

Annealing behavior of Li and Si impurities in GaAs

by

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Dedicated to my wife

Tatiana Kirilova Dimitrova

I wonder, by my troth, what thou and I

Did, till we lov'd?

John Donne (1572-1631)

Ágrip

Áhrif hitameðhöndlunar á hegðun litín (Li) og kísil (Si) aðskotaatóma í gallín arseni (GaAs) voru könnuð með raf- og ljósmælingum.

Einkristölluð lög af holu- og rafeindaleiðandi kísil-íþættu GaAs voru ræktuð úr vökvafasa við 700°C og 840°C. Hitun á kristöllum í kjölfarið við háan arsen hlutþrýsting breytir holuleiðandi sýnunum yfir í rafeindaleiðandi en eykur styrk rafeinda í sýnum sem voru rafeindaleiðandi fyrir. Deilt hefur verið um ástæður þessarar hegðunar en niðurstöður okkar gefa til kynna að flutningur Si frá grindarsæti As yfir í grindarsæti Ga geti skýrt hana.

Sveim litíns inn í rafeinda- eða holuleiðandi GaAs við 800°C gerir efnið hálfleitan- grandí. Hin litla rafleiðni í slíkum sýnum á sér stað þegar holur í gildisborða seytla milli smárra einangrandi útfellinga í kristallinum. Viðbótarhitun gerir sýnin holuleiðandi. Hitun við lágt hitastig (200-300°C) veldur stökkleiðni þar sem hleðsluberar stökkva frá hlöðnum til hlutlausra veilna í kristallinum. Eftir hitun við hátt hitastig (> 600°C) er aftur um hefðbunda holuleiðni í gildisborða að ræða.

Abstract

The annealing behavior of Li- and Si-related impurities in GaAs was studied by means of electrical and spectroscopical measurements.

Epitaxial *p*-type Si-doped GaAs and *n*-type Si-doped GaAs samples were grown from a liquid phase at 700°C and 840°C, respectively. Subsequent annealing of the crystal, in the presence of As overpressure, converts the *p*-type sample into *n*-type whereas the *n*-type material remains *n*-type but with increased carrier concentration upon annealing. The reason for this type-conversion has been debated but our results suggest that it may be explained by Si-atoms switching their lattice position from As- to Ga-site.

Li diffusion into either Zn- or Si-doped GaAs (*p*- and *n*-type, respectively) turns the material semi-insulating. A subsequent annealing results in *p*-type conduction. The electrical conduction in the as-diffused material is governed by holes in the valence-band percolating around insulating regions of Schottky-barriers attributed to metallic precipitation. After annealing at low temperatures (200-300°C) a new conduction mechanism, dominated by carrier hopping between defects, takes over. Annealing at high temperature (600°C) result in conventional conduction of thermally activated holes in the valence-band.

List of papers

This dissertation is based on the following papers:

1. H. G. Svavarsson, J. T. Gudmundsson, G. I. Gudjonsson and H. P. Gislason, The effect of Si site-switching in GaAs on electrical properties and potential fluctuation, *Physica B* **308 - 310** (2001) 804-807
2. H. G. Svavarsson, J. T. Gudmundsson, G. I. Gudjonsson and H. P. Gislason, Potential fluctuations and site switching in Si-doped GaAs studied by photoluminescence, *Physica Scripta* **T101** (2002) 114 - 118
3. H. P. Gislason, K. Leosson, H. Svavarsson, K. Saarinen and A. Mari, Lithium induced vacancy formation and its effect on the diffusivity of Lithium in Gallium Arsenide, *Materials Science Forum* **258-263** (1997) 1810-1820
4. H. G. Svavarsson, J. T. Gudmundsson and H. P. Gislason, Impurity band in lithium-diffused and annealed GaAs: Conduction and Hall effect Measurements, *Physical Review B* **67** (2003) 205213
5. J. T. Gudmundsson, H. G. Svavarsson, S. Gudjonsson and H. P. Gislason, Frequency-dependent conductivity in lithium diffused and annealed GaAs, accepted for publication in *Physica B* (2003)
6. H. G. Svavarsson, J. T. Gudmundsson and H. P. Gislason, Lithium diffused and annealed GaAs: Admittance spectroscopy study, submitted to *Physical Review B*

Other publications not included in the thesis:

7. H. O. Olafsson, J. T. Gudmundsson, H. G. Svavarsson and H. P. Gislason, Hydrogen passivation of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ studied by surface photovoltage spectroscopy, *Physica B* **273-274** (1999) 689 - 692

8. J. T. Gudmundsson, H. G. Svavarsson and H. P. Gislason, Lithium-gold-related complexes in p-type crystalline silicon, *Physica B* **273-274** (1999) 379 - 382

9. H. G. Svavarsson, S. Olafsson, N. Hellgren and U. Helmersson, Electrostatic powder impact deposition (EPID) of Ge on Si and Cu substrate, micro-structure and morphology study, *Journal of Physics D: Applied Physics* **33** (2000) 1155-1160

10. J. T. Gudmundsson, H. G. Svavarsson and H. P. Gislason, Hopping conduction in lithium diffused and annealed GaAs, *Proceedings of the 12th Conference on Semiconducting and Insulating Material (SIMC XII)*, (IEEE, Smolenice Castle, Slovakia, 2002) 9 - 12

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Chapter 1

Introduction

Semiconductors made of elements from groups III and V in the periodic table are among the technologically most important compound semiconductor materials for microelectronic applications. Of these, gallium arsenide (GaAs) and aluminum gallium arsenide (AlGaAs) have found the widest use, owing to their highly developed technology. The well known phrase “GaAs is the material of the future and will always remain so” reflects the current status of GaAs among semiconductors. Despite the interesting properties of GaAs for the production of integrated circuits for memory devices and processors, silicon (Si) is still the dominant material in the semiconductor industry. The greatest impact of compound semiconductors has, so far, been in areas where their unique properties allow functions that cannot be performed by silicon. III-V semiconductors are commonly used in the fabrication of opto-electronic devices, e.g. red laser- and light-emitting-diodes in the visible spectrum (AlGaAs) and in the infrared spectrum (GaAs) as used for CD and DVD drives. Fiber-based data transport also relies on GaAs laser diodes. GaAs is also of interest for high frequency applications [Nguyen and Micovic, 2001]. Its electron effective mass is only 1/16 of

that of Si, consequently with higher mobility of electrons. This makes GaAs a prospective candidate for the production of future integrated circuits despite its technologically more elaborate processing.

The widespread use of satellite receivers for television and radio is closely related to the introduction of integrated receiver- and amplifier devices based on GaAs. These devices are capable of operating at microwave frequencies [Nguyen and Micovic, 2001]. Analog integrated circuits have also become very important in mobile telephone communication. All these applications make use of several superior properties of III-V semiconductors as compared to Si. In optoelectronic applications the most important properties are mainly the direct band-gap of GaAs (in contrast to that of Si) with band-gap energy E_g in the near-infrared portion of the spectrum which can be modified in a relatively wide range by alloying the GaAs with aluminum to produce $\text{Al}_{1-x}\text{Ga}_x\text{As}$ [Matsueda et al., 1990]. AlAs has a wider band-gap than GaAs and the energy-gap can be changed by varying the amount of Al in the $\text{Al}_{1-x}\text{Ga}_x\text{As}$ compound. Both GaAs and AlAs crystallize in the zincblende structure with nearly the same lattice constant which makes it easy to grow heterostructures with low defect concentration. At the hetero-interface a sharp potential change confines electrons into two-dimensional electron gas. In such a system the mobility can be made very high.

When growing or depositing electrically or optically active layers it is necessary to be able to control the carrier type, carrier concentration and mobility. Thus, examining the fundamental microscopic processes in growth, incorporation of impurities, formation of intrinsic defects and neutralization of defects, provides the basis for understanding the technologically relevant properties.

This work is divided into two main subjects: Annealing behavior of Si impurities in GaAs and the conduction mechanism of lithium-diffused (Li-diffused)

GaAs. The first main subject (chapter 3) is devoted to the behavior of Si impurity in GaAs and discussions of possible reasons for the p - to n -type conversion which occurs during annealing. Scientist have argued whether this occurs by switching of Si atoms between As and Ga lattice sites or by creation of native defects. It is well known that n -type Si-doped GaAs can be converted into p -type by thermal annealing but the mechanism has not been clarified. Here we start with p -type Si-doped GaAs, convert it to n -type and try to identify the type-conversion mechanism. Commercially available Si-doped GaAs is usually n -type where the Si-atoms occupying Ga-sites are in majority. Therefore the sample preparation had to start by growing the crystal in order to obtain crystals with the desired properties.

The second main subject (chapters 3 and 4) considers the electrical conduction in an impurity-band in Li-diffused and annealed GaAs. Special emphasis is put on the effects of high Li concentration. Lithium forms many defect complexes with native defects and other dopants in GaAs. It has been observed that such a system exhibits unexpectedly high conduction, particularly at low temperatures (below room temperature). Many models have been made in order to explain this behavior but the observed conduction mechanism remained unexplained over a range of temperatures. Among the phenomena used to describe the carrier transport mechanism in Li-diffused GaAs are *hopping*, *percolation* and *quasi-metallic* conduction.

Chapter 2

Semiconductors

Solid materials are classified as insulators or conductors on the basis of their electrical properties. Conductors are typically (but not solely) metals and are able to carry electrical current, in contrast to insulators. Semiconductors are a group of materials having electrical conductivities between metals and that of insulators. Figure 2.1 shows the portion of the periodic table where most semiconductors appear. The conductivity of semiconductors can be varied over several or many orders of magnitude by changing the temperature, optical excitation and impurity content, which makes semiconductors a natural choice for electronic devices. The difference between the electrical resistivity of a good conductor and a good insulator is striking. For a metal, the resistivity can be as low as 10^{-10} Ωcm at a temperature of 1 K, disregarding the possibility of superconductivity. For an insulator the resistivity can be as high as 10^{22} Ωcm . This range of 32 orders of magnitude may be the widest of any physical property of solids [Kittel, 1986]. The conductivity is caused by electrons and holes, which are released from the donors and acceptors by ionization, respectively. Such ionization can be produced thermally, by light, other particles or an electric field [Böer, 1990]. Depending on

	IIIB	IVB	VB	VIB
	B	C	N	O
IIB	Al	Si	P	S
Zn	Ga	Ge	As	Se
Cd	In	Sn	Sb	Te
Hg	Tl	Pb	Bi	Po

Figure 2.1: A selected portion of the periodic table where most common semiconductors appear. Si and Ge are the best known elementary semiconductors but compound semiconductors from columns II and VI or columns III and V are important in device applications.

the material and the smallest structural size used in a device, the electrical and optical properties can be significantly altered by defects which are present with a concentration as low as 10^{12} cm^{-3} (compared to the typical concentration of $10^{23} \text{ atoms/cm}^3$ in solids). Electronic transitions are the basic processes of interest in semiconductor physics. As dictated by Pauli's exclusion principle no two electrons in a given interacting system can occupy the same quantum state. Thus electrons in solids are restricted to certain energies and are not allowed at other energies. As the inter-atomic spacing decreases, when isolated atoms are brought together to form a crystal, the energy levels form a band which spans a range of energies. If the levels are spaced closely enough, *Heisenberg's uncertainty principle* no longer permits distinction between individual levels [Böer, 1990]. Since the inner core electrons are tightly bound to the nucleus they are not easily removed and only the valence electrons have to be taken into account.

Energy bands

As well known, energy levels of electrons form bands of energy states, separated by gaps where no energy levels exist, as the individual atoms are brought together to form a crystal [Böer, 1990; Blakemore, 1985]. This highest occupied band at zero temperature is called the *valence-band* while the first unoccupied band just above the energy-gap is denoted *conduction-band* (see figure 2.2). These are the most important bands to consider for semiconductors.

An insulator has an empty conduction-band and a full valence-band at zero temperature, separated by large energy-gap E_g (≥ 4 eV). In a perfect crystal no energy states exist between these bands and, hence, the gap is called the forbidden gap. Semiconductors are similar to insulators except that their energy-gap is smaller. Empty or full bands cannot carry electrical current, but electrons from the valence-band can be excited up to the conduction-band, resulting in an electron-hole pair capable of electrical transport. In metals the uppermost band is only partially full so electrons are free to move. A schematic expression of the band-model, introduced here above, is given in figure 2.2.

Defects

If an atom, either foreign or native, is accommodated in the crystal outside a host lattice site it is referred to as *interstitial* but a foreign atom in a lattice site is called *substitutional*. Foreign atoms in semiconductors are referred to as impurities and a deliberate addition of foreign atoms is called *doping*. Such impurity- and native-atoms create defects in the host-lattice and introduce new energy-states into the forbidden gap. The most common native defects are classified as vacancies and anti-sites. As the name implies, vacancies are simply empty lattice sites whereas anti-site refers to a native host atom substituting the other atomic site. A

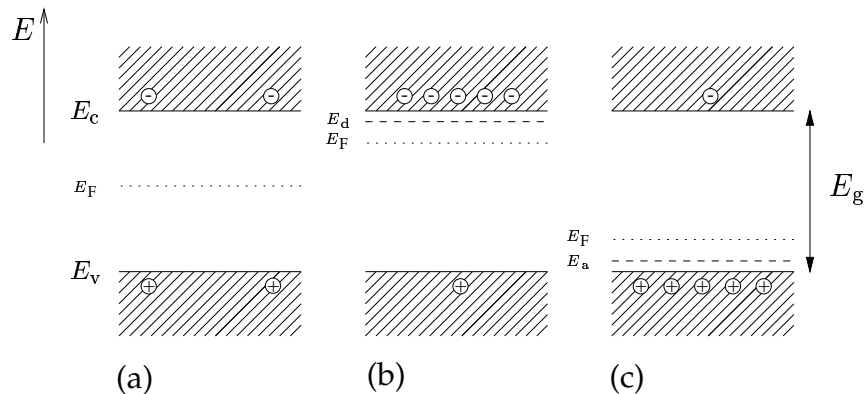


Figure 2.2: Energy band diagrams of semiconductors. (a) E_c is the bottom of the conduction-band, E_v is the top of the valence-band and E_F is the Fermi-level. Here, the position of the Fermi-level in the middle of the band-gap indicates an intrinsic semiconductor. (b) In an n -type semiconductor shallow donor energy levels, E_d , contribute their electrons to the conduction-band and the Fermi-level E_F (to be defined in section 2.1.2) is in the upper half of the band-gap. (c) In p -type materials, shallow acceptor levels, E_a , create holes in the conduction-band and the Fermi-level is located in the lower half of the band-gap.

graphical representation of vacancy- and interstitial-defects is given in figure 2.3.

In GaAs the anti-sites are either a Ga-atom on an As site (Ga_{As}) or vice versa, As

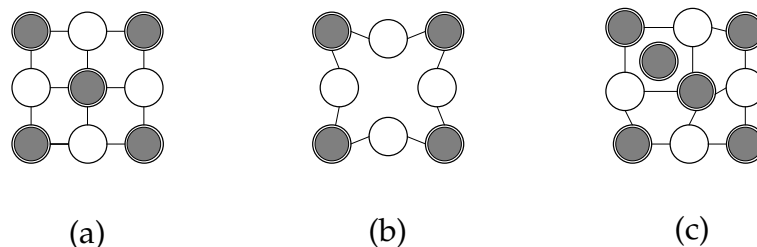


Figure 2.3: Defects in a binary compound crystal: (a) a perfect crystal, (b) a vacancy and (c) an interstitial atom.

on a Ga site (As_{Ga}). In addition there may be a variety of complex defects formed by any two or more of these aforementioned individual defects. Depending on whether the defects donate or accept electrons in the crystal medium they are classified as *donors* or *acceptors*, respectively. A donor ionizes by donating an electron to the conduction band, leaving behind a positively charged impurity center. If the energy needed for ionization is low the defect is called *shallow* but

deep otherwise. An acceptor may capture an electron from the crystal and become negatively charged. Consequently a positively charged hole appears in the valence-band.

In most cases both donors and acceptors are present but not necessarily in equal amounts. If the donors are in majority the semiconductor is *n*-type but *p*-type otherwise. The ratio between the total donor-concentration N_d and the total acceptor-concentration N_a is defined as the compensation ratio K . For *n*-type material K is written as N_a/N_d but as N_d/N_a for *p*-type.

2.1 Transport in semiconductors

A simple model of the electrical conductivity in semiconductors assumes the conductivity to depend on the carrier type (electrons or holes), their concentration and their mobility. The electrical conductivity can therefore be written as;

$$\sigma = e(n_0\mu_n + p_0\mu_p) \quad (2.1)$$

where n_0 and p_0 are the concentrations of free electrons and holes, respectively, μ_n and μ_p their corresponding mobility and e the electron charge. The subscript 0 denotes thermal equilibrium.

2.1.1 Mobility

In an electric field, carriers in solids acquire the velocity $\mathbf{v}_d = \hbar\mathbf{k}/2\pi m_0$, referred to as the drift velocity where \hbar is the Planck constant, m_0 is the rest mass of the carrier and \mathbf{k} its wavevector. In the absence of scattering processes v_d should increase continuously with time. However, due to elastic and inelastic scattering processes the direction and magnitude of the wavevector change. In reality the crystal lattice is disturbed and the electron (or hole) movement may be described as random scattering from lattice atoms, neutral and ionized defects, other carriers, acoustic phonons and optical phonons [Böer, 1990, pages 778–779]. These types of scattering mechanism act as a friction component causing constant carrier drift velocity and heating of the crystal [Böer, 1990, chapter 32]. When a force (i.e. electric field) is applied to an electron (or a hole), its acceleration can be described by a modified Newton's law where the perfect periodic crystal potential is taken into account by an effective mass m^* instead of its rest mass m_0 . The

resulting average drift velocity has the following form

$$\bar{v}_d = -\frac{e\tau}{m^*}E, \quad (2.2)$$

where τ denotes the mean time between scattering events (*mean free time*) and E the strength of the electric field.

The proportionality factor between the drift velocity and the electric field strength is called the electron mobility μ

$$\mu = -\frac{e\tau}{m^*}. \quad (2.3)$$

For GaAs the mobility is nearly isotropic (independent on crystal directions) and at 300 K the value of μ for electrons may be up to 8000 cm²/Vs in undoped GaAs [Look, 1989, page 3] and as high as 2.40×10^5 cm²/Vs in high-purity GaAs at 77 K [Wolfe et al., 1970].

The way in which the electron (hole) mobility behaves as a function of the temperature depends on which processes dominate the scattering. Most of these scattering events are elastic because of the large mass ratio between defect and carrier. In elastic scattering only the momentum of the carrier is changed; its energy is not. Inelastic scattering causes a change in momentum and energy. Scattering by emitting optical phonons and intervalley scattering are the only inelastic scattering processes during which the carrier can lose a significant amount of its energy to the lattice [Böer, 1990, chapter 32]. Usually, ionized impurity scattering is dominant at low temperatures whereas scattering by acoustic phonons dominates at high temperatures [Look, 1989, pages 76–83]. Their functions can be explained as follows: In the case of lattice scattering a carrier moving through the lattice encounters atoms which are out of their normal positions due to ther-

mal vibration. The frequency of such scattering events increases with increasing temperature. Therefore we expect the mobility to decrease when the semiconductor is heated. On the other hand, scattering from lattice defects (such as ionized impurities) dominates at low temperatures. Since the atoms of the cooler lattice are less agitated, lattice scattering becomes less important. At the same time the thermal motion of carriers is slower. Since a slowly moving carrier is likely to be scattered more strongly through an interaction with a charged ion than a carrier with greater momentum, impurity scattering events cause a decrease in mobility with decreasing temperature. It can be derived theoretically that at low

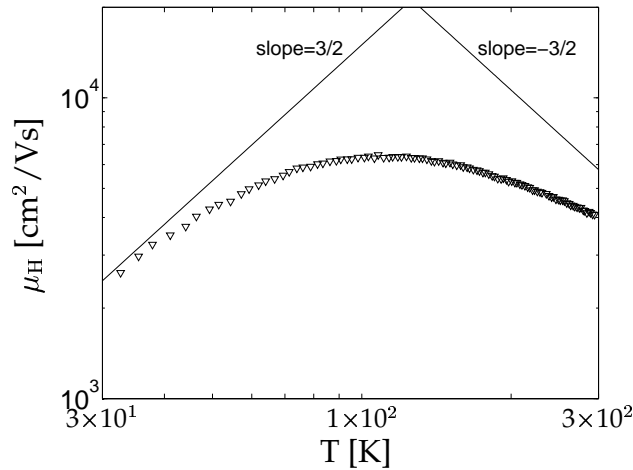


Figure 2.4: Temperature dependence of electron mobility of bulk Si-doped GaAs with $n = 2 \times 10^{16} \text{ cm}^{-3}$.

temperatures when lattice scattering dominates $\mu \propto T^{3/2}$. At high temperatures where scattering of ionized impurities dominates $\mu \propto T^{-3/2}$ [Look, 1989, pages 76 – 83]. The mobility curve in figure 2.4 shows the experimental value of the Hall-mobility of electrons in Si-doped GaAs. The solid lines are drawn to ease a comparison to the simple model $\mu \propto T^{\pm 3/2}$ presented here above. In reality the ideal behavior is rarely observed, especially for high defect concentrations. Note that in papers II and IV the temperature dependency of the mobility is presented

on a semi-logarithmic scale, as conventionally done, instead of log-log scale as in figure 2.4.

2.1.2 Semiconductor statistics

For a system of indistinguishable particles which occupy quantum states in accordance with the Pauli principle, the probability of occupancy for a state of energy E at thermal equilibrium is given by the *Fermi-Dirac* distribution function [Blakemore, 1987]

$$f(E) = \frac{1}{1 + \exp\left(\frac{E - E_F}{k_B T}\right)}. \quad (2.4)$$

A plot of the Fermi-Dirac distribution is shown in figure 2.5. The quantity E_F is

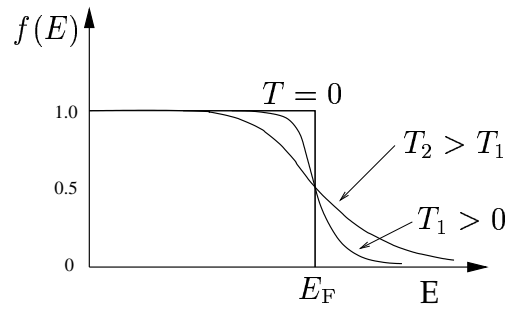


Figure 2.5: The Fermi-Dirac probability function $f(E)$ as a function of energy for finite temperatures and for an absolute zero temperature.

commonly known as the *Fermi* energy-level and represents the energy at which the probability of electron occupation is $1/2$. It may be described as a normalizing parameter, characterized by the number of electrons per unit volume n_0 and the density of states function $N(E)$ [Blakemore, 1987, pages 10–16]. The concentration of electrons with energy in the range dE is given by the product of the density of allowed states $N(E)$ in that range and the probability of occupation

$f(E)$. Thus the density of occupied electron states N_e in dE is

$$N_e dE = N(E) f(E) dE. \quad (2.5)$$

We then derive an equation for the electron concentration n_0 in the conduction-band at a given temperature by integrating equation (2.5),

$$n_0 = \int_{E_c}^{\infty} N(E) f(E) dE, \quad (2.6)$$

with the subscript 0 denoting thermal equilibrium. The result of the integration is the same as that obtained if we represented all of the distributed electron states in the conduction-band by an *effective density of states* N_c located at the conduction-band edge E_c . Then equation (2.6) can be rewritten as

$$n_0 = N_c f(E_c). \quad (2.7)$$

For electrons with effective mass m_n^* in the conduction-band the effective density of states is

$$N_c = 2 \left(\frac{2\pi m_n^* k_B T}{h^2} \right)^{3/2}. \quad (2.8)$$

A similar equation is used for the effective density at the valence-band N_v with m_n^* replaced with m_p^* , the effective mass of a hole. When $E_c - E_F \gg k_B T$ and $E_F - E_v \gg k_B T$ equation (2.7) simplifies to

$$n_0 = N_c \exp[-(E_c - E_F)/k_B T] \quad (2.9)$$

and

$$p_0 = N_v \exp[-(E_F - E_v)/k_B T] \quad (2.10)$$

for electrons and holes, respectively.

Another important relation is the *law of mass action*

$$n_0 p_0 = N_c N_v \exp(-E_g/k_B T) = n_i^2 \quad (2.11)$$

where n_i is the intrinsic concentration at the corresponding temperature.

Chapter 3

Gallium arsenide

GaAs is a compound semiconductor which belongs to a group of semiconductors commonly referred to as III-V. It crystallizes in the zincblende structure in a diamond-like array which can be described as two face-centered cubic cells, interpenetrating each other. The effective mass of electrons in GaAs is small which makes it feasible for high speed application. Its band-gap is direct with $E_g = 1.52$ eV at 0 K. At room temperature E_g is 1.42 eV which limits its use in opto-electronic devices to the infrared region. Figure 3.1 illustrates the qualita-

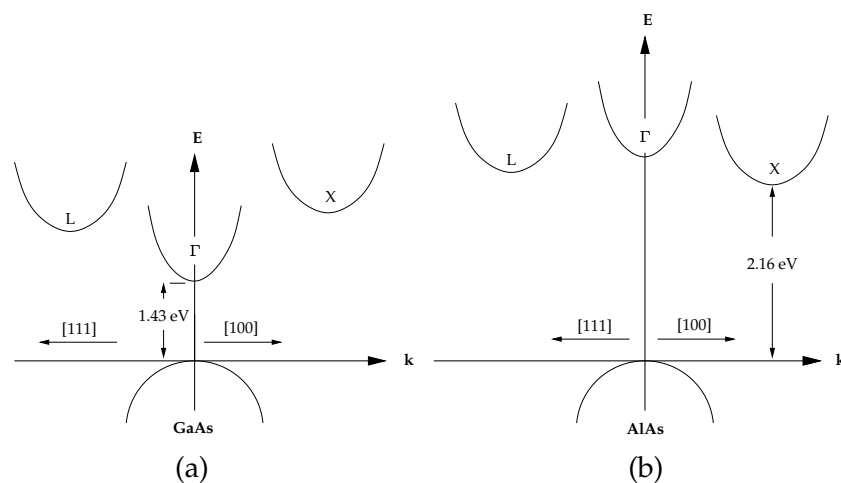


Figure 3.1: Schematic picture of (a) the direct energy-gap of GaAs and (b) the indirect energy-gap of AlAs.

tive differences between a direct- and an indirect-gap semiconductor. In a direct band-gap semiconductors, an electron making a smallest-energy transition from the conduction- to the valence-band, can do so without a change in its \mathbf{k} value. Indirect gap, on the other hand, requires a change of \mathbf{k} for the transition to occur which corresponds to a change of momentum for the electron. Point defects, to be distinguished from line- or surface-defects, can be grouped into two principal categories: impurities and native defects (see also Chapter 2). Impurities induce either deep localized electronic levels in the band-gap or shallow and delocalized levels. Native defects, on the other hand, are usually deep and thus induce localized levels. The defect may be a complex including foreign atoms and native defects. Several elementary native point defects, known in GaAs, are listed in

Table 3.1: Native point defects in GaAs

Defect	Below E_c [eV]	Above E_v [eV]	Reference
V_{Ga}^-		0.13	Hurle [1999]
V_{Ga}^{2-}	0.49		Hurle [1999]
V_{As}^{2+}	0.7		Hurle [1999]
Ga_i^+	0.3		Hurle [1999]
Ga_i^{2+}	0.5		Hurle [1999]
Ga_{As}^-		0.068-0.077 (0.077)	Bugajski et al. [1989] (Yu et al. [1982])
Ga_{As}^{2-}		0.200 (0.23)	Bugajski et al. [1989] (Yu et al. [1982])
As_{Ga}^+	0.74		Silverberg [1988]

table 3.1. These are vacancies in the Ga sublattice (V_{Ga}), vacancies in the As sublattice (V_{As}), interstitial Ga atoms (Ga_i), interstitial As atoms (As_i), and anti-site defects formed by either a Ga atom on a As site (Ga_{As}) or an As atom on a Ga site (As_{Ga}). Most of these defects have energy levels located deep in the forbidden gap as can be seen in table 3.1. The arsenic anti-site has been determined to be the famous defect EL2 which is known to compensate other defects in bulk-grown GaAs producing semi-insulating material [Silverberg, 1988].

3.1 Si in GaAs

Silicon is a group-IV element in the periodic table between the columns of Ga and As. Basically all of the elements of group IV can be used as amphoteric dopants in GaAs since their valence of IV lies just between the valences of Ga(III) and As(V). Consequently they can serve as shallow donors when on Ga-site or shallow acceptors when on As-site. Interstitial Si is rarely observed unless at very high doping level. Substitutional Si may form variety of complexes involving Ga vacancies or anti-sites such as $\text{Si}_{\text{Ga}}\text{-V}_{\text{Ga}}$ pairs and possibly $\text{V}_{\text{Ga}}\text{-Si}_{\text{As}}\text{-As}_{\text{Ga}}$. The variety, however, depends on the crystal-growth method. A basic difference is observed, for example, between melt-grown and LPE (liquid phase epitaxy) grown GaAs in that different acceptor species (other than Si_{As}) are present [Kachare et al., 1975]. The favored substitutional site of Si dopants can be controlled by growth method and growth temperature. The temperature dependency is, however, not trivial. In MBE (molecular beam epitaxy), growth at temperatures below 400°C mainly produces Si_{Ga} and hence n -type but Si_{As} and p -type at higher temperatures. The opposite is true for LPE, where growth temperatures below 840°C result in p -type. Typical activation energies of the most common Si-related defects in GaAs are listed in table 3.2.

Table 3.2: Si-related defects in GaAs

Defect	Below E_c [eV]	Above E_v [eV]	Reference
Si_{Ga}^+	0.006		Madelung et al. [1982]
Si_{As}^-		0.032	Ha et al. [2000]
$(\text{Si}_{\text{Ga}}\text{-V}_{\text{Ga}})^-$		0.10	Hurle [1999]
$(\text{Si}_{\text{As}}\text{-V}_{\text{As}})^+$	0.089		Ha et al. [2000]
$(\text{Si}_{\text{As}}\text{-Si}_{\text{Ga}})^-$		0.1	Kachare et al. [1975]

Si-doped GaAs is always compensated to some extent and at high doping

levels auto-compensation limits the concentration of free carriers [Maguire et al., 1987]. The reasons for this has been disputed and many contradictions in the literature can be found. A simple model assumes that the high Si concentration leads to the occupation of both Ga- and As-sites by Si in almost equal amounts [Kirchner et al., 1985]. In the model the Si_{As} acceptors compensate the Si_{Ga} donors which results in a self-deactivation of electrical activity. It has, however, been shown that this kind of auto-compensation can only partially explain the observed compensation. Hence, an additional mechanism must be present [Scuppler et al., 1994], e.g. dimerization ($\text{Si}_{\text{As}} + \text{Si}_{\text{Ga}} \rightarrow \text{Si}_{\text{As}}\text{-Si}_{\text{Ga}}$) and Si clustering. In *p*-type LPE grown GaAs:Si it has been observed that the concentration of Si_{Ga} does not commensurate with the carrier concentration and an additional shallow acceptor has to be present [Spitzer and Panish, 1969; Kachare et al., 1975]. Information on the lattice sites occupied by Si is most easily obtained by *local vibrational mode* (LVM), infrared absorption spectroscopy or from Raman scattering [Newman, 1994]. LVM measurements of *n*-type silicon-doped GaAs have shown that the Si_{Ga} donors are predominantly compensated by a [Si-X] acceptor complex where X must be a native defect (see for instance Maguire et al. [1987]). Today it is generally accepted that the compensating defect is a Si atom in a complex containing another point defect which is most likely a gallium vacancy [Laine et al., 1996; Domke et al., 1996; Birkmann et al., 2002]. The role of the Si solubility in GaAs has also been argued. The formation energy of a Si-Si nearest neighbor pair is 0.4 eV with respect to the isolated Si_{Ga}^+ and Si_{As}^- while the formation energy of $\text{Si}_{\text{Ga}}\text{-V}_{\text{Ga}}$ is 0.77 eV [Northrup and Zhang, 1993]. In *scanning tunneling microscope* study on bulk grown *n*-type Si-doped GaAs, Domke et al. [1996] identified microscopically five different defects; V_{Ga} , Si_{Ga} , Si_{As} , $\text{Si}_{\text{Ga}}\text{-V}_{\text{Ga}}$ and Si clusters. The Si clusters were found to be created above certain critical Si concentration where the Coulombic

interaction forces between Si_{As} and Si_{Ga} become strong enough to create neutral Si-Si pair and consequently a Si cluster. As a result all Si atoms added to the crystal, in excess of the critical concentration, precipitate as Si clusters. Thus, the solubility limit of Si in GaAs is governed by screened Coulomb interaction and the free carrier concentration remains unaffected by the Si concentration above a critical limit. Somewhat different results for LPE and MBE grown *p*-type GaAs were obtained by Ashwin et al. [1994] where LVM spectra implied only one type of shallow acceptor, Si_{As} . The $\text{Si}_{\text{Ga}}-\text{V}_{\text{Ga}}$ and Si-X defect complexes were absent. These anomalies do reflect the differences between *p*- and *n*-type material and the complication introduced by different between growth techniques.

The samples investigated in Paper I and II were Si-doped GaAs grown by LPE technique.

3.1.1 Si site-switching

The possibility of changing the carrier type by thermal annealing is well known and has been observed in GaAs for various dopants e.g. Cu [Moore et al., 1992]. Conversion from *n*-type to *p*-type in Si-doped GaAs is well established [Ky et al., 1991, 1994] but few reports exist on *p*-type to *n*-type conversion. Piazza et al. [1992], however, reported that As overpressure during MBE growth of Si-doped GaAs induced site-switching of Si from As-site to Ga-site. This is however misleading since in their demonstration Si does not move from As site to Ga site but instead a different thermal equilibrium was obtained by changing the As-pressure. Many authors have reported a type conversion in MBE grown [Pavesi et al., 1992; Pashlay and Haberern, 1991] and melt grown GaAs [Asom et al., 1988; Hwang, 1968] but the reason for it has been debated. It has been argued whether the type conversion results from Si-atom switching from Ga position to an empty

As-site or from the creation of native defects or Si_{Ga} -native defect complexes during the annealing. Si site-switching has been mentioned as a likely reason for n -type to p -type conversion during annealing of MBE grown GaAs:Si [Newman, 1994]. Northrup and Zhang [1993] provide theoretical support for the proposal that the donor-vacancy complex $\text{Si}_{\text{Ga}}\text{-V}_{\text{Ga}}$ in Si-doped GaAs, mediates Si diffusion in GaAs under As-rich conditions. Similar opinion was viewed by Ky et al. [1994] in annealed samples grown by the horizontal Bridgman (HB) method. The possibility of Si site-switching governed by V_{Ga} has also been mentioned. Pavesi et al. [1992] came to the conclusion that the motion of Si_{Ga} would occur on the Ga sublattice by successive hopping into vacancies and thus would be governed by the concentration of V_{Ga} . A possible site-switching may also be inferred by co-dopants. Chen and Spitzer [1980] concluded, in their LVM study of Li-diffused Si-doped GaAs, that the presence of Li might induce transfer of Si from one type of lattice site to another.

The maximum equilibrium free-carrier concentration, obtained in a heavily doped n -type GaAs is typically $(4 - 7) \times 10^{18} \text{cm}^{-3}$, limited by self-compensation of donors [Domke et al., 1996; Theis et al., 1988]. In the case of column-IV dopants, compensating acceptors are produced when the dopant atoms occupy the As lattice-sites [Theis et al., 1988].

It is discussed in papers I and II whether the p - to n -type conversion, observed during thermal annealing of LPE grown Si-doped GaAs, may be caused by Si atoms moving from As- to Ga-site. The following model has been suggested by us: Ga vacancies are created at the GaAs surface during thermal annealing in As-rich and Ga deficient ambient $\text{Ga}_{\text{Ga}} \rightarrow \text{Ga}_i + \text{V}_{\text{Ga}}$. Arsenic vacancies, also created in the process, will have high probability of being instantly filled with an As atom in the presence of As rich ambient. Consequently we expect higher

supply of V_{Ga} than V_{As} .

Under the aforementioned conditions some Si_{As} will have V_{Ga} as a nearest neighbor and Si atom may jump from its As position into the adjacent V_{Ga} leaving V_{As} behind. The solubility of Si_{As} is expected to be much lower than that of Si_{Ga} except at very high Si concentration levels [Chen et al., 1999] so that the reverse jump of Si_{Ga} to V_{As} should occur at much lower rate. Hence, the equilibrium ratio $K = [Si_{As}]/[Si_{Ga}]$ will be lower after annealing under As-rich conditions. We do not believe, however, that Si site-switching is solely responsible for the changes observed in the carrier concentration during annealing. V_{Ga} is an acceptor and its role as a compensating agent may also be significant even though it has not been fully clarified in which way.

3.2 Li in GaAs

Due to its small size and reactive character lithium is an extremely fast diffuser in most semiconductors. In general group I impurities, such as Li, are expected to be able to compensate the electrical conductivity of semiconductors. This can be both through directly neutralizing (passivating) the impurity or providing charge of polarity opposite to that of the dominating one (compensation). Lithium has been known for decades for its ability to reduce the free carrier concentration of both *n*- and *p*-type GaAs which has made it a popular co-dopant in LVM measurement for reducing the free carrier concentration. Chen and Spitzer [1980], for instance, inspected the possible Si site-switching in GaAs via the local modes of Si-impurities compensated by Li. They also found that the presence of Si inhibits the formation of certain complexes of Li and native defects. LVM measurements of the GaAs:Li system in order to identify the lattice position of Li have not supplied conclusive information due to the complexity of the Li-related defects [Gislason, 1997]. In *n*-type GaAs it passivates deep native donor levels and compensates shallow donors [Egilsson et al., 1994b]. In *p*-type GaAs, Li passivates both shallow [Yang et al., 1993] and deep levels [Egilsson et al., 1994a]. In *p*-type material the passivation has been attributed to the formation of Li-Zn and Li-Cd complexes [Egilsson et al., 1994b]. The compensation phenomenon is caused by the action of Li_i^+ which permeates the crystal and tends to form donor-acceptor complexes [Milnes, 1983]. When GaAs crystals are saturated with Li by diffusion at temperature greater than 500°C and cooled down to room temperature, they become highly resistive. The maximum resistivity is obtained at diffusion at $\sim 700^\circ\text{C}$ as shown in figure 3.2 for *p*- and *n*-type starting material. The cross-over temperature for the *n*-to-semi-insulating (or *n*-to-*p*-type) behavior depends on the diffusion time and the concentration of Li present during the

diffusion process but under certain conditions it may be below 400°C [Leósson, 1996]. A subsequent annealing of the sample results in *p*-type behavior [Gislason et al., 1997, 1992; Gudmundsson, 1991]. The most weakly bound Li-atoms are released from the complexes already at 100°C [Leosson and Gislason, 1997] A somewhat contradictory results have however been obtained by Zazoui et al. [1992] for unintentionally doped AlGaAs where Li-diffusion at 300°C increased the donor concentration which reflects the complexity of the Li related defects.

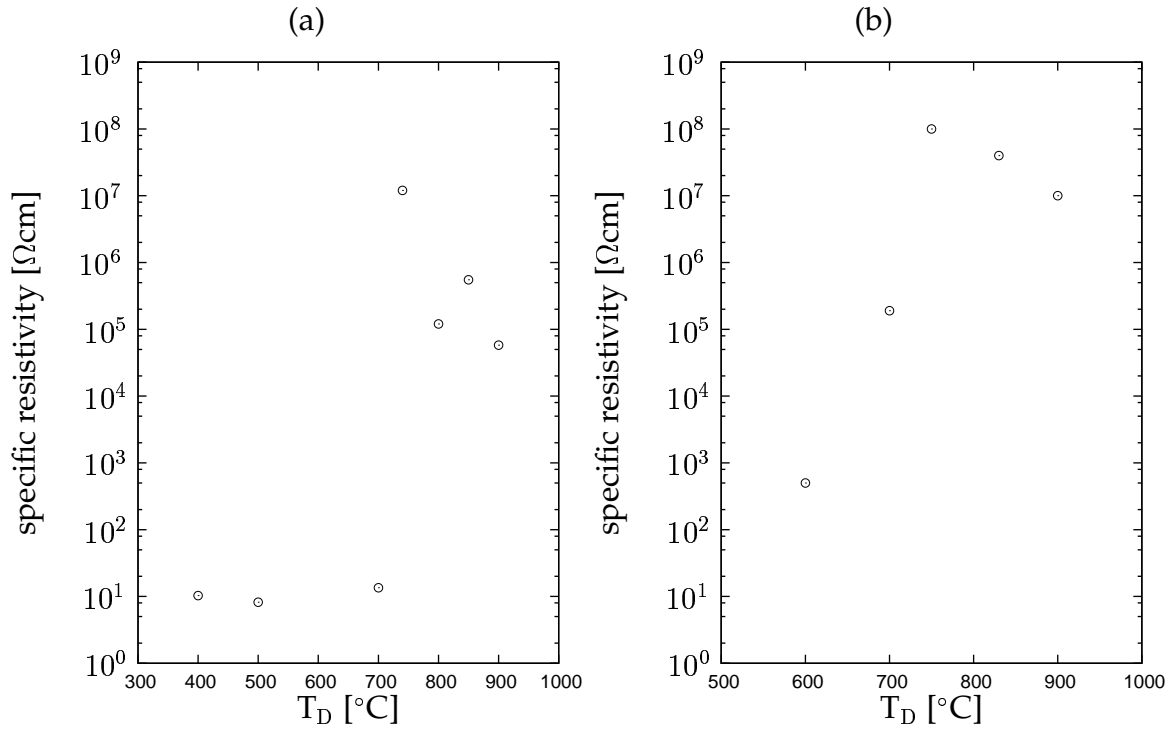


Figure 3.2: Specific resistivity of Li-diffused GaAs as a function of the diffusion temperature (data from Gislason et al. [1992]). (a) Zinc-doped starting material with $p = (2 - 4) \times 10^{17} \text{ cm}^{-3}$. (b) Un-doped starting material with $n = 2.2 \times 10^{16} \text{ cm}^{-3}$.

Defect mechanism

Lithium in GaAs is believed to exist as a double acceptor on Ga site and an interstitial donor, $\text{Li}_i^{0/+}$, although to date there exists no report of a Li donor level

in GaAs. The presence of the interstitial Li donor has, however, been confirmed in AlGaAs by Zazoui et al. [1992]. A negative charge state of interstitial Li is not expected to exist [Gislason, 1997]. Lithium, in excess amount needed to neutralize the original defects, auto-compensates [Fuller and Wolfstirn, 1962]. Thus, depending on the diffusion temperature a fraction of the Li will always remain electrically inactive. In GaAs Li mainly diffuses via an interstitial mechanism as a positive ion. Using conductivity and flame analysis, Fuller and Wolfstirn [1962] measured the effective diffusion coefficient D near the solubility limit of Li as

$$D = 0.53 \exp(-1.0/k_B T) [\text{cm}^2/\text{s}].$$

In Li-rich, nominally undoped starting material the diffusion is limited by the formation of complexes involving several Li-atoms and native-defects [Leosson and Gislason, 1997]. The validity of the above equation has been confirmed for heavily Li-doped material (within a model of trap-limited diffusion) by Leosson and Gislason [1997] who measured the effective diffusion coefficient of Li in Zn-doped HB grown GaAs by using capacitance-voltage techniques. At lower doping level of Li, under conditions of weak pairing interaction, the situation is considerably different and the activation energy of intrinsic diffusion reduces from 1.0 eV to 0.67 eV [Gislason et al., 1997]. A plot of D according to the equation of Fuller and Wolfstirn is shown in figure 3.3 (a). Fuller and Wolfstirn [1962] also determined experimentally the solid solubility of Li in GaAs and found it to follow the equation

$$[\text{Li}] = 7.0 \times 10^{21} \exp(-0.57/k_B T) [\text{cm}^{-3}]$$

where T is the in-diffusion temperature in the range of 700-1250 K. At 700°C $[\text{Li}] = 8 \times 10^{18} \text{ cm}^{-3}$ and at 800°C $[\text{Li}] = 1.5 \times 10^{19} \text{ cm}^{-3}$. A plot of the Li concen-

tration versus reciprocal temperature is shown in figure 3.3 (b).

Shallow acceptor levels have been attributed to $\text{Li}_i\text{-Li}_{\text{Ga}}$ complexes. Fuller and Wolfstirn [1962, 1963] observed a shallow acceptor level in their Li-diffused and annealed GaAs 23 meV above the valence-band and attributed it to a $\text{Li}_i^+ \text{Li}_{\text{Ga}}^{2-}$ defect but later spectroscopic investigations failed to confirm the existence of such simple configuration [Levy and Spitzer, 1973]. It is commonly accepted that V_{Ga}

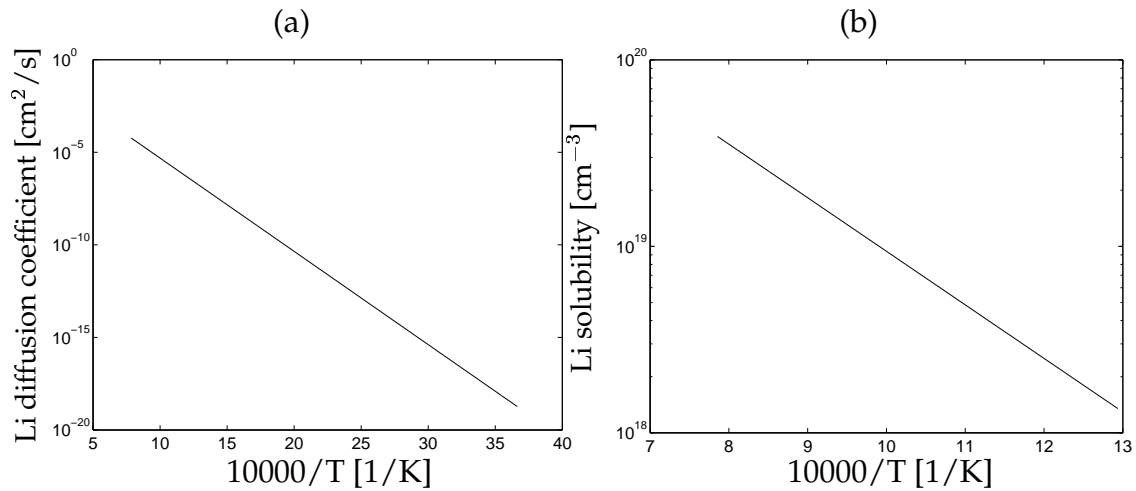


Figure 3.3: (a) Diffusion coefficient of Li in GaAs and (b) the solid solubility of Li in GaAs. The solid lines are plotted from equations given by Fuller and Wolfstirn [1962].

plays a vital role in the observed electrical behavior of Li-diffused GaAs [Lindner et al., 1989]. Norris and Narayanan [1977], who reported on Li-saturation of GaAs at high temperatures observed that during cooling to room temperature the Li super-saturation was readily removed by precipitation of Li. They also found that the size and density of the precipitation decreased with decreasing diffusion temperature. Post-annealing at 400°C for prolonged period did not produce significant changes in the as-diffused microstructure, indicating that the complexes were stable. Post-diffusion at 600°C , on the other hand was shown to form additional precipitates, vacancy-type prismatic dislocation loops on the (110) planes and extrinsic stacking faults in the (111) planes. This was related to dissociation

of Li_i-vacancy complexes. Milnes [1983] reported on similar precipitation during cooling, after high temperature Li in-diffusion, where excess Li⁺ readily precipitates because of its high mobility.

Explanation of the *p*-type behavior after annealing

A recent model, presented by Arpiainen et al. [1999], to explain the mechanism of the *p*-type behavior in Li-diffused and annealed GaAs, summarizes most of the above discussions. In their positron annihilation spectroscopy of originally *p*- and *n*-type GaAs they found the concentration of V_{Ga}^- and Ga_{As}^- to increase upon Li in-diffusion at 700-800°C but to remain passivated by Li prior to out-diffusion at 400°C. The passivation was accounted for by formation of neutral acceptor pairs like $V_{\text{Ga}}^- \text{-Li}^+$ and $\text{Ga}_{\text{As}}^- \text{-Li}^+$. During annealing the Li is effectively removed from the complexes and the acceptors V_{Ga} and Ga_{As} remain in the sample which explains the final *p*-type conductivity of the samples. Furthermore, it was noticed by Arpiainen et al. that the As anti-site (EL2) and the As vacancy disappeared totally during the diffusion and did not appear again during post-diffusion at 400°C.

The samples investigated in Papers III-VI were Li-diffused and annealed GaAs. In paper III it was observed that diffusion of Li into GaAs is trap-limited due to formation of complexes containing Li and native defects. A significant concentration of V_{Ga} and Ga_{As} before and after annealing was demonstrated. In Papers IV-VI a conduction in Li-related defect band is demonstrated.

Chapter 4

Impurity conduction in GaAs

Free carriers, holes in the valence-band and electrons in the conduction-band are created by thermal activation. Thus, cooling of a semiconductor towards zero temperature is expected to result in the recapture of every mobile electron or hole to give infinite resistivity. Conductivity, higher than can be explained by the number of free carriers, has however been observed in many semiconductors, especially those containing high defect concentration [Look et al., 1990]. For simplification the following discussion will concern p -type semiconductors but similar argument can be applied to n -type semiconductors. The reason for the unexpectedly high conductivity is that at low temperatures holes may travel from an occupied (neutral) defect to another empty (ionized) in a band formed by defects whose wave-functions overlap, without entering the valence-band. This requires the defects to be in high concentration and the resulting band to be only partially ionized. Such transport is known as *hopping conduction*. Obviously the compensation must play a role in the hopping since we need alternating ionized and unionized defect centers. At high degree of compensation K , where $1-K \ll 1$, and at low degree where $1-K \sim 0$ the hopping conduction becomes impossible.

In weakly doped semiconductors electrons localized near any of the impurity centers do not spread out in time over other centers constituting the impurity band. The term *impurity conduction* usually refers to a conduction in a band made up of shallow impurities. A deep-level band usually consists of native defects or complexes of native defects and impurities. The presence of a deep-level defect-band is however much more improbable since the wave-functions of deep-levels are more localized and do not spread out as much as in the case of shallow impurities. Here it must be pointed out that the term *band* does not have the same meaning as in *valence-* or *conduction-band* where the wave-functions of the carriers are non-localized.

If an impurity-band is present it will contribute to the total electrical conductivity but its relative impact will depend on temperature. Normally the relative influence of a defect-band decreases with increasing temperature due to ionization and at room temperature it can often be neglected [Shklovskii and Efros, 1984]. Since the overlap of the wave-functions becomes larger as the donors are closer to each other the defect-band conduction should be a function of defect concentration.

One of the characteristics of an impurity-band is its *density of states*, but the term must be used with precaution. In a macroscopic system the density of states is a continuous function of energy, even if one speaks of an impurity system which represents a set of discrete levels. Thus, the density of state function does inform how to distinguish a true band from a set of discrete levels unrelated to each other and randomly scattered in space.

At sufficiently high impurity concentration the (shallow) acceptors impurity-band merges with the conduction-band and the electrical conductivity of the material changes from a semiconductor to a quasi-metal. In the following discus-

sions these two forms of defect-band conduction, *hopping* and *metallic*, will be treated separately. Furthermore, percolation will be discussed.

In paper VI an observation of defect-band conduction is discussed for Li-diffused GaAs after annealing at low temperature ($< 400^\circ\text{C}$). Annealing at intermediate temperature (430°C) resulted in quasi-metallic conduction. After annealing at high temperature (600°C) the conduction was mainly due to holes in the valence-band. This is demonstrated in figure 4.1 for GaAs Li-diffused at 800°C and annealed at various temperatures. The activation energy of the sample after

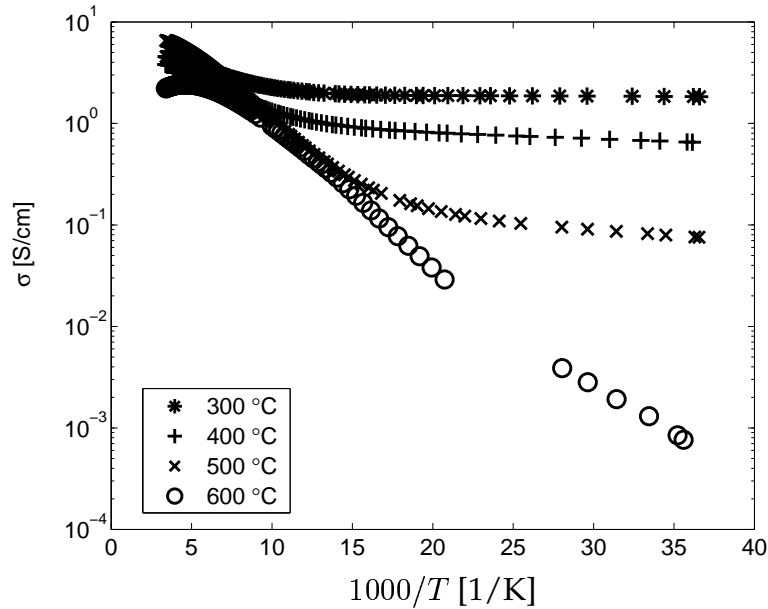


Figure 4.1: Temperature dependence of the specific resistivity ρ for GaAs Li-diffused at 800°C and annealed at various temperatures (paper IV).

annealing at 600°C is typical of a shallow acceptor whereas the activation energy drops to zero below $\sim 100\text{ K}$ after annealing at 430°C which is characteristic of metallic-like conduction. In paper V and VI the defect-band conduction is treated in terms of the percolation theory.

4.1 Hopping conduction

Hopping conductivity is a variation of impurity conduction and was described in the fifties by Conwell [1956] but Miller and Abrahams [1960] treated the hopping conductivity more theoretically a few years later. The electrical transport consists of phonon-assisted hopping among localized defect centers. This hopping mechanism is often very important for conduction and may even dominate at low temperatures in moderately doped materials.

For simplification the following discussion will be of n -type semiconductors but the discussion of p -type semiconductors is comparable. When impurity conduction takes place among the donors, the total conductivity can be expressed approximately by [Blakemore, 1985, page 343]

$$\sigma = n_0 e \mu_n + \sigma_2 \exp(-\epsilon_2/k_B T) + \sigma_3 \exp(-\epsilon_3/k_B T). \quad (4.1)$$

where n_0 is the net electron density in the conduction-band, k_B is the Boltzmann constant and μ_n the mobility of electrons in the conduction-band. The first term is the normal contribution from electrons in a conduction-band and may also be written as $\sigma_1 \exp(-E_d/k_B T)$ where E_d is the donor activation energy which is observed to decrease with increasing donor concentration and to increase with compensation [Davis and Compton, 1965]. The second and third terms describe two different kinds of electron transport among the donors (acceptors). The actual *hopping conduction* is given by the third term and arises from electrons tunneling from neutral to ionized donors in a partially compensated semiconductor and ϵ_3 is the energy necessary to hop from an occupied defect or impurity site to one which is unoccupied. The second term is impurity conduction of a type which requires closer proximity of the participating donors or acceptors but does not

require compensation to keep them partially ionized. This mechanism works in the intermediate temperature range between the band and hopping conductivity regime [Shklovskii and Efros, 1984, pages 78–80]. Some alternative explanations for the ϵ_2 mechanism have been proposed. Davis and Compton [1965] proposed the energy ϵ_2 to be associated with the energy necessary to place a second electron onto neutral donors of double occupancy states. Woodbury and Blakemore [1973] assumed it to be associated with the energy necessary to place a second hole onto a neutral acceptor. Thus the band, in which conduction takes place, may consist of negatively charged donors (a D^- band) or of positively charged acceptors, (an A^+ band). The idea of a D^- band is, however, much more likely since the radius of D^- states is larger and they will overlap stronger [Shklovskii and Efros, 1984, pages 78–80]. Due to its large radius, the D^- band has much higher mobility than hopping conduction and may exceed the ϵ_3 -conductivity, despite the exponential small number of electrons. The most favorable conditions for ϵ_2 conduction are in the absence of any compensation, when the ϵ_3 conductivity vanishes.

In principle, hopping involves two limiting factors [Look et al., 1996], the energy ϵ_3 and the overlap of wave-functions. Random variation in donor-donor separation means that some paths for an electron are connected from one end of the sample while others are not. The general motion of electrons in the defect band in the presence of an electric field is then in the nature of a percolation process [Blakemore, 1985, page 347]. In his study of conduction in glasses, Mott [1968] pointed out that an electron gains or loses energy from phonons of amount W_d which corresponds to the width of the impurity-band (see figure 4.2) and may be calculated as

$$W_d \approx f(K)e^2/\epsilon R, \quad (4.2)$$

where $f(K)$ is a function of the compensation K , ϵ is the dielectric constant and R

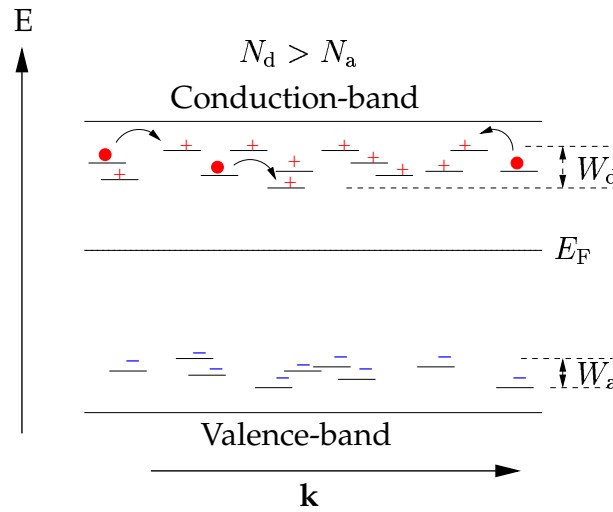


Figure 4.2: Energy levels in an n -type compensated semiconductor. W_d is the spread of the energy of the donor levels and W_a similarly that of acceptor levels. The circles represent electrons jumping between adjacent empty impurity states by emitting or annihilating phonons. The Fermi energy E_F is slightly above the middle of the forbidden gap.

the distance between donors (for n -type semiconductors). If the wave-functions of the donors are localized then conduction at low temperature is governed by thermally activated hopping. Every time an electron moves, it hops from one localized state to another, whose wave-function overlaps that of the first state [Mott, 1990]. Since the states have quantized energies, the electron must exchange energy with a phonon (or possibly a spin wave). Even though the hopping mechanism is not responsible for a large conduction it can be strikingly dominant at low temperature, especially in a shallow impurity system. Figure 4.3 shows schematically the inverse temperature dependence of the resistivity of a moderately doped semiconductor. At high temperature semiconductors possess an intrinsic conduction (range A). In the case of shallow impurities, there exists a temperature range B, called the saturation range. In this range all the impurities are ionized and consequently the carrier concentration in the band is almost independent of temperature. The electron mobility in this regime is typically increased due to weaker

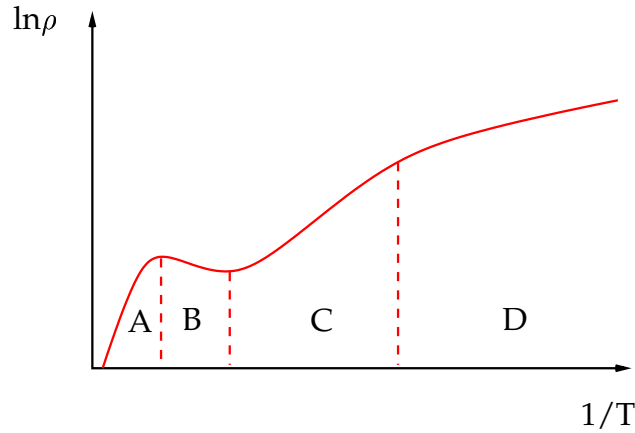


Figure 4.3: Schematic temperature dependence of resistivity of a lightly doped semiconductor. (A) intrinsic conduction range, (B) saturation range of impurity conduction, (C) freeze-out range, and (D) hopping conduction range (adopted from Shklovskii and Efros [1984]).

defect scattering which results in a lowering of the resistivity. A further decrease in temperature (range C) leads to a gradual freeze-out of impurity electrons, i.e. they are recaptured by donors. The gradual freeze-out of conduction electrons with decreasing temperature eventually leads to a regime *D* where the main contribution to conduction comes from electrons hopping directly between impurities and without entering the conduction-band. Above certain temperature, in heavily doped *n*-type material, the predominant electrical transport mechanism results from conduction by electrons thermally excited from shallow donors into the conduction-band. For lower temperatures the dominant mechanism is due to frozen-out electrons (i.e. neutral donors) in an impurity-band formed by these same shallow donors. In the case of compensated material the concentration of electrons, $N_d - N_a$, frozen-out in the donor impurity-band can hop from a full to an empty donor. Since the impurity states are spatially distributed in the \mathbf{k} space each jump between different states must involve a change of the electron momentum with participation of phonons. The hopping mechanism of conduction corresponds to a very low mobility since the electron jumps are associated with

a weak overlap of wave-function tails from neighboring donors. Nevertheless, it may have stronger effect than band conduction at low enough temperature because only a very small number of free carriers can participate in the latter.

Earlier studies were mostly concerned with impurity-bands made up of shallow defects with extended (hydrogenic) wave-functions providing the base for the classical hopping model [Woodbury and Blakemore, 1973; Shklovskii and Éfros, 1971]. Since electrons are weakly bound to shallow donors their wave-functions are extended. The shallow donor-band may be assumed to be formed from extended hydrogenic wave functions of the donor electrons. The classical hopping model, which is based on such wave-functions, does quite well in explaining most of the observed features, with a few exceptions however [Look et al., 1994]. More recent studies have been focused on impurity-bands composed of deep centers with tightly bound wave-functions [Look et al., 1994; Betko et al., 1996]. In this case the hopping takes place between deep centers with localized wave functions instead of the extended wave functions of shallow defect. Therefore a smaller overlap between the wave functions of deep centers is expected. Deep-level conduction has gained much more interest lately. One of the first observations made was on a neutron-irradiated semi-insulating GaAs [Coates and Mitchell, 1972]. Later, high temperature hopping in GaAs was investigated by Look et al. [1994] who reported conduction dominated by hopping between closely spaced As_{Ga} (EL2) in GaAs grown by MBE at temperatures below 300°C. Recently Khirouni et al. [1999] also reported on deep-level hopping in comparable samples. In agreement with Look et al. they attributed the hopping to a band of As_{Ga} defect centers. Morvic et al. [1998], who also reported on deep-level hopping, observed that a GaAs layer grown at 250°C exhibits hopping conductivity whereas a layer grown at above 400°C showed dominant band-conduction.

Around 300°C, the electrical conduction was found to be a combination of both hopping and valence-band conduction.

So far hopping conductivity has not been fully explained in terms of a simple model. Detailed calculation of $\sigma(T)$ in the vicinity of hopping has proven difficult to perform. Two separate hopping mechanisms are commonly recognized: the nearest neighbor hopping (NNH) and the variable range hopping (VRH) but an additional mechanism of a multi-phonon hopping has also been mentioned [Emin, 1974]. A brief introduction of the NNH, VRH and multi-phonon mechanism will be given in the following subsections.

Nearest neighbor hopping

In a system of randomly localized donors of concentration N_d , among which electrons hop from occupied to unoccupied sites, the standard theory predicts a NNH conductivity of [Look et al., 1996]

$$\sigma_{nn} = C_{nn} \exp(-\alpha R/a_d) \exp(-\epsilon_3/k_B T) \quad (4.3)$$

where C_{nn} is a constant independent on T , a_d is the extent of the donor wave-function, R is an average distance between neighbors, α is a constant close to 1.8 and ϵ_3 is the hopping activation energy as before. Notice that equation (4.3) corresponds to the third term of equation (4.1). Look et al. [1996] measured ϵ_3 for deep center hopping in GaN and obtained values from 0.016 to 0.38 eV for the defect concentration N_D in the range of $1.1 \times 10^{18} \text{cm}^{-3}$ to $1.6 \times 10^{22} \text{cm}^{-3}$.

Assuming hydrogenic wave-functions the extent of the donor function a_d can be estimated [Look et al., 1994]

$$a_d \approx h/(2m_n^* E_d)^{1/2} \quad (4.4)$$

for the activation energy E_d . Below a certain critical temperature [Look et al., 1996]

$$T_c = e^2 N^{2/3} a_d (N_a/N_d)^{1/3} k(4\pi\kappa), \quad (4.5)$$

the hopping process is found to change from NNH to VRH type.

Variable range hopping

When the temperature becomes so low that typical resistance between neighboring impurities becomes larger than those connecting more remote impurities whose energy levels happen to be very close to the Fermi level the hopping mechanism changes from NNH to VRH [Shklovskii and Efros, 1984, page 203]. In this case the hopping occurs between more distant sites which are closer in energy however [Look et al., 1996].

Éfros and Shklovski have argued that due to Coulomb interactions of defect electrons, the density of states approaches zero (Coulomb gap) near the Fermi level [Éfros and Shklovskii, 1975]. If this effect of the electron-electron interaction is not taken into consideration and a nonvanishing density of states near the Fermi level assumed, the temperature dependence of the conductivity is expressed by the Mott law

$$\sigma_{vr} = \sigma_0 \exp[-(T_0/T)^{1/4}] \quad (4.6)$$

where

$$T_0 \approx \frac{1}{N(E_F)a^3}. \quad (4.7)$$

Here $N(E_F)$ is the density of states at the Fermi level and a the localization radius of the wave-function. Other forms of T_0 have also been suggested but it is

difficult to define this quantity precisely. Including the long-range Coulomb interaction the density of states has a parabolic dependence $N(E_f) = N_0(E - E_F)^2$ and vanishes as $E \rightarrow E_F$. In this case the low-temperature conductivity becomes proportional to $\exp[-(1/T)^{1/2}]$ instead of being proportional to $\exp[-(1/T)^{1/4}]$ as assumed in equation (4.6). Some contradictory results on hopping conductivity in GaAs have been published and it has been stated that $\sigma \propto \exp[-(1/T)^{1/2}]$ gives better fit near the *metal insulator transition* [Rentzsch et al., 1986]. The result of Benzaquen and Walsh [1984] showed however that the Coulomb gap plays at best a minor role in hopping conductivity above 1.4 K for lightly doped ($N_d \approx 5 \times 10^{15} \text{ cm}^{-3}$) and moderately compensated (30-60%) GaAs.

Multi-phonon hopping

It has been pointed out by Emin [1974] that the theory leading to equations (4.3) and (4.6) is in fact only valid under the conditions of single-phonon hops at low temperatures. By assuming multi-phonon hopping Emin further showed that the term C_{nn} in equation (4.3) is not a constant, but can vary as $\exp[(-T_0/T)^{1/4}]$. Thus, the multi-phonon picture can include both the $\exp[(-T_0/T)^{1/4}]$ and $\exp(-\epsilon_3/k_B T)$ factors, at least over certain temperature range. Look et al. [1996], for instance, have reported on multiphonon hopping between deep-levels in GaN.

4.2 Percolation theory

In the early nineteen sixties Miller and Abrahams [1960] proposed a model called *random resistance network* to account for hopping conductivity in semiconductors. Based on the model, the hopping mechanism was reduced to that of calculating the conductivity of a random network which has its vertices at the donors

in an n -type semiconductor (or acceptors in p -type) and in which resistance connects each pair of vertices. This resembles a situation of dealing with dielectric islands immersed in a conducting sea. An improved method of calculating the random network conductivity, based on the mathematical theory of percolation, was proposed a few years later by Pollak [1972]. A good description of the *random resistance network* is provided in a book of Shklovskii and Efros [1984, pages 83–93].

The percolation theory is known as one of the simplest models of a disordered system. The most easily solved problem in the percolation theory is a lattice problem which can be formulated as follows: Consider a square lattice, where each site is randomly occupied with the probability x or being empty with probability $1-x$. Occupied and empty sites may stand for very different physical properties. For simplicity, assume that the occupied sites are electrical conductors, the empty sites insulators, and that electrical current can flow between nearest neighbor conductor sites (see figure 4.4). At low occupancy x , the conductor sites are

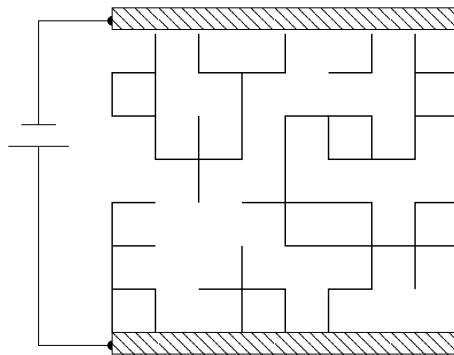


Figure 4.4: A random resistor network between two electrodes (adopted from Shklovskii and Efros [1984, page 103]).

either isolated or form small clusters of nearest neighbor sites. Two conductor sites belong to the same cluster if they are connected by a path of nearest neighbor conductor sites, and a current can flow between them. At sufficiently low

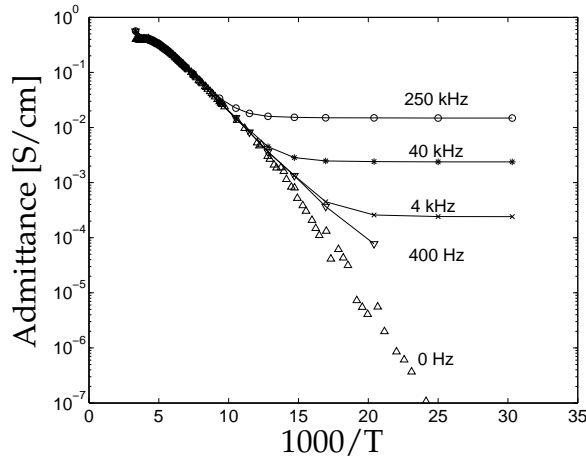


Figure 4.5: Temperature dependence of admittance for GaAs:Si, Li in-diffused at 800°C for various frequency after annealing at 300°C for 10 h (from paper VI).

values of x a conducting path connecting opposite edges of the lattice does not exist and the matrix is an insulator. At large values of x many conducting paths, where electrical current can flow, exist between opposite edges and the matrix is a conductor. At some intermediate concentration a threshold concentration x_{crit} exists where electrical current can, for the first time, percolate from one edge to the other. Below x_{crit} the matrix is an insulator and above x_{crit} a conductor. The threshold concentration is called a percolation threshold or, since it separates two different phases, a critical concentration. A detailed discussion on the percolation theory is given by Shklovskii and Efros [1984, chapter 5]

One consequence of percolation is that only a part of the total volume contributes to (low temperature) conduction when a DC voltage is applied to the semiconductor. Under AC condition the carriers move back and forth between the insulating regions. The contributing volume and the conductivity can thus increase dramatically when measurements are made with AC voltage. This is shown in figure 4.5, where the temperature dependence of conductivity at several different frequencies is illustrated for Li-diffused GaAs. As seen the con-

ductivity increases with increasing frequency below certain temperature level. Below that level the conductivity becomes independent of temperature at a given frequency. The physical reason for the strong frequency dependency can easily be understood in the language of percolation theory [Bleibum et al., 2002]. In a strongly localized, disordered system, the current between two electrodes in a constant electric field chooses the optimal path. Thus, the current writhes somehow through the sample and somewhere it passes a critical resistor (that is the piece of the path with the highest resistance). If the distribution function for the resistor is wide enough the critical resistor exceeds all the other resistors on the path by orders of magnitude, and thus, determines the resistivity of the whole sample. In an alternating electric field a substantial part of the current is composed of a displacement current (the changes in charge density as a function of time and hence in the internal electric field). The displacement current can be used to eliminate the most resistive parts of the current path merely by increasing the frequency. Since with increasing frequency the resistors are excluded according to their strength, at first the critical resistor and thereafter the next smaller ones, the resistance of the whole network decreases. In a review article by Hunt [2001] the AC hopping conduction is discussed in relation to the percolation theory where it describes charges hopping between ionized and neutral defects. Both classical hopping over potential barrier and a phonon-assisted tunneling were considered. A somewhat different approach to the percolation theory was introduced by Khirouni and Bourgoïn [1997]; Khirouni et al. [1997, 1999]. They applied the theory to low-temperature MBE-grown GaAs where conduction was limited by free electrons percolating around depleted macroscopic layers formed around metallic precipitates [Khirouni and Bourgoïn, 1997]. As Hunt's approach applies to a hopping or tunneling of charges between individ-

ual atoms (neutral and charged) but Khirouni's approach applies to charges percolating around clusters of many atoms we will refer to the former approach as a microscopic one and the latter as a macroscopic one.

Correlated barrier hopping model

A universal behavior of the frequency of the AC conductivity $\sigma(\omega) \propto \omega^s$ with s in the range of 0-1 is observed in many semiconductors [Hunt, 2001]. This makes percolation processes easily inspected by measuring the frequency dependence of the conductivity (admittance spectroscopy). Many models, compatible with the percolation theory, have been designed to explain such AC conductivity. In many cases the different models may be distinguished on the basis of the predicted behavior of the exponent s . The models can be divided into two main categories depending on whether they treat the charge transport in terms of classical hopping over a barrier or by quantum-mechanical tunneling (QMT) *through* a barrier [Hunt, 2001]. The tunneling can be due to electrons, large- or small-polarons (electron plus elastic deformation [Kittel, 1986, page 281]) and atoms. What is common to the QMT models is that they assume s to be independent of T or to increase with increasing T in addition of being frequency dependent. Classical hopping is treated in terms of thermal activation *over* the barrier separating two sites.

In papers V and VI it is observed that the exponent s is strongly temperature dependent and approaches unity value for the Li-diffused and annealed GaAs. This means that after annealing the hopping (or tunneling) length is a function of temperature. According to Elliott [1987] only two realistic models for the AC conduction have such a property. The first model is the *overlapping large polaron* (OLP), which refers to tunneling by polarons whose spatial extent is large

compared to the interatomic spacing. The second one is *correlated barrier hopping* (CBH) which refers to a classical hopping of carriers between different sites. Of these two only the CBH model assumes s to decrease with increasing temperature. A detailed discussion on the CBH model is given in a review article by Elliott [1987].

The CBH model is based on three main assumptions [Elliott, 1978; Abdel-Wahab, 2002]. First, the electrons in charged defect states hop over the Coulomb barrier whose height W is related to the separation of two hopping sites separated with a distance R by

$$W = W_M - \frac{2e^2}{\pi\epsilon_0\epsilon R}, \quad (4.8)$$

where W_M is the maximum barrier height, ϵ_0 the permittivity of free space and ϵ the dielectric constant of the bulk material. Second, the relaxation time τ for the electron to hop over a barrier W is given by

$$\tau = \tau_0 \exp(W/k_B T), \quad (4.9)$$

where τ_0 is assumed to be an inverse optical phonon frequency ($\sim 10^{-13}$ s). Third, N defect centers per unit volume are randomly distributed so that the probability of finding a center at distance R is

$$P(R)dR = 4\pi NR^2 dR. \quad (4.10)$$

Combining these assumptions and using some approximations the relation of s is deduced [Elliott, 1978, 1987; Abdel-Wahab, 2002]

$$s = 1 - \frac{6k_B T}{W_M + k_B T \ln(\omega\tau_0)}. \quad (4.11)$$

Equation (4.11) is plotted in figure 4.6 for variable W_M but at constant $\omega\tau_0$. The

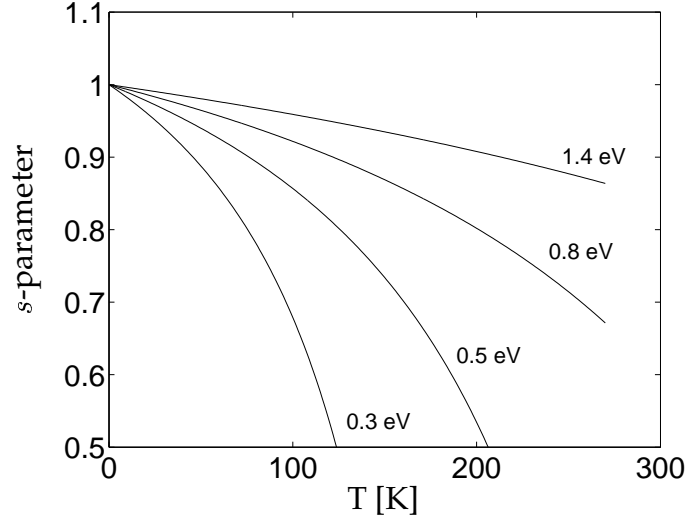


Figure 4.6: Temperature dependence of the exponent s for several different values of W_M at constant frequency $\omega = 10^6$ rad/s and $\tau_0 = 10^{-13}$ s.

above assumption is based on single-electron hopping. Within the CBH model it has been argued that in the presence of charged defects D^+ and D^- the model would have to be modified. Instead of being randomly distributed the defects would be paired due to Coulomb interactions and hopping of two polarons simultaneously between D^- and D^+ have been proposed. In case of such bipolaron transport the value of W_M would be lowered to one fourth of its value for a single polaron but the functional form of equation (4.11) would remain the same [Elliott, 1987].

In paper V and VI percolation is identified in Li-diffused GaAs by its response to alternating current. The as-diffused samples exhibited conduction which resembles a percolation of free holes in a sea of insulating regions. On the basis of this the presence of Li-related metallic precipitates was suggested. After thermal annealing the conductivity is governed by carrier hopping from ionized to neutral defects within a band consisting of defects whose wave-functions overlap.

Due to irregularly dispersed ionized and neutral defects some hopping directions are not possible and the movement of the carriers are in a way of percolation.

4.3 Metallic conduction

The term *metal insulator transition* (MIT) refers to the situation where the electrical conductivity of a material changes from a metal to an insulator as a function of an external parameter, which may be composition, pressure, strain or magnetic field [Kittel, 1986, page 268]. Heavy doping decreases the ionization energy of the carriers (donors or acceptors) and at some critical carrier density N_{cr} the ionization energy vanishes and no thermal activation is needed for the electrons. The semiconductor becomes an *impurity metal* and the free carrier density is quite insensitive to temperature. Such an MIT transition is also referred to as Mott transition. The term impurity metal is used since the number of carriers in non-localized states is constant throughout the extrinsic temperature range, just as a metal has a temperature-independent electron density [Blakemore, 1987, page 169]. In doped semiconductors the Fermi energy E_F is in the energy band-gap and energy is required to activate the carrier in order to achieve conduction. In the dark and at zero temperature the conduction becomes zero. In the case of shallow defects, such as donor impurities, individual localized levels are close to the conduction-band (similar for acceptors). A band of such impurities can be large enough to overlap with the conduction-band which in turn becomes metallic since it is partially filled. The critical concentration N_{cr} needed to achieve such metallic conduction is reached when the binding energy of the isolated donor (acceptor) is on the order of the average interaction energy [Bourgoin and Lannoo,

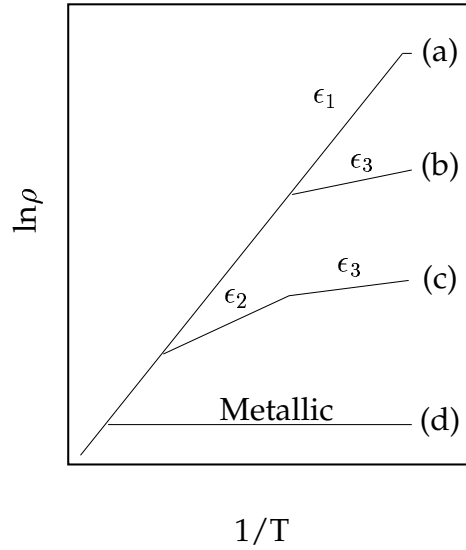


Figure 4.7: Schematic temperature dependence of the resistivity of a semiconductor. (a) Lightly doped, with activation energy ϵ_1 , (b) moderately doped, impurity band activated at low temperature with activation energy ϵ_3 , (c) highly doped, and (d) very heavily doped. Metallic-type conduction with zero activation energy

1983, page 133]. For a Coulomb interaction this gives

$$E_d \sim e^2/\epsilon R, \quad (4.12)$$

where R , the mean distance between impurities, is given by

$$3/4\pi R^3 N_{cr} = 1. \quad (4.13)$$

In general it can be stated that materials with deeper impurities need higher impurity concentration to achieve the MIT. A typical range of N_{cr} is given by the results of Rentzsch et al. [1986] for neutron irradiated n -type GaAs ($K = 0.7$) and Look et al. [1996] for deep center n -type GaN who observed $2 \times 10^{16} \text{cm}^{-3}$ and 10^{18}cm^{-3} , respectively.

Chapter 5

Experimental apparatus

Three major types of samples were used in this work: Si-doped GaAs grown with LPE on semi-insulating GaAs, bulk Si-doped GaAs, grown by HB method, and bulk Zn-doped GaAs, also grown by HB method. The LPE grown samples were used in papers I and II but HB grown samples in papers III-VI.

5.1 Crystal growth in liquid phase

Various methods are used for crystal growth, both for bulk material and thin films. The two most widely used methods for bulk production are Czochralski and Bridgman. Epitaxial growth is a specific type of thin film processing. The term *epitaxy* can be defined as the deposition of a single crystalline layer on a single crystalline substrate in such a way that the crystalline structure of the substrate continues into the layer [Astles, 1990, page 2]. In short it refers to a coherent structure between the grown layer and the substrate. Within the field of epitaxial crystal-growth there exists many different methods. The best known ones are molecular beam epitaxy (MBE), chemical vapor deposition (CVD) and magnetron sputtering. Liquid phase epitaxy is also a well known method for epitaxial crys-

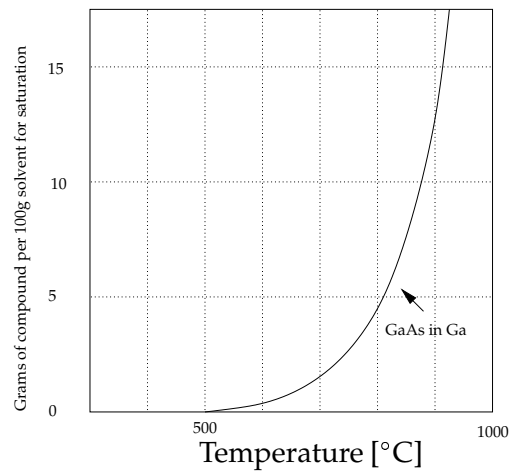


Figure 5.1: Weight percent of GaAs dissolved in Ga at saturation level as a function of temperature. Below 500°C the solubility is practically zero.

tal growth and was popular in its prime two decades ago. It has however some unique features superior to other methods which has ensured its continuing use to date. Since the LPE technique was used to produce many of the samples investigated in this work a brief introduction will be given here. LPE material has mostly been used for opto-electronic devices such as lasers, light emitting diodes, photo-cathodes and solar cells. For more detailed discussion of the LPE technique the reader is referred to the works of Astles [1990] or Hsieh [1974].

One of the main advantages of the LPE method is the fact that a crystal can be grown at temperatures well below its melting point. This is of great importance since high temperatures may cause decomposition of the material under growth. The GaAs system is especially well suited for LPE growth since As can be dissolved in molten Ga-metal, which reduces the number of constituents involved. As we see from figure 5.1 the solubility of GaAs (or just As) in Ga increases very rapidly with temperature above 500°C. The solubility is, for example, almost ten times higher at 870°C than at 700°C. The Ga metal itself has very low melting

point (27°C) and acts as an excellent getterer for impurities. Special precaution has to be paid to the high As partial pressure during growth. At the melting point of GaAs (1238°C) the As pressure reaches approximately 0.9 atm. Elementary As sublimates at 613°C at normal pressure (1 atm). However the melting point of pure As is $\sim 810^\circ\text{C}$ and can only be obtained under high pressure (28 atm.). Prior to LPE growth the desired dopant is dissolved in As-saturated Ga-melt at elevated temperatures (typically 700-900°C). A single-crystalline bulk material, preferentially with a flat surface, is brought into contact with the solution. Placing the substrate with the (100) direction normal to the surface alternate planes of Ga and As can be grown. Lowering of the temperature causes supersaturation of the solution with respect to As. The supersaturation disappears through precipitation of GaAs in (almost) stoichiometric ratio along the solidus line shown in figure 5.2. The growth conditions during LPE growth of GaAs have to involve an As source to compensate for As loss from the solution. The loss is due both to the volatile nature of As and to the atoms precipitating from the solution. An active As source may be provided by placing sufficient amount of solid GaAs in the Ga melt to exceed the saturation level of As in Ga. A crucial step in the growth process is the transport of Ga and As. When the transport to the surface surpasses the diffusion velocity at the surface, the atomic particles do not have time to find their proper ordered position before more arriving atoms block their movement and freeze in a disordered state [Böer, 1990, pages 67–70]. Since the environment at the substrate is very rich of Ga but deficient of As one would expect few vacant Ga-sites but more likely some concentration of empty As-sites. In general the total concentration of native point defects is low in epitaxial growth [Hurle, 1999]. GaAs grown by LPE from gallium melt is expected to be low in gallium vacancies and possibly high in arsenic vacancies [Milnes, 1983]. The growth

solution was placed in a carbon crucible which, unfortunately, is a potential contaminater of the crystal. During growth and prior to heating a constant flow of palladium-purified H_2 gas was maintained, giving a hydrogen of 7N purity.

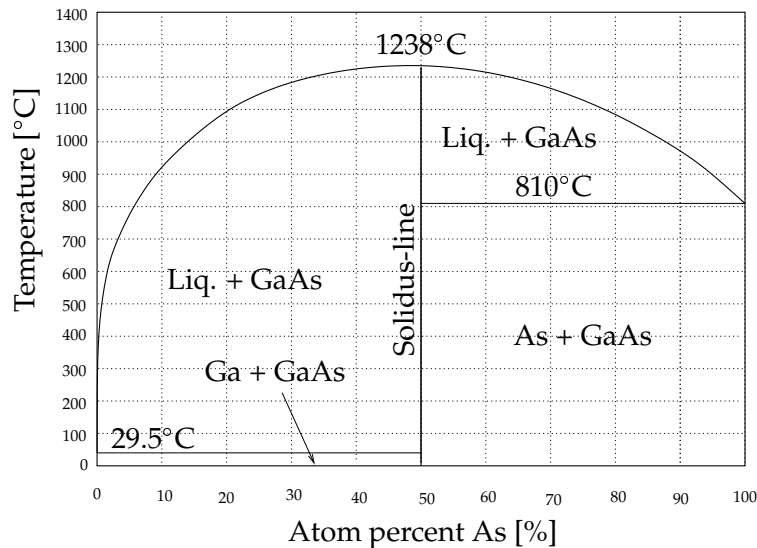


Figure 5.2: Phase diagram of the Ga-As system.

The main problems of the LPE systems are nonuniformity of layer thickness, and surface perturbation in the form of facets, ridges, and scallops. On a microscopic scale, a number of different faces (i.e. crystal planes) on the substrate are exposed to the solution during growth. In-situ etching is therefore necessary to achieve uniformly flat surfaces. During growth, the addition of extra atoms to these faces results in a large change in the free energy of the planes. Generally, this causes clustering of atoms on the faces, and leads to growth irregularities, such as faceting. Imperfections in the substrate can act as sites for spurious nucleation during early stages of growth. Dopants such as silicon and chromium are particularly bad, since they tend to form inclusions which result in large spiral growth patterns [Gandhi, 1983, pages 280–281]. Improved morphology can be

obtained when there is a large number of nucleation sites on the surface. Therefore a substrate with a slight off orientation (2°) towards the (110) plan was used in the work presented here.

Native defect such as anti-sites, dislocations and vacancies, are always created during growth. Of these defects, vacancies are of highest concern here. The ratio between V_{Ga} and V_{As} is of interest in this work because it affects the acceptor/donor ratio for the amphoteric dopant Si.

Since higher temperatures increase the solubility of As in the melt the concentration of V_{As} in the crystal growth should decrease. However, LPE growth at high temperature (above $\sim 840^\circ\text{C}$) results in n -type conduction while growth at low temperatures results in p -type conductivity, indicating that the $[\text{Si}_{\text{Ga}}]/[\text{Si}_{\text{As}}]$ ratio increases with increasing growth temperature. This can easily be understood by considering the solubility curve of As in Ga in figure 5.1 [Ghandhi, 1983, page 266]. From being close to zero at 500°C the solubility rises rapidly above that temperature. Increased arsenic concentration in the melt lowers the concentration of empty As-site available for Si-atoms. The $[\text{As}]$ increases while $[\text{Ga}]$ stays constant so that the available As-sites will be occupied more rapidly by As. Therefore $[\text{Si}_{\text{Ga}}]$ eventually exceeds the $[\text{Si}_{\text{As}}]$ if the $[\text{As}]$ is increased sufficiently by increasing the growth temperature. Here we assume that Si in GaAs mainly appears on lattice sites and in fact interstitial Si is rarely found in GaAs due to its relatively large size.

The LPE growth-machine used in this work was produced by Epigress AB and is of the *horizontal sliding boat* type [Astles, 1990]. The samples were grown at 700°C or 840°C . Those grown at 700°C exhibited p -type but those grown at 840°C were n -type. A subsequent annealing at 840°C in As-rich environment turned the p -type samples into n -type. A similar treatment of the n -type samples increased

their *n*-type conductivity. An *in-situ* etching was performed by immersing the substrate in an Ga solution just before it was brought in contact with the growth solution. A schematic set-up is shown in figure 5.3. A typical thickness of the

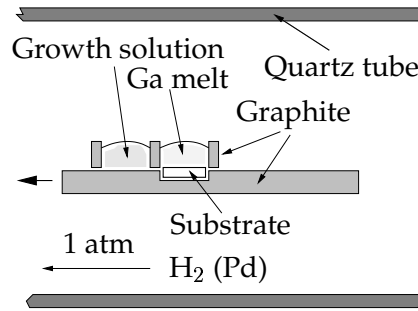


Figure 5.3: Crystal growth from liquid phase. The substrate is brought in contact with the Ga melt just before it gets in contact with the growth solution.

epilayer was 1-5 μm .

5.2 Annealing of Si doped GaAs

Silicon doped GaAs samples grown with the LPE technique were closed in an quartz ampoule together with solid As. A typical size of the LPE samples in the ampoule was $4 \times 4 \text{ mm}^2$ but the amount of solid As was roughly 0.3 mg. The estimated interior volume of the quartz ampoule was $\sim 1 \text{ ml}$. A sketch of the procedure is given in figure 5.4. After annealing at 840°C for 20 h (figure 5.5) the ampoule was subsequently quenched in liquid nitrogen.

5.3 Li diffusion and annealing

Lithium metal, which had been kept in oil bath, was de-greased and rinsed with trichlorethylene. Bulk HB-grown GaAs, either Zn- or Si-doped, was cut from wafers and immersed in molten Ga in a quartz boat, together with a piece of

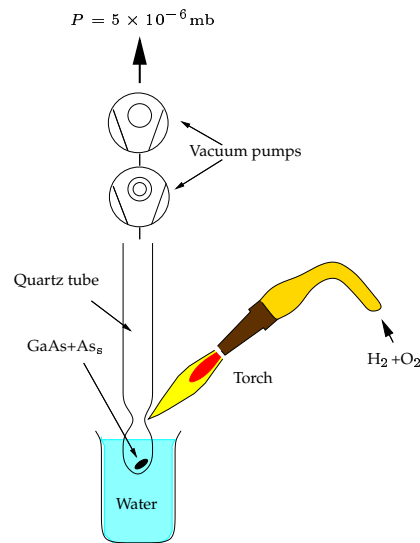


Figure 5.4: Si-doped GaAs and As(s) are placed in a quartz tube. The ampoule is closed under vacuum.

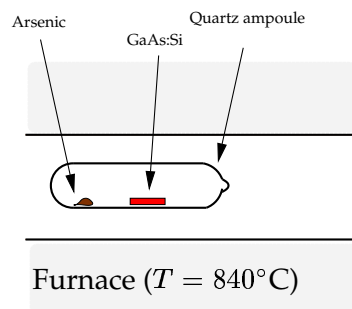


Figure 5.5: Annealing of Si-doped GaAs in ampoule in the presence of solid As.

the Li metal (see figure 5.6). The Ga melt had previously been saturated with As by placing sufficient amount of GaAs as a solute and heating the solution to a temperature exceeding the Li in-diffusion temperature. This was done to reduce loss of our samples due to melt-back during the Li in-diffusion. The diffusion took place under a flow of argon gas to prevent oxidation of the samples not to mention the very reactive lithium. The as-diffused samples were cooled to room temperature, washed with deionized water and ground to remove solidified Ga. The occurrence of a $\text{Li} + \text{H}_2\text{O}$ reaction, when the sample got in touch with the deionized water, was taken as an indication that an adequately active Li-source

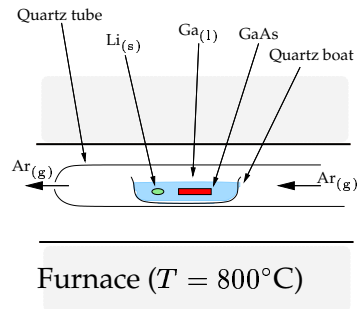


Figure 5.6: Li in-diffusion of bulk Si-doped GaAs. Solid Li and GaAs are immersed in liquid Ga and heated under flow of Ar-gas.

had remained in a diffusive contact with the samples throughout the diffusion. For the annealing process the ground sample was placed in a As-saturated Ga-melt and heated at the desired temperature under flow of Ar-gas.

5.4 Ohmic contacts

Ohmic contacts were welded to the four corners of square samples using zinc (Zn)- or tin (Sn)-coated gold-wire with a Biorad HL5400 bonding machine. A controlled current, fed through the wire (typically $50\ \mu\text{m}$ in diameter), melted the wire and alloyed it to the semiconductor. This produces a very localized heating of the sample instead of annealing the whole sample as is conventionally done. It was particularly important to avoid heating of Li-diffused samples since Li is an extremely fast diffuser. Zn of the valence II and Sn of IV diffuse onto Ga-sites where they act as acceptors and donors, respectively. Therefore, Zn-coated gold wire was used in the case of *p*-type samples and Sn-coated gold wire in the case of *n*-type samples.

Chapter 6

Experimental methods

In the following subsections a brief introduction will be given to the electrical and spectroscopical methods performed by the author. The Hall and conductivity measurements were applied in all papers I-VI. Photoluminescence (PL) measurements were applied in papers I and II and admittance spectroscopy was carried out in papers V and VI. Other methods such as positron annihilation spectroscopy, secondary ion mass spectroscopy and deep-level transient spectroscopy which were performed by others will not be described.

6.1 Hall and conductivity measurements

A Hall field is an electric field developed across two faces of a conductor, in the direction $\mathbf{j} \times \mathbf{B}$, when a current \mathbf{j} flows perpendicular to a magnetic field \mathbf{B} [Kittel, 1986, page 148]. When a current with a density j_x is passed through a semiconductor, perpendicular to a magnetic field B , the stream of charged particles is deflected by B . Let us consider a long, uniformly doped layer through which a current flows. A magnetic field is applied across the layer, of right angle to the direction of current flow, as shown in figure 6.1. For this condition, there exists

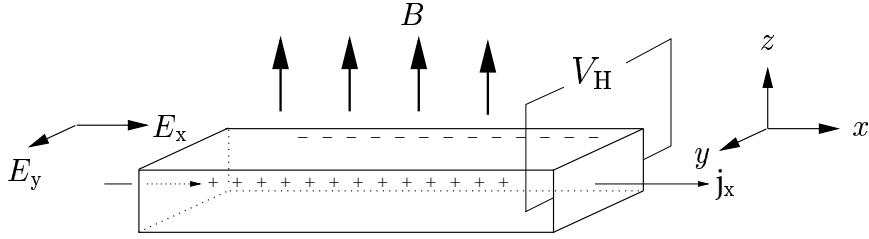


Figure 6.1: The basis of the Hall effect. The electrons accumulate on one side of the bar and holes on the opposite side.

an electric field E_H which is mutually perpendicular to both the current and the magnetic field [Ghandhi, 1983, page 288]. The value of this electric field is given by

$$E_H = \frac{R_H I B}{A} \quad (6.1)$$

where R_H is the Hall-coefficient, I the current, A the cross-section area and B the magnetic induction. If V_H is the voltage drop across the bar (figure 6.1) and t the thickness of the bar the Hall-coefficient is

$$R_H = \frac{t}{IB} V_H. \quad (6.2)$$

The value of R_H is obtained by connecting ohmic contacts onto each corner of square samples and measuring the Hall-voltage between any two contacts while current is passed through the other two contacts. Electrons traveling in the direction of \mathbf{j} respond to the Hall field by moving in the direction of $\mathbf{j} \times \mathbf{B}$. Holes, traveling in the opposite direction of electrons, accumulate on the other side of the current media. Thus, a potential difference is created across the bar. In fact, electrons in GaAs will have random thermal velocities of about 10^7 cm/s with only a small *net* velocity in the x -direction ($\sim 10^4$ cm/s for an electric field of 1 V/cm) [Look, 1989, page 2]. All samples investigated in this work were measured by the Hall method in order to obtain the carrier concentration, the carrier

mobility and the carrier type. The Hall coefficient R_H is estimated from the slope of the Hall-voltage versus the magnetic field. Electron and hole concentrations are calculated from the Hall coefficient R_H as $n = -r_H/eR_H$ and $p = r_H/eR_H$, respectively, assuming the Hall scattering factor r_H to be isotropic, temperature independent and of unity value ($r_H \equiv 1$). In addition, the sign of the Hall-voltage (positive or negative) gives the carrier type. By combining the Hall measurements and the specific resistance of the sample, the carriers mobility can be obtained. Moreover, an Arrhenius plot of the carrier concentration provides the activation energy of the majority carriers.

Classically the Hall-voltage is measured between ohmic contacts on a bridge shaped sample but in practice it is much more convenient to apply the method of van der Pauw [1958] which allows more freedom in the sample shape. The method has some restrictions however; it requires the contacts to be at the circumference of a sample, they have to be small (\ll sample area) and the sample has to be homogeneous in thickness and not perforated (no isolated holes or regions). Since GaAs is conveniently cleaved along the crystallographic (110) and (100)

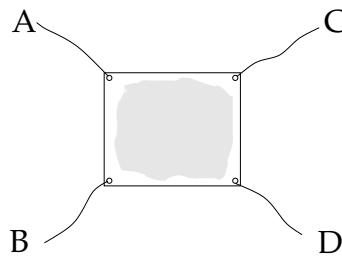


Figure 6.2: Van der Pauw configuration of semiconducting sample. Four wires, A, B, C and D are welded onto the corners of a square sample.

planes, the preferred sample is a square with contacts in the corner, as shown in figure 6.2. A detailed discussion of the Hall-effect and the van der Pauw method is given by Look [1989, pages 1–62].

6.2 Photoluminescence

When electron-hole pairs are generated in a semiconductor and when carriers are excited to higher impurity states from which they fall to their equilibrium state, light can be given off by the material [Streetman, 1995, page 100]. This is a general property of light emission and is called luminescence. If carriers are excited by photon absorption, the resulting radiation is called photoluminescence. If the recombination occurs directly rather than via a defect level, light of energy corresponding to the band-gap is given off in the process as visualized schematically in figure 6.3(a). In the figure an incoming photon with $h\nu_1 > E_g$ is absorbed by the crystal, creating an electron-hole-pair. The excited electron gives up the excess energy $h\nu_1 - E_g$ as lattice scattering until it reaches the bottom of the conduction-band. The electron may then recombine directly with a hole in the valence-band (band-to-band) giving up a light of energy $h\nu_2 \approx E_g$. The transition may also involve donor or acceptor states present in the band-gap (not shown in the figure). A deep defect-level (figure 6.3(b)) may trap the electron which in turn may be thermally re-excited to the conduction band a number of times before it recombine with a hole in the valence band. In practice, however, electrons and holes which are optically excited across the energy-gap can recombine radiatively by a variety of mechanisms. The most important transitions are shown schematically in figure 6.4. Due to Coulomb attraction between electrons and holes the emission due to electron-hole pair transition (exciton) is slightly smaller than the energy-gap. Details of the transitions are given e.g. by Bishop [1990]. The recombination energy of a donor and acceptor (DA) pair, $h\nu$, follows the relation

$$h\nu = E_g - E_a - E_d + \frac{e^2}{4\pi\epsilon\epsilon_0 r} \quad (6.3)$$

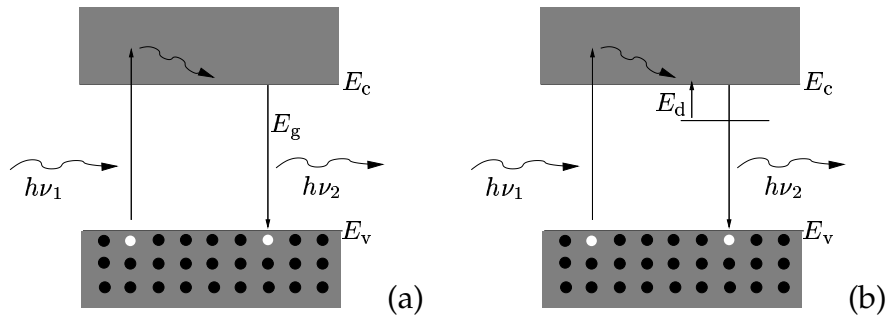


Figure 6.3: (a) Direct excitation and recombination mechanisms in PL and (b) excitation and recombination mechanisms in PL with a trapping level for electrons.

where E_g is the band-gap energy, E_a the acceptor binding energy, E_d the donor binding energy, r the spatial separation of the donor and acceptor pair and ϵ the bulk dielectric constant. The spectrum of emitted light contains peaks whose

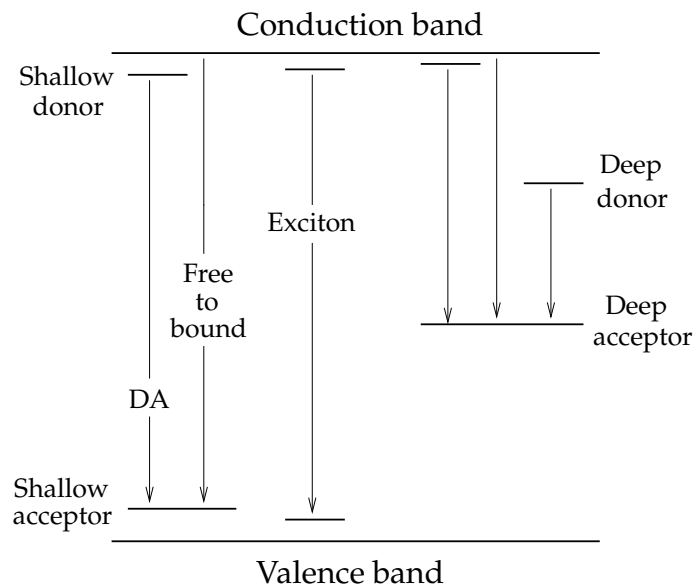


Figure 6.4: Energy-level diagram for a semiconductor showing the most important recombination processes.

wavelength can be related to the positions of defects within the band-gap. An emission spectrum, characteristic for each material, is therefore obtained. Commonly this emitted light is detected by a detector made of a semiconductor with

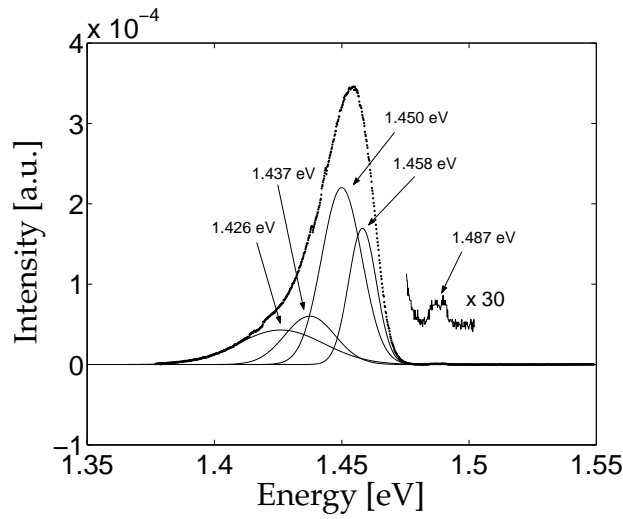


Figure 6.5: A broad PL spectrum measured at 2 K of Si-doped GaAs grown by LPE grown at 700°C. The dotted line represents experimental values whereas solid lines are mathematical fit to the experimental data assuming a Gaussian shape of the peaks.

a small band-gap (relative to the emitting material). When the thermal energy is above the defect's energy-level, the defect is more or less constantly ionized and no longer capable of emission. A PL spectra of LPE grown GaAs is shown in figure 6.5. The broad peak is due to several transitions whose emission spectra overlap.

6.2.1 Fluctuating potential

Usually semiconductors contain both donors and acceptors and thus are compensated to certain level. What happens in such cases can be explained as follows: Assume that we have semiconductors with $N_d > N_a$ and consequently the Fermi-level is in the upper part of the band-gap. An acceptor state, occupied with a valence-band electron, creates a hole in the valence-band. The hole will be filled by recombination with one of the conduction-band electrons. Extending this to all the acceptor atoms, the resulting concentration of free electrons in

the conduction-band at room temperature will be $n_0 = N_d - N_a$ instead of the donor concentration N_d . When the thermal energy $k_B T$ is larger than the ionization energy of the donor and acceptor, the number of free carriers is $(N_d - N_a)$ in n -type material and $(N_a - N_d)$ in p -type material. In strongly compensated material $N_a \simeq N_d$. Instead of being ideally distributed in the crystal, donors and acceptors are Poisson distributed throughout the crystal which means that some acceptors lack donors in their nearest surrounding. Such irregularity in the dispersion of donors and acceptors creates localized electric fields in the crystal. Free charges shield these microscopic fields but in strongly compensated crystals only a few free charges will exist and thus the shielding is poor. In such cases the energy-bands will bend due to the localized electric fields, causing irregularities in the band shape. As a result the potential difference between the conduction-band minima and the valence-band maxima will be altered which is referred to as *fluctuating potential*. Light of higher energy than the energy-gap

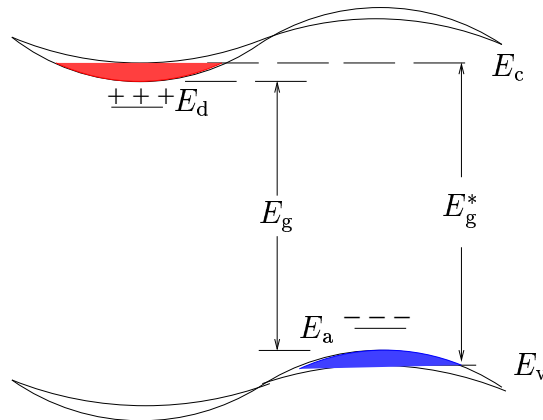


Figure 6.6: Compensated semiconductor. The energy-bands bend because of ionized defect-states irregularly dispersed in the energy-gap. Light of energy above E_g raises the electrons from the valence-band to the conduction-band. Increased light intensity increases the energy-gap from E_g to E_g^* .

E_g creates free carriers of electrons and holes which contributes to the shield-

ing of the localized electric fields and reduces the band bending. As a result the band-gap is increased and we observe a shift of *band-to-band* and *donor-to-acceptor* transitions in the PL emission-spectra to higher energy (a blue-shift) accompanied with broadening of the spectra. A schema of the fluctuation and the effect of light illumination is visualized in figure 6.6. A presence of potential fluctuation is commonly inspected by PL spectroscopy. For systems which have a long-range Coulomb-fluctuating internal field the recombination energy of donor-to-acceptor pair transition is lowered. The system energy becomes dependent on a coordinate \mathbf{r} through local values of the fluctuating potential $\varphi(\mathbf{r})$, which is the sum of the electric potential at \mathbf{r} due to all ionized species in the material [Kuskovsky et al., 1998]. In the case of a donor-level, equation (6.3) changes into

$$h\nu = E_g - E_a - E_d + \frac{q^2}{4\pi\epsilon\epsilon_0 r} + U(\varphi), \quad (6.4)$$

where $U(\varphi)$ is the so-called fluctuation term. An alternate, but more transparent, way of expressing equation (6.4) is given in paper II.

In paper I and II the presence of compensation in Si-doped LPE-grown GaAs was monitored through the shift of the PL bands with excitation intensity as shown in figure 6.7 of Si-doped GaAs grown by LPE before and after annealing. A blue-shift of 5 meV per decade of change in the excitation light intensity was observed prior to annealing but up to 24 meV change per decade after annealing. Such a large shift is a clear sign of high compensation and thus indicating that the concentration of Si_{Ga} and Si_{As} might be of a comparable level after annealing. This was further interpreted as a support for the Si site-switching theory.

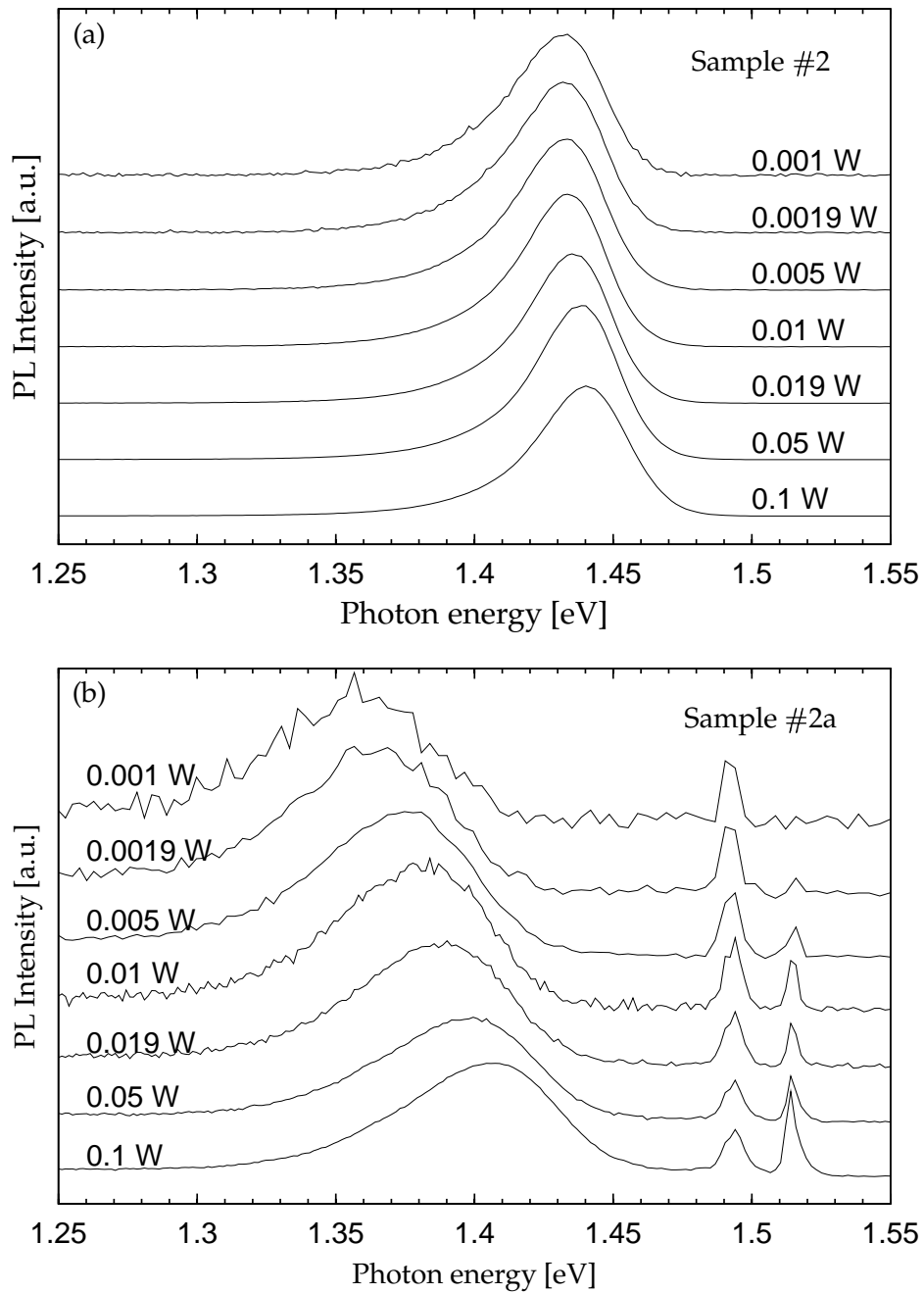


Figure 6.7: Peak shift with excitation intensity of a PL band measured at 14 K in (a) an as-grown p -type Si-doped GaAs grown with LPE and (b) the same sample n -type after annealing at 840°C for 24 h.

6.3 Admittance spectroscopy

In electrical circuits the terms *resistance* and *impedance* denote an opposition to the flow of electrons or current. For a direct current only resistors produce this opposition while for an alternating current two other circuit elements, capacitors and inductors, impede the flow of electrons. Impedance can be expressed as a complex number, where the resistance is the real component and the combined capacitance and inductance is the imaginary component. In some cases it may be more convenient to perform calculations using the reciprocal of impedance which is then called *admittance*. The admittance Y is composed of the frequency response of the real (conductance) and imaginary (susceptance) and it provides direct information on the mechanism by which conduction occurs. The admittance can thus be written as a vector sum of the real and imaginary part

$$Y(\omega) = G(\omega) + iS(\omega) \quad (6.5)$$

where $G(\omega)$ is the conductance and $S(\omega)$ the susceptance [Blood and Orton, 1992, pages 492–577]. The measurement of conductance and capacitance as a function of frequency is called admittance spectroscopy. The admittance spectroscopy is sensitive to space charges built at the interfaces between a conductor and insulator and thus very applicable to a percolation system.

In paper V and VI admittance spectroscopy was applied to explore the existence of carriers percolating within a band of defect and to free carriers percolating around insulating precipitates in Li-diffused and annealed GaAs.

Chapter 7

Summary of papers

Papers I and II discuss the annealing behavior of LPE grown Si-doped GaAs in relation to type-conversion occurring during annealing. Papers III-VI discuss the role of defect mechanism in electrical conduction in Li-diffused and annealed GaAs.

Paper I: The effect of Si site-switching in GaAs on electrical properties and potential fluctuation

Si-doped GaAs grown by LPE at 700°C was *p*-type while a sample grown at 840°C was *n*-type. Thermal annealing at 840°C in the presence of As overpressure converts the *p*-type GaAs into *n*-type while the *n*-types GaAs remain *n*-type. The electrical properties were investigated by Hall- and conductivity and the optical properties by photoluminescence. We discuss the possibility of Si site-switching from As-site to Ga-site as a cause of the type-conversion.

Paper II: Potential fluctuations and site-switching in Si-doped GaAs studied by photoluminescence

Si-doped GaAs grown by LPE at 700°C was *p*-type but converts to *n*-type during thermal annealing. A photoluminescence study of thermal type-converted LPE-

grown GaAs:Si exposed increased fluctuation of the energy-bands. This was related to increased compensation and possible site-switching of Si on As-site to Si in Ga-site.

Paper III: Lithium induced vacancy formation and its effect on the diffusivity of Lithium in Gallium Arsenide

Positron annihilation spectroscopy was applied on Li in-diffused and annealed GaAs to identify native defects and defect complexes. After annealing the GaAs is always *p*-type due to Li-related acceptor complexes. A dissociation energy of 0.85 eV, found by using reverse- and zero-bias annealing, was attributed to the Li-Zn complexes. Diffusion of Li was found to be trap-limited due to formation of complexes containing Li and native defects. The same defect complexes were found in Li in-diffused SI-GaAs as in Zn-doped GaAs, provided that the Li concentration exceeded that of the Zn. A diffusion activation energy of Li was found to be 0.67 eV.

Paper IV: Impurity band in lithium-diffused and annealed GaAs: Conduction and Hall effect measurements

A temperature dependent Hall- and conductivity measurement of Li-diffused and low-temperature annealed GaAs reveal a conduction controlled by carrier hopping between defect-sites in a band made up of defects whose wave-functions overlap. At intermediate annealing temperature the sample exhibited a quasi-metallic behavior and after high-temperature annealing a conventional valence-band conduction by holes was achieved.

Paper V: Frequency-dependent conductivity in lithium-diffused and annealed GaAs

A measurement of the AC conductivity of Li-diffused and annealed GaAs indicated a conduction mechanism in a defect-band which could be described by

the CBH model of carriers hopping between sites over the Coulombic barrier separating the. It was further concluded that prior to annealing the conduction mechanism might be described by holes in the valence-band percolating around insulating regions of Schottky-barriers created by metallic precipitates.

Paper VI: Lithium-diffused and annealed GaAs: Admittance spectroscopy study

Annealing of Li diffused Zn- and Si-doped GaAs creates a band of impurities and native-defects. Before annealing the defect-band is neutralized and conduction is governed by holes in the valence-band percolating around insulating precipitates. After annealing at low temperature a partially filled defect-band is invoked and a conduction by carriers hopping between ionized and neutral defects takes over. The defect-band conduction can be described as well by percolation of carrier within the defect-band. Both the valence-band conduction and the defect-band conduction are treated in the framework of the percolation theory.

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