CHAPTER 3

DETERMINATION OF THERMAL DIFFUSIVITY OF R.F. PLASMA POLYMERIZED THIN FILMS USING PROBE BEAM DEFLECTION METHOD

3.1 Introduction

Development of new and improved materials and their characterization is one of the most active areas of research in the progress of science and technology. The conventional thermal characterization techniques include differential scanning calorimetry, contact transient methods, etc. These techniques are time consuming and need large sample quantity. In these methods the sample must be in contact with the detector, producing fluctuations in the thermal field to be measured. This can explain the thermal data dispersion which appears in the literature. Non-contact tools like laser flash methods where temperature is measured as a varying function of time are also used [1-3]. Here IR radiation emitted from the hot sample is detected. Radiation losses, destructive tendencies of the sample, etc. are some major disadvantages of the technique.

Meanwhile, a set of highly sensitive non-contact techniques, which are non-destructive also are developed and are commonly known as photothermal techniques [4, 5], as mentioned in chapter 1. These PT techniques are best suited for thermal characterization of solids, liquids and gases. Thermal diffusivity is an important parameter which is measured by applying the suitable technique depending upon the thermo-optical properties and structure of samples. Photoacoustic methods [6-9] and photothermal beam deflection methods [10-15] are widely used for thermal diffusivity measurements. Thermal diffusivity of the plasma polymerized thin films described in chapter 2 are measured here using a transverse probe beam deflection experimental setup.
3.2 Importance of Thermal Diffusivity

Thermal conduction is a process by which heat is transferred from one part of the sample to another as a result of the temperature gradient. Both electrons and phonons are instrumental in transferring energy from one place to another in a solid. Electrons are primary carriers in metals and these materials have fairly large thermal conductivities. Heat conduction in insulators can be considered as the diffusion of phonons from the hot to the cold end. Jean Fourier derived a basic law defining the one-dimensional propagation of heat in solids as

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

This equation is known as the Fourier equation. Here Q is the quantity of heat conducted, A is the conducting area normal to the flow path, $\frac{\partial T}{\partial x}$ is the temperature gradient along the path and k is thermal conductivity of the conducting material. The formal definition of thermal diffusivity arises from the expression for a transient temperature field in a conducting solid, which is given by

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

where the thermal diffusivity $\alpha$ is given by $\alpha = \frac{k}{\rho C}$

Here ‘k’ is the thermal conductivity, ‘$\rho$’ is the density and ‘C’ is the specific heat of the material. The thermal diffusivity ($\alpha$) is expressed in m$^2$s$^{-1}$. It is evident from the units that, $\alpha$ represents the rate of heat flow.

Thermal diffusivity is an important physical parameter in thin film characterization. In the case of polymers, knowledge of thermal diffusivity is required for studying the relation between molecular structures and crucial thermal properties [16]. Moreover thermal diffusivity or thermal conductivity are often vital parameters in the applications of polymers [17]. In superconductivity studies,
3.3 Experimental Configurations

As discussed in chapter 1 the photothermal beam deflection (PBD) technique uses two laser beams, one for heating the sample (pump) and the other to probe the refractive index gradient produced (probe). According to the alignment of pump and probe with respect to each other we have collinear PBD and transverse PBD [4]. The pump and probe are parallel to each other in collinear PBD while they are perpendicular to each other in transverse PBD. The probe beam can be directed to the sample surface in two ways. They are the skimming configuration and bouncing configuration [25-27].

Skimming configuration: In this configuration, the probe beam just grazes the sample surface. This implies that the probe beam travels at a certain height above the sample surface, which is determined by the size of the probe beam. The main problem connected with the skimming configuration is related to the size of the probe beam. Though the probe beam is focused to a small spot size, it increases at the edge and in order to avoid probe beam scattering the beam has to travel a distance ‘z’ far from the surface which is at least $z = \sqrt{\lambda L/\pi}$. Here $\lambda$ = wavelength of the probe beam and $L$ = sample size along the probe beam path.

Bouncing configuration: This is also called surface reflection scheme. Here the probe beam impinges on the sample surface at a certain angle and the deflection of the reflected beam is noted. The height of the probe beam above the sample surface is zero. In the bouncing configuration, the probe beam deflection is obtained as a result of two different mechanisms, the thermal gradient in the areas near to the heated sample (mirage) and the sample deformation due to thermal expansion. The
bouncing scheme however cannot be applied to absorbing, rough or non-reflecting samples where there is no relevant probe reflection.

The effects introduced in both the configurations by the finite size of the heating beam, finite height of the probe beam above the sample surface, the secondary effects like finite size of the probe beam, sample temperature, optical misalignment, diffusivity of the deflecting medium, etc. are discussed in detail by Salazar et al. [25].

In the present work in order to measure the deflection, the transverse scan method is preferred. In this method, the pump beam is fixed to a particular position on to the sample surface. The probe beam is then scanned across sample surface perpendicular to the pump beam. Hence the separation between the pump and the probe beams (transverse offset ‘y’) is a variable. Thus, the normal and tangential beam deflection profiles are measured about the center position of the exciting laser beam.

3.4 Methods of Analysis

As already explained, photothermal beam deflection experiment consists of a pump source for excitation of the sample, which is modulated using a chopper and a probe source to probe the refractive index gradient. The deflection of the probe beam is detected using a position sensitive detector. The vectorial nature of the deflection implies that the magnitude has two spatial components. The components are referred to as the normal component $\varphi_n$ and tangential component $\varphi_t$ [4, 12]. Different methods are developed by many workers to analyse the amplitude and phase data for the determination of thermal diffusivity. They are zero crossing [14], multiparameter fitting, thermal wave coupling, phase method [28, 29], amplitude method [30, 31], etc. In the present work the phase and amplitude methods are used.

**Phase method:** This method utilizes the phase of the tangential component of deflection signal $\varphi_t$. Theoretically,

$$\varphi_t = \varphi_n \exp \left[ -j \left( \frac{y}{l} + \phi \right) - j\omega t \right]$$
This implies that the phase varies linearly with the pump-probe offset \( \gamma \). \( l_c \) is the characteristic length, which is the distance corresponding to one radian phase shift. From the slope \( s \) of the plot of phase vs. \( \gamma \), the thermal diffusivity of the sample can be determined using the relation

\[
D = \pi f / s^2
\]

Direct determination is possible only if the thermal diffusivity of the sample is greater than that of the coupling medium. On the contrary, if the thermal diffusivity of the sample is lower than that of the coupling medium, modified phase method must be applied. In such a case, slope \( s' \) is determined for various modulation frequencies \( f \) and a graph is plotted between \( 1/s \) and \( 1/\sqrt{f} \). The slope of this straight line graph, \( s' \), gives the thermal diffusivity using the relation

\[
D = \pi s'^2
\]

**Amplitude method:** The method developed by Quelin et al. took into account the linear variation of logarithm of amplitude of the tangential component of the deflection signal with the pump-probe offset. The three-dimensional thermal conductivity tensor of a polymer crystal is determined in the front configuration where the pump and probe runs on the same side of the sample [30]. This is similar to the Phase method and the thermal diffusivity is obtained from the relation \( D = \pi f / s'^2 \) where \( s' \) is the slope of graph between \( \ln[A_t] \) and \( \gamma \). Further they observed that only a numerical simulation led to the thermal conductivity coefficient perpendicular to the sample surface. Hence in order to determine the thermal conductivity coefficient in the normal direction, they used amplitude of normal component of deflection in the rear configuration, which means that the pump and probe are running on either side of the sample [31].

### 3.5 Transverse PBD Setup

The essential components for the mirage (PBD) setup are: 1) pump source 2) probe source 3) chopper 4) sample cell 5) detection & data acquisition assembly consisting
of the position sensitive detector (bicell, quadrant cell, etc.), preamplifier and lock-in amplifier.

1) **Pump source:** Lasers are used as light sources in photothermal experiments. Besides the monochromaticity, high spectral brightness, etc., the laser output is highly collimated with cylindrical beam symmetry. The basic theory of the probe beam refraction treats the excitation beam as gaussian. The strength or amplitude of the photothermal signal is directly proportional to the amount of laser light absorbed and to the laser power. However the high excitation power is found to cause deformation of the probe beam [30]. In the present work, a He-Ne laser ($\lambda=6328$ Å, power 20mW) with geometrical dimensions of length 50 cm and diameter 5 cm is used as the excitation source. The ($1/e^2$) beam diameter is .7mm and the divergence is 1.2 milliradians. The beam is focused using a lens of focal length 10 cm and hence the beam is focused to a spot size of $\approx 110 \mu m$.

2) **Probe source:** Usually all the traditional setups use He-Ne laser as the probe source. Since the power required for the probe source in mirage experiment is small, only a low power semiconductor laser is required. Here a diode laser ($\lambda= 6328$ Å, 5mW) is used as the probe beam. The size of the laser is about 7 cm long and 1.5 cm in diameter and is focused using a lens of focal length 5cm to a spot size of $\approx 52 \mu m$. The other advantages of using the semiconductor lasers include easy power stabilization and absence of high frequency pointing noise.

3) **Chopper:** Light from the excitation source should be modulated for observing the photothermal signal. The two main types of modulation are amplitude modulation and frequency modulation of which the former one is the most common technique. The amplitude modulation can be achieved by mechanical, electrical, electro-optic or acousto-optic choppers. In the present set up, a mechanical chopper (Stanford Model SR 540) is used, which is the most inexpensive, efficient and easy way to modulate with the depth of modulation being 100%. The unit can chop light beam at rates of 4Hz-4 kHz. The whole frequency range operation requires two blades: a 6-slot blade
for operation in the frequency range 4Hz-400 Hz and 30-slot blade for 400 Hz - 4 kHz.

The modulation frequency has a major role in determining whether the sample is thermally thick or thermally thin. This is due to the fact that the thermal diffusion length follows an inverse relation with the square root of modulation frequency. As mentioned earlier in chapter I, the sample is classified into thermally thick or thermally thin according to whether the thermal diffusion length is less than or greater than the thickness of the sample. Hence by controlling the modulation frequency, the sample can be changed from thermally thick to thermally thin or vice versa. However, in the mirage measurements for thermal diffusivity, the technique can be applied irrespective of whether the sample is thermally thin or thermally thick. Only the analysis of the deflection signal must be made appropriately.

4) Sample cell: The sample cell used is a quartz cuvette of dimensions 1cm x 1cm x 5 cm. High purity carbon tetrachloride is used as the coupling fluid surrounding the sample, mainly due to the high value of dn/dT compared to air. This implies that for each degree temperature rise there will be considerable change in the refractive index, which will lead to an appreciable beam deflection. The comparatively low values of thermal conductivity (k=0.099 Wm⁻¹K⁻¹) specific heat capacity (Cₚ = 0.85 Jg⁻¹K⁻¹) and thermal diffusivity (0.731x10⁻³cm²s⁻¹) also make carbon tetrachloride an ideal coupling fluid for thermal diffusivity measurements.

5) Detector & data acquisition assembly: This assembly consists of a position sensitive detector, a pre-amplifier and a lock-in amplifier. Silicon photodetectors are commonly used for light power measurements in wide range of applications such as spectroscopy, photography, optical remote control, optical switches, analytical instrumentation, medical imaging, laser printers, bar code readers and many more. However there is another application that utilizes the photodetectors as optical position sensors and hence are referred to as position sensitive detectors (PSD). Under this head they are widely used in ultra fast accurate auto focusing schemes for a variety of optical systems, human eye movement monitoring, etc. The position of
beam with fractions of microns can be obtained using PSDs and hence are conveniently used in beam deflection or mirage experiments. The PSDs are broadly classified into segmented PSDs and lateral effect PSDs.

Segmented PSDs are common substrate photodiodes divided into either two or four segments or photodiode elements separated by a gap or dead region and are referred to as bicell and quadrant cell respectively. The photodiode elements are generally masked onto a common substrate so that their cathode is shared. A symmetrical optical beam generates equal photocurrents on all segments, if positioned at the centre. The relative position is obtained by measuring the output current of each segment. The bicell is used for one dimensional measurement where as the quadrant cell is used for two dimensional measurements. A quadrant cell with segments A, B, C and D are shown in the figure below. The light spot diameter should be larger than the gap between the photodiode elements.

Lateral effect PSDs are continuous single element planar diffused photodiodes with no gaps or dead areas.

In the present work a bicell (SPOT 2D from M/S UDT Sensors Inc.) is used as the position sensitive detector for the probe beam deflection measurements. The important features of this bicell include high accuracy, excellent resolution, high-speed response, ultra low dark current and excellent response match. They have fast response times necessary for high speed or pulsed operation and position resolutions of better than 0.1 μm.

A pre-amplifier is used to obtain the amplified output since the deflection signal is usually small. The block diagram of the pre-amplifier circuit used in the present set up is as shown in Fig. 1. Giving common signal from a function generator to the two different inputs initially tests the pre-amplifier and it is ensured that the output is zero. Furthermore, two different inputs are fed to obtain the same result as expected theoretically.
The output of the pre-amplifier is fed to a lock-in amplifier for detection. The lock-in amplifier is used to detect and measure very small a.c signals using a technique known as phase-sensitive detection in order to single out the component of the signal at a specific reference frequency and phase. The signals at other frequencies regarded as noise are rejected and do not affect the measurement. Lock-in amplifiers use a phase locked loop (PLL) to generate the reference signal. The PLL locks the internal reference oscillator to the external reference signal provided to the lock-in amplifier resulting in a reference sine wave of a particular frequency and a fixed phase shift. In the present work, SR830 (Stanford Research Model) is used. The SR 830 operates from 100 V, 120 V, 220 V or 240 V nominal a.c. power source having line frequency 50 Hz or 60Hz and can measure voltage from 2 nV to 1 V.

Fig. 1. Block diagram of the pre-amplifier
Schematic of the experimental setup: The schematic of the experimental setup used for the measurement of thermal diffusivity is as shown in Fig. 2. A photograph of the same is shown in Fig. 3. In the present work, the transverse scan method is employed. The measurements are performed by varying the distance between the pump and probe beams. This is achieved by fixing the pump beam and scanning the probe beam across the sample surface, since our pump source is bulky compared to the probe source. In traditional mirage experimental set ups, usually the probe beam is fixed and the pump beam scans across the sample surface with the help of a mirror arrangement. This is because probe beam scanning requires a synchronous movement.

Fig. 2. Schematic diagram of the experimental setup
of the lens focusing the probe beam and the detector, which makes the system complex, especially when the probe source is bulky. Here since the probe laser is of small size that, it together with the focusing lens and detector could be fixed on an aluminium flat of length 30 cm and width 1cm, which in turn is fixed onto an XYZ translation stage, so that all the three move in synchrony. The sample placed in the cuvette is also fixed on a translation stage. The pump laser and these two translation stages are fixed on an optical breadboard with honeycomb structure, placed on a granite table so as to minimize the errors due to mechanical vibrations. The experimental setup is standardized for thermal diffusivity using InP wafer [32].

Fig. 3. Photograph of PBD experimental setup
3.6 Therma Diffusivity of Plasma Polymerized Thin Films

As mentioned in Chapter 2 plasma polymerized thin films find innumerable applications ranging from corrosion free adhesive coating materials to sensor technology and microelectronics [33-38]. The thermal diffusivity (and hence conductivity) is an equally important parameter like electrical conductivity, which is to be known for effectively applying these materials for different purposes. The thermal conduction parameters of polymers are very low that the determination is really challenging and the sample being in thin film form adds to the difficulty. By employing the photothermal beam deflection setup described in section 3.5 the thermal diffusivity values of the three r.f plasma polymerized thin films namely, poly 2,6-dimethylaniline, poly diethylamine and poly dimethylamine are determined. We have used the phase method and amplitude method for analysis. The measurements were performed at two different modulation frequencies for each sample. Here carbon tetrachloride is used as the coupling medium. Figs. 4-15 show plots between ln(amplitude) versus offset and phase versus offset. All the graphs are linear as expected. The slopes evaluated from these graphs are the inverse of the characteristic length and thermal diffusivity values obtained from the slopes are tabulated in Table I.
Fig. 4. In(amplitude) vs. pump-probe offset for 2,6-dimethylaniline at 8 Hz

Fig. 5. Phase vs. pump-probe offset for 2,6-dimethylaniline at 8 Hz
Fig. 6. ln(amplitude) vs. pump-probe offset for 2,6-dimethylaniline at 12 Hz

Fig. 7. Phase vs. pump-probe offset for 2,6-dimethylaniline at 12 Hz
Fig. 8. In(amplitude) vs. pump-probe offset
for diethylamine at 8 Hz

Fig. 9. Phase vs. pump-probe offset
for diethylamine at 8 Hz
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**Fig. 10.** $\ln(\text{amplitude})$ vs. pump-probe offset for diethylamine at 10 Hz

**Fig. 11.** Phase vs. pump-probe offset for diethylamine at 10 Hz
Fig. 12. ln(amplitude) vs. pump-probe offset for dimethylamine at 4 Hz

Fig. 13. Phase vs. pump-probe offset for dimethylamine at 4 Hz
Fig. 14. $\ln(A)$ vs. pump-probe offset
for dimethylamine at 6 Hz

Fig. 15. Phase vs. pump-probe offset
for dimethylamine at 6 Hz
Table 1
Thermal diffusivity values obtained for the three samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Method of Analysis</th>
<th>Frequency (Hz)</th>
<th>Thermal Diffusivity ($10^{-2}$ cm$^2$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly 2,6-dimethylaniline</td>
<td>Phase Method</td>
<td>8</td>
<td>.365 ± .016</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>.391 ± .020</td>
</tr>
<tr>
<td></td>
<td>Amplitude Method</td>
<td>8</td>
<td>.343 ± .018</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12</td>
<td>.312 ± .019</td>
</tr>
<tr>
<td>Poly diethylamine</td>
<td>Phase Method</td>
<td>8</td>
<td>.374 ± .010</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>.384 ± .010</td>
</tr>
<tr>
<td></td>
<td>Amplitude method</td>
<td>8</td>
<td>.319 ± .007</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10</td>
<td>.327 ± .006</td>
</tr>
<tr>
<td>Poly dimethylamine</td>
<td>Phase Method</td>
<td>4</td>
<td>.187 ± .012</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>.166 ± .011</td>
</tr>
<tr>
<td></td>
<td>Amplitude Method</td>
<td>4</td>
<td>.155 ± .006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6</td>
<td>.156 ± .005</td>
</tr>
</tbody>
</table>
Two basic factors that need to be considered in the photothermal beam deflection technique are the effects of coupling media and substrate on which the samples are coated. If there were any contribution from the coupling media, then the thermal diffusivity value calculated would have been different for different modulation frequencies [28]. The contribution from the coupling fluid to the photothermal signal becomes dominant in the skimming configuration only when the thermal diffusivity of the coupling fluid is greater than that of the sample. In the present work, although the thermal diffusivity of the samples under study are low, the carbon tetrachloride (D_{CCl4} \approx 0.731 \times 10^{-3} \text{ cm}^2\text{s}^{-1}) which is used as the coupling medium in our measurements has still a lower thermal diffusivity value. In conclusion, in our measurements, the thermal properties of the coupling medium do not influence the photothermal measurements. However, in the present work, the samples are coated onto a glass substrate, which is perfectly non-absorbing at the pump beam wavelength. Hence the effect of substrate on the photothermal measurements can also be neglected [39].

While dealing with the polymer samples, another important factor to be dealt with is the effect of the temperature rise on the expansion of the samples. However, the temperature rise in the heated area is estimated to be approximately 1 degree, which can cause a surface deformation of only < 1 nm. This expansion can affect the photothermal measurements only when the bouncing configuration is employed. In the present work skimming configuration is used where the probe beam skims the sample surface and the height of the probe beam above the sample surface is limited by the spot size of the probe beam. Due to the large spot size of the probe beam compared to the surface deformation, any error in the photothermal measurements caused by the thermal expansion of polymers also is completely eliminated.

In conclusion, the thermal diffusivity values of r.f. plasma polymerized thin films of poly 2, 6-dimethylaniline, poly diethylamine and poly dimethylamine are determined. The values obtained for all the samples lie in the same order as those of polymer thin film samples [40, 41].
REFERENCES


