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Plasma based nitrogen ion implantation to hydrogenated diamond-like carbon films

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ABSTRACT

Surface modification of hydrogenated diamond-like carbon films prepared by C_7H_8 plasma is carried out by the implantation of nitrogen ions in pure nitrogen plasmas, changing the modification time from 0 to 30 min. A negative high voltage pulse with a value of 10 kV, a width of 10 µs, and a repetition rate of 2 kHz is applied to the substrate. The electrical resistivity decreases from 2.1 Ωcm to 0.08 Ωcm with increasing the modification time. The film hardness also decreases from about 11 GPa to about 7.5 GPa. The near surface region in the films modified by the nitrogen implantation is expected to contain the relative nitrogen content of about 10%, based on the results of X-ray photoelectron spectroscopy (XPS). The XPS measurements in the depth direction show that the nitrogen content depends on the modification time and the depth of nitrogen implantation is approximately 20 nm or more at the modification time longer than 18 min. The relative content of carbon increases from 80% on the surface to 99% except for the content of hydrogen and sp^2 C bond is always dominant in the XPS. The estimated resistivity of the nitrogen ion implanted layer decreases to 0.008–0.013 Ωcm with increasing the modification time.

1. Introduction

Diamond-like carbon (DLC) films have attracted much attention in various industrial areas owing to excellent mechanical properties such as high hardness, a low friction coefficient with a low wear rate, biocompatibility and chemical inertness [1,2]. The mechanical properties of the DLC films strongly depend on microstructures such as the hydrogen content, the bonding ratio of sp^3 C to sp^2 C and the film density. A lot of coating techniques for hydrogen-free and hydrogenated DLC films have been proposed, because the properties of the DLC films depend on the preparation methods [3,4]. The DLC films prepared by plasma chemical vapor deposition (CVD) of hydrocarbon gas contain large amounts of hydrogen. The large amounts of hydrogen in the films can reduce the internal stress of the films, resulting in good adhesion on various substrates, but the film hardness and the electrical conductivity decrease due to the hydrogenation of the films. In general, DLC films usually have high electrical resistivity, which ranges from 10^2 to 10^{16} Ωcm. The electrically conductive DLC films are required for industrial applications such as antistatic film and protective films of electrical probe tip and some electrodes. The plasma based ion implantation (PBII) technique was proposed to increase the electrical conductivity of the hydrogenated DLC films and to reduce the internal stress of the films [5]. In the bipolar-type PBII technique, a high negative pulse voltage with the value of 5–20 kV was applied to the substrates. The addition of small amount of other elements also can modify the electrical properties of DLC films. The electrical conductivity of DLC films was varied over the wide range by incorporating metals such as titanium and tungsten [6–9] into DLC films. We also prepared the conductive DLC films with a small titanium dopant using the high power pulsed magnetron sputtering combined with the bipolar pulse voltage source for the substrate [10]. The addition of nitrogen to DLC films can cause the increase in film hydrophilicity and surface roughness [11], whereas the film hardness depends on the amount of nitrogen contained in the films [12,13]. The nitrogen doped DLC films were prepared using bipolar-type PBII system of N_2 and C_7H_8 mixture and the electrical resistivity of the films, which depended on the nitrogen content, reached a minimum value of about 0.03 Ωcm at a nitrogen-content of 11.5% [14]. Several studies on electrically conductive carbon nitride films have been reported by various preparation methods. The carbon nitride films prepared by radio frequency plasma enhanced chemical vapor deposition [15] had electrical conductivity and its conductivity reached a maximum at a nitrogen content of

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12.8%. The electrical resistivity of the films grown by direct current (DC) plasma of N_2 and C_6H_6 [16] monotonically decreased with the increase in the nitrogen content in the nitrogen content up to 9.5%. The nitrogen content of the films prepared by a combination of pulsed DC plasma of N_2 and C_2H_4 and PBII was lower than 12% [17] and the resistivity of the films reached a minimum at a nitrogen content of about 8%.

Ion implantation technique has been utilized to improve surface mechanical properties such as hardness, friction and wear resistance [18–22]. The ion implantation can cause the change of the chemical composition in surface/subsurface layers and the generation of the dislocation, resulting in the formation of hard phase and the strain hardening. As for the nitrogen ion implantation into hydrogenated DLC films, the implantation of N_2^+ ions with an energy of 80 keV was reported. The experimental results indicated that the electrical resistivity increases due to amorphization caused by nitrogen implantation at room temperature [23]. However, it is expected that the DLC films with relatively high hardness and low resistivity may be created by adjusting nitrogen implantation conditions such as ion energy and implantation temperature. Such a preparation method of conductive DLC films is expected to take some advantages such as the suppression of the large reduction in the film hardness due to the complete graphitization of the DLC films and the easy control of the electrical conductivity by adjusting the implantation conditions. Therefore, the experimental studies on the effect of the surface modification due to the implantation of nitrogen ions on the electrical and mechanical properties of the hydrogenated DLC films are necessary.

The mechanical and electrical properties of the films prepared on the glass substrates were investigated by the nanoindentation method and van der Pauw method. The microstructures of the films were investigated by Raman spectroscopy, and the composition of films and their bonding states were examined by X-ray photoelectron spectroscopy (XPS). In XPS measurements, the films were investigated not only on the surface but also in the depth direction by Ar ion etching.

2. Experimental setup

Fig. 1 shows the illustration of the bipolar-type PBII system. The system was composed of a bipolar high voltage source for the substrate, a vacuum pumping system and a cylindrical vacuum chamber with an inner diameter of 650 mm and a height of 500 mm. The sample holder was connected to the bottom side electrode of PBII system in order to apply the bipolar pulse voltage to the sample holder with a diameter of 150 mm and a thickness of 2 mm. The borosilicate glass with a thickness of 1 mm was used as the substrate to make accurate the resistivity measurements. The substrate, which was approximately 25 mm × 15 mm in size, was placed on the surface of the sample

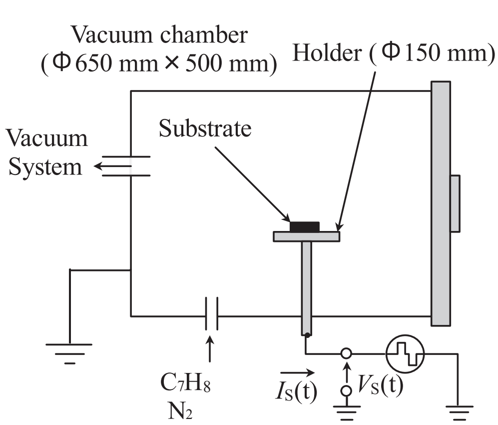

Fig. 1. Illustration of the bipolar-type plasma based ion implantation (PBII) system.

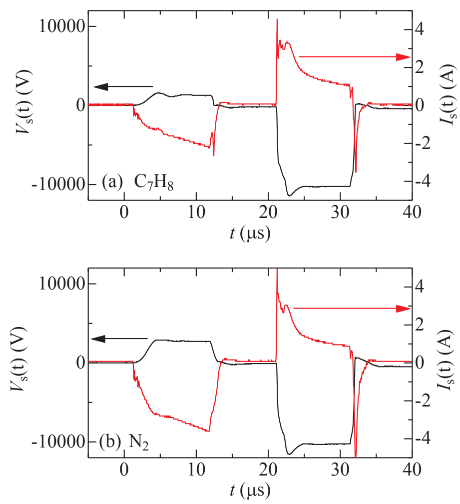

Fig. 2. Waveforms of the voltage applied to the holder and the current flowing to substrate holder in (a) C_7H_8 and (b) N_2 discharges, where black and red lines respectively correspond to the voltage and the current.

holder. At first, the hydrogenated DLC films were prepared by PBII system, where C_7H_8 gas pressure was about 0.2 Pa. The thickness of the DLC films prepared for 50 min reached about 0.2–0.24 μm. The waveforms of the current detected by a current transformer and the voltage divided into 1/1000 by a voltage divider were monitored with a digital oscilloscope. Waveforms of the current flowing to the substrate holder and the voltage applied to the holder are shown in Fig. 2(a), where C_7H_8 gas was used. The repetition rate f_r of the bipolar pulse high voltage source was 2 kHz and the average power was about 420 W. After the positive pulse voltage with a value of 1.4 kV was turned off, the negative voltage with a value of 10 kV was applied for 10 μs and then the negative voltage reached 0 V at about 100 μs after the negative voltage was turned off due to the characteristics of the pulse power supply system. After the preparation of the hydrogenated DLC films, the nitrogen gas pressure in the chamber was maintained at about 0.05 Pa by flowing only nitrogen gas into the chamber with a flow rate of 15 sccm. Surface modification of the DLC films using plasma-based nitrogen ion implantation was carried out. Waveforms of the current flowing to the substrate holder and the voltage applied to the holder are shown in Fig. 2(b), where N_2 gas was used. The repetition rate of the bipolar pulse voltage source for the surface modification was also same as that for the preparation of the hydrogenated DLC films and the average power was about 450 W. The plasma discharges was generated by the positive pulse voltage, and the ion implantation was carried out by applying the negative pulse voltage with a pulse width of 10 μs. The power dissipated in the nitrogen discharges was about 140 W and the power dissipated by the application of negative pulse voltage was 310 W. Here the high negative voltage pulse was applied, changing the modification time (implantation time) $T_{m.}$ The values of T_m corresponded to 0, 3, 6, 18 and 30 min. In this experiment, the temperature T_s of the substrate holder, which was measured by thermocouple, reached 570–600 K without any active heating mechanism. The heating was a consequence of the plasma process. The temperature T_s was measured immediately before and after the modification and the slight increase in T_s during the modification was observed.

The microstructure of the film surface was investigated by Raman spectroscopy and the composition and bonding states were investigated by XPS. Moreover, sputtering of Ar ions with a kinetic energy of 1 keV was employed to investigate the depth of nitrogen implantation. In this study, the hydrogenated DLC films with and without the surface modification were etched for about 60 min by the energetic Ar ions and then the sputter etching rate E_r of Ar ion was estimated to be E_r = 0.6 nm/min from dividing the thickness difference between the before and after