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Argon-dominated plasma beam generated by filtered vacuum arc and its substrate etching

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Abstract

A new technique to etch a substrate as a pre-treatment prior to functional film deposition was developed using a filtered vacuum arc plasma. An Ar-dominated plasma beam was generated from filtered carbon arc plasma by introducing appropriate flow rate of Ar gas in a T-shape filtered arc deposition (T-FAD) system. The radiation spectra emitted from the filtered plasma beam in front of a substrate table were measured. The substrate was etched by the Ar-dominated plasma beam. The principal results are summarized as follows. At a high flow rate of Ar gas (50 ml/min), when the bias was applied to the substrate, the plasma was attracted toward the substrate table and the

substrate was well etched without film formation on the substrate. Super hard alloy (WC), bearing steel (SUJ2), and Si wafer were etched by the Ar-dominated plasma beam. The etching rate was dependent on the kind of substrate. The roughness of the substrate increased, when the etching rate was high. A pulse bias etched the substrate without roughening the substrate surface excessively.

Keywords: T-shape filtered-arc-deposition (T-FAD) system, carbon vacuum arc, Ar-dominated plasma beam, substrate etching, DLC film

1. Introduction

Amorphous carbon film which has an sp^3 structure is a so-called diamond-like carbon (DLC) film and has gradually spread in use as a protective film in various fields, such as cutting tools (razor, knife, drill, end mill), sliding parts (fork absorber in motorcycles, faucet valve, valve lifter in engines, slider in hard disk drives), molds, PET bottles for winter version tea, and decollation (watch) [e.g. 1-6]. DLC has various unique properties; high hardness, low-friction, harmless, etc. The hardness strongly corresponds to the density of the film, and some properties are associated with the hardness and density. For example, harder DLC is electrically non-conductive due to rich sp^3 structure, but softer DLC without hydrogen is conductive since the sp^2 (graphite) structure is rich. DLC films have been prepared by various physical vapor depositions (PVDs) and plasma enhanced chemical vapor depositions (PECVDs). The properties of DLC films depend somewhat on the preparation method as well.

It is well known that the harder DLC is difficult to adhere firmly to the substrate. The hardest DLC, the so-called ta-C (tetrahedral amorphous carbon), is especially difficult. In order to attain practical firm adhesion, the substrate is typically slightly etched by argon (Ar) ions irradiation or bombardment for the purpose of surface cleaning. In general, an ion gun [7] or RF plasma [8] is employed for supplying Ar ions. However, in the case of RF plasma, a micro-discharge sometimes

occurs at the edge of the substrate and the vapor generated by the micro-discharge is re-deposited on the substrate, making the surface rough and contaminated. Ion guns are known to be quite expensive. We have been developing the T-shape filtered arc deposition (T-FAD) system, which is a type of PVD system with a solid graphite target, based on cathodic vacuum arc discharge plasma with macro-particle filtering geometry [9]. It can provide all kinds of DLC films of high quality, hydrogen (H) free, H-rich, hard and soft, by controlling the substrate temperature, substrate bias, and introduction gases [10-12]. Recently, we have also been developing a small table-top type T-FAD, called μ T-FAD, for R&D in the laboratory or for on-site coating of a DLC film in the manufacturing field. In order to supply a lower priced, mass-production-type T-FAD and laboratory-scale μ T-FAD, auxiliary facilities or devices should be excluded as much as possible, such as an RF generator or ion gun.

From this background, we developed a new pre-treatment method using an Ar-dominated plasma beam, which is described in this paper. The Ar-dominated plasma beam was generated by transforming the cathodic carbon arc plasma beam formed in T-FAD. The plasma condition was spectroscopically evaluated as a function of the Ar flow rate and substrate bias. The etching rates were obtained for super hard alloy, bearing steel, and silicon (Si) substrates.

2. Experiment

The experimental setup of the T-FAD system is depicted in Fig. 1. The carbon cathodic arc plasma was generated between a high-purity graphite cathode and stainless anode in the arc source part. The plasma was bent and guided to the process chamber through a T-shape duct by magnetic and electric fields, where macro-particles (so-called droplets) emitted from the cathode spot were filtered from the plasma.

Experimental conditions were as follows: arc current, 30 A; base pressure, less than 5×10^{-3} Pa; gas, Ar; flow rate, 0 to 50 ml/min; process pressure, 0.005 to 0.4 Pa; duct bias, +15 V; substrate

bias, 0 (grounded), DC –100 to –400 V, and pulse –500 V (frequency, 10 kHz; width, 50 μ s; duty, 50%). The substrates used were well-polished super hard alloy, tungsten carbide (WC) with cobalt (Co) binder 6%, and bearing steel, SUJ2, as well as a Si (100) wafer (n-type, 525!25 μ m thick, 2 to 10 Ω). The substrate table was made of stainless steel, 100 mm in diameter, and 1 mm thick. The back side of the substrate table was insulated. The ion current monitor plate biased at DC –100 V was located at the entrance to the chamber, and it also acted as a mechanical shutter. In this study, the T-FAD system was not baked out and the leakage of the system was 8.5×10^{-5} Pa·m³/s.

The substrate surface was analyzed with a stylus surface profiler (Veeco, Dektak3) and Laser Raman spectroscopy (JASCO, NRS-1000; Laser wavelength, 532 nm; laser output, 80 mW; exposure time, 30 s). The radiation spectra emitted from the plasma was measured with a multi-channel spectrometer (Soma Optics Ltd., Fastvert S-2400 customized; blaze wavelength 500 nm; slit width, 30 μ m; resolution, 1.1 nm; wavelength range, 200 to 900 nm). The emission from the plasma at 15 mm in front of the substrate was focused on a quartz optical fiber with a quartz lens and guided to the spectroscopy. The exposure time and number of repetitions of the spectrometric measurement was 1.6 s and 30, respectively, and thus the total measurement time was less than 1 min per time.

3. Results and Discussion

3.1 Plasma behavior

After the chamber was open to the atmosphere, the chamber was closed and evacuated. Then, the carbon arc was ignited by contacting a mechanical trigger under the condition of no gas introduction. The emission spectra as well as pressure and voltage between the cathode and anode were measured for more than 10 min. The results are shown in Figs. 2 and 3. The spectra detected were identified based on spectral data books [13-16]. The identified spectra were the same as in previous reports [10, 11]. All of the identified spectra were a molecular type; carbon monoxide

(CO), carbon monoxide ion (CO^+), and carbon nitride (CN). These particles were combinations of carbon and air ingredients, indicating the existence of air leakage in the system. Incidentally, other spectra did not appear. Thus, from another perspective, the spectral intensity of CO is considered to indicate the relative amount of carbon transported from the source. Hereafter, the CO Third Positive band (0, 2) is used as a relative index, since the spectra was not overlapped by another spectra.

The chamber pressure was immediately raised at the ignition of the arc and gradually decreased. Three minutes after arc ignition, the pressure became constant at a value higher than the pressure before the arc ignition. Such pressure changes over time are frequently observed in vacuum arc deposition systems [17]. The spectral intensity change over time behaved the same as the pressure change relative to the CO Third Positive band (0, 2), as shown in Fig. 3. These results indicate the experiment of plasma irradiation to the substrate should be carried out at least 3 min after the ignition. Thereafter, all experiments were carried out 3 min after ignition. The arc voltage did not significantly change during the arc ignition regime.

The spectral distribution emitted the plasma beam as a function of the Ar gas flow rate without substrate bias. The chamber pressure depended on the Ar gas flow rate so the pressure is indicated as well in the figure. When the Ar gas was introduced, the obvious spectra of Ar were detected at 738.9, 750.4 (U3), 801.5, 810.4, and 811.5 nm (U2) as typical spectra. The spectral intensities of Ar (U2) and CO Third Positive band (0, 2) as a function of the Ar gas flow rate are shown in Fig. 5. The intensity of CO gradually decreased with the Ar gas flow rate, although the intensity of Ar increased with the lower Ar gas flow rate, which reached a maximum at 10 ml/min, and then decreased with the higher Ar gas flow rate. Figure 5 shows the arc voltage and ion current. The arc voltage slightly decreased with the Ar gas flow rate. The ion current more significantly decreased. These results indicate that Ar (ionization potential, 15.75 eV) is easier to ionize than carbon particles so that the arc voltage was lower. The ionization potential of carbon particles was estimated to be at least 17.26 eV as follows.

As the Ar gas flow rate increased, the pressure increased so that the amount of transported plasma decreased. As a result, the ion current and spectral intensity decreased.

Then, the emission spectra in front of the substrate table were measured when the substrate table was biased. The result is shown in Fig. 7. As the bias voltage increased negatively, the intensity of the Ar spectra increased. Figure 8 shows the intensity of Ar (U2) and CO Third Positive band (0, 2) as a function of the substrate bias. This clearly indicates that the intensity of the Ar spectra increased with the negative bias voltage, although that of the CO spectra was almost constant.

3.2 Substrate etching

From the above results, we considered that an Ar-dominated plasma beam was obtained when Ar gas was introduced to the carbon filtered arc plasma. Then, the Ar-dominated plasma beam was irradiated on a WC substrate with a different flow rate of Ar gas. Half of the side of the substrate was masked. Resulting photographs of the substrate surface are shown in Fig. 9. When the Ar gas flow rate was lower or at lower pressure, as shown in Fig. 9 (a), a thin solid film was formed on the substrate. The film remained on the un-masked surface (area B) and peeled off from some parts (area C) without external factor. On the other hand, when the Ar gas flow rate was higher or at higher pressure, as shown in Fig. 9 (b), no film was observed on the surface. As for area A, C, and D, no significant Raman spectrum was observed, indicating that no film existed on the substrate. As for area B, the typical Raman spectra of a ta-C film were observed.

From the results of Fig. 9 and section 3.1, the plasma behavior against the substrate was considered as follows. An explanatory schema is shown in Fig. 10. When no gas was introduced, C plasma reached the substrate and a DLC film formed on it. With a lower flow rate of Ar gas, Ar-dominated plasma was obtained, although a considerable amount of carbon atoms and ions

remained in the plasma. As a result, the deposition rate of carbon was still higher than the etching rate by Ar so that a DLC film was formed on the substrate. With a higher flow rate of Ar gas, the plasma had difficulty reaching the substrate, since the pressure was relatively high and the mean free path was shorter. However, in this condition, if a negative bias was applied to the substrate, Ar ions, the dominant ion in the plasma, were attracted to and reached the substrate. Accelerated Ar ions were bombarded to etch the substrate. In this case, the etching rate was faster than the deposition rate.

Further etching tests were carried out for various substrates and biases. The Ar gas flow rate and process pressure were 50 ml/min and 0.4 Pa, respectively. For comparison, the substrate was also etched by Ar RF-plasma (400 W; Ar gas flow rate, 20 ml/min; pressure, 1.0 Pa), where the substrate itself was an RF antenna and the vacuum arc was not discharged. Etching depth and difference of surface roughness before and after plasma irradiation as a function of treatment time were measured. The results are shown in Fig. 11. All substrates were etched almost proportionally with treatment time. It was found that the fastest to be etched was SUJ2 and the slowest was Si under the same conditions. This process was found to have almost the same ability as Ar RF-plasma treatment. The surface roughness was found to increase almost proportionally with treatment time as well. From these results, the relation between etching depth and surface roughness was obtained, as shown in Fig. 11 (c). The relation indicates that when the slope is gentler, the treatment process is milder so that the surface does not get rough. From the comparison of DC bias, pulse bias, and conventional RF plasma treatments, it was found that the pulse bias realized the etching without roughening the surface. This relation is also an available dataset for how much the surface roughness increases for a certain etching depth, especially for the WC substrate to be used as a precise press mold, because the surface roughness must be as low as possible even after the etching treatment.

4. Conclusions

The Ar-dominated plasma beam was generated from the filtered carbon arc plasma by introducing an appropriate Ar gas in a T-FAD system. The radiation spectra emitted from the plasma beam in front of the substrate table were measured. The substrate was etched by using an Ar-dominated plasma beam. The principal results are summarized as follows.

- (1) When no gas was introduced, CO, CO⁺, and CN spectra were observed due to a small regular air leakage, and these spectra were used as a relative index of the amount of carbon transported.
- (2) The radiation intensity of Ar spectra increased at lower flow rates of Ar gas, and decreased at higher rates.
- (3) At a high flow rate of the Ar gas (50 ml/min), when the bias was applied to the substrate, the plasma was attracted toward the substrate table and the substrate was well etched without film formation on the substrate.
- (4) Super hard alloy (WC), bearing steel (SUI2), and Si wafer were etched by the Ar-dominated plasma beam. The etching rate was dependent on the kind of substrate. The roughness of the substrate increased when the etching rate was high. The pulse bias etched the substrate without roughening the substrate surface excessively.

This study provides a new technique to etch the substrate as a treatment prior to functional film deposition instead of using RF power supply and an ion gun. In this process, a common power supply can be used for pre-treatment and film preparation. Unlike a pre-treatment using the substrate itself as an antenna or electrode in a local plasma such as RF-plasma or pulsed plasma, the Ar-dominated plasma beam can be easily controlled to irradiate various objects. This process can also be used in small and low-price filtered arc deposition systems to prepare various kinds of functional film, not just DLC, but also metals, nitrides, oxides, etc.

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Figure Captions

Fig. 1. Schematic diagram of T-FAD and experimental setup.

Fig. 2. Temporal change of radiation spectra emitted from plasma beam in front of substrate table, in case of first ignition after chamber was once opened (no gas introduction; substrate bias, 0 V).

Fig. 3. Temporal change of chamber pressure, voltage between electrodes, and spectral intensity of CO Third Positive band (0, 2) in case of Fig. 1.

Fig. 4. Radiation spectra as a function of Ar gas flow rate (substrate bias, 0 V).

Fig. 5. Arc voltage and ion current as a function of Ar gas flow rate (substrate bias, 0 V).

Fig. 6. Spectral intensity of Ar (U2) and CO Third Positive band (0, 2) as a function of Ar gas flow rate (substrate bias, 0 V).

Fig. 7. Radiation spectra as a function of substrate bias (Ar gas flow rate, 50 ml/min).

Fig. 8. Spectral intensity of Ar (U2) and CO Third Positive band (0, 2) as a function of substrate bias (Ar gas flow rate, 50 ml/min).

Fig. 9. Photographs of ta-C coated WC substrate treated by Ar-dominated plasma beam and Raman shift on the surface. Ar gas flow rate, (a) 10 ml/min (pressure, 0.1 Pa) and (b) 50 ml/min (pressure, 0.4 Pa). Substrate bias, DC -400 V; treatment time, 20 min.

Fig. 10. Explanatory schema of Ar-dominated plasma beam behavior. (a) no gas, 0.005 Pa, (b) Ar, 10 ml/min; 0.1 Pa, and (c) Ar, 50 ml/min; 0.4 Pa.

Fig. 11. Results of etching experiment for various substrates with various biases. (a) Etching depth

as a function of treatment time, (b) change of surface roughness before and after treatment, and (c) relation between change of surface roughness and etching depth. Ar gas flow rate, 50 ml/min; pressure, 0.4 Pa. RF plasma treatment was carried out without filtered arc.

Figures

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11(a)

Fig. 11(b)

Fig. 11(c)