MASS SPECTROSCOPIC AND OPTICAL DIAGNOSTICS OF THE ARC DISCHARGE WITH EVAPORATED GRAPHITE CATHODE

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The density of the chemically active radicals have been measured in the low pressure arc discharge with evaporated graphite cathode in the atmosphere of methane (argon/methane), employing the methods of mass-spectroscopy and optical actinometry. Dependences of the intensity of mass-spectroscopic signals corresponding to the radicals and stable molecules: C, CH, CH_2, CH_3, CH_4, H_2O, as well as the absolute density of atomic hydrogen have been studied as a function of the discharge parameters.

INTRODUCTION

In recent years the development of plasma sources for the various thin films deposition schemes received a wide-spread applications. For example, different kinds of gas discharges are using for diamond, diamond-like and amorphous carbon thin film deposition. The quality of the coatings are strongly depends on the plasma parameters. It has been established that presence of the hydrogen atoms and various hydrocarbon radicals are promoted (in various proportions) the formation of the amorphous carbon or diamond-like bonds. Therefore, for the optimization of the deposition processes it is important to know the internal plasma parameters, i.e. the plasma chemical composition and the radicals density. For the various schemes of carbon thin film deposition the quantitative information on the radical and stable molecule densities is required, which can not be observed by emission spectroscopy, and, of course, the information on hydrogen atom ground state density in the plasma represent a special interest.

EXPERIMENTAL

The experimental set up described in detail elsewere [1]. The discharge has been organised between the evaporated graphite cathode and the metal walls of vacuum vessel (anode). The arc current was 40-60 A, the voltage was 18-20 V, the gas pressure (methane or argon/methane mixture) can be changed in the range of $1 \cdot 10^{-4} - 5 \cdot 10^{-3}$ Torr. Study of the radical and stable monomer densities, which can not be observed by the emission spectroscopy, were carried out by using of quadrupole mass-spectrometer MX-7304. Emission spectra of the plasma were studied by the optical system, which consists of monochromator (dispersion 13 A/mm), photomultiplier, lock-in-amplifier and recorder.

RESULTS AND DISCUSSION

Mass-spectroscopy

The following mass spectra (MS) (from M = 2 - 45) have been investigated. Neutral gas MS at lowest possible pressure in the vessel $\simeq 10^{-5}$ Torr, MS of the discharge under the same condition, i.e. at $P \simeq 10-5$ Torr, MS of the working gas (methane) without discharge at pressure $P \simeq 5 \cdot 10-4$ Torr, I = 60 A, and MS of the discharge in atmosphere of methane in the pressure range between $1 \cdot 10^{-4} - 5 \cdot 10^{-3}$ Torr. Dependences of mass-spectroscopic signals corresponding to M = 12 (C), 13 (CH), 14 (CH_2), 15(CH_3), 16 (CH_4) and 18 (H_2O) on total gas pressure were studied. Because these mass-spectroscopic peaks were observed also without discharge, for the determination of influence of the discharge on the plasma chemical composition we used the following procedure for the results processing. As a first step the neutral gas MS without the discharge have been measured at a certain fixed pressure. Then the similar MS have been measured with the discharge at the same pressure. Finally, the ratio of the mass-spectroscopic peaks with (I) and without discharge (I_0) has been calculated. I/I_0 pressure dependences are presented on Fig.1 and

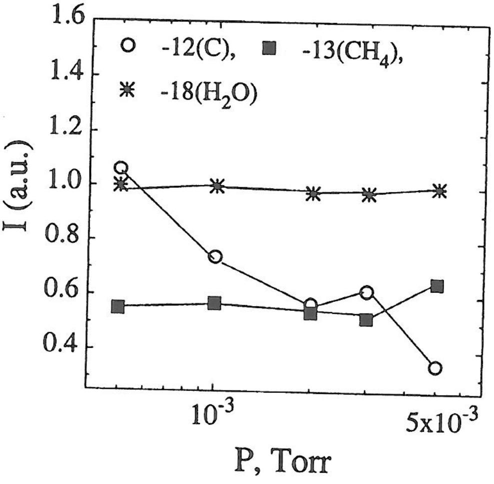

Fig. 1

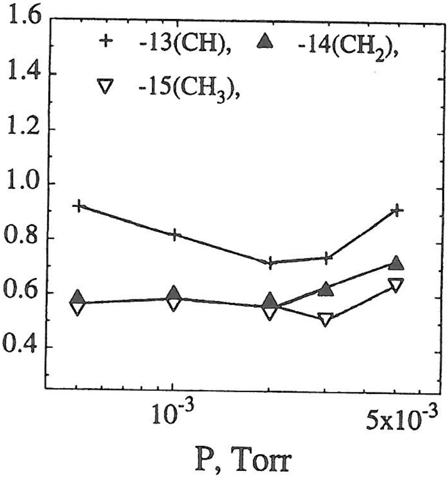

Fig. 2

2. Since it was not possible to make an absolute calibration of the mass-spectroscopic system, from the results presented we can only judge on the relative change of the particle densities.

Comparison of the pressure dependences for the C* and CH* radicals, obtained in the same plasma conditions by emission spectroscopy (see [2]) clearly shows, that the relative density of C and CH radicals in the ground state as derived by mass-spectroscopy have quite different pressure dependence. We believe that the main reason for this discrepancy is that the emission spectroscopy provides the information on the particle density in the excited states, however the mass-spectroscopy reflects the radicals behaviour in the ground electronic state. Since in the weakly-ionized plasma the most of the radicals are concentrated namely in the ground states, the main subject of interest for the plasma diagnostics is the ground state radicals density. In order to get information on the absolute density of H atoms in the plasma the method of optical actinometry can be employed [3].

Optical actinometry

The method of optical actinometry consist of admixture to the plasma under investigation a small controlled amount of actinometer, i.e. the gas with known spectra, and excitation and de-excitation rate constants of the electronically-excited radiative states. If the radiative states of actinometer and analysed gas are excited from their corresponding ground states by a direct electron impact, and the radiative states have close to each other excitation potentials, the same group of electrons will be responsible for the excitation of those states. Thus it is crucial for the applicability of the method, that the relationship between the excitation rates of the radiative states of the radical and the actinometer should not be dependent on the plasma parameters [3].

The method of optical actinometry has been employed to measure the absolute density of hydrogen atoms in the discharge. Argon have been used as an actinometer. To determine the absolute density of hydrogen atoms the relative intensities of the spectral lines of HI 6562 A (excitation potential E = 12.09 eV), and ArI 6965 A (E = 13.32 eV) were measured as a function of the discharge current, pressure and various percentage of argon in the gas mixture). It is important, that with increasing of argon partial pressure, from 0 to 30 % of the total gas pressure, the intensity of argon spectral line also increased linearly, whereas the intensity of hydrogen spectral line remains constant. It is testify that the addition of argon to methane in the amount less than 30 %, not strongly influence the shape of electron energy distribution function in the plasma, and admixture of small amount of argon can be used without perturbing a discharge. Additional experimental measurements and kinetic calculation also showed, that the technique of optical actinometry can be applied to atomic hydrogen density measurements, and all the requirements of the method [3] have been fulfilled. Finally, the absolute density of hydrogen atoms in the ground state N_{02} can be determined from the corresponding spectral lines intensities ratio I_2/I_1 and the absolute density of the actinometer N_{01}:

$$N_{02} = k \cdot \frac{I_2}{I_1} \cdot N_{01}, \tag{1}$$

$$k = \frac{\sigma_1^{max} \cdot A_1 \cdot \tau_1 \cdot \nu_1}{\sigma_2^{max} \cdot A_2 \cdot \tau_2 \cdot \nu_2} = const, \tag{2}$$

where σ_i^{max} are the maximum values of the excitation cross sections of the radiative states by direct electron impact, A_i are the radiative transition probabilities, τ_i are the radiative lifetimes, and ν_i are the wavenumbers of the radiative transitions.

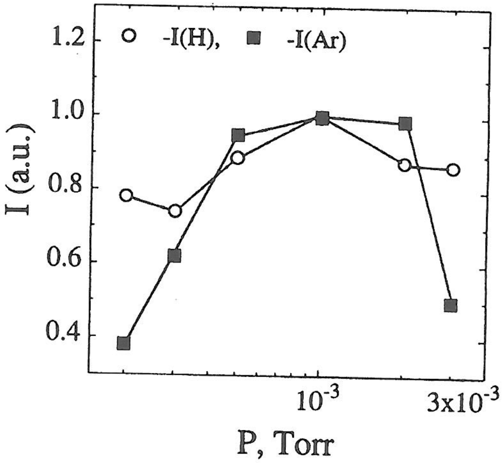

Fig. 3

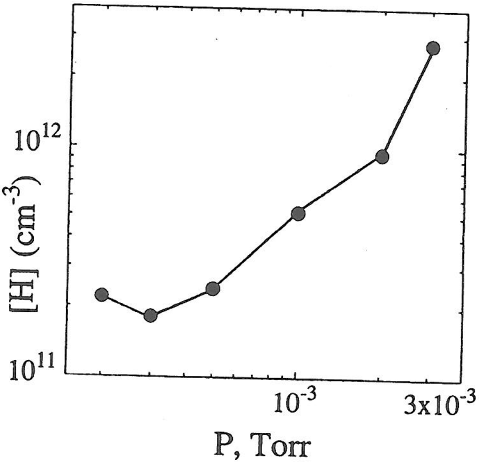

Fig. 4

In the experiments the gas mixture Ar-CH_4 (1:5) has been used. The relative intensities of HI and ArI spectral lines as function of the gas pressure are presented on Fig. 3. The absolute density of actinometer (Ar) has been determined from the absolute pressure of the gas mixture. The gas temperature in vacuum arc discharge is assumed to be close to 300 K [1,2]. The results of calculation of the hydrogen atoms density from (1) are presented on Fig. 4. The values of the rate constants, which were necessary for the H density determination are presented in Table.

Component	λ, A	A, $10^8\ s^{-1}$	τ, 10^{-9}, s	σ^{max}, 10^{-19}, cm^2
H	6562	0.647 [5]	15.5 [5]	57.1 [4]
Ar	6965	0.067 [6]	28.0 [7]	12.6 [8]

An accuracy of the discussed procedure as it can be seen from the relations (1) and (2), is limited both by the experimental accuracy (spectral line intensities, electron temperature, and spectral selectivity of the optical system), and by the uncertainty in the kinetic coefficients (electron excitation cross sections, radiative transition probabilities). Taking into account the experimental errors and the accuracy in the kinetic coefficients, we estimate the relative error in the plasma dissociation degree determination from Eqs. (1) and (2) within a factors from 2 to 3.

CONCLUSIONS

Based on the results of the mass-specroscopy investigations it has been shown that the carbon atoms density is decreasing and CH_x radicals density are slightly increasing with increase of the total gas (methane) pressure. The hydrogen atoms absolute density as determined by optical actinometry is growing with increase of the total gas pressure. On the basis of obtained dependences it can be suggested that increase of the total gas pressure in the particular low pressure arc discharge with evaporated graphite cathode will enhance the formation of the carbon films [9].

ACKNOWLEDGEMENTS

This work was partially supported under grant No. 713-224 of Netherlands Organization for Scientific Research (NWO), and partially under grant No. 94-2922 of INTAS.

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