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Modification of diamond-like carbon films by nitrogen incorporation via plasma immersion ion implantation

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ABSTRACT

The addition of nitrogen to diamond-like carbon films affects properties such as the inner stress of the film, the conductivity, biocompatibility and wettability. The nitrogen content is limited, though, and the maximum concentration depends on the preparation method. Here, plasma immersion ion implantation was used for the deposition of the films, without the use of a separate plasma source, i.e. the plasma was generated by a high voltage applied to the samples. The plasma gas consisted of a mixture of C_2H_4 and N_2, the substrates were silicon and glass. By changing the experimental parameters (high voltage, pulse length and repetition rate and gas flow ratio) layers with different N content were prepared. Additionally, some samples were prepared using a DC voltage. The nitrogen content and bonding was investigated with SIMS, AES, XPS, FTIR and Raman spectroscopy. Their influence on the electrical resistivity of the films was investigated. Depending on the preparation conditions different nitrogen contents were realized with maximum contents around 11 at.%. Those values were compared with the nitrogen concentration that can be achieved by implantation of nitrogen into a DLC film.

1. Introduction

Diamond-like carbon (DLC) films are widely used as coating material. They offer chemical inertness, a low friction coefficient combined with a low wear rate and biocompatibility [1,2]. The properties of DLC films can be tuned by the addition of other elements [3]. Added nitrogen causes increased film hydrophilicity and roughness [4] and thus better cell adhesion and biocompatibility [4,5]. The hardness of the film decreases with the addition of nitrogen [6], and the optical properties of the film [7,8] as well as the electrical properties [7,9] are changed. With its changed electrochemical characteristics, nitrogen containing DLC (N-DLC) films are considered to be promising electrode material for electrochemical analysis [10].

The nitrogen content is limited, though, and depends on the preparation method. By implanting N into a DLC film a temperature dependent saturation level was found, with 23% at room temperature and 10% at 900 °C [11]. Maximum nitrogen contents that can be achieved by deposition are in the few ten percent range only when higher temperatures are involved [12,13] and/or a technique is used that produces a high number of ions such as pulsed vacuum arc [13] or a plasma beam source [14]. Most published results are in the range of around 10 at.% nitrogen, e.g. 12.8% for an RF plasma CVD method [15], 8% for a combination of an RF discharge and C_2H_2 plasma immersion ion implantation (PIII) [16], 10% for an N_2 electron cyclotron resonance plasma source combined with PIII [17], 9.5% for a DC plasma of N_2 and C_6H_6 with an additional electron source to facilitate the plasma generation [18].

All of the experiments mentioned above employed a dedicated plasma source or at least an electron source. Here, we applied plasma immersion ion implantation without any further plasma or electron source, i.e. the plasma was ignited by a high voltage applied to the sample holder. Co-deposited N-DLC films were prepared and characterized. The results were compared to those of samples where the nitrogen was implanted (also via PIII) into DLC films. As the plasma gas, C_2H_4 was used. DLC films can be grown with this gas, but it is also a small enough molecule to be used for implantation [19]. The handling of the gas is more convenient than that of the otherwise widely used C_2H_2. For the same reason N_2 was used here instead of ammonia, pyridine or cyanides.

2. Material and methods

Substrates of silicon and glass with a size of 2×2 cm and 1×2 cm, respectively, were fixed onto a metallic holder of 10 cm

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diameter. The glass substrates were cleaned before in an ultrasonic bath with ethanol. The sample holder was fixed in the middle of a high vacuum chamber (base pressure 5×10^{-5} Pa) by connecting it to a high voltage feedthrough. The flow of the gases (N_2 and C_2H_4) was controlled by separate mass flow controllers with rates of 6–12 sccm for C_2H_4 and 0–18 sccm for N_2. The pressure inside of the chamber was set to a value between 0.7 and 1.4 Pa by reducing the pumping via a gate valve. A plasma was generated by applying a voltage to the sample holder, either a pulsed (pulser RUP 6-25, GBS Elektronik) or a DC voltage (power supply HCP 5000-3500, FuG Elektronik). The pulsed voltage was −10, −15 or −18 kV with a pulse repetition rate of 100, 250 or 1000 Hz, combined with a pulse length of 100, 40 or 10 μs, i.e. keeping a constant duty cycle. The DC voltage was −2 kV. The process time varied between 45 and 270 min. A schematic of the experimental setup can be found in [20].

Implantation of nitrogen was performed at −15 or −20 kV with pulses of 10 μs and a repetition rate of 1000 Hz. The pressure was 0.7 or 1 Pa, the implantation time was 15, 30 or 45 min. Due to the peculiarities of the preparation technique (plasma generation by a high voltage, sample holder at high negative potential), it is not possible to measure the nitrogen fluence during the experiment.

Different preparation methods were realized: N-DLC films were prepared with a simultaneous flow of N_2 and C_2H_4 combined with either a pulsed or a DC voltage. Additionally, DLC films were prepared with only a flow of C_2H_4. Afterwards, nitrogen was implanted by introducing N_2 into the chamber and applying high voltage pulses to the substrate. For one sample, the sequence of DLC preparation (20 min) and nitrogen implantation (30 min) was performed four times. A few samples were prepared by depositing an N-DLC film first via a simultaneous flow of N_2 and C_2H_4 and implanting nitrogen afterwards.

The samples were characterized by Raman spectroscopy (Horiba LabRAM HR) with an Ar laser of 514.5 nm wavelength and FTIR spectroscopy (Varian HR8800) in transmission. Depth profiling was performed by SIMS (Cameca ims 5f) using 5.5 keV Cs primary ions detecting positive secondary ions of the type MCs^+. The composition of the films was determined by AES (Jeol JAMP-30) and XPS (Shimadzu ESCA), employing Ar sputtering with an energy of 3 and 2 keV, respectively. The electrical resistivity was measured with a Parstat 2273 (Princeton Applied Research) and a four point probe. The film thickness was determined with a profilometer (Dektak XT Advanced), scanning over the transition of an uncovered area (due to the fixing of the samples to the sample holder) to the film or using a sputter crater from a SIMS measurement that was stopped at the interface. The friction coefficient was determined by a ball-on-disc setup (CSM Instruments Tribometer) with a WC ball of 6 mm diameter and a force of 1 N.

3. Results and discussion

The co-deposited N-DLC films show a uniform composition with depth as evidenced by the mostly parallel intensities of the main components, C, H and N, in the SIMS depth profiles. In Fig. 1, an example is shown for the sample prepared by co-deposition with the parameters 6 and 12 sccm of C_2H_4 and N_2, −15 kV pulse with 100 μs and 100 Hz. Only at the beginning of the profile and in the vicinity of the interface there are some variations in intensity. The former are mainly measurement artifacts due to the implantation of the primary ions. For the latter, there is also the implantation effect of the preparation method to consider which changes the composition; here, it is probable that some nitrogen enrichment occurred in the interface. Some silicon can be seen throughout the profile. However, it should be noted that the intensity scale is logarithmic. For the implanted samples,

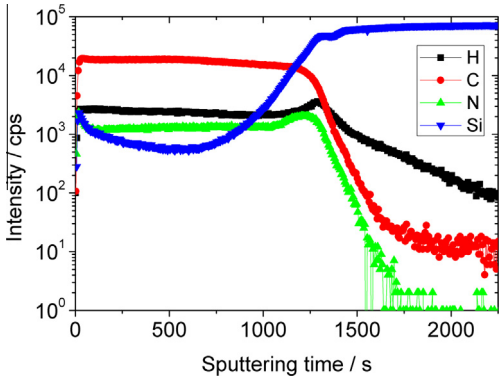

Fig. 1. SIMS depth profile of a sample prepared by co-deposition with −15 kV pulses. The intensities are derived from the MCs^+ signals.

a typical implantation peak near the surface can be observed. Alternating the DLC deposition and the nitrogen implantation four times results in a continuous nitrogen distribution with some variation in intensity with depth. Implantation of nitrogen into an N-DLC film does not produce a very distinct implantation peak, though, but only a small increase in intensity.

The deposition rate of the co-deposited films decreases linearly with the flow ratio of $N_2/(N_2 + C_2H_4)$ as can be seen in Fig. 2 for samples prepared at 0.7 Pa with a −15 kV pulse with 40 μs length and 250 Hz repetition rate. This behavior has also been observed for other deposition methods [5,12]. The general influence of a certain experimental parameter on the deposition rate is indicated in Table 1. The deposition rate can be increased by a higher pulse voltage – which generates more plasma – and a higher pressure which provides more gas atoms to be ionized. The apparent deposition rate in the case of implantation, i.e. regarding the film thickness after the implantation, decreases due to the pulse voltage and nitrogen pressure because of the same effect, i.e. more nitrogen is available with higher pressure and the number of ionized particles increases with the pulse voltage. The nitrogen ions in turn are responsible for sputtering of the surface which leads to a decreased film thickness.

The nitrogen content of the samples depends on the process parameters. The general trend is also shown in Table 1. Due to the same reasons as mentioned above, the nitrogen content increases with higher nitrogen flow ratio, pulse voltage and

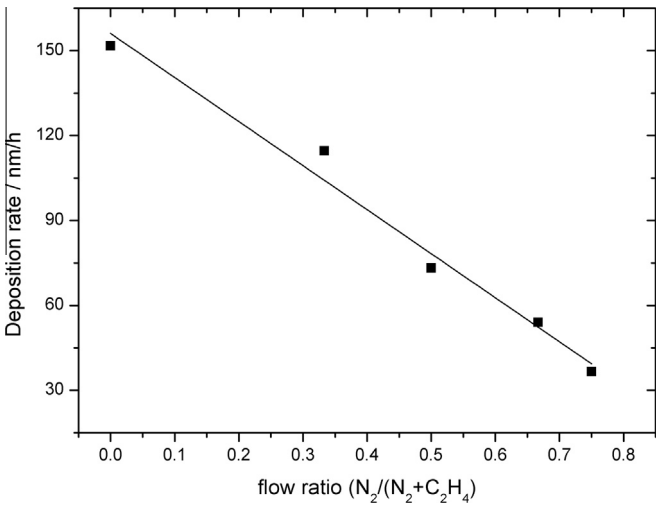

Fig. 2. Deposition rate of co-deposited N-DLC films as a function of the flow ratio, including a linear fit to the data.