

# Simple model for the thermal conductivity estimation on the basis of Raman and ESR spectroscopy measurements

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The diamond films were grown at different working gas pressure in the range of 20–80 mbar by using hot filament chemical vapor deposition (HF CVD) technique. It was observed that the film morphology was dependent on deposition pressure and changed from so called “ball-like” via (111) and (100) type to the morphology of mixed character. The diamond film quality was studied by means of Raman and ESR (electron spin resonance) spectroscopy measurements. Within the presented work a simplified model for heat conductivity was proposed which allows to estimate the value of the thermal conductivity on the basis of Raman and ESR measurements. The obtained results are in good agreement with those reported in literature.

Keywords: diamond film, chemical vapor deposition (CVD), Raman spectroscopy, electron spin resonance (ESR), thermal conductivity.

## 1. Introduction

Due to excellent unique combination of physical properties diamond is an interesting material for many potential applications including mechanics, optics, heat management, passive and active electronic devices [1].

The properties of interest in this context include the wide band gap (5.45 eV), exceptional thermal conductivity (5 times higher than that of copper), high electrical resistivity ( $\sim 10^{16}$   $\Omega$ cm) and extreme hardness.

During the last few years the progress in chemical vapor deposition (CVD) of continuous diamond films has enhanced the prospects for many potential applications

of this material. However, the diamond films synthesized by various CVD techniques appear polycrystalline in nature and contain high defects concentration which is a limiting factor for applications in microelectronics and optics. In spite of this CVD diamonds are ready to be applied in mechanics as the abrasives and in thermal management as the heat sinks [2, 3].

The diamond structure ( $sp^3$ -covalently bonded carbon atoms) is metastable during the CVD growth process therefore the CVD diamond films can contain high concentration of defects such as voids, grain boundaries, lattice strain, impurity inclusion including, for example,  $sp^2$ -bonded carbon structures admixture. All these defects reduce the phonon life time and in consequence the thermal conductivity of the diamond films [4].

The thermal conductivity of CVD diamond film depends on films quality and in general is much lower than that of diamond monocrystal but is still higher than that of copper considered as a very good heat conductor.

Most of experimental techniques for the thermal conductivity measurements are based on the temperature gradients measurements. In the case of diamond the temperature gradient can be very small which causes some experimental problems in precise thermal conductivity measurements.

In present work we have developed a simple model for thermal conductivity estimation based on the Raman and ESR spectroscopy measurements. We believe, that the proposed model provides a quick and reliable method for CVD estimation of diamond films thermal conductivity.

## 2. Experimental

The present studies were carried out on the diamond films synthesized by the hot filament chemical vapor deposition (HF CVD) method from a gas mixture of  $CH_4$  (1%) and  $H_2$  (99%) with total gas pressure varying from 20 to 80 mbar. The tungsten filament was operated at 2000°C and was placed 8 mm above the substrate. The substrates 0.5 cm × 0.5 cm × 0.25 cm were cut from (100) single crystal silicon wafer.

In order to enhance diamond nucleation density the standard procedure was applied, *i.e.*, the substrate surface was polished mechanically and than cleaned in acetone, methanol and distilled water.

ESR measurements were carried out at room temperature in air by using X-band spectrometer with 100 kHz field modulation and modulation amplitude of 0.05 mT. The absolute number of spins in the samples was obtained by comparison under the same experimental conditions, with an  $\alpha$ ,  $\alpha'$ -diphenyl- $\beta$ -picrylhydrazyl (DPPH) reference.

The Raman spectra were recorded at room temperature in back scattering geometry using Jobin-Yvon T64000 Raman micro-spectrometer. The samples were excited by 514.5 nm argon laser line. The spectral resolution was set below 2  $cm^{-1}$ .

### 3. Results and discussion

The morphology of the synthesized diamond films was found to depend on the total pressure of the working gas. All synthesized films were thicker than  $20\ \mu\text{m}$ . The diamond films deposited at higher pressure than 20 mbar exhibit clear crystalline feature, while those grown at 20 mbar have a ball-like morphology without clear crystalline feature.

From the scanning electron microscopy (SEM) observation point of view the morphologies of the best and worst diamond film are presented in Figs. 1a and 1b. The Raman spectrum presented in Fig. 2 corresponds to the diamond film shown in Fig. 1a. It is dominated by the diamond Raman line peaked at  $1333.9\ \text{cm}^{-1}$  with FWHM (full width at half maximum) equal  $14\ \text{cm}^{-1}$  and contains also broad band at the maximum around  $1530\ \text{cm}^{-1}$  attributed to the  $sp^2$ -hybridized graphite-like carbon structure.

The Raman spectrum of the diamond film presented in Fig. 1b is shown in Fig. 3. This spectrum with a flat background is characterized by sharp diamond line at the

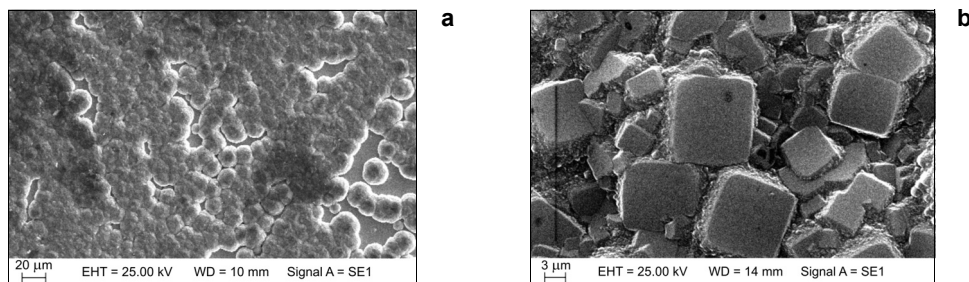


Fig. 1. Morphologies of diamond film synthesized at: 20 mbar (a), 80 mbar (b).

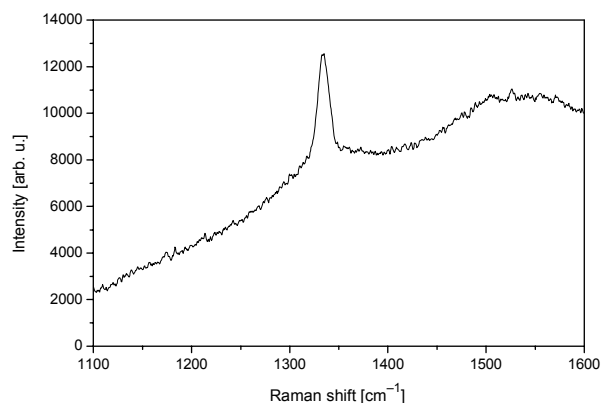


Fig. 2. Raman spectrum of the diamond film shown in Fig. 1a.

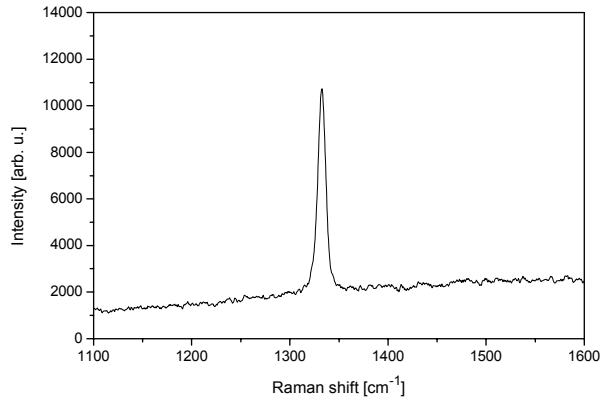


Fig. 3. Raman spectrum of the diamond film shown in Fig. 1b.

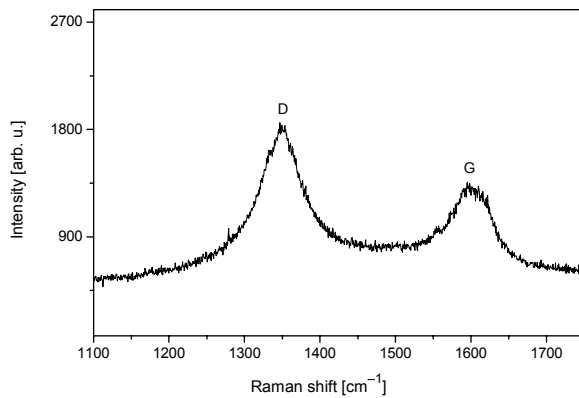


Fig. 4. Raman spectrum of the amorphous carbon film.

position of  $1332.6 \text{ cm}^{-1}$  with FWHM of  $7 \text{ cm}^{-1}$  and does not exhibit any broad band attributed to graphite-like phase admixture. The Raman spectrum of diamond monocrystal consist of single line at the position  $1332.5 \text{ cm}^{-1}$  with  $\text{FWHM} \leq 2 \text{ cm}^{-1}$  and is associated with triply degenerate phonon of  $F_{2g}$  symmetry [5]. The broadening of the diamond Raman line of the CVD diamond film is attributed to the reduction of the phonon life time due to different phonon scattering processes.

As it is seen in Fig. 2 the CVD diamond film contains some admixture of the non-diamond (graphite-like) phase. An example of the Raman spectrum of amorphous carbon (graphite-like carbon phase) is shown in Fig. 4 and it is composed of two broad bands having maxima around  $1340$  and  $1560 \text{ cm}^{-1}$ , respectively. These two bands are respectively called *D* and *G* line. The CVD diamond films contain always some amounts of amorphous carbon phase and its existence is reflected in the corresponding Raman spectrum. In order to estimate the diamond volume fraction  $\Phi_D$  the Raman

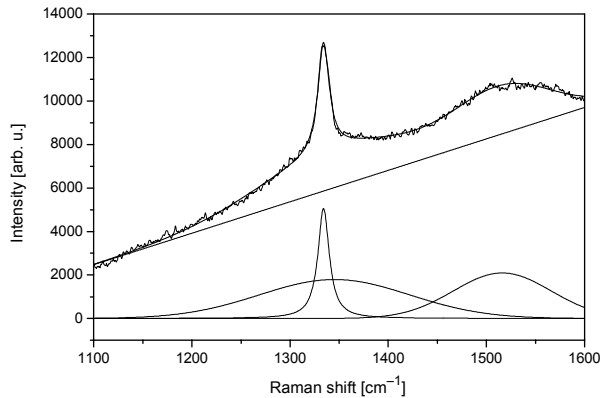


Fig. 5. Decomposition of the Raman spectrum shown in Fig. 2.

Table. Diamond Raman line parameters and estimated values of  $\Phi_D$  for diamond samples synthesized at different pressures.

Working gas pressure [mbar]	Diamond Raman line position [cm <sup>-1</sup> ]	Diamond Raman line FWHM [cm <sup>-1</sup> ]	Diamond phase volume fraction $\Phi_D$
20	1333.9	14.2	0.912
40	1333.1	12.3	0.938
50	1332.8	10.4	0.9604
60	1332.6	9.5	0.971
70	1332.5	7.2	0.986
80	1332.6	6.85	0.991
100	1332.3	7.35	0.975
120	1332.4	10.6	0.964

spectra of CVD diamond films were decomposed into three components as it is shown for illustration in Fig. 5. The value of  $\Phi_D$  (or amorphous carbon volume fraction  $\Phi_N = 1 - \Phi_D$ ) was calculated using procedure described elsewhere [6, 7] and the results are collected in the Table.

The graphite-like phase is a paramagnetic in nature [8] and the majority of point defects in diamond structure are also paramagnetic [9] therefore they can be detected by using ESR spectroscopy. An example of ESR signals of the CVD diamond film (*a*, *b* – corresponds to the films synthesized at 80 and 20 mbar respectively) are shown in Fig. 6. All investigated films were found to show symmetrical resonance line shape with peak-to-peak  $\Delta B_{pp}$  width ranging from 0.3 to 0.8 mT depending on the film quality. The estimated spin densities for diamond films deposited at different pressure are presented in Fig. 7.

The best diamond film synthesized at 80 mbar, contains lowest spin concentration. All defects in the diamond film reduce its thermal conductivity.

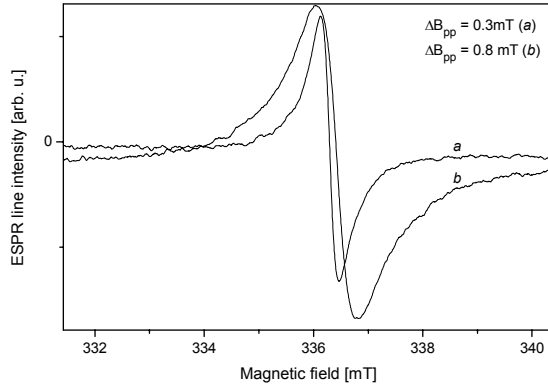


Fig. 6. ESR spectra of the diamond films synthesized at: 80 mbar (a), 20 mbar (b).

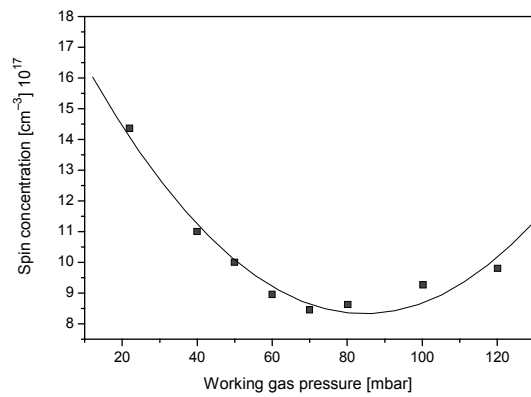


Fig. 7. Spin concentration in diamond film vs. deposition pressure.

In general the thermal conductivity of solids is temperature dependent and according to the model developed by CALLOWAY [10] and refined by HOLLAND [11] is given by formula:

$$\lambda = \frac{1}{3} V^2 \int_0^{\theta_0/T} C_v \tau dx_\omega \quad (1)$$

where:  $\theta$  – Debye temperature,  $C_v$  – specific heat per volume,  $V$  – phonon velocity,  $\tau$  – phonon relaxation time,  $x_\omega = \hbar\omega/kT$ ,  $k$  – Boltzmann's constant,  $T$  – temperature,  $\hbar = h/2\pi$ , ( $h$  – Planck's constant).

According to formula (1) the thermal conductivity in crystalline solids is governed by the temperature dependence of specific heat and rates of phonon scattering on other phonons, impurities, defects, grain boundaries and dislocations [10–12].

At room temperature the main mechanism contributing to thermal resistance is phonon–phonon scattering. The phonon boundary scattering limits the phonons free path and plays an essential role at lower temperatures [13].

At room temperature the thermal conductivity of solid can be represented by the expression

$$\lambda = \frac{1}{3} \sum C_i V_i^2 \tau_i \quad (2)$$

where  $i$  – denotes the type of heat carrier.

The main heat carrier of an insulator such as diamond film is the phonon and according to Debye approximation the heat conductivity is described by:

$$\lambda = \frac{1}{3} C V^2 \tau \quad (3)$$

$C$  – specific heat,  $V$  – speed of phonons (can be taken average sound velocity equal 13500 m/s [13]),  $\tau$  – effective relaxation time.

The relaxation time is determined by the three scattering processes. These are: scattering by phonon collisions, crystal lattice defects and grain boundaries and according to Mathiessen's rule [14] one can write:

$$\tau^{-1} = \tau_{\text{phonon}}^{-1} + \tau_{\text{defect}}^{-1} + \tau_{\text{boundary}}^{-1} \quad (4)$$

As it was mentioned earlier, the grain boundaries play essential role only at lower temperature, and at room temperature their influence on  $\tau$  value is negligible, so we can rewrite Eq. (4) in the form:

$$\tau^{-1} = \tau_{\text{phonon}}^{-1} + \tau_{\text{defect}}^{-1} \quad (5)$$

By multiplying Eq. (5) by sound velocity  $v$  we will find the mean free paths to particular scattering process:

$$l^{-1} = l_{\text{phonon}}^{-1} + l_{\text{defect}}^{-1} \quad (6)$$

Taking the above consideration into account we can rewrite the Eq. (3) in the following form:

$$\lambda = \frac{1}{3} C V^2 \tau = \frac{1}{3} C V l = \frac{1}{3} C V \frac{l_{\text{phonon}} l_{\text{defect}}}{l_{\text{phonon}} + l_{\text{defect}}} \quad (7)$$

On the basis of phonon confinement model, FABISIAK [15] showed that there exists a following relationship between the FWHM of the diamond Raman line and phonon free path:

$$\text{FWHM} \times l_{\text{phonon}} \approx 90 \quad [\text{nm cm}^{-1}] \quad (8)$$

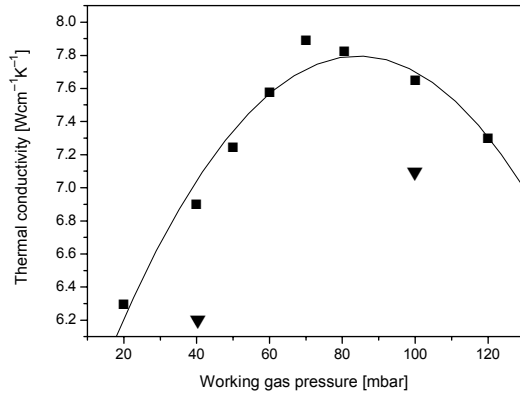


Fig. 8. Values of thermal conductivities as a function of deposition pressure (■ – the estimated values, ▼ – the measured values).

Using this relationship one can estimate  $l_{\text{phonon}}$ . Let us assume that  $l_{\text{defect}}$  is in a simple relationship to defect density  $N_s$  as measured by ESR:

$$l_{\text{defect}} = N_s^{-\frac{1}{3}} \quad (9)$$

Having estimated values of  $l_{\text{phonon}}$  and  $l_{\text{defect}}$ , and using formula (7) one can estimate the heat conductivity. The results as a function of deposition pressure are shown in Fig. 8.

The obtained values of heat conductivities are in the range of 6–8  $\text{Wcm}^{-1}\text{K}^{-1}$  and are very similar to values reported in literature [16–21]. In Figure 8 the values of thermal conductivities measured for two our samples are shown as well. As it is visible measured values are only about 10% lower in comparison to estimated values.

BACHMANN *et al.* [19] found that the thermal conductivities of the thin diamond films are always below 8  $\text{Wcm}^{-1}\text{K}^{-1}$  independently of deposition conditions. ONO *et al.* [20] measured the maximum value 10  $\text{Wcm}^{-1}\text{K}^{-1}$  of thermal conductivity of the diamond films having thickness in the range of 7–30  $\mu\text{m}$ .

KAENEL [21] has carried out the thermal conductivity measurements on the films of thickness ranging from few to 50  $\mu\text{m}$  and has found that thermal conductivity depends on films thickness. According to his measurements the thermal conductivity increases from 1  $\text{Wcm}^{-1}\text{K}^{-1}$  for few  $\mu\text{m}$  thick film to 8  $\text{Wcm}^{-1}\text{K}^{-1}$  for 20  $\mu\text{m}$  thick film. After exceeding the thickness of 20  $\mu\text{m}$  the saturation is observed, *i.e.*, for thicker films the thermal conductivity is independent of film thickness and has constant value equal to about 8  $\text{Wcm}^{-1}\text{K}^{-1}$ .

The values of thermal conductivities estimated on basis of our simplified model are in very good agreement with the data reported in literature.



#### 4. Summary

The diamond films were synthesized by using HF CVD method. The films quality and morphology, as studied by SEM, Raman and ESR spectroscopy, was found to be dependent on the deposition pressure.

For thermal conductivity estimation, the simplified model of heat conductivity was proposed.

It was shown that proposed model provides a quick and reliable method for thermal conductivity estimation giving results being in good agreement with the data reported in literature.

The estimated results are about 10% higher in comparison to measured values.

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