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ON IONIZATION PROCESSES Ar-HEXAMETHYLDISILOXANE (HMDS) DISCHARGE[1)]

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The measurement of the axial electric field in the positive column of a low pressure glow discharge in Ar with small admixtures of HMDS has shown a minimum of electrical field strength for admixtures of 10^{-3}. The influence of several ionization processes is evaluated using the diffusion theory of the positive column. The effective PENNING ionization of HMDS molecules by metastable Ar-atoms is responsible for the decrease of the electric field with increasing HMDS admixture up to 10^{-3}.

INTRODUCTION

Plasma processing is a fast developing field in technology. Nowadays thin film production and etching processes are often connected with the application of plasmas. Film formation without a pyrolysis of the used monomers and without a thermal stress of the plasma confining surfaces is only possible under nonisothermal conditions. The electron gas as the hot component transfers the energy obtained in the electric field to the cold neutral gas. According to this the knowledge of the parameters of the electron gas is very important for studying the elementary processes taking place in the plasmachemical system.

The effective control of such processes demands the knowledge of the plasma properties. Plasmas are determined by the ionization processes, often the formation of the reactive species is connected with ionization reactions. In this paper the different ionization processes in the positive column of the Ar-hexamethyldisiloxane (HMDS) low pressure glow discharge are discussed for low admixtures of the HMDS. Hexamethyldisiloxane is an important monomer in plasma polymerization. The discussion of the ionization processes is based on results of experimental investigations of the electric properties of the positive column [1]. Also the results of measurements of the electron impact ionization cross — section of the HMDS-molecule [2] and investigations into the determination of ionization cross — sections of molecules by semiempirical formulas [3] and by applying the additivity rule for the estimation of the ionization cross-section of molecules are used [4].

The quantitative evaluation of the action of several ionization processes is possible by the diffusion theory of the plasma of the positive column in rare gases with small admixtures of molecular gases [5].

II. APPARATUS AND EXPERIMENTAL RESULTS

Experiments were carried out in a flowing argon dc glow discharge in a glass tube with a diameter or 3.8 cm and a length of 47 cm by varying the discharge current (5—10 mA), the monomer input (0.02—20 %), the argon gas flow (6×10^{-2}—1.2×10^{-1} m/s) and the probe position along the axis of the positive column up to distances of 30 cm from the monomer input. In all experiments the pressure in the discharge tube was 70 Pa. Directly heated cylindrical probes with a diameter of 0.025 mm and a length of 4 mm movable in the flow direction were used.

The potential gradient, the mean electron energy and the electron density are systematically determined by electric probe measurements.

Before carrying out investigations in the discharge of the argon HMDS mixture measurements of plasma parameters in the flowing argon discharge

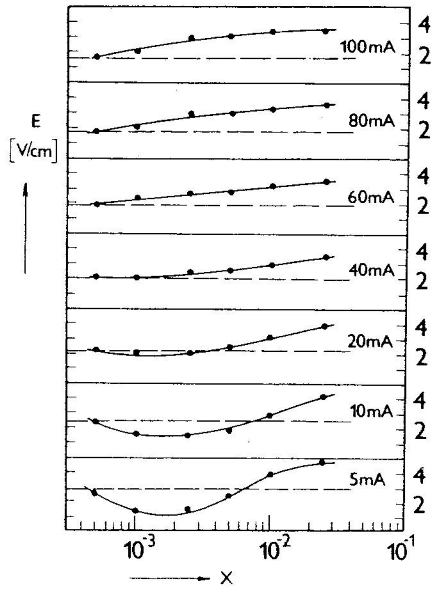

Fig. 1. Minimum electric field in the positive column with flowing gas in dependence on HMDS admixtures (X) for different discharge currents.

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were made using single probe methods. The discharge is significantly changed if an organic component is introduced in the discharge system. Simultaneously a film formation takes place on all solid surfaces which are in contact with plasma. The film formation on the probe surface after the monomer input will have for the probe measurements serious consequences. Unstable surface conditions as a disadvantageous result of probe surface contamination are known to be a source of errors in probe measurements. A sufficient cleaning of the probe surface under conditions of a polymeric plasma is possible by probe heating. In the present case a surface temperature of about 900 °C was sufficient to obtain reproducible probe characteristics.

After monomer input the plasma parameters show a typical behaviour. At monomer admixtures smaller than 5 % inhomogeneities particularly of mean electron energy and gradient are observed in the flow direction. Thus the mean electron energy decreases with increasing monomer input because of the lower ionization energy of HMDS. The influence of the monomer on the discharge is reflected especially by the behaviour of the gradient. Fig. 1 illustrates the behaviour of the lowest value of the gradient in dependence on the monomer admixture. The gradient minimum lies below the reference value at small discharge currents and small monomer admixtures.

III. IONIZATION REACTIONS

The ionization processes in the plasma of the positive column are determined by electron collisions of the ground state atoms and/or molecules and by a stepwise ionization of excited, mainly metastable atoms. But also collisions between heavy particles lead to ionizations, that are collisions between excited, expecially metastable atoms, collisions between ground state and highly excited atoms with formation of molecular ions (HORNBECK—MOLNAR-process) and collisions of metastable atoms with molecules or atoms with a sufficient low ionization energy (PENNING-ionization).

For the positive column of an Ar-hexamethyldisiloxane discharge the cross-sections for the direct ionizaiton of Ar-atoms, the excitation and the deexcitation of the metastable levels are known. The reaction rate $Z_{AA} = 5 \times 10^{-9}\,\mathrm{cm^3/s}$ of pair collisions of metastable Ar-atoms is estimated by comparison with the rate for pair collisions of metastable Ne-atoms [6] taking into account the different gas kinetic cross-sections. The electron impact ionization cross-section of the HMDS molecule was measured in a mass spectrometer by comparison with well-known inert gas atoms of Ar and Xe [2] (Fig. 2, EXP). By the calculation of the cross-section with the GRYZINSKI-formula [3] using the energy levels determined by ERMAKOV [7] with two electrons in each case in one energy state we obtain the cross section G also in Fig. 2., which is somewhat higher than the measured one. With the additivity rule [4] we get an ionization cross-section value (*FS*) for a 70 eV electron energy near the GRYZINSKI curve. Hence we suppose that the experimental values are too small. The reason may be the different energy distributions of the inert gas ions (Ar^+, Xe^+) and the HMDS-ions, which results in a different width of the ion beams [8]. For the calculation of the rate coefficient of direct ionization a linear approximation of the ionization cross-section is used as shown in Fig. 2. The PENNING ionization of the HMDS-molecule by metastable Ar-atoms can occur because of the difference in the ionization energy of the molecule (9.6 eV) and the excitation energy of the metastable atom (11.5 eV). Reaction cross-section are not available for this process, but an estimation is possible by comparison of the gas kinetic and the PENNING reaction cross-sections for other systems using values from HASTED [9], BEIJERINCK [10] and SABADIL [11] (Fig. 3). In a first approximation the PENNING cross-section is equal to the gas kinetic one. The gas kinetic cross-section can be estimated from the density of liquid HMDS, we obtain $Q_{GK} = 6 \times 10^{-15}\,\mathrm{cm^2}$. From this value a rate constant can be deduced for collisions with argon atoms at room temperature $Z_{pm} = 2.5 \times 10^{-10}\,\mathrm{cm^3\,s^{-1}}$. The HORNBECK—MOLNAR process may be neglect-

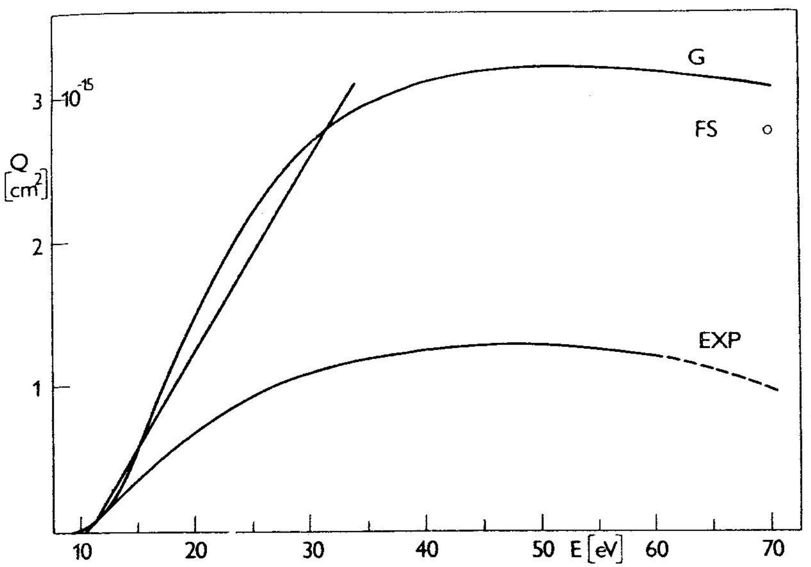

Fig. 2. Electron impact ionization cross-section of HMDS in dependence on electron energy. Calculated according to the GRYZINSKI formula G [3], additivity rule FS [4]; experimental values EXP [2] and linear approximation.

ed owing to the difficulties of balance of the highly excited states of the Ar-atoms and the known low concentrations of the molecular ions in the positive column of a low pressure glow discharge [12].

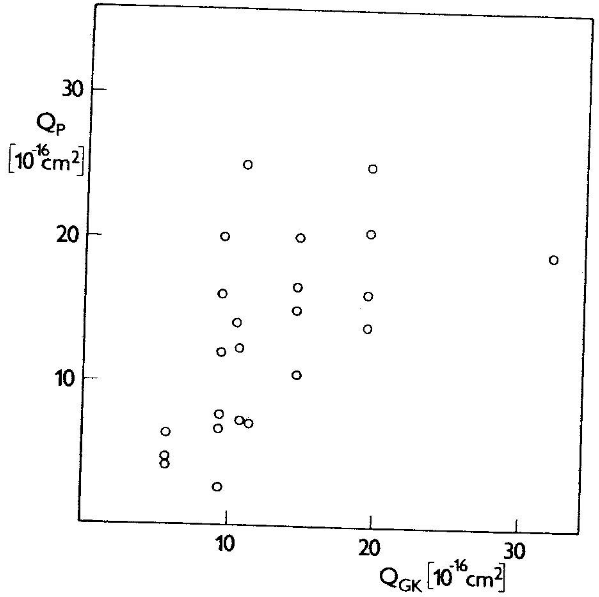

Fig. 3. PENNING ionization cross-section for reactions of excited He with Ne, Ar, Kr, Xe, H_2, N_2, O_2; Ne with Ar, Kr, Xe, H_2, N_2, C_6H_6 [9, 10, 11] in dependence on the gas kinetic cross-section Q_{GK}.

The particle balance equations are derived by **PFAU** and **RUTSCHER** [5] for a plasma with two gaseous components in a cylindrical discharge tube and concentrations averaged over the tube cross section. Taking into account the discussed ionization reactions we obtain the balance equations for the Ar^+ ions (1), the metastable atoms (2) and the HMDS-ions (3)

$$\frac{\lambda_1^2 b_1^{(1)} a D_e/b_e}{(1+a)(Nr_0)^2} = Z_{0\infty}^{(1)}(1-x) + 1.45\,Z_{m\infty}^{(1)}\frac{N_a}{N} + 1.45\,Z_{AA}^{(1)}\frac{(N_a/N)^2}{N_e/N} \qquad (1)$$

$$\frac{\lambda_1^2 D_{m1}}{N_e/N(Nr_0)^2} + 1.45\,Z_{m\infty}^{(1)} + 1.45\,Z_{AA}^{(1)}\frac{N_a/N}{N_e/N} + 1.45\,Z_{m0}^{(1)} + Z_{pm}^{(2)}\frac{x}{N_e/N} = Z_{0m}^{(1)}\frac{1}{N_a/N} \qquad (2)$$

$$\frac{\lambda_1^2 b_1^{(2)} D_e/b_e}{(1+a)(Nr_0)^2} = Z_{0\infty}^{(2)} + Z_{pm}^{(2)}\frac{N_a/N}{N_e/N}x;\; a = \frac{N_{(1)}^+}{N_{(2)}^+},\; x = \frac{N_{(2)}}{N_{(1)}+N_{(2)}}. \qquad (3)$$

Index (1) is connected with Ar, index (2) with HMDS. The balance and transport-coefficients which depend on the electron energy distribution function were calculated by means of the distribution function of electrons in pure Ar [13]. For admixtures of molecular gases to inert gases $x \lesssim 10^{-3}$ this approximation is valid [14]. The rate coefficients of the electron collision processes and the electron — drift velocity in dependence on E/N are shown in Fig. 4. The following ion mobilities b_i $(s^{-1}V^{-1}cm^{-1})$ at unit gas density are used for the calculation of Ar^+ in Ar: 4×10^{19}; in HMDS: 4×10^{19} HMDS-ion $(CH_3)_5Si_2O^+$ in Ar: 5.4×10^{19}; in HMDS: 1×10^{19}. In gas mixtures the mobilities were calculated by BLANC's law. Results of the solutions of the balance equations are presented in Figs. 5, 6. The ion production rate P/N_e is the production of ions per cm^3 and second averaged over the cross-section of the discharge tube divided by the averaged electron density. The most effective ionization processes are the PENNING ionization of the HMDS-molecules and the stepwise ionization of the Ar-atoms. The behaviour of the calculated axial electric field in the

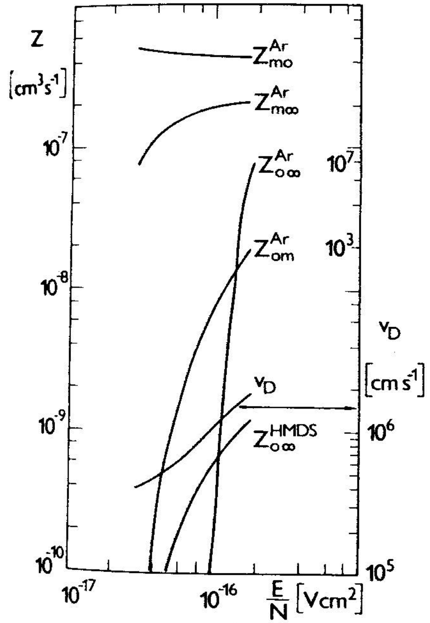

Fig. 4. Rate coefficients electron impact excitation (Z_{0m}^{Ar}), deexcitation (Z_{m0}^{Ar}) and ionization ($Z_{0\infty}^{Ar}$, $Z_{m\infty}^{Ar}$, $H_{0\infty}^{HMDS}$) processes and electron drift velocity in dependence on E/N. Calculated with electron energy distribution function in pure Ar [13].

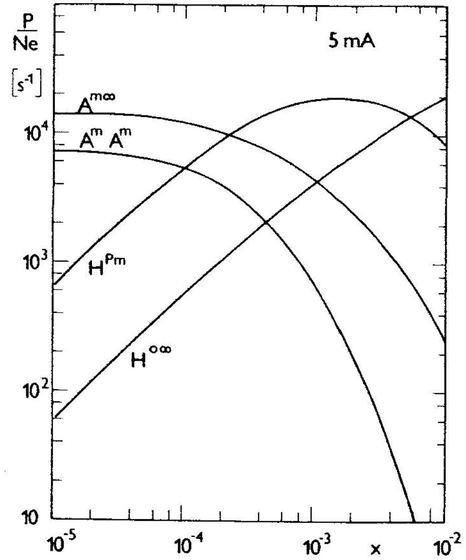

Fig. 5. Ion production rates according to stepwise ionization (A^m) and pair collisions of Ar (A^mA^m), Penning (H^{Pm}) and direct ($H^{0\infty}$) ionization HMDS in dependence on HMDS admixture (X) ($i = 5$ mA, $P = 60$ Pa, $r = 2$ cm).

positive column corresponds with the experimental results. The decrease of the gradient starts for the HMDS-admixtures near $x = 10^{-4}$. The decrease becomes smaller with increasing discharge current as a consequence of the decrease of the PENNING ionization. The increase of the electric field with a growing HMDS-admixture owing to the increase of the energy loss processes in the electron collisions with the HMDS molecules is not apparent in the calculated results, these processes had to be neglected since the cross sections are not available. It is obvious that for the neglected PENNING ionization the calculated decrease of the electric field is not in accordance with the experimental results (Fig. 6, 1).

A more detailed discussion of the results is given in [15] also with regard to the electron density and the thin film formation rate.

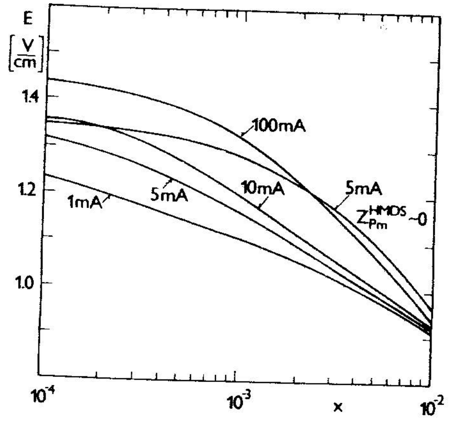

Fig. 6. Calculated axial electric field in dependence on HMDS admixture (X) for 1, 5, 10 and 100 mA. For 5 mA with and without PENNING ionization.

IV. CONCLUSION

This paper shows that by comparison of the experimental results and a simple modelling of the chemical active plasma an evaluation of the different ionization reactions is possible. A stepwise ionization of the metastable Ar atoms and PENNING ionization are essential. A direct ionization of the Ar atoms is negligible, for the HMDS-molecules this process may be important only for higher HMDS admixtures.

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