

# Photoacoustic investigation of intrinsic and extrinsic Si

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**Abstract.** An open-cell configuration of the photoacoustic (PA) technique is employed to determine the thermal and transport properties of intrinsic Si and Si doped with B (*p*-type) and P (*n*-type). The experimentally obtained phase of the PA signal under heat transmission configuration is fitted to that of theoretical model by taking thermal and transport properties, namely, thermal diffusivity, diffusion coefficient, and surface recombination velocity, as adjustable parameters. It is seen from the analysis that doping and also the nature of dopant have a strong influence on the thermal and transport properties of semiconductors. The results are interpreted in terms of the carrier-assisted and phonon-assisted heat transfer mechanisms in semiconductors as well as the various scattering processes occurring in the propagation of heat carriers. © 2004 Society of Photo-Optical Instrumentation Engineers. [DOI: 10.1117/1.1814357]

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## 1 Introduction

Recently, thermal wave physics has become an active area of research, particularly in characterizing the material parameters.<sup>1–3</sup> The laser induced nondestructive and nonintrusive photoacoustic (PA) and photothermal methods are widely used to investigate the thermal, transport, and optical properties of matter in all its different states.<sup>4,5</sup> The PA technique has emerged as a very valuable tool for semiconductor research, especially after the invention of lasers and advanced signal processing and data acquisition systems.<sup>6–8</sup> Since the PA technique can directly monitor the nonradiative processes, it is widely used for the surface characterization and investigation of deep-level impurities in semiconductors.<sup>9,10</sup> The thermal waves generated in the coupling medium within the PA cell following the illumination of the sample with chopped optical radiation induce density fluctuations in the sample and the coupling medium, which can be detected using a microphone or piezoelectric transducer.<sup>10,11</sup> The PA technique, using the heat transmission configuration or the so-called open-photoacoustic-cell (OPC) technique is found to be more useful than that employing the reflection detection configuration to evaluate the structural and transport properties of the materials, especially in the low-chopping-frequency range.<sup>12–16</sup>

Si is an extremely important semiconductor, which has wide applications in the electronic and optoelectronic industries.<sup>17</sup> The power-handling capability and the electrical as well as electro-optical properties of these semiconductors depend greatly on the thermal and transport properties of these materials. A large number of PA investigations of the thermal, transport, and optical properties on both direct-bandgap and indirect-bandgap semiconductors have already been reported.<sup>18–20</sup> However, the very

recent investigations show that the thermal and transport properties are substantially influenced by the doping concentration as well as by the nature of dopant.<sup>21,22</sup> It was also reported that doping can alter even the optical properties such as the bandgap of the semiconductor devices, which has wide applications in the electronic and optoelectronic industries, especially from the device fabrication point of view.<sup>23,24</sup> In this context, a more detailed investigation of the thermal and transport properties of intrinsic Si and the influence of the nature of the dopant has great physical and practical significance.

This investigation focuses on the measurement of thermal and transport properties of intrinsic Si and Si doped with B (*p*-type) and P (*n*-type). The thermal and transport properties, namely, thermal diffusivity, diffusion coefficient, surface recombination velocity, and nonradiative recombination time, are evaluated by fitting the experimentally obtained phase under the heat transmission configuration to that of the theoretical model proposed by Pinto Neto et al.<sup>19</sup>

## 2 Experimental Setup

Figure 1 shows a schematic view of the OPC employed here. Optical radiation from an argon ion laser (Licam 5000 series) was used as the source of excitation, which was intensity modulated using a mechanical chopper (Stanford Research Systems SR 540) before it reached the sample surface. Detection in the PA cell cavity was made using a sensitive electret microphone (Knowles BT 1754). The phase of the PA signal was measured using dual-phase lock-in amplifier (Stanford Research Systems SR 830). In all cases, the laser was operated at 80 mW with a stability  $\pm 0.5\%$ , and the optical radiation was unfocused to avoid the lateral diffusion of heat.

782

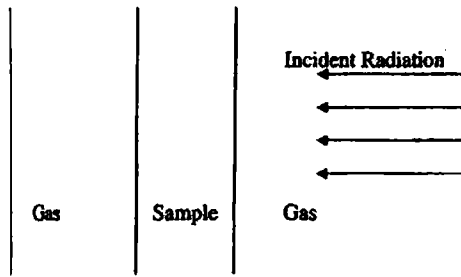


Fig. 1. PA cell geometry for the heat transmission configuration.

The samples used for the present investigation were intrinsic Si and Si doped with B (*p*-type) and Si doped with P (*n*-type). Intrinsic Si has a carrier concentration of  $10^{10} \text{ cm}^{-3}$ , whereas the doped specimens have a doping concentration of  $10^{18} \text{ cm}^{-3}$ .

**Theoretical Background**

In our semiconducting samples, we resort to the piston model of Rosencwaig and Gersho (RG), which the pressure fluctuation  $\delta P$  in the PA cell due to the heating of the sample is given by the

$$\frac{\partial \Theta}{\partial x} = \frac{P_0}{T_0} e^{j\omega t} \quad (1)$$

where  $P_0(T_0)$  is the ambient pressure (temperature);  $l_g$  is the length of the gas chamber;  $\sigma_g = (1+j)a_g$ , where  $a_g = (D/\mu_g)^{1/2} = (1/\mu_g)$  with  $\mu_g$  as the thermal diffusion length in the gas with thermal diffusivity  $\alpha_g$ ;  $\Theta$  is the temperature fluctuation at the sample-gas interface; and  $\omega = 2\pi f$ , where  $f$  is the modulation frequency. The geometry of the PA cell used for this study is given in Fig. 1.

In the case of semiconductors, if we excite the sample with energy greater than the bandgap energy, the heat generation and hence the temperature fluctuation  $\Theta$  can be due to three processes, namely, thermalization, bulk recombination, and surface recombination processes. The thermalization component is due to fast intraband transition of the electrons in the conduction band. Bulk and surface recombination are due to nonradiative recombination of photoexcited carriers in the bulk and surface of the specimen, respectively. Taking into account all these distinct processes, the expression of PA signal is

$$\frac{\partial \Theta}{\partial x} = \frac{P_0}{T_0} \left[ \frac{\epsilon - 1}{\epsilon} \right] \exp(-l_s \sigma_s) \frac{F \sigma_s}{D \gamma \tau} \left( \frac{1}{\sigma_s^2 - \gamma^2} + \frac{v \tau}{\sigma_s} \right) \quad (2)$$

The first term represents the thermalization component, which dominates in the low-chopping-frequency range, followed by the bulk and surface recombination processes.

In Eq. (2),  $\sigma_s = (1+j)a_s$ ,  $a_s = (\pi f/\alpha_s)^{1/2} = (1/\mu_s)$ , where  $\mu_s$  is the thermal diffusion length of the sample,  $\gamma = [(1+j\omega\tau)/D\tau]^{1/2}$  is the carrier diffusion coefficient,  $\epsilon = E_g/h\nu$ ,  $r = v/D\gamma$ ,  $r_0 = v_0/D\gamma$ , and  $F = 1/(1+r_0)(1+r)e^{\gamma l} - (1-r)(1-r_0)e^{-\gamma l}$ , where  $E_g$  is the bandgap energy; and  $h\nu$  is the incident energy; and  $v$  and  $v_0$  are the recombination velocity of photoexcited carriers at  $x = -l_s$  and  $x = 0$ , respectively;  $D$  is the diffusion coefficient; and  $\tau$  is the nonradiative recombination time.

It is reported in Ref. 19 that the PA signal under the heat transmission configuration for semiconductors in the thermally thick ( $l_s \sigma_s \gg 1$ ) region is essentially determined by nonradiative recombination processes. Thus, the expression for pressure fluctuation is given by

$$\delta P = \frac{2\epsilon f_0 P_0 F}{T_0 l_g k_s D \gamma \tau \sigma_g} \left( \frac{1}{\sigma_s^2 - \gamma^2} + \frac{v \tau}{\sigma_s} \right) \quad (3)$$

and in the experimental frequency range for which  $\omega\tau \ll 1$ , we can show that the phase of the PA signal is given by

$$\Phi = \frac{\pi}{2} + \Delta\Phi, \quad (4)$$

where

$$\tan \Delta\Phi = \frac{(aD/v)(\omega\tau_{\text{eff}} + 1)}{(aD/v)(1 - \omega\tau_{\text{eff}}) - 1 - (\omega\tau_{\text{eff}})^2} \quad (5)$$

with  $\tau_{\text{eff}} = \tau[(D/\alpha_s) - 1]$  and  $a = (\pi f/\alpha_s)^{1/2}$ .

We took thermal diffusivity, diffusion coefficient, surface recombination velocity, and relaxation time as adjustable parameters and then we fitted the variable part of Eq. (5) with the experimentally obtained phase angle  $\Delta\Phi$ .

**4 Results and Discussion**

Figures 2, 3, and 4 represent the best theoretical fits to the experimentally obtained phases of the PA signal for intrinsic Si and Si doped with B and P, respectively. The fitting procedure essentially follows the least square fitting procedure developed using MATLAB. Table 1 contains the values of parameters obtained by the fitting procedure for all the specimens under investigation. The fitting analysis resulted in the following accuracy of the fitted parameters: thermal diffusivity,  $\pm 2\%$ ; diffusion coefficient,  $\pm 5\%$ ; surface recombination velocity,  $\pm 8\%$ ; and nonradiative recombination time,  $\pm 3\%$ .

It is obvious from Table 1 that the thermal diffusivity value of the doped samples is less than that of the intrinsic sample. Thermal diffusivity is an important thermophysical parameter, which essentially determines diffusion of heat through the specimen.<sup>26</sup> The inverse of thermal diffusivity is a measure of the time required to establish a thermal equilibrium in systems for which a transient temperature change has occurred. The reduction in the thermal diffusivity value of the doped samples can be understood in terms of the phonon-assisted heat transfer mechanism in semicon-

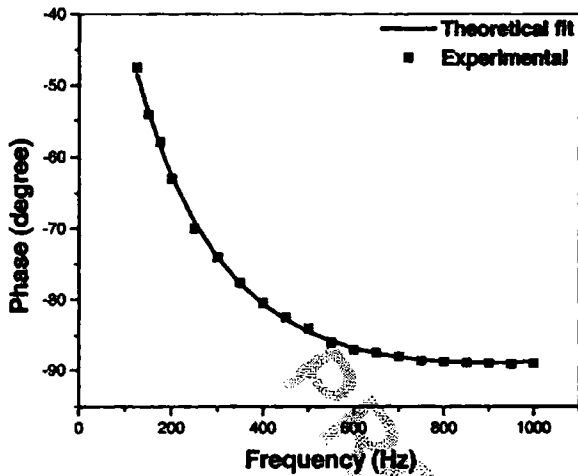


Fig. 2 OPC phase angle for intrinsic Si versus modulation frequency. The solid lines represents the data fitting to Eq. (5) of the text.

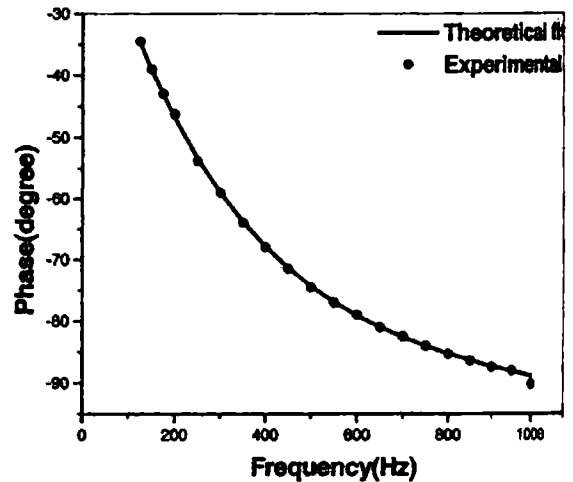


Fig. 4 OPC phase angle for Si doped with P versus modulation frequency. The solid lines represents the data fitting to Eq. (5) of the text.

ductors. For semiconductors having a carrier concentration less than  $10^{20} \text{ cm}^{-3}$ , the contribution from electrons to lattice thermal conductivity is small as compared to the contribution from electrons.<sup>27</sup> However, phonon scattering is the key source that limits the performance of electronic and optoelectronic devices. The addition of a dopant introduces scattering centers in the lattice, which, in turn, reduces the phonon mean free path. It was reported<sup>28</sup> earlier that the lattice thermal conductivity  $k$  is governed by lattice thermal resistivity  $W$  through the relation  $k = 1/W = AT^{-n}$ . At constant temperature,  $A$  is a parameter that decreases with doping. The lattice thermal conductivity (thermal diffusivity), which is proportional to phonon mean free path, also decreases with the introduction of a dopant. Thus, the doped samples show a reduced value for thermal diffusivity. We also see from the table that, for a given doping concentration, the thermal diffusivity value of the  $n$ -type specimen is

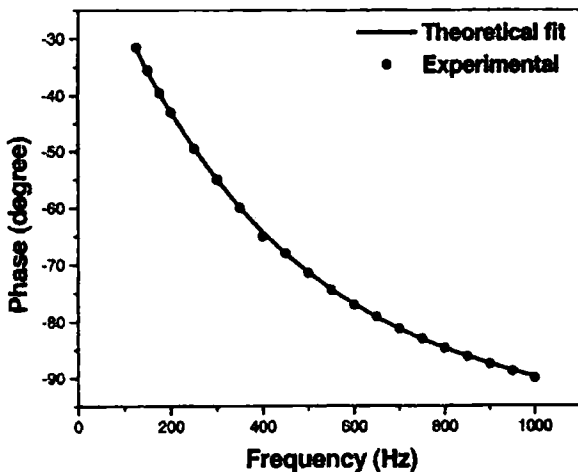


Fig. 3 OPC phase angle for Si doped with B versus modulation frequency. The solid lines represents the data fitting to Eq. (5) of the text.

greater than that of the  $p$ -type specimen. The impurity scattering rate in the case of doped samples is proportional to the mass difference between the atom in the host lattice and the impurity atom. In the present case, the mass difference between B and Si is greater than that of P and Si. Thus, the increased scattering rate in B-doped Si as compared to P-doped Si results in a reduced value for thermal diffusivity for a given doping concentration. In addition, in the case of a  $p$ -type specimen, phonons suffer large scattering from holes having greater effective mass as compared to the electrons in the  $n$ -type sample. Thus, the  $p$ -type B-doped Si shows a reduced value for thermal diffusivity in comparison to P-doped  $n$ -type Si.

Diffusion coefficient ( $D$ ) is an important physical parameter, along with recombination time, because it determines the distance traveled by the photoexcited carriers before their recombination. Thus, the value of diffusion coefficient greatly depends on the scattering processes suffered by the photoexcited carriers. An increase in scattering centers due to doping results in a decreased value of diffusion coefficient. It is seen from the values obtained for the diffusion coefficient that under the present experimental condition, it is not the ambipolar diffusion coefficient but the diffusion of minority carriers that essentially determines the PA signal. This also implies that for the laser power used in the present investigation, the population of photoexcited carriers is less than that of the carrier concentrations of the samples used here. The diffusion coefficient is directly proportional to the mobility of the carriers through Einstein's relation  $D = (\mu k_B T)/e$ , where  $\mu$  and  $e$  are the mobility and the charge of the carriers at a particular temperature  $T$ , and  $k_B$  is the Boltzmann constant.<sup>29</sup> Thus, the doping reduces mobility and hence the value of the diffusion coefficient. It is also seen from the table that the diffusion coefficient of the  $n$ -type specimen is less than that of the  $p$ -type sample. This is because in the case of  $n$ -type sample, the minority carriers are holes, which have low mobility due to its greater effective mass as compared to electrons in the  $p$ -type specimen.

Table 1 Thermal and transport properties of intrinsic and doped Si.

Thermal Diffusivity ( $\text{cm}^2 \text{s}^{-1}$ )	Diffusion Coefficient ( $\text{cm}^2 \text{s}^{-1}$ )	Surface Recombination Velocity ( $\text{cm s}^{-1}$ )	Relaxation Time (s)
0.882	11.5	446	$5 \times 10^{-6}$
0.815	10.6	632	$9 \times 10^{-7}$
0.846	10.1	536	$2 \times 10^{-6}$

surface recombination velocity has great impact on performance of electronic and optoelectronic devices. The introduction of a dopant has a significant effect on surface recombination. In general, the surface contains a large number of recombination centers due to the presence of dangling bonds at the surface. In addition, the impurities can also act as recombination centers for the photoexcited carriers. It is reported earlier that the surface recombination velocity of semiconductors increases with increase in doping concentration.<sup>22,30</sup> We see from Table I that the surface recombination velocity of the doped samples is greater than that of the intrinsic sample. This can be understood from the equation  $v = \sigma v_{th} N_{st}$  (where  $\sigma$  is the capture cross section of the photoexcited carriers,  $v_{th}$  is the thermal velocity of photoexcited carriers, and  $N_{st}$  is the number of trapping centers per unit area) that the surface recombination velocity is proportional to the density of surface trapping centers. The introduction of a dopant results in an increase in the number of trapping centers for photoexcited carriers, which consequently increases the surface recombination velocity, which agrees well with the present experimental observations. However, for a given doping concentration, the surface recombination velocity is proportional to the thermal velocity of the photoexcited carriers, and thus, it has an inverse relation with the square of effective mass of photoexcited carriers. In the case of the *p*-type specimen, the majority carriers are electrons with lower effective mass. Hence, the surface recombination velocity of photoexcited carriers in a *p*-type material is greater than that of an *n*-type

material. The nonradiative recombination time of semiconductors is an important physical parameter, which ultimately determines the quantum efficiency of light sources and optoelectronic materials. The nonradiative lifetime  $\tau_{nr}$  is related to the total lifetime  $\tau_T$  through its relation with the radiative lifetime  $\tau_r$ , given by  $1/\tau_T = (1/\tau_r) + (1/\tau_{nr})$ . The total lifetime depends on various recombination mechanisms such as the direct nonradiative recombination mechanism, the Shockley-Read-Hall recombination mechanism, etc.<sup>6</sup> In the case of indirect-bandgap semiconductors such as Si, nonradiative recombination is the dominant recombination process, whereas in direct-bandgap materials like GaAs, the radiative recombination process is the dominant recombination mechanism of photoexcited carriers. Hence, the evaluation of the nonradiative recombination time of Si and the study of the influence of doping on the nonradiative recombination time have great physical significance, especially with respect to the design and fabrication of optoelectronic devices. The nonradiative recombination time is directly related to the thermal velocity of the photoexcited carriers as well as to the number of scattering centers, which can be expressed through the expression  $\tau_{nr} = 1/N_{st} v_{th} \sigma$ . The intro-

duction of a dopant increases the scattering centers in the specimen, which, in turn, results in a decrease of nonradiative recombination time, as observed in the present investigation. However, for a given doping concentration, the nonradiative lifetime is inversely proportional to the thermal velocity of minority carriers. Hence, in the case of the *n*-type specimen, where the minority carriers are holes with lower thermal velocity due to their greater effective mass, we see a higher value for nonradiative recombination time as compared to a *p*-type specimen, as observed in the present measurement.

## 5 Conclusion

We demonstrated the effectiveness of the PA technique in general and the OPC technique in particular to study the influence of doping on the thermal and transport properties of semiconductors. The thermal and transport properties of intrinsic Si as well as Si doped with B and P were studied using the thermal wave transmission technique. Thermal and transport properties such as thermal diffusivity, diffusion coefficient, surface recombination velocity, and nonradiative recombination time were evaluated by fitting the experimentally obtained phase to that of the theoretical model. From the analysis of data, it is obvious that doping can influence the thermal and transport properties of semiconductors in a significant manner. The nature of the dopant also alters these properties in a considerable way. It is seen from the analysis that the doping decreases the thermal diffusivity value of semiconductors, whereas the variation of transport properties depends on the nature of dopant.

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