

INVESTIGATION OF NANOCRYSTALLINE
DIAMOND FILMS PREPARED BY MICROWAVE
PLASMA CHEMICAL VAPOR DEPOSITION

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Two approaches have been described in literature for the preparation of nanocrystalline diamond (NCD) coatings by microwave plasma chemical vapor deposition (MWCVD). The first approach involves an increase of the methane concentration in the conventional CH₄/H₂ gas mixture, leading to enhanced secondary nucleation rate (4-8), the second one – partial or complete substitution of hydrogen by argon or nitrogen, resulting in change of the growth mechanism by inclusion of new film-forming species (9-15).

We have investigated the deposition of NCD films by MWCVD combining the two approaches mentioned above: by increasing the methane concentration in the gas mixture up to 17% and by complete replacement of hydrogen by nitrogen. The influence of the gas phase composition on the properties of the deposited NCD films (films **B** and **C**) was investigated and they were compared to that of polycrystalline diamond films (films **A**). All deposition conditions are listed in Table I.

Table I. Deposition parameters throughout our experiments

Parameter	A	B	C
Working pressure, Torr	20		
Input MW power, W	800		
Substrate temperature, °C	770		
CH ₄ /H ₂ flow rate ratio	1:100	-	-
CH ₄ /N ₂ flow rate ratio	-	1:10	1:5
CH ₄ concentration, %	1	9	17

The SEM pictures show large well-defined crystals for polycrystalline diamond films **A** (Fig. 1 (a)) and the absence of well-formed crystalline facets in the micron scale for NCD films **B** and **C**. Films **B** exhibited rounded nodules of submicron size which entirely covered the substrate surface (Fig. 1 (b)), while films **C** possessed smooth and uniform surface (Fig. 1 (c)). The different morphology reflected the influence of the methane concentration on the growth mechanism and respectively on the structure of the NCD films. The growth process during MWCVD from gas mixtures without hydrogen, e.g. CH₄/N₂ (X), CH₄/Ar (Y), as well as from CH₄/H₂ mixtures with higher methane concentrations (J,K) involves carbon dimers (C₂), as revealed by optical emission spectroscopy. The structures observed in Fig. 1 (b) and (c) are a result of the secondary nucleation with C₂ species leading to the growth either of sub-micron crystals from initial nuclei at the film-substrate interface (films **B**) or of uniform films due to high renucleation rate at increased methane concentration (films **C**). The high secondary nucleation rate affects the growth rate of the nanocrystalline diamond films; it increases from 0.11 μm/h for films **B** to 0.57 μm/h for films **C**.

Further information on the surface roughness and topography of the NCD films was obtained by AFM investigations. Films **C** were very smooth with rms

roughness of 11.9 nm and grains height of 43.2 nm, while films **B** possessed rms roughness of 33.6 nm and grains height of 381.7 nm. The obtained roughness of 11.9 nm (for films **C**) is in the range of the typical values for NCD films deposited by MWCVD (N,M,L).

The Raman spectrum of the polycrystalline diamond films **A**, presented in Fig. 2, shows the characteristic diamond peak at 1336 cm⁻¹ together with a broad peak around 1500 cm⁻¹ originating from small amount amorphous phase. The Raman spectra of the NCD films **B** and **C**, show three bands, irrespective of the methane concentration. The band around 1150 cm⁻¹ can be assigned to the presence of nanocrystalline diamond phase (V,B,N). The intensity of the band at 1150 cm⁻¹ increases with the increase of the methane concentration (films **C**) which, as already discussed, leads to smaller diamond crystallite size. For films **C** an additional peak is observed around 1480 cm⁻¹ which is also attributed to NCD (L). The other two broad bands, at about 1350 and 1560 cm⁻¹ are signed to the *D* and *G* bands of disordered carbon, respectively. The diamond peak at 1336 cm⁻¹ observed in the Raman spectrum of the polycrystalline films **A** cannot be seen in the spectra of NCD films **B** and **C** due to the presence of amorphous and/or graphitic phase in the latter, which has much greater Raman scattering efficiency than the diamond.

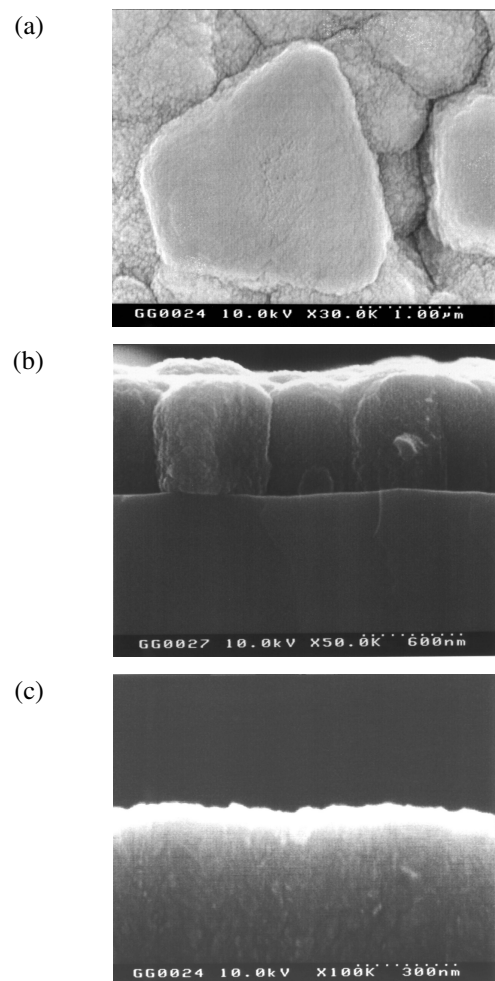


Fig. 1 SEM micrographs of films **A**, **B** and **C** prepared by MWCVD

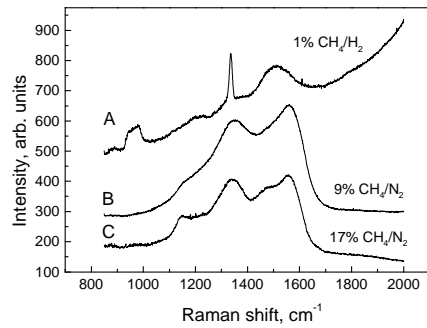


Fig. 2. Raman spectra of films **A**, **B** and **C** prepared by MWCVD

The FTIR spectra of films **B** and **C** showed significant absorption bands in the region $2800\text{--}3000\text{ cm}^{-1}$ in contrast to films **A**. Different CH_x ($x = 1\text{--}3$) asymmetric and symmetric stretching vibrations are superimposed in this broad band and it is important to note that the films were deposited without addition of hydrogen. In general, sp^3 -carbon atoms bonded to 1, 2 or 3 hydrogen atoms give rise to stretching modes in the region below 3000 cm^{-1} , while the $\text{sp}^2\text{-CH}_x$ – above 3000 cm^{-1} . In our case the C-H band is below 3000 cm^{-1} indicating predominant amount of sp^3 -carbon atoms bonded to hydrogen.