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3D DIAMOND GROWTH FILM SIMULATION : CORRELATIONS BETWEEN NUCLEATION AND SURFACE PARAMETERS

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Abstract

The development of a three-dimensional simulation of the diamond nucleation and growth presented in a previous paper has been used in this study to determine surface parameters as roughness (R_a , R_q , S_k) and porosity (filling factor Q) of diamond film, according to the crystal size (via the radius R) and the nucleation density N . Evolutions of these surface parameters are correlated to values obtained by a statistical treatment (Poisson's law) based on the random nucleation and subsequent growth of hemispheres. We particularly study the roughness variations with the parameter $\lambda = \pi R^2 N$ which seems to be the key variable in the case of coatings whose nucleation and growth are in agreement with the Volmer-Weber mechanism. From these results, we validate the three-dimensional model and calculate some surface parameters useful for tribological and optical applications whose evolutions with synthesis time have not been reported to our knowledge.

1. Introduction

Some optical electrical and mechanical applications of chemical vapour deposition (CVD) diamond coatings strongly depend on the surface properties. For example, tribological phenomena such as friction and wear are directly linked to the nature of the real area of contact between the surfaces which is, in turn, dependent upon the distributions, sizes and shapes of the asperities [1-3]. On the other, optical devices such as I.R windows and lenses need antireflection diamond coatings whose characteristics are determined by the uniformity and the smoothness [4]. Independently of diamond applications, the realisation of highly oriented diamond films by means of plasma assisted CVD techniques needs a cathodic polarisation of the substrate [5-8]. This cathodic polarisation induces a bias plasma on the diamond crystals whose physical and electrical characteristics strongly depend on the diamond surface roughness [9-12]. In this context, the determination of surface parameters in relation to the CVD diamond growth conditions seems to be fundamental. In this paper, we have chosen to study the theoretical variations of C.L.A roughness (R_a), R.M.S roughness (R_q), and Skewness (S_k) which constitute classical tribological parameters. We have likewise studied the filling factor Q that we have defined in previous papers in the case of an optical monitoring performed during the diamond growth [13-14]. These surface

parameters are studied according to the synthesis time (i.e. the crystal size via the growth rate) and the nucleation density N by means of two theoretical approach's: a numerical three-dimensional simulation of diamond film growth detailed in section 2 which is based on the homothetic growth of single faceted diamond crystals, and an hemispherical model developed in section 3 where diamond crystals are considered as hemispheres. The section 4 gives results of the surface parameters evolutions established with the two models and shows the good correlation's between these ones.

2. Determination of surface parameters with numerical growth model

The three-dimensional simulation of CVD diamond film growth has been previously presented [15]. This model is based on the homothetic growth of single diamond crystals (limited by $\{100\}$ and $\{111\}$ facets) in an Euclidean space, and the selection of the enveloping surface obtained after the crystal interpenetration. The resulting topography is constituted by a succession of bidimensional sections including each of them a series of segments, and separated to each other by a fixed distance. Each segment is defined by two doublets (x_i^j, z_i^j) and (x_f^j, z_f^j) that fix the position of the j th segment inside a given section. The determination of the surface parameters is performed for each bidimensional section and averaged on the all sections. As developed by Guillemot and Patte [16], the filling factor Q is calculated by the relationship:

$$Q = \frac{\sum_j A_j}{L * z_{\max}} \quad [1]$$

Where A_j is the area located between the j th segment and the substrate ($z = 0$), and z_{\max} the higher z coordinate obtained for the section considered. The factor L corresponds to the total length of a section (in our case $L = 100 \mu\text{m}$). In the case of the C.L.A roughness and according to its definition [1], Ra is estimated by the relationship:

$$Ra = \frac{1}{L} \sum_j \frac{(x_f^j - x_i^j)}{2} . F(Z_i^j, Z_f^j) \quad [2]$$

$F(Z_i^j, Z_f^j)$ is a function depending on the relative Z co-ordinate defined for a point of a segment j by the relation $Z^j = (z^j - \bar{z})$ where \bar{z} is the average centre line calculated with all the segments of a section. The function $F(Z_i^j, Z_f^j)$ is expressed as follow:

$$F(Z_i^j, Z_f^j) = |Z_f - Z_i| \quad \text{if } (Z_f \cdot Z_i) \geq 0$$

$$F(Z_i^j, Z_f^j) = \frac{(Z_i^2 + Z_f^2)}{|Z_f - Z_i|} \quad \text{if } (Z_f \cdot Z_i) < 0 \quad [3]$$

According to the R.M.S roughness definition [1], Rq is calculated by the relationship:

$$Rq = \sqrt{\frac{1}{L} \sum_j \frac{(Z_i^2 + Z_f^2 + Z_i Z_f)(x_f^j - x_i^j)}{3}} \quad [4]$$

Where Z corresponds to the relative co-ordinate previously defined. The Skewness Sk which is a measure of the departure of a distribution curve from symmetry [1], is defined by the relationship:

$$Sk = \frac{1}{R_q^3} \frac{1}{L} \int_0^L Z^3 .dZ = \frac{1}{R_q^3} \frac{1}{4L} \sum_j (Z_i^3 + Z_f^3 + Z_i^2 Z_f + Z_f^2 Z_i)(x_f - x_i) \quad [5]$$

In this study, we have chosen to perform simulations in the case of perfect cubo-octahedrons (i.e.

$\sqrt{3} \frac{v_{100}}{v_{111}} = 1.5$) whose nucleation densities are contained between 10^7 and 10^8 cm⁻². The v_{100} growth rate

has been chosen equal to 0.42 μm/hr and corresponds to value classically measured in practice.

3. Determination of surface parameters with the theoretical growth model

3.1. Introduction

The simulation of diamond film growth by means of hemispheres has been presented before [14]. In this model, we assume that the diamond crystallites can be globally considered as N small identical hemispheres with a radius equal to R(t) randomly distributed per unit substrate area. The description of the surface parameters in this case needs the statistical determination of \bar{h} which corresponds to the average height between the film and the substrate when hemispheres join and cover the whole surface of the substrate. This determination consists to define the point P belonging to the surface of the film and separated from the substrate by the height h (Fig. 1). This point belongs to a hemisphere whose centre is the nearest to the point M. We demonstrated that the probability for the point M to be distant from the centre C₂ of a particle by the length r is given by the relationship [6]:

$$P(r, N) = 2.\pi.r.N.e^{-\pi N r^2} \quad [6]$$

Where N is the nucleation density. The height h is directly deduced in Fig. 1 from simple geometric considerations; that is $h = \sqrt{R^2 - r^2}$. Therefore, the average height \bar{h} is given by the relationship:

$$\bar{h} = \int_0^R \sqrt{R^2 - r^2} 2.\pi.r.N.e^{-\pi N r^2} dr \quad [7]$$

We limit the integration to R since h can be considered as null for higher values of R.

3.2. Determination of filling factor Q

The filling factor Q can be easily expressed as a function of \bar{h} :

$$Q = \frac{A}{L * h_{\max}} = \frac{\bar{h}}{h_{\max}} \quad [8]$$

Since we work on a unit surface ($A = \bar{h} . L$ and $L = 1$). It is possible to calculate that h_{\max} does not strongly differ from R (difference below 3%) when the number of intersected hemispheres in a bidimensional section is higher than 5. According to the studied values of growth rate ($v = 0.42 \mu\text{m/hr}$) and nucleation densities ($10^7 < N \text{ (cm}^{-2}\text{)} < 10^8$), we can substitute h_{\max} to R. Therefore, we can develop the expression of \bar{h} given by the relation [7] by performing the changes of variables $u = (r/R)^2$ and $\lambda = \pi R^2 N$:

$$\bar{h} = \lambda R \int_0^1 \sqrt{1-u} . e^{-\lambda u} du \quad [9]$$

By using equation [8], we obtain the filling factor:

$$Q = \lambda \int_0^1 \sqrt{1-u} . e^{-\lambda u} du \quad [10]$$

From the previous relation, we can deduce that Q has limit $\frac{2}{3} \lambda$ as R tends to 0 and $1 - \frac{1}{2\lambda}$ as R tends to infinity. It is important to underline that Q only depends on the parameter λ whatever the nucleation density and the growth rate are.

3.3. Determination of C.L.A roughness Ra

The determination of Ra consists to calculate the average value of the vertical deviation of the profile from \bar{h} previously obtained by the relation [7]:

$$Ra = \int_0^R \left| \sqrt{R^2 - r^2} - \bar{h} \right| . 2 . \pi . r . N . e^{-\pi^2 N} dr \quad [11]$$

\bar{h} is taken as a line, which divides the profile in such way, that the sums of the enclosed areas above and below are equal. Therefore, Ra is expressed as:

$$Ra = 2 \int_0^{\sqrt{R^2 - \bar{h}^2}} \left| \sqrt{R^2 - r^2} - \bar{h} \right| . 2 . \pi . r . N . e^{-\pi^2 N} dr \quad [12]$$

By performing the changes of variables $u = (r/R)^2$ and $\lambda = \pi R^2 N$ as previously described and by using the relation [8], we obtain:

$$Ra = 2R \left[\left(\lambda \int_0^{1-Q^2} \sqrt{1-u} \cdot e^{-\lambda u} du \right) - Q(1 - e^{-\lambda(1-Q^2)}) \right] \quad [13]$$

This relation only depends on λ if we consider the ratio Ra/R (i.e. the relative C.L.A. roughness).

3.4. Determination of R.M.S roughness Rq

In the same manner as Ra , the R.M.S roughness is obtained by the relation:

$$Rq^2 = \int_0^R \left(\sqrt{R^2 - r^2} - \bar{h} \right)^2 \cdot 2\pi \cdot r \cdot N \cdot e^{-\pi r^2 N} dr \quad [14]$$

By performing the same variable changes, we obtain:

$$Rq = R \sqrt{1 - 2Q^2 + \left(\left(Q^2 - \frac{1}{\lambda} \right) (1 - e^{-\lambda}) \right)} \quad [15]$$

As specified in the case of Ra , the R.M.S roughness only depends on the λ parameter if we study the ratio Rq/R (i.e. the relative R.M.S. roughness)..

3.5. Determination of Skewness Sk

According to the Sk definition [1], we can write:

$$Sk = \frac{1}{Rq^3} \int_0^R \left(\sqrt{R^2 - r^2} - \bar{h} \right)^3 \cdot 2\pi \cdot r \cdot N \cdot e^{-\pi r^2 N} dr \quad [16]$$

By using the variable λ , we finally obtain:

$$Sk = \frac{1 + Q^3(2 + e^{-\lambda}) - \frac{3Q}{2\lambda}(2\lambda + 2e^{-\lambda} - 1)}{\left(1 - 2Q^2 + \left(Q^2 - \frac{1}{\lambda} \right) (1 - e^{-\lambda}) \right)^{3/2}} \quad [17]$$

From equations [10], [13], [15] and [17], it seems clear that the studied parameters mainly depend on the parameter $\lambda = \pi \cdot R^2 \cdot N$ which integrates the growth rate (via R) and the nucleation density (via N). In order to validate the two theoretical approaches', we have studied these parameters according to λ . In the case of hemispherical model, we have directly drawn Q , (Ra/R) , (Rq/R) and Sk from previous relationships. In the case of numerical growth model, we have calculated each surface parameter for four nucleation densities, and deduced the ratios (Ra/R) and (Rq/R) by assuming $R = v_{100} \cdot t$ (where t is the synthesis time).

4. Surface parameter evolutions with the two growth models

Fig. 2 shows the evolution of the filling factor Q according to λ for the hemispherical model (solid line) and for the four numerical simulations (dotted lines). The global Q evolution is in agreement with previous paper in which the filling factor tends to one when the synthesis time increases [14]. In our case, Q tends to one when λ raises and λ is proportional to the time t for a fixed nucleation density. We can remark that the filling factor is effectively linked to λ since the four numerical simulations give practically the same curve (see dotted lines in Fig. 2). It is important to point out that the Q evolution in the case of the numerical simulation is in agreement with the hemispherical model although the curve of this last tends more rapidly to 1. This difference can be attributed to the fact that the volume of a hemisphere is not strictly equivalent to the volume of a cubo-octahedron for a given radius R .

Fig. 3 and 4 show the respectively evolutions of (Ra/R) and (Rq/R) according to λ for the hemispherical model (solid lines) and the numerical simulations (dotted lines). These relative roughness parameters have the same evolution with λ and the numerical simulations give similar curves, which are in agreement with the curves of the hemispherical model. If we describe the (Ra/R) evolution, we observe a good correlation between the two models with a rapid increasing of the relative roughness parameter to $\lambda_{\max}^{Ra/R}$ (approximately equal to 0.7), then a slow decreasing for higher λ values. It is important to note that the maxima of the relative roughness parameters do not exactly correspond to the maxima of the roughness parameters. For example, the evolution of Ra according to λ in the case of the four numerical simulations is shown in Fig. 5. We observe the same evolution of the relative roughness (Ra/R) with a maximum of Ra , but the corresponding λ_{\max}^{Ra} is located for a higher value (approximately equal to 1.25). In the case of the numerical simulation where we can separate R and N from λ , we can draw the evolution of Ra roughness according to the time (Fig. 6). Since λ_{\max}^{Ra} is constant and equal to 1.25 in this case, the time $t(\lambda_{\max}^{Ra})$ for which the Ra roughness is maximum is all the more weak that the nucleation density increases. It is important to precise that the maxima of Ra in these four numerical simulations do not correspond to the coalescence step, which is located earlier. We can estimate the coalescence time t_c by considering that two particles join each other when the distance r between their centres strictly corresponds to the diameter of these particles (with the hypothesis that the growth rate v is identical for all the crystals). Consequently, we can write:

$$t_c = \frac{r}{2v} \quad [18]$$

In the case of a random distribution of the particles on the substrate, the distance r can be considered as the average distance \bar{r} between a point on the substrate corresponding to a nucleation site and the nearest nucleation site. Therefore, \bar{r} can be deduced from equation [6] by the relationship:

$$\bar{r} = \int_0^{\infty} r \cdot e^{-\pi N r^2} \cdot 2\pi r N dr = 2\pi N \int_0^{\infty} r^2 \cdot e^{-\pi N r^2} dr \quad [19]$$

By performing the change of variables $x = r\sqrt{\pi N}$ we finally obtain:

$$\bar{r} = \frac{2}{\sqrt{\pi N}} \int_0^{\infty} x^2 \cdot e^{-x^2} \cdot dx = \frac{1}{2\sqrt{N}} \quad [20]$$

By using equations [18] and [20], we can estimate the coalescence time for a nucleation density N by the relationship:

$$t_c^N = \frac{1}{4v\sqrt{N}} \quad [21]$$

Table 1 reports the time of the maxima of Ra $t(Ra_{\max})$ for each nucleation density and the corresponding coalescence time t_c^N when $v = 0.42 \mu\text{m/hr}$. From these results, it is clear that the presence of a maximum of Ra does not correspond to the coalescence step, which always occurs earlier. The invariance of $\lambda_{\max}^{Ra/R}$ in the case of the Ra/R curves can be pointed out on the curves reported in Fig. 6 since $\lambda_{\max}^{Ra/R}$ is obtained by the condition:

$$\frac{\partial(Ra/R)}{\partial\lambda} = 0 \quad [22]$$

By considering $\lambda = \pi R^2 N$ and $R = v \cdot t$, we obtain:

$$\left(\frac{\partial Ra}{\partial t} \right)_{t(\lambda_{\max}^{Ra/R})} = \left(\frac{Ra}{t} \right) \quad [23]$$

Where $t(\lambda_{\max}^{Ra/R})$ corresponds to the time for which the relative parameter Ra/R is maximum. Therefore, $t(\lambda_{\max}^{Ra/R})$ for each curve (for each nucleation density) is obtained in Fig.6 by drawing the line having the slope (Ra/t) and which touches each curve with the same slope at $t(\lambda_{\max}^{Ra/R})$. For example this operation is performed in Fig.6 in the case of the curve corresponding to a nucleation density $N = 10^7 \text{cm}^{-2}$. The table 1 summarises the values of $t(\lambda_{\max}^{Ra/R})$ deduced from the Fig.6, and gives the corresponding values of $\lambda_{\max}^{Ra/R}$ calculated from N and $t(\lambda_{\max}^{Ra/R})$ with the relation $\lambda_{\max}^{Ra/R} = \pi R^2 N = \pi [v \cdot t(\lambda_{\max}^{Ra/R})]^2 N$.

Fig.7 shows the Sk evolution in the cases of the hemispherical model (solid line) and the four numerical simulations (dotted lines). The global evolutions of the numerical curves are in agreement with the hemispherical curve excepted for the end of the curve corresponding to $N = 10^8 \text{cm}^{-2}$. The behaviour of Sk

is difficult to interpret but it is clear that a perfect symmetrical profile of the roughness ($S_k = 0$) in the case of the four numerical simulations is reached when λ is equal to 0.7. In the case of the hemispherical model, this symmetric profile is obtained for a higher λ value ($\lambda \approx 2.25$). For the all simulations, we can observe that for high λ values, the skewness does not vary very much and is characteristic of an unsymmetrical profile where the average height of the film is lower than the median co-ordinate which divides the area under the distribution curve into two equal parts.

5. Conclusions

The determination of some surface parameters such as C.L.A roughness (R_a), R.M.S roughness (R_q), Skewness (S_k), and the filling factor Q has been performed by using two diamond growth models: a numerical three-dimensional simulation where single cubo-octahedral crystals randomly located on an unit surface grow, and a theoretical model where the crystals are represented by hemispheres whose spatial distribution is conform to a Poisson's law. The presented results show that these two approaches' give similar surface parameter evolutions. Therefore, it is possible to describe the diamond surface roughness by means of hemispherical model, which is easier to bring into operation than the numerical simulation. The study of the relative surface parameter R_a/R or R_q/R shows that the roughness only depends on the parameter $\lambda = \pi R^2 N$ which contains the main characteristics of these coatings; i.e. the particle size proportional to R and the nucleation density N . The evolution of R_a with λ shows that the roughness initially increases, reaches a maximum value located at $\lambda = 1.25$ whatever the nucleation density, and then decreases for higher λ values. If we separate the parameters R and N , we observe that the time t for which the R_a roughness is maximum is all the weaker that the nucleation density increases. The evaluation of the coalescence time from the growth rate and the nucleation density shows that this maximum does not correspond to the coalescence step, which occurs earlier. It is important to emphasize that to our knowledge, this behaviour has not been reported before and can be extended to other coatings if the nucleation and growth are consistent with the Volmer-Weber mechanism. Complementary studies will be performed to experimentally determine these surface parameters.

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Figures

Figure 1

Schematic representation of hemispherical growth of two particles C_1 and C_2 having a identical radius equal to R . The point P of the resulting surface belongs to the C_2 particle since its projection M is located nearest to the centre of C_2 as the particle C_1 .

Figure 2

Evolution of the filling factor Q versus the parameter λ in the case of the hemispherical model (solid line) and the numerical simulations (dotted lines).

Figure 3

Evolution of the relative roughness parameter Ra/R versus the parameter λ in the case of the hemispherical model (solid line) and the numerical simulations (dotted lines).

Figure 4

Evolution of the relative roughness parameter Rq/R versus the parameter λ in the case of the hemispherical model (solid line) and the numerical simulations (dotted lines).

Figure 5

Evolution of the C.L.A roughness Ra versus the parameter λ in the case of the numerical simulations for four nucleation densities.

Figure 6

Evolution of the C.L.A roughness Ra versus the synthesis time in the case of the numerical simulations for four nucleation densities. The growth rate v is equal to $0.42 \mu\text{m/hr}$.

Figure 7

Evolution of the skewness Sk versus the parameter λ in the case of the hemispherical model (solid line) and the numerical simulations (dotted lines).

Table 1

Summarise of the characteristic parameters deduced from the four nucleation densities corresponding to the numerical simulations. $t(Ra_{\text{max}})$ is deduced from Fig.6 and corresponds to the time associated with the maximum of Ra . t_c^N corresponds to the coalescence time (for a nucleation density N), $t(\lambda_{\text{max}}^{Ra/R})$ the time

deduced from Fig.6 which corresponds to the maximum of Ra/R , and $\lambda_{\max}^{Ra/R}$ the calculated value of lambda from N and $t(\lambda_{\max}^{Ra/R})$.