

# Deposition of thick and thin nanocrystalline diamond films by microwave plasma enhanced chemical vapor deposition

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## Abstract

Thick (around 3  $\mu\text{m}$ ) and thin (48-310 nm) nanocrystalline diamond (NCD) films have been produced from Ar-rich  $\text{CH}_4/\text{Ar}/\text{H}_2$  (1/89/10 %) and  $\text{H}_2$ -rich  $\text{CH}_4/\text{H}_2$  (1/99 %) microwave plasmas, respectively. The thick NCD films were obtained with and without an initial buffer layer (BL). The BL is easily obtained under typical microcrystalline diamond growth conditions ( $\text{CH}_4/\text{H}_2$  mixtures). The effect of the deposition temperature ( $T_D$ , 630-900°C) was investigated on the morphology, the surface roughness and the bonding characteristics of the films grown with and without BL. The thin NCD films were grown on Si substrates treated by two different methods, i.e. ultrasonic agitation in a suspension of diamond powders of 40-60  $\mu\text{m}$  or combinatorial approach in a suspension of mixed diamond powders of 250 nm and 40-60  $\mu\text{m}$ . The present experimental results show that the buffer layer procedure allows a good preservation of the surface of treated Si substrate and the combinatorial approach promotes effectively the seeding of the Si surface.

## Introduction

In the last years, nano- and ultranano-crystalline diamond (NCD and UNCD) films have attracted great interest as smooth materials. The advantage of these two types of nanostructured diamond over microcrystalline diamond (MCD) films consists in the smaller grain size and lower surface roughness.

The strategies to produce smooth thin NCD films consist in enhancing markedly the primary nucleation at the beginning of deposition process [1,2] or to promote the secondary nucleation during the growth process [3]. Usually diamond nucleation is difficult to occur on non-diamond substrates. For this reason the substrate surface must be treated in-situ (bias enhanced nucleation technique) or ex-situ (ultrasonic agitation, seeding and/or deposition of carbon/silicon carbide interlayer) in order to enhance the primary nucleation density. This paper

focuses on the nucleation and growth of nanocrystalline diamond. The NCD films used in this work have been produced at two different thickness scales: micrometer (around 3  $\mu\text{m}$ ) and submicrometer (48-310 nm). Micrometer-thick NCD films were obtained from a  $\text{CH}_4/\text{Ar}/\text{H}_2$  (1/89/10 %, with modest renucleation process) gas mixture with and without a diamond interlayer of about 500 nm, called buffer layer (BL), between the NCD films and the treated Si substrate. Additionally, the effect of the substrate temperature was investigated on the morphology, the surface roughness and the bonding characteristics of films grown with and without a BL.

Nanometric-thick (48-310 nm) continuous films were produced under conventional conditions of microcrystalline diamond films ( $\text{CH}_4/\text{H}_2$ , 1/99 %, with suppression/reduction of renucleation process) by precisely stopping the growth at the planned thickness by means of an in-situ, real time and non

invasive optical technique, i.e. laser reflectance interferometry (LRI) [1,2,4]. The NCD films were grown on Si substrates treated by two different methods, i.e. ultrasonic agitation in a suspension of diamond powders of 40-60  $\mu\text{m}$  or combinatorial approach in a suspension of mixed diamond powders of 250 nm and 40-60  $\mu\text{m}$ .

## Materials and methods

The NCD films were deposited by the microwave plasma enhanced chemical vapor deposition technique in a home-made cylindrical stainless steel Astex-type reactor. Thick NCD films (Sets1 and 2 in Table 1) were produced using  $\text{CH}_4/\text{Ar}/\text{H}_2$  (1/89/10%) gas mixtures, whereas very thin films were obtained using conventional  $\text{CH}_4/\text{H}_2$  (1/99%) plasmas. During the deposition the working pressure and microwave power were 140 mbar and 950 Watt for  $\text{CH}_4/\text{Ar}/\text{H}_2$  plasmas, and 50 mbar and 1000 Watt for  $\text{CH}_4/\text{H}_2$  plasmas.

Table 1. Experimental parameters for the deposition of thick NCD films of Sets1 and 2. For all the samples the pressure ( $p$ ), microwave power ( $P$ ), total flow rate ( $\Phi_{\text{tot}}$ ) and percentages of  $\text{CH}_4/\text{Ar}/\text{H}_2$  gas mixture were maintained constant at 140 mbar, 950 Watt, 100 sccm and 1/89/10%, respectively. For Set 2 films, the thickness ( $t_{\text{BL}}$ ) of the buffer layer (BL) were fixed at 500 nm. The heater temperature ( $T_{\text{PID}}$ ) and deposition temperature ( $T_{\text{D}}$ ) were varied and listed with total film thickness ( $t_{\text{film}}$ ) as evaluated by in situ PI measurements.

Sample	$T_{\text{PID}}$ ( $^{\circ}\text{C}$ ) at plasma		$T_{\text{D}}$ ( $^{\circ}\text{C}$ )	$t_{\text{film}}$ (nm) PI
	OFF	ON		
<b>Set 1 without BL - 27min Ar/<math>\text{H}_2</math> plasma exposure for parameters stabilization</b>				
1A	25	462	652	2750
1B	585	585	748	2660
1C	700	700	823	2540
1D	780	780	875	2640
<b>Set 2 with BL - 10min <math>\text{H}_2</math> plasma exposure for parameters stabilization</b>				
2A	25	473	653	2880
2B	585	585	775	3570
2C	700	700	833	3370
2D	780	780	884	3230

In the experiments the total flow rate ( $\Phi_{\text{tot}}$ , 100 sccm) was held constant. For the thick films without and with a buffer layer the deposition temperature ( $T_{\text{D}}$ , 630-900  $^{\circ}\text{C}$ ) was varied. For the thin films (Sets3 and 4 in Table 2) the process time of deposition was varied from 7 to 66 min by keeping constant the deposition temperature around 815  $^{\circ}\text{C}$ . In all the experiments the nucleation time, the deposition rate, the thickness and the

Table 2. Experimental parameters for the deposition of thin NCD films of Sets 3 and 4. The pressure ( $p$ ), microwave power ( $P$ ), total flow rate ( $\Phi_{\text{tot}}$ ), deposition temperature ( $T_{\text{D}}$ ) and percentages of  $\text{CH}_4/\text{H}_2$  gas mixture were maintained constant at 50 mbar, 1000 Watt, 100 sccm, 815  $^{\circ}\text{C}$  and 1/99%, respectively, whereas the Si substrate pretreatment was varied. The process time ( $t_{\text{p}}$ ), nucleation time ( $t_{\text{N}}$ ), deposition rate ( $r_{\text{D}}$ ) and thickness ( $t_{\text{film}}$ ) were measured by laser reflectance interferometry (LRI) and the surface roughness by atomic force microscopy (AFM).

Sample	$t_{\text{p}}$ (min)	$t_{\text{N}}$ (min)	$r_{\text{D}}$ ( $\mu\text{m}/\text{h}$ )	$t_{\text{film}}$ (nm)	Roughness $3\times 3\mu\text{m}^2$ (nm)
Untreated Si	----	----	----	----	0.17
<b>Set3</b>					
<b>Si substrate treatment with 40-60 <math>\mu\text{m}</math> diamond powder</b>					
3Treated Si					5.70
3A	7	----	----	----	9.79
3B	28	18	0.29	48	45.07
3C	31	14	0.29	81	25.71
3D	54	17	0.30	185	40.06
3E	63	15	0.36	290	39.43
<b>Set4</b>					
<b>Si substrate treatment with 250 nm (50%) + 40-60 <math>\mu\text{m}</math> (50%) diamond powder</b>					
4Treated Si					15.98
4A	7	7	----	----	16.14
4B	28	----	----	48	17.92
4C	24	6	0.28	84	21.11
4D	44	10	0.29	165	19.58
4E	66	4	0.30	310	19.50

deposition temperature were monitored in-situ and in real-time during the process by the pyrometric interferometry (PI) technique. Squared pieces of single crystal (100) p-type silicon wafers of 2.6 cm x 2.6 cm size were used as substrates and placed on a

molybdenum holder set on a graphite susceptor. Prior to the deposition, the substrate surface of the thick films was ultrasonically treated in an ethanol suspension containing diamond powders of 40-60  $\mu\text{m}$  to obtain a high density of the initial diamond nucleation [5]. For Set4 samples the Si surface was ultrasonically treated in an ethanol suspension containing a mixture of diamond powders composed of 250 nm (50%) and 40-60  $\mu\text{m}$  (50%) to cause a further nucleation enhancement [6,7].

The BL of all the films of Set2 was easily obtained under the typical conditions of microcrystalline diamond growth (gas mixture  $\text{CH}_4/\text{H}_2$  1/99sccm; 50mbar; 1000W; heating at TPID 700 $^\circ\text{C}$ ), and was characterized by a very short nucleation time as monitored through pyrometric interferometry. Successively, the deposition was continued on the buffer layer in Ar-rich  $\text{CH}_4/\text{Ar}/\text{H}_2$  gas mixture.

The very thin thickness of samples (Sets3 and 4) was well monitored in-situ and in real-time by LRI rather than by pyrometric interferometry not usable for monitoring film thickness less than 140 nm.

The chemical-structural features of all the films were determined at room temperature by means of a Raman confocal micro-spectrometry apparatus (Labram from Jobin-Yvon Horiba). The morphology of the coatings was evaluated by AFM (Park Systems Nanotechnology Solution Partner). The average values of root-mean-square (RMS) surface roughness were estimated on  $10 \times 10 \mu\text{m}^2$ ,  $5 \times 5 \mu\text{m}^2$  and  $3 \times 3 \mu\text{m}^2$  surface areas by sampling three different regions for each film.

## Results

All the Raman spectra of the Set 1 and 2 films, see Fig.1a-b, show typical features of nanocrystalline diamond. A typical NCD spectrum has a less intense diamond peak at  $1332 \text{ cm}^{-1}$  and different contributions of non-diamond phase, that are the D and G graphite bands (at  $1360 \text{ cm}^{-1}$  and  $1550 \text{ cm}^{-1}$ ,

respectively) and the transpolyacetylene (t-PA) bands at  $1140 \text{ cm}^{-1}$  and  $1480 \text{ cm}^{-1}$  [8,9]. In particular, the t-PA bands increase at the highest deposition temperature.

The AFM images clearly show the difference

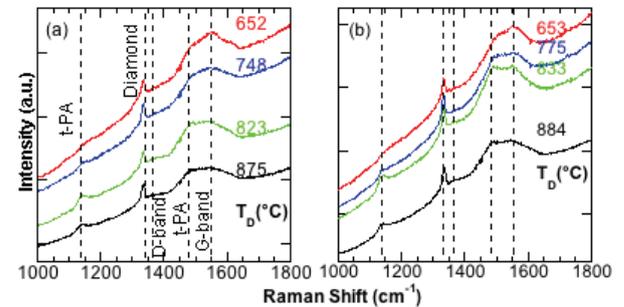


Fig.1a-b Raman spectra of thick NCD films without (a) and with (b) a buffer layer obtained at different deposition temperatures ( $T_D$ ).

between the film without BL (Fig.2, Set1) and with BL (Fig.2, Set2).

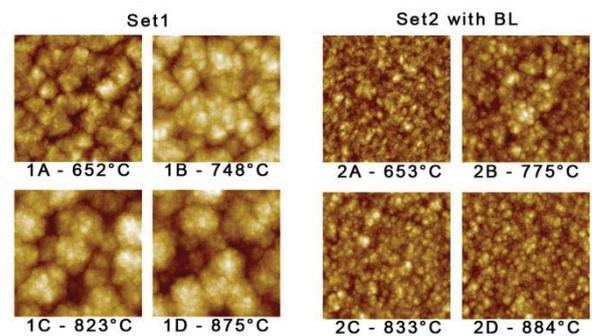


Fig.2 AFM images of thick NCD films on  $10 \times 10 \mu\text{m}^2$  surface areas without (Set 1) and with (Set 2) a buffer layer (BL) obtained at different deposition temperatures ( $T_D$ ).

The surface morphology of the samples without BL consists of cauliflower-shaped crystallites composed of small grains, as frequently observed in many NCD films.

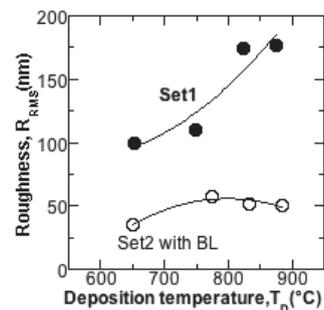


Fig.3 Root mean square (RMS) surface roughness ( $R_{RMS}$ ) determined by AFM  $10 \times 10 \mu\text{m}^2$  measurements of thick NCD films without (filled circle, Set 1) and with (empty circle, Set 2) a buffer layer (BL) as a function of deposition temperature ( $T_D$ ).

On the contrary, the samples obtained in the same conditions, but deposited on a buffer layer, are also nanocrystalline and show uniform small grains of nanometric size. In Fig.3 the RMS surface roughness ( $R_{RMS}$ ) data, estimated from the AFM images on  $10 \times 10 \mu\text{m}^2$  areas, are shown for all the samples as a function of the  $T_D$ . The roughness values for films without BL are high (100-190nm) and increase by increasing the temperature, whereas for films with BL these are low ( $\leq 50$  nm) and show a weak dependence on the temperature.

Figs.4a and b show the evolution of Raman spectra with increasing thickness of samples of Sets3 and 4. A sharp diamond peak at  $1332 \text{ cm}^{-1}$  is evident with a weak and broad G band

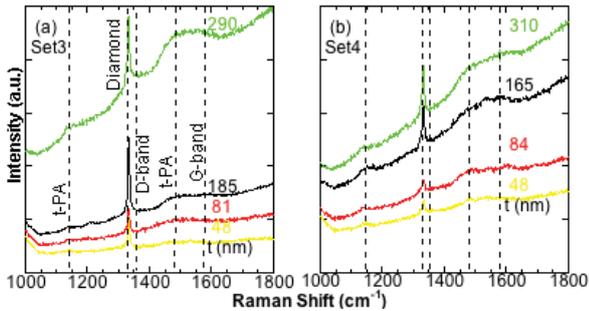


Fig.4a-b Raman spectra of thin NCD films grown at different thicknesses on Si substrates treated with a suspension containing diamond powders of  $40\text{-}60 \mu\text{m}$  (a, Set3) and mixed diamond powders of  $250 \text{ nm}$  and  $40\text{-}60 \mu\text{m}$  (b, Set4).

and new weak bands of t-PA of the non-diamond components. The features of the Raman spectra of Sets3 and 4 films are very similar, but the films of Set4 are more nano than those of Set3 due to the lowering and broadening of the diamond peak.

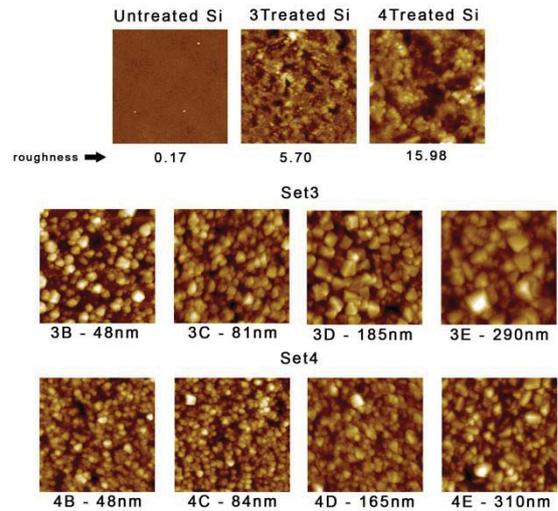


Fig.5 AFM images on  $5 \times 5 \text{ mm}^2$  surface areas of untreated, treated Si substrates and AFM images on  $3 \times 3 \text{ mm}^2$  surface areas of thin NCD films grown on Si treated with a suspension containing diamond powders of  $40\text{-}60 \mu\text{m}$  (Set3) and mixed diamond powders of  $250 \text{ nm}$  and  $40\text{-}60 \mu\text{m}$  (Set4) at different thicknesses.

Fig.5 displays the morphology of AFM images on surface areas of untreated, treated Si substrates and of films grown on Si wafers for the two treatments at different thicknesses (48-310nm). The AFM images of the nanometric films show that the diamond grain sizes of the Set3 are larger than those of the Set4.

Fig.6 reports the surface roughness of Sets3 and 4 NCD films as a function of the process time. The surface roughness of the diamond films is around  $40 \text{ nm}$  and  $20 \text{ nm}$  for samples of Sets3 and 4, respectively.

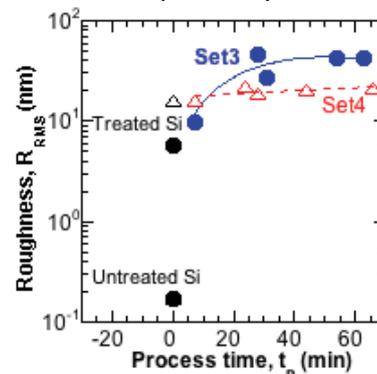


Fig.6 Root mean square (RMS) surface roughness ( $R_{RMS}$ ) determined by AFM measurements of thin NCD films grown on Si treated with a suspension containing diamond powders of  $40\text{-}60 \mu\text{m}$  (filled circle, Set3) and mixed diamond powders of  $250 \text{ nm}$  and  $40\text{-}60 \mu\text{m}$  (empty triangle, Set4) vs process time.

## **Discussion**

The above described results may be explained by assuming that the ultrasonic and combinatorial treatments of the Si substrate using diamond powders provide sites for nucleation with either embedment of diamond powder fragments or diamond seeds besides scratches and morphology changes of the substrate surface. The AFM topography of the Si surface treated by ultrasound in an ethanol suspension of 40-60  $\mu\text{m}$  diamond powders and of mixed diamond powders composed of 250 nm and 40-60  $\mu\text{m}$  shows that the dominant process is scratching and seeding, respectively.

The proposed initial deposition of a BL from  $\text{H}_2$ -rich  $\text{CH}_4/\text{H}_2$  mixture at a power of 1000 W and a pressure of 50 mbar is shown to facilitate the nucleation process of diamond reducing the nucleation time and forming easily the first layer of diamond. This because the 10-min  $\text{H}_2$ -plasma exposure would leave the seed sites unmodified on the treated Si substrate. Although the deposition conditions are typical of MCD films, the low thickness (about 500 nm) of the BL ensures the formation of small grain sizes with surface roughness of 45 nm that is preserved during the subsequent deposition of NCD films from Ar-rich  $\text{CH}_4/\text{Ar}/\text{H}_2$  mixture. The BL procedure, therefore, shortens the times for nucleation. The absence of BL and the long time of nucleation result in cauliflower-like films. On the contrary, the presence of BL brings to the formation of nanometric grain sizes thus improving markedly the smoothness of films obtained.

The different method used for the Si surface treatment in Set3 and 4 samples is well depicted by AFM images of treated Si in Fig.5, in which the scratching and seeding process becomes dominant in the mono-dispersed and poly-dispersed suspensions, respectively. Additionally, the comparison of AFM images of the nanometric films grown on Si surface in the two treatments shows that the film grain sizes of Set3 are larger than those of

Set4. The films of Set3 grown on Si treated in suspension of 40-60  $\mu\text{m}$  diamond powders exhibit a surface roughness of 40 nm for the larger grain size, whereas the films of the Set4 show a roughness of about 20 nm for the smaller grain sizes.

## **Conclusions**

The production of thick NCD films with the use of the BL procedure results in a fast nucleation stage, facilitates the growth process of nanocrystalline diamond and reduces the roughness of deposited material. The obtained films are smooth, continuous and uniform in comparison to those produced in the same conditions but without growing the buffer layer.

The production of thin NCD films with roughness around 20 nm from  $\text{CH}_4/\text{H}_2$  (1/99 %) plasmas was easily performed when the Si substrate surface was treated with the combinatorial approach. This method exploits the hammering effect of large grains with respect to the small ones that are effectively seeded on the substrate surface promoting a primary nucleation density higher than that obtained on Si treated in suspension of mono-dispersed diamond powder.

## **References**

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