

THERMAL WAVE AND RAMAN CHARACTERIZATION OF DIAMOND FILMS

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INTRODUCTION

Diamond films possess many of the attractive properties of bulk diamond such as hardness, thermal conductivity and wide band transparency. This fact plus the recent progress in making these films inexpensively[1,2] has attracted much renewed interest in using them in many different applications which include coatings to machine tools and optical components, heat sinks for high power semiconductor devices. The challenge is then placed on material characterization techniques intended to measure their electrical, optical, thermal, and elastic properties. The challenge on the measurement of thermal properties is especially acute because none of the conventional techniques are appropriate for thin films. The films are usually very thin (of the order of a few to tens of microns) and in intimate thermal contact with the substrate. Even though the diamond films are supposed to have superb thermal conductivity, their contribution to the thermal conductivity of the combined film/substrate composite may still be too small to be detectable by conventional methods. Lifting the film from its substrate and measuring its thermal properties in isolation is not sufficient, because not only is this a destructive procedure, but also it misses the main point. For many applications, it is the *in situ* thermal properties, together with the coupling to the substrate, which constitute the main focus of interest. The thermal wave mirage method of measuring the thermal diffusivities of solid materials[3,4] meets this challenge very well. In this method a thermal wave is launched at the surface of the sample by a periodic, focused laser beam. The amplitude and phase of the gradient of the temperature field in the surrounding area are then measured with the mirage technique. The thermal properties of the sample/substrate are then deduced by comparing measured values with theoretical model predictions.

Another nondestructive, *in situ*, but complimentary to thermal wave, measuring technique is the Raman spectrograph. It measures the nature of chemical bonds between adjacent atoms in the material. A Raman spectrum can give information on the relative content of diamond, graphitic or some other intermediate amorphous bonds in a polycrystalline diamond deposit.

We present results of *in situ* thermal wave mirage effect measurements of the thermal diffusivities of thin polycrystalline diamond films on silicon substrates. These results are correlated with microfocus Raman measurements of the diamond/graphitic content of the same films. The diffusivities are obtained from a multi-parameter, non-linear fit to a three-dimensional analytical model. We also present similar data for thick, free-standing diamond films, in addition to data for bulk, high pressure diamond.

THERMAL WAVE TECHNIQUE

The basic setup for the thermal wave mirage method of measuring the thermal diffusivities of materials has been described before[3]. The new experimental features used in this work include the following: (a) Two lock-in amplifiers are used to record simultaneously the transverse and normal components of the mirage signals derived from a quad-cell photo detector. (b) A differential micrometer is used to adjust the height of the optics to assure that a good Gaussian beam profile is obtained at the sample. (c) The intensity of the probe beam is monitored and the information is used to normalize the output of the lock-ins. Two configurations of the probe beam are used dependent on the surface condition of the sample. If the sample surface is smooth enough to permit specular reflection at a grazing angle ($\sim 1^\circ$), the probe beam is bounced from the sample surface before striking the detector[4]. This arrangement allows the probe beam to interrogate the temperature gradient very close to the heated region of the sample surface without being obstructed by it. For samples whose surfaces do not permit bouncing, the skimming configuration is used. In this case the probe beam is also placed so close to the sample surface that part of the beam (up to $\sim 50\%$) is obstructed by it in order to maximize the signal strength. In a typical experimental run on a given sample, multiple scans are made with different frequencies and different sample-to-probe beam heights.

The equation for a thermal wave emanating from a point source in a layered material can be solved analytically. The theoretical model for the transverse and normal deflections of the probe beam as functions of the perpendicular distance between the probe and the heating beam have been given as the Fourier transform of explicit complex functions in k-space[3]. This theoretical model is based on the assumption that the entire probe beam is deflected by the temperature gradient and is detected by the quadcell. If an incomplete gaussian integral (error function with a complex argument) is introduced into the k-space function the situation of deep skimming configuration mentioned above can be accurately simulated. If two such terms are used, one for the bounced part of the probe beam, the other for the unbounced part, the bouncing scheme can also be handled.

We analyze the data by using a multi-parameter least squares fit that involves all the physical constants of the materials: the diffusivities of the film, of the substrate, the relative thermal conductance of the film to the substrate, the thickness of the film. Since the theoretical model provides analytic expressions for the mirage signals in k-space, one has a choice to do this in k-space or x-space. There are at least two reasons to choose k-space rather than x-space. The first one is that of computational speed. By choosing the k-space as the meeting ground between theory and experiment, only the experimental data need to be transformed into k-space. The k-space expression, which is evaluated many times in searching for the best set of parameters, need not be transformed further. The second reason for choosing k-space has to do with sensitivity to various kinds of errors. There are two kinds of errors that are most difficult to eliminate. The first kind is due to imperfections of sample surface which produce high (spatial) frequency noise in data. The second kind of error is due to slow modulation of sample surface property (e.g. optical absorption) which causes the signals to lose their proper symmetry. (The transverse deflection should be antisymmetric while the normal deflection should be symmetric with respect to the point at which the heating and probe beams coincide.) When the experimental data are converted into k-space, errors of the first kind are relegated to high k values and errors of the second kind disappear entirely.

In carrying out the least squares calculation a number of geometrical parameters are also included as fitting constants. They include the radii of heating and probe laser beams, the height of probe beam above the sample, and the thicknesses of the film and the substrate. Even though some of them can be independently and more reliably determined, they serve as control parameters to check the consistency of the least squares program. Data from different scans of the same sample with different frequencies and different probe beam heights are grouped together for the multi-parameter least squares fit calculation. In such calculations the relative heights of the probe beam are regarded as known parameters because they are accurately known from settings of the differential micrometer. The absolute height, however, is more difficult to ascertain and is left as a single free parameter to be determined by the fitting process.

RAMAN TECHNIQUE

Raman spectroscopy is a well known and widely utilized non-destructive technique for the characterization of materials and will only be described briefly here. As shown schematically in Fig. 1, the beam of an Ar ion laser is focused to a spot (~ 50 mW, ~ 1 μ m in diameter) on the sample surface by a conventional microscope. The Raman scattered light is collected by the same objective lens and sent through a 2 m double monochromator to produce a spectrum. In this case, the primary interest is the quantification of polycrystalline diamond materials which contain some non-diamond material [5]. Diamond materials, as deposited using any of the techniques available currently, contain some non-diamond material. That material can be graphitic, amorphous or in some intermediate state. Figure 2 shows a typical Raman spectrum of a diamond film.

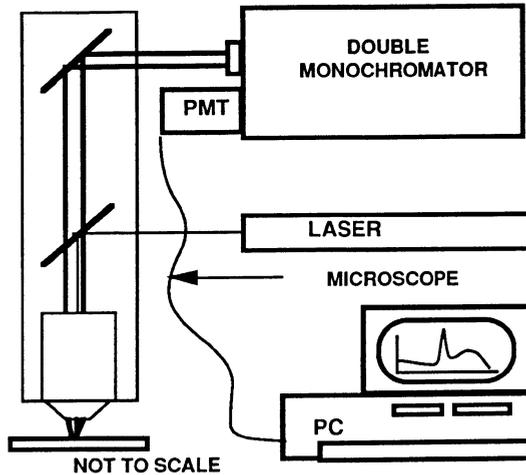


Fig. 1. Microfocus Raman spectrometer

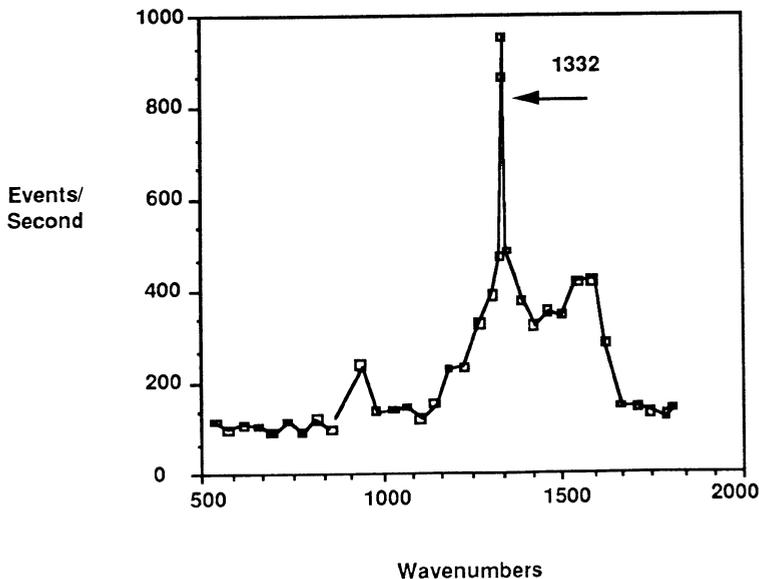


Fig. 2. WSU Raman diamond spectrum

This spectrum differs from that of pure, single crystal, diamond, since the pure diamond spectrum contains only the peak at 1332 wavenumbers. The additional information on the graph in Figure 2 results from the presence of non-diamond material. To first order, if a comparison is made of the ratio of the peak heights of the diamond material at 1332 cm^{-1} and that of the non-diamond (graphitic) material at 1550-1600 cm^{-1} , then that ratio is an indication of the graphitic content. Also, the difference in Raman scattering efficiency for graphite and diamond (~50 to 80: 1) needs to be taken into account to calculate the correct ratio.

RESULTS AND DISCUSSION

We report results of applying the thermal wave technique to two groups of diamond films. The samples of group A are polycrystalline, diamond films are grown on 200-300 μm thick silicon wafers by microwave plasma enhanced chemical vapor deposition (MPECVD). These films are approximately 25 μm thick, with crystallites range 2-10 μm in diameter. Samples A1-3 are deposited at Astex in a bell-jar reactor while sample A4 is fabricated at the Pennsylvania State University, in a tubular reactor. Table 1 lists the measured diffusivities measured with the bouncing method. The samples of group B (from General Electric Corporation) are thick, synthetic, free-standing diamond films (approximately 200 μm) with a thin layer of graphite/carbon (approximately 10 μm) on one side. Even though the thick diamond films were substantially transparent to the Argon laser beam, the 10 μm graphite/carbon layer acted as an heat absorber and allowed thermal waves to be generated. Since these samples were substantially "all-diamond", the probe beam can be made to scan on the opposite side from the heat source, thereby measuring the transmitted thermal wave. The sample surface was, however, too rough to allow the bouncing technique to be used. The skimming method was used instead. In a control experiment, a silicon wafer of similar thickness was used in the transmitted thermal wave measurement, and the measured value for the diffusivity (0.8 cm^2/s) was in good agreement with values found in the literature. The measured thermal diffusivities are summarized in Table II. In Figs. 3 and 4 we show examples of the fit of theoretical model to data for the diamond film sample B3 and a silicon wafer.

Table 1 Measured diffusivities of the four Diamond-on-Silicon samples. Two measurements are made for Sample A3 which has two distinctly different morphological regions.

SAMPLES	A1	A2	A3a	A3b	A4
THERMAL DIFFUSIVITY (cm^2/s)	3.30	2.30	0.73	4.90	3.08

Table 2 Measured diffusivities and their "fitted" thicknesses for the thick diamond film samples. The physical thickness of each sample is noted in parenthesis.

SAMPLES	B1(215 μm)	B2 (230 μm)	B3 (480 μm)
THERMAL DIFFUSIVITY (cm^2/s)	3.03	3.05	3.04
THICKNESS (μm)	215	230	250

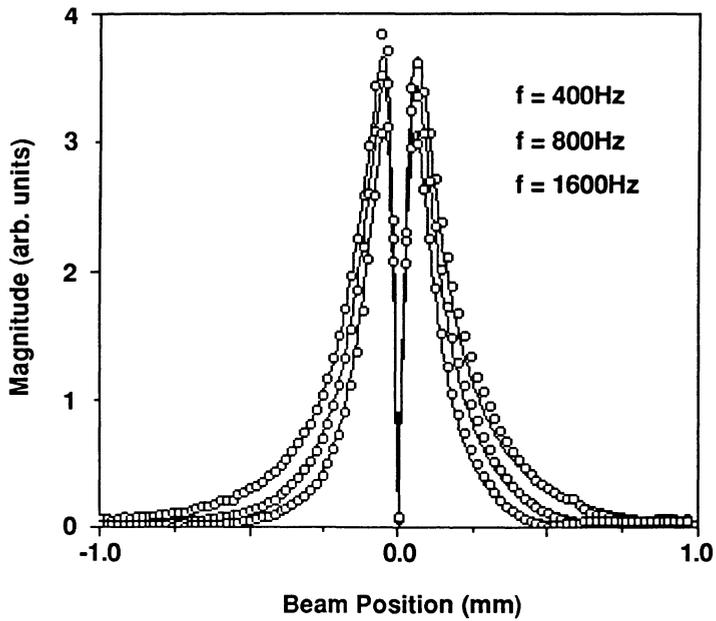


Fig. 3. Comparison of theory and experiment for data on diamond film (transverse deflection of reflected thermal wave).

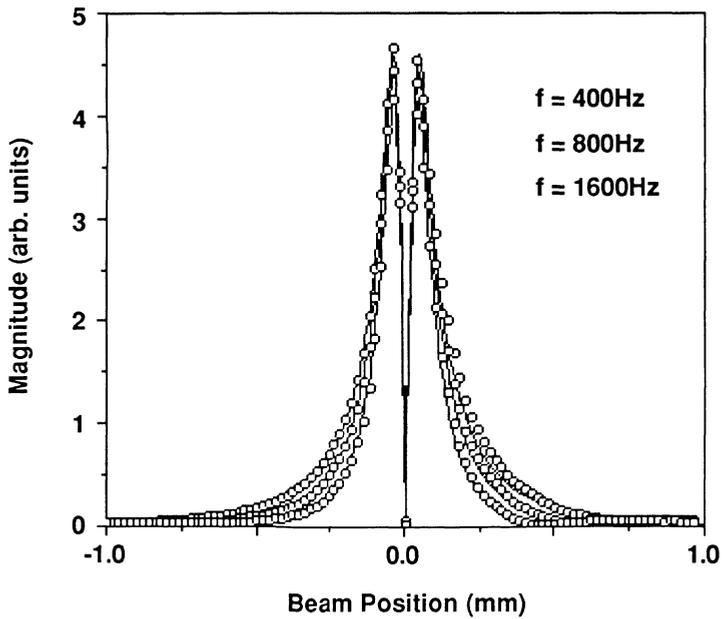


Fig. 4. Comparison of theory and experiment for data on silicon wafer (transverse deflection of reflected thermal wave).

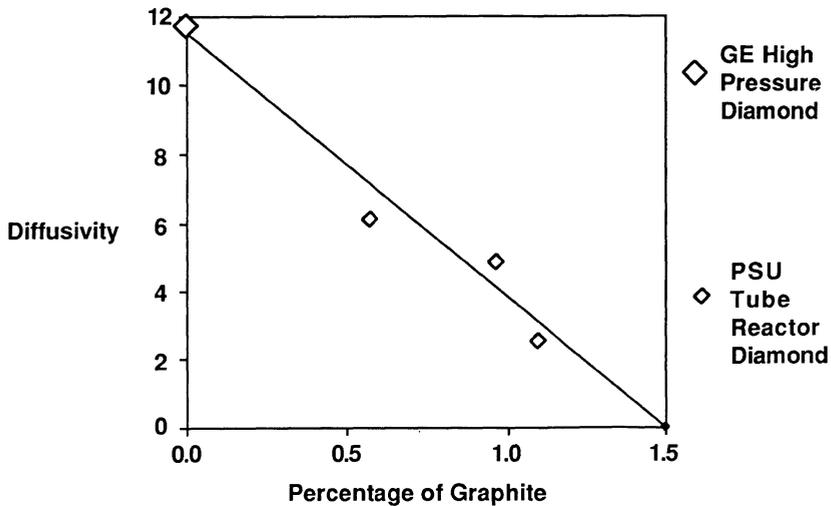


Fig. 5. Correlation between the graphitic content and the measured diffusivity of thin film and bulk diamond.

Both the thermal wave and microfocus Raman methods are applied to yet another group of diamond films. They are prepared by the same process as sample A4, except that the nominal thickness is 16 μ m. Figure 5 shows the correlation between the graphitic content and the measured diffusivity. An additional data point on the graph is for the GE high pressure synthetic diamond sample, which shows a diffusivity of 11.5 cm²/s by our thermal wave method. Although a linear relation is not necessarily what one would expect, it is clear a general trend is suggested.

In conclusion we have demonstrated a non-contact, non-destructive, *in situ* method for measuring the thermal properties of diamond films. This method is flexible enough to handle many different types of film/substrate combinations. The measured diffusivity values correlate well with the estimate of graphitic content from Raman spectra.

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