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Thermal Properties of Diamond Films Deposited by Chemical Vapor Depositon

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Four diamond films were deposited by the microwave plasma assisted chemical vapor deposition method varying CH_4 concentration from 2.5 to 10% in the feeding gases. Thermal conductivity was measured on these free standing films by the steady state method from 80 K to 400 K. They showed higher thermal conductivity as the film deposited with lower methane concentration. One exception, 7.79% methane concentration deposited film, was observed to be the highest thermal conductivity. Phonon scattering processes were considered to analyze the thermal conductivity with the full Callaway model. The grain size and the concentration of the extended and the point defects were used as the fitting parameters. Microstructure of diamond films was investigated with the scanning electron microscopy and Raman spectroscopy.

Key words : Thermal conductivity, MW-CVD diamond film, Phonon scattering, Callaway model, Point defect, Extended defect, Umklapp process, Normal process

I. Introduction

Diamond has the highest atomic density and the highest atomic bond energy density of any known solid. With these physical properties, diamond has the highest Young's modulus and the highest Debye temperature.[1] The thermal conductivity of diamond is the highest of known materials above 100 K. At room temperature, thermal conductivity of the single crystal diamond (type IIa) and nitrogen containing natural diamond (type Ia) are 20 and 10 W cm^{-1} K^{-1}, respectively.[2] These extreme physical properties are useful in mechanical, tribological, thermal and electronic applications.[3]

After develpment of low pressure synthesis, usually chemical vapor deposition (CVD) method, large area diamond coatings are possible. Early CVD diamond film was poor quality and showed lower values of thermal conductivity than type Ia.[4-6] Recently, the quality of CVD diamond films improved much and the thermal conductivity is approaching gem quality type IIa diamond.[7,8]

It has been known that the deposition with high CH_4 concentration enhances the defect level in CVD diamond film and cause a reduction in the thermal conductivity.[4,9-11] The initial attempt to measure thermal conductivity of CVD diamond films was carried out by Ono *et al.*[4] using infrared thermography. They found a rapid increase of thermal conductivity by reduction of CH_4 concentration below 1%. Studying Raman spectra, they found that the level of the graphitic carbon or sp^2-bonded carbon was increased as the methane concentration was decreased. They suggested that the decrease in thermal conductivity might be caused by an increase in the microscopic defect concentration.

Baba *et al.*[10] measured thermal conductivity of diamond films that were synthesized with CH_4 concentration in the range of 1 to 5% using the hot filament method. Using Rutherford backscattering, they observed an exponential increase of hydrogen content in the films with increasing methane concentration. They also found peaks in the infrared spectrum, which they attributed to C-H stretchbands. They correlated the increase of thermal conductivity in the diamond film with the decrease of the impurity of hydrogen. Their film thickness was thinner than 10 μm so that the grain boundary - phonon scattering might also be high. In order to get the thermal conductivity from the measured thermal diffusivity, they used literature values of specific heat of single crystal diamond instead of their CVD diamond film's specific heat.

A similar result was obtained by Gu *et al.*[11] They measured thermal diffusivity with a photothermal deflection method at room temperature. Their films were deposited with a hot filament method by varying methane concentration from 0.5 to 5%. They showed the relative decrease of thermal diffusivity with longer period of polishing time on the same film.

For a better understanding of thermal conductivity in conjunction with the deposition condition thicker films are needed and the thermal conductivity has to be

measured over a wider temperature range.

We prepared four CVD diamond films which were deposited with 2.5 to 10% CH_4 in the gases with the microwave plasma CVD method. The thickness of these diamond films ranged from 70 to 160 μm. Thermal conductivity of these free-standing diamond films was measured with steady state method in a temperature range from 80 K to 400 K. Scanning electron microscopy and Raman spectroscopy were used to study the diamond films. The thermal conductivity of the film was analysed with the full Callaway model.

II. Experiments and Results

1. Sample preparation

A microwave plasma assisted chemical vapor deposition reactor of power 5 kW was used. The deposition conditions for each film are presented in Table 1. The concentration of CH_4 in the source gases were increased from 2.5 to 10% in 2.5% increment. They are labeled as increasing order of the methane concentration from MW1 to MW4. Thus, MW1 and MW4 are the diamond film deposited with 2.5 and 10% of CH_4 concentration, respectively. The ratio between CH_4 and O_2 in the gases was fixed at 6 to 1. The pressure and the microwave power were fixed at 110 Torr and 5 kW, respectively, during growth. Each diamond film was deposited on a Si substrate which had a thickness 3 mm and area 30×30 mm^2. A thicker than usual Si-wafer was used for the substrate to avoid an accidental curvature on the film due to the internal stress generated by the high temperature deposition process. After deposition, the diamond film was removed from the substrate by chemical etching. Laser cutting was used to cut the diamond film to 5×15 mm^2.

2. Thermal conductivity

A heater was attached on one end of the film with Ag paste and the other end was thermally grounded to the Cu-block of the sample holder. Strain gauge of resistance 350 ohms, 2×4 mm^2, was used for the heater. The schematic diagram for thermal conductivity measurement is presented in Fig. 1. The resistance of the heater was monitored throughout the range to measure the Joul heating power input to the sample. Three calibrated T-type thermocouples were attached on the sample, 2~3 mm apart each to measure the thermal gradient with a temperature resolution ±10 mK. The distance between the thermocouples was measured by a cathetometer within ±10 μm.

In Fig. 1, the junction size of the thermocouple is drawn larger than the real size. The thermocouples were attached by small amount of Ag-epoxy. The diameter of the junction including Ag-epoxy is less than 80 μm. The diameter of Cu-wire from the heater and the thermocouple wires were 0.025 mm. Heat losses through the wires were less than 1% of the total power input The sample holder is mounted in the insert of the vacuum cryostat. Thermal conductivity was measured in vacuum to avoid the heat loss by convection. Thermal stability of the cryostat was ±10 mK throughout the entire temperature range. Thermal conductivities for all diamond films and natural diamond type IIa are shown in Fig. 2 Thermal conductivity of natural diamond type IIa was taken from Berman *et al.*[9] MW3 shows the best thermal conductivity. For the diamond films of MW1, MW2, and MW4, higher thermal conductivity is observed as the methane concentration is decreased.

Table 1. Deposition Conditions for each CVD Diamond Films Pressure and the Microwave Power was 110 Torr and 5 kW, Respectively During Deposition. The Substrate Temperature was Measured by an Optical Pyrometer. Raman Ib/Id is the Ratio of the Peak Height of Diamond Signal to the Background

	MW1	MW2	MW3	MW4
CH_4 concentration (vol. %)	2.46	4.92	7 79	9.85
O_2 concentration (vol. %)	0.41	0.82	1.29	1.64
H_2 concentration (vol. %)	97.13	94.26	90.91	88 51
Substrate Temperature (°C)	980	1011	842	950
Growth rate (μm/h)	0 6	2.8	3.5	5.7
Thickness (μm)	68	130	125	160
Raman FWHM (cm^{-1})	1.6	3.0	4.6	6.2
Raman Ib/Id	0.10	0.12	0 16	0.32

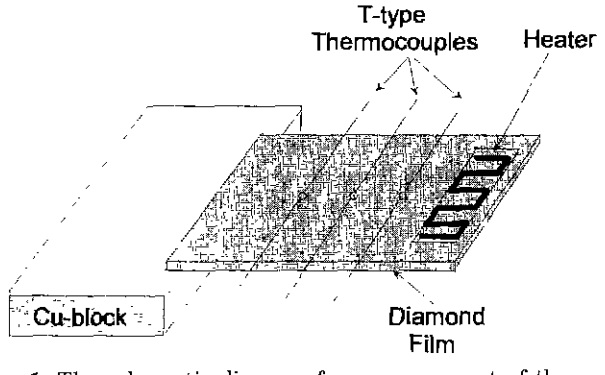

Fig. 1. The schematic diagram for measurement of thermal conductivity of the CVD diamond film. One end of the diamond film is thermally grounded to the Cu-block. The other end was attached by an electric resistance heater (strain gauge with resistance 350 Ohms) Three thermocouples were attached 2~3 mm apart each to measure thermal gradient Heat loss through the wires is less than 1% of total input power.

3. Raman spectroscopy

We investigated the diamond films with Raman spectroscopy. In Table 1, full width at half maximum (FWHM) of the diamond peak and Ib/Id ratio for each diamon films are listed. Ib is the background level and Id is the peak height of the diamond peak near 1332 cm^{-1} in Raman spectra. For all diamond films, non-diamon carbon phase near 1550 cm^{-1} was not detected or might be

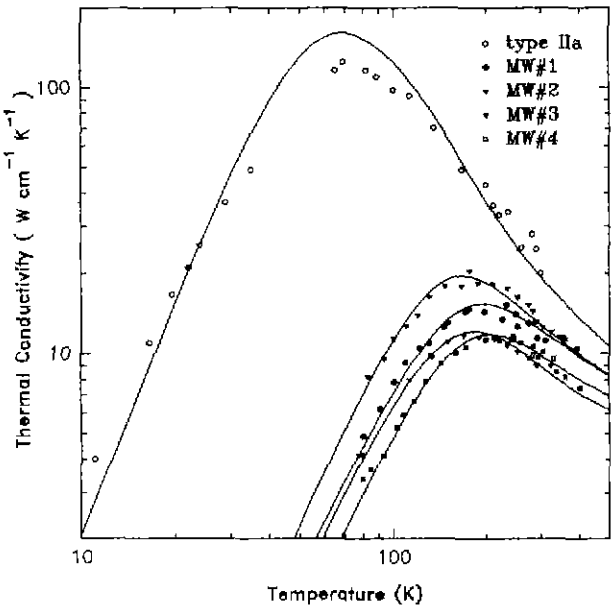

Fig. 2. Thermal conductivity of natural diamond type IIa (Ref. 3) and CVD diamond films deposited with different concentration of CH_4. The labels of the film with the methane concentration in parenthesis are MW1 (2.46%), MW2 (4.92%), MW3 (7.79%), and MW4 (9.85%). Lines are the fitted curves using the full Callaway model. Three adjustable parameters, the grain size, D; point defect concentration, c; and the extended defect concentration, E; were used. The values of the parameters are listed in Table 2.

very small if it was. FWHM and Ib/Id ratio are observed to be increased as the concentration of CH_4 is raised. The results of Raman spectroscopy are in accordance with the expectation of the increment of defect level as methane concentration is raised. In the same manner, thermal conductivity of MW1, MW2 and MW4 is decreased as the defect level is raised with increment of methane concentration. This is a similar result as Herb *et al.*[12] showed. They investigated that the diamond films with low values of FWHM of Raman showed high thermal conductivity.

Herb *et al.* also studied a correlation between the ratio of diamond peak to non-diamond peak (sp^3/sp^2) of Raman and the thermal conductivity of CVD diamond films. For our diamond films, there is not a detectable non-diamond peak. For the thermal conductivity of MW3, it's not in the line with the expectation.

4. Scanning electron microscopy

In the SEM (scanning electron microscopy), the microstructure of the top surface of morphology of each film could be observed. MW1 which has thickness 68 μm, showed the smallest grains with high density of 5-fold twins and steps. For MW2-4, grains are larger than MW1 due to their larger film thickness. It's not easy to estimate the average grain size, since the crystal was grown as a columnar structure and the grain size increases gradually along the height from the substrate.

III. Analysis and Discussion

We used the full Callaway model[13,14] to analyze the thermal conductivity of diamond film. This model can take into account the differences among the longitudinal and transverse phonon modes and was recently used to analyze the thermal conductivity of high purity synthetic diamond[15,16] and CVD diamond.[17,18] In this model, the combined mean-free path l_C^{-1} is written as the sum of the normal, l_N^{-1} and the resistive mean-free path, l_R^{-1}, such as

$$l_C^{-1} = l_N^{-1} + l_R^{-1}$$

We choose the normal process from Landau and Rumer,[19] such as

$$l_N^{-1} = A\frac{x}{\upsilon}T^5$$

where $A=0.011\ s^{-1}K^{-1}$, $x=\hbar\omega/k_BT$, k_B is Boltzmann's constant, $\hbar$ is Planck's constant, and υ is the sound velocity. In each mode, different values of the Debye temperature and the sound velocity were used.[13,20] The assumption is made that the resistive scattering rates add, so that

$$l_R(x) = (l_B^{-1} + l_P^{-1} + l_U^{-1} + l_E^{-1})^{-1} + \frac{\lambda}{2}$$

The individual mena-free paths l_B, l_p, l_U and l_E are associated with the grain boundaries, point defects, umklapp processes and the extended defects,[17] respectively. The term $\lambda/2$, half the phonon wave length, is included to avoid the unphysical case where the mean-free path becomes short compared to the phonon wave length. The functional forms of each mean-free paths are chosen to be

$$l_B^{-1} = 1/D$$

$$l_P^{-1} = 4\pi^3 V_0 c(1-c)\left(\frac{1}{12+C}\right)^2\left(\frac{k_BT}{\hbar}\upsilon\right)^4 x^4$$

$$l_U^{-1} = B\left(\frac{k_BT}{\hbar}\upsilon\right)^2 x^2 T e^{-\frac{C}{T}}$$

$$l_E^{-1} = \begin{cases} \dfrac{E}{(2\pi\upsilon)^4}\left(\dfrac{k_BT}{\hbar}\right)^4 x^4 & x < x_c \\ \dfrac{E}{(2\pi\upsilon)^4}\left(\dfrac{k_BT}{\hbar}\right)^4 x_c^4 & x \geq x_c \end{cases}$$

where $x_c=\hbar\upsilon/k_BTF$, F is the diameter of the extended object,[17] and V_0 is the volume per atom (5.68×10^{-24} cm^3). We used the parameters $B=1.5\times10^{-12}$ cm K^{-1}, C=670 K, F= 15.0×10^{-8} cm to be fixed.

Three adjustable parameters D, c and E are the grain size, the point defects concentration and the concentration of the extended defects, respectively, which

Table 2. Thermal Conductivity of CVD Diamond Films and Natural Diamond type IIa at room Temperature. The Parameters were used to Fit data with the full Callaway Model

	MW1	MW2	MW3	MW4	typeIIa
k(298 K)(W cm^{-1} K^{-1})	11.5	8.5	12.6	9.2	20.0
D, Grain size (μm)	7	6	10	4	1000
c, Point defect level (%)		7	3	5	1.1
E, Extended defect (10^{-22} cm^3)	15	10	5	13	0

are listed in Table 2 for a good fit The fitted curves are presented in Fig. 2. Low temperature thermal conductivity (left side of the thermal conductivity peak) is directly proportional to the grain size, since the phonon mean free path is longer than the size of the grain boundary. Near the peak region, phonon scattering with the point defect and the extended defect is dominant. ^{13}C is the major source of point defect scattering in Rayleigh scattering.

Without the extended defect, the fitting curves over shoot. But, the nature of the extended defects is not known yet. Probably, the extended defect is a cluster of foreign atoms or disordered atoms [17,21] The intrinsic phonon-phonon scattering which is known as the umklapp process is dominant at higher temperatures (the right side of the peak). Except MW3, thermal conductivity is inversely proportional to the CH_4 concentration. MW3 showed the highest thermal conductivity even though the CH_4 concentration was 7.79%. Among four films, MW 3 has the largest grain size, 10 μm, the lowest extended defect and point defect concentrations, The next highest thermal conductivity film, MW1, which was deposited with the lowest methane concentration, showed the next largest grain size, 7 μm and the same level of the point defect as MW3, but the extended defect level was the highest. Between MW1, MW2, and MW4, the grain size and the thermal conductivity were shown to be decreased as the methane concentration was increased.

Considering the synthesizing condition of each diamond film, except CH_4 concentration, the only difference in the deposition process for MW3 was the substrate temperature. The substrate temperature of MW3 was 100 K lower than other film's substrate temperature which was 950°C or higher. It is known that good quality diamond film is obtained when the substrate temperature is 900~1000°C.

IV. Conclusions

Four diamond films were prepared with a microwave plasma assisted chemical vapor deposition method. Methane concentration was varied from 2.5 to 10%. Thermal conductivity of these films was measured by the steady state method between 80 and 400 K. Raman spectroscopy and SEM were used to characterize CVD diamond films.

FWHM and Ib/Id ratio of Raman peak of diamond were increased as the methane concentration increased. Except for the diamond film deposited with 7.79% of methane concentration, three diamond films showed that their thermal conductivity decreased as the methane concentration was raised. The diamond film deposited with 7.79% of CH_4 concentration at the substrate temperature 850°C showed the highest thermal conductivity. Thermal conductivity was analysed with the full Callaway model. In this model, the point defect as well as the extended defect is an important factor to have a good fit to the thermal conductivity of CVD diamond.

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