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Fabrication of diamond-like carbon films using short-pulse HiPIMS

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ABSTRACT

Diamond-like carbon (DLC) films were fabricated by sputtering a graphite target using a short-pulse-operated high-power impulse magnetron sputtering (HiPIMS) technology. The pulse duration was 7 μs with a maximum source voltage of −2400 V, which efficiently facilitated the ionization of the sputtered carbon species. In order to show the effectiveness of the short pulse operation, the fabricated DLC films were investigated by Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and spectroscopic ellipsometry. XPS spectra were curve-fitted using three Gaussian functions of sp^3-C, sp^2-C and C–O bonding. The information from the Raman and XPS spectra showed that the sp^3 fraction in the DLC films fabricated using a pulse duration of 7 μs was larger than that obtained using a pulse duration of 50 μs. It was found that the sp^3/sp^2 ratio was larger than 40%, which was approximately 1.5-fold compared to that obtained using a pulse duration of 50 μs. A high sp^3 fraction was realized due to application of high voltage without arc generation transferred from a magnetron sputtering (MS) glow discharge. To obtain the high sp^3 fraction in the fabricated DLC films, a parametric survey was performed, in which the background gas pressure, bias voltage applied to the substrate, power-source voltage and the distance between the target and the substrate were varied. There were optimum deposition parameters for lowering the D-band and G-band intensity ratio (I_D/I_G) in Raman spectra. The optimum source voltage was in the range of −1200 to −1600 V. For voltages higher than −1600 V, energetic carbon and argon ions may deteriorate the film properties. The hardness of the fabricated DLC films at 7-μs-pulse-width and −1200 V source-voltage were obtained as 37 GPa measured with a nano-indenter. The hardness decreased to a range from 20 to 27 GPa with increasing the pulse width in range from 40 to 60 μs.

1. Introduction

Physical vapor deposition (PVD) is a film-coating method for depositing metal or nonmetal (such as carbon) particles supplied in physical manners such as sputtering, abrupt vaporization, heating and metal irradiation. This technology has been used in many fields, such as the automotive and biomaterial fields [1,2]. Electron beam, vacuum arc [3–6] and magnetron sputtering (MS) glow plasma [7–9] have primarily been used as the plasma sources for the industrial deposition of films using PVD. In the case of vacuum arcs, metallic species are ejected by violent evaporation from the cathode and are simultaneously fully ionized. In contrast, magnetron sputtering glows are based on the sputtering resulting from bombarding energetic gas ions onto the target.

Carbon-related materials are promising for applications in a wide variety of fields, such as electronics, mechanics and bio-industries. Because there are different allotropes of carbon-related materials, such as graphite, graphene, diamond and diamond-like carbon (DLC), the properties of these materials differ from those of their atomic three-dimensional structures. In particular, DLC films have attracted a considerable amount of attention as hard coatings because of their excellent properties, such as high hardness, high elastic modulus, low friction, optical transparency and chemical inertness [10,11].

DLC films with high hardness and high density have been obtained using vacuum arc technology. However, the films often contain droplets and macro-particles, which are simultaneously produced at the initiation of the plasma. These species significantly deteriorate the properties of the deposited film. A filtering system has been used to exclude these species [6,12]. However, the filtering system decreases the efficiency of transmitting the deposited particles from the plasma source to the substrate. The density of the charged particles becomes 20–30% compared to those at the cathode region owing to ion transmittance limit by the filtering system [13].

Magnetron sputtering is known to not producing macro-particles. The deposited films experience no deterioration from macro-particles [14]. The sputtered atoms, with energies as high as 10 eV, travel toward a substrate located near the target. In general, the sputtered metallic materials have a weak ionization rate in a direct-current magnetron sputtering (dcMS) system. However, it is desired to have ionized

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species, as they can be controlled and collimated by an electric field produced by the voltage applied to the substrate.

The properties of the sputtered species should be controlled to produce high-quality films. To realize easy control over the species, a pulse-operated magnetron sputtering system [15–18] was developed to obtain a high-density of sputtered metal ions, in which a higher power can be consumed during the pulse without overheating the target by pulsing the power. This system is called high-power impulse magnetron sputtering (HiPIMS), [18] or high-power pulsed magnetron sputtering (HPPMS) [17]. The power density and current density at the target are usually on the order of approximately kW/cm^2 and A/cm^2, respectively. Both densities of current and the consumed power are by a factor of 10 to 1000 higher than those of dcMS glow plasma [1]. The densities for the actual plasma generation area are higher than those values considering the target utilization during the plasma generation. The high values of electrical parameters impart a high adhesion ability, enhancement of corrosion characteristics, uniform deposition on the substrate and high-dense structures [1]. Recently, DLC films have been prepared using HiPIMS [19–23]. To improve the mechanical properties and microstructure of the deposited films, modifications of the applied voltage [19] and changes in the gas pressure [20] and substrate bias voltage [11], [21–23] have been explored. A high sp^3 fraction has been proposed by applying a pulsed substrate-bias voltage on the order of several kilo-volts [23]. To increase the deposition rate, a mixed gas of argon and methane has been used to prepare hydrogenated DLC films [24]. A hybrid system of HiPIMS with a vacuum arc has also been employed [25,26]. A high carbon film density has also been obtained by increasing the argon ion content [27].

It is well known that sputtered carbon species are difficult to ionize [1,26,28–31]. This difficulty is due to the low ionization rate [2], the low sputtering yield [32] and the high ionization potential of carbon compared to metals. To obtain a high ionization rate of sputtered carbon species, the use of a short pulse operation of a HiPIMS discharge was proposed [33]. A study previously investigated the enhancement in the ionization of sputtered carbon species by changing the background gas [34].

In the present paper, DLC films are deposited using a short-pulse HiPIMS glow plasma containing abundant carbon ions based on the results of previous studies [33]. The film characteristics are analyzed using Raman spectroscopy, X-ray photoemission spectroscopy (XPS) and spectroscopic ellipsometry. The structure of films deposited under various conditions is compared to that with a long pulse HiPIMS operation with a duration of 50 μs [20,22]. A significant improvement in the sp^3-C fraction can be realized, and there are appropriate deposition conditions in terms of gas pressure and the source voltage to increase the sp^3-C fraction. The sp^3 bond fraction estimated by XPS analysis is greater than approximately 40%, which is 1.5-fold greater than the fraction in the film fabricated using a 50 μs pulse duration. A hardness and a mass density of the fabricated DLC films have also enough high values compared to those previously obtained. Thus, a short pulse operated HiPIMS technology shows to be an effective way to prepare DLC films with high sp^3 fraction.

2. Experimental details

Fig. 1 presents a schematic diagram of the DLC film deposition system. The system is divided into film deposition system and plasma control circuits. The latter is two circuits; plasma generation and application of a bias voltage to a substrate. The detailed configuration of the magnetron sputtering plasma source is described in [33]. The use of a self-made unbalanced magnetron sputtering (MS) apparatus, in which totally 30 magnets were placed outside of the vacuum chamber in the atmosphere, allowed the spatial distribution of the magnetic field to be easily changed into different patterns [33]. The electric power was supplied from a pulsed power supply to the target through a water-cooled copper plate, as shown in "Plasma generation system". The bias voltage was applied to a substrate-holder electrode (SHE) with a diameter of 60 mm. A direct current (dc) voltage or a pulsed dc voltage was used as substrate bias voltage (V_b). In the case of $V_b = 0$ V, the SHE was grounded directly. Thus, three methods were employed, as shown in "Bias application system" in Fig. 1.

The stainless steel (SUS) vacuum chamber had a diameter of 350 mm and a height of 250 mm. The throw distance (TD) between the target and SHE was varied from 35 to 170 mm. The substrate was Si (100) with dimensions of 20 mm × 20 mm. The magnetron was operated in pulsed mode and was configured as HiPIMS. The target

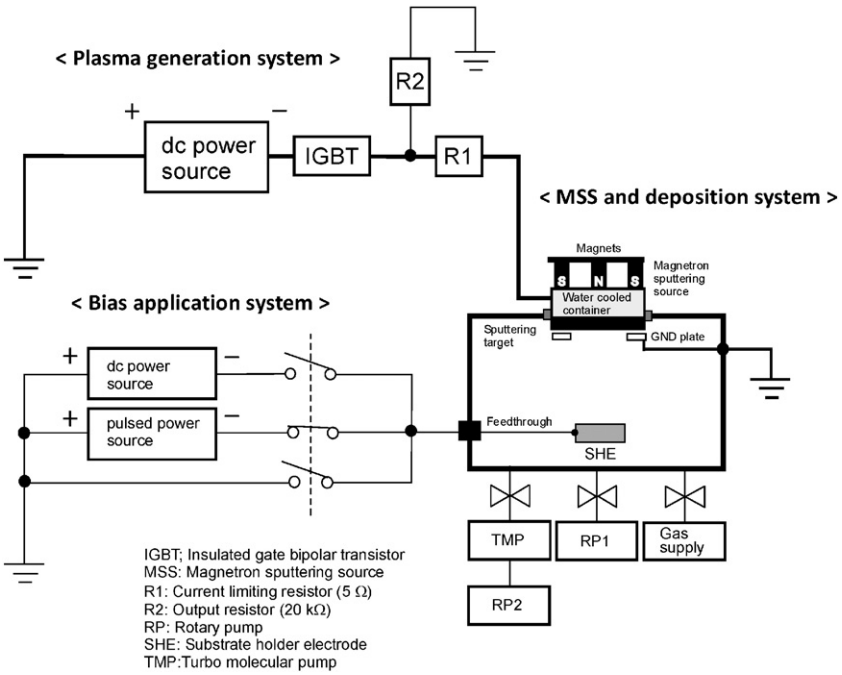

Fig. 1. Experimental arrangement.