

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

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Evidence is presented for a significant influence of electrode surface material and condition on the measurement of the kinetic energies of ions sampled from discharges through an orifice in the electrode. Significant differences in ion energy shifts and/or discrimination of low-energy ions are found using aluminum and stainless-steel electrodes in a radio-frequency (rf) discharge cell. It is argued that the observed differences in energy shifts may be attributable in part to differences in charging of oxide layers on the electrode surface around the sampling orifice. © 1995 American Institute of Physics.

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. In parallel-plate, rf glow discharges, ions have been sampled through both the grounded²⁻⁵ and powered electrode^{6,7} and with probes inserted into the side of the discharge volume.^{8,9} Difficulties with ion sampling through a small aperture, manifested by errors or distortions in measured ion energy distributions (IEDs), have been encountered in previous investigations of both dc^{10,11} and rf^{8,12} 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 an rf discharge in argon⁸ 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 suggested¹⁰ 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, oxygen, and a mixture of helium and nitrogen at different gas pressures.

The rf discharges were produced in a parallel-plate, capacitively-coupled rf (13.56 MHz) discharge cell (a GEC rf Reference Cell¹³) 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.³ Measurements of the voltage and current waveforms at the surface of the powered electrode were made in order to define the plasma conditions.¹⁴ All data presented here were obtained for an applied peak-to-peak rf

voltage (V_{pp}) of 200 V. 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 material did not significantly affect the measured voltage and current waveforms, i.e., any change was less than the observed scatter in the voltage and current amplitudes measured over several months. This indicates that observed differences in the IEDs using the two types of electrodes are due primarily to differences in the conditions of ion sampling rather than differences in discharge characteristics. Only the grounded electrode was changed to stainless steel, since it has been documented that GEC cells with stainless-steel powered electrodes exhibit current-voltage characteristics¹⁴ and electron densities¹⁵ that differ from those for an aluminum powered electrode.

Figure 1 shows a comparison of kinetic-energy distributions measured for Ar^+ ions from argon discharges at a pressure of 13.3 Pa using stainless-steel and aluminum electrodes. The IED obtained with the aluminum electrode exhibits a maximum near 8 eV with a decreasing signal down to 0 eV. By contrast, the IED measured with the stainless steel electrode exhibits a maximum near 2 eV. The results obtained for stainless steel are more consistent with theoretical models,¹⁶ and with measurements made using re-

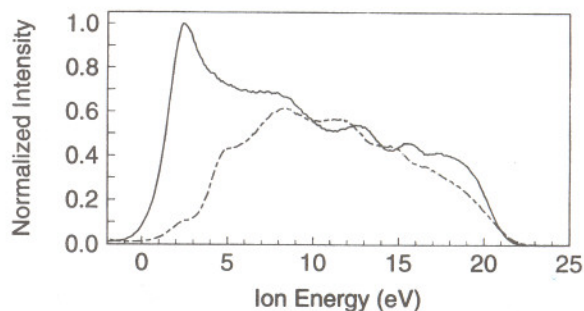


FIG. 1. Kinetic energy distributions for Ar^+ ions sampled from argon plasmas with stainless-steel (solid line) and aluminum (dashed line) grounded electrodes at a pressure of 13.3 Pa and V_{pp} = 200 V.

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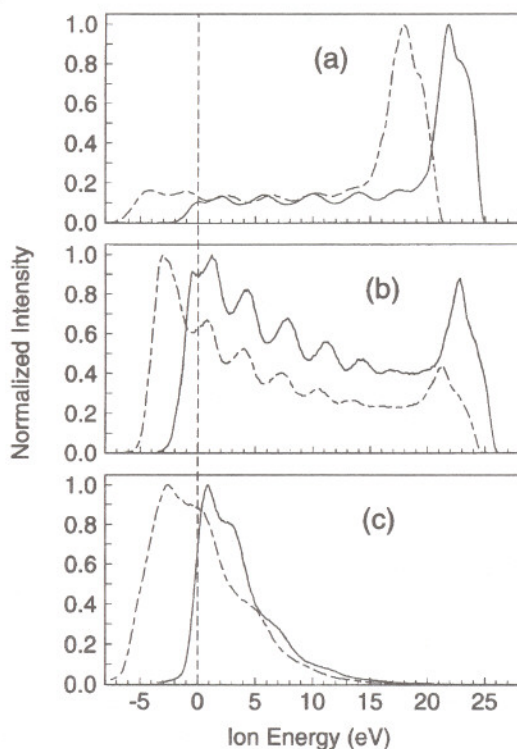


FIG. 2. Kinetic energy distributions for O_2^+ ions sampled from oxygen plasmas at a pressure of (a) 4.0 Pa and (b) 8.0 Pa, and N_2^+ ions sampled from a 50/50 helium-nitrogen plasma at a pressure of (c) 33.3 Pa with $V_{pp} = 200$ V. IEDs are shown for both stainless-steel (solid lines) and aluminum (dashed lines) grounded electrodes.

tarding potential analyzers,^{12,16} 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 fact that the observed maximum ion energies (~ 22 eV) are nearly the same for both electrodes suggests that significant energy shifts seen for other gases reported below are not evident in the case of argon.

The occurrence of energy shifts is demonstrated by the O_2^+ IEDs shown in Figs. 2(a) and 2(b) for an oxygen discharge at 4.0 Pa and 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 peaks 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. A similar shift is shown in Fig. 2(c) for N_2^+ ions sampled from a plasma generated in a 50/50 mixture of helium and nitrogen at 33.3 Pa. We have observed these apparent shifts in ion energies with aluminum electrodes for *all* ions from O_2 , N_2 , He, H_2 , SF_6 , and in various mixtures of these gases, as well as in mixtures with Ar, over a wide range of rf plasma conditions. By contrast, the IEDs obtained with clean stainless-steel electrodes tend to exhibit little or no apparent energy shift. The extent of the ion signal below 0 eV for the stainless-steel electrode is, in most cases, close to that expected from the energy resolution of the analyzer (1.5 eV full width-at-half maximum).

All of the IEDs presented in Figs. 1 and 2 for the

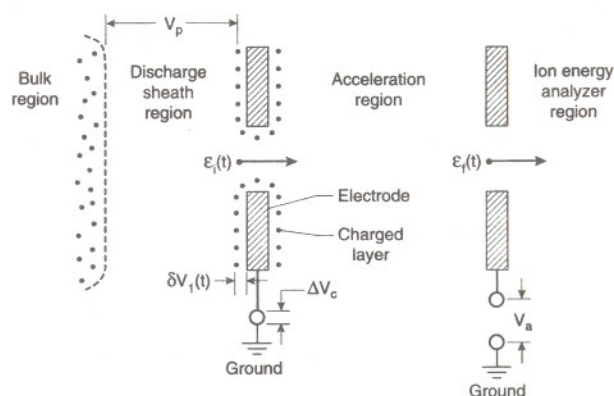


FIG. 3. Diagram showing different regions of ion acceleration from the plasma bulk (glow) to the analyzer entrance aperture.

stainless-steel electrode were obtained during the first 10 hours of plasma operation after a cleaned and polished electrode was installed. For longer discharge operation, the shapes of the measured IEDs using the stainless-steel electrode slowly changed until they resembled the IEDs obtained with the aluminum electrode. It is speculated that this change resulted from deposition of sputtered aluminum onto the grounded electrode as observed by Ganguly and Bletzinger¹⁷ for hydrogen discharges in a GEC cell. Additional evidence for sputtering of aluminum was obtained from tests made using stainless-steel electrodes that had been repolished after being exposed to the discharge for more than 10 hours. Ions sampled through repolished electrodes exhibited the same energy distributions as seen using "new" stainless-steel electrodes.

The cause of low-energy discrimination as seen in Fig. 1 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 effects of oxide formation on aluminum surfaces has been observed in electrical measurements from argon discharges containing oxygen that display a hysteresis effect when gas-phase oxygen is added and then removed from an argon discharge.¹⁴

The apparent shift in energy as seen in Fig. 2 might be explained by the existence of charge on the surfaces surrounding the sampling aperture. The possible influence of electrode surface charge is illustrated in Fig. 3. An ion is assumed to enter the aperture with a kinetic energy $\epsilon_i(t)$ at some time t in the rf cycle, which is also the energy that it would have if it had struck the electrode surface. The ions that enter the energy-analyzer region after acceleration then have an energy given by

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

where V_a is the acceleration voltage *relative to ground* and $\delta V_1(t)$ and ΔV_c are the shifts of the electrode potential *relative to ground* due respectively to phase-dependent surface charge and a constant contact potential. The term in brackets represents an error in the *recorded* kinetic energy, $\varepsilon_f(t)$. Under stationary conditions, surface charge density may vary periodically with rf phase, and this would imply that the energy shift need not be the same for all energies.¹⁸ The maximum ion energy that defines the upper limit of the IED is determined by the mean (time-averaged) plasma potential, denoted by V_p in Fig. 3. If V_p remains constant but adjusts to the presence of electrode surface charge by shifting to a value $\delta V_1(t) + \Delta V_c$ relative to ground, then the recorded maximum ion energy will also shift by this amount. Based on Eq. (1), "negative" ion energies are recorded if $[\delta V_1(t) + \Delta V_c] < 0$.

Negative recorded energies are also possible if a significant fraction of the ions is created in the acceleration region of the analyzer. However, there is no evidence to support this possibility because (1) the negative shifts become progressively greater *during* deposition of aluminum on a stainless-steel electrode; (2) no significant dependences on V_a , ion species, or discharge cell pressure are observed (see Fig. 2); (3) previous estimates³ indicate that an insufficient number of ions will experience collisions in the analyzer region for the conditions considered here to produce the observed effect; and (4) the profiles (structure) of the IEDs for all ions are not significantly modified when negative shifts occur.

The smaller apparent energy shift in the case of argon may be related to the kinds of ion-surface interactions that occur in this case that influence surface composition and the distribution of surface charge at the aperture site.¹⁹ Other factors to be considered in comparing aluminum and stainless steel are differences in secondary electron emission, and gas adsorption. It is equally interesting that discrimination against low-energy ions observed for argon was not as clearly evident for other gases that produce large energy shifts (see Fig. 2).

The present results suggest that IEDs measured through an aperture in a clean stainless-steel electrode are more representative of the ions striking the electrode than those measured using an aluminum electrode. Regardless of the electrode used, evidence is provided here for questioning the assumption that an aperture through which ions are sampled in a discharge can be treated as a grounded equipotential region.

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