INFLUENCE OF LONG TIME NUCLEATION ON HOMOGENEITY OF DIAMOND FILMS GROWN ON SILICON SUBSTRATES[*]

A. Kromka[1], V. Malcher

Department of Microelectronics, Slovak University of Technology Ilkovičova 3, 812 19 Bratislava, Slovak Republic

I. Červeň

Department of Physics, Slovak University of Technology Ilkovičova 3, 812 19 Bratislava, Slovak Republic

The nature of the nucleation centers formed during the so-called bias enhancement nucleation (BEN) of chemical vapor deposited diamond is still an open question. We address this problem by studying a long time nucleation process and its impact upon the nucleation density and quality of grown films deposited on Si substrates by hot filament chemical vapor deposition (HF CVD) method. It was found that the nucleation density of the growth centers on silicon wafers increased drastically with the increasing process time up to a few hours.

1   Introduction

Nucleation is the first step of a diamond film growth. However, the control and understanding of diamond nucleation on non-diamond substrates remains still problematic. In an effort to enhance diamond nucleation during chemical vapor deposition (CVD), extensive work has been performed, and a number of nucleation enhancement methods have been developed [1]. Nucleation density can be increased from less than 10^5 cm^{-2} on untreated substrates up to 10^{11} cm^{-2} on scratched or biased substrates.

Recently, S.T. Lee *et al.* [2] have even shown that very-low-pressure condition can be advantageous for the diamond nucleation. Using a pressure of H_2/CH_4 as low as 10 Pa in HF CVD system, they obtained on an untreated, mirror-polished Si a diamond nucleation densities as high as 10^{10}-10^{11} cm^{-2}. Interesting results also have been shown in the work of W.L. Wang *et al.* [3], where substrate biasing and electron emission via hot filament chemical vapor deposition are considered to be a significant technology because they not only lead to a high diamond nucleation density but also represent a critical step in the growth of heteroepitaxial diamond films.

---

[*]Presented at the Workshop on Solid State Surfaces and Interfaces II, Bratislava, Slovakia, June 20 – 22, 2000.
[1]E-mail address: kromka@elf.stuba.sk

The formation mechanism of diamond crystallites under the effect of a substrate bias voltage is presently still under discussion [4]. Generally, the nucleation of a new phase requires the formation of a nucleus exceeding a critical size and becoming thermodynamically stable. The critical size of nuclei depends on the total free entalphy of formation related to the free energies of the surfaces of nuclei and substrate. The mechanism by which the enhancement of nucleation density occurs is not yet fully clear.

In the following work we would like to present the results demonstrating the important role not only of substrate biasing for diamond nucleation but also the effects of long time nucleation period on density and quality of diamond films.

2   Experimental

2.1   HF CVD reactor

The simplest deposition technique of diamond films is hot filament CVD. Crucial factors in HF CVD are filament material, filament temperature, input gas mixture, substrate temperature, filament-to-substrate separation distance, and gas flow dynamics.
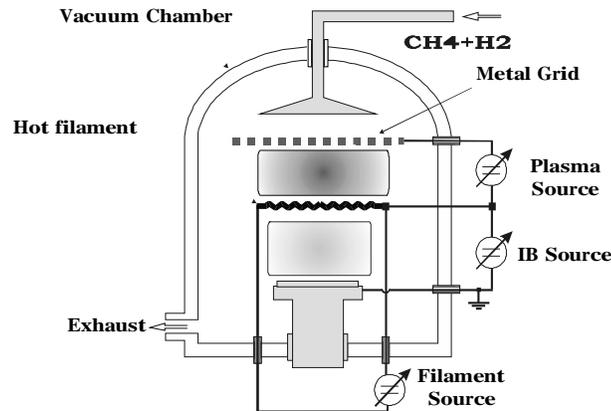

Fig. 1. Schematic diagram of the HF CVD reactor.

In Fig. 1 is viewed a simplified block diagram of an apparatus for deposition of diamond thin films by the HF CVD process. This HF CVD reactor has been designed, developed and constructed at the university.

First, methane and hydrogen mixed gas are *i)* led into a stainless steel chamber and *ii)* controlled by a mass flow unit consisting of mass flow meters, types 258C and 1258C and of a four mass flow controller MKS type 247C. The rotary pump displaces the gas in the chamber to balance the inside pressure and the total gas pressure is adjusted by a needle valve. The mixed gas is thermally activated by tungsten filaments (120 mm in length, 0.6 mm in diameter) heated to more than 2000 °C. The filaments temperature is measured optically with a two color pyrometer, type METRA.

The filaments are set up at a distance of 8 mm above the substrate. The substrate surface temperature is measured with K-type thermocouples positioned in the molybdenum block. The

substrate material is directly heated from the filaments and placed on a rotating (~12 turns/min) substrate holder. The substrate holder consists of the molybdenum block (50 mm in length, 110 in diameter) and a water cooled cooper block.

Over the d.c. heated filaments a plasma-grid is placed and by applying DC power source plasma can be generated between this grid and the filaments. Furthermore, an additional d.c. power supply is connected between the filaments and substrate holder to control bombardment of the substrate surface by positively charged ions and/or by electrons. All process parameters are automatically monitored and controlled by PC unit.

Prior to deposition of diamond films, the tungsten filaments were carburized in a methane atmosphere to enhance the formation of a tungsten carbide layer. This process step reduces tungsten evaporation and stabilizes the carbon flux to the substrate during the deposition process.

2.2   Sample preparation

Mirror polished (111) silicon wafers were used as substrates. The wafers were first ultrasonically cleaned in acetone. Then they were rinsed in NH_4OH for 15 min and washed in de-ionized (DI) water. Then they were etched in 30% HF acid for 1 min to remove the natural oxide. After rinsing in DI water, the substrates were introduced into the HF CVD chamber. The reactive gases were a mixture of CH_4 and H_2. The methane concentration in hydrogen was 1 % (3:300 flow ratio of $CH_4 : H_2$ (in sccm) and the total gas pressure was kept at 3000 Pa.

The deposition process consisted of two stages – *a)* nucleation period and *b)* growth period. The nucleation was utilized at negative substrate biasing of -170 V (at current density of 7.8 mA/cm^2) with varied process time. The film growth was realized at positive substrate biasing of +100 V (at current density of 2.6 mA/cm^2) for 4 hours. All experimental parameters are summarized in Table 1.

Gas flow rate: hydrogen	[sccm]	300
methane	[sccm]	3
Filament temperature	[°C]	2200
Substrate temperature	[°C]	850
Filament-substrate distance	[mm]	8±1
Total gas pressure	[kPa]	3
Methane concentration	[%]	1
i) Nucleation time (U_s=-170V)	[min]	0-240
ii) Growth time (U_s=+100V)	[min]	0-480

Tab. 1. Diamond deposition conditions

3   Results and discussions

The deposited films were characterized by micro-Raman spectroscopy, optical microscopy (OM) and X-ray diffraction.

Conventional micro-Raman measurements of the deposited materials were performed using a Dilor system and 632.817 nm line from a He-Ne laser in the backscattering geometry. A ×100
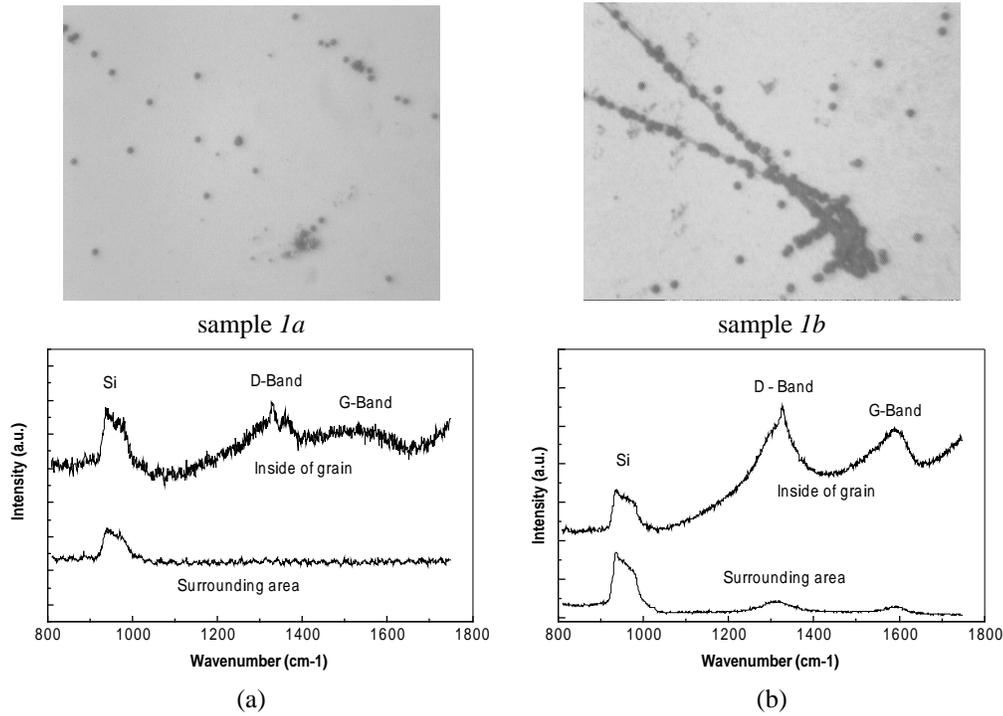
Fig. 2. Surface morphology and Raman spectra of deposited films for (a) 280 min (sample 1a) and (b) 480 min (sample 1b).

microscope objective was used to focus the laser onto a spot of approximately 1 μm in diameter, and to collect the scattered light, which then passed through the spectrometer onto a CCD detector. The X-ray diffraction data were collected by a horizontal goniometer HZG3 equipped with a graphite monochromator in the primary beam tuned for Cu-Kα radiation ($\lambda = 0.1542$ nm).

Figure 2 shows the surface morphology and Raman spectra of diamond films grown at different growth times, i.e. 280 and 480 min, respectively. In this case, only the growth process was activated without any nucleation stage. A few microscopic grains are observed over the substrate surface. The density of these grains is not influenced by the deposition time and no coalescence of the grains is achieved after a long time period. However, the size of these grains increases with increasing the deposition time. Generally, these grains are preferentially formed near the energetically favorable sites like substrate defects and/or scratching lines, like in Fig. 2 for sample *1b*.

The Raman spectrum of the formed grains over sample *1a* shows two broad bands centered at 1300 and 1597 cm^{-1}, respectively (Fig. 2 - sample *1a*). The area surrounding these grains seems to be free of any carbon deposit and only a silicon characteristic band is detectable by the Raman spectroscopy.

The Raman spectrum of sample *1b* (inside the grains) shows three basic bands centered at
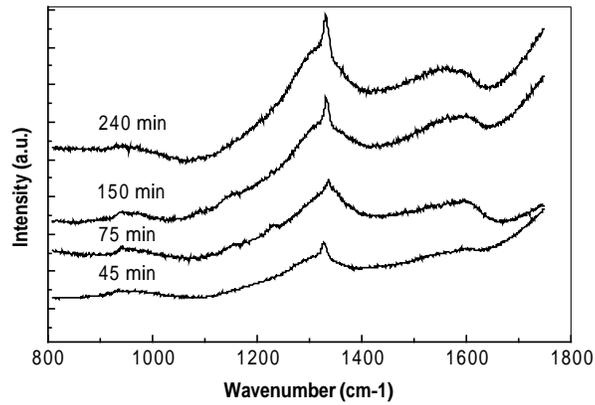
Fig. 3. Raman spectra of samples nucleated at different times (45-240 min) followed by a growth regime for 4 hours.

1310, 1331 and 1585 cm^{-1} with a left shoulder (Fig. 2 - sample *1b*). The area surrounding these grains seems to be featureless as observed by optical microscopy. However, the Raman spectra of this part is characterized by two carbon bands centered at about 1300 and 1590 cm^{-1} and by a signal from the substrate material which indicates poor thickness of the deposit.

These results are similar to previous works [5,6]. The band at 1350 cm^{-1}, called as the D-band, was assigned to polycrystalline graphite with the presence of small sp^3 amount within the bulk of the film. The broad band between 1500 and 1550 cm^{-1} was attributed to amorphous graphite regions, G-band. This G-band could be located either between 1510-1560 cm^{-1} referred to the G$_a$ band or between 1590-1610 cm^{-1} referred to the G$_d$ band (disordered graphite) [9,10].

The shift of the band center at 1310 cm^{-1} may be a result of induced stresses in the deposited films. The second broad band, centered between 1530-1590 cm^{-1} indicates the presence of disordered carbon and defective graphite mixture. The band centered at 1331 cm^{-1} is attributed to diamond characteristic line [6].

Raman spectra of the films deposited at different nucleation time are shown in Fig. 3. These spectra are collected from the area inside of the grains. Samples were grown at different nucleation times followed by growth process for 4 hours. These spectra were recorded at identical conditions, i.e. constant laser power and integration time, and no offset or scaling was introduced. All the samples show similar spectra, with two broad bands. One is centered between 1310 and 1320 cm^{-1} and the second is centered between 1580 and 1590 cm^{-1}. Also a "weak" band centered at about 1330 cm^{-1} is observed. This indicates that the nucleation time does not affect substantially the quality of the grown grains. These Raman spectra are similar to the Raman spectra inside the grain of sample *1b*. In Fig. 4 is shown the surface morphology of these films. The grain density (dark points over substrate) increases with increasing the nucleation time. After nucleation pretreatment for 4 hours coalescence of the individual grains could be observed. In this case a long time nucleation process successfully results in homogenous deposition of films and seems to be only slightly dependent on the substrate material used such a WC-Co, TiC/TiN, plates [7]. Fig. 5 shows the XRD pattern of the samples *2c* and *2d*. The XRD pattern of the samples prepared by combined process, i.e. nucleation and growth stage, reveals the (111)

sample *2a* - 45 min   sample *2b* - 75 min

sample *2c* - 150 min   sample *2d* - 240 min
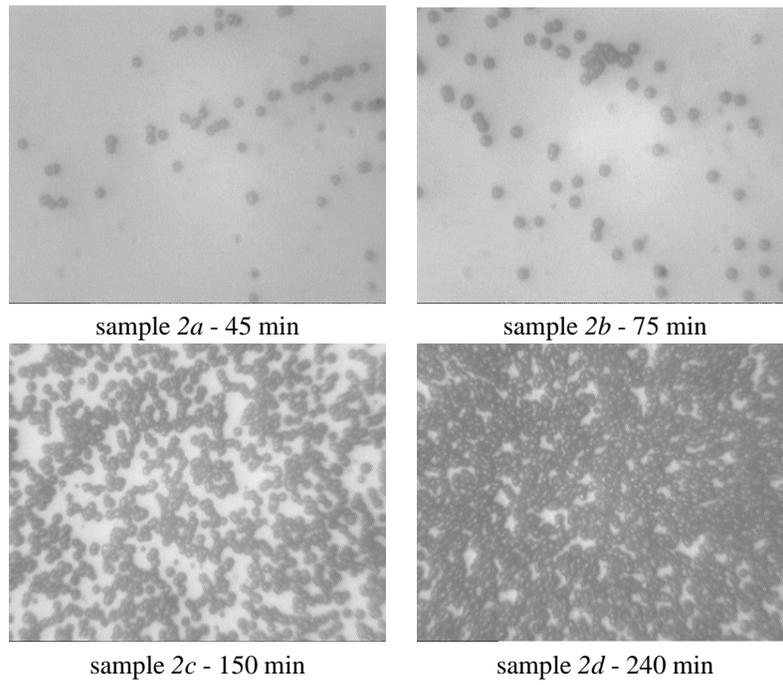
Fig. 4. Surface morphology of samples nucleated at different time followed by a growth regime for 4 hours.
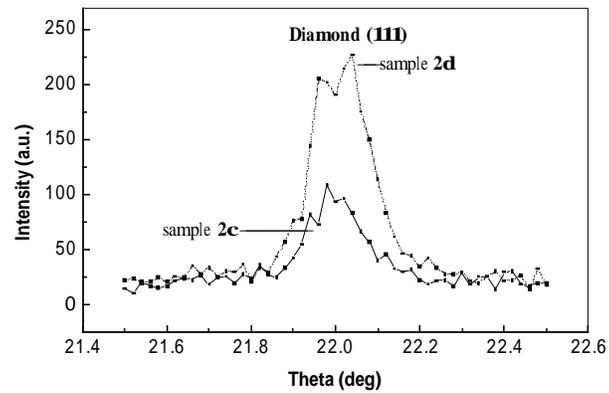

Fig. 5. X-ray diffraction pattern of diamond films nucleated for 150 min (sample *2c*) and 240 min (sample *2d*), and followed by a growth regime for 4 hours.

diamond plane. However, the intensity of (111) diamond line for both samples is small and the line is broad, which indicates only an "early" stage of diamond growth. The XRD pattern of all other samples showed only silicon substrate line and no diamond diffraction peaks could be detected.
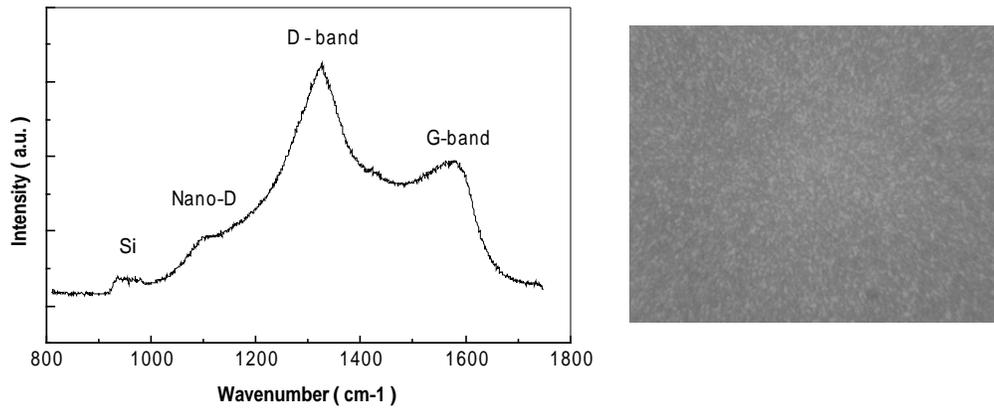
Fig. 6. The Raman spectra and the surface morphology of the sample nucleated for 480 min and grown for 60 min.

The Raman spectra and surface morphology of the sample nucleated for 480 min and grown for 60 min is shown in Fig. 6. There are observed four basic bands: one weak centered at about 1114 cm^{-1}, one broad band centered at 1325 cm^{-1} with a left shoulder up to 1114 cm^{-1}, one also broad band centered at 1580 cm^{-1}, and one silicon band. The higher relative intensity of 1325 cm^{-1} absorption line indicates higher content of sp^3 bonded carbon than sp^2 bonded carbon. The band centered at 1114 cm^{-1} could be assigned to small size (1-2 nm) sp^3 bonded clusters [8].

This investigation has shown that an ion bombardment of the substrate plays an important role in enhancing of the diamond nucleation and reaching homogenous deposition. The deposition process without any nucleation pretreatment leads to the growth of grains at energetically favorable sites. These grains are in the early stage of growth identified as amorphous carbon by Raman spectroscopy, sample *1a*. Further increasing of the deposition time could lead to a possible conversion of sp^1→sp^2→sp^3 and/or more efficient etching of unstable phases. Raman spectra show an additional peak centered near natural diamond (1332 cm^{-1}), Fig. 2 - sample *1b*. However, this effect occurs only over the formed grains indicating preferential three-dimensional growth. The area between these grains is characterized by a delay of the growth of amorphous carbon.

When the ion bombardment of the substrate is included, the density of the formed grains increases, Fig. 4. Ion bombardment could result in *i)* higher local saturation for amorphous carbon, *ii)* an increase of the surface mobility of adsorbed species, *iii)* induction of local stresses and *iv)* enhanced reactions above the substrate and/or conversion of surface composite to small sp^3-bonded clusters, Fig. 6. The required time to achieve homogenous deposition drops down. However, the main mechanism of the diamond nucleation enhancement is not clear yet. On the other hand, accelerated positive ions to much high energy could lead to an unwanted effect, i.e. distortion of sp^3 cluster and resulting in graphitization or only deposition of a-C. Therefore, it is important to define optimal deposition parameters for nucleation and diamond growth independently.

4   Conclusions

University developed an advanced hot-filament chemical vapor deposition reactor that was described in detail. This system allows deposition in both regimes of substrate bombardment, i.e. electron and/or ion bombardment. The diamond nucleation was examined in BEN process. It was found that the film quality and the homogeneity was influenced in its early growth stage. Film deposition without any nucleation pretreatment results only in formation of grains. The density of these grains is nearly independent of the deposition time and their size increased with an increasing process time. However, films deposited under combined stages, i.e. nucleation and growth stage, show time dependence of the grain density on the nucleation time. The density of these grains increases with increasing of nucleation time. The quality of films is not substantially affected. Further investigations are required for a better understanding of the nucleation process via an ion bombardment. We have found that the nucleation period is an important process stage for homogenous diamond growth at the deposition conditions described above.

References

[1] H. Liu and D.S. Dandy: *Diamond Rel. Mater* **4** (1995) 1173

[2] S.T. Lee, Y.W. Lam, Z. Lin, Y. Chen, and Q. Chen: *Phys. Rev. B* **55** (1997) 15937

[3] W.L. Wang, K.T. Liao, J. Wang, L. Fang, P.D. Ding, J. Esteve, M.C. Polo, and G. Sanches: *Diamond Rel. Mater.* **8** (1999) 123

[4] X. Jiang and C.-P. Klages: *Physica Status Solidi (a)* **154** (1996) 175

[5] W.N. Wang, N.A. Fox, P.W. May, M.P. Knaper, G. Meaden, P.G. Partridge, M.N.R. Asgfold, J.W. Steeds, I.P. Hayward, and G.D. Pitt: *Physica Status Solidi (a)* **154** (1996) 255

[6] S. Bühlman, E. Blank, R. Haubner, and B. Lux: *Diamond Rel. Mater.* **8** (1999) 194

[7] V. Malcher *et al.*: *Vacuum*, to be published

[8] A.V. Komich, P.I. Perov, V.I. Polyakov, I.G. Teremtskaya, V.P. Varnin, E.D. Obratztsova, S.M. Pimenov, and V.G. Balakirev: in *Applications of diamond films and related materials*, 3rd International Conference 1995, eds. A. Feldman, Y. Tzeng, W.A. Yarbrough, M. Yokishawa, and M. Murakawa, *NIST* **885** (1995) pp. 597-600

[9] S. L. Heidger: *Mat. Res. Soc. Symp. Proc. Vol.* **383** (1995) 319

[10] M. Nishitami-Gamo, T. Tachibana, K. Kobashi, I. Sakaguchi, K.P. Loh, K. Yamamoto, and T. Ando: *Diamond Rel. Mater.* **7** (1998) 783