



Near-surface hydrogen depletion of diamond-like carbon films produced by direct ion deposition



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ABSTRACT

Amorphous atomically flat diamond-like carbon (DLC) coatings were produced by direct ion deposition using a system based on a Penning ion source, butane precursor gas and post acceleration. Hydrogen depth profiles of the DLC coatings were measured with the ^{15}N R-NRA method using the resonant nuclear reaction $^1\text{H}(^{15}\text{N}, \alpha\gamma)^{12}\text{C}$ ($E_{\text{res}} = 6.385$ MeV). The films produced at 3.0–10.5 kV acceleration voltage show two main effects. First, compared to average elemental composition of the film, the near-surface region is hydrogen depleted. The increase of the hydrogen concentration by 3% from the near-surface region towards the bulk is attributed to a growth model which favours the formation of sp^2 hybridised carbon rich films in the film formation zone. Secondly, the depth at which the maximum hydrogen concentration is measured increases with acceleration voltage and is proportional to the penetration depth of protons produced by the ion source from the precursor gas. The observed effects are explained by a deposition process that takes into account the contributions of ion species, hydrogen effusion and preferential displacement of atoms during direct ion deposition.

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1. Introduction

Diamond-like carbon (DLC) refers to carbon films that are composed of a significant amount of sp^3 hybridised carbon. Such materials are gaining interest in the field of thin film technology [1–4]. The sp^3 hybridised carbon in these films gives rise to “diamond-like” properties such as chemical inertness, high hardness, wear resistance and are directly proportional to the sp^3 content in the films [5]. The production of DLC films is technically less challenging compared to that of diamonds and thus more cost-effective [5].

The properties of DLC films are strongly influenced by the carbon deposition process [5]. It can be inferred from the works of Robertson [5] and Lifshitz [6] for example, that deposition energy and hydrogen content play a significant role in film properties. Several methods have been developed to achieve low sp^2/sp^3 ratios [5]. Tetrahedral amorphous carbon with sp^3 content above 85% can, for example, be produced by mass selective ion beam deposi-

tion [6], which allows precise control over impurities and energy of deposition.

Carbon atoms can attain sp^3 hybridisation only under metastable conditions that can for example be reached under high pressure–high temperature conditions [7]. This poses a significant challenge for the production process. The most stable configuration for carbon is the graphite phase dominated by sp^2 hybridisation. Thus in order to maximise sp^3 hybridisation in the films, the synthesis process should generate the required metastable conditions during the deposition of carbon atoms. This aspect limits widespread uptake of DLC films in industrial applications. However, it is possible to increase the sp^3 content in the films by other means. For example, preventing the carbons from relaxing to the sp^2 states can enhance the sp^3 content in the films. This can be achieved through passivation of the dangling bonds. One such method is to use hydrogen in the deposition process. Thanks to its monovalent electronic configuration hydrogen can attach to the dangling bonds of the carbon atoms, thereby preventing them from clustering with other carbon atoms and relaxing to the sp^2 states. Hydrogen thus plays an important role in DLC film fabrication and it is useful to quantify and study the hydrogen present in such films.

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We note that C–H sp^3 bonds do not directly contribute to the physical hardness but can significantly reduce graphitisation and the friction coefficient of thin DLC films [5,6,8].

The hydrogen content in the films can be determined by a variety of methods such as resonant nuclear reaction analysis (R-NRA) [9–11], elastic recoil detection analysis (ERDA) [12], reflection electron energy loss spectroscopy (REELS) [13], nuclear magnetic resonance (NMR) [14], secondary ion mass spectroscopy [10], and infrared spectroscopy [15]. R-NRA in particular is an interesting method of analysis because quantitative hydrogen depth profiles can be measured over more than 1 μm thickness in a non-destructive manner [9]. In this contribution, we used R-NRA to improve the understanding of the role of hydrogen in the growth process of DLC films by direct ion deposition.

2. Experimental

2.1. DLC film deposition

DLC films can be fabricated by direct ion beam deposition techniques [16–18]. The system we have used for the experiments described here consists of a Penning ion source with associated power supplies and a gas feed for the precursor gas, an electrostatic steerer-scanning unit, a vacuum chamber, a sample stage with post acceleration and a charge integrator to control the deposition process. The ion source has a solenoid magnet surrounding the plasma chamber that incorporates the high voltage anode and two electrically conductive solid cathodes. Carbon cathodes were used for the experiments. The front of the cathode that faces the sample (at a 250 mm distance) has a 2–3 mm hole to allow extraction of ions from the plasma that is sustained by a combination of static electric and magnetic fields. A negative bias voltage can be applied to the sample deposition stage to increase the ion energy. $C_xH_y^+$ ions are predominately generated in the plasma from butane gas [16]. Additionally, 23% of the ions are H^+ and H_2^+ , with a H_2^+/H^+ ratio of 6.5. Upon impact with the sample surface, molecular ions dissociate into atomic fragments. The final kinetic energy of these molecules is distributed amongst these fragments according to their atomic mass. $^{12}C^+$ ions from the 3.0 kV C_3H_6 molecule receive an energy of 857 eV. According to SRIM calculations, this leads to $R_p = 3.3$ nm ($\Delta R_p = 1.7$ nm) in carbon considering the density $\rho = 2.2$ g cm^{-3} [19]. $^{12}C^+$ ions emitted by the source receive the full acceleration energy of $E = 3.0$ keV. Apart from the low probability of higher charge states, there is no mechanism by which carbon ions can impact on the sample with a higher kinetic energy. Therefore, the maximum range of carbon atoms in carbon is $R_p = 8.8$ nm ($\Delta R_p = 4.0$ nm) and the DLC growth zone is restricted to $d = 12.8$ nm. Increasing the acceleration voltage to $U = 10.5$ kV increases the growth zone to $d = 27.1$ nm ($\Delta R_p = 9.8$ nm). Protons from H_2^+ with 3 keV energy have a range of $R_p = 24.2$ nm ($\Delta R_p = 14.8$ nm), which extends well beyond the growth zone. Initially, carbon ions are implanted into this material. The implantation profile extends to the surface. Once the surface incorporates carbon atoms, the different sputtering yields of Si and C cause a depletion of silicon [16]. Over time a film builds up that contains only hydrogen and carbon atoms. The substrate-film interface will have a mixture of silicon, carbon and hydrogen atoms. This intermixing of atoms results in strong adhesion of the film to the substrate. The set-up with the four-plate electrostatic scanner enables a laterally homogeneous deposition onto any substrate material across $d = 50$ mm. For this study, we have chosen Si(100) wafer material as substrate. Other commonly used substrates are steel, stainless steel, chromium, titanium, glass and plastic materials.

The films are produced under high-vacuum conditions. In the experiment, the ion current was set to $i = 0.3$ mA using a $U = 1.5$ kV anode voltage and an electromagnetic coil current of

$I = 2$ A. Further details about ion species distribution produced by this ion source, sp^2/sp^3 ratio, surface roughness and other properties of the films are described in [16].

2.2. Hydrogen depth profiling

Hydrogen depth profiles of the DLC films were measured with R-NRA. The nuclear reaction $^1H(^{15}N, \alpha\gamma)^{12}C$ has a sharp resonance at $E_{res} = 6.385$ MeV allowing a hydrogen depth profile analysis by varying the ^{15}N ion energy [9–11]. In the experiment, the ion beam was focussed to a diameter of $d = 2$ mm. γ -rays produced by the nuclear reaction were detected with a NaI detector. The fraction of hydrogen atoms in each step can be calculated by the formula $H_{sample} = Y \times K \times \epsilon_C / (1 + K \times Y \times (\epsilon_C - \epsilon_H))$, where H_{sample} corresponds to the hydrogen concentration of the sample, Y refers to the gamma yield from the specific sample step after an appropriate background subtraction, K is a constant factor of $K = 7.1 \times 10^7$ $\mu\text{C eV}^{-1} \text{cm}^{-2}$. K includes the resonance properties as well as the details of the experimental set up and ϵ_H and ϵ_C refer to the stopping cross section of the ^{15}N beam ions in hydrogen and carbon respectively as can be obtained from SRIM [19,20]. The factor K has been determined using a standard of an amorphous Si-layer with a hydrogen concentration of $C = 12.5$ at.%. The detection limit of hydrogen by the system is 100 ppm [21]. The depth resolution at the surface is governed by the energy resolution of the ion beam and the Doppler broadening. The resonance width of $\Gamma = 1.8$ keV adds very little to the depth resolution. The settings used in the experiment resulted in an energy resolution of 16 keV [21]. The stopping cross section of 6.4 MeV ^{15}N ions in DLC films is calculated to be 145×10^{-15} eV $\text{at}^{-1} \text{cm}^2$. Considering a DLC film with an atomic density of $\rho = 1.11 \times 10^{23}$ $\text{at} \text{cm}^{-3}$ this corresponds to a depth resolution of 10 nm. Ion straggling inside the DLC film will increase the depth resolution to, e.g., 15 nm in the depth of 150 nm.

2.3. Structural analysis

Transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDXS) and electron energy loss spectroscopy (EELS) were used to obtain structural information and additional compositional data of the films. The samples were processed for TEM analysis using an eight steps preparation protocol that uses 120 °C for the preparation steps that involve epoxy gluing [22]. The cross-sectional samples were analysed with an image-aberration-corrected Titan 80–300 transmission electron microscope at the Helmholtz-Zentrum Dresden-Rossendorf, Germany. This microscope is characterised by a point resolution of 0.1 nm [23,24].

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows a representative cross-sectional TEM image of a DLC film produced with the direct deposition system.

The DLC film has a homogeneous thickness of $t = 138$ nm as shown in Fig. 1. The film is amorphous and shows no signs of ordering, thereby inhibiting ion channelling during R-NRA. (Channelling would have biased hydrogen concentration analyses towards lower concentrations.) The surface and the interface to the substrate are smooth to the 2–3 nm scale. An abrupt change in amorphous to crystalline structure is observed at the interface, as shown in the high-magnification inset in Fig. 1. A dark band in the DLC film is visible near the interface to the substrate. This band is caused by the presence of Si atoms from the substrate. As

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