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Measurements of thermal diffusivity of boron-silicon film-on-glass structure using phase detection method of photothermal deflection spectroscopy

B. X. SHI
State Key Laboratory of Modern Optical Instrumentation, Zhejiang University, People's Republic of China

C. W. ONG,* K. L. TAM
Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, People's Republic of China

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The phase detection method of photothermal deflection spectroscopy in the transverse configuration was used to measure the overall thermal diffusivity of silicon-boron (Si-B) alloy film on Corning 7059 glass substrate. Results were attained by observing the phase of deflection of the probe beam when it scanned above the film surface relative to the pump beam. Measurements were repeated for different modulation frequencies of the pump beam. Furthermore, both bouncing and skimming configurations were used. The effect of varying the distance between the probe beam and film surface was investigated. © *1999 Kluwer Academic Publishers*

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1. Introduction

Photothermal deflection spectroscopy (PDS) is widely used in the investigations of thermal diffusivity of bulk solids and thin films [1, 2]. Results of great scientific and application interest have already been achieved and reported by many authors. For example, Anthony *et al.* employed the multi-parameter least-squares-fitting procedure to determine the thermal diffusivity of diamond by matching the results of theoretical calculations and experimental data [3]. On the other hand, Salazar *et al.* and Bertollotti *et al.* employed PDS in collinear as well as transverse configurations with the related mathematical formulations to investigate solid samples with known thermal diffusivity [4–6]. They demonstrated the success of the zero-crossing and phase detection methods. On this basis, the formulations for examining the thermal properties of film samples (thermally thin and thick) on substrates were proposed.

In this study, the authors measured the overall thermal diffusivity of a film-on-glass configuration by using the phase detection method of PDS in transverse mode. The film-on-substrate configuration was regarded as a whole system instead of separating the thermal properties of the film from the substrate. Such kind of results could have already satisfied the needs in some practical applications. The phase detection method is employed since it is irrespective to the thermal thickness of a film sample. The coating is an amorphous silicon-boron (Si-B) alloy film prepared by chemical vapor deposition.

The main goal of this investigation is to compare the data attained from different measurement schemes, such that the method of producing reliable results can be proposed. The phase of deflection of the probe beam was observed when the probe beam scanned above the film surface relative to the pump beam. Experiments were repeated for different modulation frequencies of the pump beam. Skimming and bouncing configurations were used, and the results were compared. Finally, with the system in the skimming mode, the influence of varying the separation between the probe beam and film surface was investigated and discussed.

2. Sample preparation

The film sample used for the PDS measurements was prepared by chemical vapor deposition. A Corning 7059 glass substrate was placed in a graphite susceptor, positioned at the center of a quartz tube. The susceptor was heated up to 460 °C by an induction heater [7]. Admixture of diborane and siliane in the ratio of 0.004 : 1 was admitted into the reactor, and was thermally decomposed. The film has a thickness of $t = 880$ nm. X-ray diffraction data show that the film has an amorphous structure analogous to that of amorphous silicon [8]. According to the data of energy dispersive X-ray analyses, the film was found to contain about

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* Author to whom all correspondence should be addressed.

20 at % B. The optical absorption coefficient α of the film was determined to be 3.2×10^4 cm^{-1} at the incident photon energy of 1.95 eV [9]. The product $t \cdot \alpha$ has a magnitude of around 3, so that the film can be regarded to be optically opaque [1]. The thermal diffusivity of Corning 7059 glass is known to be 0.47 mm^2 s^{-1}.

3. Principles of measurements

Fig. 1 shows the typical setting of PDS in transverse mode employed. In our case, the whole film-on-glass structure is the sample of interest, which is in touch with air as the medium. When a modulated laser beam (pump beam) is focused on the absorbing film, thermal waves are excited and propagate in the interior of the sample and the surrounding medium, which decay very fast as propagating. Three-dimensional time-varying distributions of temperature and refractive index are set up. At the same time, a probe beam scans across the air layer just above film surface around the incident point of the pump beam, and is thus deflected. The deflection of the probe beam contains a tangential component Φ_t, which carries the information on the propagation of the thermal waves in the sample and medium, and is thus related to the thermal diffusivity of the sample. In principle, the solution of the 3-dimensional heat conduction equations gives [5]:

$$\Phi_t = |\Phi_t| \exp[j\omega t - j(y/\mu_t - \psi_o)]. \tag{1}$$

In (1), ω is the angular frequency $= 2\pi f$ with f being the modulation frequency of the pump beam. μ_t is the characteristic length, and is close to the thermal diffusion length $\mu_s = \sqrt{k_s/\pi f}$ of the sample when μ_t is large. k_s denotes the thermal diffusivity of the sample. ψ_o is a slowly varying function of f, the pump beam diameter, the separation between the probe and pump beam y, and the separation between the probe beam and the sample surface z_o etc. [6].

From Equation 1 with fixed ω, the phase Arg Φ_t is linearly proportional to y, such that the slope (m') of the plot of Arg Φ_t against y is:

$$m' = \frac{\partial \operatorname{Arg} \Phi_t}{\partial y} = 1/\mu_t. \tag{2}$$

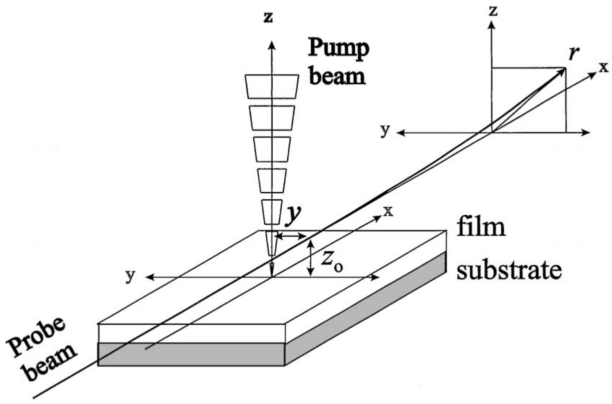


Figure 1 Schematic diagram of photothermal deflection spectroscopy in transverse mode.

Since

$$1/m' = \mu_t \approx \mu_s = \sqrt{\frac{k_s}{\pi f}},$$

k_s is determined as:

$$k_s = \frac{\pi f}{m'^2}. \tag{3}$$

Nevertheless, according to the results of numerical calculations carried out by Salazar *et al.* [4], the linear relationship (3) is valid only when the radius a of the pump beam and the vertical offset z_o are close to zero. Indeed, the influence of the finite magnitudes of a and z_o on the result would be more serious if k_s is much smaller than that of air. Theoretical calculations illustrate that the increase in z_o and a can even disrupt the linear relationship between Arg Φ_t and Δy (Fig. 8 of reference [4]), as well as altering the magnitude of m'. Therefore, Equation 3 may not be applicable if the sample has a low thermal diffusivity.

Bertolloti *et al.* proposed a method to eliminate z_o based on an empirical relation [5]:

$$\mu_t = \mu_s + K z_o, \tag{4}$$

with K to be a constant. This expression reflects that μ_t would not approach μ_s when k_s is small, but differing by a term in proportional to z_o. By eliminating z_o from Equations 3 and 4, one obtains:

$$\begin{aligned} k_s &= \pi \left[\frac{\Delta \mu_t}{\Delta(1/f^{1/2})} \right]^2 \\ &= \pi \left[\frac{\mu_t(f_i) - \mu_t(f_j)}{1/f_i^{1/2} - 1/f_j^{1/2}} \right]^2, \quad i \neq j \end{aligned} \tag{5}$$

where $[\frac{\Delta \mu_t}{\Delta(1/f^{1/2})}]$ is the slope of the plot of $\mu_t(f_i)$ against $1/f_i$ in the linear region. This idea can be implemented practically by repetitive measurements of Arg Φ_t against y at different modulation frequencies f_i'. For each plot of Arg Φ_t against y, a $\mu_t(f_i)$ is obtained. k_s can thus be determined from the slope of linear region of the plot of $\mu_t(f_i)$ against $1/f_i^{1/2}$ according to Equation 5.

The above method is based on the assumption of Equation 4, where z_o is presumed to appear in the second term only and affects μ_t linearly. However, this may not be true in general in broad range of z_o, so that we repeated the above measurements at different z_o, and took a closer look on the validity of the above analysis as follows. Equation 4 implies that:

$$\mu_t \cdot f_i^{1/2} = \sqrt{\frac{k_s}{\pi}} + K z_o \cdot f_i^{1/2}, \tag{6}$$

so the plot of $\mu_t \cdot f_i^{1/2}$ against z_o gives a straight line. One may check the correctness of Equations 4 and 6 by observing whether curves with different f_i would intercept at the same point ($= \sqrt{k_s/\pi}$ if valid) when

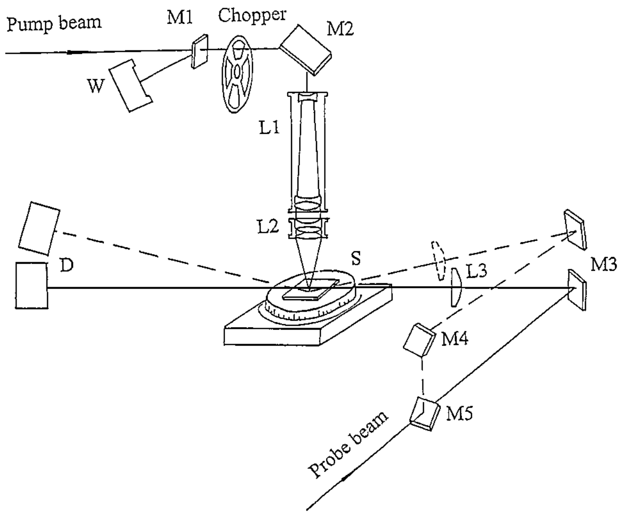


Figure 2 The optical arrangement of the photothermal deflection spectroscopy system used for the study. Solid line: skimming. Dash line: bouncing.

$z_o = 0$. The influence of changing z_o in determining k_s can also be explored.

4. Experimental set-up

Fig. 2 shows the experimental set-up. A 18 mW He–Ne laser is used as the pump beam. The beam is reflected by a mirror M2 and focused by a specially designed focusing lens system (L1 + L2) with a focal length of 30 mm. The focused spot size is 2 μm in diameter. The beam shines perpendicularly to the film surface. The probe beam is a thermally stabilized He–Ne laser with an output power of 1.5 mW (maximum shift 1–3%). It combines with the mirror M3, the focusing lens L3 (focal length = 50 mm) and a four-quadrant position sensor D to form the detection system of the probe beam. The change in the horizontal offset y is precisely controlled using a precision computer controlled horizontal translation stage. The vertical offset z_o is varied by means of a precision manually operated vertical translation stage. In the bouncing method, the variation of the horizontal offset y is implemented by moving the probe beam instead of moving the pump beam, such that the degree of scattering of the pump beam from the sample surface is not altered throughout the measurement. The time-varying deflection signal detected by the four-quadrant detector is analyzed by a lock-in amplifier (Stanford Research System, Model SR830), such that both Arg Φ_t and $|\Phi_t|$ can be recorded. The intensity of the pump beam is monitored by detecting the intensity of a beam reflected from the beam splitter M1 using a power meter W.

5. Results and discussions

Fig. 3a and b show the plots of Arg Φ_t against y of the Si-B film-on-glass configuration, associated with the bouncing and skimming methods respectively. The modulated frequencies of the pump beam are 4, 5, 7 and 9 Hz respectively. From these curves, we obtain the plots of $1/m'$ against $1/f^{1/2}$ in Fig. 4a and b, where z_o has already been eliminated as presented by Equation 5. The results of the overall thermal diffusivity of the Si-B film-on-glass structure (k_s) are summarized in Table I. By averaging the data of three repetitive measurements for the bouncing and skimming_configurations respectively, the results are found to be $k_s = 0.6169$ and 0.6153 mm^2 s^{-1}. These values are higher than that of the Corning 7059 glass (0.47 mm^2 s^{-1}), indicating that the thermal diffusivity of the Si-B alloy film alone is higher than that of the glass substrate.

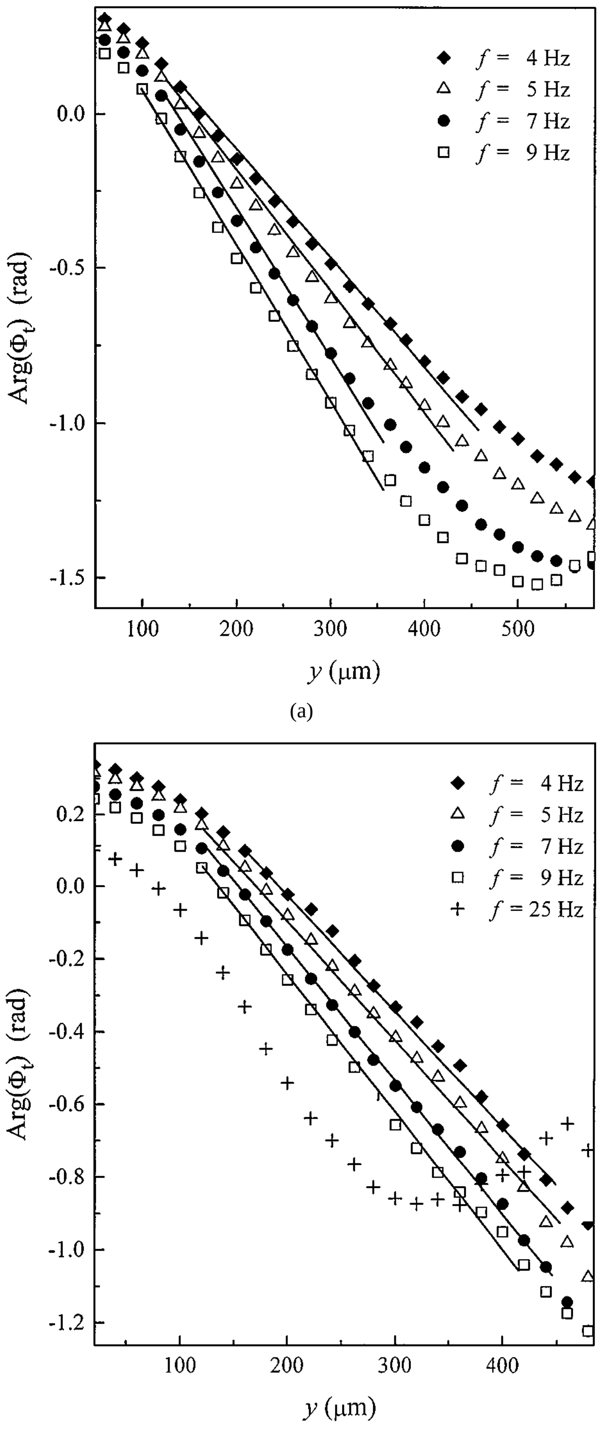


Figure 3 Arg Φ_t against the horizontal offset y for (a) bouncing and (b) skimming configurations.

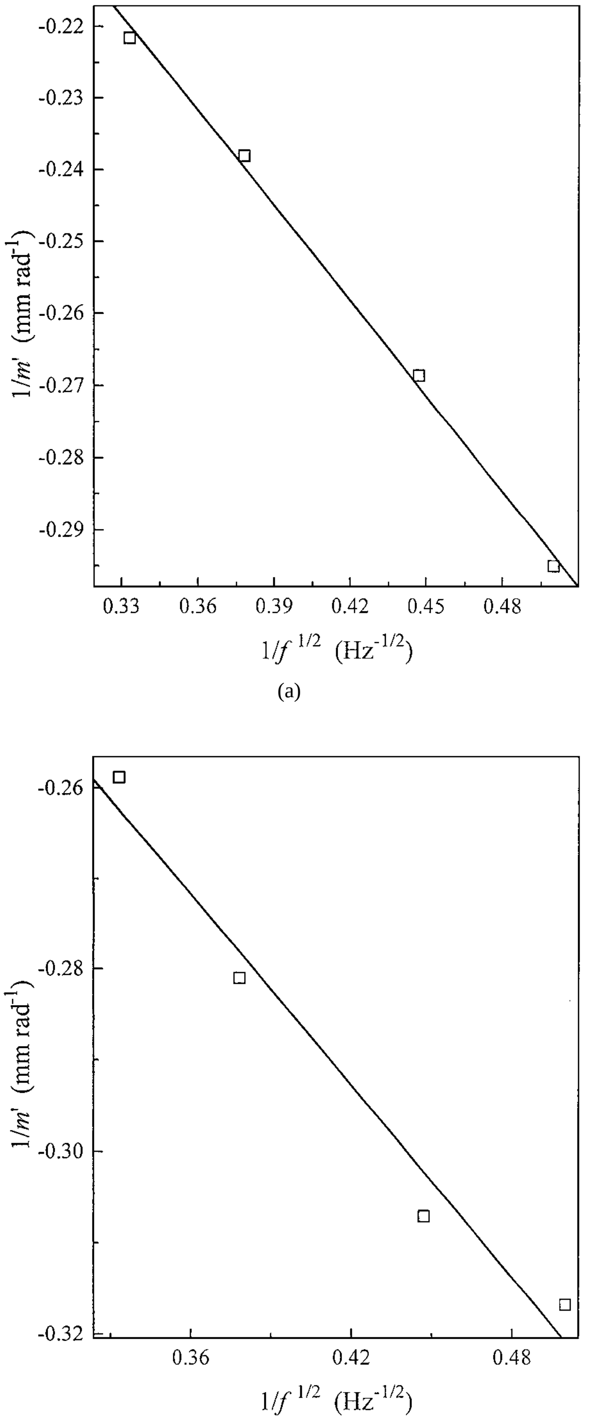
Fig. 5 shows the plots of $\mu_t(f_i) \cdot f^{1/2}$ against z_o at various $f_i = 4$, 5, 7 and 9 Hz. It appears that at the region of low z_o, all the four curves merge together. However, a magnified diagram (inset in Fig. 5) illustrates that the curves do not coincide at a single point, but

TABLE I Results of the thermal diffusivity of Si-B film-on-glass obtained by different experimental schemes

Method measurements[a]	Bouncing		Skimming		From the intercept of the plots of $\mu_t(f_i)\cdot f_i^{1/2}$ against z_0 at various f_i	
	k_s	$\bar{k}_s$	k_s	$\bar{k}_s$	k_s	$\bar{k}_s$
1	0.6124		0.6140		0.6375	
2	0.6251	0.6169	0.6180	0.6153	0.6511	0.6507
3	0.6131		0.6134		0.6636	

k_s is given in mm^2 s^{-1}.

[a] Measurement conditions: Pump beam: He–Ne laser, output power 18 mW, focus dia. 2 μm; Probe beam: He–Ne laser, output power 1.5 mW, focal length of the focusing lens = 50 mm.



(a)

(b)

Figure 4 $\Delta\mu_t$ against $\Delta 1/f^{1/2}$ deduced from Fig. 3 for (a) bouncing and (b) skimming configurations.

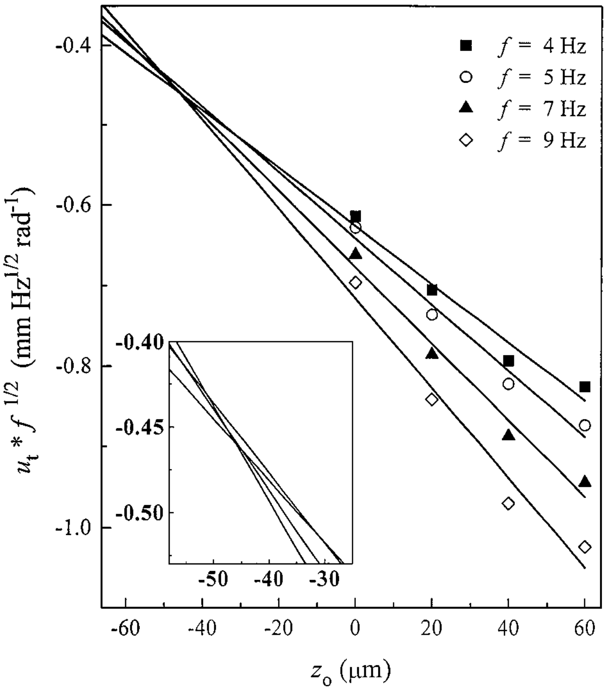


Figure 5 $\mu_t(f_i)\cdot f_i^{1/2}$ against z_0 for various modulation frequencies f_i.

the intercepts between pairs of the curves distribute in an area. Therefore, the position of $z_0 = 0$ is not defined accurately. Furthermore, the probe beam itself has a finite size, giving additional uncertainty in determining the position of the film surface. We averaged the three data of k_s corresponding to the intercepts located at the central region, leading to an average value of $\bar{k}_s = 0.6507$ mm^2 s^{-1}. This result deviates noticeably from those attained from the bouncing and skimming methods. From the engineering point of view, the accuracy of Equation 4 and the ensuing analysis may not be satisfactory enough, such that the influence from the non-zero z_0 in the determination of k_s may not be eliminated completely as predicted by Equation 5. Indeed, Equation 1 reflects that Arg Φ_t not only depends on z_0, but also on the modulated frequency and the spot size of the focused pump beam. The influences of these parameters are more prominent when the thermal diffusivity of the sample is small. Furthermore, Fig. 4 shows that for both bouncing and skimming configurations μ_t may not always linearly depend on $1/f^{1/2}$, elucidating the proximity of Equation 4. We further investigated the influences of increasing the spot size of the focused pump beam and modulation frequency. Results show that k_s could be as large as 0.8862 mm^2 s^{-1} for a spot size of 50 μm in diameter. Furthermore, the curve corresponding to $f = 25$ Hz in Fig. 3b shows a narrower linear region compared with others with lower modulation frequencies, and the value of k_s deduced from the curve is as large as 3.7519 mm^2 s^{-1}. This greatly deviates from those obtained using the bouncing and skimming methods, indicating that Equation 4 is no longer valid.

6. Conclusions

From the results of this work, we propose the following points in measuring the overall thermal diffusivity of film-on-glass configuration when the phase detection method of PDS in transverse mode is used.

(1) The phase detection method is advantageous since it is less dependent on the thermal thickness of the sample.

(2) To get more reliable value of k_s of the structure, it is recommended to measure Arg Φ_t as a function of the offset y at many different modulation frequencies f_i, and then determine the slope m' of the plot of Arg Φ_t against y for each f_i, and then calculate k_s by using Equation 5. It is utmost important to focus the pump beam as small as possible, and to use low modulation frequency in the measurements.

(3) With small pump beam size and low modulation frequency, the results obtained by the bouncing and skimming methods, and from the intercept of $\mu_t \cdot f^{1/2}$ at $z_o = 0$ for different f give rather similar values of k_s.

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