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Surface modification of nanocrystalline diamond/amorphous carbon composite films

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Abstract

The surfaces of nanocrystalline diamond/amorphous carbon (NCD/a-C) nanocomposite films deposited from a 17% CH_4/N_2 mixture have been subjected to a variety of plasma and chemical treatments, namely H_2 and O_2 microwave plasmas, a CHF_3 13.56 MHz plasma, and a chemical treatment with aqua regia ($HCl:HNO_3$ 3:1). The resulting surfaces have been studied with respect to their chemical nature by X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (TOF-SIMS), concerning their morphology with atomic force microscopy, and by contact angle measurements to study their hydrophobicity and their stability. As-grown surfaces are hydrogen terminated, but the number of C–H bonds can slightly be increased by a H_2 microwave plasma, while treatment with aqua regia considerably lowers the number of C–H bonds at the surface. O_2 and CHF_3 plasmas, on the other hand, lead to a replacement of the terminating C–H bonds by C–O or C–OH and C–F_x groups, respectively. Finally, by contact angle measurements over a period of 150 days it could be shown that the H-terminated surface is very stable whereas the contact angle of the O-treated surface changed considerably with time, probably due to the adsorption of contaminants.

Keywords: Nanocrystalline diamond films; Surface characterization; Surface modification; Contact angle measurements

1. Introduction

Owing to their mechanical, electrical and electrochemical properties, and biocompatibility, polycrystalline diamond films (PCD), and especially nanocrystalline diamond films (NCD) due to their reduced surface roughness [1,2] are most promising candidates for applications in fields such as electrochemistry, MEMS, biotechnology, biosensors, etc. [3,4]. One of the advantages making diamond films especially useful for these purposes is their chemical inertness guaranteeing stability [5,6]. This however, bears the inherent disadvantage that PCD and NCD surfaces cannot be easily modified for a given application. E.g., owing to the stability of hydrogen terminated surfaces (almost all NCD surfaces are H-terminated after growth), modification is not possible by simple chemical treatment but requires either photo-, thermo- or electrochemical processes [7,8]. Another possibility is of course the application of plasmas, making use of their non-equilibrium character and the presence of highly excited species. With the exception of hydrogen plasmas (in most cases applied at elevated temperatures in the same set-up as used for deposition), which are meanwhile routinely used to improve the H-termination of NCD surfaces, there is only a limited number of investigations on the modification of NCD surfaces by plasma methods, e.g. by oxygen [9], air [10] and *N*-(6-aminohexyl) aminopropyl trimethoxysilane plasmas [11].

In this contribution we report on the modification of nanocrystalline diamond/amorphous carbon (NCD/a-C) composite films by H_2, O_2, and CHF_3 plasmas. For comparison purposes, also a room temperature chemical treatment with aqua regia was applied. The resulting surfaces have been characterized by X-ray photoelectron spectroscopy (XPS), time of flight secondary ion

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Table 1
Parameters used for the growth of the NCD/a-C films and the treatment with various plasmas

Parameter		Growth	H_2 plasma	O_2 Plasma	CHF_3 Plasma
Plasma		2.45 GHz	2.45 GHz	2.45 GHz	13.56 MHz
Power	[W]	800	800	200	70
Gas		17%CH_4/N_2	H_2	O_2	CHF_3
Gas flow	[sccm]	300	250	–	5
Pressure	[kPa]	2.2	6	0.2	0.066
Temperature	[°C]	600	400	rt	rt
Duration	[min]	390	30	10	10

mass spectrometry (TOF-SIMS), atomic force microscopy (AFM) and contact angle measurements.

2. Experimental

2.1. Deposition

NCD/a-C nanocomposite films have been deposited by microwave plasma chemical vapour deposition (MWCVD) from a 17% CH_4/N_2 mixture using the set-up and the process described previously [12,13]. The parameters used for the samples of the present investigation are summarized in Table 1. Prior to the deposition, the (100) silicon substrates were pre-treated with a suspension of a 1.6:1 mixture of ultradispersive diamond powder (3–5 nm grain size) and nanocrystalline diamond powder (250 nm grain size) in n-pentane in order to increase the nucleation density. This leads to a nucleation density $\geq 10^{10}$ cm^{-2} [14]. The resulting films consist of diamond nanocrystals of 3–5 nm diameter which are embedded in an amorphous carbon matrix with a width of 1–1.5 nm. The crystal/matrix ratio is about unity [15].

2.2. Surface treatments

Four different surface treatments have been applied hitherto in the course of this investigation: i) a MW hydrogen plasma at 400 °C applied in the deposition set-up (in the following: HP); ii) a O_2 MW plasma treatment at room temperature in a Technics Plasma E 100 system (OP); iii) a CHF_3 plasma treatment in a 13.56 MHz parallel plate reactor also at room temperature (FP); and iv) a chemical treatment (CT) with aqua regia (HCl/HNO_3 with a ratio of 3:1) for 90 min at room temperature. The parameters of the plasma treatments are listed in Table 1. After the treatments, the samples, as well as an as-grown one (AG) were sealed in vacuum until the measurements described below were started.

2.3. Characterization

The composition of these surfaces has been investigated by XPS and TOF-SIMS measurements. An AXIS ULTRA spectrometer (KRATOS, UK) using monochromatic Al Kα X-rays and an ION-TOF (IV) TOF-SIMS system using 25 keV Bi_3^+ ions have been employed for this purpose, respectively. Atomic force microscopy (Solver P47H from NT-MDT Co., Russia) performed in tapping mode in air was used to establish the surface topography. Details of the measurement set-ups and procedures can be found in Ref. [16]. Finally, contact angle measurements were performed with a Digidrop Model MSE (GBX Instruments) with ultrapure analytical grade water. The results presented here are the average of several measurements performed with each surface.

3. Results and discussion

3.1. XPS

The surface compositions of the five samples of this investigation as determined by XPS are listed in Table 2. If one takes into account that—according to elastic recoil detection (ERD) measurements—the films possess bulk concentrations of O and N in the range of 0.5–1% [15], it must be stated that the as-grown and the chemically treated surfaces are very clean, with oxygen and nitrogen concentrations of about 2 and 1%, respectively. This is in agreement with observations of other authors [6,17]. Surprisingly, the O concentration of the hydrogen plasma treated surface was about 4%; in addition there is a slight Si contamination of about 1.4%. A closer examination of several samples and measurements revealed that this contamination has the overall formula $SiO_{1.5}$; most probably it is caused by an etching of the quartz window, through which the MW plasma is coupled into the chamber, by the hydrogen plasma. The oxygen content of the O_2 plasma treated sample is about 12%, indicating an oxidation of the surface. Finally, plasma treatment with CHF_3 leads to fluorine concentration of almost the same value (12±2%, Table 2), indicating that a fluorination process has taken place. For this surface, a slightly increased oxygen content was observed; at the present time it is not clear whether this is due to the process itself or to post-process contamination.

Table 2
Surface composition of the five samples of this investigation as determined by XPS

Sample	C	O	N	Si	F	θ_1 [°]	θ_{150} [°]	rms [nm]
AG	96.9±0.6	2.2±0.4	0.8±0.1	–	–	86±2	80±2	10.0
HP	93.3±0.2	4.1±0.3	1.2±0.3	1.4±0.1	–	88±2	87±2	12.1
OP	87.4±0.1	12.0±0.4	0.7±0.1	–	–	7±1	23±2	12.1
FP	81.9±2.3	4.8±0.2	0.8±0.2	–	12.5±2.4	100±3	–	–
CT	97.6±0.5	1.8±0.1	0.7±0.1	–	–	67±2	78±2	10.5

The values given are the average of two measurements each; the errors present the maximum deviation. The table also contains the contact angle after 1 (θ_1) and 150 days (θ_{150}), respectively, and finally the rms roughness.