*Optica Applicata, Vol. XXXIX, No. 4, 2009*

# Electron paramagnetic resonance and scanning electron microscopy characterization of diamond films fabricated by HF CVD method

Kazimierz FABISIAK[1*], Maciej SZREIBER[1], Cezary UNISZKIEWICZ[1],
Tomasz RUNKA[2], Dobrosława KASPROWICZ[2]

[1]Institute of Physics, Kazimierz Wielki University, Weyssenhoffa Sq.11, 85-072 Bydgoszcz, Poland

[2]Faculty of Technical Physics, Technical University of Poznań, Nieszawska 35A, 60-965 Poznań, Poland

[*]Corresponding author: kfab@ukw.edu.pl

Defects in diamond films, produced by the hot filament chemical vapour deposition (HF CVD) of methanol and hydrogen mixture as function of gas composition, were investigated by electron paramagnetic resonance (EPR), scanning electron microscopy (SEM) and Raman spectroscopy measurements. We found an isotropic $g$-value ($2.003\pm0.0002$) independent of growth conditions. The peak-to-peak of EPR line width changes from 0.3 to 0.6 mT and the spin density increases from $2.3\cdot10^{17}$ to $3.2\cdot10^{18}$ spin/cm$^{-3}$ with increasing concentration of methanol vapour. The EPR line in general shows double character and was found to be superposition of two components, a narrower Lorentzian and a broader Gaussian, suggesting the existence of two different types of defects in diamond layer. EPR measurements were supported by SEM observation.

Keywords: hot filament chemical vapour deposition (HF CVD), diamond, electron paramagnetic resonance (EPR), Raman spectroscopy.

## 1. Introduction

The growth of diamond at low pressures, using chemical vapour deposition (CVD) methods, is an interesting problem both in the growth of crystals and potential applications. The mechanical, thermal, optical and electrical properties of diamond are extremely attractive to technological interest [1–3]. While the mechanical and thermal properties of thin diamond films may not be strongly dependent on point defects, the optical and electrical properties may be dominated by such type of defects. Despite the significant progress in the field of diamond growth, the fundamental scientific problems remain still unresolved. One of them is the question of diamond nucleation and growth under conditions where diamond should be thermodynamically unstable relative to graphite. In such conditions the co-deposition of amorphous carbon phase is very probable. This phase of carbon structure in the diamond film is an additional source of defects, which could be paramagnetic in nature. Electron paramagnetic resonance (EPR) is a powerful technique to study the paramagnetic point and extended defects.

Natural and high-pressure high-temperature synthetic diamonds were extensively studied by EPR and an excellent review article was published by Loubser and van Wyk [4]. In this paper, we have studied the defect structures in different quality diamond films using EPR and SEM techniques.

## 2. Experimental

The randomly-oriented polycrystalline diamond films were grown in hot filament CVD reactor. All the films were grown on (100) oriented *n*-type Si substrate with resistivity of 2 Ωcm. The growth conditions were almost the same for all samples, namely: hot filament was operated at a temperature of 2400 K, $CH_3OH/H_2$ flow ratio changed from 0.5 to 2.0%, substrate temperature was kept at 1100 K. Before diamond deposition, in order to enhance diamond nucleation density, the substrate was mechanically polished with diamond powder in order to introduce the surface defects acting then as diamond nucleation centers. After polishing the substrate was washed in ultrasonic bath with methanol and deionized water. The total gas pressure in the reactor was 50 mbar. SEM picture was taken using Jeol-820 scanning electron microscope working at 25 kV. The EPR spectra were recorded in air at room temperature by Varian X-band EPR spectrometer.

## 3. Results and discussion

The surface morphology of the diamond films investigated was found to depend on methanol concentration in working gas mixture (see Figs. 1–3). The diamond film

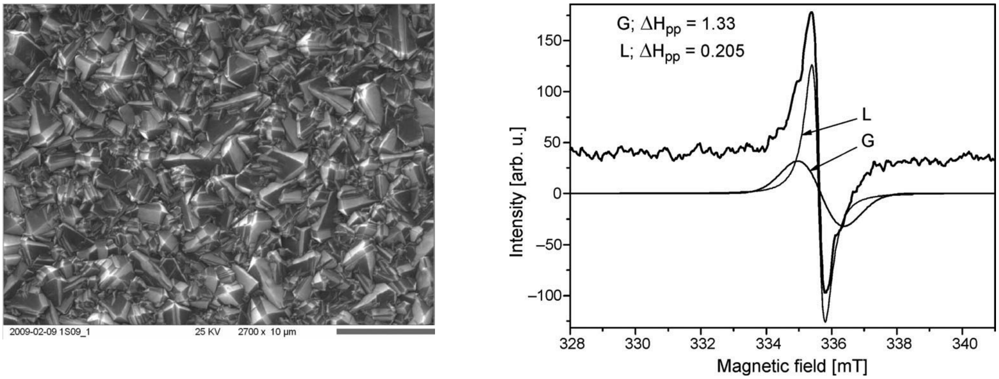

Fig. 1. SEM picture of diamond morphology synthesized at: 0.5% concentration of methanol vapour and corresponding EPR spectrum (inset: peak-to-peak line widths for Lorentzian ($L$) and Gaussian ($G$) components).

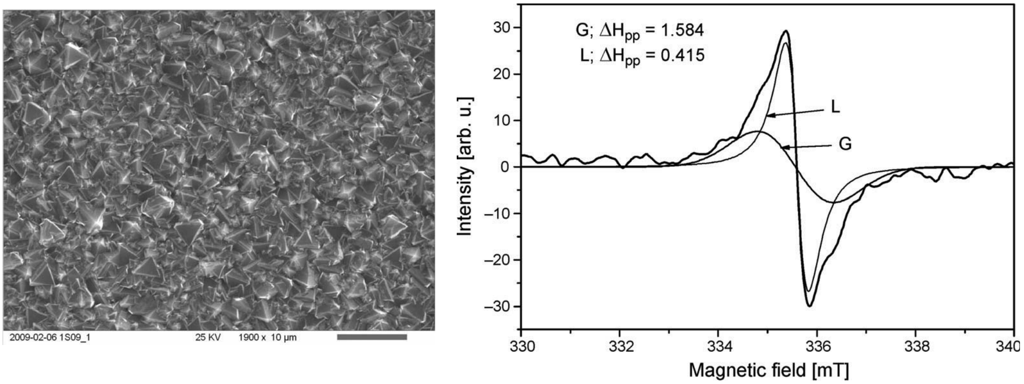

Fig. 2. SEM picture of diamond morphology synthesized at: 1% concentration of methanol vapour and corresponding EPR spectrum (inset: peak-to-peak line widths for Lorentzian ($L$) and Gaussian ($G$) components).

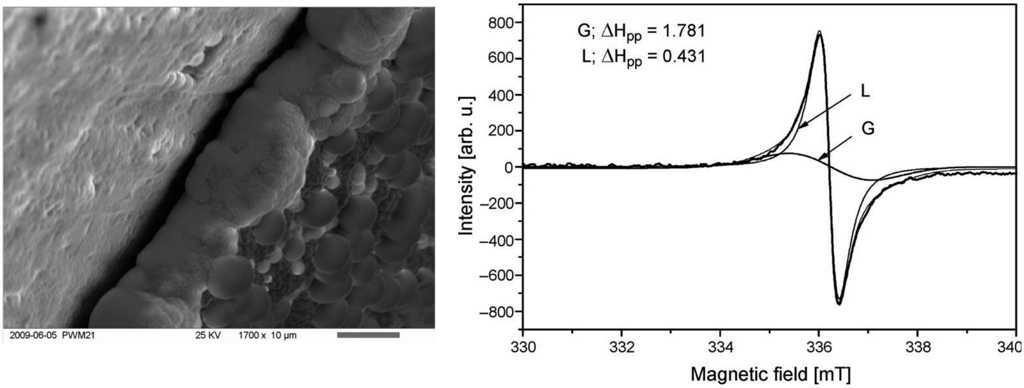

Fig. 3. SEM picture of diamond morphology synthesized at: 2% concentration of methanol vapour and corresponding EPR spectrum (inset: peak-to-peak line widths for Lorentzian ($L$) and Gaussian ($G$) components).

synthesized at the methanol vapour concentration of 0.5% shows clear, well-faceted crystal features. The sizes of the microcrystals are of the order of 3–6 µm. With increasing methanol vapour concentration to 1% the microcrystals have still clear crystalline feature but their sizes decrease to the value of 1 µm or even less. At the highest methanol vapour concentration equal to 2% the morphology of the film obtained loses the crystalline character and shows “ball-like” feature. Each of the balls is composed of many crystallites of the nanometer in size.

All the diamond films investigated were found to show symmetrical EPR resonance line shape which can be deconvoluted into two components, a narrower Lorentzian ($L$) and a broader Gaussian ($G$) component, as shown in Figs. 1–3.

The procedure used for deconvolution is a nonlinear best fit based on the Marquardt method [5]. From Figures 1–3 it is clearly seen that the EPR line changes its shape, *e.g.*, intensity (this must be normalized taking the mass of the samples into account) and peak-to-peak line width with increase of methanol concentration.

The estimated spin densities from the EPR spectra presented in Figs. 1−3 are respectively: $2.3 \cdot 10^{17}$ spin/cm$^{-3}$, $7.8 \cdot 10^{17}$ spin/cm$^{-3}$ and $3.2 \cdot 10^{18}$ spin/cm$^{-3}$. This means that diamond films become more and more defective, which was already observed [6].

The most important aspect of this study is that the HF CVD technique of diamond synthesis results in a variety of their morphologies, which strongly depends on the working gas composition. During the diamond growth process there is a competition between the diamond and graphite phase deposition. At higher hydrocarbon concentrations in the working gas the co-deposition of amorphous, graphite-like phase becomes more probable. This is clearly seen in EPR spectra (Fig. 2). Generally, it is assumed that $G$ component of EPR spectrum is responsible for paramagnetic defects associated with amorphous carbon phase and $L$ component is ascribed to the point defects in diamond crystal lattice [7−9].

The ratio of integral intensities of $L$ to the $G$ components of EPR spectra decreases with hydrocarbon concentration increasing, indicating an increase of the amorphous carbon admixture. The EPR lines broaden especially their $G$ components, which is in agreement with the fact that spin concentration also increases. EPR observations are in agreement with an evolution of the morphology of diamond films. As is seen from Figs. 1−3, with increasing hydrocarbon concentration in the working gas the morphology changes dramatically and microcrystals become smaller and density of grain boundaries increases. We speculate that the amorphous carbon phase is deposited between grains rather than inside the diamond structure.

## 4. Conclusions

This work demonstrates the use of EPR and SEM techniques as a powerful tool for characterization of diamond films. SEM pictures show the evolution of diamond film morphology from the well defined polycrystalline structure to the ball-like structure depending on hydrocarbon concentration in the working gas.

Each diamond sample is characterized by symmetrical EPR line having double character.

Each EPR spectrum was composed of two components, Lorentzian and Gaussian. Gaussian component increases faster with an increase of hydrocarbon concentration than Lorentzian one, indicating faster co-deposition of amorphous carbon phase. EPR and SEM observation are in good agreement and confirmed that EPR technique is a powerful technique for diamond quality estimation.

*Acknowledgement* – This work was supported by the Ministry of Higher Education and Science, Grant No. R02 022 01.

## References

[1] Kalish R., *The search for donors in diamond*, Diamond and Related Materials **10**(9–10), 2001, pp. 1749–1755.

[2] Mizuochi N., Ogura M., Watanabe H., Isoya J., Okushi H., Yamasaki S., *EPR study of hydrogen-related defects in boron-doped p-type CVD homoepitaxial diamond films*, Diamond and Related Materials **13**(11–12), 2004, pp. 2096–2099.

[3] Pei Sann Siew, Kian Ping Loh, Wei Choong Poh, Heng Zhang, *Biosensing properties of nanocrystalline diamond film grown on polycrystalline diamond electrodes*, Diamond and Related Materials **14**(3–7), 2005, 426–431.

[4] Loubser J.H.N., van Wyk J.A., *Electron spin resonance in the study of diamond*, Reports on Progress in Physics **41**(8), 1978, pp. 1201–1248.

[5] Marquardt D.W., *An algorithm for least-squares estimation of nonlinear parameters*, Journal of the Society for Industrial and Applied Mathematics **11**(2), 1963, pp. 431–441.

[6] Duosheng Li, Dunwen Zuo, Wenzhuang Lu, Rongfa Chen, Bingkun Xiang, Min Wang, *Effects of methane concentration on diamond spherical shell films prepared by DC-plasma jet CVD*, Solid State Ionic **179**(21–26), 2008, pp. 1263–1267.

[7] Orzeszko S., Bała W., Fabisiak K., Rozpłoch F., *DC conductivity and ESR of hydrogenated amorphous carbon films*, Physica Status Solidi (a) **81**(2), 1984, pp. 579–584.

[8] Viana G.A., Lacerda R.G., Freire F.L., Marques F.C., *ESR investigation of graphite-like amorphous carbon films revealing itinerant states as the ones responsible for the signal*, Journal of Non-Crystalline Solids **354**(19–25), 2008, pp. 2135–2137.

[9] Stesmans A., Nouwen B., Iakoubovskii K., *Electron spin resonance characterization of a divacancy-related centre in CVD diamond*, Journal of Physics: Condensed Matter **12**(35), 2000, pp. 7807–7818.

*Received June 23, 2009*
*in revised form July 29, 2009*