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Influence of duty ratio of pulsed bias on structure and properties of silicon-doped diamond-like carbon films by plasma deposition

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A B S T R A C T

We have investigated the influence of the duty ratio of pulsed substrate bias on the structure and properties of Si-doped diamond-like carbon (Si-DLC) films deposited by radio frequency plasma-enhanced chemical vapor deposition using CH_4, Ar, and monomethylsilane (CH_3SiH_3) as the Si source. The Si/(Si + C) ratios in the Si-DLC films deposited using pulsed bias were higher than that of the dc-biased Si-DLC film, and the Si fraction increased with decreasing pulse duty ratio. Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy analyses revealed that Si-C, Si-H_n, and C-H_n bonds in the Si-DLC films increased with decreasing duty ratio. The internal stress decreased as the duty ratio decreased, which is probably due to the increase in Si-C, Si-H_n, and C-H_n bonds in the films. The Si-DLC films deposited using pulsed bias had higher adhesion strength than the dc-biased Si-DLC film because of the further reduction of internal stress. At higher duty ratios, although the Si fractions of the pulse-biased Si-DLC films were higher than that of the dc-biased Si-DLC film, the wear rates of the former were less than that of the latter.

1. Introduction

Diamond-like carbon (DLC) films have attracted considerable attention because they have unique properties such as high hardness, low friction, chemical inertness, high wear resistance, and optical transparency. Therefore, DLC films are used in a wide range of industrial applications such as protective coatings in devices such as magnetic storage disks. They are also of significant interest as coatings for soft polymer materials such as the resins used in the medical field and as substrate materials for micro-electro-mechanical systems [1–3]. One of the issues in the use of DLC films as wear-resistive coatings is their high internal stress. A higher internal stress in DLC films causes the deformation of coated substrates. It is also causing delamination when the higher load at the film/substrate interface is exceeding the adhesion strength of the interface. Secondly, under dry sliding conditions, DLC films generally shows friction coefficients of ~0.1 – ~0.3, but those are not very low compared with the other solid lubricants. Si doping to DLC films has been intensively studied because of the improvements of adhesion strength, thermal stability, and friction performance in air; specifically friction coefficient $\mu \sim 0.05$ [4–8]. However, its drawback is that wear protection and hardness were reduced by Si doping [9–11]. It is, therefore, strongly required to provide Si-DLC with high wear resistance as well as low friction. Meanwhile, it has been reported that the use of pulsed substrate bias was effective in improving the mechanical and tribological properties of DLC films by plasma-enhanced chemical vapor deposition (PECVD) [12–14]. We found that the pulse-biased Si-DLC films were found to have a higher wear resistance than the dc-biased Si-DLC films [13]. However, few studies have clarified in details the influence of pulsed-bias parameters such as voltage, duty ratio, and frequency on the structure and properties of the Si-DLC films.

In this study, to overcome the problems of Si-doped DLC (Si-DLC) films and to further improve their properties, we investigated the influence of the duty ratio of pulsed substrate bias on the structure and properties of Si-DLC films deposited by radio frequency (rf) PECVD using CH_4, Ar, and monomethylsilane (MMS; CH_3SiH_3) as the Si source.

2. Experimental methods

Si-DLC films were deposited in an rf PECVD chamber, whose base pressure was 8.0×10^{-5} Pa. The reactor consisted of two electrodes, and rf power (13.56 MHz) was capacitively coupled to one of the electrodes (cathode). The substrate used was a Si wafer. The substrate was mounted on the other electrode (anode). A negative dc bias or a negative pulse bias applied to the substrate was used to increase incident ion energy. The substrate was rinsed with ethanol, acetone, and ethanol in an ultrasonic container. Prior to the deposition, the substrate was cleaned by sputtering with Ar (99.999%) discharge under a negative dc bias voltage of −500 V and an rf input power of 40 W for 10 min. The Ar flow rate and pressure were 10 sccm and 0.3 Pa, respectively. The deposition of DLC films was carried out at an rf input power of 40 W and a pressure of 0.3 Pa. A negative dc bias (voltage, −500 V) or a negative pulse bias (voltage, −500 V, frequency: 25 kHz) was applied to the substrate during the deposition. MMS (99.99%) flow ratio to the total

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flow rate [MMS + CH_4 (99.999%)] was 5%, and Ar gas was introduced into the chamber at an Ar flow rate of 22 sccm. The total flow rate was kept at 44 sccm. The substrate temperature was lower than 75 °C during the deposition, which was measured by a thermocouple attached to the substrate holder. The DLC films for electron probe microanalysis (EPMA) measurements were 1 μm thick and the films for other measurements were 300 nm thick.

The deposition rate of the DLC films was determined from the profilometric measurement of a step formed during deposition using a laser scanning microscope (Olympus LEXTOLS 4000). The Si content of the DLC films was measured by EPMA (JOEL JXA-8230). The EPMA operating voltage was 8 kV.

X-ray photoelectron spectroscopy (XPS) was employed to investigate the chemical bonding of the films using a Shimadzu ESCA-1000 system with a Mg Kα X-ray tube and a hemispherical electron analyzer. The spectrometer was operated in the fixed-analyzer-energy transmission mode. Fourier transform infrared spectroscopy (FTIR) measurements were carried out using a JASCO FTIR-6100 system to investigate the Si-H_n and C-H_n, and Si-C stretch bands. The resolution of FTIR spectra was 4 cm^{-1}.

A conventional beam-bending method was used to estimate the internal stress of the deposited films. The deformation of the substrate owing to the stress in the deposited films was measured using a thin Si wafer as a substrate and a laser scanning microscope (Olympus LEXTOLS 4000). Internal stress was then calculated from the radius of curvature of the beam using Stoney's equation.

Adhesion measurements of the deposited films were performed using a scratch tester (Rhesca CRS-2000). The strength of adhesion to the substrate was evaluated by determining the load required to peel off the films. A diamond stylus was used and the radius of curvature of the stylus was 15 μm. The scratch furrow morphology of the films was observed using an optical microscope to find the peeling of the films.

The tribological properties of the films were investigated by ball-on-plate reciprocating friction tests (Heidon Tribostation Type32) using a stainless-steel (SUS304) ball of 10 mm diameter. The sliding speed was 60 cycles/min at 600 mm/min. The ball was placed in contact with the films at a load of 0.98 N. Specific wear rate was calculated from the profile of wear tracks measured using a laser scanning microscope (Olympus LEXTOLS 4000).

3. Results and discussion

Fig. 1 shows the deposition rate of DLC films as a function of duty ratio. Solid and open circles denote undoped DLC and Si-DLC films, respectively. The dotted lines show the deposition rates of the films deposited using the dc bias. The deposition rate increases by the introduction of MMS. The increase in deposition rate is chiefly due to the difference in bond dissociation energy between CH_4 and MMS. The mean bond dissociation energy of C-H in CH_4 is 410.5 kJ mol^{-1}, while those of Si-H in SiH_4 and Si-C in $Si(CH_3)_4$ are 316 and 317 kJ mol^{-1}, respectively [15]. The amount of activated precursors contributing to the deposition of the films increases by the introduction of MMS because organosilane molecules dissociate more easily than CH_4 molecules. On the other hand, the deposition rate of the pulse-biased films decreases with decreasing duty ratio. We have shown that the deposition rate of DLC films increased with increasing dc bias voltage [16]. This is because positively charged ion species are further accelerated by increasing the negative bias, resulting in an increase in ion flux on the depositing surfaces. As the time of the bias application is shorten, the impinging rate of ion species on the surfaces decreases, resulting in a decrease in deposition rate.

Fig. 2 shows the dependence of Si/(Si + C) ratio in DLC films on duty ratio. The dotted line denotes the Si/(Si + C) ratio (approximately 15%) of the film deposited using dc bias. The Si ratios in the films deposited using the pulsed bias are higher than those of the films deposited using the dc bias. The Si/(Si + C) ratio increases with decreasing duty ratio. Specifically, the Si ratios are approximately 16% and 21% at duty ratios of 90% and 5%, respectively.

Fig. 3 shows the C 1 s spectra of the Si-DLC films deposited at various duty ratios. The dotted lines in the figure denote the binding energies corresponding to C-O (286.6 eV), sp^3 C-C (285.2 eV), sp^2 C = C (284.3 eV), and C-Si (283.2 eV) bonds [17–20]. The binding energy of C-Si bonds is that of C 1 s in amorphous SiC films [19]. The C-O bonding component is attributed to some residual contaminations formed on the surfaces due to air exposure [20]. It is known that the binding energy of C-H is 284.9–285.5 eV [16,21,22]. It is difficult to separate the sp^3 C-C and C-H bonds because of the binding energy superposition. Therefore, the sp^3 C-C and C-H bonds are considered to be one component. It is expected that the C-Si position shifts to a lower binding energy with increasing the number of Si atoms bound to C atoms. The position of maximum intensity in the C 1 s envelope shifts towards lower binding energies with decreasing duty ratio. The width of the C 1 s spectra increases with increasing duty ratio. The broadening of the C 1 s spectra can be attributed to the increase in the number of C-Si components and the increasing magnitude of each C-Si component in the C 1 s spectra with an increase in duty ratio.

FTIR spectroscopy provides variable information on local chemical bonding. The infrared absorption spectra of C-H_n [Fig. 4(a) and (b)], Si-H_n [Fig. 4(c)], and C-Si [Fig. 4(d)] bond stretching modes are shown for the films deposited at various duty ratios. In Fig. 4(a) and

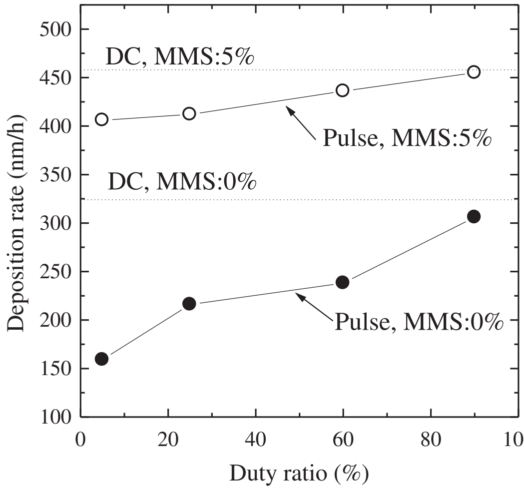

Fig. 1. Deposition rate of DLC films plotted as a function of duty ratio.

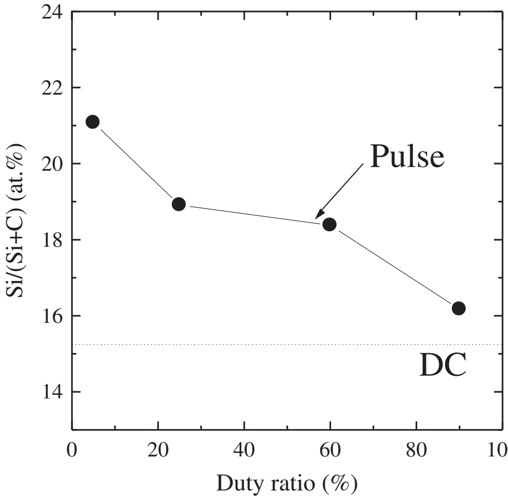

Fig. 2. Si/(Si + C) ratio in DLC films plotted as a function of duty ratio.