Diamond & Related Materials 55 (2015) 52–63

Contents lists available at ScienceDirect

Diamond & Related Materials

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

Improved surface coverage of an optical fibre with nanocrystalline diamond by the application of dip-coating seeding

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ARTICLE INFO

Article history:
Received 2 November 2014
Received in revised form 20 February 2015
Accepted 5 March 2015
Available online 7 March 2015

Keywords:
Plasma CVD
Diamond film
Optical fibre coatings
Dip-coating seeding
Optical properties characterization
Long-period grating

ABSTRACT

Growth processes of diamond thin films on the fused silica optical fibres (10 cm in length) were investigated at various temperatures. Fused silica pre-treatment by dip-coating in a dispersion consisting of detonation nanodiamond (DND) in dimethyl sulfoxide (DMSO) with polyvinyl alcohol (PVA) was applied. Nanocrystalline diamond (NCD) films were deposited on the fibres using the microwave plasma assisted chemical vapour deposition (MW PA CVD) method. The longitudinal variation of NCD morphology, structure and optical parameters were specifically investigated. The evolution of the film morphology and film thickness along the fibre length was studied using scanning electron microscopy (SEM). The chemical composition of the NCD film was examined with micro-Raman Spectroscopy. The sp^3/sp^2 band ratio was calculated using the Raman spectra deconvolution method. An approximately 5 cm-long homogeneous diamond film has been obtained on the surface of the fibre sample. Thickness, roughness and optical properties of NCD films in the VIS–NIR range were investigated on the reference quartz slides using spectroscopic ellipsometry. The samples exhibited relatively low deviations of refractive index (2.3 ± 0.25) and extinction coefficient (0.05 ± 0.02) along the length of 5 cm, as estimated at a wavelength of 550 nm. In order to show the effectiveness of deposition process on optical fibres, diamond films were also grown on the fibre with induced long-period grating (LPG). The results of transmission measurements demonstrated that an LPG with diamond overlay exhibits the appropriate dependency on the optical properties of external medium. Thus, the deposition process has a negligible effect on the fibre transmission properties.

1. Introduction

Optical fibres have been extensively used for developing a number of sensing devices [1]. The advantages of fibre-based sensors include the resistance to high temperature, immunity to high electromagnetic field and electrical inertness. Various physical and chemical optical fibre sensors as well as devices capable of detecting gases [2,3], pH [4], temperature [5,6] or presence of biological molecules [6,7] have been developed. Optical fibres designed and fabricated mainly for the applications in telecommunication systems are typically covered with polymer coatings which protect the fibre against mechanical damages and harsh environmental conditions. However, the coating does not protect the fibre well against some acids.

Diamond films show a combination of properties which makes them attractive candidates for the application in sensing devices. These properties include, e.g., optical transparency in a broad wavelength range [8,9], chemical stability [10] and biocompatibility [7,11]. Moreover, the properties of diamond films can be easily tuned, i.e., in situ doping during the chemical vapour deposition (CVD) process effectively changes their electrical conductivity [12,13]. Diamond is also known for its high hardness. Diamond thin films can protect optical fibres against either mechanical damage or a chemically harsh environment. Thanks to their optical properties, which include a high refractive index and low optical absorption in the infrared spectral range, diamond thin films can also be applied for enhancing sensing properties of optical fibre devices [14].

Seeding is a key parameter influencing the diamond growth on various substrates [15–17]. This process can be performed via a number of methods [18], where the most commonly applied are ultrasonic treating of the substrate with the diamond slurry [19,20], coating the substrate with carbon-based materials [21], and the application of an interlayer that contains nanodiamond [22,23]. Poor seeding results in a lack of continuity of the deposited films, the appearance of cracks, partial coverage of the substrates, large thickness gradient, or even a lack of film growth. Alberto et al. [24] reported the application of the Taguchi

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http://dx.doi.org/10.1016/j.diamond.2015.03.007
0925-9635/

method as an efficient tool for targeting the appropriate conditions for fibre coating with nanocrystalline diamond. On the other hand, it is not trivial to achieve a good quality diamond–fibre interface due to a large difference in the properties and composition of the optical fibre material, i.e., fused silica, and diamond films [25]. May et al. [26] demonstrated that it is possible to deposit highly-resistive diamond films on optical fibres. Later, Rabeau et al. [27] produced nitrogen-doped diamond films deposited on the optical fibre end-face for fluorescence waveguiding. However, in the SEM images shown in [27] it can be seen that there is still room for improvement with regard to the homogeneity of diamond films produced. In our previous work we applied high-power sonication seeding in different suspensions (water/DMSO) for obtaining diamond films [28]. We have noticed that high power seeding can induce the erosion/cavitation of optical fibres. The application of titanium dioxide interlayer was also investigated; it was shown that a ~20 nm thick interlayer enhanced the growth of film on fused silica substrates [29].

Dip-coating seeding seems to be a promising method for the efficient seeding of optical fibres. This method does not employ any treatment that may damage the optical fibre. Moreover, it allows for easy treatment of long fibre sections. Scorsone et al. proposed seeding in a solution composed of polyvinyl alcohol (PVA) and detonation nanodiamond (DND) particles. PVA was chosen due to its ability to form thin films as well as its high viscosity and high solubility in water and surfactants [30,31].

To the best of our knowledge, neither the effect of dip-coating seeding in PVA/DMSO solution nor a study of spatial variation in morphology, structure and optical properties of diamond grown by chemical vapour deposition (CVD) on fused silica optical fibres has been reported yet. In the present study, we used PVA mixed with diamond slurry, the latter based on diethyl sulfoxide (DMSO) and diamond nanoparticles. The dispersion of particles in DMSO enables to achieve the higher concentration and low diameter of diamond particles (4–5 nm in size) [19,20]. Since optical fibres have a cylindrical shape we had to adopt a dip-coating method instead of typically used spin coating.

In this paper, we also discuss the spatial distribution of properties in nanocrystalline diamond (NCD) thin films deposited on long-period gratings that had been induced in fused silica. In our previous works, we investigated the properties of diamond films as determined at a single position only, and by using a different seeding pre-treatment [28,29]. Moreover, the measurements were performed on relatively short sections of optical fibres. High power sonication [28] enables to seed a short section of the fibre so it can only be used in tip sensing devices. Furthermore, the use of a TiO_2 interlayer [29] complicates the refractive index profile of LPG coverage, which additionally complicates the transmittance signal.

In the present work, we investigated several points on the substrate surface that correspond to the plasma distribution in the CVD chamber. Hu et al. [32,33] demonstrated that the optical properties of NCD films strongly depend on the deposition temperature. The substrate temperature has a crucial effect on the diamond film synthesis and the kinetics of pyrolytic reaction at the growth surface [34]. For this reason, the temperature dependence of plasma distribution and the homogeneity of diamond film growth on optical fibres have also been studied. In order to demonstrate the effectiveness of the deposition process on optical fibres, films were also grown on the fibre with induced long-period grating (LPG) for sensing purposes. The LPG is a periodic modulation of refractive index within the core of an optical fibre [35]. The modulation results in coupling of a core mode and a series of cladding modes. The coupling effect is observed as a series of resonances in the LPG transmission spectrum. Due to interactions between the modes, the resonance wavelengths depend on the fibre properties as well as the optical properties of external medium, which in this experiment is diamond the overlay [36].

The NCD films were grown on fibres by microwave plasma assisted chemical vapour deposition (MW PA CVD). Scanning electron microscopy (SEM) imaging was applied to investigate the morphology of nanocrystalline diamond films. The chemical composition of the deposited layers was investigated by means of micro-Raman spectroscopy, while the deconvolution of Raman spectra was used to calculate the sp^3/sp^2 band ratio. The film growth rate, film thickness, and optical properties in the VIS–NIR range, i.e., refractive index and extinction coefficient were estimated on reference quartz slides by using spectroscopic ellipsometry (SE).

2. Experimental section

2.1. Dip-coating system

In order to investigate the influence of dip-coating seeding on diamond growth, we prepared a single mode optical fibre (cleaved Corning SMF28, cladding diameter of 125 μm, approx. 10 cm in length) where the outer soft polyamide jacket was removed mechanically and the inner polyimide jacket was etched in the hydrogen plasma. The investigated optical fibre was composed of the fused silica cladding as an outer medium, which is high quality amorphous SiO_2, and of germanium-doped fused silica core as an inner medium (diameter of 8.2 μm). The quartz slides were used as reference samples for the deposition process on optical fibres. The fibres and quartz slides were cleaned for 5 min in an ultrasonic bath containing acetone, rinsed in 2-isopropanol and then dried.

Next, the optical fibres were subjected to hydrogenation. The process was performed in the microwave H_2 plasma at 1300 W for 60 min. During the process the total flow of gas was reaching 300 sccm and the pressure was kept at a level of 50 Torr. Hydrogenation was supposed to remove polyimide, which hinders the growth of diamond thin films. The seeding process included a double immersion of the optical fibre in the suspension, each time for 1 min. In the second step, the fibre was turned around and its other end was dipped. The automatic dip-coating system was used for these purposes. Moreover, the reference quartz slides were seeded in the same seeding media by means of spin-coating. The suspension was prepared in a two-step procedure. Firstly, 1 g of solid PVA (average molar mass of 18,000 g mol^{-1}) was suspended in 99 g of DMSO at a temperature of 80 °C, resulting in a 1% w/w solution. Secondly, after the suspension had reached room temperature, 100 g of nanodiamond suspension (DMSO–DND 0.5% w/w) was carefully added.

2.2. Nanocrystalline diamond growth

Diamond films were synthesized using the MW PE CVD system (SEKI Technotron AX5400S, Japan). The optical fibres and reference quartz slides were placed in the CVD chamber on a molybdenum stage (see Fig. 1).

The base pressure inside the chamber was 10^{-4} Torr. The chamber was filled with a mixture of hydrogen and methane. The chamber pressure was kept at 50 Torr with the total flow rate of gases reaching 300 sccm at the molar ratio of methane equal to 4%. The plasma was generated with microwave radiation (2.45 GHz) and optimized for diamond synthesis at a power level of 1300 W [37–39].

The deposition time was kept at 60 min. The influence of the substrate temperature on the fibre coating with diamond was specifically investigated. To this end, the molybdenum stage was heated by an induction heater and controlled by a thermocouple to reach T_c of 300, 475 or 550 °C during the process. Kromka et al. [40] reported that the low-temperature process (430 °C) results in a growth of well-faceted continuous films after the polymer-based seeding pre-treatment. The high-temperature process (830 °C) results in the formation of voids and openings in the deposited diamond layer. After reaching the desired temperature, the heating process was carried on for over 1 h before starting the plasma. The procedure was aimed at ensuring the equal temperature distribution across the Mo holder. After the growth process, the substrate temperature was slowly reduced (2 °C·min^{-1}) to room temperature. The temperature was adjusted by