Available online at www.sciencedirect.com
SCIENCE DIRECT
Diamond & Related Materials 14 (2005) 589–593
DIAMOND AND RELATED MATERIALS
www.elsevier.com/locate/diamond

Thermal conductivity of CVD diamond at elevated temperatures

A.V. Sukhadolau[a], E.V. Ivakin[a], V.G. Ralchenko[b,*], A.V. Khomich[c], A.V. Vlasov[b], A.F. Popovich[b]

[a]*Institute of Physics, Academy of Sciences of Belarus, 70 Skaryna Ave., 220072 Minsk, Belarus*
[b]*A.M. Prokhorov General Physics Institute RAS, Vavilov str. 38, Moscow 119991, Russia*
[c]*Institute of RadioEngineering and Electronics RAS, 1 Vvedenskogo sq., 141190 Fryazino, Russia*

Available online 8 January 2005

Abstract

Transient thermal grating and laser flash techniques have been used to measure in-plane ($k_{||}$) and perpendicular ($k_{\perp}$) thermal conductivity of 0.3–0.6 mm thick polycrystalline MPCVD diamond films. A small (<20%) anisotropy in k is revealed, and a correlation of k (8–20 W/cm K at RT) with optical absorption and hydrogen impurity concentration is established. The temperature dependence $k(T)$ between 293 and 460 K follows the relationship $k \sim T^{-n}$ (n=0.17–1.02) depending on the diamond quality.

Keywords: Diamond film; Thermal conductivity; Transient thermal grating; Laser flash technique

1. Introduction

Due to superior thermal conductivity of diamond, it is ideally suited for heat spreaders for electronic devices, e.g. laser diodes or microwave semiconductor devices. CVD diamond is especially promising for heat dissipation from large size thermal sources such as multichip modules (MCM) [1], since, unlike to HPHT and natural diamonds, the CVD films can be produced in planar dimensions exceeding 100 mm. The thermal properties are important also for performance of diamond optics of IR and radio frequency ranges. Typically, the thermal conductivity (k) of polycrystalline CVD diamond shows some anisotropy due to columnar crystallite growth [2]. In the present paper, we used the transient thermal grating [3] and a laser flash [4] non-contact techniques to measure in-plane and perpendicular thermal conductivity of thick diamond films of different qualities grown in a microwave plasma CVD reactor. The correlation of thermal and optical properties is traced. Since in some cases thermal spreaders must operate at temperatures up to 450–500 K, we measured the temperature dependence of thermal conductivity for the diamond films between 293 and 460 K and compared the results with the data of Burgemeister [5] for natural single crystals, in which nitrogen impurities determine the k value.

2. Experimental

The diamond films of different qualities (k=8–20 W/cm K at RT) with thickness in the range of 0.3 to 0.6 mm have been grown by microwave plasma CVD in CH_4/H_2 mixtures, with methane content varied from 1.5% to 5%, as described elsewhere [6]. The hydrogen and nitrogen impurity concentrations in the films were determined from UV (peak at 270 nm) and IR (stretching C–H vibrations in the range from 2800 to 3100 cm^{-1}) of optical absorption spectra, respectively, on the polished free-standing samples [7].

The in-plane thermal conductivity ($k_{||}$) was measured with the transient thermal grating (TTG) technique [3] that is based on the thermal grating recording in the sample by two interfering laser beams, and monitoring the thermal decay of the grating with a probe He–Ne beam diffracting on the TTG. The TTG with the period of 30–120 μm were

* Corresponding author. Tel.: +7 095 1328229; fax: +7 095 135 7672.
E-mail address: ralchenko@nsc.gpi.ru (V.G. Ralchenko).

0925-9635/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2004.12.002

excited in bulk by Nd:YAG laser pulses at 1064 or 266 nm wavelengths. The thermal diffusivity $D_{||}$ is determined from the exponential decay of the diffraction signal.

The laser flash technique (LFT) is based on measurement of travelling time of the thermal wave excited by a laser pulse, from one side of the plate to another [4,8,9]. In this case, the diffusivity $D_{\perp}$ in the direction perpendicular to the sample surface is determined. A pulsed YAG:Nd laser (wavelength 1.06 μm, pulse width 8 ns) was used for sample surface heating, while the temperature kinetics was monitored with a HgCdTe detector. Ti coating was deposited on both sides of the sample to enhance the laser absorption and IR emissivity. The thermal conductivity was found according to relation $k=D\rho C$, where ρ and C are density and the temperature-dependent specific heat of diamond, respectively.

3. Results

3.1. Room temperature measurements

A collection of samples grown upon a variety of synthesis conditions has been measured, and an inverse correlation of thermal conductivity and hydrogen impurity in the film has been established [9]. This finding is in a good agreement with the earlier result of Coe and Sussmann [10]. The thermal conductivity at room temperature is controlled by phonon scattering rate on various defects, grain boundaries and phonon–phonon interactions. Since hydrogen decorates the defects, the hydrogen impurity concentration is a convenient indicator of imperfections in CVD diamond [9–11]. Thermal conductivity vs. bonded H content in our diamond samples is shown in Fig. 1. The conductivity varies from 21 to 8 W/cm K when the bonded (C–H) hydrogen concentration ranges from 70 to 1000 ppm. The perpendicular values $k_{\perp}$ are systematically higher by 10–15% than the in-plane values $k_{||}$.

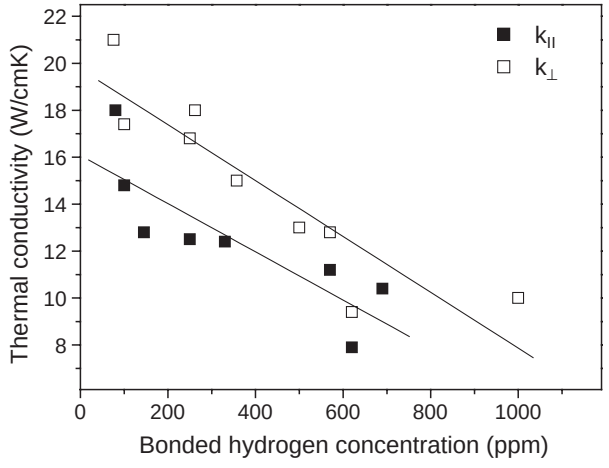

Fig. 1. Thermal conductivities $k_{||}$ and $k_{\perp}$ vs. concentration of bonded (C–H) hydrogen impurity in diamond films as measured from integrated IR absorption of stretching C–H modes between 2800 and 3100 cm^{-1}.

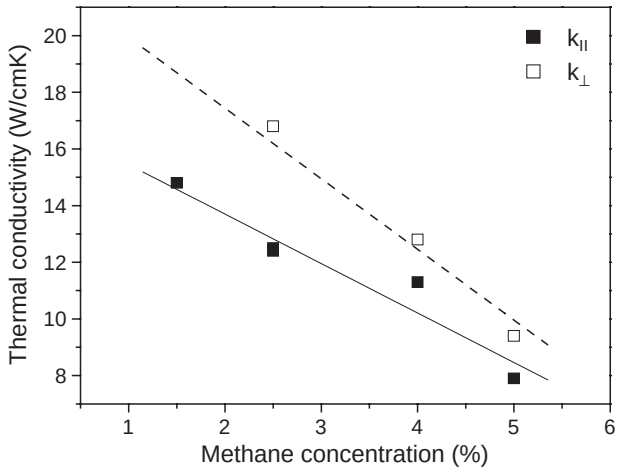

Fig. 2. Dependence of thermal conductivities $k_{||}$ and $k_{\perp}$ on CH_4 concentration in CH_4/H_2 mixture used for diamond deposition with other growth parameters kept constant: microwave power 5 kW, substrate temperature 717 °C, gas flow rate 400 sccm, pressure 100 Torr.

The source of anisotropy is a preferred location of defects at or near boundaries of columnar grains directed perpendicular to the film plane [2,12]. The enhanced concentration of defects, including extended ones, has been revealed along grain boundaries with transmission electron microscopy even in high quality films [13]. The thermal resistance would be less for phonons propagating along the columns than for those crossing the grain boundaries and the defect "atmosphere" around. Indeed, thermal barriers at the grain boundaries have been revealed [14] by local measurements of thermal diffusivity by photothermal microscopy and TTG.

The conductivity is found to decrease with the methane concentration in the source gas, as might be expected, since the supersaturation with hydrocarbons in gas phase leads to more defective material. This is illustrated in Fig. 2 for a set of the films produced at different CH_4 percentages in H_2, while keeping constant other deposition parameters. The bonded H in the films has been found to increase with CH_4 concentration in the gas mixture (not shown here), so the trend in Fig. 2 is in line with that in Fig. 1. As the unpurified hydrogen generated by an electrolyzer has been the H_2 source in these particular deposition runs, some nitrogen impurity was present in reaction chamber. While the CH_4 content in the gas mixture increased from 1.5% to 5%, the growth rate increased from 2.6 to 5.0 μm/h, however, by the cost of reduced thermal conductivity. Again, the anisotropy in k values is clearly seen for this series of the films.

Various point and extended defects impact not only the thermal conductivity, but result in enhanced optical absorption as well. In particular, since the nitrogen is the main impurity in natural diamonds, the correlation between the conductivity and characteristic absorption peaks in infrared region in nitrogen-contaminated natural single crystals of type Ia is well known [5]. Besides the specific absorption peaks, a continuous absorption background may exist in polycrystalline CVD diamond because of disordered regions