

Optical properties of diamond films grown by MPCVD method with alternating nanodiamond injection

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ABSTRACT

Transparent polycrystalline diamond films with grain size ranging from a few tens to hundreds of nanometres were prepared on fused silica substrate by Microwave Chemical Plasma Vapour Deposition method (MPCVD). The new technique, called alternating nanodiamonds injection, was applied for substrate pretreatment. It was demonstrated that nanodiamonds injected on fused silica substrate serve as nucleation centres and make possible an increase in nucleation density to 10^{10} cm^{-2} . The influence of MPCVD parameters such as methane concentration, total pressure and substrate temperature on the crystalline structure and optical properties of diamond films were investigated by using micro-Raman spectroscopy and scanning electron microscopy, transmittance and reflectance measurements in the wavelength range of 400-1000 nm. Under appropriate MPCVD parameters, diamond films with optical transmission $\sim 70\%$ from 650 to 1000 nm and high content of diamond phase were fabricated.

Keywords: diamond films, nucleation density, Raman spectroscopy, nanodiamond

1. INTRODUCTION

Diamond possesses many outstanding properties, including broad-band optical transparency from near-UV to far infrared, extreme hardness, chemical stability and ultra-high thermal conductivity. Therefore, diamond films grown by CVD method are very attractive for many industrial applications, such as optical windows and protective/antireflection coatings on optical elements^{1,2}. Transparent diamond films grown on optical substrate with little content of non-diamond carbon and strong adhesion are needed for practical application.

It is known that conventional polycrystalline diamond films with a grain size from one micron to several microns have a rough film surface. This rough surface increase optical scattering and consequently reduces the optical transparency drastically. This problem can be overcome by either polishing the film surface or growing a film with nanometer size grain should be adopted. Polishing of polycrystalline diamond by either chemical or mechanical methods seems impractical due to its extreme hardness and chemical inertness. Therefore thin nanocrystalline diamond films with characteristic grain size of a few dozens nanometers and smooth surface are considered the most suitable for optical applications^{3,4}. It is well known that substrate pretreatment is needed for increasing the nucleation density of diamond. For example, the nucleation density of silicon and fused silica is only about 10^4 cm^{-2} . In order to roughness of diamond films to be smaller than the wavelength of visible light the nucleation density should be at least 10^{10} cm^{-2} . Among pretreatment techniques, scratching of substrates with diamond powder or paste⁵, biasing enhanced nucleation (BEN)³, ultrasonic agitation in a diamond slurry^{2,6} and nanodiamond seeding^{7,8} are the most widespread.

Scratching of the substrate with diamond gives rise to unacceptable damage of substrate and does not provide high nucleation density⁶. In work³ reported that nanocrystalline diamond films with maximum transmittance over 60% were fabricated on quartz substrate scratched by diamond powder. Wang et al.⁹ reported that nanocrystalline films with a mean grain size of 20 nm were prepared by MPECVD on silicon substrate with scratching of its surface using 2.5 μm and 5 nm diamond powder. Only the free-standing diamond film was reported to possess high optical transmittance of 70%.

The BEN technique involves the substrate biasing at a negative voltage at the beginning of diamond deposition to form nuclei in a carbonaceous layer upon bombardment with accelerated ions. Although negative biasing technique

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allows nucleation density up to 10^{11} cm^{-2} to be achieved on conducting and semi-conducting substrate, when it is applied to isolating substrates, the nucleation density is not high and usually not uniform⁶. The authors¹⁰ pointed out that the optimal parameters for the diamond nucleation with negative biasing might not be optimal for the CVD growth of films with a high diamond content, which is indicated by an increased non-diamond phase and a higher defect concentration in the film.

There are a number of works devoted to the enhancement of nucleation density with ultrasound agitation of silicon substrate in slurry of diamond powder^{2,6}. Recently, Hao et al.⁶ reported that using slurry of 30-40 μm diamond powder a nucleation density of 10^{10} cm^{-2} on fused silica substrate and optical transmittance 73-84% of diamond film were obtained. In that work it was demonstrated that nano-damaged sites, rather than residual crystal seeds, mainly serve as active sites to induce high nucleation density.

The application of nanodiamonds as nucleation sites for diamond film growth allows the nucleation density up to 10^{10} cm^{-2} to be achieved⁷, a reduction in the incubation time and provides CVD growth without preliminary nucleation stage. It is suggested, that owing to a high surface energy and a small particle size nanodiamond precursors provide growth of the continuous diamond films on various substrate materials. The substrate may be pretreated simply by evaporating the nanodiamond suspension deposited on it^{11,12} or by treating it with ultrasound in the suspension¹³. Some researchers have reported the ND deposition from a suspension using electrophoresis¹⁴. The most important problem in the application of substrate pretreatment with nanodiamonds is that in suspension nanodiamonds aggregate in particles of about 300 nm¹⁵. Ralchenko et al.⁸ reported that after the treatment of Si substrate in the nanodiamond suspension in an ultrasonic bath nanodiamond particles agglomerated in clusters of 40-50 nm have been found on the substrate.

In this work, the recently developed technique of alternating nanodiamond injection¹⁶ was applied to enhance nucleation density of diamond film on fused silica substrates. The nanodiamond cluster has a complex structure consisting of a diamond core of about 2.5 nm in size and a shell made up sp^2 -coordinated carbon atoms. The fused silica was chosen as optical substrate having little chemical affinity to carbon. The nanodiamonds injected on substrate serve as nucleation centers. The analysis of light reflection from the growing film at the initial growth stage as a function of growth time was applied to estimate the nucleation density. It was suggested that the injected nanodiamond aggregates are broken when they hit a substrate causing high nucleation density of about 10^{10} cm^{-2} . Diamond films with high transmittance were fabricated by MPCVD method from a CH_4+H_2 mixture. The effect of MPCVD parameters on the phase composition and optical properties of diamond films was studied.

2. EXPERIMENTAL

The diamond films were grown in home-made 2.45 GHz MPCVD system, as shown in Fig. 1. The typical parameters of MPCVD process were as follows: substrate temperature 600-800°C; total pressure in chamber 10 – 50 Torr; methane concentration 0.3 – 10%; hydrogen flow 200-500 sccm, the microwave discharge power 300-500 W. The film growth rate was found to be 0.1-0.4 microns per hour. The substrate temperature was controlled by a Pt-PtRh thermocouple inserted into the substrate holder. Before growth the chamber was pumped down to 10^{-3} Torr. Fused silica of $10 \times 10 \times 1 \text{ mm}^3$ was used as a substrate.

The thickness of the diamond films was determined *in-situ* by interferometric technique based on measuring the intensity evolution of light reflection from the growing film. The white lamp was used as a light source and narrow-band filter was applied to get 970 nm wavelength of reflection light. Micro-Raman spectra were measured in backscattering geometry using a RENISHAW 1000 micro-Raman system. An argon laser at wavelength 514.5 nm was used for excitation. The 50 times magnifying objectives of the Leica microscope focuses the beam into spot of about 1 μm in diameter. The morphology of surface of the diamond films was examined by scanning electron microscope (SEM). The transmittance spectra of diamond films in visible range from 400 to 110 nm were recorded with AvaSpec-2048 spectrometer.

The nanodiamonds used in this work were extracted by etching the non-diamond material with nitric acid at 200-230 °C from carbon black soot ('detonation carbon') produced by the detonation of explosives containing excess of carbon (mixture TNT and hexogen). The size of the coherent scattering region of the nanodiamond powder, measured by X-ray diffraction method, to be used for making the suspension was about 4.5 nm. The nanodiamond particles injection was made to enhance nucleation density on substrate prior to the growth. In order to inject nanodiamond the water suspension of nanodiamond was prepared. The nanodiamond powder concentration in suspension was varied from 0.003 to 3 wt. %.

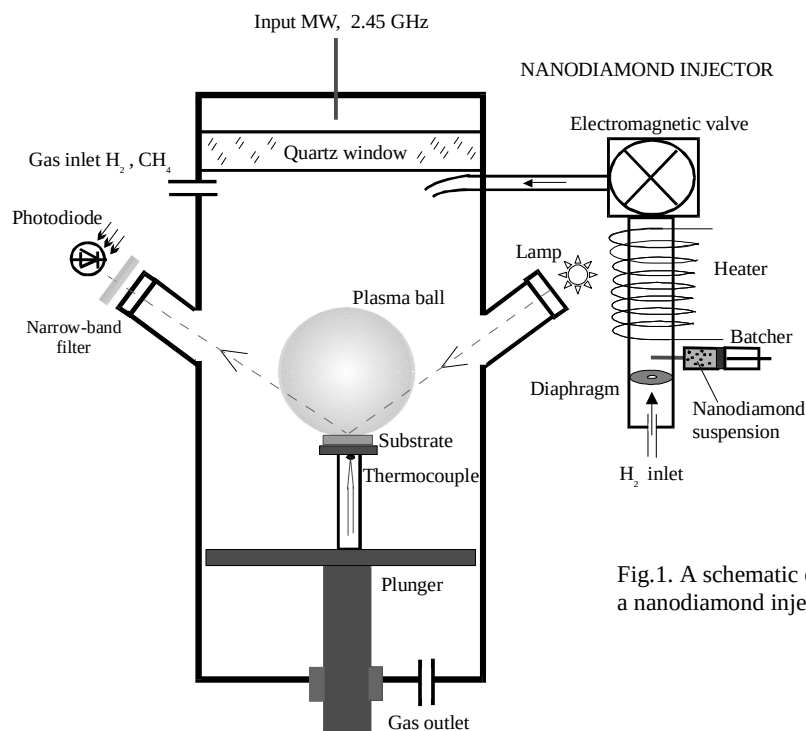


Fig.1. A schematic of MPCVD system with a nanodiamond injector.

The alternating nanodiamond injector operates as follows. The nanodiamond suspension was placed above a diaphragm using batcher. The diaphragm separates the injector vessel into two parts and has a hole of 1.5 mm in diameter. Hydrogen was pumped in the lower part. When an electromagnetic valve is closed the pressure in the upper part is lower than in the bottom one. During periodical opening of the electromagnetic valve for approximately 50 ms, suspension was delivered to the chamber in a pulse mode by the hydrogen flow, which transports the suspension droplets containing nanodiamond particles. The water was evaporated when the droplets passed through the heater. Then the flow of hydrogen and water vapour with nanodiamond particles was directed by a nozzle into the chamber towards the substrate. The time interval between the injection pulses was varied from 1 to 10 sec. The concentration of nanodiamond in suspension, the size and the speed of injected droplets and the nozzle direction were optimized to achieve maximum nucleation density. The plasma discharge was generated during injection.

3. RESULTS AND DISCUSSION

The dependence of *in-situ* light reflection from growing film versus growth time is shown in Fig. 2. Parameters of MPCVD process were follows: substrate temperature - 700°C; total pressure in chamber - 25 Torr; methane concentration -2.5%; hydrogen flow - 500 sccm. Obviously, the scattering by individual particles on initial growth stage must decrease the reflection (Fig.2a). However, the first interference extreme to appear with the formation of a continuous film should be a peak because the refractivity of quartz is lower than that of diamond, so the reflection must increase (Fig. 2b). The change from the initial reflection decrease to its increase results from the formation of a continuous film. If we assume that that growth rate practically is the same for islands and continuous film then a continuous film starts to form at an island height of about 90 nm. The nucleation density can be estimated using also the assumption that the growth rate of the diamond islands is isotropic, i.e., the islands are hemispherical. Under appropriate parameters of nanodiamond injector the nucleation density will be about 10^{10} cm^{-2} . Attenuation of reflection (Fig. 2,b) from the film with growth time can be attributed to an increase of the roughness of the film surface. Using interference fringes shown in Fig.1a the diamond films thickness was estimated to be about 600 nm. In order to compare correctly transmittance the diamond films with practically the same thickness were grown.

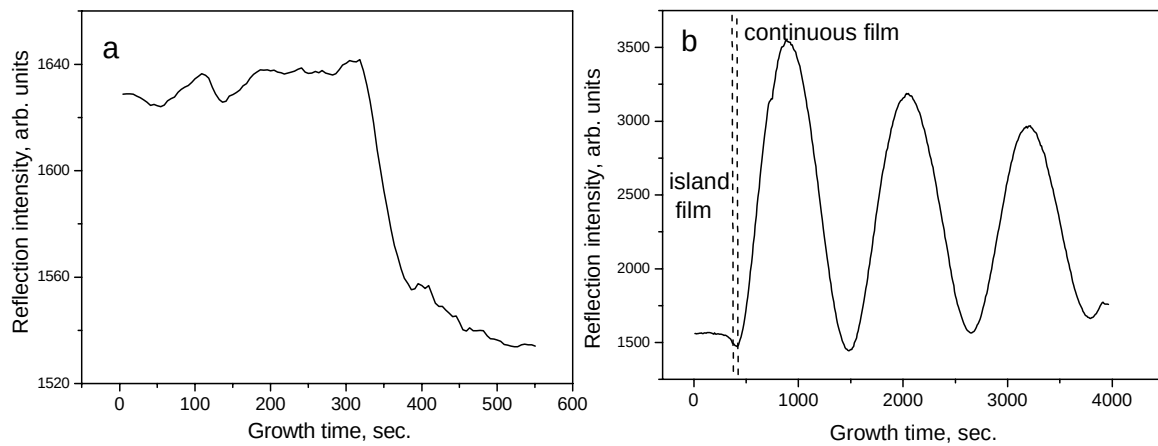


Fig.2. The dependence of diamond film reflectivity on time of growth: a- during initial growth stage, b- during total time of growth.

As is well known the structure and morphology of a diamond film are determined by the parameters of MPCVD process. In order to obtain the diamond films with various diamond phase content and surface roughness, two sets of experiments were carried out. For the first set of experiments MPCVD parameters such as the gas flow rate – 500 sccm, substrate temperature – 650°C and the pressure – 14 Torr were maintained, while the methane concentration varied from 0.5 to 10%. For the second set of experiments MPCVD parameters by etching the non-diamond material with nitric acid at $200\text{--}230^{\circ}\text{C}$ as the gas flow rate – 500 sccm, substrate temperature – 700°C and the pressure – 25 Torr were maintained, while the methane varies from 0.5 to 5%. The change in methane concentration permits to vary the size of diamond grain from nanocrystalline to submicron. Fig. 3 and 4 shows the Raman spectra of the diamond films obtained for the two sets. The formation of crystalline diamond phase is demonstrated by the occurrence of a diamond peak near 1332 cm^{-1} corresponding to a zone centre mode of T_{2g} symmetry. We also observed broad peaks near 1140 cm^{-1} , 1350 cm^{-1} , 1470 cm^{-1} , 1550 cm^{-1} . The lines at 1350 cm^{-1} and 1550 cm^{-1} can be assigned to the well-known D- and G-modes which are due to sp^2 -hybridized carbon¹⁷. The D-mode appears to be due to the relaxation in the momentum selection rules of the Raman scattering process due to small domain size in graphite. The 1470 cm^{-1} line corresponds to the presence of amorphous sp^2 -hybridized carbon¹⁸. It should be noted that there is some controversy in the interpretation of the peaks at 1140 cm^{-1} in diamond. Most researchers compare its position with the single phonon density of the diamond states and attribute it to the presence of nanocrystalline diamond in the film. The authors of Ref. ¹⁹ believe that the 1135 cm^{-1} peak is due to transpolyacetylene inclusions at the boundaries of diamond grain.

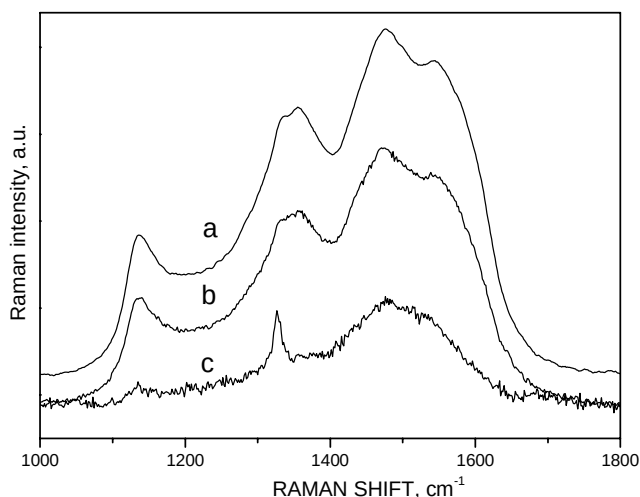


Fig.3. Raman spectra of diamond films grown at substrate temperature – 650°C , the pressure – 14 Torr and at methane concentration: a – 10%, b- 5%, c- 0.5%

Note that diamond peaks in spectra shown in Fig.3(c) and Fig.4 (c,d) are shifted relatively to the peak of natural diamond at 1332 cm^{-1} toward lower phonon frequencies by 4 cm^{-1} , 2 cm^{-1} and 5 cm^{-1} , respectively. These shifts result from the compressing stress caused by the difference between the thermal expansion coefficients of fused silica and diamond. The occurrence of such stress indicates the film adhesives

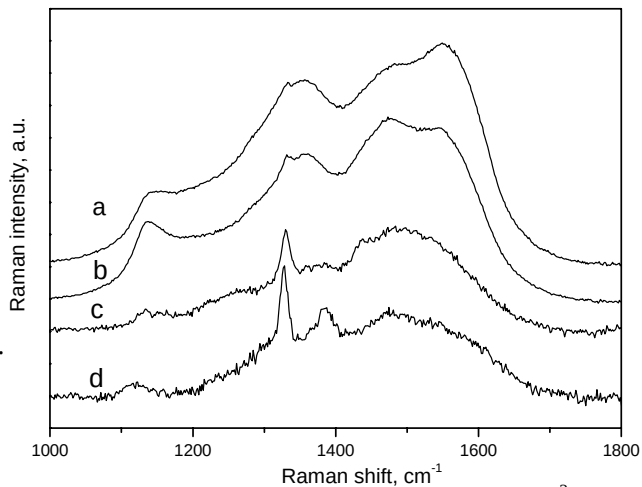


Fig.4. Raman spectra of diamond films grown at substrate temperature of 700°C , the pressure of 25 Torr and at methane concentration: a – 5%, b- 2.5%, c- 1%, d- 0.3%.

The cross section for light scattering by sp^2 -bonded carbon is approximately 50 times larger than that by sp^3 -bonded carbon³. Consequently, even a weak diamond peak near 1332 cm^{-1} indicates that the grown films consist of diamond grain and sp^2 -hybridized carbon which is most likely present only in the grain boundaries. The highest content of the diamond phase is found in the films grown at a methane concentration of 0.5% (Fig 3, spectrum b) and 0.3% (Fig 4, spectrum d). In Fig. 4 a,b the diamond peak at 1332 cm^{-1} is hardly seen on the background of sp^3 - hybridized carbon that is typical for nanocrystalline diamond films^{3,20}.

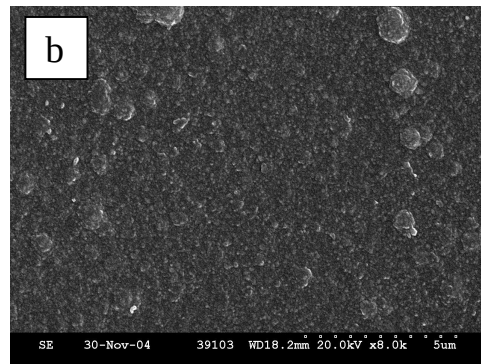
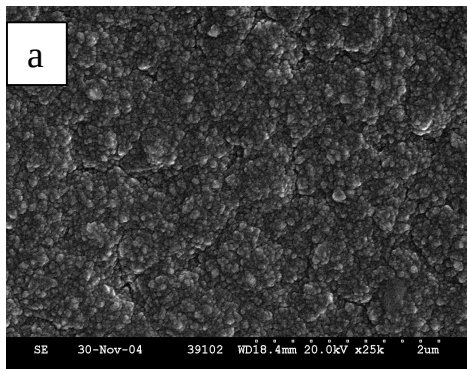


Fig.5. SEM images of the diamond films grown at substrate temperature – 700°C , the pressure – 25 Torr and at methane concentration -2.5%: a- magnification 20kV, b- magnification 8 kV.

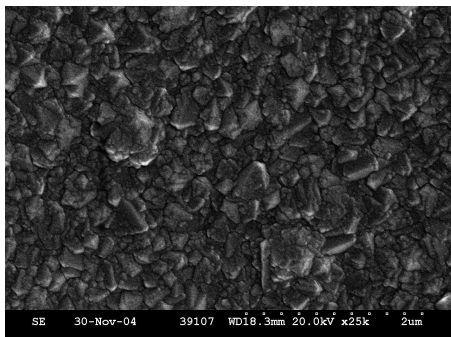


Fig.6. SEM images of the diamond films grown at substrate temperature – 650°C , the pressure – 14 Torr and at methane concentration - 0.5%.

SEM images of the diamond films are shown in Fig.5 and 6. For diamond films grown at methane concentration more than 2.5%, grain size is reduced to a few tens nanometers (Fig.5). The size of diamond grains in the film grown at methane concentration less than 2.5% are a few hundred nanometers (Fig.6). A large cauliflower particle spread with density 10^4 cm^{-2} over the film surface can be seen (Fig.5, b). These particles may originate from a huge nanodiamond aggregate, which was injected from suspension and were not broken when they hit a substrate.

Fig. 7 and 8 show the transmittance spectra of the diamond films. Let us briefly discuss the effect of methane concentration on transmittance of the films for the first set (Fig.7). It is seen that the diamond film with sub-micron grain size grown at methane concentration of 0.5% is more transparent than the diamond films grown at methane concentration of 5% and 10%. It can be related to a lower concentration of sp^2 -hybridized amorphous carbon as confirmed by Raman results (Fig. 2).

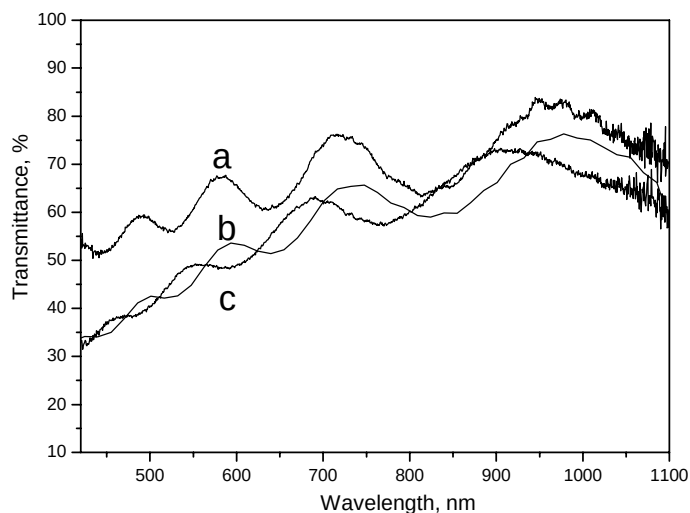


Fig. 7. The transmittance spectra of the diamond films grown at substrate temperature – 650°C , the pressure – 14 Torr and at methane concentration: a – 0.5%, b- 10%, c- 5%.

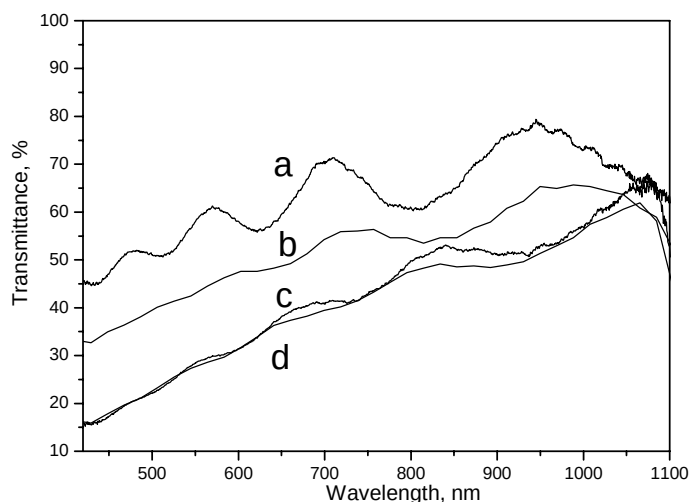


Fig. 8. The transmittance spectra of the diamond films grown at substrate temperature – 700°C , the pressure – 25 Torr and at methane concentration: a – 2.5%, b- 0.3%, c- 5%, d- 1%.

Among the films fabricated in the second set of samples the diamond films grown at methane concentration of 2.5% has the highest transmittance. The diamond film grown at methane concentration of 0.3% possesses a lower transmittance and the transmittance of the diamond films grown at methane concentration of 1% and 5% are the lowest. This result of the second set can be explained as follows. The diamond films grown at high methane concentration (more than 5%) have smooth surfaces but relatively high contain of sp^2 -hybridized carbon. Otherwise, the diamond films grown at methane concentration of 2.5% and less demonstrate lower content of sp^2 -hybridized carbon but due to

their microcrystalline structure they have rougher surface resulting in higher light scattering. We can conclude that there are optimal MPCVD parameters that provide the highest transmittance. These parameters compromise between content of sp^2 -hybridized carbon concentration, promoting light absorption in film, and grain size, which determines the film roughness.

The rms surface roughness of most transparent film (Fig.8a), as measured by atomic force microscope in $5 \times 5 \mu m^2$ area, was observed to be approximately 30 nm.

The transmittance spectra of the films exhibit a sharp absorption edge in the short wavelength region, which is close to the band gap edge of natural diamond (220 nm). In this region light scattering is more efficient as well. Therefore it is not surprising that the most prominent differences of transmittance for various diamond films were observed in the short wavelength region.

The transmittance oscillations due to the interference pattern originate from the reflections on surfaces between film and air, film and fused silica and fused silica and air (on the backside of the sample), were established. The thickness of diamond films calculated by the optical interference pattern (Fig. 7 and 8) is in good agreement with the data of thickness value obtained by the dependence of *in-situ* light reflection as function of growth time. It was observed that the greater the transmittance of films is the greater amplitude of interference fringes.

The absorption coefficient (α) of most transparent film (Fig.8a), fitted using Fresnel equations for system of diamond film on fused silica substrate, appeared to be 2000 cm^{-1} . The following parameters were used for fitting: the reflection index of film – 2.3, incidence angle - 90° , film thickness - 600 nm. The obtained value of absorption coefficient is close to ones of 10^3 - 10^4 cm^{-1} reported in Ref. ³ for nanocrystalline diamond films grown at substrate temperature of 600°C . The extinction coefficient can be estimated by the formula $k = \alpha \cdot \lambda / 4 \cdot \pi$, where λ - wavelength. For a wavelength of $1 \mu m$, the extinction coefficient is approximately 0.01.

4. CONCLUSION

This study has demonstrated that the alternating injection of nanodiamond can effectively increase nucleation density on fused silica substrates. A nucleation density of up to 10^{10} cm^{-2} has been achieved. Due to the high nucleation density, thin continuous films with high content of diamond phase have been grown by MPCVD method. The optical and structural properties of the obtained diamond films have been investigated. Appropriate MPCVD parameters to fabricate the diamond films with optical transmission of $\sim 75\%$ in the range from 650 to 1000 nm were found. The suggested alternating nanodiamond injection is non-destructive to the substrate surface and can be profitably applied in the growth of adhesive diamond films for optics.

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