

XXII International Conference on Phenomena in Ionized Gases

Hoboken, USA July 31st - August 4th, 1995

Editors: K. H. Becker, W. E. Carr, and E. E. Kunhardt

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Influence of electrode material on measured ion kinetic-energy distributions in radio-frequency discharges

R. J. Van Brunt, J. K. Olthoff, and S. B. Radovanov^a

National Institute of Standards and Technology, Gaithersburg, MD 20899

The measurement of ion kinetic energies is important for understanding processes that occur in discharges, e.g., the influence of ions on the etching of semiconductor materials in plasma reactors.¹ Direct measurements of ion kinetic energies striking surfaces exposed to the discharge requires sampling through an orifice in a surface. Difficulties with ion sampling through a small aperture, manifested by errors or distortions in measured ion kinetic-energy distributions (IEDs), have been encountered in previous investigations of both dc^{2,3} and radio-frequency (rf)^{4,5} discharges. The errors are usually most significant at relatively low ion energies.

Previous measurements in our laboratory of IEDs for ions sampled through a 0.1-mm hole in a grounded, aluminum electrode for rf discharges in argon⁴ showed evidence of reduced detection efficiency (discrimination) for low energy ions (< 10 eV), and apparent shifts in the measured ion energies for plasmas generated in other gases. It has been suggested² that surface charging at or near the sampling orifice can cause both discrimination and energy shifts. The existence of an insulating, or partially insulating, layer of aluminum oxide on the surface of an electrode allows the possibility of surface-charge accumulation. In the present work, IEDs were measured at both aluminum and 304 stainless-steel grounded electrodes with 0.1 mm sampling orifices in rf plasmas generated in argon and oxygen.

The rf (13.56 MHz) discharges were produced in a parallel-plate, capacitively-coupled GEC rf Reference Cell⁶ with 10.2-cm diameter electrodes spaced 2.5 cm apart. The grounded electrode assembly was modified to house a quadrupole mass spectrometer preceded by an ion energy analyzer.⁷ The aluminum and stainless-steel electrodes were cleaned and polished prior to use in the discharge. The IEDs were measured under ostensibly identical plasma conditions with each electrode as specified by applied voltage, pressure, and flow. Changing the grounded electrode from aluminum to stainless steel did not significantly affect the measured voltage and current waveforms.

Figure 1a shows a comparison of kinetic-energy distributions measured for Ar⁺ ions from argon discharges using grounded electrodes made of stainless steel and aluminum. The results obtained for stainless steel are more consistent with theoretical models,⁸ and with measurements made using retarding potential analyzers,^{5,8} that indicate an increasing ion signal down to 0 eV for comparable conditions. The results for aluminum would, therefore, appear to be more significantly affected by low-energy discrimination.

The occurrence of energy shifts is demonstrated by the O₂⁺ IEDs shown in Fig. 1b for an oxygen discharge at 8.0 Pa. In the case of the aluminum electrode, the IED exhibits peaks that are approximately 2 eV lower in energy than the corresponding peak observed with the stainless-steel electrode. Moreover, the results for the aluminum electrode show significantly more ion signal below 0 eV than those for stainless-steel. We

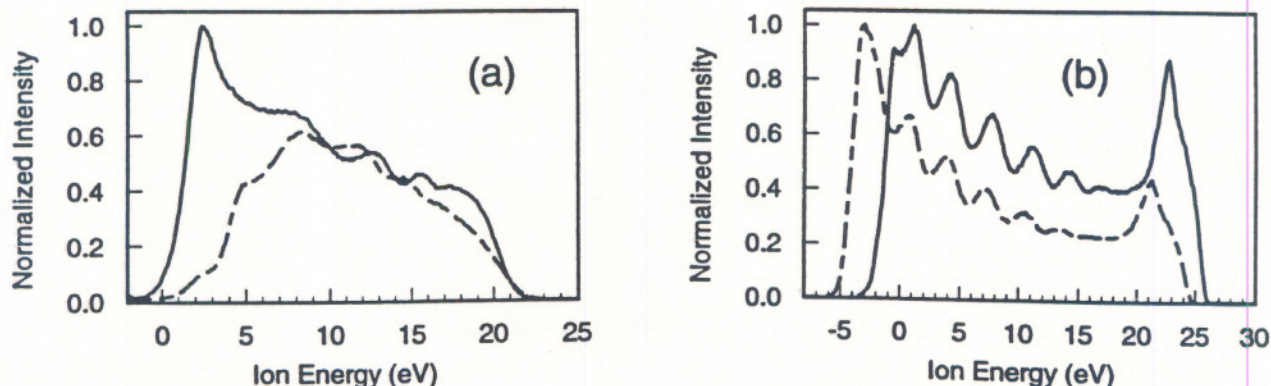


Figure 1. Kinetic energy distributions for (a) Ar⁺ ions sampled from argon plasmas at 13.3 Pa, and (b) O₂⁺ ions sampled from oxygen plasmas at 8.0 Pa with stainless-steel (solid lines) and aluminum (dashed lines) grounded electrodes for an applied rf voltage of 200 V.

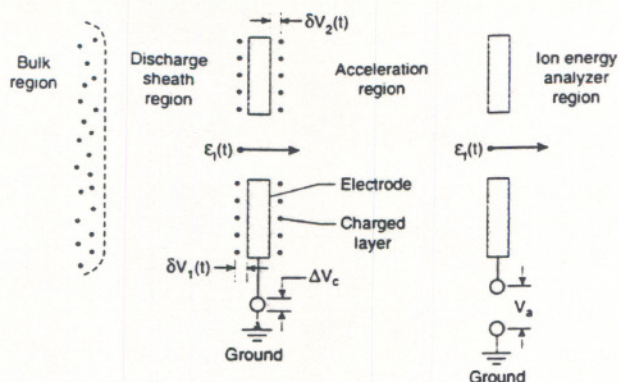


Figure 2. Diagram showing different regions of ion acceleration from the plasma glow to the analyzer entrance aperture.

have observed these apparent shifts in ion energies with aluminum electrodes for all ions sampled from rf discharges in oxygen, nitrogen, helium, hydrogen, and in various gas mixtures, over a wide range of plasma conditions. By contrast, the IEDs obtained with clean stainless-steel electrodes tend to exhibit little or no apparent energy shift.

The cause of low-energy discrimination as seen in Fig. 1a for Ar^+ from an aluminum electrode is not clear but could result from defocusing of ions outside of the narrow acceptance angle ($\sim 3^\circ$) of the energy analyzer-mass spectrometer. It is difficult to understand why defocusing is more significant for aluminum than stainless steel unless there is a difference in perturbation of the local electric field near the sampling aperture for the two materials such as might result from different charge retention properties of the surfaces. Surface charging of aluminum is expected to be greater than for stainless steel since an oxide coating can form on the aluminum surface.

The apparent shift in energy as seen in Fig. 1b might be explained by the existence of charge on the surfaces surrounding the sampling aperture. The influence of electrode surface charge on either side of a sampling aperture is illustrated in Fig. 2. When ions enter the aperture they have, at some time t in the rf cycle, a kinetic energy $\epsilon_i(t)$. After passing through the aperture, the ions can experience an energy shift $e[\delta V_1(t) + \delta V_2(t)]$, where $e\delta V_1(t)$ and $e\delta V_2(t)$ are respectively the charged surface-to-ground potential differences on the "front" and "back" sides of the aperture at time t . The ions that enter the energy analyzer region after acceleration then have a final energy given by:

$$\epsilon_f(t) = \epsilon_i(t) + eV_a + e[\delta V_1(t) + \delta V_2(t) + \Delta V_c] \quad (1)$$

where V_a is the applied acceleration voltage and ΔV_c is a contact potential. The term in brackets is an error in the recorded energy due to surface charge and contact potential.

The present results suggest that IEDs measured through an aperture in a clean stainless-steel electrode are more likely to represent the true distributions than those measured using an aluminum electrode. Regardless of what type of electrode is used, the present results provide evidence for questioning the assumption that an aperture through which ions are sampled in a discharge can be treated as an equipotential region.

^aPresent address: Dept. of Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, NM 87131

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