



# Growth dynamics of nanocrystalline diamond films produced by microwave plasma enhanced chemical vapor deposition in methane/hydrogen/air mixture: Scaling analysis of surface morphology

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## ABSTRACT

Nanocrystalline diamond (NCD) films were produced by microwave plasma enhanced chemical vapor deposition (MPCVD) in methane/hydrogen/air plasma. The thickness of the films was varied from 0.15 to 22  $\mu\text{m}$ . X-ray diffraction (XRD), Raman spectroscopy and atomic force microscopy (AFM) were used to investigate the structure and surface morphology of the films. During a short initial period of the deposition, i.e. from 2.5 min to 60 min, the growth dynamics involve relatively strong non-local effects, followed by a growth stage, which is characterized by a contribution of non-local and non-linear effects to the growth dynamics. The later regime of growth with roughness exponent  $\alpha \sim 0.35\text{--}0.4$  and growth exponent  $\beta \sim 0.25$  can be related with the Kardar–Parisi–Zhang (KPZ) scaling regime of growth. The morphological peculiarities observed on the NCD film surface after already 2.5 min of deposition influence the morphology of the films for prolonged deposition time. Therefore, control over the size and distribution of these peculiarities by systematic variation of the deposition parameters allows to optimize the surface morphology for specific applications. The mountain-like patterns observed on the NCD films surface can be related to conformal KPZ growth regime, in contrast to the cusp-like patterns caused by non-local effects and noise.

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## 1. Introduction

Diamond and diamond films have attracted increasing interest for tribological, electrical, optical, thermal and biomedical applications [1–3] due to a unique combination of material properties including high hardness, chemical inertness, high thermo-conductivity, etc. The high roughness of microcrystalline diamond (MCD) films is a main obstacle to use this type of diamond films for applications where the roughness needs to be minimal. For instance, the film roughness is an essential property for tribological applications. Nanocrystalline diamond (NCD) and ultra-nanocrystalline diamond (UNCD) films possess lower surface roughness [4] compared to MCD films and therefore considered as more suitable materials for applications involving contacting surfaces.

The NCD films are grown under deposition conditions leading to a high secondary nucleation rate [5]. The diamond grain size of NCD

films varies between 10 and 300 nm [6,7]. The NCD films can be prepared in a pure form, i.e. with a small fraction of non-diamond carbon [3], as well as with a composite structure of diamond grains embedded in an amorphous carbon matrix [5,7–10]. NCD grown with high methane concentration may contain as much as 50% non-diamond carbon [6]. The diamond film structure can be effectively controlled from micro to nanocrystalline by adding nitrogen and oxygen in the  $\text{CH}_4/\text{H}_2$  gas mixture [8,11]. The NCD films with composite structure possess often characteristic irregular cauliflower-like surface morphology [5–10]. In general, the diamond grain growth can be described by chemical reactions involving radicals ( $\text{CH}_x$ ) and free hydrogen atoms (H) [12]. The understanding of the NCD film growth dynamics is further complicated by the fact that the NCD film structure consists of diamond grains and grain boundaries.

The scaling concept is related to the properties of a fractal surface and shows high versatility and applicability to describe different growth phenomena [13], including diamond film growth [9,14]. In this method, the deposition process is characterized by a finite set of scaling exponents derived directly from experimental data,

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which is a great advantage of this concept. In addition, the surface area on the micrometer-scale can be studied, in contrast to kinetic Monte Carlo models [15] which enable presently only nano-scale simulations.

The present study aims to investigate the growth dynamics of NCD films prepared in CH<sub>4</sub>/H<sub>2</sub>/air plasma by MPCVD using the scaling concept. The evolution of film roughness and surface morphology is studied along with a structural characterization of the grown films. The influence of growth dynamics at early stages on the succeeding growth stages is elucidated. This study is important, because an improved understanding of the NCD film growth dynamics eventually enables a better control of the film roughness and morphology, which are important aspects in tribology, in the preparation of smooth surfaces, multilayered structures, etc.

## 2. Theoretical background

The scaling concept is based on the Family–Vicsek scaling relation [16]:

$$S_q(L, t) \sim L^\alpha f(t/L^z) \quad (1)$$

where  $S_q$  is the (root mean square) surface roughness or interface width,  $t$  is the deposition time and  $L$  is the length scale. The growth exponent  $\beta$  and the coarsening exponent  $z$  are interrelated as  $z = \alpha/\beta$ , where  $\alpha$  is the roughness exponent.  $S_q(L, t) \sim t^\beta$  for the small deposition time and it scales like  $\sim L^\alpha$  for  $t \rightarrow \infty$ , i.e. when the interface width saturates [13].

Very good agreement between theory and experiment was shown by Castro et al. [17] in the study of cauliflower-like amorphous hydrogenated carbon (a-C:H) film growth. The authors discussed the universality of cauliflower-like fronts in different contexts, namely real plant growth, combustion front and CVD growth. Related publications by Nicoli et al. [18] and Cuerno and Castro [19] provide a theoretical basis of CVD growth of films with cauliflower-like surface morphology. After spatial Fourier transform of the surface  $h_{\mathbf{k}}(t) \equiv \mathcal{F}[h(\mathbf{x}, t)]$ , where  $h(\mathbf{r}, t)$  is the height of the film at time  $t$  and position  $\mathbf{r}$  above the reference plane, the model growth equation can be represented as follows [17]:

$$\frac{\partial h_{\mathbf{k}}}{\partial t} = \left[ V\mathbf{k} + \sum_{j=2}^4 C_j k^j \right] h_{\mathbf{k}} + \frac{V}{2} \mathcal{F} \{ (\nabla h)^2 \}_{\mathbf{k}} + \eta_{\mathbf{k}}. \quad (2)$$

In this equation  $V$  is the growth velocity of the interface,  $k$  is the spatial frequency in reciprocal space,  $C_j$  are coefficients and  $\eta_{\mathbf{k}}$  represents a fluctuation (noise). Concerning the CVD method, the variation of height during the growth can be understood by taking into account next the four main ingredients [17]. *First*, a non-locality is caused by competition between diffusing particles, i.e. particles with higher probability will be attached more frequently to the surface protrusions than to surface valleys, in other words, the former regions are under higher flux of incoming particles than the latter ones. The effect of non-locality is expressed in above equation by odd powers of  $\mathbf{k}$ , i.e. by  $V\mathbf{k}h_{\mathbf{k}}$  and  $C_3 k_3 h_{\mathbf{k}}$  terms. *Second*, an instability due to non-locality of CVD growth can be stabilized by different mechanisms. In general, the overall effect due to these mechanisms can be described by a surface kinetics regime. High/slow kinetics regimes are defined by the value of the mass transfer rate  $k_D$  or equivalently by the effective sticking coefficient  $s$  [19]. High kinetics regime (or instantaneous kinetics) is characterized by  $k_D \rightarrow \infty$  [19] or  $s \sim 1$ , with the meaning that incoming particles will be attached immediately on the arriving place. Such kinetics regime leads to the formation of rough surfaces. On the contrary, in the case of low kinetics regime,  $k_D < \infty$  [19] or  $s \leq 1$ , particles incoming to protrusions diffuse to valleys, and therefore an instability of CVD growth caused by non-locality of growth can be stabilized. *Third*, a non-linear term ( $\lambda/2$ )

( $\nabla h$ )<sup>2</sup> in Eq. (2) describes a lateral growth. This term was introduced by Kardar, Parizi and Zhang [20] and accounts, for instance, for non-conservative effects including broken up-down ( $h \rightarrow -h$ ) symmetry. *Fourth*, fluctuation in the growth system is described by white uncorrelated Gaussian noise  $\eta_{\mathbf{k}}$ .

The scaling behavior of Eq. (2) depends on the surface kinetics regime [18,19]. In the case of instantaneous kinetics regime, no KPZ scaling was found for asymptotic times. Indeed, the scaling exponents  $\alpha = \beta = 1$  (which define the cauliflower-like surface morphology) were revealed for (a-C:H) films [17] grown under high kinetics growth regime, and in this case coefficients  $C_2$  and  $C_4$  in Eq. (2) are equal to zero. These values of exponents differ from the scaling exponents of the KPZ equation in 2d (surface growth), namely  $\alpha \sim 0.4$  and  $\beta \sim 0.25$  [13]. However, in low kinetic regime the coefficients  $C_2$  and  $C_4$  may not be zero and KPZ scaling can be revealed [19]. For instance, it was shown that diamond films with cauliflower-like surface morphology grown by HF-CVD show a growth dynamics with scaling exponents corresponding to KPZ scaling [9]. To summarize, the model Eq. (2) falls into the KPZ equation universality class in the case of the low kinetics regime and does not for the high kinetics regime. KPZ scaling corresponds to conformal lateral growth or the growth along local normal direction, which is an important asset for applications in the micro and nano domains [19].

The KPZ scaling regime was also reported for microcrystalline diamond film growth [14], although the growth dynamics was described by the KPZ equation [20] which differs from the model Eq. (2).

In the context of the present study it is worth to mention the universality of cauliflower-like fronts [17,18]. The roughness exponent  $\alpha < 1$  corresponds to self-affine surfaces and  $\alpha \geq 1$  to surfaces that are self-similar and super-rough. In the case of self-similar surfaces, the geometrical structure of the surfaces is statistically invariant for any lateral observed scale  $L$ , i.e.  $L \rightarrow \infty$ . Self-affine surfaces obey to Family–Vicsek scaling [13] for sufficiently large  $L$ . Castro et al. [17] also stress that a broad spectrum of cauliflower-like surface patterns can be prepared due to a variation of non-linear effects in the growth dynamics.

It was suggested that three stages in the growth dynamics can be distinguished in the case of a-C:H film growth [17,18]. During the short first regime of growth, Mullins–Sekerka linear instabilities [21] play an important role in the formation of a cusp-like surface morphology with characteristic length scale  $l_c$ . It is followed by non-linear growth dynamics due to the competition between cusp coarsening/annihilation and cusp formation induced by noise. Finally, such non-linear growth can be stabilized by the KPZ nonlinearity and asymptotic behavior to KPZ regime can be observed.

## 3. Experimental method

Polished (100) silicon wafers with  $10 \times 10 \times 0.5$  mm<sup>3</sup> dimensions were used as substrates for the deposition of NCD films. The substrates were subjected to a “seeding” ultrasonic treatment in a nanodiamond powder suspension (particle size  $\sim 20$  nm) to form a layer with diamond nanocrystal density of  $10^9$ – $10^{10}$  particles per cm<sup>2</sup> on the substrate surface. The synthesis of diamond films was carried out in a microwave plasma CVD system ARDIS-100 (2.45 GHz, 5 kW) using a CH<sub>4</sub>/H<sub>2</sub>/air mixture as the process gas under the following deposition parameters: substrate temperature of 800 °C, total flow rate of 500 sccm, pressure of 80 Torr, microwave power of 3.0 kW, volume fraction of methane of 4%. Air was added to the chamber through a separate gas flow meter with a concentration equal to the concentration of methane (4% of the gas mixture) to form a nanocrystalline film structure. A series of the films with thickness 0.15, 0.3, 0.6, 1.2, 2.7, 4.8, 9 and 22  $\mu$ m (corresponding to 2.5, 5, 10, 20, 60, 120, 240 and 840 min of deposition time) were produced in identical deposition conditions to monitor surface relief evolution with the deposition time. The film thickness was evaluated from Scanning Electron Microscopy (SEM) images of the film cross-section. Continuous NCD films were only obtained with

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