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# Conductive diamond-like carbon films prepared by high power pulsed magnetron sputtering with bipolar type plasma based ion implantation system

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ABSTRACT

Diamond-like carbon (DLC) films are prepared by high power pulsed magnetron sputtering (HPPMS) combined with bipolar type plasma based ion implantation (PBII). The microstructure, electrical and mechanical properties of the films are examined as a function of positive pulse power ($P_p$) by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), four-point probe resistivity measurements and nanoindenter tests. In addition, the effect of the pulse sequence is also examined. For comparison, some samples are annealed in vacuum in the range of 200 to 400 °C. The results of resistivity measurements clearly show that electrically conductive DLC films are formed by applying bipolar pulse voltages, and the resistivity decreases with increasing $P_p$. The temperature is at most estimated to be 200 °C using vacuum thermo-labels. The Raman and XPS analysis reveal that $sp^2$ clusters increase as $P_p$ increases. However, the hardness of the conductive DLC films is kept approximately 12 GPa. The comparison of pulse sequence suggests that the microstructure and properties of the films are affected by ion bombardment effects. In the case of annealed samples, $sp^2$ clusters are also increased with increasing temperature. However, the annealed films are still electrically insulating and the hardness is slightly decreased with increasing temperature. From these results, it is concluded that the bipolar pulse voltage application is effective for the formation of conductive DLC films at relatively low temperature in the HPPMS-PBII system.

## 1. Introduction

Diamond-like carbon (DLC) films have attracted much attention because of their excellent properties, such as high hardness, high wear resistance, low friction coefficient, chemical inertness, and high electrical resistivity [1]. However, the properties of DLC films depend on their microstructure, which is usually changed by the preparation conditions and methods [2–4]. For example, the hardness of the films varies from 10 to 80 GPa, depending on the microstructural features such as the $sp^3$ bonding ratio and hydrogen concentration. Therefore, many researchers have investigated the preparation of suitable DLC films by various methods [5,6].

Both chemical and physical vapor deposition methods are used for the preparation of DLC films. In the case of chemical vapor deposition (CVD) methods such as direct current (DC), pulse-DC, and radio-frequency (RF) plasma CVD [7–10], electron cyclotron resonance (ECR) plasma CVD [11], and plasma based ion implantation (PBII) [12–14] the deposited films include large amounts of hydrogen, because hydrocarbon gases are usually used as the source. Inclusion of hydrogen reduces the internal stress of the films. This allows better adhesion on various substrates. However, the hardness of the films becomes relatively low owing to the hydrogenation. On the other hand, in the case of physical vapor deposition (PVD) methods such as sputtering [15–18], ion beam deposition (IBD) [19], pulse laser deposition (PLD) [20], filtered cathodic arc (FCA) deposition [21,22], and arc ion plating (AIP) [23,24] the films include less hydrogen and the film hardness is usually higher than those obtained by the CVD methods. However, these films are relatively brittle and the adhesion ability tends to deteriorate. Therefore, it is necessary to optimize the preparation conditions of both CVD and PVD methods. A relatively high hardness and sufficient adhesion is essential for practical application.

In general, DLC films prepared by both methods are electrically insulating in nature. Industrial applications sometimes require electrically conductive DLC films. For example, a conductive DLC coating on the electrode of a separator is expected to increase the durability of fuel cells. To obtain conductive DLC films, the films are prepared by the

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sputtering method at high temperatures. The films indicate a relatively low resistivity. However, the hardness of the films is also decreased owing to the formation of a graphite-like structure. Another alternative is the incorporation of metal into the films. Various metals such as Ti [25–28], Cr [29,30], W [27,31,32] and other metals [26,33–35] can be incorporated into DLC films and the resistivity could be decreased with increasing metal concentration. However, the mechanical properties of the metal-incorporated DLC films tend to deteriorate with increasing metal concentration. Therefore, realization of conductive DLC films without any metal incorporation is preferred.

A bipolar-type plasma-based ion implantation (PBII) has been developed at AIST-Chubu [36,37]. Conductive DLC films can be prepared by the system without metal incorporation [38]. Negative and positive pulse voltages ($v_n$ + $v_p$) are alternately applied to substrate, and the surface of the deposited film is sequentially bombarded by ions and electrons. In this system, amorphization due to ion bombardment competes against graphitization due to electron heating. As a result of this competition, a turbostratic structure (amorphous graphite) is developed and electrical conductivity is induced by an increase in the delocalized electrons [38,39]. It has been recognized that the hardness of these conductive films is approximately 10 GPa, which is sufficiently larger than those of graphitic carbon films. However, relatively high $v_n$ + $v_p$ (∼−20 and ∼+4 kV) is necessary for the formation of such conductive DLC films. The films are hydrogenated because of the hydrocarbon gas used in the system. To promote high conductivity, hydrogen concentration in the films should be reduced, which is achieved by increasing the deposition temperature more than 400 °C, owing to high pulse voltage (power) application.

In the case of the CVD process, effects of dopant elements such as Si, B, and N were also examined to modify the properties of the DLC films, including the electrical resistivity. The incorporation of Si into the films does not seem to reduce the electrical resistivity, although the thermal stability may be improved [40–42]. The possibility of reducing the resistivity of the films by the incorporation of B and N has been reported [43–46]. However, the doping effects are not always clarified, and in any event, it requires high input power, which leads to increased deposition temperature. Therefore, decreasing the deposition temperature remains challenging. A possible solution is to supply carbon without any hydrogen to prevent the hydrogenation of the films as in the case of sputtering. In this case, a relatively high ionization rate of carbon is required for sufficient ion bombardment to maintain the amorphous nature.

Sputtering is likely to be an appropriate technique for the preparation of conductive DLC films at low temperatures. However, in conventional magnetron sputtering, the ionization rate of the sputtered particles remains low and the ion bombardment of the sputtered particles is not always sufficient upon applying the substrate bias voltage. Recently, high power impulse or high power pulsed magnetron sputtering (HPIMS or HPPMS) has been developed at Linkorpin University. It generates high-density plasma in the vicinity of the sputtering target and a high ionization rate of sputtered particles is achieved [47–52]. Therefore, the ion bombardment effect could be expected by applying a substrate bias voltage using the HPPMS method. DLC films were fabricated using HPPMS and the microstructures were examined as a function of preparation conditions such as the gas pressure and substrate bias voltage [53–55]. It was also confirmed that the carbon ions were increased under some conditions and relatively hard films were obtained [56,57]. Unfortunately, the ionization rate of carbon is estimated to be approximately 5% even in the HPPMS system. Therefore, further increase in the ionization rate is desired. A combination of HPPMS with DCMS was also attempted to improve the properties of the films [58,59].

A new hybrid technology combining PBII with HPPMS technique was proposed and a dense CrN coating was achieved by high ionization and high-energy ion bombardment [60]. In our laboratory, the bipolar-type PBII combined with HPPMS (HPPMS-PBII) system has been constructed and attempts were made to prepare conductive DLC films at a relatively low temperature, using a carbon sputter target. Although the ionization rate of carbon is not always high in the HPPMS system as already mentioned, sputtered carbon should be ionized not only in the HPPMS plasma region but also in the bipolar pulse plasma region. Thus, the ionization effect may be enhanced compared to that in HPPMS.

The aim of this study is to prepare conductive DLC films by the HPPMS-PBII system at relatively low temperature, and the preparation conditions are optimized to achieve relatively high hardness and adhesion. As a first step, a positive pulse power ($P_p$) is chosen to clarify the effect of electron heating on the structural change in the deposited films. The structural changes and properties of the films are examined as a function of $P_p$. Further, evaluation of the microstructure is carried out using Raman spectroscopy and X-ray photoelectron spectroscopy. The electrical resistivity and hardness of the films are examined using a four-point probe resistivity measurement and nano-indenter test, respectively. For comparison, some samples annealed in vacuum are also examined. In addition, an interesting parameter is a combination of the pulse voltage application sequences between HPPMS and PBII systems. The amount of ion species arriving at the substrate has been reported to vary with time in the HPPMS system [52]. Therefore, the amount of the ionic species may be affected by the timing of $v_n$ application. The onset of $v_n$ application relative to the target pulse voltage is varied in timing, and the differences are discussed.

## 2. Experimental procedure

Fig. 1 shows the schematic of the HPPMS-PBII system. A horizontal cylinder-type vacuum chamber, 650 mm in diameter and 600 mm in length, was used. The sputter gun was located in the chamber at the backside and connected to the HPPMS power source. High purity graphite, 50.8 mm (2 in.) in diameter and 3 mm in thickness, was used as the carbon sputter target. A target negative pulse voltage ($V_T$(t)) was applied to the carbon target and a pulse current ($i_T$(t)) passes through it. An electrode of bipolar pulse was introduced into the chamber at the lower side of the cylindrical surface through the high-voltage feed. An L-shaped substrate holder was located on the bipolar pulse electrode. 1-mm-thick glass was used as the substrate to accurately measure the resistivity. The substrates were approximately 10 × 10 cm in size and

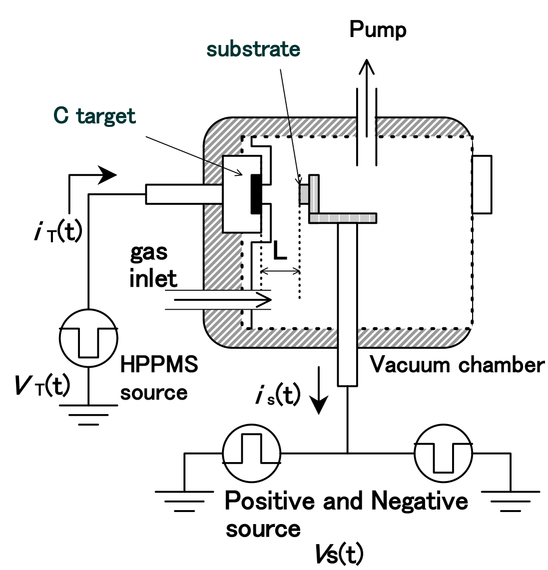


**Fig. 1.** The schematic diagram of the HPPMS-PBII system. High purity graphite plate in a diameter of 50.8 mm is used as sputter target. Ar gas is inlet into the vacuum chamber. Target and substrate are connected to the HPPMS power source and the PBII (positive and negative pulse) power source, respectively. The target pulse voltage and current are denoted by $V_T$(t) and $i_T$(t), respectively. Similarly, the substrate pulse voltage and current are denoted by $V_S$(t) and $i_S$(t), respectively.