Growth of 4″ diameter polycrystalline diamond wafers with high thermal conductivity by 915 MHz microwave plasma chemical vapor deposition

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Abstract
Polycrystalline diamond (PCD) films 100 mm in diameter are grown by 915 MHz microwave plasma chemical vapor deposition (MPCVD) at different process parameters, and their thermal conductivity (TC) is evaluated by a laser flash technique (LFT) in the temperature range of 230–380 K. The phase purity and quality of the films are assessed by micro-Raman spectroscopy based on the diamond Raman peak width and the amorphous carbon (a-C) presence in the spectra. Decreasing and increasing dependencies for TC with temperature are found for high and low quality samples, respectively. TC, as high as 1950 ± 230 W m⁻¹ K⁻¹ at room temperature, is measured for the most perfect material. A linear correlation between the TC at room temperature and the fraction of the diamond component in the Raman spectrum for the films is established.

Keywords: thermal conductivity, polycrystalline diamond, microwave plasma chemical vapor deposition, Raman spectroscopy

(Some figures may appear in colour only in the online journal)

1. Introduction
Diamond, with its extraordinary high thermal conductivity, is the material of choice for thermal management in many cases when the problem of huge heat dissipation is to be solved. Thanks to progress in the growth of polycrystalline diamond (PCD) films and wafers by the chemical vapor deposition (CVD) method, large size, CVD diamond plates are in demand to act as heat spreaders in powerful GaN transistors [1], high-frequency microwave transistors on H-terminated p-type diamond surfaces [2, 3], pixel particle detectors [4] and x-ray imaging detectors [5], windows for high-power gyrotrons [6] and infrared (IR) lasers [7, 8], thin-disk semiconductor lasers [9] and helix traveling-wave tubes (high-power, millimeter-wave radiation sources) [10]. As thermal conductivity (TC) (which is dependent on the material’s purity and transparency) is of primarily importance, the growth process should be engineered to reach a compromise between structure perfection and viable growth rate to ensure high thermal properties. The microwave plasma CVD (MPCVD) technique allows the production of both high-quality single crystal and PCD films; this is due to the clean growth environment, typically methane diluted in hydrogen, with minimized impurities in the plasma. TC at room
temperatures above 1900 W m\(^{-1}\) K\(^{-1}\) was reported for the most perfect, thick (hundreds of microns) PCD wafers produced by MPCVD [11–17]. The TC of the PCD films strongly depends on the growth process parameters and the resulting structure, grain size and defects [12, 16, 18, 19]. Most of the published studies on TC of MPCVD PCD films were performed with the samples grown on substrates, typically 2–3 inches in diameter, in a microwave plasma operated at a 2.45 GHz frequency. The necessity to increase the diamond deposition area motivated researchers to use microwave sources with longer wavelengths, such as 915 MHz systems [20–26], however, much less information about the TC of films produced with extended plasma size at 915 MHz is available. Goyal et al [27] deposited thin (300 nm) nanocrystalline diamond (NCD) films on GaN substrates in Ar/CH\(_4\)/H\(_2\) mixtures and estimated the TC for NCD to be above that of GaN (130 W m\(^{-1}\) K\(^{-1}\)), but less than 800 W m\(^{-1}\) K\(^{-1}\) in view of the small (100–200 nm) grain size. Mallik et al [28] reported on a free-standing, translucent PCD film with a TC of 660 W m\(^{-1}\) K\(^{-1}\); this relatively low value was due to the poor quality and small thickness (≈80 μm) of the material. A much higher TC of 1800–1900 W m\(^{-1}\) K\(^{-1}\) was reported for free-standing MPCVD PCD disks with diameters and thicknesses up to 119 mm and 2.2 mm, respectively, as manufactured by the Element Six Company [6]; however, no details on the growth process were given.

Here, we performed the synthesis of 100 nm-diameter PCD films with thicknesses up to ∼600 μm using MPCVD (915 MHz) at different process parameters; we measured the TC of the free-standing wafers with a laser flash technique (LFT), and studied the correlation between the thermal properties and the diamond quality as deduced from Raman spectroscopy and scanning electron microscopy (SEM) analysis.

2. Experiment

PCD films were deposited on (100) 100 mm-diameter and 6 mm-thick mirror-polished, single crystal silicon substrates with a MPCVD reactor (DiamoTek 1800 series, 915 MHz, 15 kW from Lambda Technologies Inc.) [21]. Prior to this, the silicon substrate was seeded by ultrasonic treatment in deaggregation nano-diamond slurry in methanol (1:3 ratio) for 15 min to enhance diamond nucleation density [29, 30]. The synthesis was performed in CH\(_4\)/H\(_2\) gas mixtures with a total flow rate of 500–1000 sccm, a CH\(_4\) content of 1% and 3%, a gas pressure of 152 mbar, a 9.0 kW microwave power and the substrate temperature varied in the range of 950 °C–1030 °C, as monitored with a two-color optical pyrometer (PRO 82-40-C, Williamson) focused at the center of the substrate. The growth time from 34 h to 239 h was used to obtain diamond films of different structures and qualities with thicknesses of 68 μm to 660 μm (table 1). The growth rate, as measured at the wafer center, increased from 2.1 μm h\(^{-1}\) to 3.6–4.7 μm h\(^{-1}\) for films of comparable thickness, with an increase of CH\(_4\) content in gas from 1% to 3%. A photograph of one of the deposited diamond films on the substrate is shown in figure 1. After the growth run the free-standing films were obtained by etching the Si substrate in a solution of hydrofluoric, nitric and acetic acids in a 1:1:1 ratio.

The phase purity of the samples on both growth or nucleation sides was analyzed at room temperature with micro-Raman spectroscopy using a LabRam HR800 (Horiba) instrument in a confocal configuration with a spectral resolution of 1.0 cm\(^{-1}\) and spatial resolution of ∼1 μm at the 473 nm excitation wavelength. To reliably determine the diamond Raman peak width, the spectra were taken in 20 different locations of the sample (within a 0.5 mm diameter zone) and then averaged. The surface morphology of the samples was characterized with SEM (SM-7001F, JEOL). The grain size was determined by counting the number of grains along an arbitrarily directed straight line across the SEM image. The smaller samples (∼1 cm\(^2\)) suitable for TC measurements were laser cut from a central zone of the mother wafers, without further polishing. To assess the TC spatial uniformity across the diamond disks, samples W11_c and W11_e were cut from the center and edge of the same wafer. The TC k has been measured in the temperature range of 230–380 K by a LFT, as described elsewhere [17, 31]. Briefly, the diamond plate was mounted in the cryostat in a ∼10\(^{-4}\) Pa vacuum, and the thermal wave was generated on the front side of the sample in a 5 mm spot by the laser shot (λ = 1.06 μm, 8 ns), while the temperature rise kinetics T(t) on the rear side was traced by a liquid nitrogen-cooled HgCdTe infrared detector (300 MHz).

To enhance the laser absorption and IR emissivity, a bilayer Cu–Ti coating (∼300 nm) was deposited on both sides of the sample. The thermal diffusivity D was determined by fitting the experimental T(t) curves to a modeled kinetics assuming one-dimensional heat flux [12]. The kinetics T(t) was averaged over 100 laser pulses to reduce noise and improve accuracy in the evaluation of thermal diffusivity to ±12%; this is mostly due to uncertainty about the thickness of the rough, as-grown specimens. Then, the TC was calculated as k (T) = D(T)ρC(T), where ρ and C(T) are the mass density and specific heat of diamond, the latter tabulated in [32].

3. Results and discussion

For all combinations of growth parameters used, the produced diamond films exhibited well-faceted crystallites with random orientations. Figure 2 displays SEM images of the growth surface for several samples of different qualities and thicknesses. The translucent (‘white’) sample W11_c of 520 μm thickness, taken from a central zone of the wafer produced in an optimal regime, at low (1%) CH\(_4\) content and high temperature (1020 °C), shows crystallites of ∼20 μm mean size with very smooth facets and no twins; this indicates a high crystallinity (figure 2(a)). The sample W11_e from the periphery of the same wafer revealed grains of larger size (∼34 μm) with more rough facets due to the presence of growth steps, v-shaped grooves and pentagonal dimples (figure 2(b)). A thickness variation of ∼10% over the wafer was found, owing to a radial temperature gradient (ΔT ≈ 50 °C center-edge difference). The increase of methane to 3% in
the reaction mixture results in the growth of a dark material, often with enhanced roughness of crystallite facets caused by the appearance of numerous penetration twins on (111) faces, as seen for sample W140 (figure 2(c)). Since the formation energy of twins in diamond is low, they emerge easily on CVD diamond crystallites [33]. The size of the twins varies in the range of 1–20 μm, the smallest twins being the second-order ones, while the mean grain dimension (the twins are not included in the statistics) enlarges to ≈85 μm. Similarly, the black diamond sample W18 also demonstrates roughened facets with high macrosteps (figure 2(d)). The relatively thin films #34 and #64 were both composed of (100) oriented pyramidal 12–16 μm crystallites, with stepped facets and a small number of twins.

The degradation of the structure following the addition of more CH₄ in the gas is further confirmed by Raman spectra (figure 3). The Raman spectra of all the samples reveal a strong narrow peak around 1332 cm⁻¹, characteristic of diamond, and the broad band of amorphous carbon (a-C) in the range of 1450–1600 cm⁻¹, the latter being a superposition of the G-peak (∼1550 cm⁻¹) of a graphitic structure and of the 1480 cm⁻¹ band of the trans-polyacetylene component [34]. The disorder-induced D-peak at 1350 cm⁻¹ contributes to the overall Raman spectrum only in a minor extent. The total integrated intensity of all non-diamond carbon phases (intensity of the whole Raman spectrum minus intensity of diamond peak) is designated here with I₉ (the subscript with small letter ‘g’ differentiates it from the G-peak intensity). The diamond peak width at half maximum (FWHM) Δν₁ is as small as 2.5 cm⁻¹ for the most perfect (‘white diamond’) sample W11_c, increasing to 8.8–12.8 cm⁻¹ for black diamond films produced at the highest (3%) CH₄ content (table 1). This broadening indicates a build-up of defect abundance and stress in the material. The diamond Raman peak broadening from 2.5 cm⁻¹ to 3.8 cm⁻¹ is also detected when the samples taken from the center and edge of the wafer W11 are compared, this reflecting some variation in structure.

Similarly, the non-diamond components with intensity I₉ in the Raman spectra become synchronously noticeable with the 1332 cm⁻¹ peak broadening. The ratio I₀/(I₀ + I₉) of integrated intensity (area under peak) I₀ of the 1332 cm⁻¹ diamond peak to the total intensity of carbon phases I₀ + I₉ in the spectrum over the 1150–1700 cm⁻¹ wavenumber range, can be regarded as the value proportional to the diamond content in the film. The I₀/(I₀ + I₉) ratio decreases from 0.92 for the best-quality sample W11_c down to 0.16–0.27 for the black material (table 1), confirming again the diamond’s structural deterioration.

Figure 4 shows temperature dependences of TC k(T) for four representative diamond samples of different qualities. The films with high and moderate TC reveal a decreasing trend k ∼1/Tⁿ with exponent n < 1, as the phonon–phonon scattering becomes the dominant source of thermal resistance at elevated temperatures [14–16]. In contrast, the black diamond films W18 and W140 with low k demonstrate a monotonic increase with temperature, similar to the behavior known for highly-defective polycrystalline [35] and ultra NCD (UNCD) films [36]. This trend reflects the important role of grain boundaries and defects in phonon scattering at room and lower temperatures.

A link between the TC with an abundance of a-C inclusions, the latter usually quantified as the I₀/I₀ ratio in the Raman spectrum, was reported earlier for diamond films grown by different CVD methods [18, 37]. Here, we examined the correlation between measured TC at room temperature and the I₀/(I₀ + I₉) ratio which serves an indicator for the diamond content in the film. Figure 5 displays the plot k versus the I₀/(I₀ + I₉) ratio; this fits well with the linear dependence k(W cm⁻¹ K⁻¹) = 0.54 + 19.5 I₀/(I₀ + I₉). The terminal points for the fit gives k(1) = 2008 W m⁻¹ K⁻¹ for pure diamond, and k(0) = 54 W m⁻¹ K⁻¹ for a graphite material with no diamond feature in the Raman spectrum. It is interesting that the low end of this plot k(0) is higher than...
16 W m$^{-1}$ K$^{-1}$ for UNCD [36] and is comparable to the values of 70–220 W m$^{-1}$ K$^{-1}$ for polycrystalline graphite [38]. The Raman peak broadening, as an indicator of defect abundance in the films, correlates with the TC decrease (table 1), as can be expected.

We note that the $I_d(I_d + I_g)$ ratio is not exactly the diamond fraction $f$ in the sample, since the denominator does not take into account that the cross section of Raman scattering for diamond is $\approx$50 times less than for graphite [39]. The more correctly-assessed fraction $f = I_d(I_d + 0.02I_g)$ varies between 0.998 for the highest $k$ sample to 0.905 for the lowest $k$ sample ($k = 530$ W m$^{-1}$ K$^{-1}$). Among the diamond films

Figure 2. SEM images of white diamond, samples W11_c (a) and W11_e (b), and black diamond, samples W140 (c) and W18 (d), arranged in order of structure degradation. All pictures are taken at the same magnification.

Figure 3. Raman spectra for growth side of PCD samples. The sample number is indicated for each spectrum. The dashed area denotes the integral intensity of the (a-C) component.

Figure 4. Temperature dependence of TC for diamond samples of different qualities. The lines are guides for the eye.
In summary, we used a LFT to measure the TC of large-area PCD films grown by 915 MHz MPCVD. The temperature dependence of TC $k(T)$ has been determined in the temperature range of 230–380 K for films of different structure perfections. The TC $k$ (298 K) as high as 1950 ±230 W m$^{-1}$ K$^{-1}$ for the best-quality translucent PCD is evaluated at room temperature, while a dramatic reduction in TC down to 300–600 W m$^{-1}$ K$^{-1}$ for highly defected ‘black’ diamonds was observed. The TC is found to decrease with temperature for more perfect material, as expected for phonon-phonon scattering enhancement; however, it rises for heavily defected films (having $k < 600$ W m$^{-1}$ K$^{-1}$ at room temperature). The phase purity of the films (diamond to a-C ratio) prepared in different growth regimes is assessed by micro-Raman spectroscopy, and a linear correlation between the room temperature TC and the diamond content in the films is established.

**4. Conclusions**

In summary, we used a LFT to measure the TC of large-area PCD films grown by 915 MHz MPCVD. The temperature dependence of TC $k(T)$ has been determined in the temperature range of 230–380 K for films of different structure perfections. The TC $k$ (298 K) as high as 1950 ±230 W m$^{-1}$ K$^{-1}$ for the best-quality translucent PCD is evaluated at room temperature, while a dramatic reduction in TC down to 300–600 W m$^{-1}$ K$^{-1}$ for highly defected ‘black’ diamonds was observed. The TC is found to decrease with temperature for more perfect material, as expected for phonon-phonon scattering enhancement; however, it rises for heavily defected films (having $k < 600$ W m$^{-1}$ K$^{-1}$ at room temperature). The phase purity of the films (diamond to a-C ratio) prepared in different growth regimes is assessed by micro-Raman spectroscopy, and a linear correlation between the room temperature TC and the diamond content in the films is established.

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**References**

[37] Bachmann P K et al 1995 Diam. Relat. Mater. 4 820