



# Growth of highly oriented diamond films by the MPCVD technique using CO–H<sub>2</sub>, CH<sub>4</sub>–H<sub>2</sub> and CH<sub>4</sub>–N<sub>2</sub>–H<sub>2</sub> gas mixtures

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# **Growth of highly oriented diamond films by the MPCVD technique using**

## **CO-H<sub>2</sub>, CH<sub>4</sub>-H<sub>2</sub> and CH<sub>4</sub>-N<sub>2</sub>-H<sub>2</sub> gas mixtures**

**I-H. Choi<sup>1</sup>, P. Weisbecker<sup>2</sup>, S. Barrat<sup>1</sup>, E. Bauer-Grosse<sup>1</sup>**

<sup>1</sup>Laboratoire de Science et Génie des Surfaces, UMR 7570

<sup>2</sup>Laboratoire de Science et Génie des Matériaux et de Métallurgie, UMR 7584

École des Mines, Parc de Saurupt, Nancy, Cedex 54042, France

### **Abstract**

Highly oriented diamond films were deposited on Si (001) substrates by the microwave plasma assisted chemical vapor deposition technique (MPCVD) using the bias enhanced nucleation (BEN) step. The formation of highly oriented diamond (HOD) films is often linked to the presence of few ppm of nitrogen which stabilizes the texture but deteriorates the chemical quality of the film. In this study, we show that carbon monoxide can be used without nitrogen addition to conserve the <001> texture and to promote the {100} facet extension on the top of the diamond film. After a nucleation step carried out by the BEN technique, and after a subsequent growth time limited to 30 min in a CH<sub>4</sub>/H<sub>2</sub> gas mixture avoiding the coalescence step, HOD films were synthesized using CH<sub>4</sub>/H<sub>2</sub>, CO/H<sub>2</sub> and N<sub>2</sub>/CH<sub>4</sub>/H<sub>2</sub> gas mixtures for a growth time fixed to 10~14 hrs. The effect of carbon monoxide or nitrogen on the morphologies and the texture of the diamond films is discussed from the results of scanning electron microscopy (SEM) and the texture measurements performed by X-ray diffraction.

### **1. Introduction**

Chemical Vapor Deposition (CVD) is a promising technology for the production of low-cost and high quality diamond films. The heteroepitaxy of diamond is a key challenge for future

applications as electronic devices or ionising radiation detectors. These applications require a significant increase in the electrical and transport properties such as carrier velocity and lifetime or doping-induced defect formation [1-5]. However the polycrystalline nature of diamond coatings synthesized on silicon substrates induces the formation of chemical and structural defects like grain boundaries, stacking faults and non carbon atom insertion which damage electronic performances. As reported by M.G. Donato et al.[3] and V.I. Polyakov et al.[5], the grain boundaries constitute the main locations where impurities and defects are concentrated. This effect inevitably induces a dramatic deterioration of properties like the free carrier lifetime. One way to limit it is to increase the density of epitaxial diamond particles at the first stage of nucleation to further diminish the grain boundary misorientation. In our previous studies, we obtained 26% epitaxial diamond crystals for total nucleation densities above  $10^9 \text{ cm}^{-2}$  without specific carburization step and for a low bias enhanced nucleation step duration [6].

Since HOD films have been synthesized from a limited epitaxial ratio, the natural evolutionary selection mechanism initially described by Van der Drift [7] and applicable to the diamond thickening step is still necessary to eliminate the ill-oriented diamond crystals and to favour the epitaxied ones which progressively constitute the diamond surface (texturing process). As reported by some authors [8-10], the addition of nitrogen seems to be often unavoidable to correctly carry out the texturing in the case of MPCVD processes and to obtain the  $\{100\}\{111\}\langle 100 \rangle$  microstructure according to the terminology introduced by Wild *et al.* [11]. Nevertheless, two opposite phenomena occur when nitrogen is added: a beneficial effect on the growth rate and on the growth parameter  $\alpha$  ( $\alpha = \sqrt{3} \frac{U_{\langle 001 \rangle}}{U_{\langle 111 \rangle}}$ ), but a detrimental effect due to the incorporation of nitrogen atoms mainly into  $\{111\}$  growth sectors [8,12-13]. A few ppm of nitrogen in a  $\text{CH}_4/\text{H}_2$  gas mixture drastically increases the growth rate and

seems to stabilize the growth parameter  $\alpha$  close to 3 leading to the rapid formation of the  $\{100\}\{111\}\langle 100\rangle$  structure. However, the remaining  $\{111\}$  facets are generally rough and incorporate nitrogen. Except for K. Janischowsky et al. [14] who obtain HOD films without  $N_2$  addition in the case of a hot filament assisted CVD process, the absence of nitrogen leads to the formation of near  $\langle 110\rangle$  texture [10] which is not compatible with the HOD film formation. The possibility to use other gases like CO,  $O_2$  or  $CO_2$  has been envisaged previously [15-19]. Brunsteiner et al.[18] observed that the addition of CO in a  $CH_4/H_2$  mixture can extend the range of crystal-faceted deposition with a higher deposition rate and a higher quality of diamond. Initial growth of heteroepitaxial diamond was successfully performed by Suesada et al.[16] by using a mixture of  $CH_4$  and CO where well octahedra-shaped crystals were obtained for a high carbon proportion ( $C/H_2=10\text{vol}\%$ ). Finally, some authors have reported the possibility to obtain high quality of diamond coating at low temperature by using CO gas [17,19]. The low temperature favours the development of octahedral-shaped crystals which improves the formation of the  $\langle 100\rangle$  fibre axis.

In this paper, we tried to optimise the synthesis of HOD films by using a multi-step growth process using different gas compositions:  $CO-H_2$ ,  $CH_4-H_2$  and  $CH_4-N_2-H_2$  gas mixtures. The objective is to reduce the nitrogen pollution inside the film and then to rapidly enlarge the  $\{100\}$  facets by using CO while maintaining the diamond quality and the growth rate.

## 2. Experimental procedure

Details of the experimental system have been described previously [6,20]. All samples were prepared by using a modified ASTeX MPCVD reactor equipped with a 2.45-GHz generator. The multi-step process consisted to perform a nucleation/growth step (step 1) whose conditions are constant for all samples and the duration limited to 30 min avoiding the

coalescence (see table 1). Then, two successive (step 2 and 3) growth steps were carried out using CO-H<sub>2</sub>, CH<sub>4</sub>-H<sub>2</sub> or CH<sub>4</sub>-N<sub>2</sub>-H<sub>2</sub> gas mixtures (see table 2 for the five presented samples). The other experimental conditions were similar to the growth of the step 1. Feedstock gas flows of H<sub>2</sub>(99.999%), CH<sub>4</sub>(99.99%) and CO(99.97%) were regulated by mass flow controllers. Nitrogen (99.999%) was fed into the chamber via a micro leak for a concentration of about 180 ppm.

The morphology and crystallographic orientation of the films were evaluated by scanning electron microscopy (Philips XL30S FEG) coupled with an image analysis software (APHELION, ADCIS S.A.) and X-ray diffraction pole figure measurements. The films have been characterized by a 4-circle X-ray diffraction goniometer using Co K $\alpha$  radiation. {111} X-ray diamond pole figures were measured on each specimen with a step size of 1° in  $\chi$  and 2° in  $\phi$ . The maximum tilt value was  $\chi=80^\circ$ , the azimuth angle varied from 0° to 360° with a continuous scan. {111} silicon pole figures have been recorded with the same parameters to check the instrumental characteristics and the crystal morphology was characterized using the growth parameter  $\alpha$ .

### 3. Results and discussion

#### 3.1 Morphological characterization of nucleation/growth deposit

Fig. 1 shows the SEM micrograph of the typical deposit after the step 1 (table 1). Well-defined cubo-octahedral diamond crystals have grown from a CH<sub>4</sub>/H<sub>2</sub> gas mixture with  $\alpha \approx 1.8$  as simulated in the inset. We can observe the presence of multiply-twinned particles and a lot of epitaxied crystals which present a square {100} facet parallel to the substrate surface (see for example, the crystal pointed by an arrow). In all samples, the epitaxial ratio was close to 26% and the total nucleation density is about  $10^9 \text{ cm}^{-2}$ .

### 3.2 Structural et morphological characterizations of HOD diamond films

#### 3.2.1. Growth in a CH<sub>4</sub>/H<sub>2</sub> gas mixture

Fig. 2a shows the surface morphology of the sample A obtained after a total growth sequence of 10 hrs (step 2) as reported in table 2. This morphology is characteristic of nitrogen-free gas mixtures with the presence of well-shaped grains whose facets look like rooftops [10]. The corresponding  $\{111\}$  X-ray pole figures is reproduced in Fig. 2b. The presence of a central peak fairly broad and a ring approximately located at  $X \approx 70^\circ$  can be associated to a fibre axis between  $\langle 110 \rangle$  and  $\langle 111 \rangle$ . The obtained texture is in agreement with morphological observations (Fig. 2a and 2c) where we observe large  $\{111\}$  facets tilted in relation to the sample surface. Some emerging crystals exhibit a little  $\{100\}$  facet surrounded by large  $\{111\}$  facets which is characteristic of a high value of the growth parameter  $\alpha$ . Therefore, the obtained texture is not in agreement with the evolutionary selection model which predicts that single crystals having a high growth parameter ( $\alpha$  close to 1.8 in this case) lead to the formation of a  $\langle 001 \rangle$  fibre axis. Consequently, as illustrated in Fig. 2a, epitaxied crystals do not survive during the thickening. A careful observation of sample A at higher magnification (Fig. 2c) shows that they are not single crystals but rather lamellar-twinned particles with a surprising crystallographic relationship which seems to be close to  $\{100\} // \{111\}$  and  $\langle 110 \rangle // \langle 110 \rangle$ . The occurrence a such relations, between three octahedral crystals (labelled 1, 2 and 3 in Fig. 2d), leads to the formation of rooftop morphology as schematised in Fig. 2d (grazing and normal views from top to bottom). This geometrical configuration, that we call afterwards abnormal twinning, induces that  $\langle 110 \rangle_{(1)}$  direction of the octahedron (1) is parallel to the  $\langle 112 \rangle_{(2)}$  direction of the octahedron (2). Similar considerations can be made between octahedra (1) and (3). If we consider that the film microstructure is mainly defined by these crystallographic relationships, the corresponding fibre axis must have two components  $\langle 110 \rangle$  and  $\langle 112 \rangle$ . This is almost confirmed by Ayres et

al. that observe the main  $\langle 110 \rangle$  orientation with a secondary component near  $\langle 113 \rangle$  [10]. The difference between the reported  $\langle 113 \rangle$  direction and the deduced  $\langle 112 \rangle$  from our geometrical considerations can be due to the rough evaluation of texture component by Ayres et al. that specify a near  $\langle 112 \rangle$  direction, or by a more complicated twinning as  $\{100\} // \{111\}$ . The supposed crystallographic relationship can be envisaged if we consider (111) diamond reconstruction such as C(111)2x1:H whose symmetry is compatible with a (001)2x1:H [21,22]. Further investigations are necessary to precise this microstructure

### 3.2.2. Effect of nitrogen

Fig. 3a shows the surface morphology of the sample B prepared with the same conditions as sample A except the addition of 180 ppm nitrogen during the step 2 (see table 2). A large portion of grains are  $\langle 001 \rangle$ -oriented with an azimuthal orientation characteristic of epitaxied crystals. This structure is in agreement with the growth parameter  $\alpha$  which is still close to 1.8 for this experiment. A small portion of grains are in-plane misoriented due to the incomplete selection during the thickening. The corresponding  $\{111\}$ X-ray pole figure is reported in Fig. 3b. This one is clearly dominated by the four  $\{111\}$  peaks of diamond as expected for the highly oriented diamond (HOD) films on silicon substrates.

### 3.2.3. Effect of carbon monoxide

The sample C has been prepared to investigate the influence of CO addition on the growth morphology and the microstructure. As reported in table 2, we have chosen 10% CO in  $H_2$  to ensure that well-faceted crystals develop as reported by Brunsteiner et al. [18]. As seen in Fig. 4, the obtained layer showed well-shaped crystallites, but the presence of in-plane well oriented crystals is difficult to detect. A careful observation of the crystal morphology shows that the abnormal twinning observed for the sample A in the absence of nitrogen does not

appear in this case. On the other hand, the growth parameter  $\alpha$  is decreased from 1.8 to 1.6 by using CO. This is now too low to obtain a  $\langle 100 \rangle$  fibre axis, and the thickening induces the disappearance of epitaxied crystals.

### 3.3. The multi-growth technique

From the previous results, it appears that CO can be used to avoid the abnormal twinning while maintaining a good crystal morphology. The decreasing in the growth parameter  $\alpha$  from 1.8 (with CH<sub>4</sub>) to 1.6 (with CO) can be used to extend the {100} diamond facets but is detrimental to the formation of the  $\langle 100 \rangle$  fibre axis necessary to select the epitaxied crystals.

In a first approach, we propose to carry out HOD films by using two steps with different deposition parameters. The first step is to establish the  $\langle 001 \rangle$  fibre axis by using a mixture of CH<sub>4</sub>/H<sub>2</sub>/N<sub>2</sub>, and a second step with a mixture of CO/H<sub>2</sub> to develop the (001) facets without nitrogen pollution.

Fig. 5a shows the morphology of the sample D obtained with a CH<sub>4</sub>/H<sub>2</sub>/N<sub>2</sub> mixture during 3 hrs (step 2) followed by 7 hrs (step 3) with a CO/H<sub>2</sub> mixture. Epitaxied crystals are visible on the top of the diamond surface but a significant proportion of azimuthally misoriented crystals are still present. A careful observation indicates that these crystals exhibit (100) faces which are not strictly parallel to the surface. For this sample, the establishment of the  $\langle 001 \rangle$  fibre axis is determined by the second step whose duration is limited to 3 hrs. This one is probably not sufficient to correctly define the fibre axis. The third step probably favours the development of misoriented crystals by decreasing the growth parameter  $\alpha$ . The {111} X-ray pole figure presented in Fig. 5b shows the dissymmetry of the four {111} diamond peaks which could be attributed to the preferential development of these misoriented crystals.

Fig. 5c shows the surface morphology of the sample E whose conditions are reported in table 2. We have strongly raised the duration of the second step to better develop the  $\langle 001 \rangle$  fibre axis. Very few crystals are azimuthally misoriented on the top of the surface and the  $\{001\}$  diamond facets are large and parallel to the sample surface. The  $\{111\}$  X-ray pole figure reported in Fig. 5d confirms this structure. To underline the beneficial effect of CO during the third step, we have calculated by image analysis the surface ratio ( $S_{(001)d}/S_{total}$ ) as the ratio of the  $\{001\}$  diamond surface constituted by all  $\{001\}$  facets on the top of the film to the total surface of the surface sample  $S_{total}$ . Fig. 6 shows the results of the image analysis for the samples B (single step with nitrogen), D and E (double steps). If we consider that the surface ratio does not depend on the thickness for a constant value of  $\alpha$ , it is clear that the surface ratio strongly increases when CO is used without deterioration of the fibre axis as confirmed in the case of sample E (Fig. 5c). In the case of the sample D (Fig. 5a), the presence of non epitaxied crystals for which  $\{100\}$  facets are tilted in relation to the surface, hides the effect of CO and induces a decreasing in the surface ratio. In our experiments, it is still necessary to call up a second step with the presence of nitrogen which is too long (10 hrs in our case). This limitation will be probably overcome by using experimental conditions for which CO will favour near-octahedral crystal shapes (higher growth parameter) and by increasing the nucleation density to more rapidly promote the  $\langle 001 \rangle$  fibre axis.

## 4. Conclusion

Highly oriented diamond films have been elaborated by using different gas mixtures like  $CH_4/H_2$ ,  $CO/H_2$  and  $N_2/CH_4/H_2$ . The nitrogen gas is detrimental to the electronic properties but a few quantity allows the  $\langle 001 \rangle$  fibre axis to be created by avoiding the formation of abnormal twinning. This one seems to be defined by the crystallographic relationships  $\{100\} // \{111\}$  and  $\langle 110 \rangle // \langle 110 \rangle$ , and induces a fibre axis with two components close to

<110> and <112> irrespective to the growth parameter ( $\alpha = 1.8$  in our case). The use of alternative carbonaceous gases like CO permits the growth of diamond without nitrogen, but the morphology change (growth parameter decreasing in our conditions) complicates the creation of the <001> fibre axis. We have presented HOD films elaborated by a double step process where the fibre axis is firstly created by using a  $N_2/CH_4/H_2$  mixture, followed by a growth with a  $CO/H_2$  mixture which promotes the extension of the (001) facets while maintaining the fibre axis. Complementary studies are in progress to find experimental conditions where CO could be used during the formation of the <001> fibre axis.

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