PULSED LINEAR ANTENNA MICROWAVE PLASMA – A STEP AHEAD IN LARGE AREA MATERIAL DEPOSITIONS AND SURFACE FUNCTIONALIZATION

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Abstract

A technological progress in the large area growth of diamond films and carbon nanotubes by pulsed linear antenna microwave plasma system is presented. We show a correlation between process parameters and nano- or poly-crystalline film character. Diamond coated mirrors and ATR-FTIR prisms are shown as multifunctional optical elements suitable for detection of molecules and functionalized nanoparticles. Additional positive feature of the presented plasma system is a low temperature hydrogen functionalization of diamond films. Finally, we present that combination of such plasma with radio frequency modulated substrate bias results in a growth of oriented CNTs over large area.

Keywords: microwave plasma, CVD deposition, diamond, CNT, functionalization, low temperature

1. INTRODUCTION

Carbon nanotubes (CNTs) were discovered by S. Iijima in 1991 in the form of soot [1] and since then they became probably the most popular form of carbon in the state-of-art science and technology with many promising applications from electronics to chemistry and biology. [2] In this respect, diamond as another well-known form of carbon has also gained a lot of interest in the past decade. This is because diamond features unique combination of physical (high thermal conductivity), mechanical (hardness, Young's modulus, wear resistance), chemical (chemical inertness, yet high affinity for surface covalent bonding with specific organic molecules), optical (high transparency in wide optical range, high acoustic velocity) and electrical (wide band gap semiconductor – tunable electronic behavior) properties together with high biocompatibility.[3] Nanocrystalline diamond (NCD) films represent inexpensive alternative to single crystalline diamond with ability to grow on arbitrary substrates, with tunable roughness and tunable graphite to diamond ratio (represented by sp²/sp³ bonds ratio).[4] Recent studies confirmed that tailoring of nanocrystalline diamond properties (morphological or material) has high potential of applicability in interdisciplinary fields (electronic, optics, life science, regenerative medicine, etc.).[5]

Advances in a wide range of plasma and electrical discharge deposition methods have led to a dramatic increase in diamond growth rates. Nowadays, large area deposition of NCD films with controllable morphology and material properties gains on importance. The large area deposition of NCD films is still not a trivial task due to the requirement of constant growth conditions i.e. plasma homogeneity over that area. Standard or modified hot filament (HF) chemical vapour deposition (CVD) processes are mostly employed for this task.[6] The main limitations of the HF CVD systems are: i) the filament non-stability during the CVD process (i.e. chemical and physical changes within the process time), ii) contamination of the films by impurities from filaments, and iii) restriction of using higher amounts of oxygen containing gas species due to filament burning. To grow high quality diamond films, microwave (MW) plasma CVD systems are typically used.[7] However, the “ball” character of plasma limits their extension to large area depositions. The microwave-based surface wave discharge (SWD) systems represent an alternative solution to the above mentioned systems.[7,8] Among diverse SWD configurations the linear antenna MW technique seems the most promising solution for large area deposition of NCD films. Yet the conditions for diamond growth are quite different in each type of deposition system. Our recent study has experimentally showed the ability to grow thin (100 nm), fully closed, diamond films over large area (30x30 cm²) by the linear antenna pulsed MW
plasma CVD process from the hydrogen-based gas mixture.[9] A typical size of diamond grains in the films is between 5 to 20 nm.[10]

In this paper we present the pulsed linear antenna microwave plasma (PLAMWP) system as a promising technological solution for large area depositions of carbon allotropes (NCD and CNT). We also show a low temperature hydrogen plasma treatment which can generate surface conductivity on diamond as it is common for high temperature processes. Advantages of the PLAMWP system are discussed with respect to the commonly used ball-like plasma systems.

2. EXPERIMENTAL

**Deposition system** with the pulsed linear antenna microwave plasma as used in this study is shown in Figure 1. The system employs two microwave generators (2.45 GHz, Muegge) working at a pulse frequency up to 500 Hz and maximum power up to 4.4 kW in a pulse at each side of the linear conductor located in the quartz tube. The substrate holder stage can be resistively heated up to 800°C and moved up/down to control the distance to the antenna. Next, it can be radio-frequency (RF) biased (13.56 MHz, 600W/500V) to control energy of ions impinging on the substrate surface. The deposition area is as large as 20x30 cm².

![Fig. 1](image)

**Diamond thin films** were grown on glass (Corning, AF45, microscopic slides – all in sizes up 1x3 inches) and (100) oriented silicon substrates (in diameter up to 4 inches). Before the chemical vapor deposition, substrates were pretreated by using previously reported protocol.[11] Briefly, substrates were ultrasonically cleaned 15 min in isopropyl alcohol, 10 min in deionized water and dried by nitrogen gun. Then they were immersed in a suspension of deionized water and ultradisperzed detonation diamond powder (diameter 5-10 nm, New Metals and Chemicals Corp. Ltd., Kyobashi) and ultrasonicated up to 40 min. Our previous study has shown that seeding densities as high as 10¹¹ cm⁻² are achieved. Diamond films were grown from hydrogen-rich gas mixtures of methane (0.5-2.5 %) and carbon dioxide (0-10%). Microwave power was 2.5 kW in a pulse. Total gas pressure was 1 or 0.1 mbar and the substrate temperature was kept between 650-750°C.

**Carbon nanotubes** were grown on silicon substrates (10x10 mm² large, 550 µm thick) covered with 1.5 µm thick SiO₂ layer. At first, thin Ni layer (used as catalyst) with thickness 6 nm was evaporated onto SiO₂
surface. Then the Ni layer was annealed in 2 kW microwave based hydrogen plasma at the temperature of 600°C and pressure of 0.5 mbar for 10 min. Isolated nano-islands were formed from continuous Ni layer during the plasma annealing. The Ni nano-islands were used to catalyze growth of CNTs. The growth of CNTs was performed in the methane-hydrogen atmosphere (30% of CH₄ in H₂) at the pressure of 0.2 mbar and temperature of 600°C for 30 min. The plasma was formed by microwave (2kW at each antenna side) and RF biasing (600 W).

**Hydrogen plasma treatment** of the NCD samples was carried out in order to induce surface conductivity. All NCD structures were exposed to hydrogen plasma at the same conditions (microwave power 1000 W, vacuum pressure 0.1 mbar, 100 sccm of hydrogen flow, and processing time 30 min), only the substrate temperature was varied from 150 to 400°C by resistive heating of the water cooled sample stage. Experiments with changing the NCD film wetting properties were performed applying the RF plasma at power read 84 W and 50 V biasing. Process pressure was 1 mbar at 100 sccm H₂ flow and temperature below 45°C. The process duration was varied from 30 seconds up to 1 hour.

**Material characterization** of the NCD films or carbon nanotubes was done by means of analytic techniques. Surface morphologies or grain size of the deposited NCD were characterized by scanning electron microscopy (SEM, e.LINE writer, Raith GmbH). Diamond character of the films was determined from Raman spectroscopy (Renishaw In Via Reflex Raman spectrometer, excitation wavelength of 325 nm). The surface conductivity of hydrogen-plasma treated NCD films was characterized by current-voltage (I-V) characteristics. Electrical measurements were performed at ambient conditions, i.e. atmospheric pressure and room temperature, with a DC bias swept in the range from -1.5 to 1.5V using the Keithley 237 source-measure unit. The bias voltage sweeping rate was 100 mV/s.

![Fig. 2](image.jpg) Surface morphology of diamond films grown by the pulsed linear antenna microwave plasma system at 1 mbar (a) and 0.1 mbar (b). Scale bars are 100 nm (a) and 400 nm (b).

3. **RESULTS**

3.1 **Growth of nanocrystalline and polycrystalline diamond films**

Figure 2a shows SEM surface morphology of diamond films grown by the pulsed linear antenna microwave plasma system at 1 mbar from hydrogen-based gas mixture (0.5% methane). The films exhibit clustered-like features which consist of nanograins in size < 20 nm. On the other hand, the film grown at lower pressure (0.1 mbar) from hydrogen-based gas mixture with added CO₂ (2.5% methane and 10% CO₂) exhibits large and well faceted diamond crystals in size up to 400 nm (Fig. 2b). Previously we have shown that higher pressure range resulted only in a growth of nano-sized grains for a wide range of methane (0.5-10%). This growth character occurred nearly independently of CO₂ content.[9] Decreasing of pressure down to 0.1 mbar resulted in a significant shift in growth kinetics and polycrystalline diamond films were grown as shown here. Especially, adding CO₂ to the gas mixture resulted in a considerable i) increase in the diamond quality, ii) increase of the growth rate and iii) film faceting.
3.2 Advanced optical elements with NCD coating

Possibility to covalently graft organic molecules to diamond surfaces on contrast with excellent chemical stability of diamond has significantly widened its fields of applications. However, precise characterization of chemical groups on the nanodiamonds is very important pre-requisite for optimizing such procedures as well as for further applications. We have employed the linear antenna deposition system to apply NCD coating to metal mirrors and large Si prisms for grazing angle reflection (GAR) and attenuated total reflectance (ATR) FTIR methods.[12] The schematic drawings of GAR and ATR spectroscopy are shown in Fig. 3a–3b. In diamond based GAR IR or ATR prism characterization techniques, ultra-smooth and thin NCD layers are required. However, the quality of the NCD films grown on mirror-like metallic substrates (GAR concept) is not so simple technological task as thin metal mirror films (Au or Al) are deformed either during the nucleation step or CVD growth in common plasma systems (mainly due to the overheating by plasma ball). The linear antenna microwave plasma CVD process minimally overheats the substrate surface due to larger distance of the substrate to the linear antenna (i.e. larger distance from the high density plasma region).[10,13]

Fig. 3 Schematic drawing of a) Grazing angle reflectance (GAR) spectroscopy under the Brewster’s angle (GAR IR) and b) attenuated total reflectance (ATR) spectroscopy with diamond-coated ATR prism. Optical (left-upper inset) and SEM images of diamond film deposited on 22x22 mm² aluminum mirror (c) and diamond-coated ATR silicon prism (d) (small features represent the investigated functionalized nanoparticle material). Scale bars are 400 nm (c) and 100 nm (d).

Figures 3c-3d show optical and SEM images of the diamond-coated mirror substrate and ATR silicon prism, respectively. Diamond films were deposited by the PLAMWP system. It is clearly visible that fully closed, uniform and homogeneous film without delamination or any other visible damaging of aluminum or Si layer is observed. SEM images reveal highly crystalline and continuous diamond films. The surface-related infrared (IR) absorption spectra for analysis of functionalized diamonds, especially by organosilane molecules, has been reported by our group.[14,15] Diamond coatings prepared by the pulsed linear antenna microwave plasma CVD process were superior for increasing sensitivity of GAR infrared reflection spectroscopy.[14]

3.3 Low Temperature Plasma Treatment

It is well known that hydrogen termination of diamond films is typically provided either in hydrogen microwave (MW) plasma or in atomic hydrogen produced by a hot filament source. Both methods are commonly used at relatively high substrate temperatures \(T_{\text{sub}} \geq 600^\circ \text{C}\).[16] However, such temperatures are undesired in fabrication of electronic devices because of partial or complete damage of the metal electrodes or other
Therefore, generating hydrogen termination of diamond at low temperature is essential. Pulsed linear antenna microwave plasma represents an alternative plasma source for low temperature processing. As in previous case, the main advantage of the PLAMWP system is a larger distance between the high-density plasma region and the sample surface (50÷100 mm). Thus, overheating of the temperature-sensitive substrate from the plasma radiation is minimized. Our previous study has proven that the low temperature hydrogen plasma treatment of diamond films is possible. Only briefly, induced sheet surface conductivity (SSC) was the highest ($1.7 \times 10^{-6}$ (Ω/□)$^{-1}$) when the hydrogen plasma treatment was done at the substrate temperature of 400°C. This value slightly decreased slightly down with decreasing substrate temperature down to 200°C. However, SSC dropped down by 6 order in magnitude to the value of $10^{-11} + 10^{-10}$ (Ω/□)$^{-1}$ for the substrate temperature below 200°C. The dependence of the SSC on the substrate temperature is plotted in Fig. 4. The sheet surface conductivity of quartz covered by 100% SU-8, NCD film covered with 100%, 50% and 0% SU-8, hydrogenated at 200°C are plotted for a comparison. As expected, the highest value of the SSC is observed for the sample with 0% SU-8, i.e. bare NCD film ($4.9 \times 10^{-7}$ (Ω/□)$^{-1}$). The lowest value of the SSC is $10^{-12} + 10^{-13}$ (Ω/□)$^{-1}$ for the quartz covered by 100% SU-8. The quartz substrate was used as the reference sample to avoid the influence of polymer conductivity and/or thermally induced transition of SU-8 into a conductive film. The presented results confirm that the hydrogen termination at low temperature as low as 200°C is efficient enough to induce hydrogen-terminated conductive surfaces, and at the same time to be “friendly” to metal contacts and to polymer-based encapsulation layer.

Besides the induced electrical conductivity, hydrogen-terminated NCD films exhibit hydrophobic surface character (i.e. high water contact angle). In contrast, oxidized diamond surfaces exhibit highly hydrophilic character (i.e. low water contact angle) and insulating properties. Ability of NCD film to have different surface wettability without surface morphology changes is crucial feature for selective cultivation of living cells. Here, controllable tuning of NCD wetting properties was performed by applying a hydrogen RF plasma treatment. The wetting character of diamond surface was characterized by measuring the diamond/water contact angle. Figure 5 shows the contact angle on NCD films as a function of the plasma treatment time. As initial stage (0 min) the treatment is equal to the oxidized surface with a contact angle ~10°. It is clearly observed that prolonging the hydrogen plasma treatment time increases the contact angle up to 90°, as found for 1h treatment. These observations confirm that wetting properties of diamond surface can be precisely controlled by applying the hydrogen treatment procedure while the whole process is done at as low temperature as 50°C and lower.

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**Fig. 4** Comparison of the sheet surface conductivities for samples passivated by SU-8 polymer and hydrogen-terminated at 200°C.

**Fig. 5** Dependence of calculated contact angle from treatment time.
3.4 Growth of carbon nanotubes

In contrast to diamond (sp$^3$ hybridization), CNTs are composed from sp$^2$ hybridized carbon atoms into tubular structures with one or several walls (graphene sheets). CNTs are routinely grown by variety of deposition techniques.[23] In CVD techniques the CNTs growth is enabled by catalysts where iron, cobalt, nickel or their derivatives are the most often used.[24]

![SEM images of CNTs grown by CVD method where plasma discharge was ignited employing (a) microwaves, (b) radiofrequency waves, (c) combining MW and RF waves.](image)

**Fig. 6** SEM images of CNTs grown by CVD method where plasma discharge was ignited employing (a) microwaves, (b) radiofrequency waves, (c) combining MW and RF waves.

Here we compare the influence of different plasma discharge types, i.e. microwaves (MW), radiofrequency (RF) and their combination (RF/MW), on CNTs synthesis by PLAMWP system. Surface morphology of resulting structures is shown in SEM images in Fig. 6. The SEM images show clearly that only isolated nano-islands with no sign of nanotubes appear after CVD in the microwave plasma only (Fig. 6a). Employing CVD in the RF plasma results in poor CNTs growth (Fig. 6b). Finally, in the case when RF and MW plasma are combined we observed dense, vertically oriented nanotubes with the diameter of 20-30 nm (Fig. 6c). Thus we conclude that for efficient synthesis of CNTs in the linear antenna system employing both plasma MW and RF generators is essential. The microwave energy effectively decomposes working gases to active species and RF drives the species to substrate surface where synthesis reactions take place.

4. CONCLUSIONS

The present work summarized advanced application of the pulsed linear antenna microwave plasma CVD process in the field of growth and functionalization of carbon allotropes. We showed that the large area diamond growth is possible and variation of process parameters, mainly pressure and gas compositions, allowed tailoring diamond film properties in the terms of crystal size and chemical purity. Lowering of the process pressure from 1 to 0.1 mbar increased the mean free path in the linear antenna plasma and expanded the plasma volume towards the substrate. These changes were found crucial for enhancing the
diamond growth reactions on the substrate. Due to the larger distance between “high density” plasma region and the substrate surface we were able to grow diamond film on thin metal layers, i.e. metal mirrors, and new optical element were successfully fabricated. Due to large area plasma uniformity, diamond coated ATR silicon prisms were fabricated, hereby providing improved mechanical and chemical stability, excellent IR transmittance, and possible surface functionalization. Both GAR mirrors and ATR Si prism were successfully further used for analyzing the functional groups, chemical bonds and organic molecules adsorbed or chemically attached to diamond surfaces by FTIR spectroscopy. Similarly, hydrogen plasma treatment in the pulsed linear antenna microwave plasma system was successfully done at low temperature as low as 200°C which was found efficient enough to induce hydrogen-terminated conductive surfaces, and at the same time to be “friendly” to metal contacts and to polymer-based encapsulation layer (SU-8 polymer). Similarly, and to our knowledge the first time, we were able to tailor the diamond surface wettability from highly hydrophilic (contact angle 10°) to hydrophobic character (contact angle ~100°). The step in increasing contact angle was approx. 15°. Efficient synthesis of oriented CNTs, another carbon allotrope form, was achieved at plasma conditions where microwave and RF plasma were ignited in the PLAMWP system. We assumed that microwaves effectively decomposed the working gases to activate growth species and RF drove the species to substrate surface where synthesis reactions took a place. Finally, we expect that the PLAMWP system is also suitable for the growth of graphene layers over large areas and the work is in progress. The pulsed linear antenna microwave plasma system thus represents a universal and powerful tool for the low temperature growth of carbon nano-allotropes and low temperature surface functionalization.

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LITERATURE


