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Ion energy distribution measurements in glow discharges

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The energy distribution of ions hitting the cathode of dc and pulsed dc discharges were investigated under conditions typically for PACVD and plasma diffusion treatment. Energy and mass analysis was performed, using a two-stage differentially pumped plasma monitor. Gas atmospheres containing nitrogen, hydrogen and argon were investigated in the pressure range of a few mbar. The observed amount of ions with energies exceeding the sputtering threshold is considerably higher than theoretically expected. The density of ions striking the cathode in a low frequency pulsed discharge has proved to be strongly dependent on the average discharge current, whereas the operating voltage mainly affected their energy distribution functions.

1. Introduction

Plasma chemical vapour deposition (PCVD) and plasma diffusion treatment are now widely used for improving the tribological properties and corrosion resistance of materials. Low frequency (some kHz) or dc plasma excitation is preferred, the typical pressure is up to some mbar [1]. The properties of the growing films are mainly governed by the plasma–surface interactions. The energetic ions and neutrals striking the cathode are of crucial importance since they initiate and activate many surface processes: sputtering, desorption, etching, adatom migration, implantation [2,3]. To control these processes detailed knowledge on their energy distribution function and their dependence on the plasma parameters is necessary.

During the last two decades there has been considerable theoretical and experimental research into the energy distribution of particles arriving at the cathode. After having made simplifying assumptions, Davis and Vandersclice [4] derived an expression for the distribution of ion energies in a dc glow discharge. They assumed that (a) all ions originate in the negative glow, (b) symmetrical charge transfer is the dominant collision mechanism and (c) the electric field varies linearly within the cathode dark space. The experimental test demonstrated that the theory is able to explain the main features of their measured energy distribution. In order to improve the theory further collision processes were taken into account by many authors: elastic ion–atom collisions and atom–atom collisions [5,6]. Monte Carlo simulations showed that both the energy and angular distribution of ions and neutrals are affected by elastic momentum transfer [7–9]. Due to the complexity of the system investigated the theoretical and experimental effort was mainly restricted to pure noble gas plasmas excited by dc or RF.

In the present work, dc, low frequency pulsed dc and pulsed ac discharges were studied. Pulsed discharges are characterized by a stable behaviour in the abnormal range of the current–voltage characteristic, which is the range of most technical importance. Varying the pulse width–repetition ratio,the operating voltage U_B and the average discharge current I can be decoupled from each other. Thus, at constant pressure and current the cathode potential can be varied independently within the limits given by the discharge characteristic.

It was previously shown that the energy distribution function is mainly governed by the cathode fall potential V_C and by the number of collisions within the sheath [10]. In an abnormal glow discharge the product pL_C (pressure × cathode fall length) depends on the operating voltage [11]. For that reason, at higher U_B the ions penetrating the sheath suffer less collisions, leading to a higher portion of fast ions.

2. Experiment

The experimental setup is shown in fig. 1. The plasma was maintained between two parallel plates with an interelectrode spacing of up to 10 cm (typically

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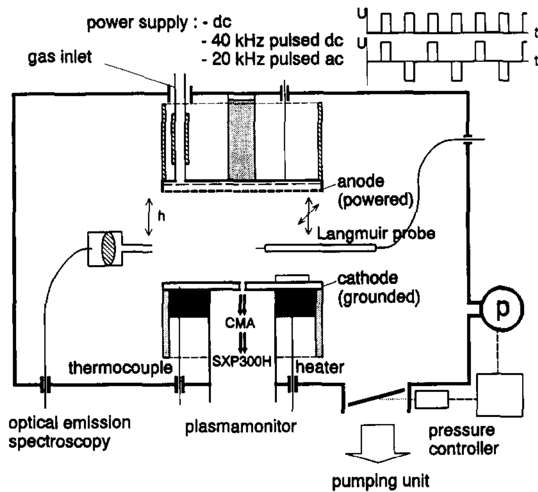

Fig. 1. Plasma CVD apparatus with diagnostic equipment.

4 cm). In order to obtain defined electrode areas quartz glass shieldings surrounded the stainless steel electrodes. The cathode temperature was adjustable up to 500°C by means of an additional resistance heater. The gases N_2, H_2 and Ar were fed throughout the powered electrode and the gas flow rate was controlled by mass-flow meters. The total pressure of 1–10 mbar, measured with a capacitance manometer, was controlled by a throttle valve with an accuracy of about 1%. In the case of deposition experiments the substrates were located on the grounded electrode.

Three different plasma excitation modes were used: dc, pulsed dc and pulsed ac. The dc discharge was stabilized using a matched serial resistor. The pulse-power supply developed in our laboratory is characterized by a fixed pulse repetition frequency. For the first time we used the pulsed dc with changing polarity. This excitation mode is referred to as pulsed ac. By using a pulsed ac excited plasma we successfully deposited insulating Si–C–N films on steel.

Mass and energy analysis of particles striking the cathode was performed, using a two-stage differentially pumped plasma monitor (V.G. Quadrupoles). The orifice of the second stage (orifice 2) is mounted in the centre of the cathode. Fig. 2 shows the system schematically. The main part of the measuring instrument is the modified cylindrical mirror analyser (CMA),in series with a quadrupole mass spectrometer (QMS). The ions enter the CMA with an energy E_{ion}. Applying a retarding or accelerating potential V_{CMA}, E_{ion} is transformed into the CMA pass energy (E_{pass} = 10–25 eV). The pass energy depends on the potential difference between the two cylindrical electrodes of the CMA. By scanning V_{CMA}, the ion energy spectrum can be measured. After passing the CMA the ions are retarded to the optimal energy of the QMS (3–4 eV) by applying the pole bias voltage V_{pb}. Due to its prefilter and its large 9-inch rod system the quadrupole mass spectrometer SXP 300H has a high sensitivity across the whole mass range of up to 300 amu.

To perform extern ion analysis the ion transfer optics, both orifices and the ion source were grounded. We confirmed the energy calibration of the plasma monitor by means of a thermally generated and electrostatically accelerated beam of sodium ions.

3. Results and discussion

3.1. Comparison of dc and pulsed discharges

Dc and pulsed dc/ac glow discharges were compared with regard to their ion energy spectra. The discharges used were in the abnormal range of the U–I characteristic (the current density was j = 0.1–3 mA cm^{-2}). The effect of the operating voltage on the distribution function of H^+ ions in a pulsed dc discharge can be clearly seen from fig. 3. The dc energy spectrum is almost symmetrical with respect to the maximum energy. Increasing the operating voltage U_B

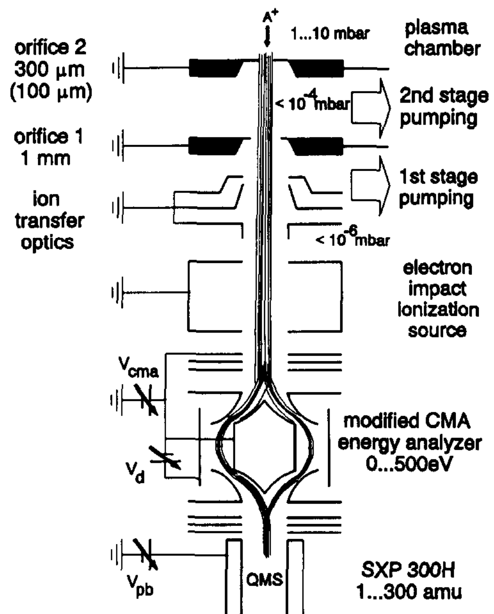

Fig. 2. Schematic of the plasma monitor system.

is equivalent to a further transition into the abnormal range of the glow discharge. The energy at maximum intensity remains unaffected. In H_2–N_2–Ar plasmas almost all of the ions strike the cathode with energies exceeding the sputtering threshold of materials deposited by plasma-enhanced techniques. A substantial part of energetic ions was found by Dexter et al. [12] in hydrogen dc discharges at a pressure of 2 mbar.

Models taking into account a certain probability of elastic ion–neutral scattering provide ion energy distribution functions with a distinct maximum [9] as it has been observed in our experiments. Unfortunately, there are no results available for dc or low frequency discharges in gas mixtures at pressures of some mbar. It is therefore not possible to compare our experimental results with theoretical considerations. There are further phenomena wich can not be explained for the time beeing. In some cases we found energy distributions showing additional maxima. Furthermore, an addition of argon to a discharge caused the energy at maximum intensity to be shifted towards higher values. For example, when argon was added to a MOCVD deposition plasma the energy at maximum intensity increased from 20 to 100 eV [13].

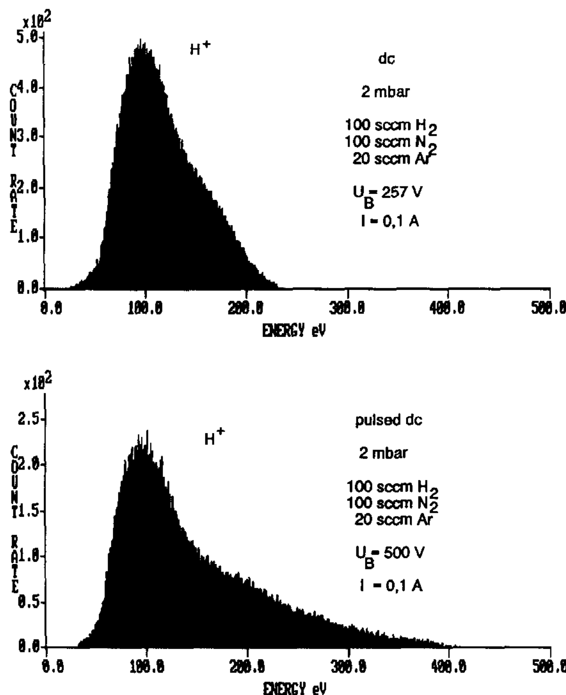

Fig. 3. Energy distribution of H^+ ions in dc and pulsed dc plasmas.

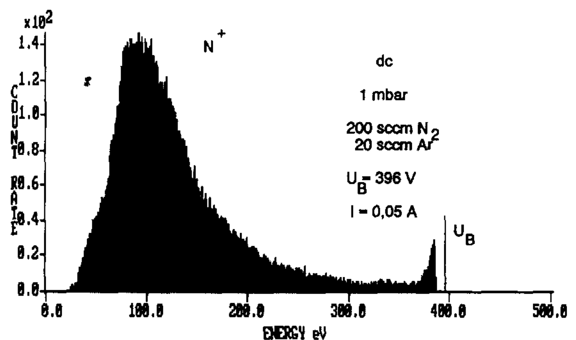

Fig. 4. Energy distribution of N^+ ions demonstrating the small angular acceptance of the two-stage plasma monitor system.

It has been found by Liu et al. [6] that low energy ions arrive at the cathode with a larger average incident angle. In our case only ions striking the cathode nearly perpendicularly are able to pass the two orifices and reach the detector assembly. The angular selectivity of the dual stage system leads therefore to a decreased sensitivity for low energy ions. The observed high energy peak in fig. 4 corresponding to the cathode fall potential is caused by ions penetrating the sheath without suffering any collisions. This sharp peak observed is due to the angular selectivity and not to a higher portion of energetic ions. This problem is hoped to be overcome by mounting an ion transfer optics between orifice 2 and orifice 1.

3.2. Predominant ions

The detected ions were assumed to be formed by different mechanisms: electron-impact ionization of neutrals and heavy-particle encounters. Typical spectra of the ions and the neutral gas composition in a H_2–N_2–Ar plasma are shown in fig. 5. The energy spectra of nearly all of the ions were similar, even those of such ions formed by ion–molecule reactions. But, the H^+ and N^+ energy spectra are characterized by distinct high energy tails.

If hydrogen was added to an Ar plasma the ArH^+ peak appeared at the expense of the Ar^+ ion. Furthermore, H_x^+ ions ($x = 1,2,3$) predominate. This is thought to be due to a reaction between Ar^+ and H_2 forming ArH^+ and H [14]. It has already been shown by Szabo and Wilhelmi [15] that the addition of hydrogen to a nitrogen discharge caused the appearence of N_2H^+ ions, whereas the N_2^+ ion peak diminished.

3.3. Dependence of the ion intensity on the discharge parameters

The electrical input power of a pulsed discharge can be varied by the discharge current as well as by the operating voltage. As it will be discussed below, these two parameters affected the ion kinetics of a discharge in a different manner. It was mentioned earlier, that the average discharge current I and the operating voltage U_B can be chosen independently by varying the pulse width–repetition ratio. Measurements were carried out in H_2–N_2–Ar mixtures. The dependence of the proportionate ion current at the cathode on the average discharge current density is shown in fig. 6. Of course, the absolute ion intensities not shown here increased with increasing discharge current density. The variation in the ion intensities reflects the changes in the neutral gas composition. Obviously, the higher the average discharge current (i.e. the electron density) the higher the formation rate of NH_x. The ionisation energies of NH_x are some eV lower than those of hydrogen or nitrogen. We concluded that NH_x^+ ions were formed by electron-impact ionisation of the respective neutrals. Furthermore, atomic hydrogen created by electron-impact dissociation is consumed by forming NH_x molecules.

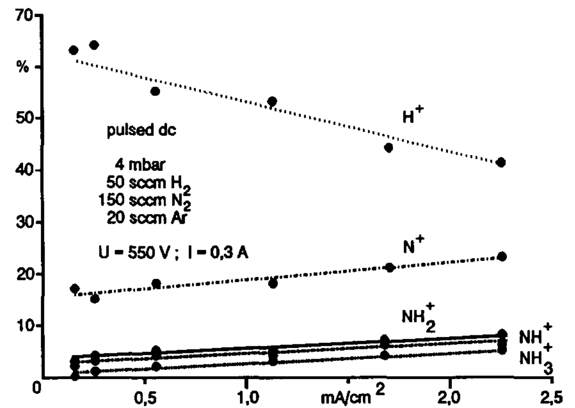

Fig. 6. Ion currents in dependence on the average discharge current.

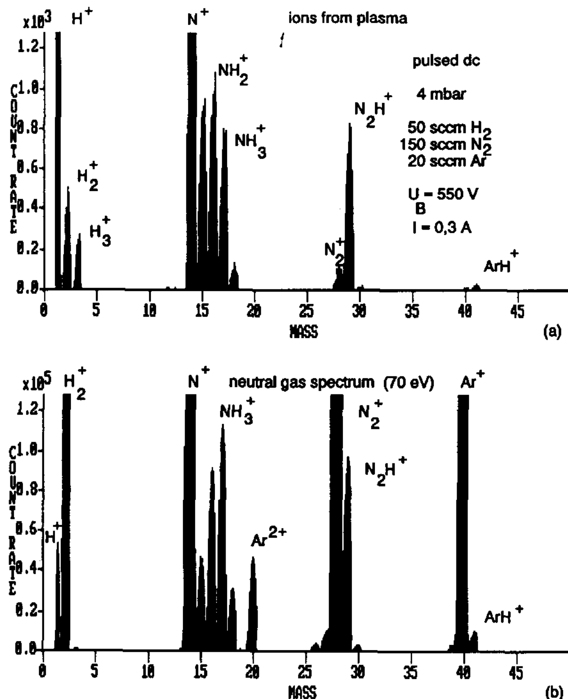

Fig. 5. Spectrum of 100 eV ions extracted from the plasma (a) and neutral gas composition (electron energy 70 eV) (b).

In contrast, when the average current density was kept constant the ion peak intensities were not dependent on the operating voltage. This can be explained by the fact that the average electron temperature is only slightly dependent on the operating voltage at pressures higher than 1 mbar [16].

4. Conclusions

Energy distributions of ions at the cathode of a glow discharge were measured using a two-stage differentially pumped plasma monitor. Different plasma excitation modes (dc, pulsed dc, pulsed ac) were investigated. The main features of the ion energy distributions obtained by computer simulations [8] were experimentally confirmed in principle. Our experiments performed at a pressure of some mbar showed the ions to be more energetic than theoretically predicted. A large amount of ions strike the cathode with energies exceeding the sputtering threshold of many materials. This has to be taken into account in the case of plasma-enhanced CVD or plasma diffusion treatment. Using pulsed dc or pulsed ac plasma excitation, the operating voltage and the average discharge current can be decoupled from each other. Both electrical discharge parameters affected the ion kinetics in a different manner, as it was shown for H_2–N_2–Ar discharges. Quantitative measurements of the ion energy distribution are planned to be carried out after having improved the plasma monitor with respect to its angular acceptance.

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