Chapter 3

Photoacoustic and photothermal deflection studies on III-V compounds

The present chapter comprises of two sections. The first section discusses the investigation carried out on sulphur doped n-type InP wafer using an open photoacoustic cell. The thermal diffusivity of the sample is evaluated from the phase data associated with the photoacoustic signal as a function of the modulation frequency. Analysis is made on the basis of the Rosencwaig-Gersho theory and the results are compared with those from earlier reported photoacoustic studies on semiconductors. Results show that, under the present experimental conditions, the pure thermal-wave component is responsible for the photoacoustic signal generation from n-type InP sample. Results obtained from a dual-beam photothermal deflection studies on n-type and p-type GaAs thin films grown on a semi-insulating GaAs substrate are discussed in the second section.
3.1. Introduction

Absorption of intensity modulated optical radiation by a sample leads to periodic heat generation, thereby causing excitation of thermal waves in the sample. Thermal wave physics is emerging as a valuable tool in the study of thermal parameters of materials, especially in the semiconductor industry [1-17]. Among the various methods used to study these thermal waves, the gas-microphone photoacoustic (PA) technique and the dual-beam photothermal deflection (PTD) technique are the most commonly employed experimental approaches [15-26]. Apart from the pure spectroscopic studies in the very beginning, the PA method has now grown to a multipurpose analytical tool for the investigation of different thermal and optical properties of a variety of materials.

In many of the earlier reported papers, PA signal amplitude data as a function of the modulation frequency has been mainly used for the thermal diffusivity measurements in semiconductors [22-28]. Since the first report of Sablikov et.al regarding the use of PA technique for heat transport studies in semiconductors, researchers are using this approach for a variety of measurements [29]. But a major renaissance in this field was made by Dramicanin et.al [30], who analytically evaluated the expression for the distribution of the periodic thermal flux originating from three principal thermal sources namely, the instantaneous thermalisation component, nonradiative bulk recombination and non radiative surface recombination. Their model is very useful for the analysis of PA signal amplitude and phase at the front and rear surfaces of a semiconductor sample. Subsequently, in more recent years, carrier transport properties such as carrier diffusion coefficient, carrier recombination velocity and mean recombination time are evaluated together with the thermal diffusivity of a large number of semiconducting samples such as GaAs, CdTe, Si solar cells, CdInGaS4, InSb, GaSb etc using the photoacoustic phase measurements [31-42].

Similar to the PA technique, PTD technique has also become mature both in the theoretical aspect as well as from the experimental point of view. The only difference between the PA and PTD techniques is in the mode of detection, but the basic mechanism of heat transport on which the two methods relies is the same [15,16]. Consequently, PA and PTD techniques can be used for similar type of studies, but each approach has its own advantages and disadvantages. Following the theoretical model developed by Sablikov et.al for the PA signal generation in semiconductors, Fournier et.al formulated a one-dimensional heat-flow model to describe the PTD signal generation in semiconductors, by taking into account the nonradiative recombination processes [43]. However, the contributions from the free carriers plays a
dominant role in the PA and PTD signal only under certain experimental conditions such as a particular frequency range, sample surface quality etc. Details of each experimental approach and the observed results are described in the respective sections.

3.2. Significance of thermal diffusivity

Centuries before, Jean Fourier (1768-1830) derived a basic law defining the propagation of heat in a one-dimensional homogeneous solid as [44-46]

\[
\frac{\partial Q}{\partial t} = -kA \frac{\partial T}{\partial x}
\]  

(1)

The above equation is known as Fourier equation. Equation (1) implies that the quantity of heat \(dQ\) conducted in the x-direction of a uniform solid in time \(dt\) is equal to the product of the conducting area \(A\) normal to the flow path, the temperature gradient \(\frac{dT}{dx}\) along this path, and the thermal conductivity \(k\) of the conducting material.

Formal definition of thermal diffusivity arises when deriving an expression for a transient temperature field in a conducting solid from the Fourier equation. The equation describing the temperature field in a homogeneous, linear conducting solid with no internal heat source is

\[
\nabla^2 T = \frac{1}{\alpha} \frac{\partial T}{\partial t}
\]  

(2)

where the thermal diffusivity \(\alpha\) is given by

\[
\alpha = \frac{k}{\rho C}
\]  

(3)

where \(k\) is the thermal conductivity, \(\rho\) is the density and \(C\) is the specific heat capacity of the material. The thermal diffusivity \(\alpha\) is usually expressed in \(m^2s^{-1}\).

The thermal diffusivity is thus a derived quantity whose significance is evident from the above relationship. The reciprocal of thermal diffusivity, \(\frac{1}{\alpha}\), expressed in \(m^2s^{-1}\) is a measure of the time required to heat-up a conducting material to some temperature level. Therefore, the ratio of heating times for two materials of the same thickness will be inversely proportional to their respective thermal diffusivity values. Obviously, \(\alpha\) is a significant thermophysical parameter that determines the heat diffusion in bulk as well as thin film samples.

Being a widely used and important substrate material in the field of semiconductor technology, measurement of the thermal diffusivity and a detailed analysis of the heat diffusion processes in InP have great practical significance. The same is the case with GaAs since it is a
widely used compound semiconductor material in electronic and optoelectronic devices. Moreover, the bandgap of semiconductors, in general, decreases as the temperature increases [47-52]. These changes have very important consequences in electronic and optoelectronic devices. The variation in the operating temperature may alter the laser frequency in semiconductor lasers, and may alter the response of semiconductor modulators and detectors. Hence, a clear knowledge of the thermal transport properties such as the thermal diffusivity of these materials assumes importance.

3.3. III-V compounds

Most semiconductors of interest for electronics and optoelectronics have an underlying fcc lattice. If two atoms of the basis are different, the structure is called the zinc-blende structure and such semiconductor materials are usually known as compound semiconductors. Usually, the compound semiconductors are denoted by the position of the atoms in the periodic table, e.g. II-IV, III-V etc. GaAs and InP are examples of III-V compounds. Both these compounds are direct bandgap materials which ensures excellent optical properties as well as superior electron transport in the conduction band. The bandgap energy in GaAs is 1.43 eV and in InP it is 1.34 eV [47-49,54]. In the field of semiconductor research the main thrust is towards III-V compounds which are widely used in solid state electronics, in particular in the manufacturing of very important types of devices such as those used in optoelectronics, microwaves, high speed integrated circuits, high efficiency solar cells etc [53-59].

Bulk crystal growth techniques are mainly used to produce large size substrates on which the thin film devices are fabricated. These techniques are widely used in the growth of semiconductors such as Si, GaAs and to some extent InP. One of the commonly employed bulk growth method is the Czochralski technique [60-65]. But, in the case of GaAs and InP the Czochralski technique has problems arising from the very high pressures of As and P at the melting temperature of these compounds. Not only the chamber has to withstand such high pressures, but also the As and P leave the melt and condense on the side-walls. To avoid the second problem, usually the melt is covered with a molten layer of a second material (e.g. boron oxide) which floats on the surface. The technique is then referred to as Liquid Encapsulated Czochralski (LEC) method. Both InP and GaAs substrates used in the present investigations are grown by LEC method.
The substrates that result from the bulk grown semiconductor boule are almost never used directly for device fabrication. Invariably an epitaxial layer is grown over the substrate, which may be a few microns in thickness. The epitaxial growth techniques have a very slow growth rate which allows precise control over the dimensions in the growth direction. One such technique is the Molecular-Beam Epitaxy (MBE) which is essentially a refined form of vacuum evaporation [54, 60-62, 66]. In this technique, elements are heated in crucibles called Knudsen cells or furnaces and directed beams of atoms or molecules are condensed onto a heated single-crystal substrate where they react chemically under ultra-high-vacuum conditions. The special merits of this technique are that thin films can be grown with precise control over their thickness, alloy composition and doping level. Using rapidly acting mechanical shutters, the composition can be changed abruptly, which permits novel structures to be prepared. MBE grown n-type and p-type GaAs double-layers on a semi-insulating GaAs wafer are used for the photothermal deflection studies.

3.4. Heat conduction in semiconductors

In general, two different mechanisms are responsible for heat conduction in a solid material. One is the heat conduction due to the charge carrier motion and is termed as electron or hole heat conductivity \(k_e\). The second mechanism is connected with the lattice vibrations [66-70]. The lattice atoms (or ions) oscillating around their respective equilibrium positions exchange energy with each other. When a temperature gradient is built up in a substance, this energy gradient proceeds in such a manner that energy is transmitted from an atom which oscillates more intensely to an atom which oscillates less intensely. Heat conductivity due to lattice vibrations is termed as lattice, or phonon, heat conductivity \(k_L\). The total heat conductivity may thus be described by the quantity \(k\) as

\[
k = k_e + k_L
\]

the value of \(k_L\) is related to the elastic properties of the solid and \(k_e\) to the charge carrier concentration. In dielectrics \(k_L \gg k_e\) and in metals opposite is the case, i.e. \(k_e \gg k_L\). In semiconductors the value of \(k_e\) strongly depends on the composition and on the temperature.

In the case of a semiconductor irradiated with an optical radiation of suitable energy, in addition to the above-described mechanisms, photogenerated carrier recombination will also contribute to the heat transport [22, 30-43]. Free-carrier generation resulting from the light absorption occurs when the incident photon energy is greater than the band gap energy. The photon is absorbed in this process and the excess energy, \(E_{ph} - E_g\), is added to the electron
and hole in the form of kinetic energy. Now, the nonradiative recombination of these carriers will result in the release of excess energy in the form of heat to the lattice. The recombination rate of majority carriers is equal to that of minority carriers since the steady state recombination involves equal number of holes and electrons. Therefore, the recombination rate of the majority carriers depends on the excess minority carrier density as the minority carriers limit the recombination rate. There exist different possible pathways for the nonradiative recombination [22,30-43]. Nonradiative band-to-band recombination depends on the density of available electrons and holes and is proportional to the product of the two densities. In this case the electrons carrying excess energy above the bandgap recombine with a hole and the energy equivalent to the bandgap energy will be liberated as a phonon. Usually this process takes place in the bulk of the material and is termed as the bulk recombination. Another nonradiative recombination process is the surface recombination. Surfaces and interfaces of semiconductors usually contain large number of recombination centers because of the abrupt termination of the crystal, which leaves a large number of electrically active dangling bonds. In addition, the surfaces and interfaces are likely to contain more impurities since they are exposed during the growth of the material. The surface recombination is also essentially an interband recombination process and the excess energy is ultimately transferred to the lattice as heat. Trap assisted recombination and Auger recombination are the other two recombination mechanisms. Apart from these interband nonradiative recombination processes there exists an instantaneous thermalisation component which arises from the intraband interaction of excited electrons with the lattice. This process is an after-effect of excitation of electrons to the higher levels in the conduction band. Such hot electrons will come back to the minimum of the conduction band by imparting the excess energy to the lattice. This thermalisation process usually takes place in ultra-short time scales (~ picosecond) and hence known as the instantaneous thermalisation process [22,66-68]. In the subsequent section of this chapter experimental investigations of heat diffusion in n-type InP carried out by PA technique and PTD studies on GaAs multi-layers are presented.
3.5. Photoacoustic investigation of heat diffusion in n-type InP

3.5.1. Theoretical outline

The open photoacoustic cell (OPC) is a renewed form of conventional photoacoustic configuration [25,40,71-82]. OPC can be used in two different configurations for the thermal characterisation of solids. They are the heat transmission configuration and the reflection configuration. The reflection configuration is equivalent to the commonly employed front surface illumination mode in conventional photoacoustic cells. The heat transmission configuration is depicted in figure 1. For an optically opaque solid, the entire light is absorbed by the sample at \( x = 0 \) and the periodic heat is generated at the same place. Assuming that the heat flow into the gas (air) in contact with the front side of the solid is negligibly small, the thermal waves generated at \( x = 0 \) will penetrate through the sample to its rear surface. The heat thus reaching the sample-air interface at \( x = -l_s \) will get attenuated after travelling a very small distance called the first thermal diffusion length in the air. The thermal diffusion length is given by \( \mu = \sqrt{\frac{2\alpha}{\omega}} \), where \( \alpha \) and \( \omega \) are the thermal diffusivity of air and modulation frequency of the incident light, respectively. Consequently, this periodic heating process arising as a result of the periodic absorption of light at the interface at \( x = 0 \) results in an acoustic piston effect in the air column in between the sample and the microphone.

According to the one-dimensional heat flow model of Rosencwaig and Gersho, for the arrangement schematically shown in figure 1, the pressure fluctuation in the air inside the chamber is given by [17,83-85]

\[
Q = \frac{\gamma P_o I_o (\alpha_g \alpha_s)^{1/2}}{2\pi^2 T_o k_s f \sinh(l_s \sigma_s)} e^{j(\omega t - \pi / 2)}
\]

(5)

where \( \gamma \) is the ratio of specific heat capacities of air, \( P_o \) and \( T_o \) are the ambient pressure and temperature, \( I_o \) is the radiation intensity, \( f \) is the modulation frequency, and \( l_s, k_s \) and \( \alpha_s \) are the length, thermal conductivity and the thermal diffusivity of the medium. \( i = g \) refers to the gas and \( i = s \) refers to the solid sample. Also \( \sigma_i = (1 + j)\alpha_i \), where \( \alpha_i = (\pi f / \alpha)^{1/2} \) is the thermal diffusion coefficient of the medium \( i \). In arriving at the above expression it is assumed that the sample is optically opaque and that the heat flux into the air in contact with the irradiated surface of the sample is negligible.
For thermally thin sample (i.e. $l_s a_s << 1$), equation (5) reduces to

$$Q = \frac{\rho P_0 I_0 \alpha_s^{1/2} a_s}{(2\pi)^{3/2} T_0 l_g l_s k_s} e^{j(\alpha - 3\pi/4)} f^{-3/2}$$

(6)

Above expression implies that the PA signal amplitude from a thermally thin sample under the heat transmission configuration varies as $f^{-1.5}$ and the phase is insensitive to the variation in the modulation frequency. On the contrary, for high modulation frequencies, when the sample is thermally thick (i.e. $l_s a_s >> 1$), equation (5) becomes

$$Q = \frac{\rho P_0 l_0 (\alpha_s / a_s)^{1/2} \exp[ -l_s (\pi f / a_s)^{1/2} ]}{\pi T_0 l_g k_s} e^{j(\alpha - \pi/2 - l_s a_s)} f^{-3/2}$$

(7)

Equation (7) suggests that for a thermally thick sample, the amplitude of the PA signal decreases exponentially with the modulation frequency according to $\left(1 / f \right) \exp(-b\sqrt{f})$, with

$$b = l_s \left( \pi / a_s \right)^{1/2}$$

while the phase $\varphi$ decreases linearly with $b\sqrt{f}$. Hence, the thermal diffusivity $\alpha_s$ can be evaluated either from the amplitude data or from the phase response with respect to the modulation frequency, provided the sample is optically opaque and thermally thick in the frequency region of interest. When the amplitude data is available, $\alpha_s$ can be obtained from the fitting coefficient $b$ appearing as the argument of the exponent $\left(-b\sqrt{f}\right)$. When the signal phase data is used, $\alpha_s$ can be obtained from the slope of the phase plot as a function of $\sqrt{f}$. However, in the case of thermally thick, disk-like solid samples the contribution from thermoelastic bending has also to be taken into account. This effect is essentially due to the temperature gradient existing along the direction of thickness, due to which the sample surface at higher temperature expands more than the other surface and
eventually the sample bends outwards [17,85-87]. In such situations the phase plot will no longer obey the linear relation with the square root of the modulation frequency. Details of the thermoelastic bending and the modifications to the phase relation with the modulation frequency are not discussed here since the sample under investigation (n-type InP) is free from this effect.

We have seen in the previous section that the charge carrier recombination (surface and bulk) is an important factor which contributes significantly to the heat conduction in a semiconductor. In such situations the expressions derived above for the amplitude and phase, obtained by taking only the dominant phonon contribution into account, are not adequate. Then, additional terms are required to accommodate the contributions from the surface as well as the bulk nonradiative recombination processes, and consequently, the above expressions will become more complex and nonlinear [29-30,32-39]. However, from the experimental observations described in the following sections, no such effects are observed for n-type InP sample and hence the corresponding theoretical model is not presented here.

![Figure 2: A schematic diagram of the experimental set-up](image)

### 3.5.2. Experimental details

A schematic diagram of the experimental set-up based on the open photoacoustic cell (OPC) configuration is shown in figure 2. The OPC employed here has provision to illuminate the sample either from the rear side or from its front side. The design and fabrication details of the OPC are discussed in the next section. The rear side illumination or the so-called heat transmission configuration is used for the present investigations. The InP wafer is fixed to the top of the air chamber of OPC using vacuum grease at the edges and laser irradiation is made on its surface facing the ambient. Modulated optical radiation at 488nm from an argon ion laser
(Liconix 5000) is used as the source of excitation. The original laser beam has a $1/e^2$ diameter of 1.2mm and is used without further focusing to avoid lateral heat flow. The PA signal is produced in a small volume of air in between the sample and the microphone. The signal is detected using a highly sensitive electret microphone (Knowles BT 1834) kept in a side chamber. The phase of the signal as a function of modulation frequency of the laser beam is recorded using a dual phase digital lock-in-amplifier (Stanford Research Systems SR830). Three different laser power levels, 50mW, 100mW and 200mW, with a stability of ±0.5% are used for the investigations. Since one surface of the sample is highly polished and the other side is roughened, separate measurements are carried out with either face for laser irradiation.

3.5.3. Design and fabrication of an open photoacoustic cell

For the study of solid samples, a simple and sensitive OPC is designed and fabricated. In the case of a conventional OPC the sample is placed directly on top of the microphone, by leaving a small volume of gas in between the two [72,79,85,88]. Such OPCs can be employed only in the heat transmission configuration. However, the design of the OPC fabricated for the present studies allows one to illuminate the sample from both sides, i.e. it can be used either as an OPC or as a conventional photoacoustic cell. In order to achieve this goal the microphone is kept in a side chamber and is acoustically coupled to the main chamber through a small cylindrical cavity. The cross-sectional view of the cell is shown in figure 3. When the sample is irradiated through the glass window, it is known as the reflection configuration and in the transmission configuration irradiation has to be made at the outer surface of the sample.

The major building block of the cell is an acrylic (perspex) disk of thickness 1cm and diameter 5.5cm. The acoustic chamber is made by drilling a bore of diameter 3mm across the thickness at the centre of the disk. One end of this cylindrical hole is closed with an optical quality glass slide of thickness 1.4mm and the other end is left open. Another fine bore of diameter 1.5mm pierced at the middle of the main chamber and perpendicular to it serves as the acoustic coupler between the main chamber and the microphone. At a distance of 8mm from the main chamber the microphone is firmly glued to the orifice of the side tube. Shielded wires are used to take the electrical connections directly from the microphone. Entire system is then fixed inside a cylindrical hollow block of aluminium, leaving half the thickness of the acrylic disk outside the aluminium holder. Plate-like solid samples having uniform surface quality can be easily stick at the top of the sample chamber (open end) by using vacuum grease. On the other hand, if the sample is very thin and requires more tight contact, then another identical acrylic disk with a 3mm hole at the centre can be used to press the sample in between the two disks.
Figure 3: Cross-sectional view of the OPC. (Top); 1: aluminium case, 2: perspex body, 3: microphone. (Bottom); 1: microphone, 2: sample, 3: perspex body, 4: glass window, 5: gas chamber, 6: incident laser beam
3.5.4. InP sample

Sulphur doped n-type InP sample grown by liquid encapsulated Czochralski (LEC) method is obtained from Sumitomo electric industries (Japan). The opposite faces of the wafer have different surface qualities, one side is polished and etched whereas the other surface is pre-etched. The wafer has a thickness of 350 \( \mu \text{m} \) and has a carrier concentration of \( 4.0 \times 10^{18} \)/cm\(^3\). Square sample with dimensions 8mm by 8mm is used for the investigations.

3.5.5. Results and discussion

As indicated earlier, the heat conduction in semiconductors is mainly contributed by three factors. If the excitation energy is more than the band-gap energy of the semiconductor material, under certain experimental conditions, apart from the pure thermal wave component, the photogenerated carriers may also contribute to the heat transport in these materials. When a modulated optical radiation is incident on a semiconductor sample, the usually observed order of different thermal diffusion processes in the thermally thick regime of the sample is as follows. The pure thermal wave component dominates in the lower frequency range, followed by the heat transfer by bulk recombination process and finally the surface recombination mechanism [30,32-43].

Even though in many studies the amplitude behaviour is used for the evaluation of thermal diffusivity of solid disk like samples, the necessary condition for employing this approach is that the detector (microphone) should have flat response over the frequency range of interest. Otherwise, complicated normalisation procedures are required as reported by Nikolic et.al [30,34,89]. Figure 4 shows the variation of OPC signal amplitude as a function of square root of the modulation frequency. It is very clear from the plot that it no longer obeys a linear relationship as predicted by the theory. The exact reason for the deviation of the observed amplitude data from the theoretically predicted behaviour is not known. The microphone response may be a contributing factor. However, a change in response of the detector with frequency will not affect the phase data and hence the measurement of phase as a function of frequency seems to be a simpler and more reliable strategy. But, a major drawback of the phase method is that the phase plot may not obey a linear relationship as predicted by the theory when thermoelastic bending of the sample contributes significantly to the signal.
Figure 5 shows the variation of the PA signal phase with square root of the modulation frequency for the n-type InP sample. In this figure we can identify a linear portion that satisfies the equation (7). The deviation from the straight line fit in the low frequency region is obviously due to the fact that the sample is thermally thin in this regime. From the slope of the phase data in the thermally thick regime the thermal diffusivity of the sample is evaluated as 0.401 (±.005) cm²s⁻¹. This measured value for the n-type InP is less than the thermal diffusivity 0.4569 cm²s⁻¹ (k = 0.68 Wcm⁻¹ K⁻¹, ρ = 4.79gcm⁻³, C = 0.3107 Jgm⁻¹K⁻¹) of pristine InP [47,49,90-94]. The decrease in the experimentally observed value of thermal diffusivity of n-type InP can be explained in terms of the dominant phonon contribution or the pure thermal wave diffusion. Addition of the dopant adds to the scattering of the phonon which results in a reduction of the phonon mean free path and consequently a decreased thermal conductivity [47,49,51,66-68,94]. Observations discussed in the following sections also confirm this dominant phonon assisted heat diffusion mechanism in the InP sample under investigation.

This linear dependence of the phase data on the square root of the modulation frequency is an important result that has to be analysed in detail. First of all, this observation implies that the thermoelastic bending is not a contributing factor to the observed PA signal. The absence of thermoelastic bending in the present sample may be due to the fact that the InP sample has a moderately high thermal diffusivity. Then the heat generated at the irradiating surface gets transmitted quickly to the other side without leaving a considerable temperature gradient along the thickness of the specimen. Also, the thickness of the sample is sufficiently high to withstand such bending effects. But in the case of materials with low thermal diffusivity, the thermoelastic bending may dominate and in such cases appropriate corrections have to be incorporated in the calculation.

It is worthwhile to note here that in many OPC studies involving a variety of semiconductors, more complex phase behaviour with a minimum in the phase plot is reported [29,30,32-42]. This nonlinear behaviour of the phase data is attributed to bulk and surface recombination processes of photogenerated carriers in those materials. However, from figure 5 it is clear that for the present sample, the photogenerated excess carriers do not contribute to the OPC signal in any significant manner in the frequency range of investigation. This is again confirmed by recording OPC phase data for different incident laser powers, namely, 50mW, 100mW and 200mW. As can be seen from the figure, for all the pump powers the plots are exactly identical and have same slopes. This implies that the OPC signal is not influenced by the increased photogenerated carrier density at 200mW compared to that at 50mW.
Figure 4: Semi-log plot connecting the OPC signal amplitude and $\sqrt{f}$ for three different pump powers.

Figure 5: Variation of the OPC signal phase with $\sqrt{f}$ for three different pump powers. Plots corresponding to different incident intensities are shifted from each other for the sake of clarity.
Apart from this it is a well-known fact that the surface quality of semiconductor samples has a pronounced influence on the carrier recombination properties such as the surface recombination velocity [36, 54, 66-68]. In order to check whether the surface quality has any influence on the OPC phase data, two different experimental configurations are used. In the first case, the polished side of the sample is illuminated and the OPC signal is detected at the rough side and in second case the sample is turned up-side down and its rough side is illuminated and the signal is detected at the polished side. But the results obtained are again exactly identical as shown in figure 6. This again confirms that throughout the frequency range of investigations, the pure thermal wave component is the major contributing factor to heat diffusion in the present sample. If the free carriers are contributing to the OPC signal, then its influence should be visible within the frequency range of investigation [32-42].

**Figure 6:** Variation of PA signal phase with $\sqrt{f}$ for two different sample surface qualities.
3.6. Photothermal deflection studies on GaAs multilayers

3.6.1. Theoretical outline

The photothermal deflection (PTD) technique can be employed in different detection configurations for the investigation of solid samples [15,23,24,95]. Probe-beam deflection in the skimming configuration is one of the widely accepted and simple approaches among the PTD techniques. A schematic representation of the probe-beam skimming configuration is shown in figure 7. In this configuration, the solid disk-like sample is irradiated with a laser beam having suitable power density and the resultant refractive index gradient generated in the coupling fluid (usually a liquid) close to the sample surface is monitored using a low power probe-beam passing through this gradient. In this scheme it is assumed that the temperature distribution in the coupling fluid, very close to the sample surface, is the same as that inside the sample. The probe-beam propagating through the spatially varying refractive index gradient suffers a deflection from its normal path and the amount of deflection is determined by a number of thermal and optical parameters of the solid sample [96-107].

![Figure 7: A schematic diagram of probe-beam skimming PTD configuration](image)

The angle through which the probe-beam deflects from its trajectory, \( \phi \) is given by [104-106]

\[
\phi = \frac{1}{n} \frac{dn}{dT} \int_{\text{path}} \nabla_{T} T(r, t) ds
\]

(8)

where "n" is the refractive index of the coupling fluid, "s" is the optical path length and \( \nabla_{T} \) is gradient transverse to the propagation direction.
Let the probe-beam make a transverse offset "$y$" with respect to the pump-beam axis and a vertical offset "$z$" with respect to the sample surface. From figure 7, it is clear that we can split the effective deflection into two components, namely the lateral or transverse ($\phi_t$) and the normal ($\phi_n$) components and are given by [104]

$$
\phi_t = \frac{1}{n} \frac{dn}{dT} \int_{-\infty}^{\infty} \frac{dT}{\partial y} \, dx
$$

$$
\phi_n = \frac{1}{n} \frac{dn}{dT} \int_{-\infty}^{\infty} \frac{dT}{\partial z} \, dx
$$

The temperature field distribution, due to the pump-beam absorption, obtained by solving the heat diffusion equations in the sample as well as in the coupling fluid, leads to the evaluation of $\phi_t$ and $\phi_n$ as [106]

$$
\phi_t = -\frac{1}{m} \frac{dn}{dT} \int_{0}^{\infty} \sin(\delta \beta) A e^{-\beta_0 z} \delta d\beta e^{jax} \quad \text{for } z > 0
$$

$$
\phi_n = -\frac{1}{m} \frac{dn}{dT} \int_{0}^{\infty} \cos(\delta \beta) A e^{-\beta_0 z} \delta d\beta e^{jax} \quad \text{for } z > 0
$$

where $A$ is a complex integration constant, $\delta$ is the spatial Fourier transformed variable, $\beta_0 = \sqrt{\delta^2 + j \omega / D_0}$, $D_0$ being the thermal diffusivity of the coupling fluid.

Salazar et al. have analysed various theoretical and experimental conditions and arrived at certain expressions which describe a linear relationship of PTD signal phase as well as amplitude with various parameters such as pump-probe offset, height of the probe-beam above the sample surface etc [107]. For $a = b = z = 0$, where $a$, $b$ and $z$ are the pump-beam spot size, probe-beam spot size and the probe-beam height above the sample surface, there exists a linear relationship between the phase of the transverse component of the probe-beam deflection and the pump-probe offset. This linearity is found to be valid for three different configurations, (1) when the probe-beam is propagated through the same side of the sample where the pump-beam falls, (2) when the probe-beam passes through the opposite face of the sample and (3) when the probe-beam passes through the sample. The experimental configuration used in the present study is of type (1). Slope of the plot connecting the phase of the PTD signal and the pump-probe offset is given by

$$
m = \frac{1}{\mu_s} = \sqrt{\frac{\sigma f}{\alpha_s}}
$$
Practically, the condition $a = b = z = 0$ cannot be achieved and a finite value of $a$, $b$ and $z$ may result in a change in the slope, especially when the sample has very low thermal diffusivity. But for samples having moderately high diffusivity the linear relationship will hold without any change in slope for finite values of $a$, $b$ and $z$ [107-109].

In the case of semiconductor samples, in addition to the above described pure thermal wave effect, electronic diffusion process and the carrier recombination process will also contribute to the PTD signal as in the case of photoacoustic effect. However, the additional terms arising from the carrier contributions come into the picture only at high modulation frequencies at which the pump-beam modulation time scale approaches the carrier lifetime [43]. But in the present investigation, the measurements are carried out at low modulation frequencies and hence the pure thermal wave approach is found to be sufficient for the analysis of the experimental results.

3.6.2. Photothermal deflection set-up

A dual-beam photothermal deflection technique is employed for the heat diffusion studies and for the evaluation of thermal diffusivity of n-type or p-type GaAs thin film double-layers grown on a semi-insulating GaAs substrate. Continuous wave laser emission at 488nm from a water-cooled argon ion laser (Liconix 5000) is used as the pump-beam. The original laser beam has a $(1/e^2)$ diameter of 1.2mm. In all the measurements a laser power of 50mW (±0.5%) is used. The excitation laser energy, 2.54eV, is very high compared to the band gap energy, 1.43eV, of GaAs and hence the sample is optically opaque at the excitation wavelength. Carbon tetrachloride (CCl4) is used as the coupling fluid to the sample, which is the most suitable and commonly used coupling fluid in photothermal deflection studies. The significant parameters that make CCl4 a potential coupling fluid in photothermal deflection technique are its low values of thermal conductivity, $k = 0.099 \text{ Wm}^{-1}\text{K}^{-1}$; specific heat capacity $C_p = 0.85 \text{ Jg}^{-1}\text{K}^{-1}$ and thermal diffusivity, $\alpha = 7.31 \times 10^{-4} \text{ cm}^2\text{s}^{-1}$. Another important parameter that favours the use of CCl4 is its very high rate of change of refractive index with respect to temperature, $(dn/dT) = 6.12 \times 10^{-4}\text{K}^{-1}$, compared to many other liquids [110-111]. The sample is placed horizontally at the bottom of a quartz cuvette having dimensions 10mm×10mm×40mm and CCl4 is filled in the cuvette up to a height of about 10mm above the sample surface.

A schematic view of the experimental set-up is depicted in figure 8. The cuvette containing the sample is firmly fixed on a heavy stand. An argon ion laser beam is focussed on to the sample surface using a convex lens of focal length 20cm. The pump-beam spot size at the
Figure 8: Schematic diagram of dual-beam photothermal deflection set-up
sample surface is estimated to be 102μm. The mirror and the lens are fixed on an XY translator and the translator is positioned in such a way that the centre of the mirror, lens and the cuvette are in a vertical line, the Z-axis. Under this experimental arrangement, the pump-beam position on the sample can be accurately varied along the X-direction by simply moving the translator in the X-direction. The resolution of the translator scale is 10μm. A mechanical chopper (Stanford Research systems SR540) is placed in the pump-beam path for modulating the pump-beam intensity at any desired frequency.

A low power (3mW) He-Ne laser emitting at 632.8nm is used as the probe-beam to detect the strength and profile of the refractive index gradient generated in the CCl₄, very close to the pump-beam irradiation site at the sample surface. The probe laser beam with a gaussian profile and having a (1/e²) diameter of 800μm is focused using a double convex lens of focal length 10cm. The probe-beam spot size at the point where it crosses the pump-beam is estimated to be 101μm. The probe laser is arranged in such a fashion that it just skims through the surface of the sample and it propagate in a direction (Y-axis) orthogonal to that of the pump-beam (Z-axis).

A plastic fiber having a circular core of diameter 1mm is used as position sensitive detector to monitor the periodic deflection suffered by the probe-beam. One end of the fiber is firmly fixed on an XYZ translator at a distance of 15cm from the sample. The other end of the fiber is coupled to a 0.25m monochromator (McPherson) tuned to the probe-beam wavelength. This ensures a perfect elimination of stray light, including the scattered pump-beam, from reaching the detector. A photomultiplier tube is coupled to the exit slit of the monochromator. The output of the photomultiplier tube is fed to a dual phase digital lock-in-amplifier, through an impedance matching circuit. A storage oscilloscope is also connected to the photomultiplier tube output in parallel to the lock-in-amplifier. This is done to optimise the position of the pump-beam, probe-beam, sample and the detector to ensure a perfect distortion free signal. The entire experimental set-up is laid out on a moderately vibration-isolated table to protect from the ambient vibrations. Whole measurements are carried out at a pump-beam modulation frequency of 10.6Hz and the probe-beam height above the sample surface is kept as minimum as possible to get non-diffracted (from the sample edge) signal. At high modulation frequencies the noise contribution from various background sources are observed to suppress the PTD signal and consequently accurate measurements are not possible in the high frequency region.
3.6.3. GaAs thin film sample specifications

Both n-type and p-type GaAs thin films grown on a semi-insulating GaAs substrate are used for the investigations. The thin films are grown by molecular beam epitaxy (MBE) method (Technical University of Eindhoven, The Netherlands). Each of the samples contains two epitaxial layers. The sample structure together with the specifications of each layer, including the growth conditions and dopants are given in figure 9.

**Sample 1**

<table>
<thead>
<tr>
<th>Layer Type</th>
<th>Thickness (µm)</th>
<th>Electron Concentration (10^16/cm³)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si doped GaAs</td>
<td>0.25</td>
<td>3.6 x 10ⁱ⁴</td>
<td>580</td>
</tr>
<tr>
<td>Si doped GaAs</td>
<td>10.00</td>
<td>3.6 x 10ⁱ⁴</td>
<td>630</td>
</tr>
<tr>
<td>Semi-insulating GaAs</td>
<td>400.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Sample 2**

<table>
<thead>
<tr>
<th>Layer Type</th>
<th>Thickness (µm)</th>
<th>Electron Concentration (10^16/cm³)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si doped GaAs</td>
<td>0.20</td>
<td>2.0 x 10ⁱ⁶</td>
<td>610</td>
</tr>
<tr>
<td>Si doped GaAs</td>
<td>2.80</td>
<td>2.0 x 10ⁱ⁶</td>
<td>695</td>
</tr>
<tr>
<td>Semi-insulating GaAs</td>
<td>400.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Sample 3**

<table>
<thead>
<tr>
<th>Layer Type</th>
<th>Thickness (µm)</th>
<th>Electron Concentration (10^18/cm³)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si doped GaAs</td>
<td>0.20</td>
<td>2.0 x 10¹⁸</td>
<td>610</td>
</tr>
<tr>
<td>Si doped GaAs</td>
<td>1.80</td>
<td>2.0 x 10¹⁸</td>
<td>695</td>
</tr>
<tr>
<td>Semi-insulating GaAs</td>
<td>400.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Sample 4**

<table>
<thead>
<tr>
<th>Layer Type</th>
<th>Thickness (µm)</th>
<th>Electron Concentration (10^18/cm³)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be doped GaAs</td>
<td>0.20</td>
<td>2.0 x 10¹⁸</td>
<td>610</td>
</tr>
<tr>
<td>Be doped GaAs</td>
<td>1.80</td>
<td>2.0 x 10¹⁸</td>
<td>695</td>
</tr>
<tr>
<td>Semi-insulating GaAs</td>
<td>400.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 9:** Structure and properties of the doped GaAs epitaxial layers on the semi-insulating GaAs substrate. Here, \( l \) corresponds to the thickness of each layer, \( n \) (p) represents the electron (hole) concentration and \( T \) is the substrate temperature at which the layers are grown.
3.6.4. Results and discussion

Photothermal deflection (PTD) measurements are carried out independently by irradiating either the thin film side or the substrate side of the samples. In PTD technique, there exist various experimental approaches to evaluate the thermal diffusivity of solids and the strategy used in the present investigation is the measurement of PTD signal phase as a function of pump-probe offset at a fixed modulation frequency in the probe-beam skimming configuration [15,105-106]. In order to achieve this goal the probe-beam as well as the position sensitive detector and the sample are firmly fixed at a particular position and the pump-beam irradiation site is varied from one side of the probe-beam to the other side. Typical variation of the signal phase with the pump-probe offset for sample 3 when the semi-insulating GaAs substrate side is facing the pump-beam is shown in figure 10. The minimum in the phase plot corresponds to the zero offset or when the pump and probe beams cross each other. Figure 11 (a) and (b) projects the linear portion of figure 10 and from the slope of these plots the thermal diffusivity of the substrate is evaluated using the relation given by equation (13). The measured value of \( \alpha \), calculated from the average of two slopes, is given in table I. We have seen in the previous section regarding the heat conduction in doped semiconductors that the photogenerated free-carrier recombination processes also contribute to heat transport in these materials. But in the case of intrinsic semiconductors, similar to dielectrics, only the phonons contribute to the heat transport due to the very low free-carrier density in these materials [66-68].

![Figure 10: Variation of PTD signal phase with pump-probe offset for sample 3 (substrate side).](image-url)
Figure 11(a): Variation of PTD signal phase with pump-probe offset for sample 3 (substrate side). Here probe is on the left side of the pump.

Figure 11(b): Variation of PTD signal phase with pump-probe offset for sample 3 (substrate side). Here probe is on the right side of the pump.
Figure 12: Variation of PTD signal phase with pump-probe offset for sample 3 (film side).

Figure 12 shows the variation of PTD signal phase with the pump-probe offset for sample 3 when the thin film side is facing the pump-beam. The n-type epitaxial layers have moderately high carrier concentrations (see figure 9) and the parameter that differentiate one layer from the other is only the temperature at which they are grown, which has some significant role in determining the thin film properties. The pure thermal wave component of the PTD signal arises from the instantaneous intraband electron-phonon interaction. Thermal energy will also be released by nonradiative recombination of the photoexcited carriers which are diffused into the semiconductor. This is the electronic component of heat transport. Fournier et al. have made a rigorous theoretical and experimental analysis in this regard and have proved that at very low frequencies, i.e. when $\omega \tau \ll 1$, only the pure thermal wave component contributes to the PTD signal and consequently the signal behaviour (both amplitude and phase) is characterised by the thermal diffusivity of the sample [43]. Here, $\omega = 2\pi f$ where $f$ is the pump beam modulation frequency and $\tau$ is the minority-carrier lifetime.

On the other hand, when the pump-beam modulation time scale is much shorter than the minority-carrier lifetime, i.e. when $\omega \tau >> 1$, the contribution from pure thermal wave component drops off and the PTD signal is now due to electronic processes. In this regime the signal behaviour is characterised by the electronic diffusivity. Usually, minority-carrier lifetime for n-type GaAs is of the order of microseconds and for p-type GaAs it is as low as nanoseconds.
Hence, at a modulation frequency of 10.6Hz (=94ms), we are far away from the requirement for the contribution from electronic diffusion and recombination to PTD signal. Intuitively, the PTD signal variation shown in the figure 12 is determined by the pure thermal wave component. Figure 13 (a) and (b) projects the linear portion of the figure 12 and from the slope of these plots the thermal diffusivity of the sample is evaluated using the relation given by equation (13). The measured value of $\alpha$, when the thin film side is facing the pump beam, is given in table I. Here, the thickness of the thin films are too small compared with the thermal diffusion length and hence the tabulated thermal diffusivity value is expected to be the effective diffusivity of the thin films and that of the substrate.

Figures 14 to 16 shows the variation of PTD signal phase with the pump-probe offset for the other samples (sample 1, 2 and 4) with either the thin film side or the substrate side facing the pump-beam. The thermal diffusivity values evaluated in each case are tabulated in table I. Though the observed thermal diffusivity values vary from sample to sample, it is rather difficult to arrive at a general conclusion regarding the heat transport in these multi-layer samples since more than one physical parameter of the thin film samples are different for different epitaxial layers. However, almost identical $\alpha$ values for the substrate side of all the four samples indicates that the thin film epitaxial layers grown on the other surface of the substrates have no influence on the measured PTD signal. The literature values of $\alpha$ of GaAs is in the range 0.2 cm$^2$s$^{-1}$ to 0.36 cm$^2$s$^{-1}$ [47,49,94,112,113] and the experimentally observed values also falls within this range. The wide range of $\alpha$ values reported in the literature is due to the large variation of thermal transport properties of semiconductor materials with the growth condition, defects etc. But, the decrease of $\alpha$ values of the epitaxial layers to a still lesser value points to some interesting but complex heat transport mechanisms in these samples. Though only phonons are contributing to the heat transport in the frequency value of investigation, the increased scattering centers arising from doping of GaAs with either Si or Be and the consequent reduction of phonon mean free path does not seem to be the only reason for the noticeable reduction in the diffusivity values of the epitaxial layers. The thin film layers are thermally very thin and hence the measured $\alpha$ values may be an effective diffusivity of the two epitaxial layers and the substrate layer. Recently, a number of research papers have come out with experimental observation of substantial reduction (up to 50%) in lattice thermal conductivity in semiconductor thin films, when the thin film thickness is of the order of the phonon mean-free-path [113-117].
Figure 13(a): Variation of PTD signal phase with pump-probe offset for sample 3 (film side). Here probe is on the left side of the pump.

Figure 13(b): Variation of PTD signal phase with pump-probe offset for sample 3 (film side). Here probe is on the right side of the pump.
Figure 14 (a, b): Variation of PTD signal phase with pump-probe offset for *sample 1* (film side). Here, probe is on the left side (a) of the pump and right side (b) of the pump beam.
Figure 14 (c, d): Variation of PTD signal phase with pump-probe offset for sample 1 (substrate side). Here, probe is on the left side (c) of the pump and right side (d) of the pump beam.
Figure 15 (a, b): Variation of PTD signal phase with pump-probe offset for sample 2 (film side). Here, probe is on the left side (a) of the pump and right side (b) of the pump beam.
Figure 15 (c, d): Variation of PTD signal phase with pump-probe offset for *sample 2* (substrate side). Here, probe is on the left side (c) of the pump and right side (d) of the pump beam.
Figure 16 (a, b): Variation of PTD signal phase with pump-probe offset for sample 4 (film side). Here, probe is on the left side (a) of the pump and right side (b) of the pump beam.
Figure 16 (c, d): Variation of PTD signal phase with pump-probe offset for sample 4 (substrate side). Here, probe is on the left side (c) of the pump and right side (d) of the pump beam.
Table I: The thermal diffusivity values of GaAs multi-layers evaluated using PTD technique

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermal diffusivity $\alpha$ in cm$^2$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Film</td>
</tr>
<tr>
<td>Sample 1</td>
<td>0.165</td>
</tr>
<tr>
<td>Sample 2</td>
<td>0.187</td>
</tr>
<tr>
<td>Sample 3</td>
<td>0.193</td>
</tr>
<tr>
<td>Sample 4</td>
<td>0.160</td>
</tr>
</tbody>
</table>

However, no such conclusions are possible with the present data since the exact values of phonon mean-free-path of the samples investigated are not available. Moreover, there exists a large discrepancy between the experimentally observed value of phonon mean-free-path and that evaluated theoretically. For example, in a very recent paper, Ju et.al have measured the effective phonon mean-free-path in Si as 300nm while that evaluated using the kinetic theory is only 43nm [114]. However, a kinetic theory expression can be used to evaluate the phonon mean-free-path in the bulk sample $\Lambda_{bulk}$ as

$$\Lambda_{bulk} = \frac{3k_{bulk}}{Cv}$$  \hspace{1cm} (14)$$

where $k_{bulk}$ is the bulk thermal conductivity, $C$ is the volumetric heat capacity and $v$ is the speed of sound in the material. For bulk GaAs, $k_{bulk} = 0.46$W/cm·°C, $C = 0.33$J/g·°C, and $v \approx 4.0 \times 10^5$cm/s, which leads to the estimation of phonon mean-free-path approximately as 100nm [47,49,94,112]. This value is smaller than the surface layer thickness of 200nm or 250nm of the samples. However, the estimated value of phonon mean-free-path need not be strictly true and hence any analysis of the observed thermal diffusivity data without knowing the exact value of $\Lambda_{bulk}$ is meaningless.
3.7. Conclusions

Two most commonly used and powerful non-destructive and non-contact analytical methods, namely the photoacoustic and photothermal deflection techniques, have been successfully implemented for the thermal characterisation of certain compound semiconductor materials. The thermal diffusivity of n-type InP is evaluated from the phase data of the photoacoustic signal under heat transmission configuration. By employing this approach and using the pure one-dimensional heat flow model of Rosencwaig and Gersho one can easily evaluate the thermal diffusivity of solid disk-like materials having moderately high diffusivity values. The results of the present investigation show that even in the case of semiconductor samples this simple and direct approach can be applied for the thermal diffusivity measurements, provided the investigations are to be done in the frequency region where the pure thermal wave component is the major contributing factor to the signal. The observation of the absence of thermoelastic bending in the case of thick InP wafer is quite reasonable and it is expected that many of the semiconductor materials will behave in this manner as most of them have moderately high thermal diffusivity values.

Dual-beam photothermal deflection technique offers a novel means of measuring the thermal diffusivity of thin films grown on bulk substrates. PTD measurements carried out on GaAs multi-layer samples prove that by employing this approach it is possible to appraise the thermal diffusivity of the substrate alone, without the influence of the thin films grown over its surface. But if the thickness of the thin film(s) is small, such that the thermal diffusion length is much greater than the film thickness, then the evaluated diffusivity value will be only the effective diffusivity of the film(s) and the substrate. In addition to this, very complex thermal wave scattering mechanisms such as the phonon scattering at the interfaces may also have a key role in determining the thermal diffusivity of the thin film(s), especially when the film thickness approaches the phonon mean-free-path.

Compared to the photoacoustic technique, the photothermal deflection method is more complicated and sensitive to ambient conditions such as vibration of the experimental set-up, properties of the coupling fluid etc, which suggests that a very careful experimental arrangement is required for the latter technique. But in the study of materials like thin films coated on bulk substrates the PTD method is more suitable since the irradiation and detection can be easily performed on the same side of the sample.
References


