

DIAMOND-LIKE CARBON THIN FILM FORMING APPARATUS AND METHOD

BACKGROUND OF THE INVENTION

This invention relates to a diamond-like carbon thin film forming apparatus and method and, more particularly, to a diamond-like carbon thin film forming apparatus and method which use a gas ion source.

A diamond-like carbon (DLC) thin film is being utilized as a hard coating film for protecting a surface of dies, tools, sliding members and recording mediums of optical-magnetic disc device or the like.

Fig. 53 is a sectional view of a DLC thin film forming apparatus utilizing a conventional microwave plasma disclosed in Japanese Patent Laid-Open No. 63-185893, for example. In the figure, 1 is a vacuum chamber for maintaining a vacuum inside thereof, 101 is a base material holder for holding a base material 3 within the vacuum chamber 1, 6 is a heater disposed on the base material holder for heating the base material 3, 103, 104 are reaction gas introducing ports for introducing reaction gases into the vacuum chamber 1, 102 is a wave guide for applying a microwave into the vacuum chamber 1 and 105 is an electromagnet for generating a magnetic field within the vacuum chamber 1.

The operation will now be described.

Within the vacuum chamber 1, the base material 3 is held by the base material holder 101. Then, the base material 3 is heated by the heater 6 to 300 - 900°C and the vacuum within the vacuum chamber 1 is maintained at 10^{-3} - 10^{-5} Torrs. Then, the reaction gases such as CH_4 and C_2H_2 are supplied into the vacuum chamber 1 through the reaction gas introducing ports 103 and 104 and a microwave plasma 600W is applied through the wave guide 102 to generate microwave plasma within the vacuum chamber 1 and a magnetic field is applied within the vacuum chamber 1 by the electromagnet 105 so that the excited carbon arrives at the base material 3, thereby forming a DLC thin film on the base material 3.

In the above-described conventional apparatus and method for forming

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diamond-like thin film using plasma C.V.D., if the temperature of the base material is made low in order to prevent thermal deformation and degrading of the base material, the film quality is degraded and the bonding strength of the film is decreased. Also, when a thin film of Si, Ti, Al or the like is to be formed as an intermediate layer between the base material and the DLC thin film for the purpose of increasing the bonding strength with respect to the base material, an additional apparatus must be used to form the films, so that the intermediate layer formed on the base material is exposed to atmosphere and the DLC thin film is formed on the exposed surface, posing the problem that the bonding strength between the intermediate layer and the DLC thin film is decreased.

Further, in the conventional apparatus, the gas is supplied to the entirety of the vacuum chamber and the micro wave is applied thereto, so that the efficiency in utilization is low.

Further, during the formation of the DLC thin film which is electrically insulating, the surface of the thin film is roughened due to electric discharging generated on the film surface due to built-up charge.

SUMMARY OF THE INVENTION

Accordingly, the present invention has been made to solve the above discussed problems of the conventional design and has as its object the provision of an apparatus and a method for forming a quality DLC thin film in which a DLC thin film which is good in bonding to a base material and high in hardness and flatness.

The apparatus for forming a DLC thin film recited in claim 1 comprises, a base material holder for holding a base material within a vacuum chamber, a base material temperature regulating device for regulating the temperature of said base material and a gas ion source disposed within said vacuum chamber to face toward said base material, said gas ion source comprises a reaction gas introducing chamber which is provided with an orifice directed toward the base material and into which gases are introduced, thermoelectron discharging means disposed within said reaction gas introducing chamber, a thermoelectron drawing electrode for drawing thermoelectrons from said thermoelectron discharging means, an accelerating electrode for accelerating ions toward the base material and bias means for applying the voltage to said base

material relative to said acceleration electrode.

The DLC thin film forming apparatus of claim 2 is the apparatus in which the bias means can provide a voltage applied to the base material relative to the accelerating electrode as a function of time.

The DLC thin film forming method of claim 3 is the method in which a DLC thin film is formed at the temperature of the base material controlled at from 100°C to 250°C after cleaning treating the surface of the base material.

The DLC thin film forming method of claim 4 is the method in which a negative voltage is applied to the base material by a bias means during the DLC thin film formation.

The DLC thin film forming method of claim 5 is the method in which an alternatively positive and negative voltage is applied to the base material by a bias means during the DLC thin film formation.

The thin film forming apparatus of claim 6 is the thin film forming apparatus for forming a diamond-like carbon thin film on a base material, which comprises: a vacuum chamber maintaining a predetermined vacuum therein and accommodating the base material, a gas ion source disposed to face toward said base material for generating dissociated carbon, carbon ions, dissociated hydrogen and hydrogen ions, said gas ion source comprises a reaction gas introducing chamber which is provided with an orifice directed toward the base material and into which gases are introduced, thermoelectron discharging means disposed within said reaction gas introducing chamber for discharging thermoelectrons, a thermoelectron drawing electrode for drawing thermoelectrons from said thermoelectron discharging means, and an accelerating electrode for accelerating said ions toward the base material, and further comprising first bias means for applying a voltage to said base material relative to said acceleration electrode as a function of time and a second bias means for applying a voltage to said thermoelectron discharging electrode relative to said acceleration electrode as a function of time.

In the thin film forming apparatus of claim 7, the voltage applied to the thermoelectron discharging means relative to the accelerating electrode by said second bias means is a positive voltage of a constant value or a value varying according to time.

In the thin film forming method of claim 8, the voltage applied to the thermoelectron discharging means relative to the accelerating electrode by said second bias means is an alternating voltage between positive and negative values.

BRIEF DESCRIPTION OF THE DRAWINGS

The present indenting will now become more readily apparent from the following detailed description of the preferred embodiments of the present invention taken in conjunction with the accompanying drawings, in which:

Fig. 1 is a sectional view of the DLC thin film forming apparatus of the first embodiment of the present invention;

Fig. 2 is a waveform diagram of the voltage applied by the bias means of the first embodiment of the present invention;

Fig. 3 is a Raman-spectrum diagram showing the temperature dependability of the thin film formation formed by the DLC thin film forming apparatus of the first embodiment of the present invention;

Fig. 4 is a sectional view of the DLC thin film forming apparatus of the first embodiment of the present invention;

Fig. 5 is a sectional view of the DLC thin film forming apparatus of the second embodiment of the present invention;

Fig. 6 is a sectional view of the DLC thin film forming apparatus of the second embodiment of the present invention;

Fig. 7 is a sectional view of the DLC thin film forming apparatus of the third embodiment of the present invention;

Fig. 8 is a sectional view of the DLC thin film forming apparatus of the third embodiment of the present invention;

Fig. 9 is a sectional view of the DLC thin film forming apparatus of the fourth embodiment of the present invention;

Fig. 10 is a sectional view of the DLC thin film forming apparatus of the fourth embodiment of the present invention;

Fig. 11 is a sectional view of the DLC thin film forming apparatus of the fifth embodiment of the present invention;

Fig. 12 is a sectional view of the DLC thin film forming apparatus of the fifth

embodiment of the present invention;

Fig. 13 is a sectional view of the DLC thin film forming apparatus of the sixth embodiment of the present invention;

Fig. 14 is a sectional view of the DLC thin film forming apparatus of the seventh embodiment of the present invention;

Fig. 15 is a waveform diagram of the voltage applied by the bias means of the eighth embodiment of the present invention;

Fig. 16 is a waveform diagram of the voltage applied by the bias means of the eighth embodiment of the present invention;

Fig. 17 is a waveform diagram of the voltage applied by the bias means of the ninth embodiment of the present invention;

Fig. 18 is a waveform diagram of the voltage applied by the bias means of the ninth embodiment of the present invention;

Fig. 19 is a waveform diagram of the voltage applied by the bias means of the tenth embodiment of the present invention;

Fig. 20 is a waveform diagram of the voltage applied by the bias means of the tenth embodiment of the present invention;

Fig. 21 is a sectional view of the DLC thin film forming apparatus of the eleventh embodiment of the present invention;

Fig. 22 is a waveform diagram of the voltage applied by the first and second bias means of the eleventh embodiment of the present invention;

Fig. 23 is a waveform diagram of the voltage applied by the first and second bias means of the eleventh embodiment of the present invention;

Fig. 24 is a waveform diagram of the voltage applied by the first and second bias means of the eleventh embodiment of the present invention;

Fig. 25 is a waveform diagram of the voltage applied by the first and second bias means of the eleventh embodiment of the present invention;

Fig. 26 is a Raman-spectrum diagram showing the Raman analysis results of the thin film;

Fig. 27 is a waveform diagram of the voltage applied by the first bias means of the twelfth embodiment of the present invention;

Fig. 28 is a waveform diagram of the voltage applied by the second bias

means of the twelfth embodiment of the present invention;

Fig. 29 is a waveform diagram of the voltage applied by the first bias means of the thirteenth embodiment of the present invention;

Fig. 30 is a waveform diagram of the voltage applied by the first bias means of the thirteenth embodiment of the present invention;

Fig. 31 is a waveform diagram of the voltage applied by the first bias means of the fourteenth embodiment of the present invention;

Fig. 32 is a waveform diagram of the voltage applied by the first bias means of the fourteenth embodiment of the present invention;

Fig. 33 is a waveform diagram of the voltage applied by the second bias means of the fourteenth embodiment of the present invention;

Fig. 34 is a waveform diagram of the voltage applied by the second bias means of the fourteenth embodiment of the present invention;

Fig. 35 is a waveform diagram of the voltage applied by the first bias means of the fifteenth embodiment of the present invention;

Fig. 36 is a waveform diagram of the voltage applied by the first bias means of the fifteenth embodiment of the present invention;

Fig. 37 is a waveform diagram of the voltage applied by the second bias means of the fifteenth embodiment of the present invention;

Fig. 38 is a waveform diagram of the voltage applied by the second bias means of the fifteenth embodiment of the present invention;

Fig. 39 is a sectional view of the DLC thin film forming apparatus of the sixteenth embodiment of the present invention;

Fig. 40 is a waveform diagram of the voltage applied by the second bias means of the seventeenth embodiment of the present invention;

Fig. 41 is a waveform diagram of the voltage applied by the first bias means of the seventeenth embodiment of the present invention;

Fig. 42 is a waveform diagram of the voltage applied by the second bias means of the eighteenth embodiment of the present invention;

Fig. 43 is a waveform diagram of the voltage applied by the second bias means of the eighteen embodiment of the present invention;

Fig. 44 is a waveform diagram of the voltage applied by the first bias means

of the eighteenth embodiment of the present invention;

Fig. 45 is a waveform diagram of the voltage applied by the second bias means of the nineteenth embodiment of the present invention;

Fig. 46 is a waveform diagram of the voltage applied by the second bias means of the nineteenth embodiment of the present invention;

Fig. 47 is a waveform diagram of the voltage applied by the first bias means of the nineteenth embodiment of the present invention;

Fig. 48 is a waveform diagram of the voltage applied by the first bias means of the nineteenth embodiment of the present invention;

Fig. 49 is a waveform diagram of the voltage applied by the second bias means of the twentieth embodiment of the present invention;

Fig. 50 is a waveform diagram of the voltage applied by the second bias means of the twentieth embodiment of the present invention;

Fig. 51 is a waveform diagram of the voltage applied by the first bias means of the twentieth embodiment of the present invention;

Fig. 52 is a wave form diagram of the voltage applied by the first bias means of the twentieth embodiment of the present indenting; and

Fig. 53 is a sectional view of a conventional DLC thin film forming apparatus.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Embodiment 1.

The first embodiment of the present invention will now be described in conjunction with the drawings. Fig. 1 is a sectional view of a diamond-like carbon (DLC) thin film forming apparatus of the first embodiment of the present invention. In the figure, 1 is a vacuum chamber maintaining a vacuum within the inside, 2 is a gas evacuating system for evacuating the vacuum chamber 1, 3 is a base material such as a super hard alloy on which surface a DLC thin film is to be formed, 4 is a base material holder for holding the base material 3 within the vacuum chamber 1 with its deposition surface (thin film forming surface) directed downward, 5 is bias means for applying a bias voltage to the base material 3 through the base material holder 4 relative to the accelerating electrode 15 which will be described later, 6 is a base material temperature

regulating mechanism disposed on the base material holder 4 for heating or cooling the base material 3 to regulate its temperature, and 7 is insulating ceramics for electrically insulating between the vacuum chamber 1 and the base material holder 4.

10 is a gas ion source disposed within the vacuum chamber 1 below and in opposition to the base material 1, 11 is a reaction gas introducing chamber into which a reaction gas is introduced, which is provided with an orifice (not shown) facing toward the base material 3 so that ions can be discharged and a large flow resistance is provided to establish a pressure difference relative to the vacuum chamber 1. 12 is thermoelectron discharging means disposed within the reaction gas introducing chamber 11 and composed of a tungsten wire for example, 13 is a thermoelectron drawing electrode disposed within the reaction chamber introducing chamber 11 and composed of parallel-arranged thin metal wires, 14 is a reaction gas introducing pipe connected to the reaction gas introducing chamber 11 for introducing the reaction gas into the inside of the chamber, 15 is an acceleration electrode disposed outside of the reaction gas introducing chamber 11 for accelerating the ions toward the base material 3, and the gas ion source 10 is composed of the reaction gas introducing chamber 11, the thermoelectron discharging means 12, the thermoelectron drawing electrode 13, the reaction gas introducing pipe 14 and the acceleration electrode 15.

Further, one end of the bias means 5, the vacuum chamber 1 and the acceleration electrode 15 are grounded.

The operation will now be described. First, the base material 3 is attached to the base material holder 4 and the vacuum chamber 1 is evacuated by the evacuation system 2 to a vacuum of about 1×10^{-6} Torr, and then the temperature of the base material 3 is regulated at about 300°C by the base material temperature regulating mechanism 6. Thereafter, in order for the cleaning treatment of the surface of the base material 3, a gas suitable for the ion cleaning such as argon gas is introduced into the reaction gas introducing chamber 11 through the reaction gas introducing pipe 14 to establish a vacuum of from 1×10^{-2} Torr to 1×10^{-1} Torr within the reaction gas introducing chamber 11.

Then, the thermoelectron discharging means 12 is operated to apply a bias voltage of about from +50 to 800 V to the thermoelectron drawing electrode 13 relative to the thermoelectron discharging means 12 by means of unillustrated electric source,

Further, in order to draw ions from the gas ion source 10, a voltage of about from +200 to 500 V is applied by means of unillustrated electric source to the thermoelectron discharging means 12 relative to the acceleration electrode 15 or to the ground potential. The electrons discharged from the thermoelectron discharging means 12 are accelerated toward the thermoelectron drawing electrode 13 to ionize the ion cleaning gas and the ions generated are radiated to the base material 3. The gas is ionized positively so that, by adjusting the bias on the base material 3 to the order of from -1 to -3 kV with respect to the ground potential by means of the bias means 5, the quantity and the energy of the ions to be radiated to the base material 3 can be controlled, whereby the cleaning treatment can be efficiently achieved.

By the treatments as above described, the impurities such as the moisture, the grease components, surface oxides and the like can be removed from the surface of the base material 3, improving the adhesive contact between the base material 3 and the DLC thin film.

Then, the supply of the ion cleaning gas to the gas ion source 10 is stopped to finish the cleaning treatment of the base material 3 surface and the temperature of the base material 3 is regulated to be from 100°C to 250°C for the reasons which will be explained later. Here, 200°C was used. Through the use of the bias measure 5, the potential of the base material 3 relative to the ground potential is given as a function $V(t)$ of time t . Fig. 2 illustrates an example of a waveform of the bias voltage supplied to the base material 3. Figs 2(a) to 2(c) show the case where the voltage applied is a negative voltage of direct current voltage, a half-wave rectified or full-wave rectified.

The voltage value is within a few kV and here it was -1kV. The frequency in (b) was of the order of from several ten Hz to several ten kHz and, here, 60Hz and 1kHz was used. By controlling the voltage value of this $V(t)$, the energy applied to the ion can be regulated. This enables the adhesive strength and the hardness of the thin film to be controlled.

Then, a gas of a hydrocarbon system containing carbon (C) is introduced through the reaction gas introducing pipe 14 into the reaction gas introducing chamber 11 to establish a vacuum of from 1×10^{-2} Torr to 1×10^{-1} Torr within the reaction gas introducing chamber 11. As for the reaction gas introduced at this time is a benzene gas for example. The thermoelectron discharging means 12 is then operated to apply

a bias voltage of the order of from +50 to 800 V to the thermoelectron drawing means 13 relative to the thermoelectron discharging means 12. A voltage of the order of from +200 to 500 V with respect to the ground potential is applied to the thermoelectron discharging means 12. The electrons discharged from the thermoelectron discharging means 12 are accelerated toward the thermoelectron drawing electrode 13 to excite, dissociate and ionize the carbohydrate gas by the discharging or the electron radiation, the dissociated carbon, carbon ions and the dissociated hydrogen and hydrogen ions are radiated toward the base material 3, thereby forming a DLC thin film on the base material 3. Since the ions are positive, they can be accelerated and drawn from the gas ion source 10 by the acceleration electrode 15 and by controlling the negative bias voltage on the base material 3, the energy provided to the ions can be adjusted.

Fig. 3 shows the results of the Raman-spectrum analysis results of a DLC thin film with the temperature of the base material used as the parameter. It is seen that while a typical DLC spectrum is obtained when the temperature of the base material 3 is 250°C, a graphite spectrum is obtained when the temperature of the base material 3 is 300°C or 400°C. Therefore, the temperature of the base material 3 should be equal to or less than 250°C, but too low temperature is not preferable for another reason. That is, the adhesive strength of the DLC thin film to the base material 3 becomes low if the temperature is less than 100°C. Therefore, the temperature of the base material 3 being formed is controlled at from 100°C to 250°C by means of the base material temperature regulating mechanism 6. By this, transforming of the DLC thin film into graphite can be controlled, allowing the formation of a hard, quality DLC thin film.

The reason that the above temperature range is different from that of the conventional apparatus shown in Fig. 53 is that the apparatus type is different.

Further, as shown in Fig. 4, a rotary mechanism 100 may be provided in the base material holder 4 to allow the base material 3 to rotate during the film formation, enabling the film thickness profile to be more uniform and the deposition unevenness at the corner portions and the like, i.e., uneven film thickness due to the direction or position of the surface can be decreased.

Embodiment 2.

Fig. 5 is a sectional view of the DLC thin film forming apparatus of the second

embodiment of the present invention. In the figure, 10a is a first gas ion source, 10b is a second gas ion source, both having a similar structure as that of the gas ion source 10 described in conjunction with Fig. 1. Other portions are similar to those shown in Fig. 1 so that their description is omitted.

The operation will now be described. Similarly to the case shown in Fig. 1, the vacuum chamber 1 is evacuated by the evacuation system 2 to a vacuum of about 1×10^{-6} Torr, and then the temperature of the base material 3 is regulated at about 300°C by the base material temperature regulating mechanism 6. Thereafter, a first gas ion source 10a is operated to achieve the cleaning treatment of the surface of the base material 3. Then, by the electric discharge or the electron radiation by the first gas ion source 10a, the hydrocarbon system gas is caused to excite, dissociate and ionize, the dissociated carbon, carbon ions and the dissociated hydrogen and hydrogen ions are radiated toward the base material 3, thereby forming a DLC thin film.

During the formation of the DLC thin film, the second gas ion source 10b is operated to cause a gas containing hydrogen element, such as methane gas to excite, dissociate and ionize by the discharge or electron radiation to radiate the dissociated hydrogen and hydrogen ions, thereby to suppress the transformation of the DLC thin film into graphite to obtain a hard, quality DLC thin film.

The reasons that this radiation is effective in suppressing the graphite transformation is that the dissociated hydrogen and the hydrogen ions selectively etch the graphite on the base material 3 and remove it.

Further, as shown in Fig. 6, is a sectional view of the DLC thin film forming apparatus of the second embodiment of the present invention;

Further, as shown in Fig. 6, a rotary mechanism 100 may be provided in the base material holder 4 to allow the base material 3 to rotate during the film formation, enabling the film thickness profile to be more uniform and the deposition unevenness at the corner portions and the like can be decreased.

Embodiment 3.

Fig. 7 is a sectional view of the DLC thin film forming apparatus of the third embodiment of the present invention. In the figure, 30 is a metallic vapor generating source, such as an electron beam evaporation source, an ion plating apparatus and a

metallic ion source, disposed in opposition to the base material 3 within the vacuum chamber 1 for forming a metal thin film or ceramics thin film, the metallic vapor generating source being a metallic ion source in this embodiment. 31 is a melting pot for placing a metallic source material, 32 is a heater for heating the melting pot 31, 33 is thermoelectron discharging means for discharging thermoelectrons, 34 is a thermoelectron drawing means for drawing the thermoelectrons from the thermoelectron discharging means 33, 35 is a thermal shield for thermally isolating these components, 36 is an accelerating electrode for drawing ions from the metallic vapor generating source 30. The metallic vapor generating source 30 is composed of the melting pot 31, the heater 32, the thermoelectron discharging means 33, the thermoelectron drawing means 34, the thermal shield 35 and the accelerating electrode 36.

Other portions are similar to those shown in Fig. 1 so that their description is omitted.

The operation will now be described. In a manner similar to that of Fig. 1, after the vacuum chamber 1 is evacuated to a vacuum of the order of 1×10^{-6} Torr by the evacuation system 2, the temperature of the base material 3 is regulated to be about 300°C by the base material temperature regulating mechanism 6. Then, similarly to the case shown in Fig. 1, the surface of the base material 3 is cleaning treated to remove the moisture, the grease, the surface oxides and the like.

Then, the supply of the ion cleaning gas to the gas ion source 10 is stopped to finish the cleaning treatment of the surface of the base material 3, and a voltage of from about -0.5 to about -3 kV is applied to the base material 3 relative to the ground potential, and the metal such as Si, Al, Ti, W or the like in the melting pot 31 is heated by the heater 32 to generate the metal vapor, and the thermoelectrons discharged from the thermoelectron discharging means 33 are drawn and accelerated by the thermoelectron drawing means 34 to generate the metallic ions which are radiated to the surface of the base material 3 to form thereon the metallic thin film of Si, Al, Ti, W or the like as an intermediate layer.

It is to be noted that the hydrocarbon system gas may be excited, dissociated or ionized by the gas ion source 10 so that the dissociated carbon and the carbon ions are radiated to the base material 3 or the vacuum chamber 1 may be filled with a hydrocarbon system gas atmosphere while the metallic vapor generating source 30 is

being operated as discussed above, whereby the thin film of ceramics such as SiC, Al_4C_3 , TiC, WC may be formed on the surface of the base material 3 as the intermediate layer.

Then, in a manner similar to that of Fig. 1, the gas ion source 10 is operated and the DLC thin film is formed on the intermediate layer on the surface of the base material 3.

As has been described, the metallic vapor generating source 30 and the gas ion source 10 are disposed in the same vacuum chamber 1, so that there is no need to expose the intermediate layer on the surface of the base material 3 to the atmosphere and the DLC thin film can be formed directly on the intermediate layer in a consecutive step, and the intermediate layer is formed on the surface of the base material 3 the adhesive bonding between the base material 3 and the DLC thin film can be established.

Also, as shown in Fig. 8, a rotary mechanism 100 may be provided in the base material holder 4 to allow the base material 3 to rotate during the film formation, enabling the film thickness profile to be more uniform and the deposition unevenness at the corner portions and the like can be decreased.

Embodiment 4.

Fig. 9 is a sectional view of the DLC thin film forming apparatus of the fourth embodiment of the present invention. The base material holder 4 is disposed within the vacuum chamber 1 at its lower portion and the base material 3 is held on the base material holder 4 with the depositing surface thereof directed downward. The gas ion source 10 is disposed in the upper portion of the vacuum chamber 1 so that the ions can be radiated downwardly toward the base material 3. In other respects, the structure is the same as that of Fig. 1 or Fig. 4 so that their description is omitted.

The operation is also similar to that of Fig. 1 or Fig. 4, and in this embodiment the base material holder 4 is disposed at the lower portion of the vacuum chamber 1 and the base material 3 is held on it, so that the base material 3 can be easily attached even when the base material 3 is large or heavy, improving the operability.

Fig. 10 illustrates an example in which a first and a second gas ion source

10a and 10b are provided and operated in the similar manner as in Figs. 5 or 6, wherein the base material 3 is mounted upwardly on the base material holder 4 at the lower portion of the vacuum chamber 1 and the first and the second gas ion sources 10a and 10b are disposed at the upper portion of the vacuum chamber 1 so as to emit the ions downwardly or diagonally downwardly toward the base material 3, so that the base material 3 can be easily attached even when the base material 3 is large or heavy, improving the operability.

Further, the first and the second gas ion sources 10a and 10b both may be arranged to operate in the similar manner as that of the gas ion source 10 shown in Fig. 1 or 4.

Embodiment 5.

Fig. 11 is a sectional view of the DLC thin film forming apparatus of the fifth embodiment of the present invention. The base material holder 4 is disposed at one of the side portions within the vacuum chamber 1 and the base material 3 is attached to the base material holder 4 with its deposition surface laterally oriented. The gas ion source 10 is disposed on the other side portions within the vacuum chamber 1 in opposition to the base material 3. In other respects, the structure is the same as that shown in Fig. 1 or 4 so that its description is omitted.

The operation is also similar to that of Fig. 1 or Fig. 4, and in this embodiment the base material 3 is laterally held by the base material holder 4, so that the base material 3 can be easily attached even when the base material 3 is large or heavy, improving the operability.

Fig. 12 illustrates an example in which the first and the second gas ion sources 10a and 10b are provided so as to operate in the manner similar to the case shown in Fig. 5 or 6, and in this case also since the base material 3 is laterally attached to the base material holder 4 and the first and the second gas ion sources 10a and 10b are arranged to emit ions laterally or diagonally laterally to the base material 3, so that the base material 3 can be easily attached even when the base material 3 is large or heavy, improving the operability.

Further, the first and the second gas ion sources 10a and 10b both may be arranged to operate in the similar manner as that of the gas ion source 10 shown in Fig.

1 or 4.

Embodiment 6.

Fig. 13 is a sectional view of the DLC thin film forming apparatus of the sixth embodiment of the present invention. The base material holder 4 is disposed at the lower portion within the vacuum chamber 1 and the base material 3 is attached to the base material holder 4. In this embodiment, the DLC thin film is to be formed on the top and side surfaces of the base material 3. Disposed within the vacuum chamber 1 are a first gas ion source 10a, a second gas ion source 10b, a third gas ion source 10c and a fourth gas ion source 10d. Out of them, the first and the second gas ion sources 10a and 10b are disposed in the upper portion within the vacuum chamber 1 so as to emit the ions downwardly or diagonal downwardly to the top surface of the base material 3 and the third and the fourth gas ion sources 10c and 10d are disposed in the side portion within the vacuum chamber 1 so as to emit the ions laterally or diagonal laterally to the side surface of the base material 3. In other respects the structure is the same as that shown in Fig. 1 or 4 so that their description is omitted.

The operation is also similar to that of Fig. 1 or Fig. 4, and in this embodiment the ions are emitted from various directions to the base material 3, so that the DLC thin film can be formed evenly even when the base material 3 is of complex shape.

Also, by rotating the base material 3 by the rotary mechanism 100, the film thickness and the like on the side surface and the like of the base material 3 may be made uniform.

When the base material 3 is small or light weight, the base material holder 4 may be disposed at the upper portion of the vacuum chamber 1 and the base material 3 is held downwardly oriented, and the first and the second gas ion sources 10a and 10b may be disposed at the lower portion of the vacuum chamber 1 so as to emit the ions upwardly or diagonal upwardly toward the base material 3 and the third and the fourth gas ion sources 10c and 10d may be arranged to emit the ions laterally or diagonal laterally toward the base material 3.

Further, the first and the third gas ion sources 10a and 10c may be arranged to operate in the similar manner as that of the first gas ion source 10a shown in Fig. 10

and the second and the fourth gas ion sources 10b and 10d may be arranged to operate in the similar manner as that of the second gas ion source 10b shown in Fig. 10.

Embodiment 7.

Fig. 14 is a sectional view of the DLC thin film forming apparatus of the seventh embodiment of the present invention. The apparatus is provided with a fifth gas ion source 10e in place of the second gas ion source 10b shown in Fig. 10. The fifth gas ion source 10e is a gas ion source that can form a metallic thin film of Si, Ti, W, Al, B or the like or a ceramic thin film of SiC, Al_4C_3 , TiC, WC or the like as an intermediate layer on the surface of the base material 3. In other respects, the structure is the same as that shown in Fig. 10 so that their description is omitted.

The operation will now be described. Firstly, the first gas ion source 10a is operated to achieve the cleaning treatment of the surface of the base material 3 in a manner similar to the case of Fig. 10.

Then, the bias means 5 establishes on the base material 3 an electric potential of about from -0.5 to -3 kV relative to the ground potential. Then, the fifth gas ion source 10e is operated to dissociate or ionize, by the electric discharging or the electron radiation, a gas containing metal element such as Si, Ti, W, Al, B or the like, such as SiH_4 , $TiCl_4$, WF_6 , $AlCl_3$ or the like, thereby to radiate the dissociated metal and the metal ions to the base material 3 to form on its surface a thin film of Si, Al, Ti, W or the like as the intermediate layer.

It is to be noted that the hydrocarbon system gas may be excited, dissociated or ionized by the gas ion source 10 so that the dissociated carbon and the carbon ions are radiated to the base material 3 or the vacuum chamber 1 may be filled with a hydrocarbon system gas atmosphere while the fifth gas ion source 10e is being operated as discussed above, whereby the thin film of ceramics such as SiC, Al_4C_3 , TiC, WC may be formed on the surface of the base material 3 as the intermediate layer.

Then, the first gas ion source 10a emits the dissociated carbon and the carbon ions and the dissociated hydrogen and the hydrogen ions toward the base material 3 to form a DLC thin film.

As has been described, the intermediate layer for improving the bonding of

the DLC thin film can be formed consecutively after the formation of the DLC thin film and the element for the intermediate layer is supplied in a gas state during the intermediate layer formation, so that the limitation on the disposition of the fifth gas ion source 10e is small and the degree of freedom is high.

Also, in the first to the seventh embodiments, graphite may be used as the material for the acceleration electrode 15 and the reaction gas introducing chamber 11 of the gas ion source, whereby the generation of the dust can be suppressed even when carbon which is a reaction product is deposited on the inner wall of the reaction gas introducing chamber 11 and the acceleration electrode 15.

Embodiment 8.

While an example of $V(t)$ of the voltage to be applied to the base material 3 is shown in Fig. 2, the voltage may have other waveforms such as shown below in stead of that shown in Fig. 2. The voltage value and frequency should be similar to that shown in Fig. 2 and the voltage is within the range of a few kV both in positive and negative directions. The waveform shown in Figs. 15 to 20 can be applied to all of the apparatus described in connection with the first to the seventh embodiment.

Fig. 15 shows an example of a waveform of $V(t)$ of this embodiment. (a) shows a sin wave and (b) - (d) show waveforms biased in the negative direction. In (a) and (b), the voltage varies between a negative and a positive value, but (c) and (d) are negative values that vary according to the time.

During the period of time in which $V(t)$ is negative energy is given to the ions and during the period of time in which $V(t)$ is positive electrons are drawn, whereby the electric charge built-up on the thin film on the base material 3 is alleviated by moderating the charges on the electrically insulating DLC thin film by supplying the electrons to the base material 3. If the electric charge is built up on the thin film, the discharge is generated and the film surface is roughened to decrease the surface flatness.

Although there is no period in which the voltage is positive in (c) and (d), the electrons have a certain energy within the gas ion source 10, so that the electrons can be supplied to the base material 3 during the period of time in which the negative voltage becomes small in (e) and (d) according to the balance between the voltage

value and the energy.

Fig. 16 shows the case in which a rectangular waveform is used instead of the sine wave of Fig. 15. Figs. 16(a) - (d) correspond to Figs. 15 (a) - (d), respectively, and exhibit similar advantageous results. The waveform may be triangular or the like.

Embodiment 9.

Fig. 17 shows an example of a waveform of $V(t)$ of this embodiment of the present invention. Both of the positive and negative half-waves are sinusoidal half-waves, but the negative period is longer than the positive period. Therefore, energy can be given to the ions and the electrons can be supplied to the base material 3 within a short positive period, so that the charge built-up can be effectively prevented.

Fig. 18 shows the case where a rectangular waveform is used instead of the sinusoidal wave of Fig. 17. Figs. 18(a) - (d) correspond to Figs. 17(a) - (d), respectively, and exhibit similar advantageous effect. The waveform may be triangular or the like.

Embodiment 10.

Fig. 19 shows an example of a waveform of $V(t)$ of this embodiment. Both of the positive and negative half-waves are sinusoidal half-waves, but the positive period is longer than the negative period just opposite to the case of Fig. 17. Therefore, mainly, the electrons can be supplied to the base material 3 and the energy can be given to the ions, so that the charge built-up can be effectively prevented.

Fig. 20 shows the case where a rectangular waveform is used instead of the sinusoidal wave of Fig. 19. Figs. 20(a) - (d) correspond to Figs. 19(a) - (d), respectively, and exhibit similar advantageous effect. The waveform may be triangular or the like.

While the waveform of the voltage to be applied to the base material 3 during the DLC thin film forming has been described, when the base material 3 is an insulating material, charge built-up takes place even during the cleaning treatment, so that the base material holder 4 may be supplied with a voltage of a waveform of Fig. 18(d) for example, whereby the electrons can be supplied to the surface of the base material 3

to provide an advantageous result in preventing the charge built-up.

Embodiment 11.

Fig. 21 is a sectional view of the diamond-like carbon (DLC) thin film forming apparatus of the eleventh embodiment of the present invention. In the figure, 1 is a vacuum chamber maintaining a vacuum within the inside, 2 is a gas evacuating system for evacuating the vacuum chamber 1, 3 is a base material such as a super hard alloy on which surface a DLC thin film is to be formed and is held on an unillustrated base material holder within the vacuum chamber 1. 10 is a gas ion source disposed in opposition to the base material 3 for generating dissociated carbon and carbon ions as well as dissociated hydrogen and hydrogen ions, 11 is a reaction gas introducing chamber into which a hydrocarbon system reaction gas containing carbon (C) which is a material for the DLC thin film is introduced and, the reaction gas introducing chamber 11 being provided at an opposing portion 16 facing the base material 3 with an orifice (not shown) for discharging ions and providing a large flow resistance for establishing a pressure difference relative to the vacuum chamber 1.

12 is thermoelectron discharging means disposed within the reaction gas introducing chamber 11 and composed of a tungsten wire or a tantalum wire, 13 is a thermoelectron drawing electrode disposed within the reaction chamber introducing chamber 11 and composed of parallel-arranged thin metal wires, 14 is a reaction gas introducing pipe connected to the reaction gas introducing chamber 11 for introducing the reaction gas into the inside of the chamber, 15 is an acceleration electrode disposed outside of the reaction gas introducing chamber 11 for accelerating the ions toward the base material 3, and the gas ion source 10 is composed of the reaction gas introducing chamber 11, the thermoelectron discharging means 12, the thermoelectron drawing electrode 13, the reaction gas introducing pipe 14 and the acceleration electrode 15.

20 is a first bias means for applying a voltage as a function of time to the base material 3 relative to the acceleration electrode 15, 21 is a second bias means for applying a voltage as a function of time to the thermoelectron discharging means 12 relative to the acceleration electrode 15, 22 is a d.c. source for positively biasing the potential of the thermoelectron drawing electrode 13 relative to the thermoelectron

discharging means 12, and 23 is an alternating source for operating the thermoelectron discharging means 12.

One end of each of the acceleration electrode 15, the first and the second bias means 20 and 21 are grounded.

The operation will now be described. First, the vacuum chamber 1 is evacuated by the evacuation system 2 to a vacuum of about 1×10^{-8} Torr, and then the temperature of the base material 3 is regulated from 100°C to 250°C by the unillustrated base material temperature regulating mechanism, and a gas of hydrocarbon system which is a reaction gas is introduced into the reaction gas introducing chamber 11 through the reaction gas introducing pipe 14 and injecting the gas toward the thermoelectron drawing electrode 13 and the thermoelectron discharging means 12 to establish a vacuum of from 1×10^{-2} Torr to 1×10^{-1} Torr within the reaction gas introducing chamber 11.

Then, the A.C. source 23 supplies an electric power to the thermoelectron discharging means 12 to heat it to the temperature of about 2000°C at which the supply of thermoelectrons is ready. Then, the D.C. source 22 applies a voltage of from about 50V to 800V relative to the thermoelectron discharging means 12 to apply a positive bias to the thermoelectron drawing electrode 13, causing the thermoelectron discharging means 12 to emit electrons of about 1 to 3A toward the thermoelectron drawing electrode 13 as shown by the arrows in the figure. The gas of the hydrocarbon system in the reaction gas introducing chamber 11 is excited, dissociated and ionized due to the contact or the like to the radiated electron and heated thermoelectron discharging means 12.

At this time, a bias voltage is applied to the base material 3 and the thermoelectron discharging means 12. Some examples of the voltage $V_1(t)$ applied to the base material 3 by the first bias means 20 and the voltage $V_2(t)$ applied to the thermoelectron discharging means 12 by the second bias means with reference to the potential of the acceleration electrode 15 are shown in Figs. 22 - 25. For either of $V_1(t)$ and $V_2(t)$, the voltage is within $\pm$ several kV and the frequency is several 10 Hz to several ten kHz.

When $V_2(t)$ is positive, ions (positive charges) can be taken from the reaction gas introducing chamber 11 and, on the other hand, when it is negative, electrons (negative charges) can be taken from the reaction gas introducing chamber 11. Therefore, by

controlling the intensity and the time ratio of the positive and negative bias voltages, the kinetic energy and ion amount of the carbon ions and the hydrogen ions affecting the film formation as well as the kinetic energy and the electron amount of the electrons for neutralizing the charge built-up on the base material 3 can be efficiently controlled.

Now, the charge built-up will be described. Since the DLC is electrically insulating, the charge built-up phenomenon occurs in which the film is positively charged by the ions during the film formation. The built up charge eventually discharges and the film surface is roughened. In order to suppress this phenomenon, the electrons are supplied to neutralize the charge and to improve the flatness of the film.

Further, the kinetic energy and quantity of ions and electrons drawn from the gas ion source 10 and injected into the base material 3 can be efficiently controlled by $V1(t)$. That is, the ions to which energy is added can be injected into the base material 3 when $V1(t)$ is negative and the electrons can be supplied when the $V1(t)$ is positive, so that the kinetic energy and the quantity of the carbon ions, the hydrogen ions and electrons can be controlled by controlling the intensity of the positive and negative bias voltages and the ratio of time during which the positive or negative voltage.

Also, the kinetic energy and the quantity of carbon ions, hydrogen ions and electrons can be controlled by making $V1(t)$ and $V2(t)$ in synchronization with each other to control $(V1(t) - V2(t))$ as a whole.

Fig. 22 shows the case where $V1(t)$ and $V2(t)$ are in synchronization with each other and a large amount of ions are drawn from the gas ion source 10 and the energy level is controlled to suite to the thin film formation.

Firstly, in order to take out a large amount of ions from the reaction gas introducing chamber 11 in the excited and ionized state, $V2(t)$ is made to be a large positive bias voltage as shown in Fig. 22(b), whereby a large amount of ions can be drawn in proportion to the bias voltage. At the same time, by positively biasing $V1(t)$ as shown in Fig. 22(a), the ions are decelerated so that $(V1(t) - V2(t))$ becomes as shown in Fig. 22(c) as a whole, whereby the kinetic energy of the ions drawn from the gas ion source 10 is controlled to an appropriate level and injected into the base material 3. Further, electrons are drawn from the gas ion source 10 when $V2(t)$ is negative and injected into the base material 3 according to $(V1(t) - V2(t))$.

Fig. 23 shows the case where, in order to increase the adhesive strength between the base material 3 and the thin film, a mixing layer is formed by the injection or the like into the base material 3 by the ion spattering for example and the kinetic energy of the ions is made at a higher energy level. In order to draw a large amount of ions from the reaction gas introducing chamber 11, $V_2(t)$ is made as a high positive bias voltage as shown in Fig. 23(b). At the same time, by making $V_1(t)$ a negative bias voltage as shown in Fig. 23(a), energy is further supplied to the ions so that a large kinetic energy as a whole as expressed by $(V_1(t) - V_2(t))$ shown in Fig. 23(c) is given to the ions to control the energy level to the level at which the ion spattering is possible and then the ions are injected into the base material 3.

Fig. 24 shows the case where $V_1(t)$ and $V_2(t)$ are alternating voltages, which are synchronized and equal intensity so that their total is zero. In this case, $V_2(t)$ is alternating between positive and negative and the ions and the electrons are taken from the gas ion source 10 but decelerated by $V_1(t)$ and is injected into the base material 3 at the kinetic energy the ions and the electrons had within the reaction gas introducing chamber 11.

Fig. 25 shows the case similar to that of Fig. 24 but where $(V_1(t) - V_2(t))$ is made a constant negative voltage, supplying energy to the ions.

In Figs. 22 to 25, the rectangular wave and the sinusoidal wave are shown, other waveform such as triangular wave may also be used.

Fig. 26 shows the Raman analysis result of the DLC thin film formed as described above. From the figure, a asymmetric Raman band having a main peak at around 1550cm^{-1} and having a shoulder band at around 1400cm^{-1} , which is a typical spectrum of a DLC, which shows that a quality DLC thin film was formed. For the reference purpose, spectrum of a graphite thin film is also shown.

Also, as a pre-treatment of the formation of the DLC thin film, a cleaning treatment of the surface of the base material 3 may be achieved. In that case, a gas such as argon gas suitable for the ion cleaning is introduced into the reaction gas introducing chamber 11 through the reaction gas pipe 14 to establish a vacuum of from 1×10^{-2} to 1×10^{-1} Torr within the reaction gas introducing chamber 11. The thermoelectron discharging means 12 is then operated to emit electrons toward the thermoelectron drawing electrode 13 to ionize the gas, the ions then are efficiently

taken from the excited and ionized reaction gas introducing chamber 11 and the kinetic energy and the amount of the ions injected into the base material 3 is controlled by the first bias means 20. At this time, an efficient cleaning treatment can be achieved when the total voltage ($V1(t) - V2(t)$) of the first and second bias means 20 and 21 is of the order of from -0.5 to -3 kV.

Through the above cleaning treatment, the moisture, grease components, surface oxides and the like can be removed from the surface of the base material 3, improving the bonding between the base material 3 and the DLC thin film.

Embodiment 12.

Fig. 27 shows a voltage waveform of voltage $V1(t)$ applied by the first bias means 20 to the base material 3 during the thin film formation in the twelfth embodiment. The description of the structure of the apparatus or the like similar to those of Fig. 21 will be omitted. $V1(t)$ is a D.C. or half-wave or full-wave rectified negative voltage, which supplies energy to the ions to obtain a hard, good-bonding DLC thin film. At this time, $V2(t)$, which is a voltage for taking out the ions or the electrons from the gas ion source 10, may be either one of Figs. 28(a) to 28(c).

Also, when both of $V1(t)$ and $V2(t)$ are voltages that vary according to time and not direct current, they should preferably be synchronized with each other.

Embodiment 13.

Fig. 29 shows a voltage waveform of the voltage $V1(t)$ applied by the first bias means 20 to the base material 3 during the DLC thin film formation. The description of the portions similar to those of the apparatus shown in Fig. 21 will be omitted. Fig. 29(a) shows a sinusoidal wave and (b) to (d) show waveforms in which the sinusoidal waveform is biased in the negative direction. In (a) and (b), the voltages are alternating between positive and negative and, in (c) and (d), they are negative voltages varying in accordance with time. The ions taken out from the gas ion source 10 are supplied with energy in the period where the voltage is negative and the electrons are supplied with energy in the period where the voltage is positive.

Fig. 30 shows the case where a rectangular waveform is used instead of the sinusoidal wave of Fig. 29, providing similar advantageous results.

In these cases, the voltage $V_2(t)$ for taking out the ions or electrons may be those of Fig. 28(b) or (c) for example.

Embodiment 14.

Fig. 31 shows a voltage waveform of $V_1(t)$ during the DLC thin film formation. The description of the portions similar to those of the apparatus shown in Fig. 21 will be omitted. The positive half-wave and the negative half-wave are both sinusoidal half-wave, but the negative period is longer than the positive period. Therefore, the energy can be supplied to the ions, which also provides a counter measure against the charge built-up.

Fig. 32 shows a case where a rectangular waveform is used instead of the sinusoidal wave of Fig. 31, providing similar advantageous results as in the case of Fig. 31.

It is to be noted that, in the case of Figs. 31(a), 31(b), 32(a) and 32(b), the voltage for taking out the ions or the electrons from the gas ion source 10 may be the voltage shown in either of Fig. 28(b), 28(c), 33(a) or 33(b), and in the case of Figs. 31(c), 31(d), 32(c) and 32(d), $V_2(t)$ may be the voltage shown in Fig. 34(a) or 34(b).

Embodiment 15.

Fig. 35 shows a voltage waveform of $V_1(t)$ during the DLC thin film formation. The description of the portions similar to those of the apparatus shown in Fig. 21 will be omitted. The positive half-wave and the negative half-wave are both sinusoidal half-wave, but the positive period is longer than the negative period contrary to Fig. 31. Therefore, this advantageously provides a counter measure against the charge built-up because the electrons can be supplied to the base material 3 as well as allows the energy to be supplied to the ions.

Fig. 36 shows a case where a rectangular waveform is used instead of the sinusoidal wave of Fig. 35, providing similar advantageous results as in the case of Fig. 35.

It is to be noted that, in the case of Figs. 35(a), 35(b), 36(a) and 36(b), the voltage for taking out the ions or the electrons from the gas ion source 10 may be the voltage shown in either of Fig. 37(b) to 37(d), and in the case of Figs. 35(c), 35(d), 36(c)

and 36(d), $V_2(t)$ may be the voltage shown in Fig. 38(a) or 38(b).

Also, while sinusoidal waves or rectangular waves are shown in Figs. 27 to 38, other waveforms such as a triangular wave may also be used.

Embodiment 16.

Fig. 39 is a sectional view of the DLC thin film forming apparatus of the sixteenth embodiment of the present invention. Comparing to Fig. 21, the first bias means 20 is not provided and the electric potential of the base material 3 is equal to the potential of the acceleration electrode 15. In other respects, the structure is similar to that of Fig. 21, so that their description will be omitted.

In this embodiment, the energy of the ions and the electrons radiated to the base material 3 is controlled only by the second bias means 21, operation is simpler and the apparatus can be made simple.

Embodiment 17.

Fig. 40 shows a voltage waveform of $V_2(t)$ applied to the thermoelectron discharging means 12 by the second bias means 21 during the DLC thin film formation. The description of the portion similar to that of Fig. 21 will be omitted. $V_2(t)$ is a D.C. or half-wave rectified or full-wave rectified positive voltage, which efficiently draw ions from the gas ion source and which provides energy to the ions.

In these cases, $V_1(t)$ which is a voltage for supplying energy to ions may be either of the waveforms of Figs. 41(a) to 41(c).

Embodiment 18.

Fig. 42 shows a voltage waveform of the voltage $V_2(t)$ applied during the DLC thin film formation. The description of the portions similar to those of the apparatus shown in Fig. 21 will be omitted. Fig. 42(a) shows a sinusoidal wave and (b) to (d) show waveforms in which the sinusoidal waveform is biased in the positive direction. In (a) and (b), the voltages are alternating between positive and negative and, in (c) and (d), they are positive voltages varying in accordance with time t . The ions are taken out from the gas ion source 10 in the period where the voltage is positive and the electrons are taken out in the period where the voltage is negative.

Fig. 43 shows the case where a rectangular waveform is used instead of the sinusoidal wave of Fig. 42, providing advantageous results similar to Fig. 42.

In these cases, the voltage $V1(t)$ for supplying energy to the ions or electrons may be those of Fig. 44(a) or (b) for example.

Embodiment 19.

Fig. 45 shows a voltage waveform of the voltage $V2(t)$ applied during the DLC thin film formation. The description of the portions similar to those of the apparatus shown in Fig. 21 will be omitted. The positive half-wave and the negative half-wave of $V2(t)$ are both sinusoidal half-wave waveform, but the positive period is longer than the negative period. Therefore, mainly the ions are supplied with energy and taken out from the gas ion source 10 and at the same time electrons can also be supplied.

Fig. 46 shows the case where a rectangular waveform is used instead of the sinusoidal wave of Fig. 45, providing advantageous results similar to Fig. 45.

It is to be noted that, in the case of Figs. 45(a), 45(b), 46(a) and 46(b), the voltage for supplying energy to the ions or the electrons may be the voltage shown in either of Fig. 41(b), 41(c), 47(a) or 47(b), and in the case of Figs. 45(c), 45(d), 46(c) and 46(d), $V1(t)$ may be the voltage shown in Fig. 48(a) or 48(b).

Embodiment 20

Fig. 49 shows a voltage waveform of the voltage $V2(t)$ applied during the DLC thin film formation. The description of the portions similar to those of the apparatus shown in Fig. 21 will be omitted. The positive half-wave and the negative half-wave of $V2(t)$ are both sinusoidal half-wave waveform, but the negative period is longer than the positive period contrary to Fig. 45. Therefore, mainly the electrons are supplied from the gas ion source 10, enabling sufficient charge built-up counter measure to be provided and the ions, of course, can be supplied.

Fig. 50 shows the case where a rectangular waveform is used instead of the sinusoidal wave of Fig. 49, providing advantageous results similar to Fig. 49.

It is to be noted that, in the case of Figs. 49(a), 49(b), 50(a) and 50(b), the voltage for supplying energy to the ions or the electrons may be the voltage shown in

either of Fig. 44(a), 44(b), 51(a) or 51(b), and in the case of Figs. 49(c), 49(d), 50(c) and 50(d), $V_1(t)$ may be the voltage shown in Fig. 52(a) or 52(b).

While Figs. 49 to 51 show waveforms of sinusoidal wave or rectangular wave, a triangular waveform may also be used.

As has been described, according to the apparatus for forming a DLC thin film, an orifice directed toward the base material is provided and a gas ion source having a reaction gas introducing chamber into which a gas is introduced is disposed within a vacuum chamber, so that the efficiency in terms of the gas consumption increases.

Also, a bias means applies a voltage to the base material as a function of time, so that the amount of the energy supplied to the ions and the electrons for suppressing the charge built-up can be regulated, allowing a quality DLC thin film to be obtained.

According to the method for forming a DLC thin film, through the use of the above DLC thin film forming apparatus, a DLC thin film is formed while the base material temperature is being kept from 100°C to 250°C after cleaning the base material, the cleaning treatment and the film formation can be achieved in the same vacuum chamber, allowing a hard DLC thin film of a high adhesive strength to be efficiently formed.

Further, by applying a negative voltage to the base material during the DLC thin film formation, energy can be given to the ions, allowing a hard DLC thin film of a high adhesive strength to be formed.

Also, by applying a voltage alternating between positive and negative, the ions are supplied with energy and the base material is supplied with electrons, allowing a DLC thin film of an improved flatness to be formed.

Also according to the apparatus for forming a DLC thin film, a first bias means for applying a voltage to a base material relative to an acceleration electrode and a second bias means for applying a voltage to a thermoelectron discharging means are provided and they are arranged to be applied with a voltage as a function of time, so that, by controlling the voltage of the first and the second bias means, energy can be supplied to the ions, electrons can be supplied to the base material as a counter measure for the charge built-up or their degree can be controlled, allowing a hard,

quality and flat DLC thin film of a high adhesive strength to be formed.

Further, by applying positive charge to the thermoelectron discharging means by the second bias means, energy can be given to the ions and the ions can be efficiently drawn from the gas ion source.

Further, by using a voltage alternating between positive and negative as the voltage of the second bias means, energy can be given to the ions and the electrons can be supplied from the gas ion source.

What is claimed is:

1. An apparatus for forming a diamond-like carbon thin film comprising:
 - a vacuum chamber for maintaining a predetermined vacuum inside thereof;
 - a base material holder for holding a base material within said vacuum chamber,
 - a base material temperature regulating device for regulating the temperature of said base material and
 - a gas ion source disposed within said vacuum chamber to face toward said base material for generating dissociated carbon, carbon ions, dissociated hydrogen and hydrogen ions,
 - said gas ion source comprises
 - a reaction gas introducing chamber which is provided with an orifice directed toward the base material and into which gases are introduced;
 - thermoelectron discharging means disposed within said reaction gas introducing chamber for discharging thermoelectrons;
 - a thermoelectron drawing electrode for drawing thermoelectrons from said thermoelectron discharging means;
 - an accelerating electrode disposed outside of said reaction gas introducing chamber for accelerating said ions toward the base material; and
 - bias means for applying the voltage to said base material relative to said acceleration electrode.
2. A diamond-like carbon thin film forming apparatus as claimed in claim 1, wherein said bias means can provide a voltage applied to the base material relative to the accelerating electrode as a function of time.
3. A method for forming a diamond-like carbon thin film through the use of a diamond-like carbon thin film forming apparatus which comprises a vacuum chamber for maintaining a predetermined vacuum inside thereof, a base material holder for holding a base material within said vacuum chamber, a base material temperature



regulating device for regulating the temperature of said base material and a gas ion source disposed within said vacuum chamber to face toward said base material for generating dissociated carbon, carbon ions, dissociated hydrogen and hydrogen ions, said gas ion source comprising a reaction gas introducing chamber which is provided with an orifice directed toward the base material and into which gases are introduced, thermoelectron discharging means disposed within said reaction gas introducing chamber for discharging thermoelectrons, a thermoelectron drawing electrode for drawing thermoelectrons from said thermoelectron discharging means, an accelerating electrode disposed outside of said reaction gas introducing chamber for accelerating said ions toward the base material, and bias means for applying the voltage to said base material relative to said acceleration electrode;

said method comprising the steps of:

cleaning treating the surface of the base material by the ions generated by said gas ion source; and then

introducing the gas of a hydrocarbon gas into said gas ion source while maintaining the temperature of said base material at from 100°C to 250°C to form a diamond-like carbon thin film on the base material.

4. A thin film forming method of claim 3 wherein a negative voltage which is constant or a function of time relative to the acceleration electrode is applied to the base material by a bias means during the DLC thin film formation.

5. A thin film forming method of claim 3 wherein an alternatively positive and negative voltage relative to the acceleration electrode is applied to the base material by a bias means during the DLC thin film formation.

6. An apparatus for forming a diamond-like carbon thin film comprising:
a vacuum chamber maintaining a predetermined vacuum therein and accommodating the base material,

a gas ion source disposed to face toward said base material for generating dissociated carbon, carbon ions, dissociated hydrogen and hydrogen ions,

said gas ion source comprises

a reaction gas introducing chamber which is provided with an orifice directed



toward the base material and into which gases are introduced,

thermoelectron discharging means disposed within said reaction gas introducing chamber for discharging thermoelectrons,

a thermoelectron drawing electrode for drawing thermoelectrons from said thermoelectron discharging means, and

an accelerating electrode disposed outside of said reaction gas introducing chamber for accelerating said ions toward the base material, and further comprising

first bias means for applying a voltage to said base material relative to said acceleration electrode as a function of time and a second bias means for applying a voltage to said thermoelectron discharging means relative to said acceleration electrode as a function of time.

7. In the thin film forming apparatus of claim 7, the voltage applied to the thermoelectron discharging means relative to the accelerating electrode by said second bias means is a positive voltage of a constant value or a value varying according to time.

8. In the thin film forming method of claim 8, the voltage applied to the thermoelectron discharging means relative to the accelerating electrode by said second bias means is an alternating voltage between positive and negative values.

This Sheet Has Been Replaced



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