

CHEMICAL SPECIES GENERATION IN RF EXCITED LOW PRESSURE DISCHARGES IN C₂H₂-N₂ AND C₂H₂-Ar MIXTURES PROBED BY MASS SPECTROMETRY AND ACTINOMETRIC OPTICAL EMISSION SPECTROSCOPY

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ABSTRACT

This paper presents the results from Actinometric Optical Emission Spectroscopy and Mass Spectrometry of RF excited plasmas in low pressure C₂H₂-N₂ and C₂H₂-Ar atmospheres. The pressure and RF power trends for CH species obtained for the same plasma parameters for both techniques are in close agreement. This shows the effectiveness of Actinometry in plasma monitoring in spite of its inherent limitation as plasma diagnostic tool.

1. INTRODUCTION

Plasma materials processing by RF excited glow discharges is of key importance in many different technological issues of microelectronics and biomaterials industry [1-8]. The main feature that makes these low temperature plasmas so attractive in materials processing is that within such kind of environment electrons may attain an energy excesses of some eV in comparison with the heavy particles present in the discharge. This unusual thermal non-equilibrium situation makes easy the molecular fragmentation by electronic impact, giving rise to a very reactive chemistry in a relatively cold environment. In fact, many chemical reactions that may occur in this regime would not occurred in a thermal equilibrium situation. Therefore the understanding of the chemical kinetics developed within low pressure RF excited discharges in hydrocarbon atmospheres used in plasma polymerization processes is of key importance for its reproducibility and for its use in industrial processes. The main feature of plasma polymerization by low pressure glow discharges that makes its understanding very difficult is the above mentioned thermal non-equilibrium among electrons and different chemical species resulting from molecular fragmentation and recombination processes. Therefore is of paramount importance for processes control to set up of different plasma diagnostics. This paper deals with the use of Actinometric Optical Emission Spectroscopy and Mass Spectrometry to follow the trends of different chemical species resulting from molecular fragmentation process in RF-excited C₂H₂ plasmas. The main purpose is to show that the results obtained with actinometry may be useful for monitoring the

plasma chemical kinetics and that they are reliable in spite of the inherent limitation of the technique.

2. EXPERIMENTAL SETUP AND PLASMA DIAGNOSTICS

The plasmas were excited by a RF power supply operating in 13,56 MHz, (Tokyo Hy-Power 0-300 W), in the range from 10 to 40 Watts in C₂H₂-N₂ and C₂H₂-Ar atmospheres with 5 % of N₂ and Ar respectively, for different values of gas pressure varying from 70 mTorr (9.31 Pa) to 190 mTorr (25.3 Pa) (C₂H₂-Ar) and from 110 mTorr (14.6 Pa) to 210 mTorr (27.9 Pa) (C₂H₂-N₂) inside a stainless steel cylindrical plasma chamber with 210 mm of internal diameter and 225 mm of length. The plasma reactor is provided with two disk-shaped stainless steel parallel electrodes and eight lateral entrances used for optical, electrical and mass diagnostics as well as for monitoring the vacuum inside the chamber. The electrodes and the entrances are placed at the chamber mid plane. The vacuum system is composed by two rotary vane mechanical and one turbo-molecular pump. The turbo-molecular pump is used for cleaning processes (pumps down the chamber up to 10⁻⁷ Torr). The gases were fed into the chamber in a flow rate of 5 sccm trough mass flow controllers and needle valves. The RF power was coupled to the chamber through an appropriate matching network (Tokyo Hy-Power model MB-300) that minimises the reflected RF power. The trends of CH species for different values of RF power and gas pressure were followed using both, i.e., Actinometric Optical Emission Spectroscopy and Mass Spectrometry. Briefly actinometry is a spectroscopic technique that consists in the insertion of a chemical inert gas like argon or an almost inert like nitrogen for instance in a relative low concentration (no more than 5 %) so that its presence does not disturb considerably the original plasma properties. The necessary condition that must be fulfilled by a chemical specie for its use as an actinometer is that the threshold for its excitation by electronic impact must be in the same range of energy as the unknown chemical specie whose concentration within the plasma one wants to probe. This ensures one that the efficiency for excitation by electronic impact will be approximately the same for the actinometer and the chemical specie whose concentration is unknown.

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Therefore the unknown concentration of a chemical specie within the discharge may be directly calculated from the rate of the light intensity emitted by unknown and the actinometer [5].

The mass spectrometry was performed using a mass spectrometer and energy analyser Hiden Analytical model EQP-300TM, operating in the mass and energy range from 1 to 300 amu and from 0 to 100 eV respectively [9]. The mass spectrometer is provided with an ionization system that allows one to separate the isomers contributions for the mass spectra. This feature of the equipment is important in the studying of a very complicated chemical kinetics that often occurs in plasma polymerization processes. The identification of many chemical species within the discharge and the correlation of its chemical kinetics with different plasma parameters is of key importance for processes reproducibility [10].

3. RESULTS AND DISCUSSIONS

Figure 1 shows the normalised relative concentration of the CH species, obtained by actinometry, for C₂H₂-Ar plasmas as a function of RF power coupled to the discharge for different values of the pressure inside the plasma chamber. It may be seen that for all values of pressure in the range between 70 mTorr (9.31 Pa) and 190 mTorr (25.3 Pa) there is a value of RF power for that the concentration of CH presents a maximum. This result means that for each value of pressure, there is an optimum value of RF power coupled to the discharge for that the electronic inelastic collisions are profitable in molecular fragmentation leading the formation of CH species.

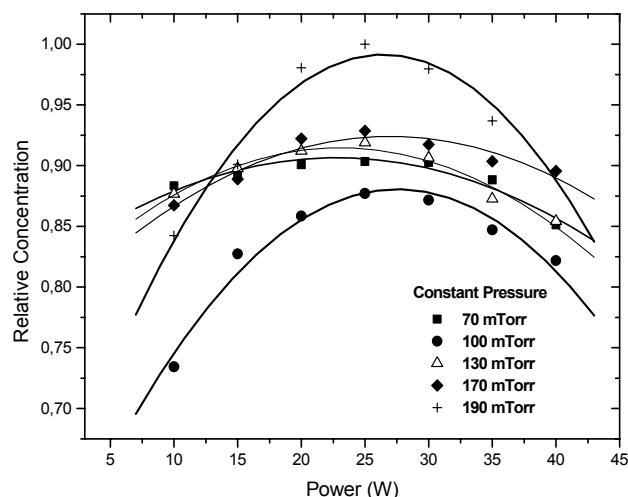


Figure 1 - Relative concentration of CH species, obtained by actinometry, in C₂H₂-Ar plasmas as function of RF power coupled to the plasma reactor.

A quite similar result for the same plasma conditions is obtained by mass spectrometry as can be appreciated in figure 2.

The trends are the same for all values of the pressure. However it can be seen that the peak value of the relative

CH concentration occurs about 10 W for 70 mTorr (9.31 Pa) and it is shifted towards higher values of RF power for higher values of pressure. This behaviour can be understood if one considers that as the pressure increases the electronic mean free-path decreases so that much more energy must be coupled to the plasma in order to obtain the same efficiency in molecular fragmentation processes by inelastic electronic collisions that lead the formation of CH species within the plasma environment.

Figure 3 shows the normalised relative concentration of CH species, obtained by actinometry, for C₂H₂-Ar plasmas as function of gas pressure inside the plasma chamber for different values of RF power coupled to the discharge.

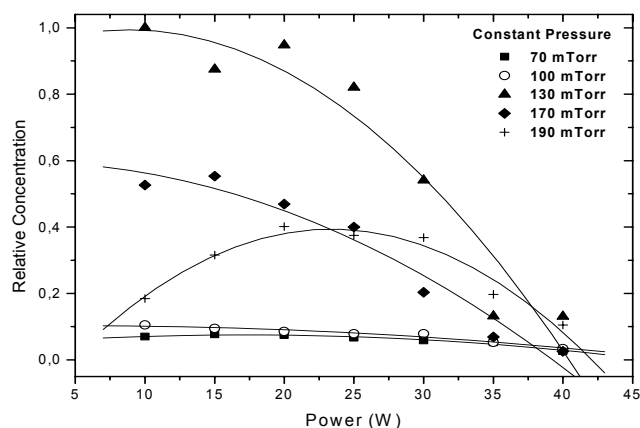


Figure 2 - Relative concentration of CH species, obtained by mass spectrometry, in C₂H₂-Ar plasmas as function of RF power coupled to the plasma reactor.

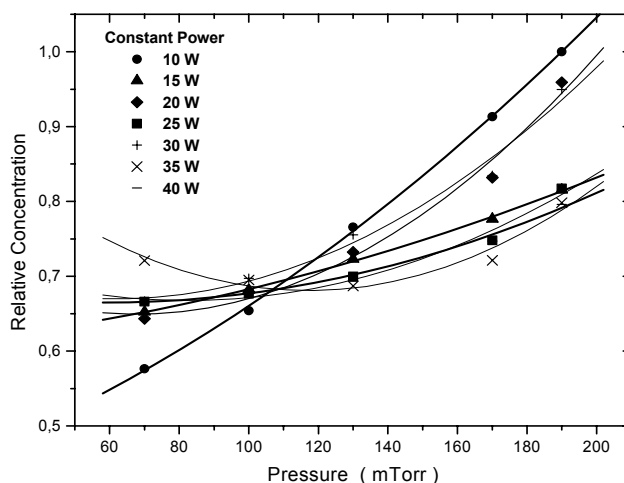


Figure 3 - Relative concentration of CH species, obtained by actinometry, in C₂H₂-Ar plasmas as function of total gas pressure inside the plasma reactor.

It can be appreciated that for all values of power within the range between 10 W to 40 W the relative concentration raises monotonically with pressure. This result is reasonable if one considers that for higher values of pressure many channels contribute for CH species formation resulting from

molecular recombination processes. It can be also seen that for 35 W the curve shows a minimum about 130 mTorr (17.3 Pa). This behaviour may be due the fact that for low pressures inelastic electronic collisions are responsible for molecular fragmentation resulting CH formation. As pressure increases the molecular recombination rate increases too leading the formation of heavy radicals and molecules. The inelastic collisions among such kind of chemical species may contribute for the formation of CH species within the discharge.

Figure 4 shows a quite similar result for the trends of CH species obtained by mass spectrometry.

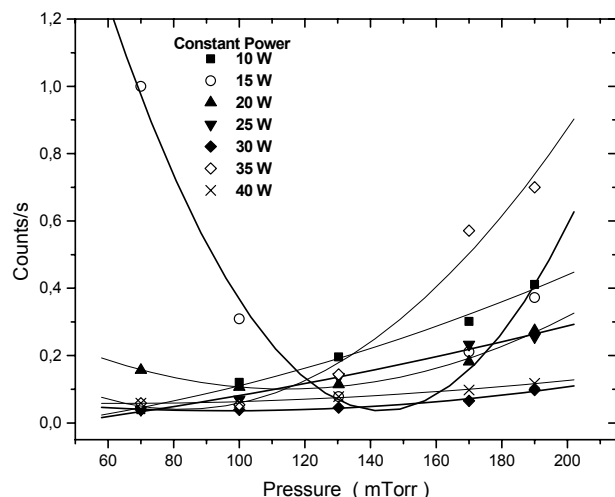


Figure 4- Relative concentration of CH species, obtained by mass spectrometry, in C_2H_2-Ar plasmas as function of total gas pressure inside the plasma reactor.

All the data corroborate the expectations that actinometry may be used in a satisfactory way for investigating the trends of the chemical species for different plasma parameters like pressure for instance.

Figures 5 and 6 show the results for the trends of CH species concentrations, obtained by actinometry and mass spectrometry respectively, in $C_2H_2-N_2$ plasmas.

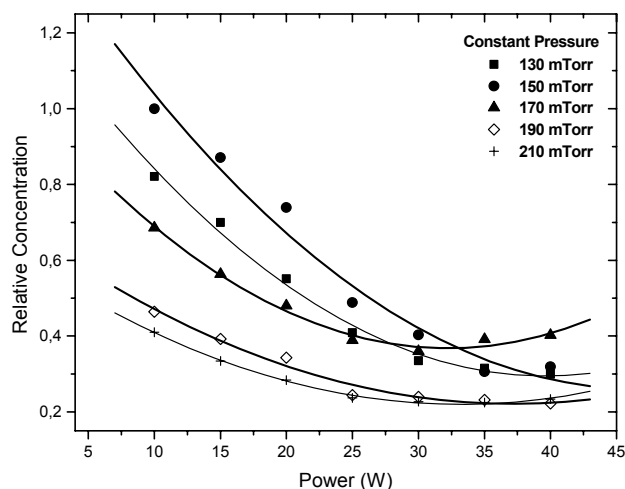


Figure 5 - Relative concentration of CH species, obtained by actinometry, in C_2H_2-Ar plasmas as function of RF power coupled to the plasma reactor.

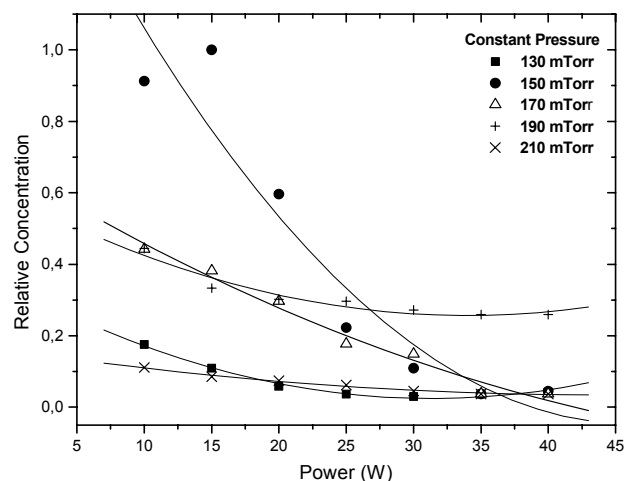


Figure 6 - Relative concentration of CH species, obtained by mass spectrometry, in C_2H_2-Ar plasmas as function of RF power coupled to the plasma reactor.

It can be seen that the trends for the CH relative concentration decreases with the increasing of RF power and that this behaviour is approximately the same for both techniques, in the same range of pressure analysed for C_2H_2-Ar plasmas. The comparison of the results obtained with mass spectrometry with those obtained with actinometry shows the effectiveness of this technique for monitoring the plasma behaviour even for 5 % of actinometer concentration. It should be pointed out that the assumption that N_2 is a chemical inert gas is not completely valid since many chemical species resulting from chemical recombination of N_2 fragments with C and H appear in the mass spectra of neutrals and ions. Nevertheless the concentrations of these chemical species in the discharges analysed are not enough to invalidate the use of N_2 as actinometer to follow the trend of CH species.

4. CONCLUSIONS

The present experimental investigation allowed one to conclude that the data from actinometric optical emission spectroscopy is reliable for the study of CH species behaviour in the $C_2H_2-N_2$ and C_2H_2-Ar plasmas and can be used as an efficient plasma diagnostic for probing the qualitative aspects of the chemical kinetics developed in the extremely reactive plasma environment. Therefore in spite of its inherent limitations, the low cost of actinometry in comparison with mass spectrometry justify its use as plasma diagnostic when the subject of the experimental investigation is to follow the trends of a chemical species in the plasma discharge.

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