Development and Testing of the Experimental Setup for Characterization of Semiconductors Using Reflectance Spectroscopy

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ABSTRACT

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Development and Testing of the Experimental Setup for Characterization of Semiconductors Using Reflectance Spectroscopy

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The last decade has seen the semiconductor industry achieve giant leaps. The III-V semiconductors including the III-nitride materials have turned out to be one of the most exciting semiconductor compounds for the realization of modern day optoelectronic devices. Prior to using these semiconductors in the realization of optoelectronic devices it is necessary to characterize them for their structural, electrical and optical properties. Reflectance spectroscopy is one of the most reliable and accurate semiconductor characterization technique which could be used for both thin films and bulk semiconductors in quest for gaining knowledge about materials opto-electrical parameters. The ability to produce sharp features indirectly representing semiconductor physical parameters like band gap, broadening parameter, defect levels etc. at given temperature is one of greatest advantage of this technique. Here, we study the reflected light from the specimen rather than the luminescence. The thesis presented will review this in detail along with the description of the experimental setup developed for the purpose of studying III-V and RE doped III-nitride semiconductors using photoreflectance spectroscopy. Furthermore, selected experimental results obtained for GaAs and GaN doped with Tb$^{3+}$ demonstrate increased sensitivity of the double modulation photoreflectance spectroscopy as compared to single modulation
photoreflectance spectroscopy when conducted at room temperature. The thesis presented will review this in details.

Approved: ________________________________________________________________

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1. INTRODUCTION

1.1 Overview

Modern optoelectronics is driven primarily by semiconductor based optoelectronic devices [1]. Semiconductors are compounds that occupy columns II, III, IV, V and VI of the Periodic Table. Silicon (Si) and Germanium (Ge) generally called elemental semiconductors are used in high speed devices and integrated circuits (IC’s) [1]. Compound semiconductors can be formed by combining elements from two or more different groups such as columns II and VI or III and V, respectively [2]. They have exciting optoelectronic properties which form the basis of most of the modern day semiconductor optoelectronics research [2].

The thesis presented focuses exclusively on III-V and III-nitride materials which have attracted considerable attention and importance due to their applications in optoelectronic devices operating in the spectral range from visible to infrared (IR). Here, an attempt has been made to characterize a sample semiconductor compound (n-GaAs) using PR spectroscopy technique. The greatest advantage of this technique is it’s sensitivity [3] and ability to perform lineshape fitting [3]. Using the genfit algorithm we have utilized the MathCAD 13.0 tool to perform the curve fitting. The source code has been pasted in the appendix section. From the modulated signal we have determined the values of bandgap and broadening parameter of transition of the material. The spectrum that we obtained by this technique is derivative in nature which explains it’s sensitivity to
small changes. We have also eventually extended this technique towards performing
defect analysis of GaN:Tb sample. The thesis is presented in the following order.

- **Overview:** This section gives a good insight into the world of semiconductor
  physics, the various types of doping techniques, advent of rare earth elements and
  it influence on semiconductor doping. It also gives a good background into the
  various semiconductor characterization techniques in the industry and the samples
  studied through them.

- **Theory:** This chapter talks about the theoretical approaches exercised to derive the
  fitting function which represents the semiconductor characterization parameters.

- **Experimental setup:** This section is about the different types of experimental
  setups used in the photoreflectance (PR) spectroscopic technique and the
  labVIEW software drivers used in data acquisition.

- **Results and Discussion:** All the experimental results obtained through the various
  PR methods are compiled here along with the genfit methodology employed.

- **Future work:** This section gives brief insight into the various potential future
  works that could be carried out in the field of PR spectroscopy.

**1.2 History of semiconductor optoelectronics**

Initial semiconductor optoelectronics research was focused on Si despite it’s
inherent limitations in light emission [3]. This was due to the fact that Si was the second
most abundant material available in the earth in the form of silica and can be easily doped
to form n- or p-type material [3]. Despite these advantages Si based optoelectronics
research had its own limitations such as weak emission of photons and inability to
operate at shorter wavelengths in the visible range [3]. Historically after Si, III-V semiconductor materials were studied for the realization of optoelectronic devices. The first high quality GaAs for a laser diode was developed by R. N. Hall at Bell Laboratory in 1962 by chemical beam epitaxy [4]. Currently GaAs has become the most suited material for the manufacturing IR lasers and light emitting diodes (LED). The physical property of GaAs is similar to Si in terms of electron velocity and electron mobility but GaAs enjoys comparatively superior noise immunity characteristics [5]. This has made GaAs one of the most favored material to be used in high frequency IC’s [5]. One of the biggest advantages of using GaAs in optoelectronics has been it’s direct bandgap structure [6]. This has made it more suitable towards light emission. Another important application of GaAs is it’s extensive use in the manufacture of solar cells [7]. The first successful large scale development of GaAs heterostructure solar cell was carried out by Z. Alferov et al. from the erstwhile USSR for space research [8]. The efficiency of GaAs solar cells is much higher than that of Si based solar cells [9]. The highest possible efficiency (24.7 %) for GaAs based solar cells was recorded by researchers at the IMEC a Belgian research organization in February 2007 [10]. The drawback with GaAs is that the cost of production of GaAs substrates is very expensive [10]. The efficient of usage of both GaAs and Si as materials in optoelectronic devices has it’s limitations as they are not suitable material for light emission in the visible spectrum due to their narrow band gap nature.

The operation of optoelectronic devices in the shorter wavelengths was realized with the arrival of III-nitride wide bandgap semiconductors. They refer to a group of
semiconductor compounds with bandgap greater than 2 [eV] [1]. These materials are grouped in III-nitride semiconductors, II-VI and IV (SiC) in the periodic table. Among them a lot of research is carried out on III-nitride semiconductors and among them GaN has already established itself as a material with a lot of promise in the semiconductor technology industry [6]. GaN is unique in many ways when compared to other classical III-V semiconductors [6]. It exhibits good strong bond strength, good electrical and thermal conductivity, and ability to form alloys [11]. The near band edge emission observed in GaN is due to the radiative recombination of the excitons [12]. The research on III-nitride semiconductors has become even more exciting after the arrival of trivalent rare earth (RE$^{3+}$) ions [13]. The RE are a group of elements that are positioned in the VI series on the Periodic Table [14]. There are 30 RE elements, 15 actinides and 15 lanthanides [14]. The optical properties of rare earth elements are due to their electronic configuration [14]. The RE$^{3+}$ ions have a unique electronic configuration with partially filled 4f orbital [14]. The higher orbitals shield the 4f orbital. The host semiconductor has only a weak influence from the 4f shell. This shielding is responsible for the sharp luminescence spectra [14]. When doped with III-nitride semiconductors, the nitride epilayers exhibit reduced thermal quenching from cryogenic to higher temperatures in comparison to semiconductor substrates like Si and GaAs [14]. This enables the fabrication of novel optoelectronic amplifiers that combines the features of both semiconductor optical amplifiers and RE-doped fiber amplifiers [14]. The RE doped III-nitride semiconductors are also attractive for LED’s and other optoelectronic devices because the emission intensity increases with bandgap value, thus enabling room
temperature operation with or without the need to introduce co-dopant impurities [15]. These spectra are almost independent of the host and temperature variations. Thus the RE$_{3}^{3+}$ ion doped III-nitride semiconductors have offered an alternative route to the realization of optoelectronic devices that operate in the ultraviolet (UV), visible and near IR part of the electromagnetic spectrum [13].

In most cases ion implantation is preferred as the prime doping technique as it is possible to precision control the dopants with it. The RE$_{3}^{3+}$ ions when doped with GaN gives rise to trap or defect centers which are nonradiative in nature and affects energy transfer between the host semiconductor and RE$_{3}^{3+}$ ion [15]. It is very important to anneal the material to remove these defects [16]. To optimize the performance of the material it is very important to study the behavior of these defect centers. The knowledge of the defects responsible for the emission is a fundamental factor in the optimization of the devices and in the conception of newer models, more efficient and less expensive [15]. Defect characterization can be carried out by various techniques such as deep level transient spectroscopy (DLTS) [16], transmission electron microscopy (TEM) [17], optically detected magnetic resonance (ODMR) [18] etc. Most often DLTS is used to characterize the deep defects that are common in III-nitride semiconductor materials. DLTS is a sensitive technique that requires a conducting material [16]. It’s drawback being extensive preparation of the sample to make Ohmic contacts. TEM requires an extremely high resolution microscope which comes with an additional burden of high costs [17]. It as well requires extensive sample preparation. ODMR is limited to sample with high defect concentrations [18]. Based on these information it is possible to draw
conclusions about the nature of the defects which can be considered responsible for the intrinsic (from semiconductor host) and extrinsic (from incorporated impurity) emission [18].

The outcome of intensive GaN:RE research started bearing fruits from the early 90’s when researchers came up with several reports regarding IR or visible light emissions from various RE ions (Er$^{3+}$: IR and green [19-22], Tb$^{3+}$: Tm$^{3+}$ green, blue, Sm$^{3+}$[23], Pr$^{3+}$[24], Eu$^{3+}$: red [25]) in GaN. Recently it has also been shown that the doping of RE$^{3+}$ ions on III-nitride semiconductors give sharp luminescence whose wavelength is almost independent of the semiconductor host [26]. This has led to GaN:RE devices to be used in the fabrication of a wide variety of optoelectronic devices operating across the visible spectrum. Research publications on the growth of RE$^{3+}$ doped GaN and AlGaN and InGaN layers on a Si substrate are an outcome of this [27]. This has also been further substantiated by the first low-voltage operation of current-injected red emission from a $p$-type/Eu-doped/$n$-GaN LED that confirmed that LDs covering the entire range of electromagnetic spectrum could be grown on a large scale [28]. Among the various types of RE doped spectra of particular interest is the sharp IR emission at 1.54 [$\mu$m] due to Er$^{3+}$ ions [19]. The IR emission is due to the electronic interaction between the excited state ($^4I_{13/2}$) and the ground state ($^4I_{15/2}$) of the Er$^{3+}$ ions [30]. This is due to the fact that 1.54 [$\mu$m] is a fundamental wavelength for telecommunication applications. Preliminary results only showed IR emissions at low temperatures [30]. However, recent advancements have permitted IR light emission at room temperature and above [25]. Despite all the demonstrated results from RE doped III-nitride materials the
main drawback lies in understanding the defects induced by the RE$^{3+}$ ions. Understanding these induced defects can lead significant enhancement of radiative yield. This thesis demonstrates that the reflectance spectroscopy is a suitable technique leading towards achieving this goal.

To implement wide band gap materials in optoelectronic devices it is very important to study their performance at room temperature. Most of the current optical techniques used for defects studies are more suited towards cryogenic temperature measurements [35] [36]. The study of deep defects associated with semiconductor materials call for a sensitive technique that can be effective at room temperature. There has been recourse to this issue in the form of a technique called Modulation Spectroscopy which is the subject of my thesis and would be explained in detail during the course of this report. The first experiment on modulation spectroscopy technique was applied to wurtzite (WZ) GaN by M. Giardano et al. in the form of photoreflectance (PR) spectroscopy and electroreflectance (ER) spectroscopy [37]. This was followed by A. Shikanai et al. reporting on the application of photoreflectance (PR) to study the effects of biaxial strain on the exciton resonance in WZ GaN [38]. Later U. Rossow et al. demonstrated the application of Reflection Anisotropy Spectroscopy (RAS) to study defects in WZ GaN [39]. The first successful demonstration of PR was carried out by A. Frova and P. Handler [40] followed by B. O. Seraphin and R. B. Hess [41].

In modulation spectroscopy the focus is on the reflected light from the material and not the luminescence. The technique is applied for bulk and thin films [43], micro and nano structures [44] including quantum wells, quantum wires, quantum dots and
superlattices [45]. This technique is gaining in relevance over the recent years mainly due to its sensitivity. In this technique values of bandgaps can be read directly from the modulation spectrum which shows the interband transitions [46]. This has made PR a powerful technique for the characterization of semiconductor compounds. The leading proponents of this technique were F. H. Pollak, H. Shen and M. Cardona [47]. The greatest advantage of this technique is its sensitivity [48] and ability to perform lineshape fitting [49]. From the modulated signal it is possible to determine the values of bandgap and broadening parameter of transition of the material. The perturbations give rise to prominent spectral features even at room temperature. The spectra that we obtain by this technique are derivative in nature which explains its sensitivity to small changes. Modulation spectroscopy can be performed via different techniques depending on the modulation parameter like electric field, magnetic field, heat pulse or stress. The various modulation spectroscopy techniques are explained in the following section.

1.3 Photoreflectance spectroscopy

The PR technique is an important optical diagnostic tool used in the study and characterization of semiconductor structures [50]. A modulated laser beam is used to excite the sample and a monochromatic source of light is used as a probe source onto the sample [50]. The laser beam creates a modulating electric field which causes a change in the dielectric function of the sample which in turn changes its reflectivity [50]. The spectrum obtained using PR is derivative and thus sharp, well resolved, sensitive to perturbations and well resolved. The data acquisition and manipulation are performed by suitable data acquisition software. Some drawbacks of PR are measuring samples with
significant PL [51]. Since the PL is typically stronger than PR it swamps the PR signal [51]. This problem can be overcome by chopping both the laser as well as the monochromatic light source and measuring the PR at the frequency which is the sum of the two frequencies [51]. The PR and PL are now at different frequencies and this technique (double modulation) isolates the PR from any PL swamping. Some other creative methods for solving this problem are carried out using a double monochromator [52], tunable dye laser [53] and sweeping PR [54] approaches. Another drawback of PL is that of background effects generated and scattered light. This typically can be overcome by placing appropriate band pass filters in front of the detector [55].

1.4 Electroreflectance Spectroscopy (ER)

Electroreflectance (ER) is among the oldest differential reflectance technique [56]. Here the sample is subjected to change in electric field [56]. The ER technique is a well known technique used in obtaining sharp and well resolved spectra [56]. The experimental setup in this case is similar to the one used in PR but the external modulation is obtained by applying a potential difference on the semiconductor surface through the electrodes placed on the surface [57]. There are two different methods of implementing the electric field in this technique, namely longitudinal and transverse [58].

In the longitudinal technique the electric field has to be applied along the surface of the sample [59]. This can be applied to semiconductor – electrolyte, metal-insulator-semiconductor (MIS), Schottky barrier and $p$-$i$-$n$ configurations [59]. The sample surface for this technique needs no special treatment thus making this technique the most
preferred and easy to implement [59]. This technique can measure changes up to $5 \times 10^{-6}$ [V] [60]. The technique was first applied by A. Frova, P. Handler, B. O. Seraphin and R. B. Hess and later extended to analyze semiconductor microstructures such as quantum wells by P. C. Klipstein and N. Apsley [62].

In the transverse ER technique the modulation is produced by applying potential differenced across the electrodes on the sample surface [63]. This technique is restricted to temperature measurements above 200 [K] and for material with resistivity greater than $10^8$ [Ωm] [63].

The ER spectra for $n$- and $p$-semiconductors would demonstrate peaks in opposite directions due to the opposite polarities of such materials [64]. Since EM can detect reflectance changes upto $5 \times 10^{-6}$ [V] it is one of strongest optical technique in semiconductor characterization.

1.5 Thermorelectance Modulation (TM)

The sample in this case is subjected to variations in temperature. This can be done by different methods like passing an alternating current [65], chopped laser beam [66] or a heat pulse [67]. The sample is placed on a heater the temperature modulation is applied on to the sample through the heater [68]. The chopper frequency is maintained to be less than 10-20 [Hz] and at such low frequency noise and background effects may play a destructive role [68]. In the case of good conductors current can be directly passed to the sample however a secondary source of light is used to heat the sample before passing current [69]. Another important factor to be considered in this technique is that unlike the other forms of modulation where the change is applied just in one direction is that in TM
the change is in all directions [70]. This technique despite its effectiveness has limited application as it requires special mounting of the sample [71].

1.6 Piezoreflectance Modulation Spectroscopy (PZR)

In this technique the modulating factor is the stress applied to the sample [68]. An alternating strain is applied onto the surface of the sample which is probed with DC light from the monochromator [68]. The sample is placed on a piezoelectric transducer which causes sample modulation by change in the lattice constant \( \Delta l/l = dE \), where \( l \) represents the lattice constant of the material and \( E \) the energy band gap [69]. The technique requires special mounting of the sample. The supply voltage for high stress generation is of the order of 100 [V] [70]. The supply voltage generates a field of about \( 10^{-5} \) [eV/cm] [71]. There are two types of stress that can be applied [72]:

a) uniaxial stress: for samples glued at the end,

b) coplanar stress: for samples glued totally to the transducer.

The PZR technique is slightly more complex than the ER but provides a different type of result which is an “oriented derivative of the reflectance spectrum with respect to the photon energy” [73].

The signal is detected via a standard lockin technique which works on phase locked loop principle with the reference frequency coming from the transducer equipment [78]. This technique like TM has limited appeal since the application of the stress might damage the surface of the sample.
1.7 Wavelength Modulation (WM)

This is the simplest modulation technique where the wavelength of the optical signal is modulated by vibrating the exit slit of the monochromator at fixed frequency or by vibrating a mirror in front of the exit slit [75]. The modulation is carried at low frequency (<100 [Hz]) [75]. The perturbation applied in this case is internal and the WM spectrum is of the form $dR/Rd(\lambda)$ where $R$ is the reflectance of the sample [76]. This is in stark contrast to the other modulation techniques where there is external perturbation of the sample environment [81]. This technique was first demonstrated at the National Central University, Taiwan by S. T. Chen et al. [81].

An electro-optical detection system is used for this purpose where a monochromatic beam of light is split into two beams by a beam splitter. Here one beam is called the sample beam ($I_A$) and the other the reference beam ($I_B$) [82]. It is possible to keep ($I_A$) and ($I_B$) approximately equal so that ($I_A - I_B$) can be maintained to a minimum value [82]. Now if $I_0(\lambda)$ is the intensity of the incident beam and $R(I)$ is the sample reflection coefficient the WM spectra can be obtained by any of the above discussed methods [82]. The modulated signal can be obtained from a lockin amplifier. The sample beam ($I_A$) intensity can be obtained through another lockin amplifier. Finally the WM of the reflectance divided by the reflectance is given by [82].

$$\frac{dR}{R(\lambda)} = \frac{1}{I_{0}(\lambda)} \frac{1dI_2}{I_{0}(\lambda)}$$

(1.1)

where $R$ is the reflectance of the sample. Wavelength modulation can explain only the derivative of a static-reflection spectrum whereas in others forms of modulation some internal parameter is modulated [79].
1.8 Cathodoreflectance Spectroscopy (CS)

This is a novel technique where the sample is modulated using an electron beam [79]. The laser beam is modulated by a low energy electron beam (200 [eV]) modulated at 1[kHz] [79]. The experimental setup is placed in a vacuum chamber [82]. This technique is more suitable towards wide bandgap materials where conventional excitation mechanisms are not very convenient [79].

Table 1: Comparison of different types of modulation techniques based on the type of semiconductor materials studied.

<table>
<thead>
<tr>
<th>Modulation Techniques</th>
<th>Modulation Parameter</th>
<th>Samples Studied</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photorelectance</td>
<td>Electric field</td>
<td>Superlattices</td>
<td>[84]</td>
</tr>
<tr>
<td>Electroreflectance</td>
<td>Electric field</td>
<td>Quantum wells</td>
<td>[85]</td>
</tr>
<tr>
<td>Wavelength Modulation</td>
<td>Wavelength</td>
<td>Bulk and thin films</td>
<td>[86]</td>
</tr>
<tr>
<td>Thermal Modulation</td>
<td>Temperature</td>
<td>Thin films</td>
<td>[87]</td>
</tr>
<tr>
<td>Piezomodulation</td>
<td>Stress</td>
<td>Strained epilayers, quantum wells</td>
<td>[88]</td>
</tr>
<tr>
<td>Cathodoreflectance Spectroscopy</td>
<td>High speed electron beam</td>
<td>Wide band gap semiconductors</td>
<td>[89]</td>
</tr>
</tbody>
</table>
2. THEORY

The most important objective of the PR technique is to obtain sharp and well resolved spectra that can correspond to the characterization parameters of the material under investigation. This is possible due to the derivative nature of the modulated spectra. In modulation spectroscopy the optical spectrum is not observed but is modulated with respect to some parameter and the change in reflectance is measured [81]. These perturbations give rise to differential spectra with sharp features even at room temperature. Due to its effective performance at room temperature as well as low temperature, PR spectroscopy has become one of the most reliable tools for semiconductor characterization. Once the experimental data is obtained it is fit to a model Lorentzian function that contains one or more fitting parameters. Then the parameter values that give the best fit are calculated [81]. This is done using the genfit algorithm function. The genfit algorithm calculates the optimum parameters to fit a defined function [81]. The best fit would give the most accurate values for the material under study. Typical modulation spectra can be amplified by a lockin amplifier which can measure down to the order of a few nanovolts [70]. The data acquisition and manipulation can be typically performed using the LabVIEW software as described in the Experimental section.

The theoretical analysis presented here is base of the principles of PR spectroscopy used to determine selected physical parameters of semiconductors [56].
laser in this case acts as probe source which causes sample modulation that causes a change in the dielectric of the sample which inturn leads to differential reflectance [56]. The PR modulation mechanism is depicted in figure 2.1 (a) and 2.1 (b). In PR technique a modulated beam causes a variation in the electric field around the sample due to the photoinjunction of the electron hole pairs as shown in figure 2.1(a). This gives rise to sensitive derivative like features near the critical points [56]. The critical point is the most important factor to be considered for the evaluation of the characterization parameters. It’s value depends on the type of sample under study. Typically the critical point of superlattices with thick barriers is two dimensional and that with thin barriers is three dimensional [56]. This spectrum observed in this case is very strong even at room temperature.

(a) LASER OFF

Figure 2.1: Schematic representation of modulation mechanism when the sample is in the dark.
Figure 2.2: Schematic representation of modulation mechanism when the sample is in excited.

The probe source can be the light from a halogen lamp which passes though a monochromator at wavelength (λ) and is focused on the sample [71]. The reflected light is collected by a detector. The light falling on the detector contains two components, the DC component represented by $I_0(\lambda)R(\lambda)$ is the intensity of the light coming out of the monochromator and $R(\lambda)$ is the DC reflectance of the sample [71]. The AC component from the lockin amplifier is given by $I_o(\lambda)R$ [71]. Since we are interested in measuring the change in the reflectance given by $\Delta R/R$ it is necessary to get rid of $I_o(\lambda)$ which can be done e.g. by a variable neutral density filter [80]. In PR care should be taken while making low temperature measurements as the PL from the sample might swamp the PR signal [80]. Furthermore, care should also be taken to prevent the scattered signal from
striking the detector. This can be done by placing appropriate filter in front of the
detector. The PR spectrum in general exhibits one positive and one negative extrema for
every critical point and the distance between the two points is the energy gap of
semiconductor. The general property of complex resonance waveforms is represented in
the form [56]:

\[
\frac{\Delta R}{R} = \text{Re}\left[Ce^{i(E - E_g)} + i\Gamma\right]^{\text{PR}}
\]  

(2.1)

where \(C\) is the amplitude of oscillation and \(\theta\) the phase factor, \(E_g\) and \(\Gamma\) represents the
energy location and broadening parameters of the PR oscillation factors, \(E\) represents the
energy parameter, \(m\) represents the critical point which varies with the material under
study respectively [56]. The broadening parameter corresponds to the width of the PR
oscillation. The phase factor \(\theta\) is the most important factor in determining the line shape.
The \(E_g\) and \(\Gamma\) are obtained directly from the recorded spectrum lineshape [56]. The \(\theta\)
parameter can be obtained from the asymmetry of that lineshape [56]. Thus, the
experimental data is fit to this model function that contains the four fitting parameters as
discussed above. The parameter values that minimize the squared deviation of the fit are
calculated. These values correspond to the physical parameter of the semiconductor
material.

2.1 Theory of the Model Function

2.1.1 Single Modulation Technique

The theoretical definition for the differential reflectance of a semiconductor
structure in the presence of the electric field perturbation contains real and imaginary
parts in a complex dielectric function \((\varepsilon)\) [56]. This is governed by the \textit{Eq.2.1.1} [56]
\[ \frac{\Delta R}{R} = a(\varepsilon_1, \varepsilon_2)\Delta \varepsilon_1 + b(\varepsilon_1, \varepsilon_2)\Delta \varepsilon_2 \]  

(2.1.1)

where \( a, b \) are the Serapian constants [56] and \( \Delta \varepsilon \) and \( \Delta \varepsilon \) are the changes in the complex dielectric function due to external and internal perturbation [56].

The Serapian constants can also be expressed as [86]

\[ a = \frac{1}{R} \frac{\delta \varepsilon}{\delta \varepsilon_1} \]  

(2.1.2)

\[ a = \frac{1}{R} \frac{\delta \varepsilon}{\delta \varepsilon_2} \]  

(2.1.3)

where \( \Delta \varepsilon_1 \) and \( \Delta \varepsilon_2 \) are related by Kramers-Kroning inversion [81] used to calculate the dielectric constants of the solid.

Near the fundamental band gap of bulk material where \( b=0 \) [87], the \( \Delta R/R = a \Delta \varepsilon_1 \) is the only term that is taken into consideration. In multilayer structures both Serapian coefficients are taken into consideration which makes both \( \Delta \varepsilon_1 \) and \( \Delta \varepsilon_2 \) parameters important [91]. The value of \( \Delta \varepsilon_1 \) and \( \Delta \varepsilon_2 \) parameters can be determined from the dielectric function and critical points [88]. The value of critical point is critical in the evaluation of the fitting parameters. Typically critical point of superlattices is two dimensional while those with thin barriers are three dimensional [88]. The PR spectra can be classified into two regimes namely: (a) high field regime and (b) low field regime, respectively.

2.1.1.1 High Field Regime

In this regime the band structure of the material under observation remains the same and the PR spectrum exhibits Franz-Keldysh oscillations [FKO] [94, 95]. The FKO
are PR oscillatory features that can be observed even below the bandgap of certain semiconductor structures [81]. It is the oscillation that is caused by the modulation in the sample. In this case $h\nu \geq \Gamma$, where $\Gamma$ is the broadening parameter and $h\theta$ is the electro-optic energy given by [56]:

$$\tag{2.1.5} (h\theta)^2 = \left(\frac{q^2 eF^2}{2\mu_2}\right)$$

where $F$ is the magnitude of the electric field and $\mu_2$ is the effective mass along the direction of the applied field [56]. From the period of the Franz-Keldysh oscillations the electric field at the sample surface is determined which helps in understanding sample physics such as surface fields [92], carrier concentrations [92], and impurity effects [92], alloy compositions [92], deep levels [92], interface quality [92] etc. One major drawback is the results from this regime cannot be used to study transition near the band edge and thus not pursued in detail generally.

### 2.1.1.2 Low Field Regime

Upon moderate excitation the PR beam can perturb the surface of the material and thus accelerates the free electrons/holes. Unlike the high field regime here the optoelectronic energy criteria is given by $h\nu \leq \Gamma$. Under this condition the $3^{\text{rd}}$ derivative modulation describes the involved phenomena in electromodulation of the sample [56]. The nature of the electron behavior in this case can be explained by Eqn. 2.1.6 [56] which is also called the time dependant Schrodinger equation given by:

$$\tag{2.1.6} (H_0 + eFr)\Psi = i\hbar \frac{\partial \Psi}{\partial \xi}$$

where $H_0$ is the crystal Hamiltonian given by:
\[ H_0 = \frac{p^2}{2m_0} + V_r. \quad (2.1.7) \]

The wavefunction at \( t=0 \) is given by the Bloch function \( \Psi(k_0, r) \) as [56]:

\[ \Psi_a(k, r, t) = \exp\left(\frac{-i(H_0 + eFr)t}{\hbar}\right) \Psi_a(k_0, r). \quad (2.1.8) \]

The generated electric field changes the wavevector from \( \vec{k}_0 \) to \( \vec{k}_0 - \frac{e\vec{F}t}{\hbar} \) [56]. After the generation of the electric field change, the electron behavior can be best explained with the help of Schrodinger equation. This can be explained by Eqn. 2.1.9 [87] as

\[ \Psi_a(k, r) = \exp\left(\frac{-i}{\hbar} \int E_a(k) \, dt\right) \Psi_a(k, r, t). \quad (2.1.9) \]

The optical constants can be determined from two factors, the time dependence of \( k \) and the broadening parameter [56]. In the extreme case of a weak electric field, \( F \), and/or a large broadening parameter the real and imaginary parts of the dielectric function are obtained [93]

\[ \varepsilon_i(E, F, \Gamma) = \varepsilon_i(E, 0, \Gamma) + \frac{(h\theta)^3}{12} E^2 \frac{\delta^3}{\delta E^3} [E^2 \varepsilon_i(E, 0, \Gamma)] + \ldots \quad (2.1.10) \]

where \( i=1, 2 \) gives the indices for real or imaginary part of the dielectric function [56]. It can be concluded that the low-field electromodulation gives a third derivative spectroscopy for band-to-band transitions and the change in the complex dielectric function is correspondingly given by [56]:

\[ \Delta E = \frac{(h\theta)^3}{12 E^2} \frac{\delta^3}{\delta E^3} [E^2 \varepsilon(E, 0, \Gamma)]. \quad (2.1.11) \]

Ultimately, Eqs. 2.1.1 and 2.11 can be combined in the form of Eq. 2.1.12 [56].
\[
\frac{\Delta R}{R} = \text{Re}(Ce^{i\phi}(E - E_g + i\Gamma)^{-m})
\]  

(2.1.12)

where \(C, \Phi, \Gamma, E_g\) represent the amplitude, phase, energy and broadening parameters and \(m\) is the line shape factor can take values based on the type of critical point. The PR spectra in general exhibit one positive and one negative extreme for every critical point and the distance between the two points is the energy gap [71]. The Eq.2.1.14 can now be used to depict the differential reflectance of the PR spectrum in the following form:

\[
\frac{\Delta R}{R} = \text{Re}(Ce^{i\phi}(E - E_g + i\Gamma)^{-m}).
\]  

(2.1.13)

The phase factor determines the symmetry of the line shape [71]. The experimental data is fit to the model function described in Eq.2.1.13 that contains the four fitting parameters. These values correspond to the physical parameters of the semiconductor material under study.

2.1.2 Double Modulation Technique

In the classical PR experiment only the laser beam is chopped at frequency \(\omega_1\). The relationship between the electric field and the sample reflectivity is given by [90]

\[
R_s(E) = R_{so}(E) + \frac{2}{\pi} \Delta R_s(E) \sin(\omega_1 t).
\]  

(2.2.14)

where \(R_{so}(E)\) is the sample reflectivity and \(\Delta R_s\) is the change in reflectivity due to the laser beam [90]. The probe beam intensity is measured as a DC value. The signal observed from the diode is represented as [90]:

\[
S_1 = I_0(E) R_{so}(E) + \frac{2}{\pi} I_0(E) \Delta R_s(E) \sin(\omega_1 t)
\]  

(2.2.15)

where \(I_0(E)\) is the probe beam intensity [90]. At frequency \(\omega_1\) the signal can be measured
proportional to \( I_0(E)(\Delta)R_s(E) \) [90]. Dividing this term by another simple reflectivity quotient correspondingly gives \( I_0(E)(\Delta)R_{so}(E) \) [90]. Finally the differential reflectivity is measured in the form \( \Delta R_s/ \Delta R_{so} \) [90]. One major issue with the conventional PR technique is the swamping of the inherent PL of the sample with affects the PR signal of the sample at low temperatures. Typically the intensity \( I \) of the direct probe beam signal is give by [90]:

\[
I = \frac{2}{\pi} I_0(E) R_{so}(E). \tag{2.2.16}
\]

However the intensity of the pump beam \( I_p \) signal is defined by [90]:

\[
I_p = \frac{2}{\pi} I_0(E) \Delta R_{so}(E). \tag{2.2.17}
\]

In most cases Eq.2.2.17 it is a few (~3 to 4) orders lesser than the pump beam in Eq.2.218 thus leading to the PL signal dominating the PR [90]. The problem can be resolved by the chopping both the probe and the pump beam at frequencies \( \omega_1 \) and \( \omega_2 \) respectively. Now the modified probe beam after double modulation can be defined by [90] (considering only the first harmonic)

\[
S_2 = \frac{2}{\pi} I_0(E) \sin(\omega_2 t + \phi) R_s(E). \tag{2.2.18}
\]

where \( \Phi \) is the phase difference. Expanding \( R_s(E) \) and \( S_2 \) one can obtain [90]

\[
S_2 = \frac{2}{\pi} i_0(E) \sin(\omega_2 t + \phi) R_s(E) + \left( \frac{2}{\pi^2} \right) i_0(E) R_s(E) \cos((\omega_1 t + \omega_2) t + \phi) ...
\]

\[
... \times \left( \frac{2}{\pi} \right) i_0(E) \Delta R_s(E) \cos((\omega_1 t - \omega_2) t - \phi). \tag{2.2.17}
\]
Here the PR signal is picked at frequency $\omega_1 + \omega_2$ which is different from the frequency of PL picked up at $\omega_1$ that does not hamper the PR measurement [90]. Typically PR signal from the double modulation AC spectrum (DACPR) spectrum is $\frac{1}{\pi}$ times of the conventional PR signal [90].

2.2 Theory of measurement using the lockin technique

The lockin technique forms the central part of the data acquisition methodology employed for the PR experiment. It is essential to understand the technique in detail for it’s optimum use. This technique is predominantly used to measure very small AC signals where standard amplification has failed to produce results. Now suppose the input is made up of signal plus noise the phase sensitive detector (PSD) which consists of a low pass filter in the lockin only detect signals whose frequencies are very close to the lockin reference frequency [91]. Noise signals at frequencies far from the reference frequency are attenuated at the PSD output by the low pass filter [91]. Noise at frequencies very close to the reference frequency will result in very low frequency AC outputs from the PSD. The low pass filter bandwidth determines the bandwidth of detection. Only the signal at the reference frequency will be amplified by the lockin [91]. This is the signal we want to measure.

In the functioning of the lockin there are two types of reference signals. The internal reference provided by the phase-locked-loop (PLL) in the lockin and the external reference frequency which is the frequency of data signal [91]. The amplification typically occurs by locking the external reference signal with the internal reference signal [91]. This is done by the PLL. The PSD in the lockin responds to signals which have
same frequency and phase as the internal reference waveform and rejects all others [91]. The lock-in amplifier now takes the input signal, multiplies it by the reference signal resulting in it's amplification [91].

![Graphical representation of the lockin amplification technique.](image)

**Figure 2.2: Graphical representation of the lockin amplification technique.**

In the *figure 2.2* the reference signal is a square wave at frequency \( \omega_r \). If the sine output from the function generator is used to excite the experiment, the response might be the signal waveform shown above. The signal is \( V_{\text{sig}} \sin(\omega_r t + \theta_{\text{sig}}) \) where \( V_{\text{sig}} \) is the signal amplitude. The SR830 generates its own sine wave, shown as the lock-in reference below. The lock-in reference is \( V_{\text{L}} \sin(\omega_L t + \theta_{\text{ref}}) \). The locking amplifier amplifies the signal and then multiplies it by the reference using a phase-sensitive detector or multiplier. The output of the PSD is simply the product of two sine waves. This is the amplified signal from the lockin.
3. EXPERIMENTAL SETUP

3.1 Single Modulation Photoreflectance Setup

The PR technique allows sensitive and non-destructive characterization of semiconductor materials at room temperature. Using the generic PR setup a wide range of materials can be studied with minimum experimental modifications. The figure 3.1.1 shows the schematic of a single modulation PR setup. The laser (pump source) used should have an operating wavelength above the band gap of the material under study for adequate number of electron-hole pairs to be generated. We have used the $n$-GaAs epilayer as a test sample. Because of that in our experiment we used a He-Ne laser with output at 632.8 [nm] as an excitation source. The laser light was chopped using an optical chopper (New Focus 3501). The chopped light was focused on the sample under investigation to the spot of $\sim$1 [mm$^2$]. The probe beam generated though a 100 [W] halogen lamp was passed though a double grating monochromator (Digikrom CM 112). The probe beam was focused using a convex lens onto the sample at the same spot as the laser beam. The reflected probe beam was focused on to a detector after passing through a filter used to prevent scattered light from reaching the photodiode. The detector used was a silicon PIN photodiode (S5343) that sends the signal to the lock-in amplifier (Standford Research Systems Inc SR 830) for AC signal detection and to a DC voltmeter to measure the DC bias voltage. The detected signal was amplified using a preamplifier (Standford Research Systems Inc SR550). The preamplifier was necessary since the signal from the diode was of the order of few nano volts. The amplified signal was passed
through an electrical band pass filter (Avens Signal Equipment AP300) tuned to the frequency of the laser chopper and having a quality factor $Q = 50$. Special care was exercised to lock the frequency of the reflected light to the chopper frequency. The locked signal was then further amplified using a lockin amplifier referenced to the chopper frequency. The lock-in amplifier was interfaced to a computer using the National Instruments GPIB communication port. To calculate the DC value (offset) a separate DC voltmeter is connected to the signal from the detector.

Figure 3.1: Schematic representation of a single modulation photoreflectance experimental setup.
The ratio $\Delta R/R$ was obtained from the lock-in amplifier and plotted versus the reflected light wavelength. From the PR spectrum plot sharp transitions were observed at the bandgap energy of the material. Accurate information about the various characterization parameters were extracted from the recorded PR spectra using genfit line shape fitting algorithm developed using the MathCAD software.

### 3.2 Double Modulation PR Setup

Double modulation is a novel technique of making PR measurements overcome PL effect that is so often pronounced at low temperatures or in samples with strong room temperature luminescence [93]. In conventional PR, the probe beam is DC and the pump beam is chopped and the signal is picked up at the frequency of the probe beam [93]. Since the PR signal is strong at the chopping frequency the PL would also be very large. This potentially may overpower the PR signal beyond detection limit [93]. The problem can be overcome chopping both the pump and the probe beam at different frequencies [93]. This let to avoid the PL which would now be at a different frequency than the PR signal. The double modulation PR produces sharper spectroscopic features and let to detect a signal with much lower amplitude than the single modulation PR technique.

The experimental arrangement for the double modulation PR measurement is similar to the single modulation PR except for the inclusion of an additional chopper between the probe beam and the sample as shown in figure 3.1.2.1 [93]. The beam is imaged onto a sample and chopped at a frequency $\omega_2$ by the 2$^{nd}$ chopper introduced between the sample holder and the monochromator [93]. It is then focused by lens onto a mirror which reflects it to the sample [93]. The reflected beam is focused onto a detector.
A low pass filter placed in front of the monochromator blocks out the scattered beam light [93]. The signal is then amplified using a preamplifier and then passed through a lock-in amplifier which is referenced to $\omega_1, \omega_2$ with a quality factor $Q = 50$ [93]. In some cases there is a possibility of the lockin getting saturated due to the intensity of the signal. This can be avoided by placing a band pass filter before the detector [93]. This is to remove the background and noise components [93]. The filtered signal is fed to a lockin amplifier. The lockin and the monochromator are interfaced to a computer which performs data acquisition and manipulation.

Figure 3.2: Schematic representation of a double modulation photoreflectance experimental setup.
The proposed technique enables PR measurement even at cryogenic temperatures where the luminescence of the sample is very strong [93]. If the background at the combined frequency (laser beam and probe beam) is of approximately the same order as the PR signal then two separate measurements should be performed, one with the probe and pump beam focusing on the same spot corresponding to the PR signal with the background effects and the other with the probe and pump beam focusing on different spots corresponding to only the background obtained in the first case from the background obtained in the 2\textsuperscript{nd} measurement [93]. Further manipulation of recorded PR spectra will result in obtaining the PR signal without the effect of intense light background [93].

3.3 Building the Data Acquisition Software for PR Measurement

The following section document how the PR data acquisition system was developed and implemented into the data collection routine. The data acquisition experimental setup contains two components, a PR intensity measurement and a graphical plot of the collected data. The flow chart shown in figure 3.2.1 gives a review of procedure to operate the software developed. The figure 3.2.2 shows the developed final graphical user interface (GUI). The data acquisition module for the PR setup was programmed using LabVIEW 8.0 (National Instruments) with active support from National Instruments technical team and the EECS Faculty at Ohio University. Four LabView modules were created in total with individual instrument drivers embedded. The hardware instruments that were automated are: (1) lock-in amplifiers (Standford Research SR 830 and SR 510), (2) DC power Supply (Hewlett Packard HP34401), and
(3) monochromator (Digikröm CM 112 and DK 242). The monochromator was communicating with a personal computer through an RS 232 port while the other instrument used the IEEE 488 (GPIB) interface for communication, respectively. Specific attention was paid to solving a few programming issues like statistical collection of data for each monochromator step and graphical visualization of the spectra during the experiment, respectively.
Figure 3.3.1: Flow chart depicting the operation of the photoreflectance spectroscopy data acquisition setup.
The developed module could control the position of the monochromator step to the precision of a nanometer while simultaneously recording and plotting data from the lock-in amplifier and DC voltmeter.

**Implementation of the Software**

This section demonstrates the implementation of the LabVIEW driver software developed by integrating the various instrument drivers. It also gives a step by step implementation of the software.

1. Before executing the software it is required to decide on the mode of communication between the computer and the hardware devices. The mode of communication can be selected from the *Port Number* drop down menu box.
2. The monochromator settings can be initialized through the Start Wavelength, End Wavelength and Wavelength Increment text boxes. Care should be taken to input the wavelength values in nanometers [nm].

3. The Software Trigger input text box enables to set the frequency of operation of the lock-in amplifier.

4. Pressing the Enable Monochromator radio button executes the software.

5. The AC values (AR) of the PR spectra in real time can be viewed at the AC Signal from the SR 830 plot graphical interface.

6. The DC values (R) are displayed in real time at the AC Signal from SR510 plot graphical interface.

7. The PR spectra deferential voltage can be viewed from the Final calibrated plot (Wavelength vs. I) graphical tool.

8. The corresponding AC and DC values can be obtained in spreadsheet format from the file path shown at Destination File file box.

9. The Software Trigger output check box gives the number of points collected.

10. Once the data acquisition is completed the final calibrated plot can obtained from the Final Calibrated Plot (Wavelength vs. I) plot.

**The VI Diagram**

The complexity of the developed LabVIEW driver requires explanation of a few critical features of it in greater details for better understanding of it’s functionality. The block diagram for the monochromator step increment has two parts as shown below:

- **Block Diagram-DK 242 Wavelength Increment Module (figure 3.2.3):** This module
carries out the monochromator step increment procedure based on the values of \textit{Start Wavelength}, \textit{End Wavelength} and \textit{Wavelength Increment} textboxes.

- \textit{GOTO execution module}: Once the wavelength specifications are entered the LabVIEW code automatically goes to the GOTO frame to enable the monochromator pointer to move to the input wavelength.

As soon as the \textit{Enable Monochromator} control is turned on it turns the case structure is set to \textit{True} Boolean value (a \textit{FOR loop}). The iteration input to the \textit{FOR loop} is the difference between the initial wavelength and final wavelength divided by the step increment. The \textit{FOR loop} contains the \textit{Insert into Array} function which is indexed to the iteration value. The current wavelength is the other constituent inserted into the array.

The frame in the bottom contains the \textit{GOTO} execution routine. This routine is executed only when the case structure is set to \textit{True} which in turn is wired to \textit{Boolean Monochromator control}. It is also very important that the \textit{Current Wavelength Control} is converted into nanometers before providing it to the VI which performs the \textit{GOTO} function otherwise this may lead to malfunctioning of the developed driver. Since a \textit{Frame Structure} is used one does not need to use a timing delay as it is necessary for the constituents of one frame to be executed before moving to the next frame. Once the monochromator \textit{GOTO} function is executed the execution moves to \textit{Frame 2}, here the GPIB string address activates the lock-in amplifier driver. This is connected to the \textit{Send Message VI}. Here \textit{VI} stands for visual interface. The execution then moves to \textit{Frame 2}. Here the \textit{Receive Message VI} receives the string from the \textit{Send Message VI} and is converted into a numeric variable by the \textit{String to Number} converter for further
manipulation. The output is now given to a Channel 1 Graph Local Variable. This point is now shown on the display screen of the computer as a Dynamic Data Plot. The developed driver also has a Final calibrated plot (Wavelength vs I) as shown in figure 3.2.1. To incorporate the dynamic plotting technique an array of all the Current Wavelength values was created which are indexed to a shift register. This array is also made into a Local Variable and used at a later stage. This local variable is called up at the final frame of execution along with the wavelength local variable. They are given as inputs to a Bundle function. The output of the Bundle function is given to a X-Y plot. Care should be taken to input the same type of variables to the inputs of the bundle function else the software hangs up. The output is given to a final Wavelength vs. Intensity Plot after completion of the execution of the program. Therefore, the AC Signal From SR 830 plot between intensity and some arbitrary incrementing value could be treated as a preview and the final calibrated plot. The same procedure is carried out for channel 2 in frames three and four. For the first increment of the Trigger counter the corresponding devices drivers are activated and with the structure explained above and the data $\Delta R/R$ is collected for the initial wavelength entered in the Start Wavelength dialog box. The collected data along with it’s corresponding wavelength from the monochromator is recorded in the file pointed at the Destination File dialog box for post experimental analysis. This marks one complete cycle in the process of data collection. Once this entire process is completed the Trigger counter is incremented by a single step. The collected PR data file is in .dat format. The data in the file also needs to be indexed. This is done by a For loop which is incremented by the Trigger counter. This loop is
active as long as the trigger counter keeps incrementing. The output array in the For Loop which stores the index values, Channel 1 numeric variable, Channel 2 numeric variable are combined in a three input Build Array function. The format used is \%.15g as it can store numbers up to the 15th decimal point. Since all the inputs are stored as rows, they are transposed using the transpose function from LabVIEW VI toolbox. The output of the transpose function is given to a Write to Spreadsheet File (Figure 3.2.5) function. This is the last frame of program execution. This frame also contains the Final Calibrated Plot which takes inputs from the current wavelength array and Channel 1 array. This is displayed as a Final Wavelength vs.I plot on the front panel of developed GUI. The final routines implement into the developed driver include the program execution stopping under the following conditions:

1. On completion of the data acquisition process.
2. When the user hits Stop Triggering control (figure 3.2.5)
3. When the value of number on the Trigger Control is higher than Trigger counter Indicator.

**Significant Programming Issues**

Among the significant challenges faced in building the module was the programming of the real time data acquisition system. The data acquisition protocol provided by the LabVIEW 8.0 was not capable of recording, plotting and displaying data in real time without the DAQ board. This shortfall was overcome using signal processing technique, mainly the sample theorem and the Nyquist criteria. According to the general sampling theorem, “In order for a band-limited (i.e., one with a zero power spectrum for
frequencies \( \nu > 2B \) baseband \((\nu > 0)\) signal to be reconstructed fully, it must be sampled at a rate \( \nu > 2B \). A signal sampled at \( \nu \) is said to be Nyquist sampled, and \( \nu = 2B \) is called the Nyquist frequency. No information is lost if a signal is sampled at the Nyquist frequency, and no additional information is gained by sampling faster than this rate” [6]. This basically implies that the signal from the lock-in has to be sampled at least at twice the original frequency for it to be reconstructed. This was implemented in LabVIEW in the following sequence:

- recording in separate storage space,
- recalling it after every scan (of the monochromator) and multiplying the locking frequency by a factor greater than two.
- Finally, storing it in a permanent storage location which is then output as a real time data acquisition plot.

This technique had other challenges such as efficient management of the limited system resources. There were three instruments that were communicating with the software module at the same time and the computer used had limited resources. Care had to be taken to selectively activate ports that were required at that point and deactivate the rest. This is implemented by putting the entire Data Acquisition (DAQ) module in a \textit{FOR Loop} which iteratively runs though the entire monochromator scan including the \textit{While Condition} inside the loop which turns \textit{on} and \textit{off} certain ports based on a few predefined conditions. This technique successfully solved the problem of real time data acquisition without using the DAQ board.
In addition to the above described module, two other modules were developed whose purpose and functionalities are discussed in the following section.

1. **Double Modulation Setup**

   Since both probe and pump beams are modulated in this case there is a need for a second lock-in amplifier to display the modulated beam from the monochromatic source. The real time data acquisition system to collect data from the second lock-in amplifier is incorporated by replacing the DC voltmeter module with the lock-in amplifier (Stanford Research 510) module.

2. **Continuous Scan Setup**

   In certain PR experiments it becomes necessary to carryout data collection in a continuous mode *i.e.* the data from the locking is recorded as a continuous stream instead of a step increment for the specified wavelength range. The **Continuous scan setup** module caters to such experiments where the monochromator is used in continuous scan mode. In this mode monochromator control is independent from the lock-in amplifier. These two constituents are treated as independent entities when the program is run. The number of points to be collected depends on the software trigger frequency and speed of the monochromator, respectively.

**Sample Details**

The sample used for testing the developed PR setup was *n*-GaAs:Si thin film with 400 µm thicknesses grown on 2 [in. diam] Si [100] wafer film by metal organic chemical vapor deposition process (MOCVD). The career concentration of the electrons in the sample was $2.6 \times 10^{16} \text{[cm}^{-3}\text{]}$. The second sample was GaN:Tb epilayer grown by
MOCVD on the basal plane of 2 [in. diam] sapphire substrates by CREE, Inc. The undoped GaN sample was high quality and semi-insulating (no intentional donor doping). It was implanted at room temperature with \(\text{Tb}^{3+}\) ions with dose of \(4 \times 10^{15} \text{ cm}^{-2}\) at multiple energies not exceeding 150 [keV]. The sample was subjected to post-implant isochronal thermal annealing treatments at 1100\(^\circ\)C in \(\text{N}_2\) at atmospheric pressure.
4. RESULTS AND DISCUSSION

4.1 Results

To test the functionality and sensitivity of the developed experimental setup we collected PR spectra of the test $n$-GaAs epilayer using both single and double modulation technique. The experiments were carried out at room temperature since GaAs shows very good optical properties at that temperature. Furthermore, studying the test $n$-GaAs sample gave us an opportunity to investigate if the double modulation technique can eliminate parasitic PL from the samples hampering the PR signal. The data collected was subjected to line shape fitting based on the genfit algorithm formula that was discussed in Chapter 2. The collected data and performed analysis depict the various characteristic parameters of studied material like band gap energy, broadening parameter and phase factor well know from the literature.

4.1.1 Photoluminescence of GaAs

The photoluminescence spectroscopy of the test $n$-doped GaAs sample was carried out to test the quality of the test sample and the sensitivity of the experimental setup. The excitation source was He-Ne laser of intensity 632.8 [nm]. Typical PL at room temperature can be observed in the near band edge region is shown in figure 4.1.
Photoluminescence (PL) spectroscopy technique is perhaps one of the most important techniques used in the estimation of sample quality [21]. The laser acts as an excitation source for the electrons from the valence band to the conduction band [6]. The recombination of holes created in the conduction band and electrons created in the valence band is radiative in nature and energy released is in the form of light [6]. The PL spectrum corresponds to a range of transition energies closely associated with the electronic levels [21]. Typically the PL spectra exhibits of highly pure GaAs shows prominent and well resolved spectra even at low temperature [21]. The signal to noise ratio in the PL spectrum was purposely selected to be low for the purpose of reducing the parasitic PL intensity. This lets us optimize the sensitivity of the PR setup by changing the entrance slit width to such a size that the PR signal could be detected.
4.1.2 Single Modulation of n-GaAs

The figure 4.2 shows the single modulation PR spectrum of n-GaAs measured at 300 [K]. Typically a PR spectrum of a semiconductor material would have one positive and one negative peak [93]. Despite of our best effort to reduce the parasitic PL signal for the test sample (see above) we were not able to completely eliminate the PL signal contribution to the PR signal using the single modulation technique. From figure 4.2 it can be noticed that the PR spectrum of n-GaAs has a positive but the negative peak is swamped by the PL which hampers the PR. The PL is much stronger than PR and overpowers it. The other concern with this setup was the effect of the scattered light and background light interferences due to strong luminescent specimen.

![Figure 4.2: Single modulation photoreflectance spectrum of n-GaAs.](image)

These are the other parasitic effects that swamp the PR signal. Due to the destructive effect of PL it is not possible to carry out any optical diagnosis using single modulation in
samples which has significant luminescence intensity. These issues have been eliminated by using a double modulation technique where the probe and pump beam are chopped and the data is collected at a different frequency than the pump beam as described in the experimental section.

4.1.3 Double Modulation of GaAs

The double modulation technique on $n$-GaAs was carried out at room temperature and the recorded spectrum is shown in figure 4.3. It shows a stark difference when compared with the one showed in figure 4.1. The PR spectrum with negative and positive features is clearly seen with no effect of the parasitic PL signal. The figure 4.3 shows the comparison between single and double modulation spectra of $n$-GaAs sample. The comparison clearly shows how the PL which swamps the PR component in the single modulation does not exist in double modulation. Sharp PR spectrum is observed at the band edge of the GaAs at 1.4 [eV]. The double PR was taken at slower scan speed and larger time constant for data collection than in the case of single modulation PR. The scattered light and the background effects were addressed using appropriate filters in front of the detector. The double modulation PR spectrum is narrow with the half width of 220 [nm] which is due to the excitonic emission of GaAs. The PR spectrum is fit to a predefined Lorentzian function to determine the characteristic parameters $C$, $E_g$, $\theta$ and $\Gamma$. Section 4.3 discusses in details how the double modulation PR was fitted to a predefined Lorentzian function with theoretical line shapes. The characteristic parameters of $n$-GaAs were calculated from the best fit values.
In conclusion we have been able to show that the problem of PL which plays a destructive role in PR measurements can be overcome by using the double modulation PR technique. Furthermore, the noise which might be introduced due the extra hardware can also be removed by using better quality electronic devices.

4.2 Discussion

The experimental analysis of PR spectrum from $n$-GaAs using both single and double modulation technique was carried out. Well resolved and sharp oscillations were observed near the critical point. A *genfit* algorithm was used to fit a Lorentzian function to the generated PR spectra. The lineshape of the PR signal of $n$-GaAs directly corresponds to the modulation of the complex dielectric function of this material [68]. The low field spectrum shown in *figure 4.1* exhibits one positive and one negative band.
for each critical point. The line shape function is given by the Eq. 2.1.14 which is the 3\textsuperscript{rd} order derivation of the PR spectrum. Since $\theta$ (phase factor) is an exponential in the equation it plays a critical role in determining the line shape. The $\theta$ for $n$-GaAs was determined from the asymmetry of the experimental data which can be further defined as the ratio of the magnitude of the positive and negative extreme of the PR spectra [68].

Finally, the $C$ and $\theta$ parameters enable us to calculate the amplitude and asymmetry of the line shape whereas the $E_g$ helps in determining the exact location of the energy and the width of the PR spectrum [68]. The value of $m$ which is a line shape factor varies with the critical point, \textit{i.e.} $m=3.5$, 3.0 and 2.5 for one, two and three dimensional critical point [94]. The value of critical point is critical in the evaluation of the fitting parameters. The critical point of superlattices with thick barriers is two dimensional while those with thin barriers are three dimensional because of [96]. In this case best fit was obtained when $m=2.5$. 

![Graph showing differential reflectance](image)
Figure 4.4: Curve fitting of photoreflectance spectroscopic spectrum of n-GaAs using genfit algorithm (The dotted line represents the PR curve and the single line represent the genfit curve fit).

The best fitting was done using genfit algorithm which is based on regression analysis [97]. It is designed to model data by an arbitrary function whose parameters much be chosen [97]. Here the function that is needed to be fitted is defined in the form of a sample curve [97]. The unknown variables of the function are given a range of guess values to try to match the actual data values. The final parameters of the data value would be the one where the data curve closely matches the function curve [97]. A typical genfit algorithm has been demonstrated below:

Suppose the data is modeled by a model function of the form $Ax^b$, where $x$ is a variable and $A$ and $b$ are the unknowns. The function genfit has the form $\text{genfit}(X, Y, \text{guess}, f)$ where:

- $X$ and $Y$ are vectors containing the x-values and the y-values, respectively, of the data.
- $\text{guess}$ is a vector of initial guess values for the parameters.
- $f$ is the model function that is to be fitted.

Subsequently a set of educated guess values are chosen for the guess vectors $A$ and $b$ on which the genfit function is applied to get the best possible fit. The best possible guess values would give the most accurate values for $A$ and $b$. The algorithm was implemented in MathCAD 13.0 environment. The figure 4.2 shows the experiment PR spectrum along with the model fit generated via an algorithm using MathCAD software (see
Appendix). The best fit values of $\Gamma$, $C$, $\theta$, $E_g$ were calculated to be $5.47 \times 10^{-8}$, $8.98 \times 10^{-8}$, 1.32 [rad], 1.42 [eV], respectively.

4.3 Conclusion

An illustrative example of the double modulation PR technique applied to $n$-GaAs along with detailed measurements and characterization is presented. It is also established that the double modulation PR spectrum can be fit to the theoretical Lorentzian fitting function to extract it’s characterization parameters [98]. The obtained fitting parameters are in good agreement with the literature [98]. The drawback regarding swamping PL was overcome with the experimental setup and the some of the optical and electronic noise improved using suitable filters and better electronic equipments [96]. The modifications implemented significantly enhance the performance capability of the system. The sensitivity of the double modulation PR technique enables it to be implemented even on semiconductors with a rough surface morphology [95].

Optimization of the experimental setup conditions to provide maximum response in the PR was accomplished by considering each component of the experimental arrangement and its influence on the spectra [56]. The characteristic parameters extracted from the experimental PR spectra are compared to the expected results and found to be satisfactory [56]. This demonstrates the reliability of the technique implemented. An alternate approach of conventional single modulation PR is demonstrated to prove the efficiency and sensitivity of the double modulation technique. The single modulation technique presents the PR spectrum swamped by the PL making it unsuitable for optical diagnosis while the double modulation PR technique presents the PR spectrum of the
same specimen with much high sensitivity and spectral resolution. This suggests that the double modulation PR technique might be useful for samples with inherently high luminescent properties [96]. The necessary software drivers used for data collection were developed in house for computerized data collection.
5. FUTURE WORK

The PR technique is a contactless, non invasive optical characterization technique with exciting applications in the semiconductor spectroscopy [56]. In future one may capitalize on the sensitivity of this technique to study in RE$^{3+}$ doped III-nitride materials. The double modulation technique can be used to study RE$^{3+}$ ions induced defect levels, determination of energy band structure affected by heavy RE$^{3+}$ ion doping, morphological changes of quantum well interfaces and structures and local strain analysis [80]. The unique feature of this technique is it’s exciting sensitivity at room temperature something that is not the case with standard optical excitation mechanisms engaged in PL and CL techniques. Furthermore, in principle the PR technique is also suitable for characterization of optoelectronic devices based on these materials.

With the use of suitable detectors operating in the UV spectra range the double modulation PR technique can be extended towards analysis of deep defect in III-Ns near the fundamental bandgap energy. However, one can utilize below bandgap excitation to test defect levels induced in band gap. We have performed successfully the preliminary test of concept using a GaN epilayer implanted with Tb ions. The double modulation PR spectrum recorded for GaN:Tb at 300 K is shown in *figure 5.1*. 
Figure 5.1: Double modulation photoreflectance spectrum of n-GaN.

The PR spectrum containing the double peaks shows deep defect levels which are mostly associated with Tb$^{3+}$ ions. It is interesting to mention that the energy of this defect (1.95 [eV]) level overlap with the 4f-4f transition of Tb$^{3+}$ ion. The nature of this deep level is still not fully understood yet, however we can speculate that it might be associated with the Tb ions implantation induced defects or some local low symmetry site of Tb$^{3+}$ ion. The data acquisition of the experimental setup used implemented GPIB ports. In future this can be extended to setting up a NI DAQ (National Instruments Data Acquisition) board which allows the input/output of both digital and analog signals on a single interface. This enables greater integration of the various components of the data acquisition system and minimizes errors due to data sampling that were discussed in this document.

It was recently shown that white light could be used as a probe source instead of monochromatic light [93]. This technique is called *bright configuration of electro*
Some headway in this technique has been carried out in the Institute of Physics, Wrocław University of Technology by R. Kudrawiec and J. Misiewicz [93]. However this technique needs more analysis [93]. To start with the results have so far not been compared with the results from classical PR [93]. Since the sample illumination has been carried out over by white light the constant PV effect affects the sensitivity of the spectra and therefore the modulation efficiency of the sample under study [93]. This technique can also be extended to replace the regular Si diode detector with CCD camera to enhance the sensitivity of the spectra [97].

Currently researchers are also concentrating on studying the third derivative of modulation spectroscopy which represents well resolved spectra where the background effects are negligible [96]. The experimental technique used in this case is called resonant quadratic electro-optic technique or low field ER and is described in detail in [96]. The setup used is similar to the one used in conventional single modulation PR but the electric field developed is transverse i.e. along the plane of the sample surface by applying high voltage between the contacts of electrodes evaporated on the sample surface [96]. Only recently developed, it can form a powerful tool in studying the properties of a wide variety of semiconductor structures.

The double modulation PR technique can also be extended further to studying samples with poor surface morphology by exploiting the freedom to modulate the pump wavelength so that we can selectively modulate specific regions in the sample morphology [103]. This technique can be used to study samples with both rough and smooth surface morphologies [103]. The modulation in this case is applied to only certain
layers in a multilayer sample thus providing more detailed information of those layers [103]. This experimental technique was developed by P. M. Amirthraj et al. [103] in 1996 to study a rough GaAs surface and was never applied to III-nitride materials.

In essence all the above techniques represent the optical response of the system to the applied perturbation. The most important information lies in the modulating parameters such as phase, modulation frequency, the modulation amplitude, and pump wavelength which have been discussed in detail in Chapter 2 and Chapter 5. Finally it is also to be noted that measuring PR with different modulation techniques can sometimes lead to decrease in the signal level. Here a signal processing approach can be taken to
REFERENCES


APPENDIX: DOUBLE MODULATION PHOTOREFLECTANCE SPECTROSCOPY OF N-GaN:Tb

The best fit analysis for the thesis presented was done using genfit algorithm. The algorithm uses a generalized least-squares fitting procedure that is built into mathCAD to find the optimal fit parameters for an arbitrary (nonlinear) model function. Steps to arrive at the optimal fitting parameters are explained below [97].

- Step 1: The PR function is first defined.
- Step 2: The fitting parameters are put into a matrix format.
- Step 3: Now we create a fitting function using the vector of parameters.
- Step 4: Now a sample data is applied to the fitting function and plot is made with the function as the y axis and excitation energy range as the x axis.
- Step 5: The point where the fitting plot matches the actual plot equals the value of fitting parameters.
- Step 6: These fitting values are unique for each sample and very accurate.
The section below shows the actual MathCAD fitting code which was developed using the genfit fitting algorithm explained above.

Here I have tried to change the values for a, b, c, d and also constant in the noise function.

\[
x = 4 \quad c = 2 \quad d = \frac{2.14}{3} \quad a = 0.01 \quad j = (c-1)^{\frac{3}{2}}
\]

\(y\) represents the differential reflectance values.

\(x\) represents the excitation energy values.

<table>
<thead>
<tr>
<th>(0)</th>
<th>(1)</th>
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<tbody>
<tr>
<td>(0)</td>
<td>(1.36)</td>
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Here is a plot of the underlying function and the actual sample data:

\[\text{Figure A.1: MathCAD code developed to implement the genfit algorithm.}\]
Figure A.2: MathCAD code developed to implement the genfit algorithm (continued from Figure A.1).
Figure A.3: MathCAD code developed to implement the genfit algorithm (continued from Figure A.2).