MASS-SPECTROMETRIC INVESTIGATION OF ION FLOW COMPOSITION ON THE WALL FROM GLOW-DISCHARGE PLASMA IN THE METHANE-XENON MIXTURE

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ABSTRACT

The composition of ion flow incident on dielectrical surface from plasma of glow-discharge produced in the flowing mixture Xe-CH_4 has been investigated by mass-spectrometric method. A possible role of ion-radicals in the process of formation of thin dielectrical films by plasmachemical polymerization has been analyzed.

I. INTRODUCTION

One of the perspective ways to obtain thin dielectrical films is the plasma polymerization method in the discharges containing organic components. However, the mechanism of this process is studied insufficiently for the present. It is shown in a number of works that the growth of such films is essentially affected by positive ions [1,2] going into the film surface from plasma. Hence, it is suggested in [3] that the centres of growth (free bonds) on the film surface are created as a result of tearing of hydrogen atoms (and perhaps functional groups) from macromolecules of the layer. The energy required for this is released by ion-electron recombination. Both hydrocarbonic ions and ions of noble gas may contribute in a such formation of the centres of growth. It is obvious that the centres of growth can capture not only the neutral radicals but the ion-radicals as well. Thus, the information on the character of particles (particulary positive ions) going into the film from plasma is highly important to understanding the phenomena proceeding on the film surface during its formation.

The results of investigations of the composition of ion flow incident on the wall from d.c. glow-discharge plasma produced in the Xe-CH_4 mixture are presented in this work.

2. EXPERIMENT

The investigations have been carried out methane concentrations in the mixture at 1 - 10 volume per cent for pressures - 0.2 - 1.0 Torr, discharge current 10 - 30 mA and flow velocity of gas mixture - 10 cm.s^{-1} (radius of discharge tube was 1 cm, distance from cathode to anode was 30 cm). The lateral surface of the glass discharge tube served as a substrate. This tube had a thin platinum diaphragm of 0.2 cm diameter with orifice in it of 4.10^{-3} cm diameter at a distance of 7 cm from anode. The ions reaching the wall entered into the mass-spectrometer

through this orifice. During the measurements the diaphragm was under the floating potential. In every new regime the measurements were carried out after 15 - 20 min. exposure to establish a stationary ion flow. In this period the diaphragm was closed by small damper.

3. RESULTS

Some results of mass-spectrometric investigations are given in the figures 1 and 2 (in fig.2 there are only data characterizing the most intensive hydrocarbonic components; $j = J_i / \Sigma J$).

Given results indicate that great series of hydrocarbonic ions $C_nH_m^+$ goes to the film side by side with xenon ions. With the increase of methane concentration in the initial mixture the hydrocarbonic ion flow increases and becomes prevailing at 10% CH_4 (P = 1.0 Torr). Under these conditions the main hydrocarbonic ions are $C_2H_3^+$, $C_2H_5^+$, $C_3H_3^+$ and $C_3H_5^+$; the amount of ions $\Sigma C_4H_m^+$ and $\Sigma C_5H_m^+$ was found considerable, m = 2-6. Thus, relatively great portion of ions with nonsaturated bonds attracts the attention. The influence of the discharge current on the ion composition was found to be insignificant in our conditions.

Along with mass-spectrometric measurements the estimated ones of the total ion current density (summary ion current $C_nH_m^+$ and Xe^+) going on the wall from plasma have been also carried out. It was found that its quantity almost does not depend both on methane concentration in the mixture and on gas mixture pressure and it does not exceed 10^{-4} A·cm^{-2} at I = 10 mA (this corresponds to ion flux equal approximately to $5 \cdot 10^{14}$ cm^{-2}s^{-1}). Add, that according to data [2] with increasing the methane concentration in the Xe - CH_4 mixture within the limits of 2 - 10% the velocity of film growth changes also slightly (it decreases roughly twice). In this case ~10^{16} particles per 1 cm^2 per 1 s are built into the film in the axial zone of discharge under conditions similar to ours; in the wall region this quantity is less by an order and a half [3], i.e. $\leq 10^{15}$.

Discuss the presented results. As it is seen from our measurements, with relatively small content of methane in the mixture the hydrocarbonic ions make up only 0.1 of the quantity of total ion flow on the wall, i.e. the quantity of their flow is $\approx 10^{14}$ cm^{-2}s^{-1}. From the comparison of this quantity with that given above it is clear that in this case the hydrocarbonic ions can not provide experimentally observed velocity of the film growth. Thus, only neutral particles can be the main particles forming the film. Probably therefore the velocity of film growth in Xe at small CH_4 concentrations can be independent on the variation of ion current into the film surface that was experimentally observed in [2] for the mixture Xe - 2% CH_4. Here and then we mean that the variation of ion flow on the film surface is realized by the change of its potential in the region negativer than floating potential (in contrast to the case of the variation of potential in the region positiver than floating potential when the growth velocity, according to data [2], always depended on the variation of ion flux). Some increase of total mixture pressure above 1.0 Torr apparently should not change the nature of film formation since the ion composition of flow in the region P = 1.0 Torr changed slightly (see fig.2).

With increasing the methane concentration in the mixture to 10% the hydrocarbonic ions mainly with nonsaturated bonds become

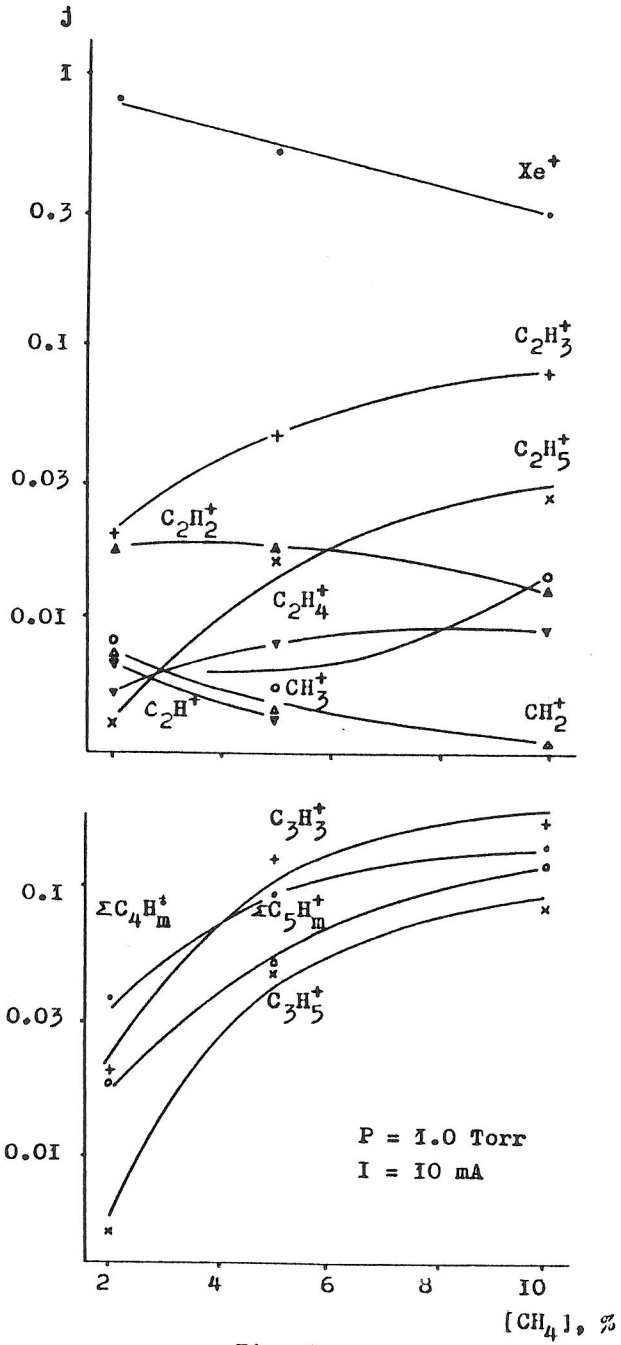
J
I
0.3
0.1
0.03
0.01
Xe+
C2H3+
C2H5+
C2H2+
C2H4+
CH3+
C2H+
CH2+
C3H3+
ΣC4Hm+
ΣC5Hm+
C3H5+
0.1
0.03
0.01
P = 1.0 Torr
I = 10 mA
2
4
6
8
10
[CH4], %

Fig. I

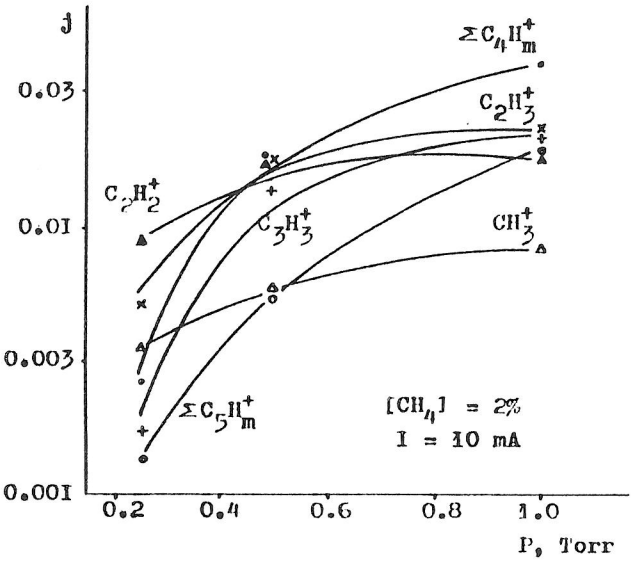

Fig. 2

prevailing in the flow. Under this the magnitude of ion flow $C_nH_m^+$ is comparable with the number of particles building into the film. It can be assumed that under these conditions the polymer film is formed to essential extent in the result of building the ion-radicals also. In this case the velocity variation of film growth with the variation of ion current on the film surface [2] to some extent confirms this assumption.

Thus, the fact in the discharge plasma produced in the Xe - CH_4 mixture at small methane concentrations (~1%) the hydrocarbonic ions couldn't be the particles responsible for the growth of polymer film upon surface has been established in the work. Apparently the ions begin to play an appreciable role in this process with increasing the methane concentration to 10% and beyond this value.

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