Mass-resolved ion energy measurements at the grounded electrode of an argon rf plasma

F. J. M. M. Snijders, M. J. M. van Sambeek, G. M. W. Kroesen, and F. J. de Hoog
Eindhoven University of Technology, Department of Physics, P. O. Box 513, 5600 MB Eindhoven, The Netherlands

(Received 6 January 1993; accepted for publication 3 May 1993)

The mass-resolved ion energy distribution (IED) at the grounded electrode has been determined in a 13.56-MHz parallel-plate plasma in argon. The IED is determined of Ar⁺, Ar²⁺, Ar³⁺, ArH⁺, H₂O⁺, and H⁺ for several plasma conditions. At pressures higher than 10 mTorr, collisions in the sheath become important. The IED of Ar⁺ is particularly defined by charge exchange collisions in the sheath while the IED of the other ions shows only features generated by elastic scattering. This is confirmed by Monte Carlo simulations. The measurements clearly show the necessity of simultaneous mass and energy separation, rather than the nonmass-resolved IED reported in the literature.

Radio-frequency (rf) plasmas are widely used in, for instance, the semiconductor industry for dry etching and deposition. Ion bombardment plays a very important role in the effectiveness of these processes. Therefore, it is desirable to know the ion energy distribution (IED) at the electrode, which depends strongly on the rf sheath conditions. Although in the last decade a number of investigations have been done on rf plasma sheaths and also on the IED, the rf sheath is not completely understood.

We have measured the mass-resolved IED at the grounded electrode. The rf plasma which has been investigated is confined in a microwave cavity (see Fig. 1). The cavity has been used to measure the electron and negative ion densities by microwave techniques and is created by extending the largest electrode around the smallest. This letter deals with a 13.56 MHz argon plasma created in a cavity with a large grounded electrode and a times-lengther, ac-coupled driven electrode. The diameter of the driven electrode is 12.5 cm and the electrode gap is 2 cm. The instantaneous voltage drop over the sheath in front of the grounded electrode is equal to the plasma potential. As a consequence of the plasma confinement, the plasma potential is time dependent and varies between 0 and Vrf + Vde, with Vrf the amplitude of the rf voltage and Vde the autobias voltage. The IED at the grounded electrode is rf modulated.

For the mass-resolved IED measurements a quadrupole mass spectrometer (Balzers, QMG311), in combination with a home-built cylindrical mirror energy analyzer, is implemented behind the grounded electrode in a differentially pumped chamber. The pressure in this chamber is kept lower than 10⁻⁶ Torr. In the grounded electrode a small molybdenum plate (diameter 2.5 cm) is situated with an orifice of 40 μm. The pressure conditions are sufficiently low so no modification of the IED is expected when ions pass the orifice. Behind the orifice the ions are focused parallel to the quadrupole axis by an ion lens. After mass selection, the ions are energy selected in the cylindrical mirror analyzer. A slit of 1 mm provides an energy resolution of 1 eV. The resolution of the quadrupole is 0.1 amu. The selected ions are detected by a channeltron and counted by a PC.

The resolution and transmission of the quadrupole and energy selector depend on the kinetic energy of the ions. To have a constant resolution and transmission during a measurement, ions are accelerated or decelerated by the ion lens before entering the quadrupole, so all ions which are detected have the same kinetic energy when passing the mass and energy selectors. Therefore, the reference (=axis) potential of the total system is adjusted when selecting different energies, while the local electric fields in the quadrupole and energy selector remain the same.

As a consequence of the geometry and the voltage of the ion lens, it is only possible to detect ions with a velocity directed nearly perpendicularly to the surface (within a space angle of 4°). From the literature it is known that in low-pressure plasmas the sheath is nearly collisionless and the angular distribution is narrow. The measured IEDs are typically saddle shaped. At higher pressures (> 10 mTorr) collisions in the sheath become important.

In the sheath of an argon plasma we distinguish charge-exchange collisions and elastic scattering. Ions produced in the sheath by charge-exchange collisions start...
with a very small (≈0) kinetic energy and are subsequently accelerated towards the electrode. The angular distribution of these ions, when they reach the electrode, is very narrow and they will all be detected. The IED of these ions shows features (peaks) at a lower energy than the saddle representing the ions which did not collide in the sheath. These peaks are also saddle shaped although at low energy the splitting is too small to be shown experimentally.

When the ions are scattered elastically in the sheath, the angular distribution becomes broader. Only those ions hit the electrode perpendicularly which, by coincidence, lose nearly all their nonperpendicular momentum during their last collision. When we consider a hard-sphere scattering model, this will nearly only happen when the last elastical collision is frontal. Ions which satisfy this condition could also generate low-energy peaks in the IED, just like the ions produced by charge exchange. From Monte Carlo simulations we know that the chance of a last frontal collision is very small and the peaks in the corresponding IED are much smaller than the peaks generated by charge exchange. As a consequence, the IED as measured under these conditions appears to be nearly similar to the one of a collisionless sheath.

The experiments have been performed in an argon plasma, and IEDs are determined for Ar+, Ar2+, and Ar3+ for several pressures and rf powers. There is always some residual water in the reactor which is responsible for the formation of hydrogen-containing ions like ArH+, H2O+, and H3+. Because of the low density of H2O, the hydrogen-containing ions hardly have any influence on the space charge in the plasma and the sheath. Consequently, the electric field in the sheath will be generated completely by the Ar+ ions. Mass-resolved determination offers the possibility to compare the IED of different ions achieved in the same sheath. Because of the low density of the hydrogen-containing ions, the signal-to-noise ratio of the corresponding IED is smaller than in the Ar+ case (when measured with the mass and energy resolution). Ar+ ions have a large cross section for charge-exchange and elastic collisions. At pressures lower than 10 mTorr the IED looks collisionless with only small collisional features, while at higher pressures the IED is complex with large low-energy peaks as shown in Figs. 2(a) and 3(a). The ArH+ ions are only scattered elastically, just like H2O+ and H3+. The measured IED of these ions shows a very well-pronounced saddle [see Figs. 2(b), 3(b), and 4]. The average energy of the saddles of all the different ions is the same (in the same plasma sheath, of course), while the splitting of the saddle appears to be proportional to \sqrt{1/m_i}. At lower powers, down to maximum sheath voltages of 80 V, the averaged energy is equal to half of the maximum sheath voltage. As shown by Kühler et al., the sheath behavior in these cases can be considered purely capacitive, which means that the ion conduction current is negligible compared to the ion-displacement current. At higher powers the sheath behavior becomes more resistive, and subsequently the averaged energy of the IED becomes less than half the maximum sheath voltage.

The IED of ArH+ ions at pressures higher than 10 mTorr show small features at lower energy. These are generated by the elastically scattered ions which bombard the electrode perpendicularly and have lost (nearly) all energy during their last collision. Figure 2(c) shows a Monte Carlo simulation of the IED of ArH+ ions for the same conditions as the measured IED shown in Fig. 2(b). The electric field used in the model was calculated from solutions of particle-in-cell (PIC) simulations and is proved to be close to self-consistency. Trajectories of 150 000 ions entering the sheath at 200 different phases were calculated. The thickness of the space-charge region is varying in time. The maximum sheath thickness is 1.56 mm and the mean free path is 0.8 mm. The collisions are treated as hard-sphere elastic scattering where the collision angle in the mass-centered system is randomly distributed and the total energy and momentum are conserved. This assumption is reasonable due to investigations of Thompson et al., who compared the hard-sphere model to more sophisticated models. The full curve represents the full angular distribution of the IED while the dotted curve represents the IED of the ions which bombard the electrode nearly perpendicularly. The IED of H2O+ and H3+ shows no collisional features. This is because these ions can never lose all their energy when they collide elastically with an...
Ar atom. The chance of these light ions hitting the electrode perpendicularly is very small. Ion-molecule reactions in the sheath, other than reactions with an Ar atom, are negligible due to the low-impurity level as determined by mass spectrometry measurements. Ar$^{2+}$ ions can gain double as much energy when accelerated in the same sheath compared to a singly charged ion, as shown in Fig. 3(c).

We have carried out experiments that confirm the distinct saddle-shaped features of IEDs known from collisionless sheaths. We found irregular structures in the low-energy part of IEDs measured at higher pressures. It is shown that various features of the IEDs can be understood from elastic and charge-transfer collisions. At higher pressures one should be aware of a considerable spread in ion energy at the electrodes in rf discharges.


FIG. 3. IED of (a) Ar$^+$, (b) ArH$^+$, and (c) Ar$^{2+}$. The pressure is 80 mTorr and the maximum sheath voltage ($V_{\text{sheath}} + V_{\text{d}}$) is 90 V.

FIG. 4. IED of (a) H$_2$O$^+$ and (b) H$_3^+$ for the same conditions as described in Fig. 3.

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