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Laser-Flash Diffusivity Measurement of Diamond Films[1]

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A laser-flash technique with fast infrared detection for the measurement of the normal diffusivity of samples, with a thickness in the range 200 to 700 μm, is presented. The experimental apparatus for such a measurement is described. Some points specific to the diffusivity measurement of semi-transparent and highly conductive materials such as diamond are discussed. Particularly, difficulties in connection with the good conductivity and low thickness of the samples we consider are pointed out. Finally, experimental results performed within the framework of the Diamond Round Robin 2 tests for both nondiamond and diamond films are presented and the influence of the coupled conductive–radiative heat transfer is shown.

KEY WORDS: coupled conduction and radiation; diamond films; diffusivity; laser-flash stimulation; semifitransparent films; transient technique.

1. INTRODUCTION

Current industrial needs concerning thin films are becoming important in many domains such as mechanics (friction), electronics (heat dissipation), or optoelectronics (light conduction) and require the development of new materials and the design of new coatings. Chemical vapor-deposited (CVD) polycrystalline diamond films are an example of such a development. Measurement of their thermophysical properties is very tricky, because of their not completely known composition and structure and of their thickness and good conductivity [1]. Their anisotropic properties [2] require

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the measurement of both in-plane [3–5] and perpendicular-to-the-plane diffusivities. The *laser-flash method* [6] is a commonly used method for the measurement of the normal diffusivity of bulk products. It has been used for the measurement of thin films of CVD diamond [7].

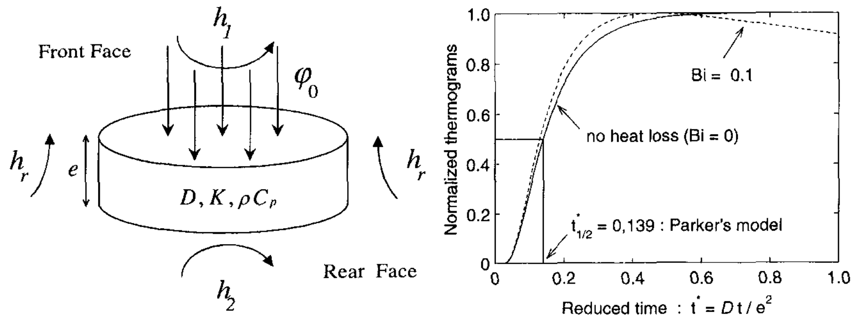
2. PRINCIPLE OF THE MEASUREMENT

The *flash method* uses heat pulse stimulation φ_0 ($\mathrm{J \cdot m^{-2}}$) of the front face of the sample (Ref. 6 and ASTM Standard E1461-92). The variation of the rear-face temperature with respect to time t is then considered. The normalized rear-face thermogram with respect to its maximum is a function of both diffusivity and heat losses (see Fig. 1). Let K be the thermal conductivity of the sample, with e being its thickness. The transient thermal response of the rear face is given by the solution of the one-dimensional heat flow equation. For a thin and good-conductivity film, the Biot number $Bi = he/K$ is low and heat losses can be neglected. In this case, the rear-face normalized temperature T^* is given by the expression

$$T^*(e, t) = \frac{T(e, t) - T_a}{\rho C_p e} = 1 + 2 \sum_{i=1}^{\infty} (-1)^i \exp\left(-(i\pi)^2 \frac{Dt}{e^2}\right) \qquad (1)$$

where D is the thermal diffusivity of the sample and T_a is the ambient temperature. Parker et al. [6] showed that the half-rise time $t_{1/2}$ is a function of the diffusivity:

$$t^*_{1/2} = \frac{Dt_{1/2}}{e^2} = 0.139 \rightarrow D = 0.139 \frac{e^2}{t_{1/2}} \qquad (2)$$



(a) (b)

Fig. 1. Theoretical model.

An alternate method has also been used with an estimation of the diffusivity by a Gauss–Newton's nonlinear least-squares method [8] based on the model given by Eq. (1) written in the Laplace domain and followed by a numerical Laplace inversion.

3. APPARATUS

Due to the very short response time and high diffusivity of the materials we consider, a wide-band and fast apparatus has been assembled. Thus, optical devices have been used for both stimulation (pulsed laser beam) and measurement (cooled infrared detector). A schematic representation of the apparatus is given in Fig. 2.

3.1. Laser-Flash Stimulation

The stimulation is produced by a Nd:glass laser (1054 nm), which delivers a pulse by an optical switch (Pockets cell) with a duration of less than 20 ns. The diameter of the flat beam is 13 mm. The 4-J maximum energy of the beam can be reduced continuously by the use of two attenuators. A two-wedge attenuator first reduces the energy by absorption. The output beam then passes through an optical isolator assembly, which prevents high power back reflection into the cavity. This is composed of three elements: half wave plate–dielectric beamsplitter–quarter wave plate. The rotation of the beamsplitter allows a continuous reduction of energy. So one can make measurements with different kinds of samples that require different levels of incident energy (conductive, dielectric, reflective or absorbing samples, with different thicknesses).

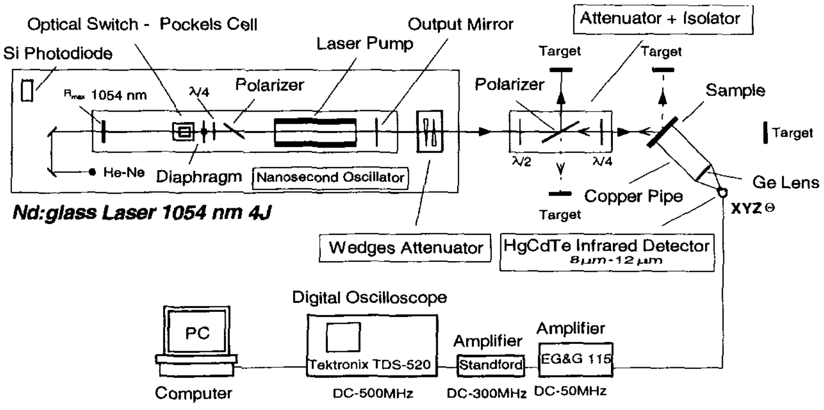


Fig. 2. Schematic diagram of the apparatus.

3.2. Temperature Measurement

Measurement of the rear-face temperature is made by a high-cutoff frequency cooled infrared photovoltaic HgCdTe detector (>500 MHz) (detector window, 8 to 12 μm). Its sensitivity is high ($D^* = 8.7 \times 10^{10}$ cm $\cdot$ Hz$^{-1/2} \cdot$ W^{-1}). The signal is then amplified by a fast preamplifier with a large bandwidth (DC, 50 MHz), matched to the fast response time of the samples and with a high input impedance (1 MΩ). This can be coupled with another amplifier to increase the amplification factor. A high-frequency digital oscilloscope (500 MHz) then digitizes the analog signal before being processed by a computer. If the sample is far from the detector, a converging germanium lens (reflective to the laser beam wavelength) can be placed between the sample and the detector to focus the rear-face emitting flux toward the sensitive element. In order to limit the influence of the outside radiative environment, a reflective cavity (copper pipe) can be inserted between sample and detector. It is especially interesting for our application, which requires a coupled DC measurement to reduce the continuous signal component and to amplify only the AC component to prevent amplifier overloading. Because of the low emissivity of the copper pipe, the ambient intensity is suppressed and the signal is composed only of the forward intensity coming from the sample. The copper pipe also allows an increase in the apparent configuration factor between the sample and the detector.

3.3. Difficulties Caused by a Nonuniform Excitation

The one-dimensional (1D) model that has been used for the measurement of the diffusivity requires that heat transfer within the medium is unidirectional. A theoretical and experimental study has been made to evaluate the two-dimensional (2D) effects on the rear-face temperature caused by the space reduced stimulation and the nonuniform laser beam (Gaussian and flat laser profiles have been considered). This study shows that if a nonuniform beam stimulates the whole face, then the local temperature measurement (with a germanium lens) is strongly affected by two-dimensional effects caused by in-plane heat diffusion at the end of recording. The thicker the samples are, the stronger are these effects. These may be partially corrected with the use of the reflected cavity pipe.

3.4. Coatings for Semitransparent Samples

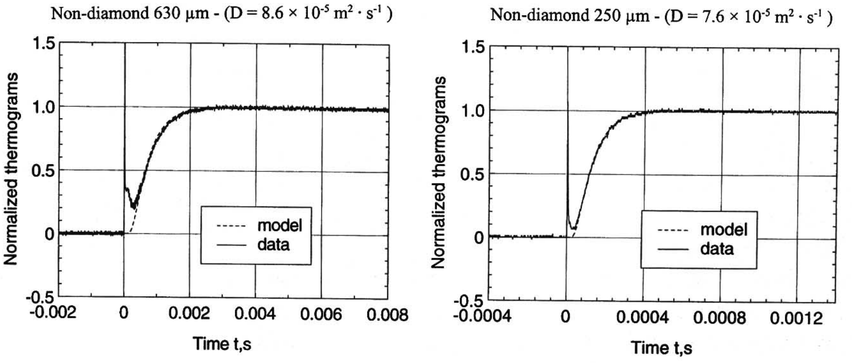
For the measurement of the normal diffusivity of semitransparent films, a coating must be deposited on the film in order to make its faces opaque. This also allows a surface absorption of the energy of the heat pulse by the sample "front face" and emission of the "rear face" in order to allow a surface temperature measurement by a contactless radiation detector. The effect of the coating is especially important for thin films. To limit the coating thermal resistance, one usually uses thin metallic coatings that are generally poor infrared absorbers and emitters. Consequently, the level of the signal (temperature) measured by the infrared detector is low. The coatings, which appear to be a compromise solution, are gold/palladium, titanium, and gold/titanium/platinum. One also uses a "*black powder*" made of monoxide of chromium and monoxide of silicon for thicker samples. This presents high absorption and emission coefficients. Its semitransparency requires the simultaneous use of titanium coating for semitransparent materials. Deposition of this powder on the two faces of an originally noncoated duraluminum sample produces an increase in the measured signal by a factor of 10.

4. RESULTS

In this section, results performed within the framework of the Diamond Round Robin 2 are presented. Titanium coatings have been used for both nondiamond and diamond films.

4.1. Nondiamond Films

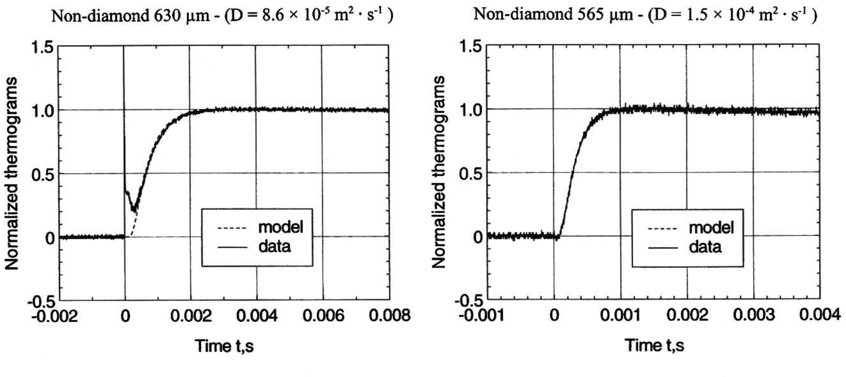
Figure 3 illustrates the thermograms obtained for titanium-coated nondiamond films with two thicknesses (630 and 250 μm). This shows the effect of the thickness on the signal/noise ratio (the thinner the film, the


Non-diamond 630 μm - ($D = 8.6 \times 10^{-5}\ m^2 \cdot s^{-1}$)

Non-diamond 250 μm - ($D = 7.6 \times 10^{-5}\ m^2 \cdot s^{-1}$)

(a) *(b)*

Fig. 3. Nondiamond films of different thicknesses.



(a) *(b)*

Fig. 4. Nondiamond films with different absorption coefficients.

larger the ratio). One can observe the semitransparent effect of the sample by a *temperature jump* at the very early times on the rear-face thermogram. One can also notice a 2D effect for the thicker sample (heat losses cannot appear at this time). The semitransparent effects are not systematic: thermograms for two ceramics (low and high absorption coefficients) of roughly the same thickness are presented in Figs. 4a and 4b. No *peak* is apparent in Fig. 4b for the more absorbing medium. The appearance of a *peak* can be explained by two phenomena: first, a direct radiative transfer between front and rear faces and, second, defects in the coatings. If the front face is partially transparent, the laser beam directly insulates the rear face. Thus, the signal measured is a combination of both front-face and rear-face responses. The effects are very important for thin and transparent samples (effect of the *optical thickness*).

4.2. Diamond Films

Figure 5 shows a perfect response for diamond film. The values obtained for diamond film diffusivities are very important, larger by a factor of 8 or 10 compared with usually good conductive materials (gold–copper–silicon) (see Table I). They vary with respect to the quality of the films. The values obtained for optical-quality films (very clear samples) are very close to the natural diamond diffusivity. As for nondiamond films, one also obtained 2D and semitransparent effects (see Fig. 6.). The methods we have implemented for the estimation give quite satisfactory results. Parker's method and the ordinary least-squares method are very close, and reproducibility tests are good. Estimations of the standard deviations on parameters are less than 5%.

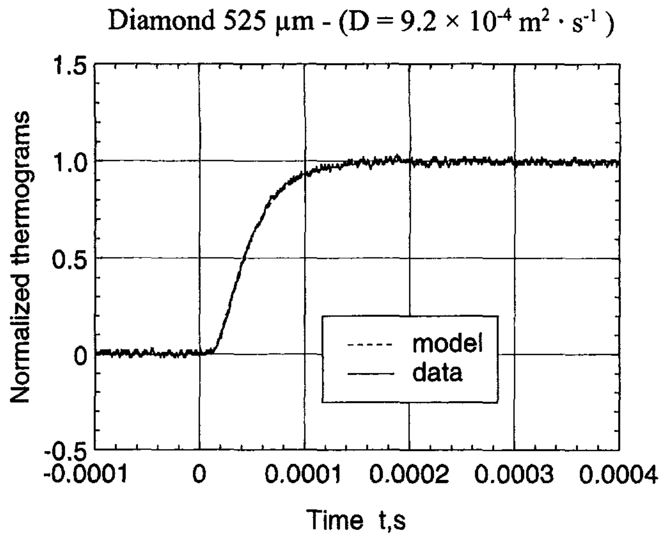
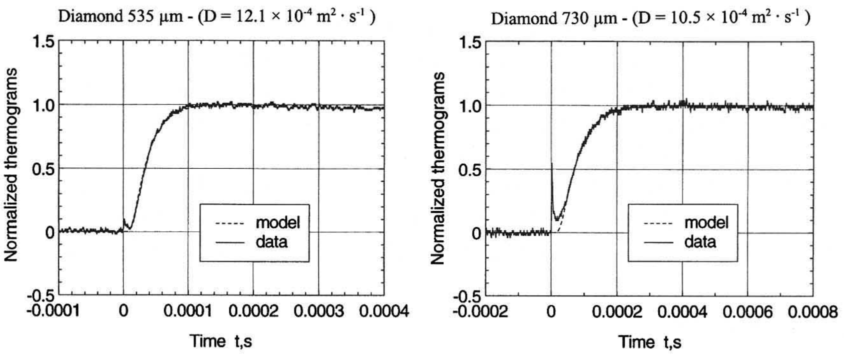


Fig. 5. Flash response of a diamond film.

Table I. Experimental Results for Nondiamond and Diamond Films

Nondiamond films				Diamond films			
		Diffusivity D (cm^2·s^{-1}				Diffusivity D (cm^2·s^{-1})	
Sample No.	e (μm)	Parker	OLS[a]	Sample No.	e (μm)	Parker	OLS[a]
1	630	0.87	0.87	1	525	9.20	9.23
2	630	0.81	0.81	2	565	*12.14*	*12.19*
10	250	0.77	0.76	3	500	9.90	9.83
15	250	0.76	0.76	4	730	10.46	10.45
20	250	0.73	0.73	5	535	9.11	9.26
25	255	0.76	0.74	6	535	11.80	11.84
3	565	1.53	1.52	7	505	8.82	8.83
4	520	1.50	1.51	8	705	10.77	10.57
5	550	1.52	1.52	Gold		1.27	
6	545	1.52	1.53	Copper		1.16	
7	565	1.53	1.56	Silicon		0.92	

[a] Ordinary least-squares method = Gauss–Newton's method.



(a) *(b)*

Fig. 6. Nonideal responses of diamond films.

5. RADIATIVE TRANSFER

The diffusivity results given above are obtained by estimations based on a purely conductive model. The semitransparent behavior of the samples can affect the diffusivity measurement technique. One can show that the interaction of radiative and conductive transfer can be reduced in the flash method by the use of reflective coatings, especially for materials whose optical thickness is low (thin film with a low absorption coefficient). In contrast, with emitting coatings, interaction is large and the diffusivity is composed of the phonon diffusivity component, related to the purely conductive transfer, and of a radiative component, which depends on the optical properties of both coatings and sample and on the sample thickness [9]. It is important to note that even though the *peak* is less pronounced for an absorbing medium (thick optical thickness), radiative transfer can also affect the thermograms. To measure this effect, a more general radiative–conductive coupled model must be implemented. An analytical solution of this model in a transient state is given in Ref. 10.

6. CONCLUSION

Diamond films exhibit anisotropy and inhomogeneity. Their characterization requires the measurement of both in-plane and perpendicular-to-the-plane diffusivities. To predict the performance of these structures in practical applications, techniques for measuring the thermal diffusivity of films and coatings and their variations with the thickness of the film are highly desirable. It is also important to use techniques that can be easily and rapidly implemented because the thermal diffusivity of a set of films with a given nominal composition may vary sufficiently to necessitate a measurement on each film. *The laser-flash technique* with *fast infrared detection* is an efficient method that can be used to perform such a measurement. The diffusivity of 500 μm-thick diamond films in the direction perpendicular to their faces has been measured by this technique. Because of the specific properties of the materials we considered, particular attention has to be given to the preparation of the sample, to the quality of the laser beam energy distribution, and to the signal that is actually measured.

REFERENCES

1. J. E. Graebner, S. Jin, and G. W. Kammlott, *Appl. Phys. Lett.* **60**:1576 (1992).
2. J. E. Graebner, S. Jin, G. W. Kammlott, B. Bacon, and L. Seibles, *J. Appl. Phys.* **71**:5353 (1992).
3. E. P. Visser, E. H. Versteegen, and W. J. P. Van Enckevort, *J. Appl. Phys.* **71**:3238 (1992).
4. P. Hui and H. S. Tan, *Surface and Coat. Technol.* **62**:361 (1993).
5. K. Plamann and D. Fournier, 4th European Conference on Diamond, Diamond-like and Related Materials (*Diamond Films '93*), Albufeira, Portugal (1993).
6. W. J. Parker, R. J. Jenkins, C. P. Butler, and G. L. Abbott, *J. Appl. Phys.* **32**:1679 (1961).
7. J. E. Graebner, M. E. Reiss, L. Seibles, T. M. Hartnett, R. P. Miller, and C. J. Robinson, *Phys. Rev. B* **50**:3702 (1994).
8. J. V. Beck and K. J. Arnold, *Parameter Estimation in Engineering and Science* (Wiley, New York, 1977).
9. S. André and A. Degiovanni, *Int. J. Heat Mass Transfer* **38**:3401 (1995).
10. S. André and A. Degiovanni, in *Heat Transfer, Vol. 3*, 2nd European Thermal-Sciences and 14th UIT National Heat Transfer Conference, G. P. Celata, P. Di Marco, and A. Mariani, eds. (ISBN 88-7741-911-3, 1996), pp. 1441–1447.