Diamond & Related Materials 101 (2020) 107635

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Preparation of silicon-doped diamond-like carbon films with electrical conductivity by reactive high-power impulse magnetron sputtering combined with a plasma-based ion implantation system

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ABSTRACT

Silicon-doped diamond-like carbon (Si-doped DLC) films were prepared by a reactive high-power impulse magnetron sputtering (HiPIMS) combined with a plasma-based ion implantation (PBII) system, in which tetramethylsilane (TMS) was used as a reactive gas. The preparation of the Si-doped DLC films was based on both plasma-enhanced chemical vapor deposition and physical vapor deposition. The incident energy of the reactive ions was controlled by applying negative pulse voltage to the substrate using the PBII system. The Si content was controlled by the flow rate ratio of TMS to Ar. The negative pulse voltage was crucial because the resistivity of Si-doped DLC films prepared under the conditions of an Ar flow rate of 75 sccm and a TMS flow rate of 1.5sccm exponentially decreased from 575 to 30 Ωcm with an increase in the negative pulse voltage in the voltage range up to −7 kV. Through X-ray photoelectron spectroscopy, it was estimated that the Si content in the films ranged between 4.3% and 11% in our experiment. The resistivity of the films, which were prepared at a negative pulse voltage of −5 or − 7 kV in the range of the flow rate ratio up to 0.043, markedly increased from 3 to 380 Ωcm with an increase in the Si content. Moreover, the film hardness ranged between 9 and 16 GPa.

1. Introduction

Diamond-like carbon (DLC) films have attracted attention in material industries owing to their unique properties, such as high hardness, low friction coefficient, and chemical inertness. However, the properties of DLC films strongly depend on their microstructure, which usually changes based on the preparation conditions and methods [1-3]. Therefore, researchers have developed a coating technology for the synthesis of suitable DLC films for various applications using plasma-enhanced chemical vapor deposition (PECVD) and physical vapor deposition (PVD) methods [4–6]. High-power impulse magnetron sputtering (HiPIMS) is an ionized PVD technique wherein numbers of ions can be produced by voltage pulses with a high-power density and low duty cycle, although the time-averaged power is the same as that in conventional magnetron sputtering [7–9]. The plasma density in HiPIMS is higher than 10^{18}–10^{19} m^{-3} during the pulse-on time. The density of carbon ions in HiPIMS with a carbon target is higher than that in a conventional magnetron sputtering system, and relatively hard DLC films can be prepared [10–14], even though the ionization rate of the carbon is less than 5% in the HiPIMS system.

DLC films generally have an electrically high resistivity, although the value of the resistivity also depends on the deposition method. However, electrically conductive DLC films are required for industrial applications, e.g., antistatic films, protection of electrical probe tips, and certain electrodes. The incorporation of metal, such as Ti [15–18] and W [15,19], into DLC films has been widely used to prepare such electrically conductive DLC films. However, the mechanical properties of metal-doped DLC films tend to degrade as the metal content increases. As such, electrically conductive DLC films have been prepared by a bipolar-type plasma-based ion implantation (PBII) system without metal incorporation [20]. In the system, negative and positive pulse voltages are alternately applied to the substrate so that the film surface is bombarded by ions, and electrons sequentially impinge on it. A high negative pulse voltage of −5 to −20 kV is applied to the substrate to improve the electrical conductivity and reduce the internal stress. The application of the positive pulse voltage is crucial in the suppression of the charging-up phenomena and crucial in the rise in the substrate temperature. An amorphous graphite structure is formed as a consequence of the bipolar pulse voltage application, and the electrical conductivity is then realized by increasing the number of delocalized electrons [20]. However, very high voltages are required for the formation of such conductive DLC films, because a relatively high temperature is necessary to suppress the hydrogenation of the films that results from the use of hydrocarbon gases. In our previous paper [21], a

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https://doi.org/10.1016/j.diamond.2019.107635
Received 27 August 2019; Received in revised form 27 October 2019; Accepted 15 November 2019
Available online 19 November 2019
0925-9635/

DLC film with hardness higher than 10 GPa and a conductivity of 0.5 S/cm was prepared by HiPIMS combined with a PBII system, in which a carbon target was used and the negative pulse voltage applied to the substrate was as low as approximately −1 kV. Moreover, Ti-doped DLC films with higher conductivity were fabricated using the same system, wherein a titanium target and acetylene as a carbon source gas were used [22].

The incorporation of Si into DLC films causes a reduction of the internal stress and improves adhesion to many kinds of substrates, such as metal alloys, steels, and glasses [23,24]. In addition, Si-dope into DLC films improves their thermal stability, and Si-doped DLC films have low friction coefficients with an insensitivity to humidity [25]. In our viewpoint, the addition of Si may promote sp^3 C bonds, but ion bombardment may not always be significant enough to form sp^3 C bonds. Therefore, there is room for investigation regarding the influence of Si addition on mechanical properties, such as the hardness and elastic modulus [26,27]. The addition of electrical conductivity to the excellent properties of Si-doped DLC films is important to widen their industrial applications, although it is well-known that the films usually have a very high resistivity due to the existence of the Si and sp^3 C bonds. It should be noted that conductive DLC films can be prepared by our equipment, and the Si content in the films is believed to be an important factor to control the total electrical conductivity. Thus, it is significant to study the feasibility of conductive Si-doped DLC film fabrication as a function of Si content. However, to the best of our knowledge, there has been one report on the electrical conductivity of Si-doped DLC films produced by the irradiation of Si ions with a high energy of 30 keV into DLC films [28].

In this study, Si-DLC films were prepared by reactive HiPIMS combined with a PBII system, and the mechanical and electrical properties were examined as a function of the negative pulse voltage to the substrate and the flow rate ratio of tetramethylsilane (TMS) to Ar. In this system, a graphite target and TMS-Ar mixture gas were used. The films were deposited through a combination of HiPIMS and PBII processes, and the Si content was independently varied by changing the respective deposition conditions. The total Si content was less than 11% in the current experiment. A negative pulse voltage of −5 to −7 kV was typically employed to ensure an electrically conductive nature as well as a reduction of the hydrogen content and internal stress of the films. The mechanical and electrical properties of the films prepared on glass substrates were measured by nanoindentation and the four-point probe method. The characterization and compositional analysis of the films were performed by Raman spectroscopy measurement and X-ray photoelectron spectroscopy (XPS), respectively.

2. Experimental setup

Fig. 1 shows a schematic diagram of the HiPIMS combined with a PBII system. The system was primarily composed of a power source of a negative pulse voltage for the HiPIMS, another power source of bipolar pulse voltage for the PBII, a vacuum pumping system, and a cylindrical vacuum chamber. The chamber had an inner diameter of 650 mm and a height of 500 mm. A graphite target with a diameter of 50.8 mm and a thickness of 5 mm was used as the sputter target. The distance between the target and the substrate was 55 mm. The substrate holder was connected to the source for the PBII through a conducting metal rod insulated from the vacuum chamber, and the target was connected to the source for the HiPIMS. Borosilicate glass with a thickness of 1 mm was used as the substrate to make the resistivity measurement accurate. The substrates, which were cut to approximately 25 mm × 15 mm in size, were placed on the surface of the sample holder.

Fig. 2(a)–(d) show typical examples of the pulse shapes of (a) the negative pulse target voltage V_T(t), (b) the target current I_T(t) for HiPIMS, (c) the bipolar pulse voltage V_S(t) and (d) the bipolar pulse current I_S(t) through the substrate for the PBII. The repetition rate f_r was 650 cycle/s. The waveforms of the currents I_T(t) and I_S(t) were

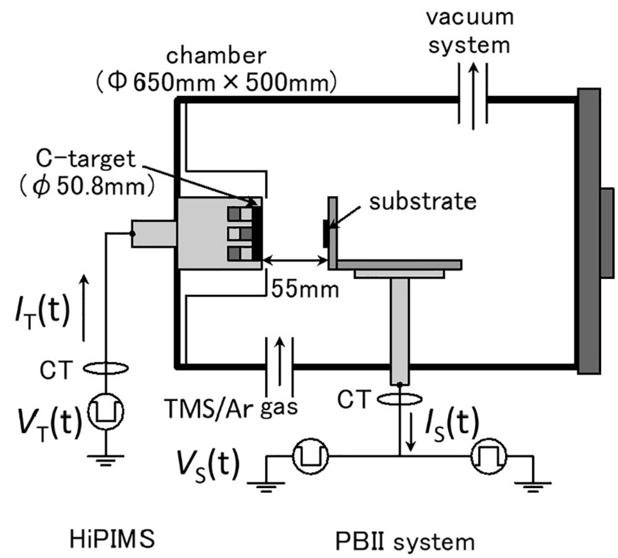

Fig. 1. Illustration of HiPIMS combined with PBII system.

detected by current transformers, whereas those of the voltages V_T(t) and V_S(t) were detected after being divided them by voltage dividers. The detected signals were monitored with a digital oscilloscope. As shown in Fig. 2(a) and (b), HiPIMS plasma was generated, and the I_T(t) evolved during the pulse-on time of V_T(t). Meanwhile, PBII plasma was also generated around the substrate, independently, as shown in Fig. 2(c) and (d). The positive pulse voltage in the V_S(t) was firstly applied to the substrate for 15 μs; then, the negative pulse voltage V_{np}(t) in the V_S(t) was applied to the substrate for 10 μs after an interval of 45 μs. The positive pulse voltage was kept constant, and the value of V_{np} was changed in the range of −2 to −7 kV. Each pulse sequence was as follows: (1) application of the positive pulse voltage to the substrate, followed by an interval of 15 μs; (2) application of V_T(t) with a width of 25 μs to the sputter target, followed by an interval of 5 μs; and (3) application of V_{np}(t) to the substrate. The plasma produced by applying the positive pulse voltage of PBII acted as an ignition for the HiPIMS discharge so that the HiPIMS discharge was easily ignited and stable. The interval of 15 μs between the positive pulse voltage in V_S(t) and V_T(t) was determined by the recovery time of the voltage source (characteristics of the power supply). The recovery time corresponded to the time when V_S(t) returned from negative voltage to zero after the application of the positive pulse voltage was finished. The negative pulse voltage in V_S(t) was applied when I_T (t) reached around zero. The average power P_D dissipated in the HiPIMS was about 90 W at any experimental condition. However, the average power P_{SN} supplied by the V_{np}(t) for the substrate ranged between 5 and 45 W. The measured temperature of the substrate stage increased as the P_{SN} increased. The substrate temperature exceeded 700 K at the value of $V_{np}(t) = -7$ kV. Ion bombardment by application of V_{np}(t) induced an internal stress relaxation in the films on the glass substrate so that no peel-off phenomenon was observed for any of the films. However, the electron impingement caused by the application of the positive pulse voltage might have played a significant role in the suppression of the charging-up effect.

The Si-doped DLC films were mainly prepared on glass substrates for 1 h using the mixture of TMS and Ar at a total pressure p of 0.6 Pa. The flow rate F_{TMS} of TMS ranged between 1.2 and 2 sccm, whereas the flow rate F_{Ar} of Ar ranged between 30 and 75 sccm. Film thickness was determined by using a surface profilometer to measure the step height made by covering a part of the substrate with a metal cover; the thickness ranged between 0.45 and 0.6 μm. The measurement of film hardness was performed by a nanoindenter with a diamond tip of trigonal shape. For each indentation, the maximum load of 400–600 μN