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Properties of iodine containing diamond-like carbon films prepared by plasma source ion implantation

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ABSTRACT

The addition of halogens to diamond-like carbon (DLC) films provides attractive film properties, e.g. a hydrophobic surface combined with an improved corrosion protection. The use of iodine is of interest in this regard because of its additional marked influence on the band gap and therefore on the optical properties of the film. Instead of solid iodine, the gaseous precursor trifluoroiodomethane (CF_3I) was used to prepare iodine containing DLC films. In contrast to our earlier experiments, a lower voltage was used in the plasma based preparation process thereby extending the iodine concentration range. The film properties, such as halogen content, bonding, water contact angle and corrosion protection were evaluated. The iodine containing DLC films are suitable to be deposited on polymer materials.

1. Introduction

Selected properties of diamond-like carbon (DLC) films, e.g. thermal stability, electrical resistivity, surface energy or optical properties, can be improved by adding doping elements [1]. Fluorine containing DLC (F-DLC) films exhibit a high water contact angle in combination with moderate hardness [2], low friction coefficient [3] and good corrosion protection [3,4]. Iodine containing DLC (I-DLC) films are of interest because the iodine reduces the optical gap and thus changes the optical properties of the films such as the photon absorption [5–7]. Comparing the results of fluorine [8] and iodine doping, the latter is more effective in this regard. There are no established suitable iodine containing precursors that are easy to handle. In fact, most experiments so far had to revert to the use of solid iodine, either for subsequent exposition of the samples to iodine vapor [5,9] or for co-evaporation during the preparation process [6]. In the latter case, it is difficult to control the dopant concentration precisely [10].

Recently, we reported on the use of trifluoroiodomethane (CF_3I, TFIM) as iodine containing precursor [11]. In a plasma source ion implantation and deposition (PSII&D) process, which ionizes the surrounding gas by applying a negative high voltage pulse to the sample, a combination of TFIM with acetylene (C_2H_2) facilitated the deposition of I-DLC films. Even though the TFIM precursor contains three times as much fluorine as iodine, the resulting halogen containing DLC films are mostly fluorine free. The maximum iodine content that could be realized was limited, though, by the occurrence of sparking at higher relative flows of TFIM. By lowering the pulse voltage from the initially used − 16 kV, higher flows of TFIM can be used. If the pulse voltage is too low, however, several disadvantages occur. This includes lower adhesion of the film to the substrate, a change of the film structure to polymer-like, and a low deposition rate. For delicate substrates, e.g. polymers, a compromise has to be found that ensures a sufficiently high deposition rate without the risk of damaging the substrate, either thermally or by sparking.

One possible application of the I-DLC films that relies on the optical properties of the films is the coating of nanostructured substrates. Here, moth-eye structures, which act as anti-reflective devices [12], are of special interest. A coating would alter the refractive index and affect the transmission properties. As an intermediate step on this way, I-DLC films were prepared and characterized regarding their iodine and fluorine content, bonding, water contact angle, and corrosion properties. After that the suitability of the preparation conditions for deposition on polymer substrates, including moth-eye structures, was tested. It has been shown that PSII&D is in general suitable for the coating of polymers, e.g. nylon and polyethylene [13].

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2. Experimental

The films were deposited onto different substrates by PSII&D. First, experiments were carried out using silicon (100) substrates. This substrate facilitated the determination of the film properties as described below. Substrates to be used in the corrosion test consisted of stainless steel (SUS304). As polymer substrate, pieces of PET (polyethylene terephthalate) foil were used. The choice of PET was motivated by the material of the moth-eye structures. In the commercial product MOSMITE™ from Mitsubishi Chemical the structures are made of PET. The structures consist of bumps on the surface with a height of 200 nm, a distance of about 250 nm and a top radius of about 50 nm. Pieces were cut from a larger sheet. All substrates had a square form with an edge length of 1–2 cm.

Acetylene and TFIM were used as process gases for plasma formation. The applied voltage was a pulse of − 14 kV with a length of 100 μs and a repetition rate of 100 Hz. Earlier samples were prepared with a pulse of − 16 kV. The gases were introduced into the discharge chamber by controlling their flow rates through mass flow controllers. The flow of C_2H_2 was held constant at 6 sccm whereas the flow of TFIM was varied between 1 and 2 sccm. The flow rate of the latter was based on N_2, i.e. no gas correction factor was applied. The gas pressure during deposition was 1.3–2.1 Pa. The base pressure in the chamber was 10^{-4} Pa before deposition. The process times were 100–120 min. Samples for the corrosion test were first treated by methane (CH_4) implantation for 180 min at − 18 kV (10 μs, 1000 Hz) to increase film adhesion. The deposition as described above followed with an extended deposition time up to 150 min. Comparison samples of pure DLC were deposited at − 14 kV with a flow of 15 sccm C_2H_2. The deposition time on the polymer substrates was reduced to obtain thinner films.

The surface morphology and the thickness, using a cross section of the film, were measured by scanning electron microscopy (SEM). Polymer samples with a thin deposited film had to be coated with platinum beforehand to reduce charging effects. The film composition was determined by X-ray photoelectron spectroscopy (XPS) using Mg K_α X-ray irradiation. Depth profiles were obtained in combination with 2 keV argon ion sputter etching. Additional elemental depth profiles of the films were recorded with secondary ion mass spectrometry (SIMS). The bonding structure of the films was evaluated by a micro-Raman spectrometer at an excitation wavelength of 514 nm (argon ion laser) and a laser power of 5 mW. The spectra were fitted with Gaussian profiles. In order to investigate the wettability of the film by water, the contact angle of a sessile drop of distilled water (volume about 1 μl) was measured using a contact angle meter. The corrosion protection potential of the samples was studied by multisweep cyclic voltammetry. The electrolytic solution was 5% H_2SO_4 at 25 °C. The potential (against an Ag/AgCl reference electrode) was changed from − 0.5 V to + 1.7 V at a scanning speed of 10 mV/s. After the electrochemical polarization measurements surface images of the samples were obtained by SEM.

3. Results and discussion

Fig. 1 shows the XPS spectra of C1s, F1s and I3d of the I-containing DLC film that was prepared with a TFIM flow rate of 1 sccm. The sputtering time of 2 min shown here corresponds to a depth of about 20 nm. For the C1s spectra a peak at about 284.4 eV can be seen, representative of C−C bonds. The peak is actually composed of sp^2 and sp^3 components [14], which are too close together to be resolved as separate peaks. Additionally, C−I bonds were reported to be located at 285.2 eV [15], the same energy as the one of sp^3 carbon. Thus, no attempt was made to determine the individual amounts. Fluorine was found only at the surface of the sample, and no clear peak was observed in deeper layers. In the I3d spectra, a peak at 620.2 eV is distributed with a near constant concentration throughout the layer. It can be ascribed to bonds of iodine with carbon or with iodine [16]. The small shoulder at higher energies is probably due to iodine bonds with oxygen [17].

In the SIMS profile, Fig. 2, it can be seen that there is some fluorine present throughout the layer but with low intensities. Assuming similar ionization probabilities for fluorine and iodine, the fluorine concentration is about fifty times lower than the one of iodine. The film thickness is 153 nm for this film. In the interface, the fluorine intensity increases and exceeds the one of iodine. At the beginning of the deposition process, ions are implanted into substrate. As the precursor contains more fluorine than iodine, the concentration of the former is accordingly higher in the implanted interface. This situation is similar to the use of pure TFIM, which leads to implantation but not to film formation. Measuring the concentrations with XPS in the implanted substrate, the F concentration exceeds the one of I with 7 and 4 at.%, respectively.

The iodine concentration in the films as a function of the flow ratio of CF_3I/C_2H_2 is shown in Fig. 3. Values for samples prepared at − 14 kV and − 16 kV are included. The iodine concentration increased linearly with flow ratio, to a maximum of 3.7 at.%. I. Comparing the iodine content of samples prepared at the same flow but with different voltages, the concentration is a bit higher for the lower voltage. Reasons for this might be found in the different amounts of molecular fragments within the plasma [18] and in different sputter yields; both factors depend on the pulse voltage. While the flow ratio of 0.25 is very close to the region where sparking occurs when using a voltage of − 16 kV, the samples could be prepared at − 14 kV without difficulties, even at the highest flow. With an iodine concentration of a few at.%, the fluorine content within the sample is likely to be less than 0.1 at.%. The lower fluorine content was explained by the reaction of hydrogen from the hydrocarbon precursor with the fluorine [11].

The bonding in the DLC films was investigated by Raman measurements. In the Raman spectra a broad peak between 1000 cm^{-1} and 1800 cm^{-1} is visible. It consists out of two peaks, the D and G peak around 1350 cm^{-1} and 1580 cm^{-1}, respectively. In Fig. 4 three spectra are shown; one of a pure DLC film and two of I-DLC films. The latter both have an iodine concentration of 3.2 at.%, but they were prepared at different voltages. The increase of the D peak as a consequence of iodine addition as well as of the use of a higher voltage is evident. After background subtraction, the curves were fitted with two Gaussian peaks. The ratio of the integrated intensities of the respective areas, I_D/I_G, is plotted in Fig. 5 as a function of the iodine concentration. The I_D/I_G value generally increases with iodine content, from around 1.3 for no iodine to about 1.9 and 2.4 at the highest TFIM flow for pulse voltages of − 14 and − 16 kV, respectively. For DLC films, a higher I_D/I_G value is equivalent to a higher sp^2/sp^3 ratio [19]. The iodine and fluorine atoms that hit the substrate introduce more disorder into the film because of their higher mass as compared with carbon. By increasing the pulse voltage, more disorder is introduced as well [20]. That the slope is different for the curves of the two different voltages can be attributed to the dependence of molecular fragmentation on the voltage, as mentioned above. The higher sp^2 content is linked to a reduced hardness of the DLC film. The sample with the highest iodine content of 3.2 at.% prepared at − 16 kV had a hardness of 10.6 GPa [11]. The hardness of a pure DLC film is about 18 GPa [21].

The wettability by water is an important factor when a film is applied as a corrosion-resistant protective film. It is preferable that the wettability is low, i.e. that the contact angle of water—which is taken as a measure of wettability—is high. As listed in Table 1, the contact angle increases by more than 20° for samples with more than 2.5 at.% iodine, as compared with a pure DLC film (50°). The highest value is 73.4°. The residual fluorine in the surface contributes to the influence on the contact angle. Values for the contact angle on pure DLC films reported in literature vary between 50° and 70°, depending on the preparation conditions and thus on the structure and composition of the DLC film. Addition of fluorine to the DLC films generally leads to an increase of the contact angle of about 20–30° [4,22–26]. It should also be noted that the absolute value that is derived in the measurement of the

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