Thermal Characterisation of doped InP using Photoacoustic Technique

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Abstract

An open cell photoacoustic configuration has been employed to evaluate the thermal diffusivity of pure InP as well as InP doped with suplhur and iron. Chopped optical radiation at 488 nm from an Ar-ion laser has been used to excite photoacoustic signals which been detected by a sensitive electret microphone. Thermal diffusivity value have been calculated from phase versus chopping frequency plots. Doped sample are found to show a reduced value for thermal diffusivity in comparison with intrinsically pure sample. The results have been interpreted in terms of the mechanisms of heat generation and transmission in semiconductors.

Keywords: thermal diffusivity, compound semiconductor, doping

Introduction

The study of photothermal phenomena has in recent years been developed into an active area of research in the field of applied physics. It has become a valuable tool in evaluating the thermal, optical and electronic properties of materials in all its different states [1-2]. In particular, photoacoustic (PA) technique which is based on the thermal wave physics has been proven to be an important method in characterizing the thermal and transport properties of materials[3]. Periodic nonradiative deexcitation following an optical absorption generates thermal waves in the sample and its propagation through the coupling gas produces acoustic waves. These acoustic waves can be detected by sensitive microphones thereby producing a PA signal. Besides being a very effective spectroscopic tool, laser induced photothermal effect has been established as a sensitive method to study the dynamics of photoexcited carriers in semiconductors.

All photothermal methods are based on the detection of one means or other of a transient temperature characterizing the thermal waves that arise in the sample as result of absorption of a periodically modulated optical radiation. The absorbed energy is converted into heat in the bulk as well as on the surface of the sample. In PA method, the experimentally measured photoacoustic signal enables us to obtain information about the heat source generating the thermal waves. Thus the photoacoustic response also enables one to gather information regarding thermal parameters, structural formations and inhomogeneities

Thermal diffusivity is an important physical property which characterizes the thermal behaviour of solids. The thermal diffusivity values of various type of semiconductors have been evaluated in past using the measurement of the amplitude of photoacoustic signal as a function of modulation frequency[4-5]. The transport properties and lifetimes, of the photoexcited carriers have also been studied using the photoacoustic technique. A detailed discussion of the contributions of various factors to thermal flux in semiconductors under periodic optical excitation is given by Pinto Neto *et.al.*[4-5]

Analytical solution of the thermal flux generated in the semiconductors is given by Dramicanin et.al [6], according to which heat is generated by three distinct processes viz thermalisation, bulk and surface recombination. The instantaneous thermalistion component that arises due to electron phonon interaction results in the intraband transition. The next two are due to nonradiative recombination of photoinduced carriers in the bulk and surface respectively. The microphone version of photoacoustic technique can be employed in two ways, either in the reflection detection configuration (RDC) or in the transmission detection configuration (TDC). It is reported that, in the low frequency range (10-10000 Hz), the TDC is more suitable than RDC to obtain the thermal and transport properties of the semiconductors [7]. The TDC, which is the basis of the design of the Open Photoacoustic Cell (OPC), is extensively used to measure both thermal and transport properties of a large number of samples such as GaAs, CdTe

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Solar cells,CdInGeS$_4$, PbTe etc[4-5,8]. However, the effect of doping on the thermal parameters of semiconductor samples has not been studied in detail except for a few reports[9].

In this paper we report the mesurement of thermal diffusivity value of the pure InP and InP doped with dopant such as sulphur and iron using an open photoacoustic cell. Thermal diffusivity, which is an important thermophysical parameter determines the distribution of temperature in systems where heat flow occurs, and this quantity is given by

$$\alpha = k/\rho C \tag{1}$$

where k is the thermal conductivity, ρ is density and C is specific heat of the sample. α measures the ability of the material to absorb heat on a transient basis, so that it appears in all the time-dependent heat diffusion problems. The heat energy developed in the sample due to the periodic excitation is transmitted to the surroundings by conduction and diffusion. Thermal diffusivity data are, therefore extremely important to every material exposed to thermal loading as in the case of semiconductor devices under actual operating conditions. InP is a well known and an important material, which is used extensively as substrate material in the semiconductor technology. InP is also a key material for high speed electronic and optoelectronic devices. Hence the measurement of thermal diffusivity of pure and doped InP and a detailed analysis of heat diffusion process in which thermal loading influences their performance have great practical significance.

Theory

If we excite the semiconductor with energy greater than bandgap energy, under certain experimental conditions photoexcited carriers also contribute to the thermal conduction mechanism. From the earlier reports it is seen that, in the thermally thick regime of the semiconductors, contributions from various processes to heat generation mechanism are as follows. If we excite the semiconductor with energy higher than band gap energy, electrons are excited to energy levels greater than bottom of the conduction band, from which they deexcite to the bottom of the conduction band through electron-phonon interaction. Nonradiative recombination of electrons and holes after they diffuse through a finite distance in the bulk of the material and the surface recombination of photoexcited carriers are other factors affecting the photothermal behaviour of the samples. For thermally thick samples, it we take the photoacoustic signal as a function of modulation frequency, it is reported that thermalisation process is followed by bulk and then surface recombination [5]. This means that in the low chopping frequency range, thermalisation is the dominant process in the heat generation mechanism. Taking into consideration, various factors to the thermal piston model of Rosencwaig and Gersho, for the thermally thick regime of the semiconductors, pressure in the coupling gas is given by the expression [4]

$$\delta P = \frac{2\delta I_0 P_0}{T_0 l_g \sigma_g k_s \sigma_s}\left[\frac{\varepsilon - 1}{\varepsilon} e^{-l_s \sigma_s} + \frac{F\sigma_s}{D\gamma\tau}\left[\frac{1}{\sigma_s^2 - \gamma^2} + \frac{\upsilon\tau}{\sigma_s}\right]\right] \tag{2}$$

The first term in the above equation is the thermal diffusion contribution from an instantaneous heat source. The second and third term are due to surface and bulk recombination respectively In the above equation $\varepsilon = E_g/h\upsilon$ and $\gamma = \left(1/D\tau\right)^{1/2}\left(1 + j\omega\tau\right)^{1/2}$ where D is the carrier diffusion coefficient. The parameter τ is the band to band recombination time and υ is surface recombination velocity and $F = \frac{1}{\left(1 + r_0\right)\left(1 + r\right)e^{\gamma l} - \left(1 - r\right)\left(1 - r_0\right)e^{-\gamma l}}$ where $r = \upsilon/D\gamma$ and $r_0 = \upsilon_0/D\gamma$.

If the thermalisation is the dominating process of the thermodiffusion mechanism, we can arrive at the expression for PA signal in the heat transmission configuration [10] as

$$\delta P = \frac{\gamma P_0 I_0 \left(\alpha_g \alpha_s\right)^{1/2}}{2\pi l_g T_0 k_s f \sinh\left(l_s \sigma_s\right)} e^{j\left(\omega t - \pi/2\right)} \tag{3}$$

Here, γ is specific heat ratio and l_s is sample thickness and $a_s = \left(\frac{\pi f}{\alpha_s}\right)^{1/2}$ is thermal diffusion coefficient of the material. Other notations have usual meaning as defined in Rosencwaig and Gersho theory[11]
For optically opaque and thermally thick sample ($l_s a_s >> 1$) the above expression reduces to

$$\delta P = \frac{\gamma P_0 I_0 \left(\alpha_g \alpha_s\right)^{1/2} e^{-l_s\left(\frac{\pi f}{\alpha_s}\right)^{1/2}}}{\pi T_0 l_g k_s f} e^{j\left(\omega t - \frac{\pi}{2} - l_s a_s\right)} \qquad (3)$$

This equation implies that, for thermally thick sample, the amplitude of photoacoustic signal decreases exponentially with the modulation frequency as $\left(\frac{1}{f}\right)\exp\left(-b\sqrt{f}\right)$, where $b = l_s\sqrt{\frac{\pi}{\alpha_s}}$, and its phase varies as

$\phi_{th} = -\frac{\pi}{2} - b\sqrt{f}$. In the case of signal amplitude, α_s is obtained from fitting the coefficient 'b' to the exponential curve where the thermal diffusivity is easily obtainable from the slope of phase plot as a function of modulation frequency. Most of the earlier studies are based on the evaluation of thermal diffusivity from the amplitude of the photoacoustic signal [4-5]. In such a procedure, the microphone should have flat frequency response in order to avoid complex normalization procedures which are needed for accurate mesurements. But the non flat response of the microphone does not affect the phase data and hence it is a more reliable strategy.

Experimental

Schematic diagram of the experimental set up used for the present studies is shown in figure1. The cross-sectional view of the open photoacoustic cell is shown in figure 2. The cell has provision to illuminate the sample from both the rear side as well as the front side. In the present studies we have used the rear side illumination or the so called heat transmission detection configuration. The sample is fixed to the top of the air chamber of OPC using vacuum grease at the edges and the irradiation is made on the exposed surface.

Optical radiation at 488 nm from an argon ion laser (Liconix 5000) is used as the source of excitation, which is modulated using a mechanical chopper (Stanford Research Systems SR 540). The laser beam has a spot size of 1.2mm and is used without further focusing to avoid lateral diffusion of heat. The photoacoustic signal is detected by sensitive microphone (Knowles BT 1834). The phase of the photoacoustic signal is recorded using a dual phase lock-in-amplifier (Stanford Research Systems SR830). The laser power used is 80mW and 160mW with a stability of ± 0.5%. As the doped samples has different surface qualities on its opposite faces, studies are done on both faces of the sample

Results and Discussions

The samples used for the present investigation are pure InP and InP doped with sulphur and iron. Pure InP has highly polished surface whereas doped samples have different surface finishing such that one surface is highly polished while other is roughened. All the samples are grown by Liquid Phase Epitaxy (LPE) technique. Specification of the samples are as follows: The undoped InP has a thickness of 510μm and is oriented in the (111) direction. It has a carrier concentration of about 10^{18} cm^{-3} at room temperature. Doped samples are InP doped with Sulphur and Iron has thickness of 390 μm and 360 μm respectively. InP doped with sulphur has a carrier concentration of 10^{18} cm^{-3} and is oriented in (111) direction. InP doped with iron has carrier concentration of 10^{7} cm^{-3} and is also oriented in (111) direction. Both the materials are doped in the saturation regime so that we can safely take carrier concentration as doping concentration [12].

Figure 3 shows the variation of phase of photoacoustic signal as a function of modulation frequency. The plot shows a curve with a minimum value. This is because in pure InP the heat is generated due to all the three components such as thermalisation, bulk and surface recombination. Thus pure InP behaves in the same manner as reported earlier for other semiconductors [4-5,7]. In the quasi thermally thick regime, thermalisation is the major component of heat generation followed by surface and bulk recombination at higher modulation frequencies. Many authors have attributed the minimum in phase plot to the nonradiative recombination of photoexcited carriers [4-5

From the figure 4 it is obvious that in the quasi thermally thick regime the phase varies linearly with the square root of the modulation frequency. From the slope of the figure 4 we can evaluate thermal diffusivity of pure InP. It is seen from the table that thermal diffusivity value of pure InP agrees well with the earlier reported value [13]. Figure 5 and 6 show the plot of phase of photoacoustic signal as a function of modulation frequency in the thermally thick regime of InP doped with sulphur and iron. In both cases, polished surface of the sample is irradiated with modulated radiation. Figure 5 and 6 show a clear linear relationship between the phase of photoacoustic signal and square root of modulation frequency. The linear nature for plot of doped samples indicates that thermoelastic bending have no influence on the photoacoustic signal. It implies that in the case of doped samples there is insufficient temperature gradient existing within the sample to produce thermoelastic bending of the sample. This may be due to the fact that InP has relatively high thermal diffusivity value and the thickness of the sample is of a few hundred micrometers so that the heat generated at the irradiating surface transmitted instantaneously to other side without leaving any temperature gradient in the sample. But for materials of very low thermal diffusivity, thermoelastic bending is an important phenomenon affecting the photoacoustic signal and in that case we should incorporate sufficient corrections.

In the steady state transport experiment, as in the case of photoacoustic effect electrons and holes continuously gain energy from the absorption of radiation and lose the same through the interaction between them. In general, photothermal signal from the semiconductors is not only dependent on how the heat is carried away by each quasi particle system but also on how energy and momentum are distributed between them. It is known that thermal conductivity contribution from phonons is much greater than that from electrons. For bulk semiconductors having carrier concentration less than 10^{20} cm^{-3}, electron-phonon interaction is the dominating process than electron-electron interaction. The time span for the electron-phonon interaction is typically of the order of 10^{-12} s which in turn suggests that instantaneous thermalisation is the major source of heat generation at low frequencies. The addition of the dopant in the host lattice enhances the probability of electron-phonon interaction and this consequently increases the contribution from instantaneous thermalisation component to the total heat generated in the semiconductor during the photoacoustic experiment. Thus for the doped samples, thermalisation component is the major source of heat thus explaining the linear nature of experimentally obtained graph. From the graphs it obvious that unlike the undoped sample, instantaneous thermalisation could be the only source of heat for the doped samples in our experimental frequency range

It is seen from Table 1 that thermal diffusivity value of the doped InP is less than that of undoped Sample. In bulk semiconductors, like InP, heat is transported by both electrons and phonons. Dopant acts as defect in the host lattice, which in turn can slightly alter the lattice parameters of the host lattice. Thermal diffusivity which is a measure of how heat diffuses through the material, is sensitive to these structural changes. The lattice thermal conductivity mainly arises due to the interaction of phonons and the scattering of phonons from the lattice. Dopant acts as point defect in the lattice, which produces additional phonon scattering. This results in the reduction of mean free path of phonons. This is applicable to electrons also. Reduction in mean free path results in a decrease in the value of the thermal conductivity. As given in the reference [14], lattice thermal conductivity is related to the doping and temperature through the relation $\left(\frac{1}{W}\right) = AT^{-n}$ where W is the lattice thermal resistivity and for InP n=1.55 at 300K. Hence at constant temperature lattice thermal conductivity is related to A. The value of A is dependent on the doping level and it decreases with increase in doping the level. Thus doped samples should have reduced value for thermal conductivity. From the equation (1) it is clear that thermal diffusivity and thermal conductivity are directly related to each other so that doped samples have thermal diffusivity less than that for undoped sample.

Table 1 also shows that thermal diffusivity of n-type sulphur doped InP has thermal diffusivity greater than that of p-type iron doped InP. In the case of p-type semiconductor scattering of phonons is more effective than n-type semiconductor due to the greater effective mass of holes. In our case of p-type InP, the number of carriers ismuch less than number of allowable state of the quasiparticle. This increases the mobility of carriers which in turn somewhat compensates the reduction in contribution from carrier concentration to thermal conductivity.

Many of the OPC studies on semiconductors [4-5,7] shows a minimum in the phase plot of photoacoustic signal as seen here in the case of pure InP. This nonlinear behaviour in the phase data of photoacoustic signal is attributed to the surface and bulk recombination, whereas the linear nature of the graph obtained for the doped samples reveals that nonradiative recombination of photoexcited carriers does not contribute in any measurable manner to the thermodiffusion process in the frequency range of the present experiment. In order to confirm the absence of the effect of the photoexcited carriers in the doped samples, we repeated the experiment at 160mW of laser power and the results were identical (not shown). For checking the effect of surface finishing of semiconductor wafer on the thermal diffusivity, we measured the same with polished and roughened surface. Nevertheless both surfaces yield same value for thermal diffusivity. This also confirms the absence of bulk and surface recombination within the experimental frequency range. If the photoexcited carriers are contributing to the signal, then their influence should be visible in the frequency range used here.

Summary

In conclusion we measured the thermal diffusivity value of pure InP and InP doped with sulphur and iron from the phase data of photoacoustic signal obtained under heat transmission configuration. It is seen that doping has clear influence on the heat generation mechanism of semiconductors. It is seen experimentally that thermal diffusivity value of doped sample is less than that for undoped sample. It is also evident that the type of doping also influences the thermal diffusivity value. From the analysis of phase data it is clear that one dimension heat flow model of Rosencwaig and Gersho can be employed for solid disc-like materials of moderately high thermal diffusivity value.

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Table 1.Thermal diffusivity value of doped and undoped InP

Sample	Thermal diffusivity in cm^2s^{-1}	Reported Value of thermal diffusivity in cm^2s^{-1}
InP (Pure)	0.443 ± 0.007	0.44
InP:S (n-type)	0.401 ± 0.004	-
InP:Fe (p-type)	0.387 ± 0.006	-

Figure Captions

Figure 1: Experimental set-up

Figure 2 : Cross-sectional view of the OPC. 1 the microphone; 2 the sample; 3 the acrylic body and 4 the glass window.

Figure 3: OPC phase versus square root of modulation frequency of polished surface of pure InP

Figure 4: OPC phase versus square root of modulation frequency of polished surface of pure InP in the quasi thermally thick regime

Figure 5: OPC phase versus square root of modulation frequency of polished surface of InP doped with Sulphur

Figure 6: OPC phase versus square root of modulation frequency of polished surface of InP doped with Iron

Figure 1

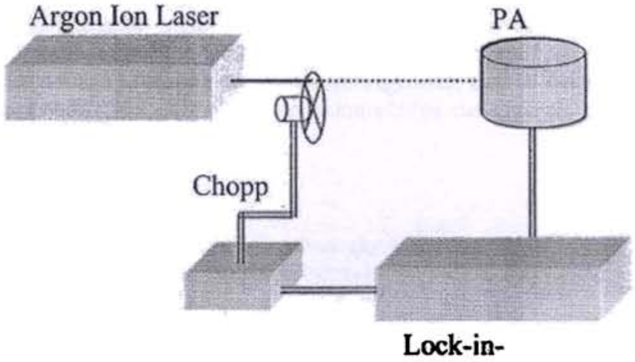

Figure 2

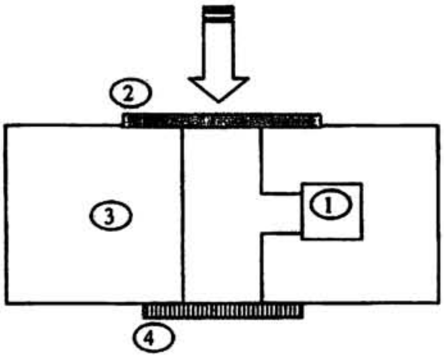

Figure 3

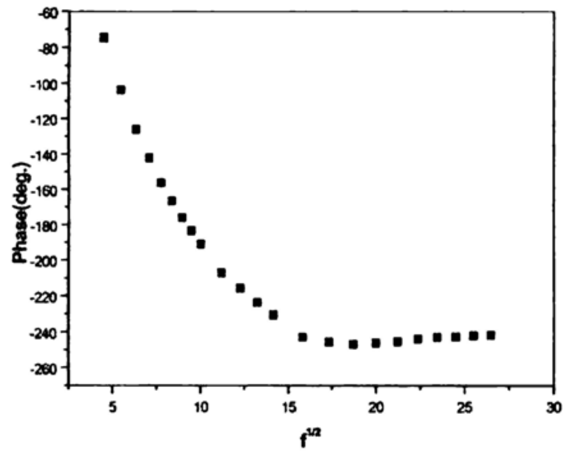

Figure 4

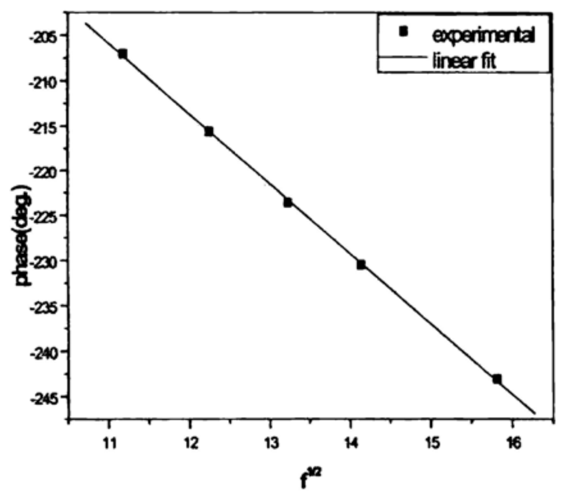

Figure 5

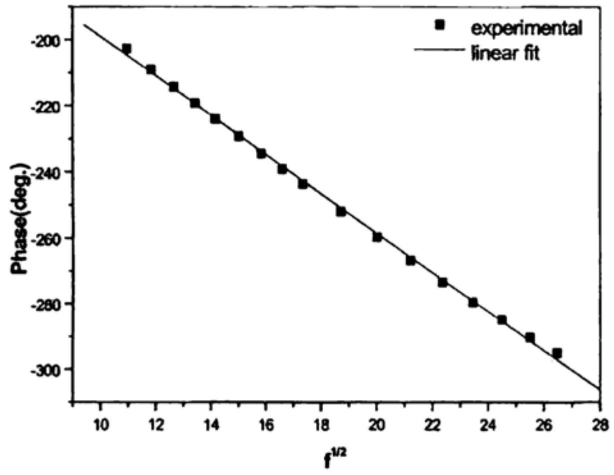

Figure 6