Diamond & Related Materials 66 (2016) 83–89

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Synthesis of single crystal diamond by microwave plasma assisted chemical vapor deposition with *in situ* low-coherence interferometric control of growth rate

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ARTICLE INFO

Article history:
Received 26 February 2016
Received in revised form 24 March 2016
Accepted 25 March 2016
Available online 9 April 2016

Keywords:
SC diamond
Homoepitaxy
Microwave plasma
Low-coherence interferometry
Growth rate
Etching

ABSTRACT

We performed synthesis of single crystal (SC) diamond by microwave plasma chemical vapor deposition in methane-enriched H_2–CH_4 gas mixtures, and achieved growth rates more than 30 μm/h, without adding nitrogen in reaction mixture. A low-coherence interferometry (LCI) was employed for precise measurements of the thickness and growth rate of the epitaxial diamond layers in the course of the process. The performance of this *in situ* technique is demonstrated by continuously monitoring the SC diamond thickness in a single growth run upon variation of CH_4 percentage in steps, up to 17%, without switching off the plasma, to produce a "multilayer" diamond film. In addition, etching rate of diamond in pure hydrogen plasma has been evaluated with the same method. The LCI technique allows quick collection of growth kinetics data upon systematic variation of a selected process parameter for the growth optimization.

1. Introduction

The continuous progress in homoepitaxial growth of single crystal (SC) diamond by microwave plasma enhanced chemical vapor deposition (MPCVD) [1–6] made high quality and very pure SC CVD diamonds available for various applications, including radiation-hard detectors [7,8], X-ray optics [9], Raman lasers [10,11], microwave transistors and other electronic devices [12], quantum devices based on color centers in diamond [13,14]. On-line control of the growth process is important to obtain the material of the desired quality. The stability of the process parameters, including the growth rate, is of primary importance to improve the diamond synthesis technology. In addition, the ability to continuously measure in real-time the thickness (and growth rate) of the crystal provides a valuable diagnostic tool to collect growth kinetics data and to study the relationship of the process parameters (pressure, gas composition, substrate temperature) with the growth rate and the crystal structure and properties. The *in situ* control of the growth rate can greatly accelerate multiparametric study of the diamond growth regimes, and allows the reduction of collection time for the experimental data to few hours as compared to the common approach when the preparation of many samples and *ex situ* characterization may take several weeks [15]. In case of polycrystalline diamond film deposition on foreign substrates, such as Si or Mo, the film thickness can be monitored *in situ* with a laser reflection interferometry based on optical reflection dynamics from the film-substrate interface [16,17]. In another version of this approach, oscillations of the film temperature in the film-substrate system are measured by a pyrometer [18,19]. In contrast, upon homoepitaxial growth of CVD diamond on a diamond substrate, the optical contrast on film-substrate interface is absent, so the total thickness of the sample (film + substrate) has to be measured by some way. Only few attempts to use the interferometry for this aim are known to date. Rawles et al. [15,20] applied *in situ* Fizeau interferometry to monitor the thickness of epitaxial diamond film deposited in a hot filament CVD system. They observed the changes in the film thickness from interference fringes formed due to reflection of He–Ne laser beam ($\lambda = 633$ nm) from the front and back sides of the growing crystal. The measurements were limited by small thickness increment of ≈2 μm with claimed best principal accuracy of 10 nm. In practice, the applicability of the method for thick diamond layers (tens or hundreds microns) is restricted by increasing of light scattering due to increasing of the surface roughness with the layer thickness. Since the CVD diamond crystals with height as large as 10 mm and significant

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http://dx.doi.org/10.1016/j.diamond.2016.03.023
0925-9635/

roughness due to terrace-and-rise surface morphology are currently produced the adequate *in situ* optical diagnostic tools should be developed. Here were applied a low-coherence tandem-type interferometry (LCI) [21,22] for real-time measurements of the thickness and growth rate of epitaxial diamond films upon deposition in a microwave plasma in methane–hydrogen gas mixtures at different process parameters. We demonstrate reliable performance of the method for CVD diamond thicknesses of the order of 100 μm (and potentially above 1 mm) and capability to collect rich kinetic data in a single deposition run for a few hours. In addition, etching rate of diamond in pure hydrogen plasma has been evaluated with the same method.

2. Experimental setup and measurement principle

The growth of SC diamond plates was performed using a MPCVD system ARDIS-100 (Optosystems Ltd., 5 kW, 2.45 GHz) [23] on polished (100) oriented type Ib commercial synthetic high pressure-high temperature (HPHT) diamond substrates (Fig. 1). The substrate facets had off-axis angle of 0.7–2.5° towards (100) surface plane as was determined by X-ray diffraction. Before the diamond deposition the substrates were pretreated in an H_2/O_2 microwave plasma (70 Torr, 2300 W, 2 h) to etch away surface defects [23,24]. The epitaxial growth then has been performed using H_2–CH_4 mixtures at pressure p = 130 Torr and total flow rate of 500 sccm. The purity of source gases was 99.99999% for H_2, 99.9995% for CH_4. The other process parameters were the following: incident microwave power P = 3.0 kW (reflected power < 60 W), the substrate temperature 930 ± 30 °C as determined by the two-wavelength pyrometer Williamson PRO-81-35-C for a side surface of the substrate *via* a side quartz viewport of the CVD chamber. The process began from heating of substrate by the plasma in pure hydrogen to a pre-determined temperature, then adding CH_4 precursor to start diamond deposition. The procedure to end the growth was reversed: first, CH_4 gas has been shut-down, and the hot sample was kept in the plasma with continuously reducing methane content and then some time more in pure H_2. This last stage causes the diamond etching by atomic hydrogen and the etching kinetics can be studied with LCI techniques as well. The CVD process time could be varied, depending on growth conditions, from a few minutes to ~100 h to produce the diamond layers with thickness up to 1 mm.

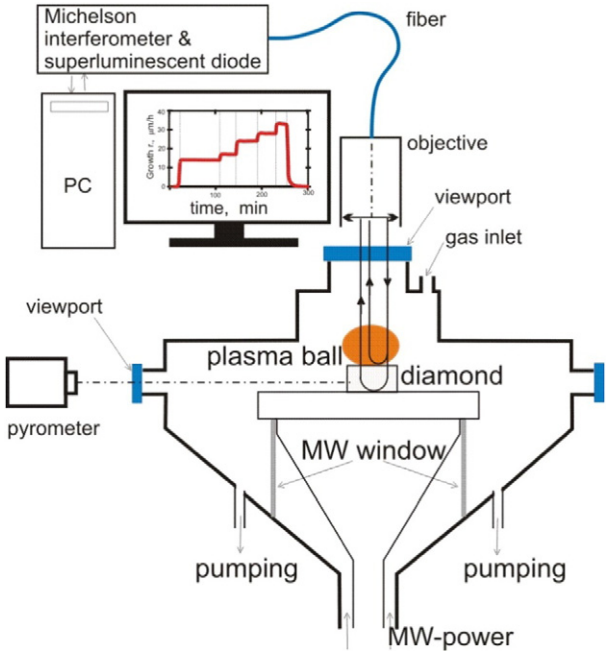

Fig. 1. Set-up for *in-situ* interferometric measurements of thickness of growing epitaxial diamond film in MPCVD reactor.

The produced samples were characterized by Raman and photoluminescence spectroscopy using the LabRam HR800 (Horiba Jobin-Yvon) spectrometer in a confocal configuration with spectral resolution of 1.0 cm^{-1} and spatial resolution of ~1 μm. The excitation laser beam (λ = 473 nm) was focused on the sample surface, and the light from the sample has been collected in backscattering geometry with microscope objective (Olympus, magnification ×100, numerical aperture NA = 0.90). The spectra were taken at room temperature at three different locations on the surface within a 1 mm zone in the sample's center. The surface topography and surface roughness of the diamond crystals were measured with an optical profilometer NewView 5000 (ZYGO) and a laser scanning microscope LSM-710-NLO (Carl Zeiss).

In particular experiment described here the HPHT diamond substrate with dimensions of 4.0 × 4.0 × 0.3 mm was placed on a Mo substrate holder within a MPCVD process chamber (Fig.1). The beam of the low-coherence infrared radiation from superluminescent diode (SLD) at λ_0 = 1.556 μm wavelength with bandwidth Δλ = 30 nm, was directed to the diamond sample through an objective of the interferometer positioned above the 10 mm thick upper quartz window of the CVD chamber. The substrate was placed on the Mo holder without any glue or brazing. No metallic layer was deposited on the back side of the substrate to enhance the reflectivity, as the Fresnel reflection of 17% from the naked diamond surface was enough to get strong enough signal. The details of the LCI principle and instrumentation are reported elsewhere [21].

The optical scheme of the measurements is shown in Fig. 2. The interferometer, designed by IPM RAS, consists of SLD and two interferometers (delay lines) optically coupled to optical fiber. The normal (≈90°) incidence of the SLD beam on the sample surface allows detection of the beams reflected back (Fig. 1). The light collected by the objective and optical fiber comes within aperture as small as ≈2°. The first delay line L_1 (reference) is based on a Michelson interferometer (MI) with two mirrors M1 (fixed), and M2 that moves back and forth with effective speed V_m of 40 mm/s over path length of 40 mm. The optical paths related to M1 and M2 are equal to l_1 and l_2, respectively. The MI produces two output beams 1 and 2, the wavelength of the beam 2 being shifted due to Doppler effect after reflection from the moving mirror M2, therefore a beating at a frequency of several 10 kHz occurs in the photodiode (PD) signal from the beams 1 and 2 after reflection from two sides of the sample, when four beams 1a, 1b, 2a and 2b are formed. The MI gives the optical path length difference $L_1 = 2[l_1 - l_2(t)]$ between beams 1 and 2, which is the time dependent value. The second delay line $L_2 = 2nd$ is formed by two beams, reflected from the front surface ("a") and rear surface ("b") of the diamond sample (S) under test (the sample itself works as a second interferometer). The 1 and 2 beams reflected back from the front surface (beams 1a and 2a) and back surface (beams 1b and 2b) of the sample are collected by the objective and coupled to a quartz optical fiber. Hereinafter, n and d are refraction index and geometrical thickness of the diamond plate. Because of low coherence length $L_{coh} = \lambda_0^2/(\Delta\lambda \times \pi) \approx 30$ μm of the SLD, the interference occurs only if the optical path length difference for two beams after both interferometers is small enough $\Delta L = |L_2 - L_1| < L_{coh}$.

While the mirror M2 moves in one direction the condition for interference $|L_2 - L_1| < L_{coh}$ in the tandem interferometer holds twice. In case (I) the optical path length difference between beams 1 and 2 in MI is zero ($L_1 = 0$), and the beams 1 and 2 reflect from the front surface "a" of the sample, *i.e.* beam 1a interferes with the beam 2a at time t_1. In case (II) beam 1b reflected from the rear surface "b" of the sample makes additional optical path $L_2 = 2nd$, while the beam 2a reflected from the front surface "a", makes the same optical path in the Michelson interferometer, thus $L_1 = L_2 = 2nd$, and the beam 1b interferes with the beam 2a at time t_2. Both interference events appear in photodiode output signal with Gaussian-like envelopes (if the spectral power density shape of SLD is Gaussian-like one) filled with beating frequency