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Jumps and Hysteresis Effects in CH$_4$-H$_2$ Plasma Discharges

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Abstract. — In typical conditions of diamond film synthesis in a EACVD device (Electron-Assisted Chemical Vapor Deposition), we report on the sudden jumps, bistability, multistability and negative resistance phenomena in methane-hydrogen mixture discharge plasma. We studied the variations of these phenomena with gas pressure, filament current. The difference of discharge characteristic between pure hydrogen and methane-hydrogen mixture system is presented.

Although the study of gas discharge is a subject which has a long history, it continues to attract considerable interest with the extensive research on plasma discharges during the last several years. In single species gas (argon or hydrogen) at very low pressure ($10^{-3}$-$10^{-2}$ Pa) many experimental research works [1-4] show that bistability, multistability, bifurcation and chaos exist in plasma discharges. Theoretical works about gas discharges are performed both by fluid model with continuum equations [5] and by particle model using particle in cell/Monte Carlo methods [6]. Especially, some numerical simulation results [7] can be used to interpret nonlinear phenomena in plasma system.

On the other hand, low temperature plasma attracts more and more attention by its vast applications in industry, such as plasma processing including synthesis of new materials by PCVD, sputtering and etching. To the best of our knowledge, few reports about DC discharge characteristic under condition of diamond film synthesis can be found in the literature. Suresh, Graves and Plano [8] studied the structure of hydrogen DC discharges between parallel plate electrodes by self-consistent particle-fluid hybrid simulation and Monte Carlo simulation. However from the view point of Fumiyoshi Tochikubo and Toshiaki Makabe etc. [9], some discrepancy of discharge structure exist between pure hydrogen and the mixture of methane and hydrogen. In this paper, we first find the multistability and negative resistance phenomena under the condition of diamond film synthesis (hydrogen and methane mixture at 100-4 000 Pa, 1 000 K).

Our experiments is performed on a PCVD device, a common device for DC glow discharge. A cylindrical quartz chamber, 70 cm in length and 6 cm in diameter, is pumped to a base pressure of less than 2 Pa ($10^{-2}$ Torr). To produce plasma, hydrogen-methane gas mixture is admitted to the chamber with neutral gas pressure from 100 Pa to 4 000 Pa. In the center of the chamber, a spiral tungsten filament of 0.5 mm diameter is placed parallel to the
stainless steel substrate holder (Ø 35 mm) which also serves as anode. The distance of the filament used as cathode from the anode is 1.2 cm. Except for special illustration, the filament heating current is 25 Amperes. The position of the electrodes and filament is maintained unchanged during the synthesis of diamond films (about 30 hours). The parameters of the DC regulated power supply used in our experiment are listed as follows: output voltage: 0-500 (Volts), output current: 0-5 (Amperes), ripple coefficient < 1 %. A 0.5 Ω series sample resistor is placed in the discharge circuit. Such a low resistor should have little influence on the gas discharge behavior. From the voltage on the 0.5 Ω resistor we can obtain the value of discharge current. The voltage versus current characteristics are obtained by X-Y recorder. The speed of recording the voltage-current curves is very high (the time of recording every characteristic curve is less than 10 seconds). When the bias voltage is increased from zero, the discharge current is increased continuously (the discharge current is changed slightly or is unchanged during this time) until a typical biased voltage $V_{1a}$ is reached. Then discharge current jumps apparently. At this time, if we decrease the biased voltage, the discharge current does not jump downward along the former trace, but it decreases continuously until a typical voltage $V_{2a}$ ($V_{2a} < V_{1a}$) appears, at which a downward jump occurs. If we increase voltage further, the discharge current is increased continuously again until another sudden upward jump occurs and so on.

In pure H$_2$ system, voltage-current characteristic is shown in Figure 1. Figure 2 shows the discharge behavior in CH$_4$ (0.75 % Vol.) and H$_2$ mixture, under typical conditions for the synthesis of diamond films. From Figure 1 and Figure 2, we can obtain the following results: with the same external parameters, plasma can be in two, three or more different states which correspond to different electron density. In the CH$_4$-H$_2$ gas mixture discharge system, the breakdown voltage increases with an increase of the gas pressure, and the higher gas pressure is corresponding with the larger hysteresis loop. The scope of jump increases with the increase of gas pressure. Figures 3a and 3b show the difference of the discharge characteristics.
Fig. 2. — Biased voltage-discharge current characteristic in CH<sub>4</sub>-H<sub>2</sub> mixture discharge system at gas pressure 2 500 Pa.

between pure hydrogen and hydrogen-methane mixture system at 400 Pa. We can see that the gas mixture of methane and hydrogen makes the breakdown voltage greater than the pure hydrogen system. This mainly results from the difference of electron emission coefficient between methane and hydrogen γ(CH<sub>4</sub>) < γ(H<sub>2</sub>) [9]. The lower electron emission coefficient causes the higher sustaining voltage in the range of gas pressure for PCVD.

Figures 4a-4b show the DC discharge behavior in CH<sub>4</sub>-H<sub>2</sub> mixture when the current intensity of the filament is 20 A and 27 A, corresponding to a maximum emission current density of 0.026 Ampere/cm<sup>2</sup> and 0.10 Ampere/cm<sup>2</sup> respectively. Our experimental results show that when the filament current intensity increases, the breakdown voltage decreases and the discharge current increases on a large scale. Option for very large discharge current density...
Fig. 4. — Biased voltage-discharge current characteristics in CH₄-H₂ mixture discharge system at different filament current. a) 20 A. b) 27 A.

(high plasma density) is an important means to increase the growth rate of diamond film. This result is quite different from that of Jiang [10], which found that the breakdown voltage is not influenced by the filament current at lower pressure. Under a quite low pressure (about 10⁻³-10⁻² Pa) the discharge current intensity does not depend on the primary emission electron density, while at typical condition of diamond film synthesis the emission electrons have an obvious influence on the formation and development of the discharge current.

A steady-state glow discharge is sustained when the ionization in the discharge is balanced by the loss of charged particles in the discharge volume by drift, diffusion and recombination. Bostch and Merlino [11] ever thought that jumps and hysteresis in discharge current can be attributed to a region of negative differential resistance in voltage-current characteristics of the discharge. They interpret that the occurrence of jumps, hysteresis and negative differential resistance are due to the slope of filament characteristic curve exceeding that of the intersecting plasma production curve. Figures 2, 3b and 4 show the existence of negative differential resistance (NDR) during the jumps (upwards and downwards) of the discharge current. We also found that NDR phenomena also existed before the breakdown in some conditions (Fig. 5). Although NDR phenomena are reproducible, the $V-I$ characteristic curves before breakdown are not reproducible, which may imply some plasma instabilities. The upward traces of $V-I$ characteristic curve are not corresponding to the downward traces before the breakdown.

Many of our experimental results first show the jumps and hysteresis effects in voltage-current characteristic of a DC discharge used in diamond film synthesis. The existence of multistability will give us some guides for the synthesis of diamond films of different quality by selecting certain conditions. If we intend to increase the thermo-conductivity of diamond films, we usually select the lower plasma state, which corresponds to the low plasma density
during the nucleation. A lower plasma density corresponds to lower nucleation density, which usually results in grain of larger scale. Whereas if we want to increase the growth rate of diamond films, we usually select higher plasma state, which corresponds to higher plasma density.

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