1 Introduction

Historically, most semiconductor devices have been created on a silicon-based crystal material. However, a growing number of electronic and optoelectronic devices are now being developed with requirements that exceed the capabilities of silicon. Lots of applications demand power-efficient high performance systems which can operate at high frequencies with lower power consumption and less noise and which can be produced cost-effectively in high volume. As a result, semiconductor device manufacturers are increasingly using compound semiconductor materials such as gallium arsenide (GaAs) and gallium nitride (GaN) to improve the performance of semiconductor devices and to enable new applications. GaAs has superior electronic and optical properties for providing high mobility of carriers and low power consumption. Moreover, GaAs-based devices can operate at microwave frequencies, whereas Si-based devices cannot. At present, GaAs has been widely used to build devices such as power amplifiers, radio frequency integrated circuits used in wireless handsets, high-brightness light emitting diodes (HBLEDs) and vertical cavity surface emitting lasers (VCSELs). Due to its wide band-gap character (3.4 eV), GaN is predicted to be one of the most promising semiconductor materials in the twenty-first century and it is expected to be applied in such areas as high-brightness blue and green light emitting diodes (LED), blue lasers, high power and high frequency electronics, high temperature electronics, ultraviolet detectors as well as electronics for microwave applications.

The first step in producing a semiconductor device is to grow a crystal or a film of the material. Historically, two main methods have been applied to grow compound semiconductor single crystals, the liquid encapsulated Czochraski (LEC) and the horizontal Bridgeman (HB) techniques. The two techniques have difficulties in producing six-inch, high-quality and low-cost semiconductor crystals. Now the producers have been tending to use the vertical gradient freezing (VGF) technique to grow compound semiconductors. Although it is still difficult to grow high-quality GaN single crystals, the techniques for GaN films are frequently vapor phase epitaxy (VPE), including metal–organic VPE and molecular beam epitaxy (MBE). During fabrication of semiconductor materials or during construction of the devices by utilizing the semiconductor materials, point and extended defects are inevitably created. It is thus essential to understand how the defects affect mechanical, electrical, and optical properties of the materials. How to minimize the possible disadvantages or how to convert them into useful effects stimulate fruitful studies all over the world.

Point defects such as impurities, vacancies and interstitial often induce localized electronic levels into the band gap of a semiconductor. The states can trap electrons or holes, thus possibly inducing compensation, scattering free carriers and introducing new luminescence bands with different energy and intensity from the near-band-edge emissions, and subsequently result in a change in electrical and optical properties. For example, parasitic optical transitions have been believed to result in luminescence bands at 1.20 eV in GaAs and at 2.2 eV in GaN, related to complexes formed by donors and gallium vacancies. Besides their influence on the electronic structure, point defects (usually charged in semiconductors) may also induce a significant lattice distortion. The magnification of a distortion depends on the charge state of defects, i.e. the Jahn–Teller effect. Consequently, all the properties related to such quantities as defect concentration at thermal equilibrium, solubility, and diffusivity as well as electron–phonon interactions are charge-state dependent.
Extended defects such as dislocations, grain boundaries and stacking faults have been widely investigated and have been revealed to have crucial influences on the mechanical, electrical and optical properties of semiconductors. Dislocations are known as non-radiative recombination centers to reduce the lifetime of excess minority carriers and to degrade the performance of GaAs- and GaN-based light emitters. The presence of space charge around dislocations was suggested to be responsible for the reduction of current gains in AlGaAs/GaAs heterojunction bipolar transistors (HBTs), lowering efficiency of solar cell, and degrading the breakdown voltage of GaAs-based power varactor diodes [1, 2]. It has been demonstrated that the threshold voltage of field effect transistors (FETs) built on the GaAs substrate depends on the distance to neighboring dislocations [3].

Dislocations are specific linear defects disturbing the regular sequence of atomic planes. Different from point defects, which disturb the short-range order of a crystal, dislocations disturb the long-range order. Dislocations are particularly generated by plastic deformation. A dislocation can be formed either by the collapse of a vacancy pancake or by incorporation of a layer of interstitials atoms. According to the relationship between Burgers vector and the dislocation line, there are two kinds of dislocations: edge or screw dislocation. The dislocations are well known as sinks of point defects (impurities or intrinsic point defects) to result in an inhomogeneous distribution in the electrical and optical properties of the materials (e.g., see Fig. 1.1). This effect, called gettering effect, shows how the dislocations may play a significant role in controlling the detrimental effects of point defects in the active regions of semiconducting devices. It is usually utilized in defect engineering to remove the unfavorable defects from the matrix or to limit the amorphization of GaAs only in dislocation regions [4]. The interactions of different defects with dislocations can have different consequences, e.g., either hindering or promoting the dislocation climb. Doping with electrically active atoms such as Si, In or B in GaAs has been found to result in a dramatic reduction of the dislocation density [5–7], which was suggested to result from the reduction of the Fermi-energy-dependent activation energy of dislocation motion or metallurgical hardening [8]. Since strongly reconstructed dislocations in Si and GaAs are widely assumed to be electrically inactive except possibly for shallow levels, any electrical effect correlated with them have to result from point defects attached to the dislocation line [10]. For example, a threefold-coordinated vacancy in the core of a 30° partial in Si has been identified as being responsible for the Si-Y line in the dislocation-related electron paramagnetic resonance (EPR) [11]. In the case of GaN, transmission electron microscopy (TEM) and atomic force microscopes (AFM) in combination with cathodoluminescence revealed that threading dislocations exhibit dark contrasts, leading to the conclusion that they act as non-radiative recombination centers to degrade the luminescence efficiency in blue-light spectra of the GaN epilayer [12]. However, other investigations showed a higher intensity of the yellow luminescence near the threading edge dislocations and that efficient light-emitting diodes and lasers are feasible by using GaN-based crystal with a high density of dislocations ($10^9 - 10^{10}$ cm$^{-2}$) [13].

\[ Figure 1.1: \text{Photoluminescence map of the near-band-edge emission (}$\lambda = 832 \text{ nm}$, revealing the influence of non-radiative recombination centers and inhomogeneous distribution of shallow-level defects on luminescence of GaAs (from Freiberger Compound Materials, Germany).} \]
The aggregation of point defects at the dislocations is generally assumed as a “Cottrell” atmosphere, i.e. a short-range increase (about tens of nm) in the number of point defects. The Cottrell atmosphere is often supposed to explain qualitatively some experimental observations although it presents poorly quantitative information. A specific instance is that it cannot interpret why the free-electron concentration in n-type GaAs:Si and GaAs:S increases from the matrix to the dislocation and why the extension in the increase is as broad as 10 \( \mu \)m around the dislocation, as revealed by the experiments presented below [14,15]. Moreover, in doped semiconductors, where there are various defects such as donors or acceptors, it is not clear how the aggregation of the defects at the dislocation affects the resultant electrical and optical properties.

In the thesis, I deal with the effect of point defects and dislocations on electrical and optical properties of III–V semiconductors, GaAs and GaN. Main emphasis is put on the interactions between point defects and dislocations. I will elucidate the spatial redistribution of point defects due to the interaction, and as a result, the variation of electrical and optical properties from the matrix to the dislocation. The influence of external conditions such as temperature and pressure on the interaction between point defects and dislocations will be addressed. For these purposes, several experimental methods such as TEM, cathodoluminescence (CL), and Raman scattering will be combined with computer simulations based on a diffusion–drift–aggregation model and molecular dynamics (MD) simulations. I will firstly focus on n-type GaAs:Si and GaAs:S with in-grown dislocations. The free-electron concentration in GaAs:Si and GaAs:S will be found to increase from the matrix to the dislocation with an extended radius of 10 \( \mu \)m. Computer simulations and theoretical analysis will suggest that whether arsenic precipitates can be formed at the dislocation or not play an important role in determining the spatial distribution of point defects and the free-electron concentration. It will be theoretically elucidated that the formation of arsenic precipitates at the dislocations is energetically and kinetically favorable.

Secondly, in order to further concentrate on the interactions of dislocations with point defects, a layer of fresh dislocations introduced by scratching the (001) surface of n-type GaAs:S with different sulfur concentrations is investigated after thermal treatments under different conditions. The results indicate that the effect of the dislocations on the spatial distribution of the point defects and on the electrical and optical properties depends strongly on temperature and the doping level. The luminescence bands and their origins will be addressed in detail. I will especially identify which defects are responsible for the luminescence bands around 0.95 eV, 1.20 eV, and 1.30 eV. The donor–gallium vacancy complexes will be revealed to be formed commonly in n-type GaAs doped with different donors occupying gallium lattice sites or arsenic lattice sites. The doping level is found to influence the charge state of a gallium vacancy and its surrounding, i.e., how many donors are bound to a gallium vacancy. As a result, three types of gallium vacancy-related complexes may be formed and the resultant luminescence bands may be located at different energies.

Lastly, the electrical and optical properties of GaN with in-grown or fresh dislocations are studied to explore the origin of the yellow luminescence band at 2.2 – 2.3 eV and the effect of dislocations on luminescence in GaN. The role of defects and dislocations in GaN will be discussed there.