structure, the material is called amorphic.

A real crystal is never as perfect as a mathematical lattice. Deviations from an
ideal structure are called defects. Defects can range from small point defects up to
large scale dislocations and macroscopic grains. Some amount of point defects are
always present due to a non-zero temperature. As atoms are constantly vibrating
at their lattice sites due to thermal energy, there is a certain probability for them
to jump off from their site. An unoccupied lattice cite is called a vacancy. An
atom between lattice sites is called an interstitial.

With alloys of two (or more) components, more complex point defects may
exist. An anti site is a point defect where an atom in a sublattice of one component
is replaced by an atom of the other component. Usually one anti site is dominating
over others for being energetically more favorable. This is the case, for example,
with low temperature molecular beam epitaxy grown gallium arsenide where there
are essentially zero native gallium anti-sites compared to arsenic anti-sites [22].

In addition to above, foreign atoms can also be found in a crystal. These defects
are called impurities. They can reside on a lattice site or between lattice sites and
they are called substitutional impurities and interstitial impurities, respectively.

3.4.2 Diffusion mechanisms

Atomic diffusion can be divided in two main categories depending on the diffusing
atom. If the diffusing atoms are of the same element than one of the elements
of the material it is diffusing in, diffusion is called self-diffusion. If the diffusing atom is a foreign one, i.e., not one of the host elements, diffusion is called impurity diffusion. Although there is no fundamental difference in diffusion of atoms depending on the category, some mechanisms can only be distinguished in the case of impurity diffusion. This is simply due to the reason that if two similar atoms switch positions, the state of the system remains the same before and after the switch and no observable diffusion has taken place. As all of the studies in this thesis are considering impurity diffusion, we shall concentrate on that.

There are two basic ways for atoms to move inside a crystal. Either they move via the lattice sites or between the lattice sites. If the atoms diffuse only through lattice sites, the corresponding mechanism is called a substitutional mechanism. Atoms diffusing solely between the lattice cites are diffusing by an interstitial mechanism. The mechanisms stem naturally from the impurity defects named in the previous chapter and are illustrated in Fig. 2. The interstitial mechanism requires atoms to push themselves between the host atom lattice sites which creates stress in the material. This stress generally increases with the size of the diffusing atom and therefore the interstitial mechanism is usually dominating for smaller atoms such as hydrogen. The interstitial mechanism is also generally much faster than the substitutional mechanism (depending on the nature of bonds). This is understandable because in order to diffuse substitutionally, from one lattice site to another, diffusing atom needs a vacant position next to it. If the number of vacancies is low, it might take a relatively long time until suitable vacancy is available.

Most of the time more complex mechanisms are taking place. This is possible due to some reactions diffusing atoms may go through with the host atoms. Basically these reactions are making it possible for diffusing atoms to switch between two main mechanisms thus creating effectively new diffusion mechanisms. For example, an impurity atom diffusing interstitially may push a host atom from a lattice site replacing it and thus creating a self-interstitial, described by

$$A_i \rightleftharpoons A_s + I,$$

where $A_i$ denotes an impurity atom in an interstitial position, $A_s$ an atom in a
substitutional position, and $I$ a selfInterstitial atom. The above mechanism is called the *kick-out mechanism*\(^3\). Essentially the mechanism is then the following: a highly mobile interstitial impurity is diffusing through the interstitial path until it is stopped by replacing a host atom in a lattice site by pushing it to interstitial position. The rate in which this takes place can then be affected by many things. If the diffusing atom is small, it may proceed very rapidly through the interstitial path and it is less probable for it to push a larger host atom off it’s lattice site. The kick-out mechanism is also affected by the energy required to push the host atoms from their lattice sites to interstitial positions - a feature depending on the crystal structure as well as the host atom element.

Another common mechanism is the *dissociative mechanism*\(^4\). In this mechanism an impurity atom in an interstitial position is recombining with a vacancy $V$ and thus creating a substitutional impurity in a lattice site:

$$A_i + V \rightleftharpoons A_s.$$  

\(^3\)also known as *interstitialcy mechanism*  
\(^4\)also known as *Frank-Turnbull mechanism*
It is obvious that with this mechanism the number of vacancies in a crystal affects the rate at which the diffusion takes place. As native vacancies are often coupled with respective self-interstitials, these interstitials can also slow down diffusion by blocking the interstitial sites making it more difficult for impurities to proceed. It must be noted that with both of the mechanisms above, also the opposite reactions are possible. For convenience, these are still labeled in the same way.

In addition to the mechanisms described above, more complex ones may take place as well. They may involve two or more vacancies, clustering of the impurities or diffusion through much faster paths such as grain boundaries. All of them are still more or less based on the basic reactions above.
4 Modified radiotracer technique

Studying solid state diffusion directly always requires some fundamental steps. First, a sample must be prepared by depositing a known distribution of the diffusing element on top or inside the material studied. Then the sample must be annealed in a controlled environment. And finally, the distribution of diffused material is measured in order to compare depth profiles before and after the annealing to gain quantitative results.

The idea of the radiotracer technique is to use radioactive isotopes of the element of interest as tracers. As the concentration of diffusing atoms is directly proportional to the activity, the depth profile can be measured by monitoring the activity. This makes it possible to use much lower impurity concentrations as methods for measuring activity are highly sensitive. The host material with stable isotopes does not interfere and counting can be performed selectively using a specific energy to diminish the background noise. In the modified radiotracer technique radioactive atoms are deployed by ion implantation.

In the following chapters modified the radiotracer technique is explained in
detail. First, implanting of radioactive ions is considered, then annealing of the samples and finally the construction of profiles by ion beam sputtering and measurement of activity.

4.1 Implantation of radioactive tracers

Ion implantation is a method where atoms are deployed inside the target material by collision. In order to achieve the high velocities required, atoms are ionised and then accelerated, usually electrostatically. The kinetic energy of this flux of ions, i.e., the ion beam, can then be controlled by the voltage used for acceleration. Usually the number of ions hitting the target can be monitored by measuring the ion current from the target. The upper limit of the dose is then limited by the ion current from the accelerator and the time available. By implanting, atoms can be deployed below the sample surface and therefore some surface effects can be avoided. For example, inevitable oxidation of surface of some materials after the sample is removed from the vacuum doesn’t directly affect the impurities inside the sample. With ion implantation it is also possible to deploy material above the solubility limit if higher concentrations are desired.

4.1.1 Radioactive ion beam

For implanting radioactive atoms, a radioactive ion beam is required. There are two ways to create radioactive ion beams. First, one can use radioactive material as an ion-source (off-line) and, second, radioactive ions can be created on-line with the implantation. Both of the methods require special facilities for the obvious health issues with radioactive material.

Implantation off-line is a straightforward procedure: radioactive atoms are provided in an ion-source (e.g., as a part of some stable molecule in a liquid), they are ionized, mass separated and accelerated to a desired energy. If samples are crystalline, they are usually positioned in front of the beam with a slight angle in order to avoid channeling effects. In this thesis, off-line implantation was used in publications II, IV and V. In publication II $^{57}$Co was provided as a part of a liquid and implanted using a separator at the university of Bonn. In publications IV and V a graphite target, previously bombarded with a 590 MeV proton beam,
was used as a source of ions for radioactive $^7$Be atoms in the ISOLDE facility at CERN [23].

Usually when we are talking about creating radioactive ion beams on line, we are talking about ISOL-method (“ion-source-on-line”). There is another alternative called the “in-flight” method. The main difference between these two methods is that in the ISOL method newly created radioactive atoms are re-accelerated but in the “in-flight” method ions get their kinetic energy from collisions of the original beam [24]. For more information about the “in-flight” method, see, e.g., [25]. In the ISOL method, radioactive nuclides are produced in spallation, fission and fragmentation reactions with target placed in front of high energy particle beam. The ISOL method is generally feasible with thick targets which thermalize reaction products before they diffuse out from the target and to be ionized. Thick targets provide large total cross-sections for isotopes and post-acceleration allows accurate control of the energy and therefore mass separation of the beam [26]. In publications I and III, $^7$Be and $^{54}$Mn ions (respectively) were implanted in ISOLDE facility at CERN using ISOL method. $^7$Be and $^{54}$Mn were created by bombarding uranium-carbide target with 1.4 GeV proton beam.

As in the ISOL method a large number of different elements and isotopes are created, the problem of selecting particles of interest gets more challenging. The standard way of separating desired ions from a beam is to use strong magnets. Charged particles are experiencing a Lorentz force and are diverted from their path according to their mass to charge ratio. With a proper adjustment of magnetic field, only desired particles can be selected to a fixed angle of beam line. With radioactive beams, where unstable isotopes are present, this is insufficient due the isobaric elements with nearly equal masses. This challenge is overcome in ISOLDE at CERN by using a resonance ionization laser ion source (RILIS) which is feasible with practically all metallic elements [27, 28].

4.1.2 Implanted depth profile

Interaction phenomena of an ion with the target are well known and studied. An ion traveling inside the material loses it’s kinetic energy by interacting with the electrons and nuclei of the target material. The ratio of the two energy loss modes
(electronic and nuclear) depends on the energy of the ion. With higher energies the interaction with electrons dominates over the interaction with nuclei [29].

An ion travelling inside the material is experiencing multiple interactions with particles inside the material. Due to the random nature of collisions, the individual path as well as the range of the ion are impossible to predict but can be estimated using statistical methods. As typically the number of implanted ions is very high, even when very low concentrations are desired (typically 2.5·10^{12} atoms for 1 ppm\(^5\)), the projected range, \(R_P\), of a monoenergetic beam can be well evaluated.

Even if the kinetic energy of the ions could be maintained at a desired level, the distribution of implanted ions, i.e., the depth profile, is still affected by the spreading of the energy due to statistical fluctuations in the collision processes. This phenomenon is called straggling. This ensures that implanted atoms always form a distribution inside the material. Sometimes a simple Gaussian distribution can be used for approximation but for more accurate description more refined functions are available [30]. In practice, however, the distribution due to the fluctuations of the energy is often a result of other variations in experimental conditions, such as non-uniformity of the sample material [29].

4.2 Annealing

Diffusion samples are annealed in order to enhance diffusion in a controllable manner. An isothermal annealing is desired as the diffusion coefficient changes as a function of temperature. The calculation of the effective temperature afterwards would require some knowledge of the behavior of the diffusion coefficient one is aiming to determine.

According to the Arrhenius law diffusion is taking place even at room temperature. However, as activation energies in semiconductors are typically around 1 eV and higher [31], one can use Eq. (10) to estimate the contribution of diffusion in room temperature compared to diffusion in higher temperatures. Just by simple calculation, one can easily see that even with 1 eV, the increase of temperature from 300 K to 400 K increases the diffusion coefficient more than four magnitudes.

\(^5\)60 keV Co in ZnO from II
As the ratio increases rapidly with increasing activation energies and as annealing of semiconductors usually takes place in much higher temperatures, it can be concluded that diffusion in room temperature can be ignored in any practical applications.

The goal with annealing is to obtain a diffusion profile that is distinctly different from an initial profile so that noticeable diffusion has taken place. If the annealing time is too short or temperature too low, one might end up with a nearly unchanged distribution greatly increasing the uncertainty of the result obtained later by fitting. However, if the time is too long or temperature too high, too much diffusion might take place. The result would then be a widely spread diffusion profile with possibly a too low concentration to be measured effectively.

The diffusion length, \( l_D \), can often be used to estimate the time needed for proper annealing. The diffusion length is defined as

\[
l_D = \sqrt{Dt},
\]

where \( D \) is the diffusion coefficient in a particular temperature and \( t \) annealing time. The diffusion length is a characteristic measure for the amount of diffusion and for Gaussian solution, Eq. (7), equals the standard deviation of the distribution. As temperature is often fixed for Arrhenius plot purposes, the annealing time can be calculated by fixing diffusion length as what is seen proper and estimating the diffusion coefficient at desired temperature. In general one has \( D = D(T) \) and with time-dependent temperature \( D = D(T(t)) \).

As annealing is typically taking place in high temperatures, protecting the sample surface is nontrivial. In most cases, annealing in air would cause a quick deterioration of the surface due to oxidation. A straightforward way to avoid this, is to anneal the samples in vacuum. This way any unwanted gaseous elements, such as oxygen, can be pumped out from the chamber before and during the annealing.

Some times annealing in vacuum introduces unwanted effects. High temperature and low pressure can enhance vaporization of some elements leading to a drastic deterioration of the surface. This is the case, for example, with GaAs where arsenic vaporizes out from the sample if annealed in vacuum [32]. This can obviously lead to distorted and unreliable diffusion profiles. However, there are ways to avoid this. One can provide arsenic inside the annealing chamber but this
is not very convenient as arsenic and many of it’s compounds are very toxic. More common way is to use capping where GaAs sample is encapsulated inside some material such as SiO$_2$ [33].

Some special cases do exist. For example, it has been shown that for ZnO, in certain temperature range, smoothest surfaces are obtained by annealing the samples in oxygen [34].

4.3 Serial sectioning by ion-beam sputtering

Serial sectioning is an effective, yet destructive, method for obtaining depth profiles. The profile is constructed by slicing the sample surface to several parallel layers. When the concentration in every slice is determined, the depth profile can be constructed. The principle is illustrated in Fig. 3. One wants to make the slices as thin as possible in order to accurately represent the actual depth profile. This is, however, limited by the sensitivity of the method used for measuring the concentrations. On the other hand, by increasing the thickness of the slices, the details of the shape of the profile are lost. This might also distort the profile if the thickness is chosen poorly as the distribution inside the individual slice is lost. A typical example of this is demonstrated in Fig. 4. There are no fundamental limitations to varying thickness of the individual slices during the sectioning of the sample and this can be done whenever technically possible.

The serial sectioning can be performed in several ways, depending on the application. If the diffusion length is at least several micrometers, mechanical techniques, e.g., grinding, can be used. However, for more subtle cases more refined methods are available. Ion-beam sputtering is a method used in the thesis and is therefore considered here.

Sputtering is a method where atoms on the surface of the material are removed due to energetic particle bombardment. The energy is transformed into the solid by collisions between incoming particles and atoms in the surface layers of the solid. The erosion in sputtering is measured by the sputtering yield $Y$, which is defined by number of atoms removed from the surface per incoming particle. The yield is a function of the target material, the incident particle and it’s kinetic energy as well as the angle of incidence of the particle beam. It has been shown
Figure 3: Schematic figure of the serial sectioning of a sample. The line represents the actual concentration profile and grey columns concentration measured in individual slices. Information about the distribution inside each slice is lost and therefore the height of a column corresponds to the average concentration in the slice.

Figure 4: Schematic figure of the importance of slice thickness in serial sectioning. Thickness of the rightmost slice is poorly chosen as the average concentration (height of the column) doesn’t correspond well to the actual concentration (line). The concentration profile appears to continue deeper inside the sample than it actually does.
that the maximum emittance can be achieved by using angles as high as $60^\circ - 80^\circ$ [35]. This also helps to increase the depth resolution as ions hitting the surface in low angles interact with thinner layers than ions approaching in higher angles yet still depositing the same total energy.

The energy, typically few keV, is chosen so that the particles hitting the surface have enough energy to break the bonds between the atom and the solid and to exceed the surface binding energy. On the other hand, with higher energies, incident particles will interact with a thicker layer on the surface decreasing the depth resolution of the technique. Also, with high enough energies, the yield will actually decrease with increasing energy as incident particles will penetrate deeper inside the solid transferring most of the energy to atoms other than ones on the surface layers.

The sputtering yield is also increasing as a function of the mass of the incident particle. This means generally that, with the same energy, the heavier the particle the higher the yield. The effect of the target material is more complicated as, in addition to atomic number of the target atoms, the yield is affected by the properties of the solid such as crystallinity, temperature and surface topography. One must also keep in mind that with single crystal materials the yield is heavily affected by the crystal orientation and the angle of incidence of the particle beam. Channeling, for example, can result in a strong decrease in the sputtering yield [35].

The schematic figure of the sputtering device used in this thesis is presented in Fig. 5. A sample is glued on to the sample holder using conductive carbon cement and the sample holder is rotated during the sputtering in order to average any inhomogeneities in the beam and crystal structure. The glue must be conducting because otherwise ion bombardment would lead to charge build up that would eventually deflect the incoming ions due to Coulomb repulsion. Conducting glue is also required for the measurement of the ion current hitting the sample.

The ion current is measured as a function of time in order to determine the relative amount of ions hitting the sample. In principle one could measure the absolute amount of ions by measuring the current but in this particular case samples are smaller than the actual sample holder from which the current is measured. Therefore part of the current measured is due to ions hitting the sample holder
instead of the sample. Once again, one could measure the relative areas of the
two but the distribution of the beam intensity would be much harder to deter-
mine. Luckily this is not necessary as only relative information about the current
is needed in order to compensate the changes in the current during sputtering.

The sputtered material is collected to the Mylar foil which is strong, transparent
plastic material. The foil is wound up in the device capable of changing the part
of the foil exposed to the sputtered material, much like the film in a camera. Each
section of the foil then corresponds to the specific slice of the sample surface. The
Mylar foil is placed in front of the sample as close as technically possible in order
to collect as much of sputtered material as possible. It is noteworthy that the
maximum intensity of the sputtered material is directed towards the normal of
the sample surface. This is independent of the angle of incidence of the beam as
long as the angle is not too high causing most of the ions to be reflected from the
surface [36].

The expose times per foil can be varied, if necessary, in order to vary the
thickness of individual slices. The voltage needed to change the foil is also mon-
tored with the ion current in order to afterwards determine the corresponding
ion charge collected per each individual foil. While processing the samples in this
thesis, typically from 20 to 30 foils were sputtered per one sample.

4.4 Measurement of activity

The construction of the impurity profiles begins with the measurement of radioac-
tivity from the foils. This gives us relative concentration of radioactive material in
each foil as the concentration is directly proportional to the activity. Although a
majority of the sputtered material consists of atoms of the sample material (as well
as the sample holder!) it does not disturb the measurements as stable isotopes are
not emitting any high energy radiation. Even if the samples were polluted with
some other radioactive material, this can be differentiated by using a multichannel
analyzer and measuring only the energy specific to the radioactive decay origin
from the material one is interested in.

The measurement of the activity sets the lower limit for the amount of im-
planted material. As the activity in each foil represents the concentration in that
specific slice, it is clear that one want’s to measure it as accurately as reasonably possible. As a rule of thumb, in this thesis, each foil was measured at least until the limit of 1000 counts in the specific peak was reached (after the background was suppressed). This gives a statistical accuracy of around 3% according to Poisson distribution [37]. The time required to reach this limit depends on the specific activity of the foil at hand. This, once again, corresponds to the half-life of the used isotope as well as the amount of the implanted material, i.e., the number of atoms. So, when making a decision of how big a dose one should consider, one must estimate the time required to measure the last foils with least material using the half-life of the isotope, the estimated time for the whole procedure and the experience from the previous experiments.

After the measurement of activities in the foils one has the relative concentration of the impurity in the sputtered slices. The final step is then to construct the profile from the measured data by determining the depth scale of the profile. First one must obtain the total thickness of the sputtered layer. This is best done using profilometer with a depth resolution around 1 nm. As can be seen in Fig. 5, the
whole sample is exposed to the ion beam and is therefore a subject of sputtering. In order to accurately measure the thickness of the removed layer, one must protect a fraction of the sample surface before sputtering. This was done by introducing a small droplet of the same conductive carbon cement used for glueing the sample to the sample holder. The thickness of the removed layer can then be determined by measuring the step between the two areas.

A thickness of each individual slice, $t_n$, is then determined by comparing the charge collected during the respective foil, $C_n$, to total charge accumulated during sputtering, $C_{tot}$, such that

$$t_n = \frac{C_n}{C_{tot}} t_{tot},$$

where $t_{tot}$ is the thickness of the sputtered layer.

To get the diffusion coefficient one must fit the proper solution of the diffusion equation with appropriate boundary conditions (see section 3.2) to the measured profile. If the solution needs an initial profile, like in Eq. (9), it must be provided either by measuring the concentration profile from an unannealed sample or by using a simulated profile obtained, for example, by a SRIM calculation [38]. With multiple diffusion coefficients measured, one can plot them against the inverse of temperature to obtain an Arrhenius plot and by fitting a straight line to obtain the temperature independent coefficients $E_A$ and $D_0$. 
5 Materials

For this thesis, a wide range of materials has been studied using the modified radiotracer technique. The main interest has been towards semiconducting materials but one study of glassy carbon has been included in order to demonstrate the feasibility of the technique for other materials as well. The most essential properties and applications of the materials are summarized below.

5.1 Zinc oxide

Zinc oxide (ZnO) is a wide, direct band gap semiconductor with a band gap of 3.3 eV and it has a hexagonal wurtzite structure. The as-grown ZnO material is naturally $n$-type, and it is widely believed that intrinsic defects such as the zinc interstitial and oxygen vacancy are acting as a source of donors making the material $n$-type [39].

ZnO is in no means a new material but has been around for a long time. Indeed, studies of its lattice parameter can be found dating back to 1935 [40] and ZnO
has had many industrial application due to it’s piezoelectric properties and the near ultraviolet band gap. The present interest towards the material has risen mainly because of the availability of high-quality substrates and studies reporting $p$-type conductivity. This has made it a possible candidate for replacing GaN as a dominant optoelectronic material. The availability of fairly high-quality ZnO bulk single crystals and a much simpler crystal-growth technology could result in a lower cost for ZnO-based devices [41].

Since the predictions of Dietl et al. [42], ZnO has become one of the most extensively studied materials for spintronics applications. Spintronics is a field of electronics aiming to employ magnetic properties of materials in addition to electronic properties. Doping with transition metals is the most promising approach to achieve the required ferromagnetism in room temperature and numerous studies have been published lately concerning transition metal doped ZnO. Most of them deal with either Mn or Co doped ZnO films [43, 44].

The available data for diffusion in single- and polycrystalline ZnO consists mostly of results from self-diffusion experiments for Zn [45–50] and O [46, 51–56]. Some impurity diffusion studies can also be found for H [57–60], Al [61], Mn [62], Ni [48], Cu [63], Ga [61] and In [64]. In addition to publication II, only one previous study concerning Co diffusion in ZnO has been presented in the literature [62]. However, the results were obtained using high Co concentrations and it is suggested that Co diffusivity is distinctly slower than the diffusivity of other impurity elements in ZnO. In publication II diffusion of Co in ZnO was examined with a much lower impurity concentration in order to obtain more reliable picture of the Co diffusion properties in ZnO.

Though it has recently been discovered that mixing Be with ZnO enables band gap engineering from 3.3 eV of pure ZnO even up to 10.6 eV of BeO [65, 66], preceding the publication I, no data for Be diffusion in ZnO was available.

### 5.2 Gallium nitride

Gallium nitride (GaN) is a III-V semiconductor with a direct band gap of 3.4 eV and like ZnO, it has a hexagonal wurztite structure. The beginning of the recent interest towards the material can be dated back to 1989 when $p$-type GaN was
realized for the first time [67]. This made it possible to fabricate working $p$-$n$
junctions and light emitting diodes (LED) out of GaN.

The success of the material relies on a solubility between other nitrides, AlN
and InN, allowing band gap engineering from 2 eV to 6 eV. This means emitted
light from red to ultraviolet [68]. The ability to create light through the whole
visible spectrum has made it possible to fabricate white light LEDs which has
made semiconductors a real alternative for light bulbs and fluorescent lighting as
well as liquid crystal display technology.

So far the best dopant for $p$-type GaN has been Mg [69, 70]. However, its
relatively large thermal ionization energy makes it a less than ideal material for
efficient use. It has been shown that substantial improvement can be gained using
beryllium instead [69]. GaN is also one of the candidates for spintronic material
[42] and ferromagnetism in room temperature has indeed already been reported.
The question still remains whether the magnetism is caused by clustering of the
implanted species instead of diluted magnetic semiconductor [71].

The available dopant diffusion data (excluding hydrogen and it’s isotopes) is
somewhat limited: Be [72], N self-diffusion [73], Mg [74, 75], Si [76], V [77], Er
[78], Pt [79] and Au [80]. As in the previous study of Be diffusion in GaN [72]
only one diffusion coefficient is presented, more research is needed to understand
Be diffusion in GaN. In publication I, a small amount of beryllium is implanted
into GaN and it’s migration is studied.

5.3 Gallium arsenide

Gallium arsenide (GaAs) is a compound semiconductor of two elements, gallium
and arsenic. It has a direct band gap of 1.4 eV and has a zincblende structure
which is a two compound equivalent the of diamond structure often found in
semiconductors.

Historically GaAs started to gain interest in 1960’s due to the appearance of
bipolar transistor superior in performance to a silicon device [81]. The downside is
that it is more expensive and harder to manufacture thus holding back it’s possi-
bilities to replace silicon in large scale. However, it was realized as a good material
for MESFET\textsuperscript{a} and microwave applications due to it’s high frequency performance. For this reason it is still a current material for modern microelectronic applications.

GaAs is also very promising candidate for spintronic applications. The realization of ferromagnetic (Ga,Mn)As in 1996 \[82\] started the experimental pursue for room temperature ferromagnetism in diluted magnetic semiconductors and it has since been one of the most prominent material for spintronics. However, diffusion properties of manganese in GaAs are not fully established.

It is also anticipated that the Ga vacancies introduced during growth can affect the diffusion properties of the material. However, there is discrepancy whether these vacancies enhance the diffusion \[22, 83\] or retard it \[84\]. In publication III diffusion of Mn in GaAs is studied in materials that have been manufactured with different techniques and therefore have different amount of excess Ga vacancies. This will hopefully shed some light on the dilemma.

5.4 Silicon germanium

Silicon germanium (SiGe) is an alloy of two most well known semiconductor materials. The potential of the material is the possibility to manufacture Si\(_{1-x}\)Ge\(_x\) with arbitrary composition \(x\) thus engineering properties of the semiconductor such as band gap varying from 0.65 eV of pure Ge to 1.1 eV of pure Si. This is possible due to the same lattice structure of the materials (diamond) and nearly matching lattice parameters differing only 4 %.

SiGe also has great economical potential for its compatibility with existing silicon technology. Though silicon is in no means superior material compared to some novel semiconductors, the huge cost of rebuilding the required infrastructure is making it hard to replace in bigger scale. For this, SiGe has a huge economical advantage compared to other new semiconductor materials.

As SiGe integrates seemingly to existing silicon technology, it can also be used to modify the properties of silicon for better performance. This is possible, for example, by strained silicon grown on top of SiGe layer. Silicon assumes the larger lattice constant of SiGe thus enhancing the electron and hole mobilities in the material \[85\]. One of the disadvantages of silicon is also its indirect band gap,
which makes it less than optimal for light emitting applications. With the lattice mismatch, it has previously been impossible to integrate efficient light emitting materials, such as GaAs, directly with silicon based components. Using SiGe in between the mismatch problems could be overcome [86].

Due to a long history of both silicon and germanium in electronics there are large amounts of data available on diffusion in both elements. Interestingly there are clear differences in dopant diffusion between the materials. As composition of $\text{Si}_{1-x}\text{Ge}_x$ can freely be adjusted, this makes it possible to study origins of the differences. Therefore SiGe is an excellent material to study fundamentals of diffusion as well.

Introducing beryllium into SiGe has recently aroused interest due to the observed improved quantum efficiency of optical emission [87]. In publication V, the diffusion of Be in $\text{Si}_{1-x}\text{Ge}_x$ has been studied as a function of a composition $x$.

5.5 Glassy carbon

Carbon is one of the elements capable of forming variable stable structures. These allotropes, such as diamond and graphite, can have drastically different properties despite the chemical similarity of the materials. As carbon bonds covalently, the strong bonds make it also possible to construct much larger and exotic entities such as fullerenes and carbon nanotubes consisting of hundreds of individual carbon atoms.

Glassy carbon (also called vitreous carbon) is a non-graphitizing allotrope of carbon. It is known that carbons produced by the solid-phase pyrolysis of organic materials fall into two distinct classes. The so-called graphitizing carbons tend to be soft with relatively high densities, and can be readily transformed into crystalline graphite by heating at temperatures in the range $2200 – 3000^\circ$C. In contrast, non-graphitizing carbons are hard, low-density materials that can not be transformed into crystalline graphite even in high temperatures [88].

In addition to the very high thermal stability, glassy carbon is chemically extremely inert and it has also been shown that the oxidation rates of glassy carbon are lower than those of any other carbon. These properties make glassy carbon a widely used material in electrochemistry as electrode material. It also has applications as high temperature crucibles and due to carbons biocompatibility makes it
a potential material for prosthetic devices [89]. It has also recently been suggested that glassy carbon could be used in nuclear applications as a protective layer on the graphite reactor core surface in molten salt breeder reactors [90].

The structure of glassy carbon has long been a subject of debate, but recent results suggest that it has a fullerene related structure [89]. It must therefore be pointed out that although glassy carbon shows a high level of disorder, it should not be confused with amorphous carbon even if the label “glassy” makes this tempting.

Prior to publication IV no previous diffusion data for glassy carbon was available. Even for carbon in general, a limited amount of diffusion data is available. However, self-diffusion and impurity diffusion studies for diamond indicate a clear difference in diffusion properties: the carbon self-diffusion activation enthalpy in the order of 7 eV [91] is of different magnitude than activation enthalpy of about 1 eV for Li diffusion in diamond [92]. As concluded in publication IV, it would seem that light impurity atom diffusion in glassy carbon is of the same magnitude than in diamond.
6 Conclusions

Beryllium diffusion in GaN, ZnO, glassy carbon and SiGe has been studied in publications I, IV and V (respectively). The isotope used in the publications, $^7$Be, has a suitable half-life of 53.3 days [31], which made it possible to carry out experiments over a relatively long period of time (in contrast to isotopes with half-lives of some hours). In practice, with longer available time this meant higher number of samples and a possibility for extended annealing of some of the samples (e.g., 12 days for Si$_{0.35}$Ge$_{0.65}$ in V) thus giving a broader range of temperature. With $^{54}$Mn and $^{57}$Co, the half-lives were even longer ($t_{1/2} = 312.2$ d and $t_{1/2} = 271.8$ d, respectively) although this had to be compensated with higher implantation doses cause activity is inversely proportional to half-life.

The long half-lives in all of the studies also allowed a proper analysis between sample measurements. Sometimes the only way to start the measurements is to make a guess, an educated one perhaps, but nevertheless a guess about the annealing temperature and annealing time. After the first measurements it is therefore important to analyze the data thoroughly before making any decisions.
on the next annealing.

The implantation of $^7\text{Be}$ also introduced implantation induced defects due to co-implantation of stable $^7\text{Li}$. This presented a challenge for diffusion studies but also an opportunity to study the fundamentals of diffusion. In fact, the role of the implantation induced defects turned out to be one of the key aspects in publications I and IV, in the studies of Be migration in GaN and glassy carbon.

Mn diffusion in GaAs was studied in several GaAs materials with different initial concentration of defects (III). The modified radiotracer technique proved to be sensitive enough to spot the small differences in diffusivity as diffusion was found faster in materials with less Ga sublattice defects.

Although diffusion in samples with more initial defects was found slower, the concentration of Mn was higher in the deeper part of the concentration profile than in samples with less initial defects. This is proposed to be caused by clustering of Mn which gives an important information for aiming towards the diluted magnetic semiconductor of Mn doped GaAs.

Co diffusion in ZnO was found to follow Arrhenius type behavior with activation enthalpy of $(2.9 \pm 0.3)$ eV, a typical value for impurity diffusion in single crystal ZnO (II). It is proposed that Co diffuses substitutionally in ZnO but it is noted that much more work is needed as both impurity as well as self-diffusion data exhibit a considerable spread.

In the future it would be interesting to continue to use the modified radiotracer technique to study the diffusion of beryllium in new materials. For example, beryllium is frequently used as an $p$-type dopant in GaAs but diffusion data for implanted beryllium in GaAs is limited [93]. Beryllium is also a good alternative for a $p$-type dopant in AlN - a material with a complete solubility with GaN and therefore a good candidate for optoelectronics [94].

For spintronic applications the studies of Mn diffusion in GaAs and Co diffusion in ZnO could be complemented with other methods such as the Mössbauer spectroscopy for better understanding of diffusion mechanisms taking place.
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