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2016 IOP Conf. Ser.: Mater. Sci. Eng. 104 012025

(http://iopscience.iop.org/1757-899X/104/1/012025)

IOP Conf. Series: Materials Science and Engineering **104** (2015) 012025 doi:10.1088/1757-899X/104/1/012025

Low temperature growth of diamond films on optical fibers using Linear Antenna CVD system

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Abstract. It is not trivial to achieve a good quality diamond-coated fibre interface due to a large difference in the properties and composition of the diamond films (or use coating even) and the optical fibre material, i.e. fused silica. One of the biggest problems is the high temperature during the deposition which influences the optical fibre or optical fibre sensor structure (e.g. long-period gratings (LPG)). The greatest advantage of a linear antenna microwave plasma enhanced chemical vapor deposition system (LA MW CVD) is the fact that it allows to grow the diamond layers at low temperature (below 300°C) [1].

High quality nanocrystalline diamond (NCD) thin films with thicknesses ranging from 70 nm to 150 nm, were deposited on silicon, glass and optical fibre substrates [2]. Substrates pretreatment by dip-coating and spin coating process with a dispersion consisting of detonation nanodiamond (DND) in dimethyl sulfoxide (DMSO) with polyvinyl alcohol (PVA) has been applied. During the deposition process the continuous mode of operation of the LA MW CVD system was used, which produces a continuous wave at a maximum power of 1.9 kW (in each antenna). Diamond films on optical fibres were obtained at temperatures below 350°C, providing a clear improvement of results compared to our earlier work [3].

The samples were characterized by scanning electron microscopy (SEM) imaging to investigate the morphology of the nanocrystalline diamond films. The film growth rate, film thickness, and optical properties in the VIS-NIR range, i.e. refractive index and extinction coefficient will be discussed based on measurements on reference quartz plates by using spectroscopic ellipsometry (SE).

1. Introduction

Optical fibres have been extensively used for development at number of sensing devices [4]. The advantages of fibre-based sensors include the resistance to high temperature, immunity to high electromagnetic field and electrical inertness [5]. 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 is a material with wide range of extraordinary properties. Transparent over a broad spectrum region, highly chemically and abrasively resistant, nontoxic and biocompatible diamond films are often used as protection coatings in various fields [6–8]. On other hand, low diamond adhesion to substrates (in particular glass or metals) or damage of substrates during chemical vapor deposition (CVD) are the limiting factors for its wider commercial use [9–11]. The use of LA MW CVD has been recently developed [1,12,13] for growth of NCD layers. In such systems, deposition of high quality diamond at lower temperatures and also on larger areas are more feasible than in ordinary systems [1]. Preparing an optical fibres for sensing system is very necessary. Substrate temperature have the crucial impact influence on diamond synthesis process and kinetics of pyrolysis reaction on the growth surface [14,15]. In our study, we proposed to use large areas and low temperature LA MW CVD system. Diamond films on optical fibres were obtained at temperatures below 350°C and optical fibre cover diamond film length more than 20 cm, providing a clear improvement of results compared to our earlier work [3].

2. Experimental

For the growth of NCD films a linear antenna microwave plasma enhanced chemical vapor deposition system (LA MW CVD) system was used. The growth chamber allows the deposition on substrates up to the size of 300 mm×300 mm. Microwaves are delivered into the growth chamber by four pairs of coaxial antennas enclosed in quartz envelopes and powered from both ends. During the deposition process the continuous mode of operation of the LA MW CVD system was used, which produces a continuous wave at a maximum power of 1.9 kW (in each antenna). The base pressure in the chamber was 10^{-4} mbar. Then the chamber was filled with a mixture of hydrogen, methane and carbon dioxide. Pressure in the chamber was kept at 0.1 mbar with the total flow rate of gases reaching 150 sccm at methane molar ratio of 2.5% and carbon dioxide molar ratio of 6%. During the process the stage was heated up to 350°C by induction heater and controlled by thermocouple. The seeding procedure took 7 hour. In order to investigate we prepared a single mode optical fibre (cleaved Coming SMF28, cladding diameter of 125 mm, approx. 30 cm in length) whose polymer coating has been mechanically stripped, and a set of reference samples, i.e., fused silica glass and p-100 Si wafers. The growth 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. 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 polyvinyl alcohol (average molar mass of 18,000 g mol^{-1}) was suspended in 99 g of dimethyl sulfoxide 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 (dimethyl sulfoxide–nanodiamond 0.5% w/w) was carefully added [16].

3. Results and discussion

3.1. Surface morphology

Scanning Electron Microscope FEI Quanta FEG 250 Scanning Electron Microscope (SEM) using 10kV beam accelerating voltage with SE-ETD detector (secondary electron - Everhart-Thornley detector) working in high vacuum mode (pressure 10^{-4} Pa) was used to observed the structure of the surface of optical fibre.

The morphology studies were performed with optical microscopy using combination with a 20x objective magnification and numerical aperture 0.4.

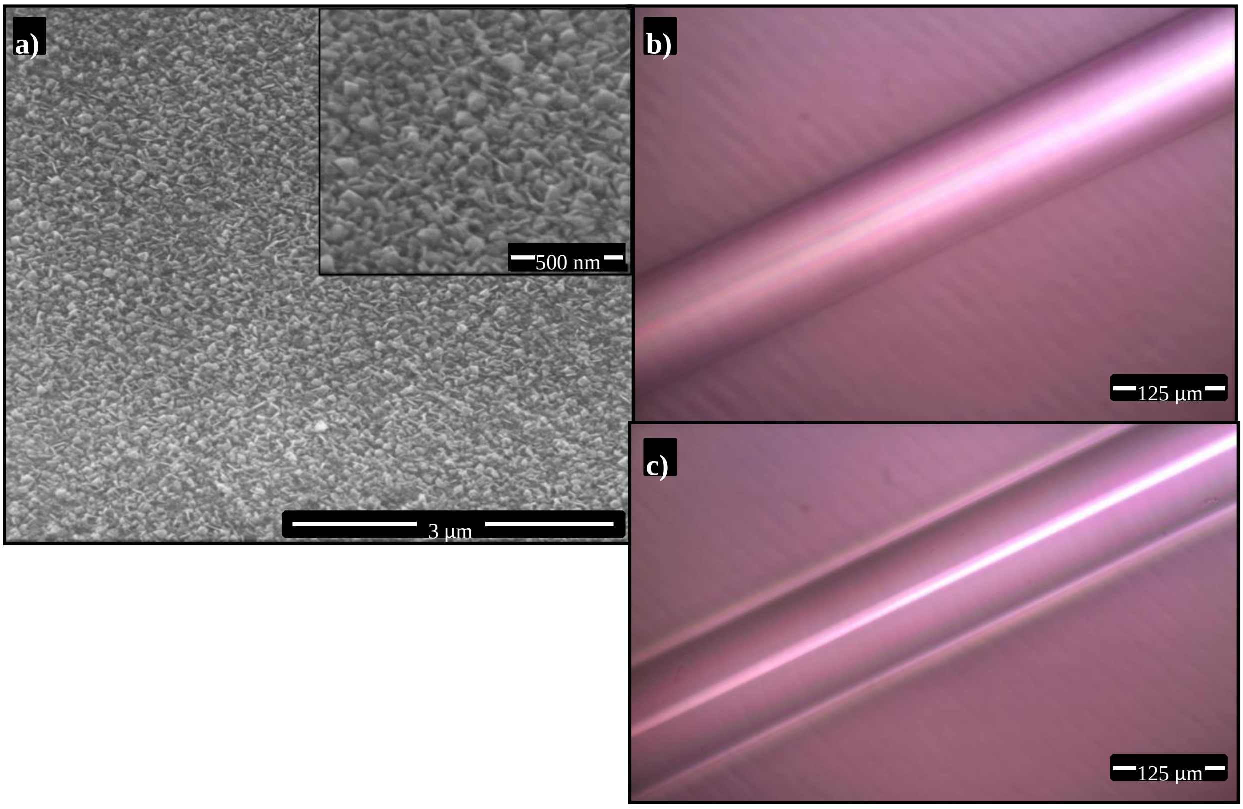

Figure 1. SEM image (a) and optical microscope image (b), (c) of diamond films on fused silica optical fibre.

Figure 1 shows the optical microscope images and SEM images of optical fibre. Use the LA MW CVD system to cover optical fibre results in continuous, homogeneous thin diamond films. Moreover, in sample it can be observed that the size as well as structure of optical fibre was not defected. The values of mean grain diameter ranged from 50 to 100 nm. Figure 1c shows the optical fibre with light guided in core. It could be concluded the core is not damaged during the process. The thin diamond films look similar in all 30cm length. The cladding diameter of optical fibre is 125 nm with core diameter of 8.5 nm. In our study, the edges of crystallites are clearly visible and the film is uniform.

3.2. Optical properties
Spectroscopic Ellipsometry (SE) investigations were carried out with a phase-modulated ellipsometer Jobin-Yvon UVISEL (HORIBA Jobin-Yvon Inc., Edison, USA). The investigated wavelength range was 260 to 830 nm. The experiments were performed at room temperature using an angle of incidence fixed at 70º. Ellipsometric fitting was based on a four-phase optical model (air/surface roughness film (SRL)/ diamond/ silica glass). The dispersion of silica glass was taken from the database [17]. The diamond film has been here assumed to be an isotropic, homogeneous material and its dispersion was fitted to the Tauc-Lorentz oscillator (TL) model. This model has been used recently for amorphous semiconductors by Logothetidis et al. [18,19]. Such materials exhibit a peculiarity due to the presence of two separated contributions of inter-band electronic transition related to sp^2 and sp^3 bonded carbon [20]. The parameters of the TL model were fitted for each of the analysed films. Finally, the assumed optical model was fitted to the experimental data using the nonlinear Levenberg-Marquardt regression method for mean-square error minimization (MSE) [21]. As a result of SE analysis, the thickness and optical constants, i.e. refractive index $n(\lambda)$ and extinction coefficient $k(\lambda)$ were obtained.

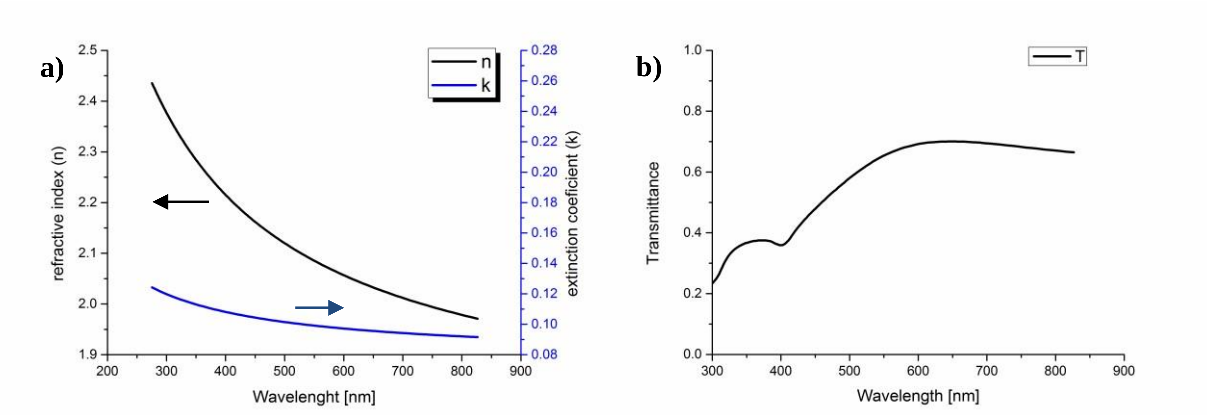

Figure 2. Dispersion of *n* and *k* (a) and transmittance (b) of diamond film measured at quartz slide.

Due to the difficulty of taking ellipsometric measurements directly on the curved surface of optical fibres, the measurements were performed on the reference diamond films deposited on quartz slides during the same deposition process. The applied fitting procedure resulted in the accurate values of film thickness, film roughness as well as dispersion of refractive index and extinction coefficient. Changes of the refractive index and extinction coefficient of the NCD films are presented in figure 2a. The obtained values of refractive index were high, ranging from 2.45 to 2.0 for the NCD films. Hu et al. [22] reported the values of n between 2.16 and 2.08 for the NCD films. The lower values of n (compared to single crystalline diamond) indicate the lower physical density of the films [23]. The k values, which correspond to optical absorption in the deposited films, were below 0.1 at 550 nm, indicating low light absorption over the entire length of the optical fibre. The transmittance in NCD films grown on quartz glass substrates were shown in figure 2b.It could be observed that the transmittance values are below 40% in the range of 300-400 nm. They increase to values above 60% over the 550 nm. The transmittance values below 60% at 550 nm. The length was optimized taking into consideration the application of NCD in the optical fibre grating devices [24]. It should be mentioned that the observed effects can be partially explained by the denser microcrystalline structure of NCD films deposited directly on quartz slides compared to that of the NCD films deposited directly on the fibres. The results obtained in our study correspond well with the SEM images shown in figure 1, which has been discussed above.

4. Conclusion

We have demonstrated that the conformal NCD films deposited on the fused silica fibres. Moreover, the growth parameters of the proposed process have been optimized, resulting in a low-temperature growth of the NCD films on 30 cm-long sections of the optical fibres. The samples exhibited relatively low deviations of refractive index (2.1 ± 0.05) and extinction coefficient (0.1 ± 0.02) along the length of 30 cm, as estimated at a wavelength of 550 nm. Diamond films on optical fibres were obtained at temperatures below 350°C.

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Acknowledgements

This work was supported by the Polish National Science Centre (NCN) under the Grant No. 2011/03/D/ST7/0354. The DS funds of Faculty of the Electronics, Telecommunications and Informatics of the Gdansk University of Technology are also acknowledge.