COMPARATIVE STUDY ON FUNCTIONALIZATION OF NCD FILMS WITH AMINE GROUPS

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Abstract

Unique semiconducting properties made from nanocrystalline diamond (NCD) films highly attractive and promising substrates for bioelectronics systems (biosensors). Nevertheless, the presence of active functional groups on the diamond surface is necessary for chemical immobilization of biomolecules, like DNA. In this paper two plasma-based processes for functionalization of oxygen or hydrogen terminated NCD surfaces with amino groups were compared. The first process was based on deposition of thin (8 nm) amine containing plasma polymer by RF magnetron sputtering of Nylon target in Ar/N2 working gas mixture. RF plasma treatment in NH3 for 10 minutes was used in the second process. The properties of NCD films before and after amination were characterized by scanning electron microscopy (SEM), wettability measurements, spectral ellipsometry, X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and current-voltage (I-V) measurements. The presence of nitrogen (and thus amino groups) on the surface was confirmed by XPS measurements in both cases. SEM images and wettability measurements indicated that the amine containing coating is continuous on both H- and O-terminated NCD surfaces. I-V measurements indicated that the NCD surface conductivity on H-terminated NCD films was preserved only after RF sputtering. The obtained results indicated that NCD surface functionalization from amine containing plasma polymer by RF magnetron sputtering is an alternative technological solution for successful functionalization of diamond surfaces for biosensor applications.

Keywords: diamond, amino functionalization, XPS, surface conductivity.

1. INTRODUCTION

It is known, that a lot of groups proved potential of diamond as an active basement useful for interaction with a biological matter by means of surface functionalization for molecular bonding (for example, DNA) [1-3]. Comparison of diamond with other commonly used surfaces such as gold, silicon, glass and glassy carbon, showed that the diamond is a promising candidate for bioelectronics and biosensor applications due to its unique electronic and chemical properties. Generally, properties of the intrinsic diamond may be altered by hydrogen or oxygen atomic surface termination with influence on its electrical conductivity, electron affinity and wettability. Hydrogenated diamond surfaces are hydrophobic and they induce $p$-type surface conductivity even on undoped diamond. After oxygen termination diamond surfaces are hydrophilic and highly resistive [4, 5]. In our experience nanocrystalline diamond (NCD) films provide economical alternative to single crystalline diamonds as they can be deposited on different large area substrates and provide properties comparable to those of single crystalline diamond. Moreover, NCD films exhibit high enough surface conductivity for biosensor applications [6, 7].

Biological applications require for the chemically inertness diamond surface an efficient and reliable functionalization [1, 2]. According to the literature, diamond surface may be modified by three common methods: wet processes (immersion into concentrated mixture) [8], plasma treatment - grafting of specific functionalities (-OH [9], -NH2 [10, 11], etc.) or organic films containing specific functional groups [12] and UV radiation (UV-enhanced photo-chemical process in liquid or gas phase [13, 14]). The main disadvantages of
these functionalization methods are connected with requirement of specific laboratory conditions (temperature, humidity, drying after immersion to mixtures, etc.) or, on the other hand, quite long time for the surface modification (from few hours to more than 1 day) [8, 14]. Moreover, the surface conductivity is essential condition for electrical signal detection. Grafting of highly electronegative atoms, i.e. fluorine and chlorine, as well as strong chemical processes may significantly degrade the diamond electrical properties. In this respect the great interest was paid for searching of new methods for the functionalization of NCD films.

Recently, RF-plasma polymerizations of N-(6-aminohexyl) aminopropyl trimethoxysilane in a vapor phase become rather interesting for surface modification of NCD films [11]. Thin plasma polymers are well known due to their pinhole free character, mechanical and chemical stability and strong adherence to substrate [15]. In this work novel method for surface functionalization of O- or H-terminated NCD films via covering them with thin amine containing plasma polymer by RF magnetron sputtering of Nylon target in Ar/N₂ working gas mixture was used. According to [16], such plasma polymers exhibit reasonable amine efficiency. Also they are relative resistant towards storing on the open air and dissolving in liquids [17]. Comparison of the presence amine efficiency in polymeric coating with commonly used radio frequency plasma treatment in pure ammonia was made. Last but not least, the possibility of preservation of the NCD surface conductivity was investigated by current-voltage measurements.

2. EXPERIMENTAL

2.1 Growth of NCD films

NCD films were deposited on Si, Si/SiO₂, and glass substrates (10×10 mm²) from a gas mixture of hydrogen, methane and CO₂ in a modified linear antenna MW plasma system (AK 400, Roth and Rau) [18]. Schematic drawing of the deposition system is shown in Fig.1. This system consists of a vacuum chamber equipped with two metal antennas (copper) located in quartz tubes. Two microwave generators (2.45 GHz, MX4000D Muegge) working at pulse-frequency up to 500 Hz and maximum power up to 4.4 kW in pulse at each side of the linear antenna (conductor) were used by the system.

![Fig. 1 Schematic drawing of linear antenna microwave PECVD system](image)

NCD films were grown on Si/SiO₂ and Si substrates for SEM, wettability tests and XPS. For Raman spectroscopy and electrical measurements NCD films were grown on glass substrates. Prior to the deposition processes all types of substrates were seeded in a suspension liquid of nano-diamond powder (5 nm) with deionized water for 40 minutes using ultrasound bath (100 % power), except of glass/Au IDC (only 5 minutes at 20 % power). The NCD films were grown under following conditions: H₂ (100 sccm), CH₄ (5 sccm), CO₂ (20 sccm), total vacuum pressure 10 Pa, deposition power 1700 W, substrate temperature 460 °C, deposition time 15 hours. Part of NCD films was exposed to the oxygen radio frequency (RF) plasma (45 W, 1 min) in order to obtain hydrophobic and electrically insulating surface properties (resistivity > 10 GΩ).
2.2 Deposition of amine containing plasma polymer

The thin (over 8 nm) plasma polymer films were deposited on NCD films by RF magnetron sputtering of Nylon 6,6 (Goodfellow) target (81 mm diameter, 3 mm thickness) in Ar/N₂ (50:50) working gas mixtures using a cylindrical plasma reactor depicted in Fig. 2 (left). Deposition equipment consisted of a cylindrical processing chamber (volume of 100 l) pumped by means of a rotary and a diffusion pump (base pressure 2×10⁻³ Pa). The pressure in the processing chamber was settled from 1 to 5 Pa. The plasma was sustained using water-cooled RF planar magnetron, operated at a frequency of 13.56 MHz, at an applied power of 40 W and at a pressure of 2 Pa. The distance from sample holder to magnetron was 100 mm [17].

Generally, after each deposition the working gas mixture flow was shut off and the samples were left in the chamber under vacuum for 30 minutes in order to avoid an oxidation after the extraction of the samples from the chamber which will cause decrease of the concentration of the radicals entrapped in the films.

2.3 Radio frequency NH₃ plasma treatment

RF plasma treatment in 100 % ammonia atmosphere was used for functionalization of few NCD films in experimental set-up presented in Fig. 2 (right). The processing chamber was pumped to the base pressure of 10⁻³ Pa by means of a turbomolecular and a diaphragm pump.

Cylindrical processing chamber (volume of 2 l) was equipped with two electrodes (diameter 100 mm). The grounded electrode was mounted on the top of the chamber opposite the other electrode which was used as sample holder. The distance between electrodes was 16 mm.

Bottom electrode was connected to RF generator (13.56 MHz) and operated at a constant power of 4 W. The pressure in the deposition chamber was tuned to 25 Pa (NH₃ gas flow was 50 sccm).

![Fig. 2 Schematic drawing of plasma reactor for fabrication of amine containing plasma polymers (left) and RF plasma reactor for treatment in NH₃ atmosphere (right)](image)

2.4 Characterization of the sample properties

The surface morphology and grain size of NCD films before and after functionalization were investigated by scanning electron microscopy (SEM, e_LINE writer, Raith GmbH). In the case of NCD films covered by thin plasma polymer film, contact angle and SEM were measured additionally in different places of the sample in order to prove the homogeneity of the polymeric coating. In addition, SEM was made in order to confirm that polymeric film was continuous. Thus, the photolithographic mask was applied on few H-terminated diamonds and the films were treated in oxygen radio frequency plasma (45 W, 1 min) to generate alternating H/O-terminated patterns of ~190 nm widths. It is known that such patterns will have different electron emission (darker/brighter parts in SEM images) and there will be clearly visible border between them. Then the half of size of these NCD films (without Si mask) was covered with polymeric coating. After that the samples were rinsed by acetone, stripper, deionized water and dried. This process removed possible surface contamination [19]. SEM images proved the quality of H/O-termination by clearly seen contrast.
The diamond character of NCD films before and after functionalization was investigated by Renishaw InVia Reflex Raman spectrometer with the excitation wavelength of 442 nm.

The hydrophobic/hydrophilic character of NCD surfaces was confirmed by wettability tests. Wettability measurements were determined by deionized water droplet (~ 3µl) at room temperature by static method. Material-water droplet system with a reflection goniometer (Surface Energy Evaluation (SEE) System) and CCD camera were used for the wettability measurements. Each measurement was repeated for 3 times in order to obtain average value of the contact angle calculated by multipoint fitting of the drop profile using SEE software.

The thickness of the amine containing coatings was determined by means of spectral ellipsometry (SE) using a variable angle spectroscopic ellipsometer (Woolam M-2000DI) in the wavelength range of λ=192-1690 nm at an angle of incidence AOI= 55-75° in air and at room temperature. In order to obtain the thickness of the coatings, recorded SE spectra were fitted with multilayer model (Si/SiO2/plasma polymer) using the CompleteEASE (Woolam) analysis software.

The chemical composition of the samples was analyzed by X-ray photoelectron spectroscopy (XPS, Specs Phobios 100). The system consists of a multi-channel hemispherical electrostatic analyser (Phoibos 150, Specs) and a dual (Al/Mg) anode X-ray source. The XPS spectra were acquired at a constant take-off angle of 90°. Wide scans were recorded using 40 eV pass energy (step 0.5 eV, dwell time 0.1 s), whereas high resolution scans were recorded at 10 eV pass energy (step 0.05 eV, dwell time 0.1 s, 10 repetitions). In the case of RF sputtered nylon coatings and NCD films treated in NH3, all the binding energies were referenced to the C 1s carbon peak at 285.0 eV. As for the non-functionalized NCD films the XPS spectra were referenced to peak at 285.3 eV, which corresponds to sp³ functional group. XPS peak positions were determined with an accuracy of 0.2 eV. Curve fitting was performed with CasaXPS software using linear baseline and Gaussian line shapes of variable widths.

The surface conductivity of the NCD films was characterized by current-voltage (I-V) measurements using interdigital metal (Au) contacts (IDCs) fabricated on their surfaces. The IDCs were prepared as six electrodes in each patterned plurality with separation distance 200 µm. Electrical measurements were performed at ambient conditions, i.e. atmospheric pressure and room temperature, with DC bias swept in the range from -2 to 2 V using the Keithley 237 source-measure unit. The bias voltage sweeping rate was 100 mV/s.

3. RESULTS AND DISCUSSION

SEM images of H-terminated NCD films before and after RF plasma treatment in NH3 are shown in Fig. 3a-b. They indicate that no significant changes in surface morphology or grain size of NCD films after RF plasma treatment in NH3 were observed. Fig. 3 c) and d) show that thin plasma polymer is continuous and completely covers the surface of NCD film with H/O-terminated patterns and there is no absolutely visible border between two patterns. SEM images and wettability measurements indicated that the amine containing coating is continuous on NCD films. The thickness measurements showed that the thickness of polymeric coating was over 8 nm. Wetting measurements confirmed the hydrophobic character of NCD films after H-termination (angle over 80°) and hydrophilic properties (angle ~ 10°) of oxidized NCD films before functionalization processes. The value of wetting angle repeated for 3 times in different places of diamond covered by polymeric coating was ~ 25° that also confirm its homogeneity.
Fig. 3. SEM images of the samples on Si substrate: a) H-NCD film, b) H-NCD film after RF NH\textsubscript{3} plasma treatment, c) visible border between uncovered side of NCD film with H/O-terminated patterns and covered with polymer, d) H/O-NCD film with patterns totally covered with plasma polymer (∼ 8 nm)

Raman spectra of NCD films before and after application of plasma polymer are presented in Fig. 4. All spectra reveal the diamond characteristic peak at 1330 cm\textsuperscript{-1} and a broad band at about 1600 cm\textsuperscript{-1} related to non-diamond phase (G band). Raman spectroscopy was not sensitive for thin polymer layer deposited on diamond surface. Raman measurements of NCD films before and after surface functionalization with amine containing plasma polymer reveal nearly identical spectra.

Table 1 summarize concentration of nitrogen detected by XPS on the surface of Nylon plasma polymer, NCD films after functionalization with amine containing plasma polymer and RF NH\textsubscript{3} treatment. The obtained results indicated presence of amino groups on the functionalized diamond surface. The XPS analysis of the high resolution C 1s peak of as-deposited hydrogenated NCD film revealed its qualified chemical composition: 90 % of sp\textsuperscript{3} and 10 % of sp\textsuperscript{2} phase. It has to be noted that no nitrogen signal was detected by XPS measurements on the diamond surface before its surface functionalization.

Fig. 4 Raman measurements of diamond films before and after functionalization with thin plasma polymer

The concentration of nitrogen detected on the NCD surface covered with polymer is nearly five times higher than the NCD surface treated by NH\textsubscript{3} plasma. The process of RF sputtering of Nylon target will promote the direct chemical incorporation of nitrogen within the formed polymeric coating [8]. Probably, for this reason polymers deposited on the NCD surface exhibit more desirable amount of amino groups than NCD films treated in RF NH\textsubscript{3} plasma. Thus, grafting of amine groups on diamond surface by means of RF plasma treatment is less effective for obtaining of high density of −NH\textsubscript{2} groups favourable for cell attachment or DNA immobilization.

Table 1 Concentration of nitrogen detected by XPS on the surface of Nylon plasma polymer, NCD films after functionalization with amine containing plasma polymer and RF NH\textsubscript{3} treatment

| Nylon plasma polymer | H-NCD + polymer | O-NCD + polymer | H-NCD + NH\textsubscript{3} plasma | O-NCD + NH\textsubscript{3} plasma |
Fig. 5 represents a comparison of surface conductivity ($\sigma$) of NCD films before and after their functionalization. A substantial decrease of the surface conductivity on the H-terminated NCD surface is observed after the deposition of thin amine containing plasma polymer (conductivity decreases from $10^{-5}$ to $10^{-7}$ S). Nevertheless, such surface conductivity is still high enough for fabrication of biosensor devices.

**CONCLUSIONS**

In this work, amine containing plasma polymer deposited by RF magnetron sputtering of Nylon target was successfully used for functionalize H- and O-terminated NCD films and its efficiency was compared with RF plasma treatment in NH$_3$ atmosphere. Basic characterization of functionalized NCD films focused on keeping initial surface conductivity and finding a favourable chemistry. XPS analysis confirmed that plasma polymer treatment of NCD film resulted in nearly 5 times higher concentration of nitrogen than for NCD samples treated in RF NH$_3$ plasma. In addition, I-V measurements showed that the surface conductivity of H-terminated NCD films decreased only by two orders of magnitude after their functionalization with plasma polymer. Consequently, the presence of sufficient amount of functional amino groups and preservation of induced surface conductivity was achieved with covering of hydrogenated NCD films with thin amine containing plasma polymer. These results show an alternative and simple way how to cover diamond films with amine-containing groups for their further application as functional layer for bioelectronics and biosensor applications.

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REFERENCES


