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Nucleation density enhancement for nanocrystalline diamond films

R. SHARMA, N. WOEHRL[a], P. K. BARHAI, V. BUCK[a*]
Department of Applied Physics, Birla Institute of Technology, Mesra, Ranchi, India
[a]Division of Thin Film Technology, Faculty of Physics, University of Duisburg-Essen, 47048 Duisburg and CeNIDE

The nucleation and the growth of diamond films are two separated stages of film deposition that follow significantly different rules. The initial nucleation step in the CVD deposition of Nanocrystalline Diamond films is considerably influencing the resulting film properties of the deposited films. Thus, specifically tailoring film properties requires understanding and optimization of both, the nucleation stage and the growth stage. In this work the influence of different pretreatment methods for the substrates on the one hand and on selected plasma properties on the other hand are shown. Substrates were ultrasonically pretreated with titanium powder, with diamond powder of different crystal sizes and with combinations of both. Additionally a low pressure nucleation step is performed prior to the deposition step to enhance nucleation. The impact of the different pretreatment methods on thickness, nucleation density and surface morphology of the growing film is determined. Additionally Raman Spectroscopy is performed to investigate the quality and the structure of the deposited films. A standard pretreatment method is suggested based on the results. Furthermore the influence of the C_2/H_α intensity of the plasma – as measured in situ by optical emission spectroscopy – on growth rate and nucleation density is investigated. The role of the C_2 in the nucleation process is discussed on the basis of the findings.

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1. Introduction

The growing interest in nanotechnology and nanostructured materials has encouraged the research of diamond films with reduced grain size. By reducing the grain size those films feature rather unique combinations of properties making them potential materials for emerging technological developments such as Nano/Micro-Electro-mechanical Systems (N/MEMS) [1] [2], optical coatings [3], bioelectronics [4], surface acoustic wave (SAW) filters [5], electron field emitters [6], and tribological applications [7].

By depositing diamond films from Argon rich plasmas it is possible to produce nanocrystalline diamond (NCD) films with grain sizes between approximately 5 nm and 100 nm [8] depending on the deposition parameters. The grain size is significantly influencing film properties such as hardness, toughness, intrinsic stress, roughness of the surface and thermoelectric properties.

Thus deposition of continuous, hole free nanocrystalline films with certain grain size requires control of the initial nucleation step in the early stages of diamond deposition. An optimization of the nucleation density is therefore essential for specific applications especially applications that require very thin continous films and films on specimen with high aspect ratio.

2. Experimental setup

Nanocrystalline diamond films were deposited with a 2.45 GHz IPLAS *CYRANNUS*® I-6” plasma source [9]. The functional principle of this microwave plasma source is based on a resonator with annular slot antennas. This special setup allows the use of a spatially fixed plasma from low pressure (10^{-2} mbar) to above atmospheric pressure. A schematic diagram of the system is shown in Fig. 1. Deposition is carried out on both side polished silicon substrates (type/dopant: P/B, orientation: <100>, resistivity: 15-25 ohm/cm) using gas mixtures of $Ar/H_2/CH_4$ (gas composition: 0.8 % CH_4; 2.5 % H_2; 96.7 % Ar, total gas flow 400 sccm). Silicon substrates are placed on a molybdenum substrate holder. The substrate temperature was measured by an IR pyrometer directly on the substrate surface and was controlled by a custom-made aerosol water cooling unit [10], because at high power levels the substrate has to be cooled and not to be heated.

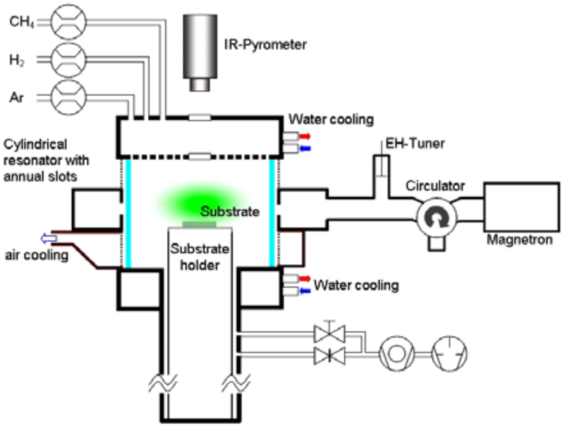


Fig. 1. Schematic diagram of Microwave PECVD system

3. Results and discussion

To investigate the influence of pretreatment methods on the nucleation of nanocrystalline diamond, eight different diamond powders were chosen for pretreatment. Because film properties depend on particle fluxes (plasma parameters) as well as on substrate properties [11] both influences have been investigated with special emphasis on substrate pretreatment.

These pretreatments differ in the type and particle size of nanocrystalline diamond powder used and in the method of the procedure. Although pretreatments of this kind can be found in literature no traceable information about specifications of these materials has been published up to now.

All diamond powders were purchased at PlasmaChem GmbH 12489 Berlin / Germany / www.plasmachem.de

The diamond powders used are shown in Table 1.

Table 1. Diamond powders used for nucleation experiments

1	Graphite / Diamond Nanomixture, raw > 16 % diamond phase (Cat. No. PL-GD-5g)
2	Graphite / Diamond Nanomixture, purfied, > 16 % diamond phase (Cat. No. PL-GD-MOF-5g)
3	Nanodiamonds, > 97 % nanodiamonds powder grade G (Cat. No. PL-D-G-5g)
4	Nanopure, 4 % Nanodiamonds aqueous suspension (Cat. No. PL-Nano)
5	Nanodiamonds, > 97 % nanodiamonds powder grade G01 (Cat. No. PL-D-G01-5g)
6	NanoPure, 4 % Nanodiamonds aqueous suspension (Cat. No. PL-Nanopure-G01-50m)
7	Nanodiamonds, Agglomerate free, positively charged, 10 % aqueous suspension
8	Sufipol BG, Nanodiamonds Super-Finish Polishing Paste

The diamond powder suspensions were mixed with a Ti Powder aqueous suspension [Ti Powder S / MaTeck GmbH 52428 Juelich / Germany / www.mateck.de] in a weight ratio of 1:1.

Samples are treated with the respective suspension for 30 min in ultrasonic vibrator. After that samples are cleaned with acetone for 15 min with ultrasonic vibrator to remove all residue.

After pretreatment all samples were exposed to typical nanocrystalline diamond growth conditions for 30 min deposition time, with 96.7 % Ar; 2.5 % H_2; 0.8 % CH_4 (total flow 400 sccm) and 1000 W microwave power to grow diamond nuclei. The nucleation density was obtained by simply counting the number of crystallites visible in the SEM picture even if more sophisticated algorithms exist [12].

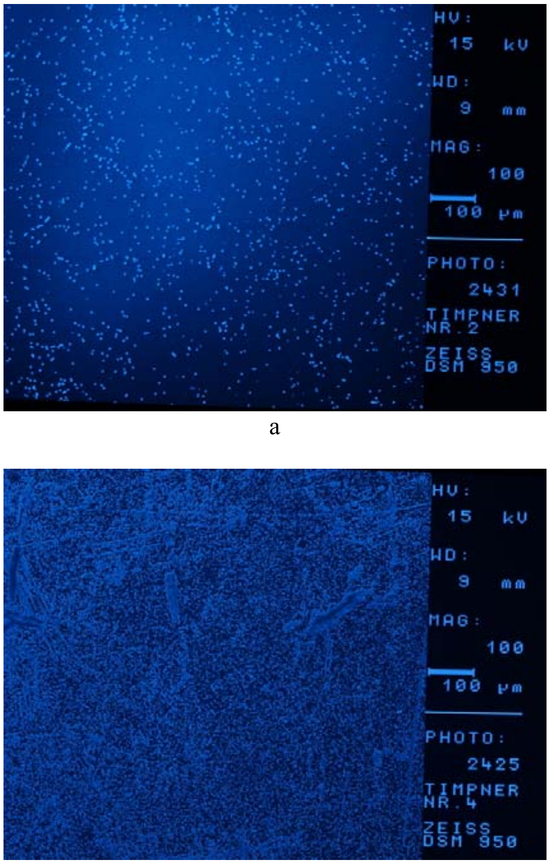
Typical SEM pictures can be found in Fig. 2 showing one sample pretreated with suspension 2 and another sample pretreated with suspension 4. The results of all nucleation density measurements are shown in Fig. 3 for the different pretreatment methods. Surprising was the very different performance of different grades of commercially available nanodiamond powder. Sample 1, 4, 5 and 7 show good nucleation density (~ 10^8 nuclei/cm^2) while all other methods show values significantly below that.

To study the effect of nucleation density on the film properties, substrates pretreated with Nanodiamond / Ti-powder suspension 1, 4, 5 and 7 respectively were also coated for 5 hours and named PRE 1 to PRE 4.

Additionally samples PRE 5 and PRE 6 are pretreated manually with diamond spray and titanium powder suspension respectively for 5 minutes.

Sample PRE 7 is exposed to a "low pressure plasma pretreatment". The sample is cleaned with acetone for 15 min in an ultrasonic vibrator followed by cleaning with deionized water for 5 min. After that it is etched with 45 % hydrofluoric acid (HF) for 30 sec and then rinsed with deionized water. The sample is then pretreated at 5 mbar pressure and 1000 W microwave power for 30 min with gas composition 96.7 % Ar; 2.5 % H_2; 0.8 % CH_4 (total 400 sccm). In this step the substrate temperature is maintained at around 250 ^{o}C.

One sample (PRE 8) is grown without any pretreatment.



a

b

Fig. 2 Nucleation density measurements PRE 2 (a) and PRE 4 (b).

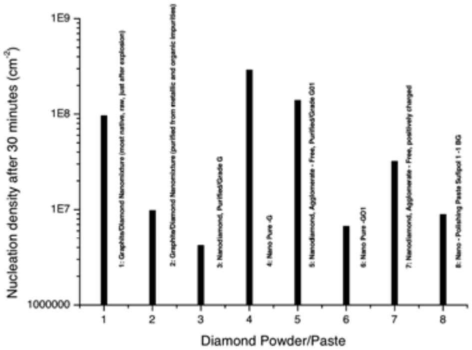


Fig. 3. Nucleation density of NCD films corresponding to different diamond powders (see Table 1).

Deposition parameters for all samples were 96.7 % Ar; 2.5 % H_2; 0.8 % CH_4 (total flow 400 sccm) at 200 mbar and 1000 W microwave power with substrate temperatures of 700 °C. Growth rate of NCD samples, deposited after different pretreatment methods, are shown in Fig. 4. The growth rate is calculated by dividing the thickness by the deposition time. Sample PRE 7 is not deposited by the conventional method. This sample is exposed to $Ar/H_2/CH_4$ plasma for 1 hour 35 minutes. First 30 minutes are only for nucleation (low pressure treatment). Next 35 minutes are to reach the actual growth condition and last 30 minutes are for growth. Nuclei grow rapidly when pressure reaches values above 100 mbar and it takes approximately 20 minutes to reach this pressure. Good growth is obtained at 200 mbar pressure. Therefore, the growth rate is calculated by considering 45 minutes as a total time.

A detailed look at the pretreatment methods used for the growth can be found in Table 2.

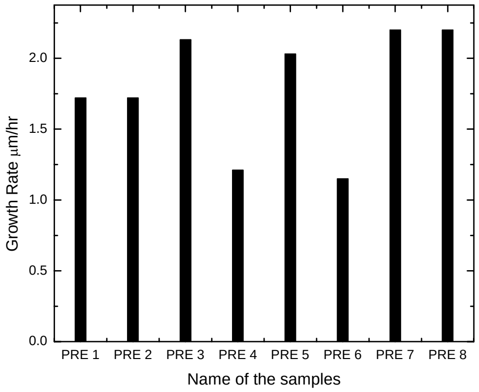


Fig. 4. Growth rate of the NCD films pretreated with different methods (see Table 2).

Table 2: Pretreatment methods used for the growth of NCD films.

Sample Name	Pretreatment method
PRE 1	50 % Graphite/Diamond Nanomixture (most native, raw, just after explosion, >16% diamondphase) [Plasmachem GmbH Berlin / Germany Cat. No. PL-GD-5g] + 50 % Ti Powder S in aqueous suspension [MaTeck GmbH / www.mateck.de]
PRE 2	50 % Nano Pure –G [Plasmachem GmbH Berlin / Germany Cat. No. PL-Nanopure-G-50m] + 50 % Ti Powder S in aqueous suspension [MaTeck GmbH / www.mateck.de]
PRE 3	50 % Nano Pure -GO1 [Plasmachem GmbH Berlin / Germany Cat. No. PL-D-GO1-5g] + 50 % Ti Powder S in aqueous suspension [MaTeck GmbH / www.mateck.de]
PRE 4	50 % Nanodiamond, Agglomerate - Free, positively charged [Plasmachem GmbH Berlin / Germany Cat. No. PL-D-GO1P-50m] + 50 % Ti Powder S in aqueous suspension [MaTeck GmbH / www.mateck.de]
PRE 5	Manually scratch with Hyprez® diamond spray 0.1µm [Joisten & Kettenbaum GmbH / www.joke.de]
PRE 6	Manually scratch with Titanium Powder S aqueous suspension [MaTeck GmbH / www.mateck.de]
PRE 7	Low pressure Pretreatment
PRE 8	No pretreatment

Raman spectra of NCD films are shown in Fig. 5. The Raman spectra confirm the deposition of nanocrystalline diamond by featuring the five typical peaks for UNCD films [Gru99]. First the two main peaks found in amorphous carbon films, the G-Peak centered at 1550 cm^{-1}, which is due to sp^2 bonded graphite [13] [14] and the D-Peak centered at 1345 cm^{-1}, which is due to disorder in graphite [14]. D and G peaks are both due to sp^2 bonded carbon situated at the grain boundaries in NCD films. Peaks centered at 1140 cm^{-1} and 1470 cm^{-1} are typical Raman features in NCD films [15] [16]. It is reported that peaks at 1140 cm^{-1} and 1470 cm^{-1} are associated with ν1 and ν3 vibration modes of transpolyacetylene co-deposited with the diamond phase [17] [18] in the grain boundaries.

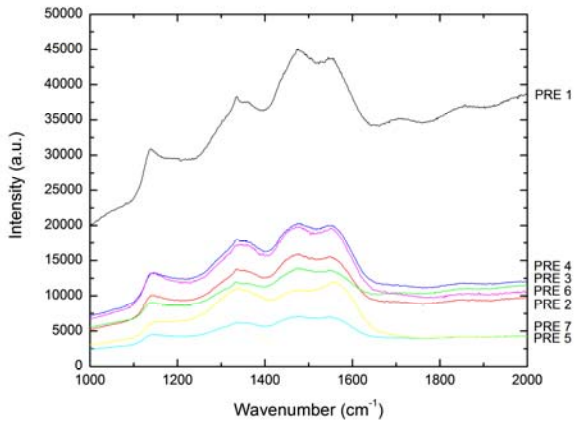


Fig. 5. Raman spectra of NCD films deposited with different pretreatment

In some of the spectra a small sharp peak at around 1332 cm^{-1} is present at the right side of the D peak representing diamond [14] [19]. Usually – because of the nanocrystalline nature of these films – the diamond peak is not visible in Raman spectra taken with 514 nm wavelength. The existence of a diamond peak in these measurements and the low intensity and the rather wide FWHM of the diamond peak are indicating that the films feature some bigger diamond grains up to 100 nm in size. The diamond peak (1332 cm^{-1}) is not present in the sample deposited with titanium powder pretreatment (PRE 6) suggesting that although the nucleation density is very poor the film grown is nanocrystalline and fine grained.

SEM images of cross sections are shown in Fig. 6. Different thicknesses and surface morphologies are found. It is clear that thickness and surface morphology depend on pretreatment method/powder or paste used. The thickness of the films grown for 5 hours with diamond powder/ paste pretreatment (PRE 1 to PRE 5) is between 6 µm and 10 µm. The sample grown without pretreatment (PRE 8) for five hours has very poor nucleation. Only few spherical balls of size about 12 µm are grown on the surface. This is an interesting result suggesting that although the nucleation density is lower, the growth rate is unchanged. This result is supporting the model of two different precursors for the nucleation and the growth of nanodiamond crystals.

The sample deposited with titanium powder suspension pretreatment (PRE 6) has low thickness (5.76 µm), this may be because of late nucleation. A reason for late nucleation may be improper pretreatment (as this sample is not pretreated with diamond powder/paste). In sample PRE 5 diamond spray of particle size 100 nm is used and good growth rate is obtained. The pretreatment process of samples PRE 5 and PRE 6 is the same, the only difference is that in PRE 5 nano diamond spray is used and in PRE 6 titanium powder suspension is used. In sample PRE 7, low pressure pretreatment is used and good growth and nucleation is obtained. In PRE 7, no diamond powder/ paste is used. Samples PRE 1 to PRE 4 have different thickness and surface morphology. These samples are pretreated with different diamond powder (all with the same method). It is also clear from Fig. 3 that nucleation density of PRE 2 is higher compared to PRE 3, however the thickness of PRE 3 is higher.

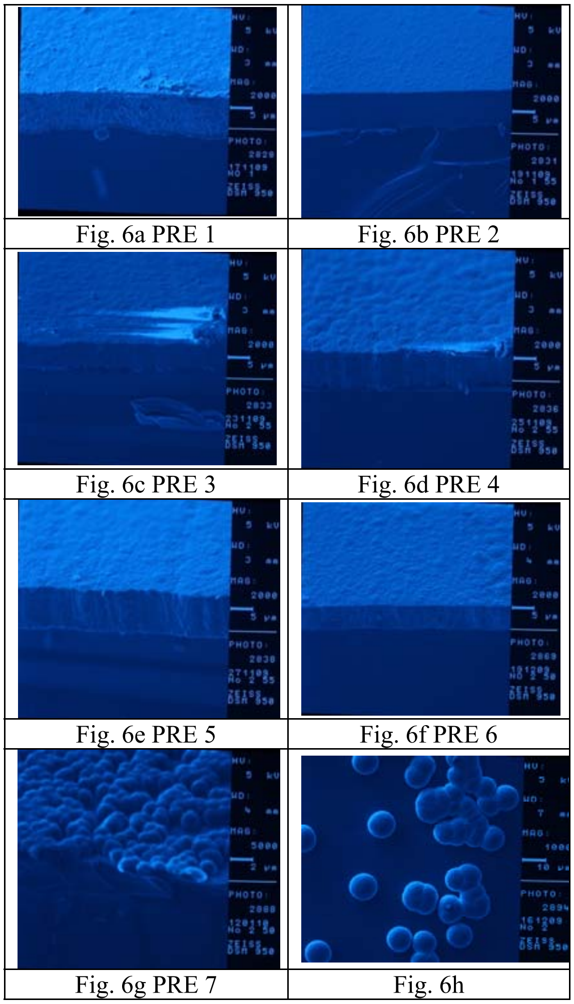


Fig. 6a PRE 1
Fig. 6b PRE 2
Fig. 6c PRE 3
Fig. 6d PRE 4
Fig. 6e PRE 5
Fig. 6f PRE 6
Fig. 6g PRE 7
Fig. 6h

Fig. 6 SEM images of the cross section of NCD films deposited with different pretreatment methods

To understand the role of the pretreatment process we discuss the importance of the nucleation precursor. Nucleation precursors are generated in the plasma near the surface. It can be considered that nucleation and growth are two independent processes. This concept has already been proposed [20] and verified by the experimental findings in this work as good growth is obtained for samples that have poor nucleation (e.g. sample PRE 8).

With the concept of specific nucleation precursors and the experimental results, a three stage model is proposed:

Stage 1: Formation of nucleation precursor

Generation of nucleation precursor starts with the generation of the plasma. The precursor is formed in the microwave plasma. Because C_2 radicals near the substrate may play a role in this step, the influence of the carbon dimer $d^3\Pi \rightarrow a^3\Pi$ Swan band emission at 516 nm on nucleation and growth is investigated using optical emission spectroscopy (it has been proved by absorption spectroscopy [21] that OES can be used for quantitative analysis of the C_2 at the given parameters. The spectrometer was coupled to the process chamber via a glass fibre and the whole system was calibrated as usual with a tungsten strip lamp.

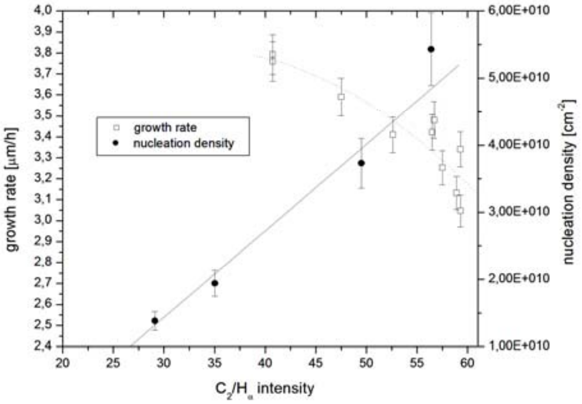


Fig. 7.Growth rate and nucleation density as a function of C_2/H_α taken by Optical Emission Spectroscopy.

As shown in Fig. 7 the growth rate is decreasing with the amount of dimers being up to 3.8 µm/h at a C_2/H_α value of 40 and dropping down to 3 µm/h for C_2/H_α of 60. Large amounts of graphitic carbon were deposited in the deposition chamber at C_2/H_α values above 60 that suggests that the deposition of graphitic carbon is favourable in these growth conditions.

Fig. 7 also shows the influence of C_2/H_α ratio on the nucleation density. It is shown that the nucleation density correlates with the C_2/H_α ratio measured by Optical Emission Spectroscopy. By increasing the carbon dimer intensity, it is possible to increase the nucleation density.

A possible explanation for this result could be found in the interplay of two competing species involved in the growth of NCD and UNCD films. It was suggested that different species for the nucleation on the one hand and the growth of diamond grains on the other hand exist. The ratios of these species determine the macroscopic structure of the growing films by influencing the rate of secondary nucleation and therefore the matrix density and the grain size of the growing crystals. A higher amount of the nucleation species leads to smaller crystals and more material between the grains. A higher amount of growth species allows the grains to grow faster (thus a higher growth rate) suppressing the secondary nucleation. In the literature, C_2 was suggested to be the nucleation species [8] as strong emission of the C_2 dimer could be found in the plasmas used for the deposition of fine-grained NCD and UNCD films. On the other hand the CH_3 radical is generally believed to be the growth species of diamond films [22]. Without taking part in the discussion concerning specific details of growth and nucleation species, Fig. 7 can be interpreted as the competition of the growth and the nucleation mechanisms: Both – nucleation species as well as growth species – are generated from the methane molecule in the process gas. The more nucleation species (correlated with C_2) is generated in the plasma, the less carbon carrier gas is available to generate the growth species.

Stage 2: Interaction of nucleation precursor with the substrate surface

Nucleation precursor interacts with the substrate. The number of precursor interacting with the surface depends on pressure, power, gas composition, biasing etc. Distance between the substrate surface and nucleation precursor and collision probability of precursor with each other or other plasma species depend on the mean free path of the system. Collision of such nuclei with other nuclei or heavy plasma species may reduce the amount of the nucleation precursor. A structured surface, e.g. by scratches, leads to an inhomogeneous distribution of the precursor, thus at places with higher concentrations these survive and at places with lower concentration are destroyed [20].

In the case of low pressure treatment, there are no scratches on the surface of silicon and nucleation is good compared to all others. The size of the nuclei indicates that these nuclei are formed at the initial stage. At low pressure (5 mbar), mean free path increases, this allows the precursors to collide with the surface and move on it. Thus, nucleation precursors have the possibility to agglomerate (as usual in growth of thin films) and thus survive also due to an inhomogeneous distribution.

Stage 3: Formation of stable nuclei and growth

As soon as stable nuclei (such as an Adamantane, the simplest diamondoid and the most stable among all the isomers with formula $C_{10}H_{16}$) exist, growth can occur by the methyl radicals just as suggested by the established growth models [22].

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[*] Corresponding author: volker.buck@uni-due.de