DIAGNOSTICS OF MAGNETICALLY-ENHANCED RF DISCHARGE PLASMAS IN METHANE: ABSOLUTE DENSITY OF HYDROGEN ATOMS

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Optical actinometry has been employed to measure the absolute density of hydrogen atoms in magnetically-enhanced assymmetric capacitive coupling RF discharge in methane. It has been shown that a main reason for the excitation of radiative states of hydrogen and argon in the particular plasma conditions is the direct electron impact from the ground electronic states, de-excitation is taking place predominantly through the radiative decay. The absolute density of hydrogen atoms was increasing function of pressure, dissipated power and magnetic field induction.

INTRODUCTION

Various modifications of the magnetically-enhanced radio frequency (MERF) discharge find a wide-spread applications in modern plasma chemistry. For example, these discharges are employed in the technology of deposition of thin carbon films from the hydrocarbon plasma [1,2]. It has been found that the hydrogen atoms play a key role in the formation of properties of the layers in all kinds of carbon deposition schemes. Their presence is very essential for the stabilization of the carbon bonds and for the selective etching of the dangling bonds during the deposition processes [3]. To understand the production and destruction kinetics of H atoms and the role of atomic hydrogen radicals in the process of formation of the carbon films properties, it is very essential to have an information on atomic hydrogen density in the plasma.

KINETIC MODEL

In the Refs. [4,5] it has been shown, that in the low pressure glow discharge plasma in the gas mixtures of hydrocarbons with the noble gases, it is possible, in principle to measure the absolute density of atomic hydrogen by optical actinometry method. The intensities of the Balmer H_α spectral line ($\lambda = 656.2$ nm), and the spectral line of argon (λ

= 696.5 nm) have been compared. However, in the same Refs. [4,5] it has been underlined that in the conditions of glow discharges plasma in the gas mixture hydrocarbon-argon not only a direct electron excitation from the ground state, but also the process of stepwise excitation of the radiative states of argon Ar($4p^3P_1$) and hydrogen H(3S, 3P, 3D) through the metastable states Ar($^3P_{0,2}$) and H($2^2S_{1/2}$) respectively, becomes important. Therefore it is essential to make an analysis of the excitation kinetics of the radiative states Ar($4p^3P_1$) and H(3S, 3P, 3D) for the particular experimental situation. The following excitation and de-excitation reations for radiative A^* and metastable A_m atomic states should in principle be discussed:

$$A + e \xrightarrow{k_1} A^* + e, \quad (1)$$

$$A + e \xrightarrow{k_2} A_m + e, \quad (2)$$

$$A_m + e \xrightarrow{k_3} A^* + e, \quad (3)$$

$$A_m + e \xrightarrow{k_4} A + e, \quad (4)$$

$$A_m + M \xrightarrow{k_5} A + M, \quad (5)$$

$$A^* + M \xrightarrow{k_6} A_k + M, \quad (6)$$

$$A^* \xrightarrow{k_7} A + h\nu, \quad (7)$$

$$A_m + wall \xrightarrow{k_8} A. \quad (8)$$

Where e means electrons, and M means heavy particles (atoms and molecules) (Ar, CH_4, H_2, etc..) in the ground and in the excited states, A_k is the atom in the excited state k.

Combining (1) - (8) the stationary density of the ground state A can be derived:

$$[A] = [A^*] \cdot \frac{k_7 + [M]k_6}{[e]k_1 + [e]^2 k_2 k_3/([e](k_3 + k_4) + [M]k_5 + k_8)}. \quad (9)$$

Finally the absolute population density of atomic hydrogen in the ground electronic state [H] can be derived from known absolute density of argon atoms [Ar], relative population densities of hydrogen [H*] and argon [Ar*] in the excited states, and the rate coefficients of elementary collisional and radiative processes:

$$\frac{[H]}{[Ar]} = \frac{[H^*]}{[Ar^*]} \cdot \frac{[k_1 + [e]k_2k_3/[e](k_3k_4) + [M]k_5) + k_8]_{Ar}}{[k_1 + [e]k_2k_3/[e](k_3k_4) + [M]k_5) + k_8]_H} \cdot \frac{[k_7 + [M]k_6]_H}{[k_7 + [M]k_6]_{Ar}}. \quad (10)$$

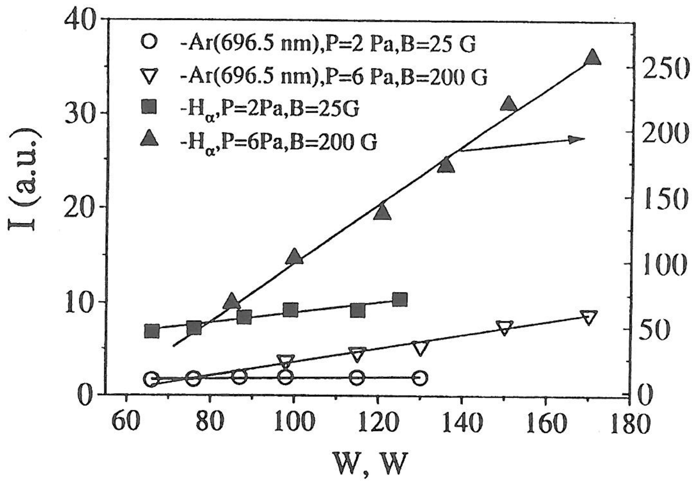

Fig. 1

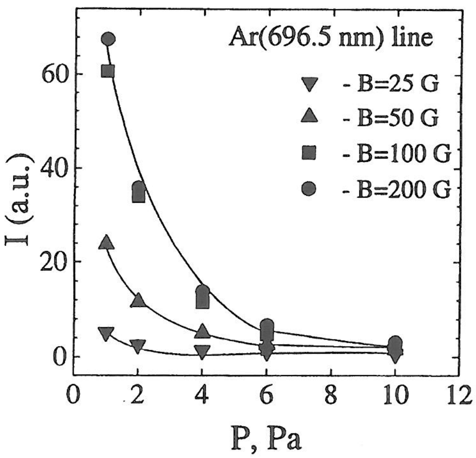

Fig. 2

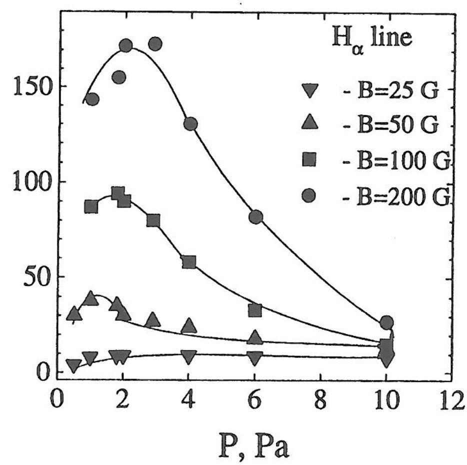

Fig. 3

The rate coefficients for the reactions (3) - (8) for Ar and H are taken from [4-12]. The rate constants k_1 and k_2 have been calculated from known excitation cross sections for the reactions (1), (2). Excitation cross section for the transition H(1S $\rightarrow$ 3S, 3P, 3D) of H was taken from Ref. [13], for the transition H(1S $\rightarrow$ $2^2S_{1/2}$) from Ref. [14]. For the Ar the excitation cross sections k_1 and k_2 were taken from Ref. [15]. The calculations have been carried out assuming the Maxwellian electron energy distribution function with a typical value of electron temperature in the RF discharge $T_e = 3$ eV, electron density $n_e = 5 \cdot 10^{10}$ cm^{-3}, and gas temperature $T_{gas} = 300$ K.

EXPERIMENTAL

The experiments have been performed in magnetically-enhanced assymetrical capacitive coupling RF reactor. RF power (frequency is 13.56 MHz) from the generator has been applied to the stainless steel plane square electrode with a side of 10 cm, which is situated in the middle of the chamber. The power supply was connected to the electrode through the special matching device. The walls of the cylindrical chamber with a diameter of 30 cm, and with a height of 25 cm were grounded. Two magnetic coils induced in the chamber a homogenious magnetic field in respect to the vertical axis of symmetry. The gas pressure (methane) can be adjusted in the range of 0.1 - 10 Pa, dissipated power between 80 - 200 W, magnetic field induction in the range of 0 - 200 G. All supplied RF power has been fully dissipated (without reflection) in the discharge, while magnetic field was higher than 50 G.

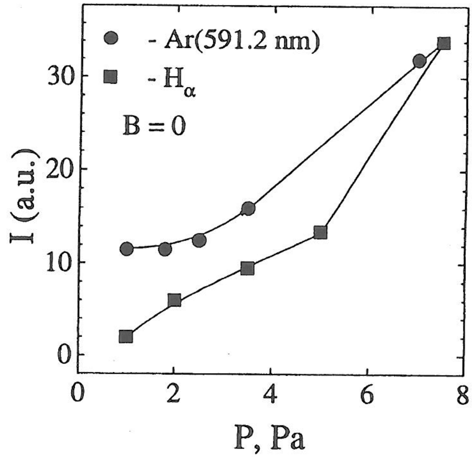

Fig. 4

To measure the spectral line intensities the optical system, based on the high resolution monochromator and photomultiplier has been used. For the determination of atomic hydrogen density in the RF discharge, argon gas as an actinometer has been added into the discharge active zone in a controlled amount (between 1 and 10 %).

RESULTS AND DISCUSSION

The intensities of the spectral lines of argon Ar(591.2 nm), Ar(696.5 nm), H_α (656.2 nm) have been measured as a function of dissipated RF power (W), total gas pressure (P), and external magnetic field induction (B). It can be seen that intensities of the spectral lines of Ar(696.5 nm) and H_α are linearly increased with the input power (Fig. 1). The intensities of both lines grew with increasing of magnetic induction, which probably is connected with increasing of the population density of the radiative states, due to the effect of magnetic confinement of the electrons by an external magnetic field (Figs. 2-3). Fact of decreasing of Ar(696.5 nm) spectral line intensity with increasing of a gas pressure is probably because of decreasing of the magnetic field confinement with pressure increasing (Hall parameter for the electrons becomes smaller). The effect of collisional deexcitation

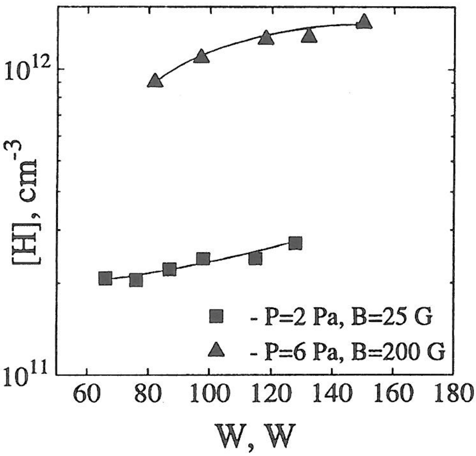

Fig. 5

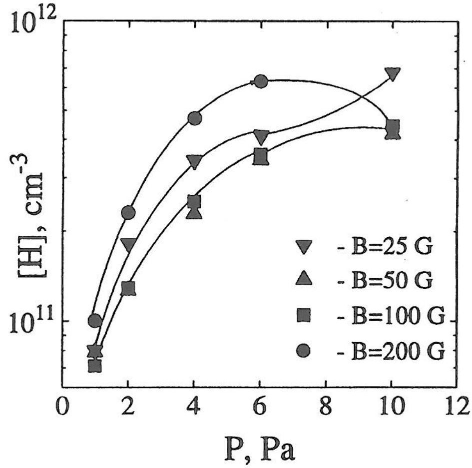

Fig. 6

of radiative and metastable states in particular experimental conditions should be small. Besides, it was confirmed, that in the case of an ordinary RF discharge without magnetic field there are inverse behaviour of I(P) (Fig. 4). Maximum of I(P) dependence for the H_α line in case of magnetically-enhanced RF discharge (Fig. 3) can be explained by two opposite trends: lowering of electron excitation of the radiative state and rising of hydrogen atomic density with increasing of total gas pressure in the discharge. Experimentally measured intensities of Ar and H spectral lines have been used to calculate the hydrogen atoms absolute density. In accordance with Eq. (10) the H atoms absolute density has been derived for the hydrocarbon plasma of MERF discharge as function of dissipated powers, total gas pressure, and induction of an external magnetic field. The data of hydrogen atoms absolute density in hydrocarbon plasma of MERF discharge as function of W, P, and B are shown in Figs. 5, 6 and 7, respectively. One can see that absolute density of hydrogen atoms becomes higher with increasing of induction of external magnetic field, dissipated power, and total gas pressure in the discharge chamber.

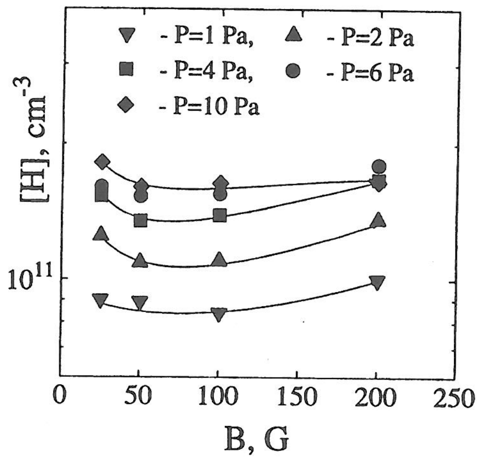

Fig. 7

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