Effect of Substrate on the Measurement of Thermal Conductivity of Diamond Films

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Photothermal deflection technique has been used to study the thermal conductivity of diamond films with the emphasis on the influence of substrate on the measurement. The effect of subrtrate could be eliminated by reducing the thermal thickness in substrate by changing the modulation frequency of the photothermal deflection measurements. The difference in thermal conductivity of films in the free surface and in the interface was studies using photothermal deflection compared with Raman scattering and X-ray diffraction measurements. The SiC and disorder structure in the interface may cause the decrease in the thermal conductivity.

1. INTRODUCTION

Diamond film is one of the most attractive advanced materials because of their novel properties. Among them the extremely high thermal conductivity of, for instance, 21 W/cm·K reported recently[1] is of great interests in the application of heat sinks. However, the study of thermal conductivity of thin films is a challenging task because the traditional thermal measurement methods are no longer active dealing with the films. The photothermal deflection (PTD) method has been developed in the recent decade[2-4] and soon be used to determine the thermal conductivity of diamond films[5-6] due to its non-destructive measurement. In the case of free standing films, this technique is successful. In the measurement of films with substrate, however, the effect of the substrate on the measured value must be taken into account, in particular for thinner films, and this problem seems not to be well solved so far. In this paper we present the study of thermal conductivity in diamond films with the emphasis on the effect of substrate on the measurements.

2. EXPERIMENTAL

Diamond films were prepared using an Electron Assisted Chemical Vapor Deposition (EACVD) system. It consists of a hot filament, substrate holder, and a DC bias between the filament and the substrate in a vacuum chamber. By changing the ratio $[CH_4]/[H_2]$ of inlet gases in the range of $1 \sim 3.5\%$, films with different structure could be obtained. The distances between the filament and the substrate were $2 \sim 4mm$.

The structure of the films was analyzed by Raman scattering and X-ray diffraction. The characteristic Raman line of diamond component

is at 1332cm⁻¹, and the X-ray diffraction peak of diamond structure is at $2\theta = 43.9°$ for (111) diffraction. The schematic diagram of the PTD system is illustrated in Fig.1, in which a 25 mW He-Ne laser is used heat the sample, another He-Ne laser (1 mW) transversely passes through the sample surface as the probe beam, and the sample is put in a quartz cell filled with alcohol instead of CCl_4 as the deflection medium. The deflection signals both of the intensity and the phase lag of the probe beam caused by the temperature as well as the refractive index gradient upon heating the sample are detected by a high sensitive site sensor. The data are analyzed by a double phase lock-in amplifier and a computer.
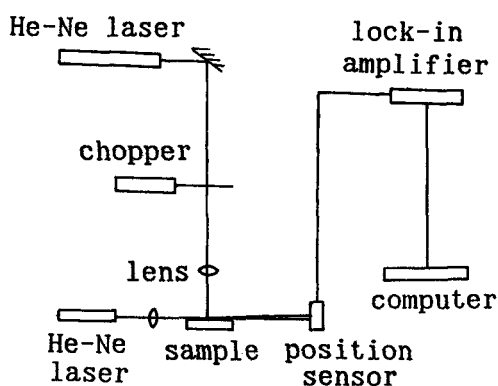

Fig.1 Schematic diagram of the photothermal deflection system

The intensity of the deflection $|\Phi|$ and its phase lag Δ can be analytically expressed as

$$|\Phi| \propto \exp[-(\omega/2K)^{1/2} \cdot y] \qquad (1)$$

$$\Delta = (\omega/2K)^{1/2} \cdot y + \Delta_0 \qquad (2)$$

where ω is the modulation frequency in PTD measurement, Δ_0 constant. By measuring the deflection phase lag as a function of distant y

from the excitation spot, the thermal diffusivity K can obtained assuming the linear relation between Δ and y mentioned above holds. The thermal conductivity κ of the sample can be obtained using the relation,

$$\kappa = K \cdot C_p \cdot \rho \qquad (3)$$

where C_p is the specific heat at constant pressure, and ρ the density of bulk materials. For thin films on substrate or surrounded by a medium, however, equation (2) holds only in the sense that the measured parameter is an apparent thermal diffusivity that includes the contributions of the film, the substrate and also the deflection medium. The apparent thermal diffusivity has been measured by varying the modulation frequency.

3. RESULTS AND DISCUSSION

The films showed a very well-behaved diamond structure characterized by the Raman line at 1332cm⁻¹ and no trace of graphitic component is shown at 1560cm⁻¹ for samples prepared at the ratio of $[CH_4]/[H_2]$ less than 1.5%. Larger $[CH_4]/[H_2]$ than 1.5% a broad band appears at 1560 cm⁻¹ corresponding to the amorphous carbon structure[7].

The relationship between the deflection phase lag Δ and the distance y from the heating site is depicted in Fig.2 for a typical free standing diamond film with the thickness about 10μm. The linear relation between Δ and y allows us to be possible to evaluate the apparent thermal diffusivity $K\alpha$ of the sample at 0.57 cm²/s, according to Eq.(2). The apparent thermal diffusivity $K\alpha$ as a function of modulation frequency ω is plotted in Fig.3 for three diamond

films: No.1 and No.2 are free standing films with different thickness, No.3 is the film on quartz substrate. It can be seen that $K\alpha$ increases with increasing modulation frequency firstly, then reaches to a saturation value at a certain frequency. These phenomena have been also
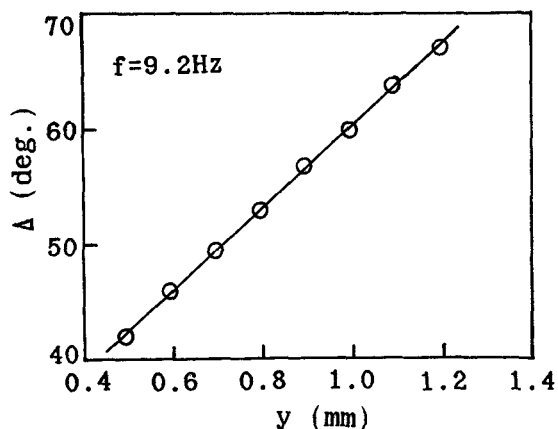

Fig.2 The phase lag Δ of deflection signal as a function of the distance y from the excitation
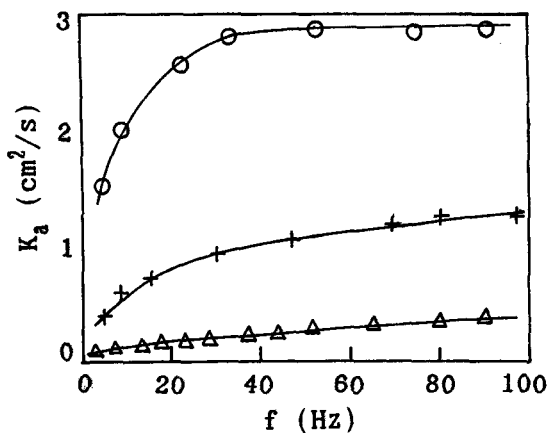

Fig.3 Apparent thermal diffusivity $K\alpha$ as a function of the modulation frequency for three samples (O:No.1 +:No.2 Δ:No.3), ———: least square method fit

found in other films with or without substrates and becomes serious at low modulation frequency. Because the thickness of the films is much less than its thermal wavelength, the influence of the substrate and the deflection medium that are also thermal conductive in some extent must be taken into account. The thermal waves can propagate either in the film or in the surrounding medium. The saturation value of $K\alpha$ is thus the thermal diffusivity of the films eliminating the influence of the substrate. The frequency at which the $K\alpha$ reaches to saturation is lower for thicker free standing film of No.1 ($\sim 30\mu$m) at 40 Hz, higher for thinner film of No.2 ($\sim 10\mu$m), and even much higher for film of No.3 with substrate because the thermal conductivity of quartz substrate is about one order of magnitude higher than that of the deflection medium. The apparent thermal diffusivity of thin films can be calculated using the photothermal deflection theory taking the effect of the interfaces between the film and the substrate and between the film (or the substrate) and the deflection medium into consideration. The dependence of the apparent thermal diffusivity on the modulation frequency calculated fits with the experimental data using the least square method as shown in Fig.3 resulting in the thermal conductivity of the films evaluated at 5.16, 3.55, and 3.67 W/cm·K for samples No.s, s=1,2,3, respectively. Assuming that the thickness of the substrate d_s is larger than its thermal wavelength, and that thermal conductivity of the substrate is poor, which is just the case in our experiments, the thermal waves propagates from the film passing through the interface to a certain distance in the substrate (or deflection medium) of basically one thermal wavelength near the interface that is called the effective thermal thickness, d_e. The dependence of d_e on

1548

the thermal diffusivity of the substrate and the modulation frequency of the excitation source can be empirically expressed as,

$$d_e \propto (K_s/\omega)^{1/2} \qquad (4)$$

It should be much less than the thickness of the substrate. Obviously, d_e decreases with increasing modulation frequency. Therefore, by increasing the modulation frequency, the influence of the substrate (or deflection medium) can be eliminated, until being neglected at the infinitive modulation frequency.

The films have been released from the substrate by etching and then measured the thermal conductivity in both sides. It is found that the thermal conductivity in the backside which is released from the interface of film and substrate is always less than that in front side. This may be originated from the different structure in the two sides as confirmed by Raman spectroscopy. There are two factors responsible for the reduction of the thermal conductivity in the backside: small crystalline grain size in the initial stage of the film growth and disordered components. The former is characterized by the broadening of the Raman line at 1332cm^{-1}, in which the full width at half maximum (FWHM) of the line is 8.5cm^{-1} for the front side, and 13.0cm^{-1} for the backside. The latter is described by the intensity increase of the broad band at 1560cm^{-1}. The thermal conductivity of the films on substrate and released from the substrate has been also examined. The influence of the substrate can be drawn in this way and a correction curve will be given elsewhere.

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