Amorphous diamond-like carbon film prepared by pulsed laser deposition with application of pulsed negative bias voltage

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Amorphous diamond-like carbon films were prepared by pulsed laser deposition with a synchronized application of pulsed negative bias voltage to the substrate. A beam from a Nd:yttrium–aluminum–garnet laser (1064 nm) was radiated to a graphite target at a laser fluence of 10 J/cm^2. The negative bias voltage was changed from 0 to 10 kV at a repetition rate of 10 Hz. The film was deposited on a Si (111) substrate at a chamber pressure of 5×10^{-5} Torr for 120 min. The effects of bias voltage on the structure of the film were discussed on the basis of the measured deposition rate, Raman spectra, refractive index, dynamic hardness, and surface roughness. The effect of self-sputtering on deposition rate was observed at a negative bias voltage above 0.6 kV. The application of bias voltage increased the fraction of sp^3 configuration in the film and made the film surface smoother. In particular, the application of 3 kV gave the largest fraction of sp^3 bonding, and formed the hardest and smoothest film. Bias voltage above 5 kV, however, drastically reduced the hardness of the film. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1334640]

I. INTRODUCTION

Unhydrogenated amorphous diamond-like carbon (DLC) films have been prepared by pulsed laser deposition (PLD)[1,2] at room temperature. The PLD method is different from that of traditional chemical vapor deposition where hydrogen plays an essential role by preferentially etching graphitic and amorphous carbon constituents. Some investigators [3–8] have correlated the degree of diamond-like film character with deposition energy.

Kasi, Kang, and Rabalais,[3] reported that the optimum C$^+$ energy range for formation of the diamond-like structure by ion-beam deposition is 30–175 eV. Below 10 eV the final diamond-like structure has not been attained and above 180 eV there is a sharp increase in the dose required to attain this final structure. Lifshitz et al.[4,5] proposed the subplantation (shallow implantation) model for film growth from hyper-thermal ($\approx 1 \times 10^3$ eV) species impinging on the substrate. The process included subsurface implantation, energy loss, preferential displacement of atoms with low displacement energies leaving high displacement energy atoms undisplaced, and sputtering of substrate material. The model, supported by ion-trajectory calculation and experimental data, was applied to diamond film formation from C$^+$ ions. Stevefelt and Collins[6] reported a model of an expanding carbon plasma ablated from graphite feedstock by a focused laser beam. They showed that, under the experimental conditions of Marquardt, Williams, and Nagel[1] that have been proven relevant for producing hard DLC films characterized by a high percentage of sp^3 bonds, the plasma is composed of multiple-charged carbon ions with kinetic energies of the order of 1 keV. Cuomo et al. [7,8] suggested that the condensation and growth of the DLC film was dependent on both the incident particle energy and a thermal quench at the substrate surface. They propose that thermally produced species of low energy will condense into the thermodynamically favored graphite structure when they reach the substrate. Alternatively, high-energy species may compact into the metastable diamond-like geometry when they impinge on the substrate. This geometry can be maintained if any excess energy that would drive it over the activation barrier toward the equilibrium structure is removed rapidly from the system.

There have been few reports about the effect of dc bias on the structure of the pulsed-laser-deposited DLC film. Sato et al.[2] reported that application of a negative dc bias (-150 to -500 V) during deposition by PLD using a XeCl laser was effective to ensure good quality of DLC film. Yamamoto et al.[9] studied the effect of substrate dc bias (-300 to 200 V) to the fraction of sp^3 bonding in the DLC film prepared by PLD using a KrF laser. Their results showed that the ion bombardment at above 200 eV was effective to form sp^3 bonding.

This study describes the effect of a pulsed bias synchronized with the pulse of a Nd:yttrium–aluminum–garnet (YAG) laser on the preparation of DLC films. The effects of negative bias voltage on the structure of the film were discussed on the basis of measured scanning electron microscope (SEM), x-ray diffraction (XRD), Raman spectroscopy, ellipsometry, atomic force microscopy (AFM), surface roughness, and dynamic hardness.

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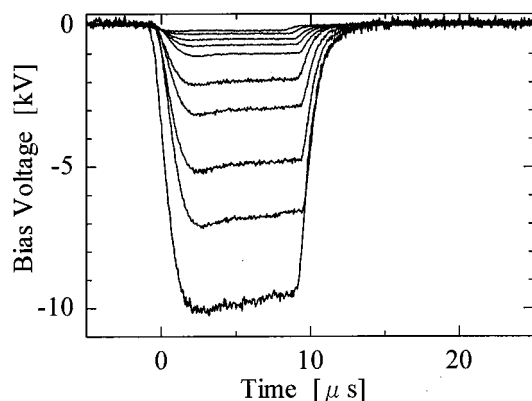
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FIG. 1. Typical wave forms of pulsed bias voltage.

FIG. 2. Deposition rate of the DLC film as a function of negative bias voltage.

II. EXPERIMENT

A Nd:YAG laser (Spectron, SL-800) was operated at 10 Hz. Pulses of 1064 nm radiation were 25 ns in duration (temporal full width at half maximum) and had energy per pulse of 150 mJ. The laser radiation was focused on the graphite target surface using a 30 cm focal length lens (Sigma Koki, SLSQ-50-300). The radiated target area, 0.0138 cm^2, was calculated from the measured radiation area of the nonconcentrated laser on the basis of the fact that the spot size is proportional to the distance between the target surface and the lens focus. Thus, the laser fluence was 10 J/cm^2, and the laser power density was 4×10^8 W/cm^2. A 99.99% graphite rod (Nilaco, C-072591) was used as a target. The target was axially moved at a speed of 3 mm/min with a motor to avoid any deep crater that may eject macroscopic graphite particle. A 10×10 mm^2 single crystal silicon was used as a substrate. The substrate was set in the position 60 mm from a target. The angle between a plane vertical to the substrate and the irradiation direction of plume was 35°. During the film deposition, the pressure in reaction chamber was kept at 5×10^{-5} Torr with a rotary pump and turbo-molecular pump. The deposition time was 120 min.

The reaction chamber and the target were grounded to make an anode, and the bias voltage was applied to the substrate holder. A pulse voltage of 10 μs in duration was used as the negative bias voltage. The 10 μs duration was selected to be long enough to cover the observed lifetime of an ablation plume. To apply the negative bias voltage to the plume, the 10 Hz voltage was triggered by the excitation lamp of the Nd:YAG laser. The trigger signal was amplified with a pulse generator (Hewlett Packard, 214B) and sent to a pulsed bias voltage source in time with the generation of the plume. Thus the rise of the pulsed bias was synchronized with that of the pulse of the laser. During the deposition, the wave form was monitored with an oscilloscope (Tektronix, TDS-620A). Figure 1 shows typical wave forms of the pulsed bias voltage. The voltage change is approximately a rectangular form with a rise time of about 1.5 μs and duration of 10 μs.

For comparison, the DLC film was prepared by radiofrequency plasma deposition process with an application of pulsed negative bias voltage to the substrate. The radiofrequency power was 0.2 kW. The applied pulse voltage was
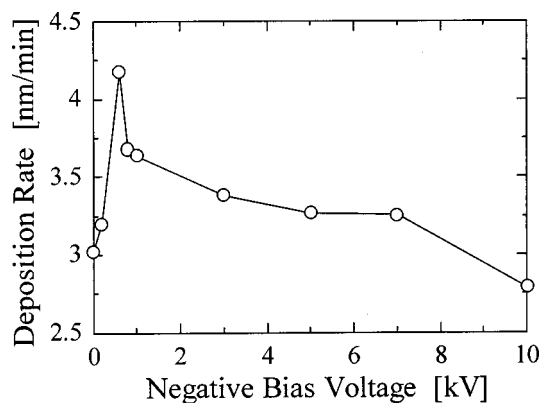
-10 kV, the pulse width was 20 μs, and the frequency was 400 Hz. The source gas was CH$_4$, the flow rate of which was 27.9 sccm. A 10×15 mm silicon substrate was placed on a 60-mm-diam copper target. The deposition was made at pressure of 10^{-3} Torr for 120 min.

The morphology of the film was observed with SEM (Hitachi, SS2460N). The crystalline character of the film was checked by XRD (Rigaku, Mini Flex) using Cu $K\alpha$ radiation. The Raman spectrum was measured with Raman spectrum meter (Renishaw, JRS-SYSTEM 2000) using the 514.5 nm line of an argon ion laser for excitation. The refractive index was measured with an ellipsometer (Mizojiri, DHA-XAVW/S6). The surface roughness and film thickness were measured with a surface roughness meter using stylus instruments (Taylor-Hobson, Form Talysurf Series 2). In the measurement of surface roughness, a 3 mm scanning was made three times in an arbitrary direction. The film thickness was measured at the step that was made by masking a part of the substrate prior to the deposition. The surface roughness was also measured with an AFM (TopoMetrix, Explorer) in contact mode using a Si$_3$N$_4$ cantilever. The average surface roughness was obtained by scanning the area of 100 μm square. The hardness of the film was measured with a dynamic ultramicrohardness tester (Shimadzu, DUH-W201S) using a Berkovich indenter (115° triangular pyramid) with a test load of 2 mN at a loading speed of 0.711 mN/s for a duration of 5 s.

III. RESULTS AND DISCUSSION

The XRD pattern showed that the prepared films were amorphous. The SEM observations confirmed that the surface of the film was very smooth and that there was not any prominent difference between the films with and without applying bias voltage. The smooth surface is characteristic of the DLC film.

Figure 2 shows the deposition rate of the film as a function of the negative bias voltage. Applying negative bias voltage in the range between 0.6 and 7 kV enhances the deposition rate. However, the enhancement effect is not proportional to the negative bias voltage. It is largest at 0.6 kV and decreases with increasing negative bias voltage. The ap-
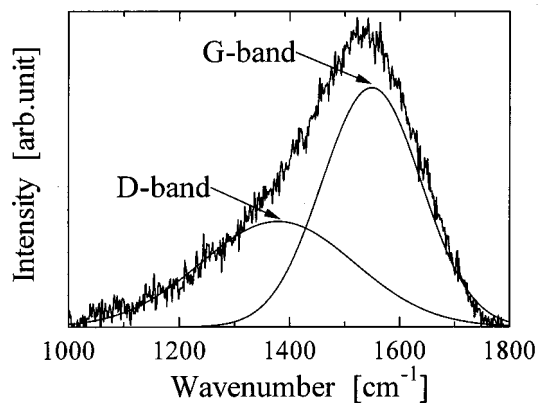
FIG. 3. Raman spectrum of PLD grown films without bias voltage.

FIG. 5. Surface roughness of the DLC film measured by using stylus instruments and by using AFM.

plication of a negative bias voltage is inferred to be effective in enhancing the deposition rate by directing the plume ions to the substrate. However, a decrease in deposition rate can also occur because of a self-sputtering effect on the deposited film by the impinging ions. The results above 0.6 kV show that the enhancement is largely overcome by the self-sputtering effect.

Figure 3 shows a typical example of the Raman spectrum for the film prepared without applying bias voltage. The spectrum shows only one broad asymmetric peak centered around 1530 cm^{-1}, which is characteristic of DLC films. Thus, the unhydrogenated DLC film is obtained at laser power density of 4×10^8 W/cm^2. It is well below the reported critical level, 5×10^{10} W/cm^2 at wavelength of 1060 nm[1], and it is equal to the critical level, $\sim 10^8$ W/cm^2 at wavelength of 248 nm[8]. The signal can be decomposed into two peaks on the assumption that it consists of Gaussian peaks. Also shown in this figure are decomposed Gaussian peaks centered at 1390 and 1530 cm^{-1}, which are called D band and G band, respectively. The D band is associated with the stretching vibration of sp^2 clusters, and the G band with the symmetric vibration mode-like contraction and expansion of the whole sp^2 cluster. The area ratio between the D band and G band, S_D/S_G, is used to express the fraction of ordered sp^2 clusters in the film.

Figure 4 shows the ratio S_D/S_G as a function of negative bias voltage. The application of negative bias voltage de-
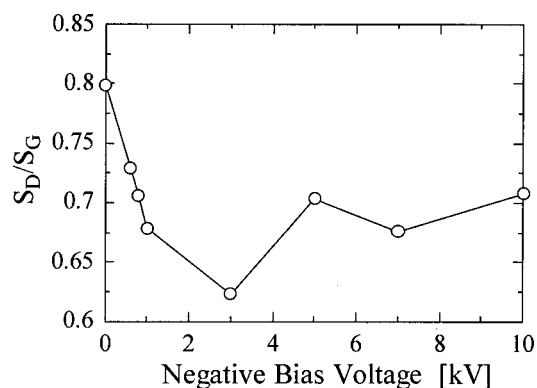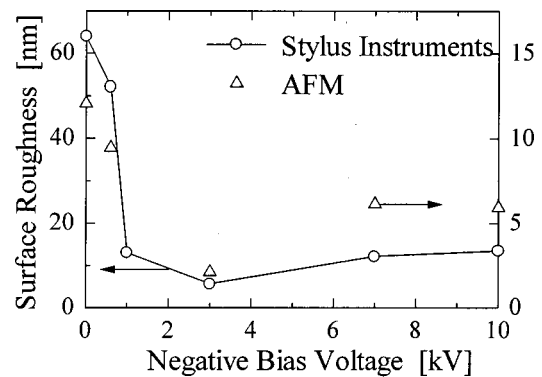
creases the ratio from that obtained without applying negative bias voltage. In particular, the ratio shows the lowest value at 3 kV, where the effect of the self-sputtering on the deposition rate is apparent in Fig. 2. Thus the ion impact on the film is effective in decreasing the fraction of sp^2 bonds in the film on behalf of sp^3 bonds. The impact of an energetic ion may locally force surface sp^2 atoms into the metastable diamond-like configuration with preferential sputtering of the more weakly bonded carbon atoms in the growing film. At a negative bias voltage above 5 kV, however, excess energy may drive an atom back over the barrier to the equilibrium sp^2 structure, because that energy cannot be quickly removed. That is, the ion bombardment at 3 keV is optimal for the reconstruction of the film. This result is consistent with the prediction of Stevenfelt and Collins[6] that the plasma is composed of multiple-charged carbon ions with kinetic energies of the order of 1 keV for producing hard DLC films characterized by a high percentage of sp^3 bonds.

Figure 5 shows the surface roughness of the film measured by using stylus instruments and by using AFM. The fact that the roughness of the former is about four times larger than that of the latter is attributable to the difference in mechanism for the measurements. The DLC film prepared by a radio-frequency plasma deposition process showed similar values of smoothness: 2.83 nm for AFM, and 15.5 nm for stylus instruments. The dependence on negative bias voltage fairly well agrees with each other, and the roughness of the film prepared at 3 kV shows the smallest value. The dependence is also similar to that for the S_D/S_G ratio, indicating that the surface of the film becomes smoother with increasing fraction of sp^3 bonds in the film. Self-sputtering by the impinging ions is also effective in making the smooth surface of the film.

Figure 6 shows the dynamic hardness and the refractive index of the film as a function of negative bias voltage. As expected, the hardness is very high and increases with increasing negative bias voltage to 3 kV, where the hardness shows a maximum value. The hardness of the DLC film prepared by radio-frequency plasma deposition process was 2000, that is, one-fourth of the maximum value. Thus, the high value is attributable to the fact that the film prepared by PLD contains no hydrogen. In the meantime, the dynamic hardness shows a lower value at a negative bias voltage

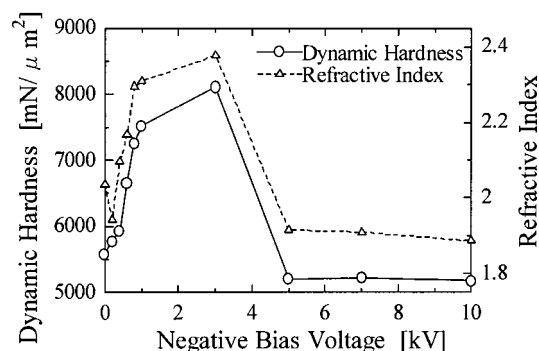FIG. 4. Ratio S_D/S_G as a function of negative bias voltage.

FIG. 6. Dynamic hardness and refractive index of the DLC film as a function of negative bias voltage.

above 5 kV. It is lower than that for the film prepared without applying negative bias voltage, being inconsistent with the dependences of the S_D/S_G ratio and the surface roughness on negative bias voltage. This fact suggests that the ion bombardment with an excessive energy induces damage such as a decrease in scale of sp^3 cluster, in addition to the decrease in the fraction of sp^3 bond. The dependence of the refractive index on negative bias voltage is similar to that of the dynamic hardness. The refractive index (2.37) at 3 kV is close to that (2.42) for the diamond, indicating that the hardest DLC film is obtained by PLD with applying negative bias voltage of 3 kV.

Thus, the ion bombardment breaks weak combinations at the surface of the film making the surface smooth. At the same time, the impact of energetic particles may locally force surface sp^2 atoms into the metastable diamond-like configuration, making the film hard with the highest refractive index. However, the ion bombardment with an excessive energy makes a structural change such as a decrease in scale of the sp^3 clusters.

IV. CONCLUSIONS

Hard diamond-like carbon films can be prepared by pulsed laser deposition from a graphite target with a synchronized application of a pulsed negative bias voltage to the substrate. The effect of self-sputtering on deposition rate at a negative bias voltage above 0.6 kV is observed. The application of bias voltage increases the fraction of sp^3 configuration in the film and makes the film surface smoother. In particular, the application of 3 kV gives the largest fraction of sp^3 bonds, and forms the hardest and smoothest film. However, excessive negative bias voltage above 5 kV drastically reduced the hardness of the film.

ACKNOWLEDGMENTS

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