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Optimization of Polycrystalline CVD Diamond Seeding with the Use of sp^3/sp^2 Raman Band Ratio

L. Golunski[a,*], M. Sobaszek[a], M. Gardas[a], M. Gnyba[a], R. Bogdanowicz[a], M. Ficek[a] and P. Plotka[b]

[a]Department of Metrology and Optoelectronics, Faculty of Electronics, Telecommunications and Informatics,
Gdańsk University of Technology, G. Narutowicza 11/12, 80-233 Gdańsk, Poland

[b]Department of Microelectronic Systems, Faculty of Electronics, Telecommunications and Informatics,
Gdańsk University of Technology, G. Narutowicza 11/12, 80-233 Gdańsk, Poland

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The influence of various nanodiamond colloids used for seeding nondiamond substrates in microwave plasma enhanced chemical vapour deposition diamond process was investigated. Colloids based on deionized water, isopropanol alcohol and dimethyl sulfoxide (DMSO) were used with different grain size dispersion: 150, 400 and 35 nm, respectively. The influence of growth time was also taken into consideration and bias enhanced nucleation. Microcrystalline diamond films were deposited on the seeded substrates in microwave plasma chemical vapour deposition using hydrogen–methane gas mixture. Seeding efficiency was investigated by means of scanning electron microscopy and Raman spectroscopy. Authors defined the new factor called as diamond ideality factor (*di*) which can give a quick estimation of quality of film and relative sp^3 content. Few main peaks were identified at the following wave numbers: diamond sp^3 peak 1332 cm^{-1}, D band peak 1355 cm^{-1}, C–H bending peak 1440–1480 cm^{-1} and G band peak 1560 cm^{-1}. The best *di* was achieved for DMSO based colloid in all cases. The application of bias enhanced nucleation increases the diamond crystals size and the sp^3/sp^2 ratio.

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1. Introduction

Due to its mechanical [1, 2] and electrical [3, 4] properties, diamond is a very interesting object of study and applications. It has been used in many different fields such as, semiconductors, biosensors, DNA sensors, etc. [5–7]. In the chemical vapour deposition (CVD) process thin-film diamond can be deposited in a pure or doped form on different substrates, particularly on silicon ones. The main trouble of the low-pressure CVD process is appearance of competing amorphous and crystalline sp^2 phases, especially during the early stage of the film growth. This is results of the mismatch of the crystalline network of substrate and the film. Even monocrystalline diamond and silicon that have the same type of crystalline network, differ in lattice constants ($\Delta = 1.86412$ Å). Therefore it is necessary to seed the non-diamond substrates in order to deposit a high quality diamond film on their surface [8, 9]. Silicon substrates can be seeded for nanodiamond growth in different ways, e.g. by mechanical polishing of the substrate with diamond powder [8, 9]. Most commonly, substrates covered in diamond slurry are treated ultrasonically [10–12]. Substrates are coated by carbon materials [13], including diamond-containing materials [14, 15]. Moreover, diamond growth can be supported by applying negative voltage to the stage which does not alter the silicon surface during the preliminary treatment and has low seed density via applying. This method is called bias enhanced nucleation (BEN) [16, 17]. The use of highly dispersed colloids increases the seed density, which should result in a measurable effect, i.e. high sp^3 content in the polycrystalline CVD diamond film, providing properties comparable to those of a natural diamond. In order to obtain seeding colloids, detonation nanodiamond (DND) powder particles could dispersed in water [10, 18], isopropanol [19] or dimethyl sulfoxide (DMSO) [20]. Isopropanol is one of the most popular solvent for DND seeding [19]. Also commonly used solvent is deionized water which was reported by Gajewski et al. [18]. Shenderova et al. showed the influence of different types of diamond in DMSO solvent on diamond seeding efficiency [20].

The influence of seeding is usually measured by density of seeding or nucleation [10, 21]. This method could be performed in two ways by counting density of seeds just after seeding or after few minutes of growth. To estimate number of seeds on selected area is necessary to use atomic force microscope or SEM for the surface imaging [10, 21]. There are a few factors proposed to determine the quality of the diamond films [22]. One of them is purity index proposed by Braga et al. [22]. Purity index is based on intensity of diamond and non-diamond bands in the Raman spectrum. It also takes into account that intensity of the band assigned to sp^2 phase has about 50 times higher value than from the band assigned to diamond lattice [22, 23]. The Raman spectra are usually deconvoluted by two profiles (Lorentzian and Gaussian) for the most important bands [24–28] and used

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[*] corresponding author; e-mail: lgolunski@gmail.com

for evaluation of deposited films. However, the optimization of seeding efficiency of diamond films formed during the early-stage of CVD process by means of the Raman spectroscopy with deconvolution of the spectra has been not reported yet.

The aim of research presented in this paper is to determine which seeding colloid provides the highest possible content of the sp^3 crystalline carbon and continuity of the growing diamond films. The investigated diamond films were deposited using microwave plasma assisted chemical vapor deposition (MW PA CVD) process. Authors defined the new factor called as *diamond ideality factor* (*di*) to estimate quality of film and relative sp^3 content. Different growth time durations of CVD processes were investigated. Three different colloids with nanodiamond particles were applied to seed the Si substrates. The influence of bias enhanced nucleation (BEN) on the growth of diamond film was also investigated. The morphology of diamond films was investigated by means of scanning electron microscope while sp^3/sp^2 relative ratio by the Raman spectroscopy.

2. Experimental

In order to study seeding different colloids, mixtures of the nanodiamond powder with deionized water, isopropanol and DMSO were prepared. The polarity index influences significantly on the stability of the colloids as well as the nanodiamond agglomerates size (see Table I). The detonation nanodiamond powder (DND, ND-50, Henan Union Abrasives, China) with prior cluster size up to 50 nm was used for experiments. Due to specificity of applied media, the nanodiamond colloids were produced using various procedures. The DI water- and isopropanol-based colloids were obtained in one-step procedure. Two 0.033 g portions of nanodiamond powder were weighed and placed in two beakers. A volume of 100 ml of isopropanol was added to one beaker, and 100 ml of deionized water was added to the other. Both mixtures were stirred with a magnetic stirrer for 10 min. A fresh colloid was prepared prior to each seeding procedure to reduce precipitation of the dispersed nanodiamond.

TABLE I

Physico-chemical parameters of utilized seeding suspensions.

Medium	Dispersion technique	Dispersed grain size [nm]	Polarity index
DMSO	high power sonication	30–35	1
DI water	high power sonication	150–200	0.88
isopropanol	high power sonication	400–500	0.55

The DMSO-based nanodiamond colloid was prepared by the multistage process. The nanodiamond powder was placed in a round bottom flask and then mixed with a solution of dimethylformamide, allyl bromide and sodium carbonate. The mixture was stirred with a magnetic stirrer and heated to the moderate boiling point. The whole process was continued for *ca.* 24 h. Subsequently, the mixture was cooled down to room temperature and subjected to vacuum filtration. The prepared colloid was centrifuged at 3000 rpm and evaporated until the color turned black. Then it was placed in the refrigerator to trigger salt precipitation. The black liquid was mixed with 5 volumes of DMSO and evaporated again until it turned black in color. The operation was repeated three times. The obtained colloid was centrifuged again and analyzed with dynamic light scattering technique to determine the dispersed grain size (30–35 nm).

Prepared colloids were used for Si wafer seeding. *p*-Si(100) substrates having resistance of 0.001–0.005 Ω cm were used during presented research. The substrates were pretreated by 5 min immersions in acetone and isopropanol. After a 1 h seeding process, the silicon wafers were rinsed in isopropanol and dried under a stream of nitrogen gas. The substrates were later placed inside a vacuum chamber of the CVD system (Seki, USA AX5400) and the pressure was brought down to 10^{-4} Torr. Subsequently, the chamber was filled with a hydrogen–methane gas mixture to reach the pressure of 50 Torr; the CH_4:H_2 ratio was 1% and the total flow rate was 300 sccm. The induced plasma was obtained by using microwave radiation (2.45 GHz) with power of 1300 W source, which is the best for the diamond growth [29–31]. The sample holder inside the chamber was kept at 700 °C. Diamond films were grown for 30 or 120 min. Each colloid and time were investigated with and without influence of BEN with negative voltage to the sample holder (−250 V).

TABLE II

Seeding and growth parameters for different types of seeding.

Sample	Medium containing diamond seeds	Growth time [min]	BEN
WAT-30	DI water	30	OFF
WAT-30-B	DI water	30	ON
WAT-120	DI water	120	OFF
WAT-120-B	DI water	120	ON
ISO-30	Isopropanol	30	OFF
ISO-30-B	Isopropanol	30	ON
ISO-120	Isopropanol	120	OFF
ISO-120-B	Isopropanol	120	ON
DMSO-30	DMSO	30	OFF
DMSO-30-B	DMSO	30	ON
DMSO-120	DMSO	120	OFF
DMSO-120-B	DMSO	120	ON

The growth and seeding parameters for each sample are presented in Table II. The morphology of each sample was evaluated by scanning electron microscopy (SEM). The secondary electrons mode was utilized with a 20 kV accelerating voltage. The Raman spectra were recorded in a spectral range of 200–3500 cm^{-1}, with an integration time of 20 s using a 532 nm diode pumped solid state (DPSS) at 10 mW power, by using a Raman microscope (Renishaw, USA, equipped with a 100 × /0.95 objective and 50 μm of pinhole). The values of the relative integral intensity sp^3/sp^2 band ratio were determined by fitting the sharp Raman peak assigned to diamond lattice (about 1332 cm^{-1}) and G band (wide band at 1560 cm^{-1}) in the Origin Pro-9.0 software. Lorentzian and Gaussian profiles were used respectively. Spectra were smoothed by the Savitzky–Golay method. The background was subtracted by the weighted end points method. The peaks were identified as 1st derivative values.

3. Results and discussion

The morphology of the growing diamond films for 30- or 120 min depositions was assessed by using a SEM (see Fig. 1). Size of crystals varied from tens nm to about 1 μm depending on process parameters. The largest of crystals were obtained in 120 min process in all colloids. Investigation of films after short time deposition (30 min) shows similar size of crystallites independently of the use of BEN. The homogeneity of these film was very high with the average size of grains around 40–60 nm. Nevertheless, deposition for long time (120 min) with active BEN shows diamond grains smaller than 1 µm. The grains were larger than observed for 30 min process but smaller than after 120 min without BEN. Their size achieved 100–200 nm. It goes to conclusion that using of BEN during the growth is changing the morphology of the film. The experiment shows that the crystal renucleation [32] on diamond grains occurs when the negative voltage is applied to the substrate. It causes also the decrease of the size of grains.

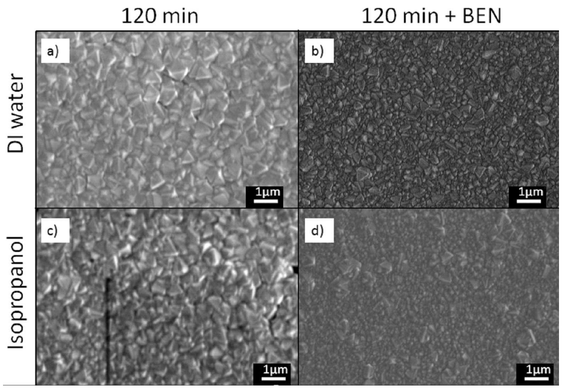

Fig. 1. SEM pictures of films after 120 min deposition: (a) WAT-120, (b) WAT-120-B, (c) ISO-120, (d) ISO-120-B. For 120 min process with active BEN (b,d) there is visible decrease of crystallites to process without BEN (a,c).

Deposited thin diamond films were examined by means of the Raman spectroscopy. Based on the results of the Raman spectroscopy (Fig. 2) relative sp^3/sp^2 band ratios were calculated for each sample. For this purpose a few main peaks were identified at the following wave numbers: 1332 cm^{-1} (peak assigned to sp^3 diamond lattice) [24–28], 1355 cm^{-1} (D band — assigned to distorted sp^3 and sp^2 lattice) [24–26, 28], 1440–1480 cm^{-1} [24, 25] (C–H bending and transpolyacetylene), and 1560 cm^{-1} (sp^2 peak corresponding to amorphous carbon G band) [24, 25, 27, 28] (see Fig. 3). The peak at 1332 cm^{-1} was fitted by a Lorentz profile, while the line at 1560 cm^{-1} — by a Gaussian profile.

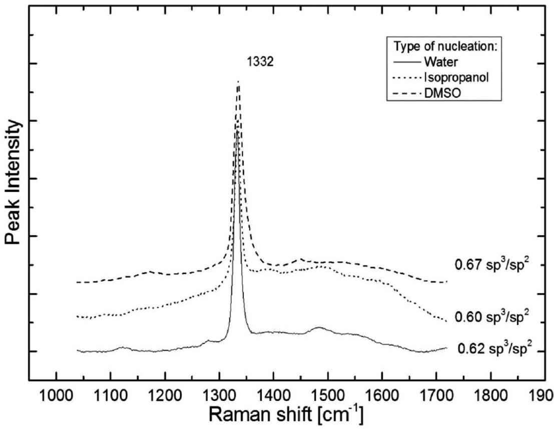

Fig. 2. Comparison of Raman spectra for 30 min deposition vs different seeding pretreatment. The highest values of sp^3/sp^2 band ratio are represented for solvent with the smallest dispersed grain size (DMSO 30–35 nm).

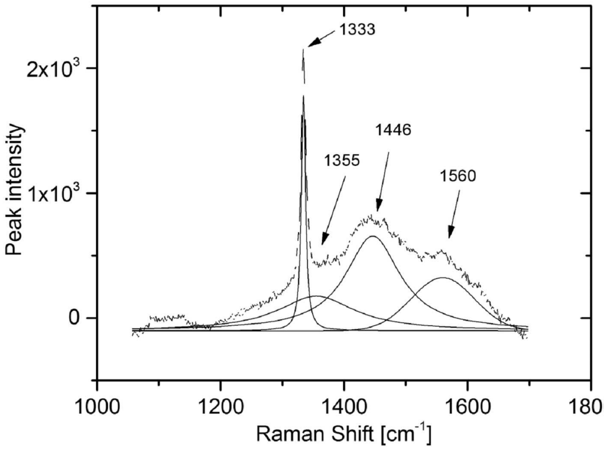

Fig. 3. Example deconvolution of Raman spectra in the range of 1000–1800 cm^{-1}, four main peaks were marked. The 120 min deposition using DMSO-based colloid seeding is presented.

Hu et al. [33] proposed to use relative factor of refractive indices (Eq. (2)) for calculating of optical density shift in polycrystalline films, which results from defects and porosity. Moreover, refractive index of the carbon material depends on sp^3/sp^2 ratio [34], therefore it is possible to introduce new material parameter which would allow for easy comparison of materials and correlation of the optical parameters and the Raman spectra.

Here, we propose to use this equation as a relative factor of sp^3/sp^2 Raman band ratios to estimate di. The di was calculated from the following Eq. (1):

$$di = \frac{\frac{sp^3}{sp^2} + 1 \, \frac{sp^3_{\rm d}}{sp^2_{\rm d}} + 2}{\frac{sp^3}{sp^2} + 2 \, \frac{sp^3_{\rm d}}{sp^2_{\rm d}} + 1}, \qquad (1)$$

where: sp^3/sp^2 — relative integral intensity ratio for the investigated film, $sp^3_{\rm d} sp^2_{\rm d}$ — relative integral intensity ratio for single crystal diamond.

Mathematical formula reported by Hu et al. [33] results in easy and direct comparison of various quality polycrystalline CVD diamond to the gold standard — high quality single crystalline diamond (e.g. CVD single crystalline diamond on HPHT diamond substrate) [31, 35]. In most of cases sp^2 is not equal to zero, but if it really reaches zero (in practice is very small) then ideality factor reaches 1 so "ideal material" means pure monocrystalline diamond.

The value of di factor increases with increasing deposition time. For the same seeding procedure, the di was about 50% higher for the 120 min long processes than for 30 min long one. In each case, the use of isopropanol based colloid resulted in the lowest value of the di. Substrates pretreated in DI water or DMSO based colloids have higher di values than prepared in isopropanol. For each case use of DMSO as solvent for diamond particles results in slightly higher di value than of water. This effects can be explained by two factors: polarity index of colloid and microscopic differences between colloids. Polarity index of the colloids and grain sizes are summarized in Table I. The main microscopic difference between the three aforementioned colloids is that diamond seeds in DMSO are dispersed throughout the medium, and the bond between the diamond particle and solvent molecule is stronger than that between the diamond particles themselves [36]. Nanodiamond grains agglomerate rapidly in media with low polarity indices [37].

Moreover, DI water- and isopropanol-based colloids were produced by ultrasound treatment. They rapidly settled in the absence of ultrasonic field. Very weak or even no interaction between the solvent and nanodiamond grains was noticed. This phenomenon can be measured as each particle in the colloid is trapped into a double electric film which, in turn, has its own potential called zeta potential. Under normal conditions, stable colloids display the absolute value of zeta potential higher than 50 mV, while these quasi-stable, around 30–40 mV. Mixtures that instantly settle usually have the zeta potential less than 10 mV.

The agglomerate size in seeding colloid influence mostly on the seeding density so changes morphology of the thin film [38]. It has a minor influence on the sp^3/sp^2 ratio, which is mostly driven by nanodiamond impurities or inefficient wetting of substrate by seeding colloid resulting from other polarity index [39].

It can be observed in Fig. 4 that using different colloids provides the same trend of changes for di in each process.

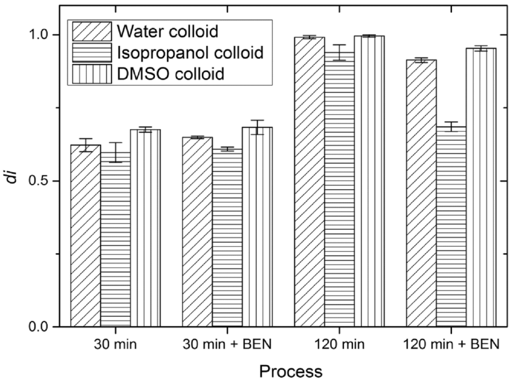

Fig. 4. Diamond ideality factor vs process parameters and various seeding colloid.

For isopropanol colloid with the biggest dispersed grains and the lowest polarity index there is observed the lowest di factor. In the opposite way DMSO works. The DMSO-based colloid with the smallest dispersed diamond grains and the biggest polarity index in each process has slightly better di than water. For pretreatment in water based colloid which has got zeta values in between DMSO and isopropanol the medium di factor is observed. The application of BEN during the diamond growth stage had different effect depending on the deposition time. In early stage of growth for a 30 min procedure, the sp^3 content increased, while for a 120 min process, it decreased. This phenomenon can be explained by effect of re-nucleation on grains by BEN application. For 30 min this effect does not show much differences in size. There are creating new seeds on the surfaces and diamond grains with similar size. It provides to high sp^3 content by faster covering of the substrate by diamond. After a 120 min procedure with BEN (see Fig. 1) new seeds are constantly created (renucleated) on surfaces of already grown crystallites which resulted in smaller dimensions of crystallites with more boundary surfaces between them [32]. Such a surfaces may contain higher amorphous sp^2 phase content. For 120 min processes with active BEN films with lower diamond ideality factor than without BEN were observed.

4. Conclusions

The various colloids for CVD diamond seeding were studied. Different growth time durations of CVD processes were investigated. The largest of crystals were obtained in 120 min process in all studied colloids. The use of bias enhanced nucleation causes the decrease of grains size. The experiment shows that the crystal renucleation [32] on diamond grains occurs when the negative voltage (BEN) is applied to the substrate. Using of BEN in early stage of growth has positive influence on diamond film quality by increasing values of sp^3 content.

Moreover, based on the results of the Raman spectroscopy (Fig. 2) relative sp^3/sp^2 band ratio were calculated for each sample. Authors defined novel factor —

a relative of sp^3/sp^2 Raman band ratios to estimate diamond ideality called here *di*. Substrates pretreated in DI water or DMSO based colloids have higher *di* values than prepared in isopropanol. For each case use of DMSO as solvent for diamond particles results in slightly higher *di* value than of water. This effects can be explained by polarity index of colloid or microscopic differences between colloids.

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