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The system for depositing hard diamond-like films onto complex-shaped machine elements in an r.f. arc plasma

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Abstract

In this paper the influence of additional carbon atom particles on the synthesis of hard carbon films in an r.f. plasma has been discussed. To estimate this, the r.f. plasma was discharged between two electrodes: one in a cylinder form made of graphite and the other formed as a substrate holder. Methane and nitrogen, argon and hydrogen in different ratios was supplied to the reactor chamber through a gas feeder with a microcomputer control.

A two-channel r.f. generator was used for plasma excitation. In addition, to obtain a plasma in the pressure range 10^{-3}–10^{-4} hPa, a gas-ionization-independent source based on the d.c. arc principle was used.

1. Introduction

It is 35 years since Schmellenmeier [1] presented the first method for the production of hard carbon layers. During that period, many competitive methods have been invented, the most interesting being the growth of carbon films from ion beams [2–4], r.f. decomposition of hydrocarbons [5, 6], magnetron sputtering of graphite [7, 8] and plasma-enhanced chemical vapour deposition [9–12]. These and many other methods have been presented in detail by Angus *et al.* [13].

In general, these methods can be divided into two groups: gas-phase and surface methods. In the gas-phase methods, the nuclei of the diamond phase produced in the gas discharge are very important [14, 15]. These nuclei are deposited on substrates by diffusion and form the basis of the carbon layers. In the surface methods, coatings are formed directly on the substrates.

Our aim was to develop such a method for producing carbon films which would include the characteristics of both those methods.

2. The system for depositing hard carbon films

The methods used to deposit the carbon films on the machine elements (substrates) are outlined in order to highlight the important characteristics

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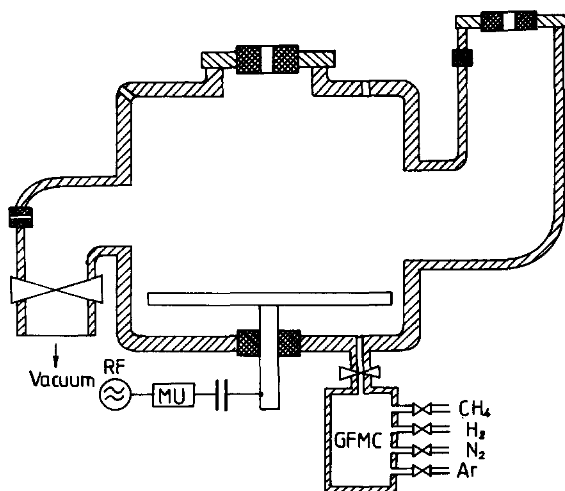

Fig. 1. The chamber of the plasma reactor with part of the systems for the r.f. decomposition of hydrocarbon: RF, first channel of the 13.56 MHz generator; MU, matching unit; GFMC, gas feeder with microcomputer control.

of the r.f. magnetron and arc plasma techniques that contributed to the positive evaluation of the hybrid plasma system.

2.1. R.f. decomposition of hydrocarbons

We have used this method to produce amorphous carbon and diamond films in our laboratory in Poland since 1978. Figure 1 shows the chamber of a plasma reactor. The energy of the r.f. electric field is supplied through a matching box to an electrode which is a substrate holder. The amount of energy transmitted owing to the collisions of electrons with the gas molecules is characterized by the r.f. peak-to-peak potential V_{pp}. However, another parameter that is more convenient, and which is proportional to V_{pp}, is the negative self-bias voltage of the r.f.-powered electrode, V_e. The negative self-bias potential V_e is indicative of the processes occurring in the gas phase [16]. The gas supply for the discharge chamber is controlled by four flowmeters with an accuracy of 0.5%.

2.2. Cylindrical magnetron sputtering

Figure 2 shows the classical method of physically sputtering positive ions from a negatively biased graphite surface. The number of positive ions (and hence the amount of material being sputtered) is increased by forming a magnetic field over the electrode surface.

In this method a relatively large flux of sputtered material particles is produced. A negative polarization of the electrode surface can be caused both by direct current and by r.f.

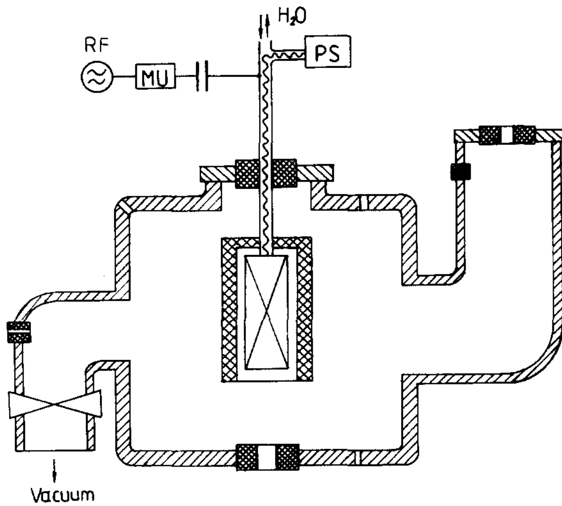

Fig. 2. The chamber of the plasma reactor with cylindrical magnetron sputtering: RF, second channel of the 13.56 MHz generator; MU, matching unit; PS, power supply for magnetron coil.

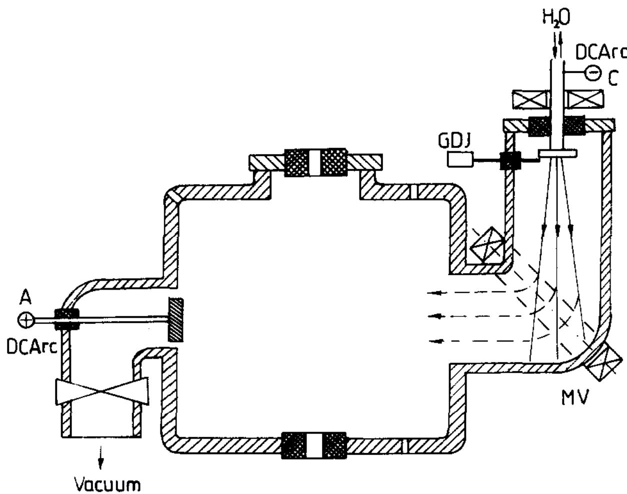

Fig. 3. The chamber of the plasma reactor with d.c. arc plasma: A, anode; C, cathode; MV, magnetic valve; GDI, gas discharge ignition.

2.3. D.c. arc plasma

The majority of modern devices for depositing hard wear-resistant coatings are constructed on the basis of the d.c. arc method, as shown in Fig. 3.

Material deposited on a surface is produced during the arcing between the electrodes. The source material is the cathode. To remove droplets of sputtered material that build up a layer, a system of magnetic coils is often used [19]. In such cases only ions reach the surface being coated. The arcing is initiated by the application of a high voltage pulse to a cathode (gas discharge ignition).

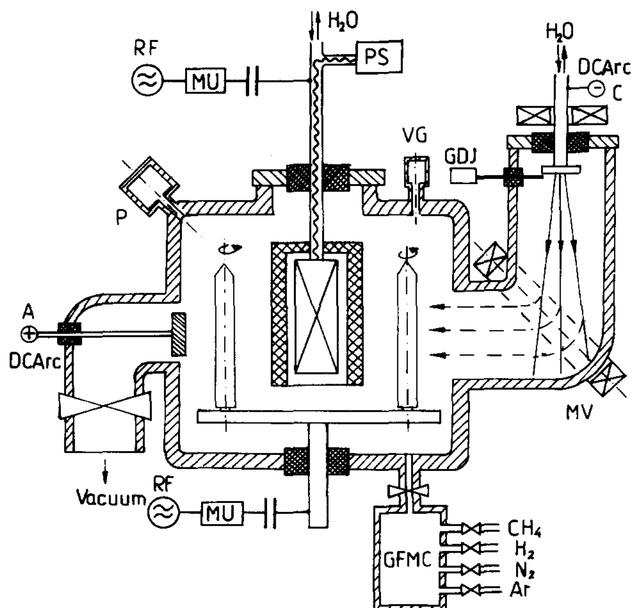

Fig. 4. The chamber of the plasma reactor with the hybrid r.f. magnetron and d.c. arc plasma systems: RF, first and second channels of the 13.56 MHz generator; MU, matching units; A, anode for d.c. arcing; C, cathode for d.c. arcing; MV, magnetic valve; GDI, gas discharge ignition; GFMC, gas feeder with microcomputer control; PS, power supply for magnetron.

The characteristics of the d.c. arc plasma method are (a) a very high rate of deposition and (b) almost 70% ionization of the material being deposited. As the beam of ions can be used in the preliminary etching of the surface, the layers of coating produced using the d.c. arc plasma method are highly adhesive [17, 18].

2.4. Hybrid r.f., magnetron and arc plasma

In the chamber of the plasma reactor shown in Fig. 4, three systems that can operate separately or together are installed: (1) an r.f. generator coupled capacitively via an impedance matching network MU to the electrode with the substrates; (2) above the electrode, a cylindrical magnetron supplied by the second channel of the r.f. generator; (3) in the pipe of the plasma guide, an arc source with a magnetic deflector coils–magnetic valve system.

Using the system of vacuum pumps it is possible to obtain an absolute pressure of the order of 10^{-5} hPa in the chamber. Methane, with additions of argon or nitrogen, or hydrogen with methane is fed to the chamber through a gas feeder with microcomputer control. Plasma in the chamber can be excited at a pressure of the order of 10^{-3} hPa. The range of parameters used in the investigation is given in Table 1.

The temperature of the substrates is measured using a pyrometer. The substrates, either fixed or spinning on their central axis, are moved in a circular orbit around the magnetron gun.

TABLE 1

Physical conditions for the hybrid r.f. magnetron and arc plasma method

Pressure	10^{-3}–10^{-4} hPa
r.f. generator	
Output power	5 kV A
Negative self-bias voltage	60–300 V
Magnetron	
Negative self-bias voltage	600–1000 V
Power supply for electromagnetic coil current	4–6 A
D.c. arc	
Electric arc current	50–300 A
Temperature of substrates	100–600 °C

In the first stage of the process the substrates placed on a spinning electrode are etched [17, 18]. The magnetron is then switched off; depending on the nature of the substrate, the first channel of the r.f. generator may also be switched off. The system of deflector coils is then switched on and the ion beam from the arc source reaches the substrate surface. Cleaning of the substrate surface now occurs; this is followed by the deposition of a very thin initial layer of coating which increases the adhesion of subsequent carbon layers [17, 20]. For optical applications (*e.g.* antireflection carbon layers on a laser mirror), parameters are set in such a way that the initial thin layer of coating is not produced on the substrate.

In the second stage of the process the magnetic valve is shut, *i.e.* the coil is switched off, and the ion beam reaches the wall of the plasma guide. In transit, the ion beam produces electrons which move to the anode. The electrons increase the ionization level in the glow space around the electrode with the substrates. Because of their presence, the electrons support plasma-chemical reactions, such as diamond synthesis.

The energy of the electric field from the second channel of the r.f. generator is supplied to the cylindrical magnetron electrode. In this way the negative potential of magnetron polarization is formed. The stream of carbon particles, produced as a result of graphite sputtering, reaches the substrate electrode and builds up into the layer formed on the substrate.

The hybrid method is superior to the r.f. decomposition of hydrocarbons in that it produces a stream of carbon particles and a beam of electrons. These change the nature of the processes that take place in the gas phase and on the substrate surface.

3. Properties of the carbon coatings produced by the hybrid method

Carbon layers obtained by the hybrid method have properties very similar to those produced by the r.f. plasma method [14, 16, 21]. Depending on

TABLE 2

Properties of the carbon coatings produced by hybrid r.f. magnetron and arc plasma method

Refractive index n	1.6–2.7
Width of the optical gap E_o	0.3–3.6 eV
Specific resistance ρ	10^1–10^{12} Ω cm
Vickers hardness	≈4000 HV
Breakdown test (0.1 μm film) (Binger Tyrod, 37 °C)	1300 V

the hydrocarbon-containing gas content in the chamber, the chamber pressure and the value of the negative self-bias potential of the r.f. electrode, carbon layers have been produced with the properties given in Table 2. The carbon layers are usually amorphous or have a superfine crystalline structure. It is also possible to obtain carbon layers with a diamond structure. This can be achieved using a pressure of the order of 10^{-2} hPa, a gas mixture containing about 99% H_2 with methane and the magnetron switched off. An example of such a coating is shown in Fig. 5.

Using this method we can produce diamond layers. For practical purposes, however, it is more reasonable to produce amorphous or superfine crystalline layers. The amorphous layers are more resistant to cracking.

4. Conclusions

The application of an independent gas ionization source allows the pressure in the plasma reactor chamber to be reduced to about 10^{-4} hPa. This

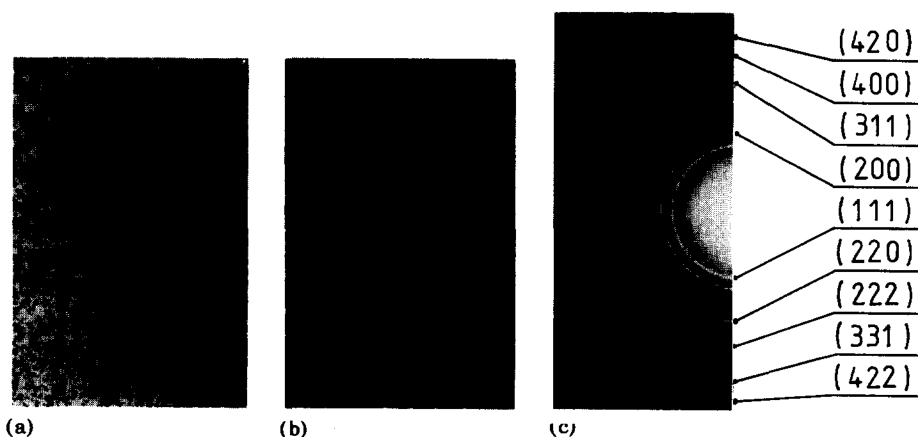

Fig. 5. TEM micrographs of diamond films: (a) bright field image; (b) dark field image; (c) electron diffraction pattern. The interplanar spacings calculated from the electron diffraction pattern are in good agreement with the value reported for cubic diamond.

facilitates the formation of carbon layers with a diamond microstructure. The gas ionization also produces ion beams that etch the original substrate: this considerably increases the adhesion of the carbon layers to a substrate of any shape. As a result, hard, thick and highly adhesive coatings of carbon layers are obtained. Deposition of the layers onto biomaterials, such as bone nail and artificial joints (*e.g.* hip joints) used as implants appear to be successful.

Acknowledgments

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