

Negative ion emission from a stainless steel surface due to positive ion collisions

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Absolute yields of negative ions and secondary electrons resulting from positive ions impacting a stainless steel surface have been determined as a function of the impact energy. The surface conditions range from those commonly found *in situ* for discharge electrodes to a surface free of any adsorbate. The implications of these findings to discharge modeling are discussed. © 1998 American Institute of Physics. [S0021-8979(98)00115-7]

The importance of ion-induced secondary electron emission from metallic surfaces in gas discharges has been well recognized. Indeed, the Townsend breakdown criterion in a uniform field gap of separation d in a nonelectron-attaching gas can be written as $\gamma(e^{\alpha d} - 1) = 1$, where α is the ionization coefficient of the gas and γ is the coefficient of secondary electron emission induced by positive ion collisions with the cathode.¹ This equation indicates that a dc discharge cannot be self-sustained if $\gamma = 0$. In a capacitively coupled rf discharge, the secondary electrons resulting from ion bombardment of electrodes are accelerated through the sheath potential into the bulk of the plasma. As the discharge voltage increases, ionization due to such secondary electrons can become dominant and lead to the so-called α - γ mode transition. These two modes differ dramatically in light emission and electron energy distributions.²

In contrast to the well-recognized importance of secondary electron emission, negative ion emission is largely neglected in the description of discharges. If ion and electron emissions from electrodes are comparable, then such an omission may compromise the accuracy of discharge simulations. For example, recent model simulations of capacitively coupled rf oxygen discharges at 13.6 MHz by Shibata *et al.*³ predicted that the O^- density would exceed that for O_2^- by several orders of magnitude. In fact, however, O_2^- and O^- concentrations are observed⁴ to be comparable in rf plasmas under conditions similar to those used for the simulations found in Ref. 3. This apparent discrepancy may be due in part to the omission of secondary negative ion emission in the simulations.

Recent studies on secondary electron and negative ion emission from well characterized elemental metallic surfaces^{5,6} have illustrated that the emission of negative ions can be comparable to that for electrons for impact energies common to discharge environments. These recent results also show that the emission of both electrons and negative ions increases dramatically with increasing oxygen coverage and, in fact, requires adsorbed oxygen as a precursor for

impact energies in the neighborhood of a few hundred eV. The purpose of this communication is to report on an extension of those measurements to stainless steel for surface conditions ranging from those commonly found *in situ* for discharge electrodes to a surface free of adsorbates.

The experimental ultrahigh vacuum (UHV) apparatus used in the present study has been described in detail elsewhere.⁵ Briefly, an alkali-metal ion gun provides the primary beam of Na^+ as the probe beam. The ions impact the surface at an angle of 60° with respect to the normal. Negatively charged secondary products ejected from the stainless steel surface are focused and collected by the extraction lens stack. In order to distinguish electrons from anions, a small electromagnet attached to the extraction stack is used to sweep the electrons from the extracted negative products without appreciably affecting the trajectories of the negative ions. A 250 nm ultraviolet (UV) source can be focused on the surface and the resulting kinetic energy spectra of the photoelectrons may be used to determine the surface work function. An electrostatic energy analyzer is employed to measure the kinetic energies of the products. Mass analysis of the sputtered anions is obtained by pulsing the Na^+ beam and collecting the negative products in a time-of-flight (TOF) spectrum. The "zero" of the TOF scale is easily identified by the secondary electron signal. Prior to insertion into the chamber, the preparation of the surface (a ribbon of 302 stainless steel) is limited to mechanical polishing and alcohol cleaning. We shall denote this as "T," a technical surface. The ribbon may subsequently be cleaned under UHV conditions by resistive heating (600 °C for 15 min) or by a combination of two consecutive cycles of heating as above followed by conventional argon ion sputter cleaning. We shall denote these latter two surface conditions as "H," heated and "S," sputter cleaned.

Shown in Fig. 1(a) is a TOF mass spectrum of the secondary negative ions that are sputtered from the technical stainless steel surface for an impact energy of 250 eV. It is interesting to note that the O_2^- signal is larger than that for O^- . The H^- signal suggests the presence of adsorbed water on the surface, and the Na^- signal (about 10% of the total

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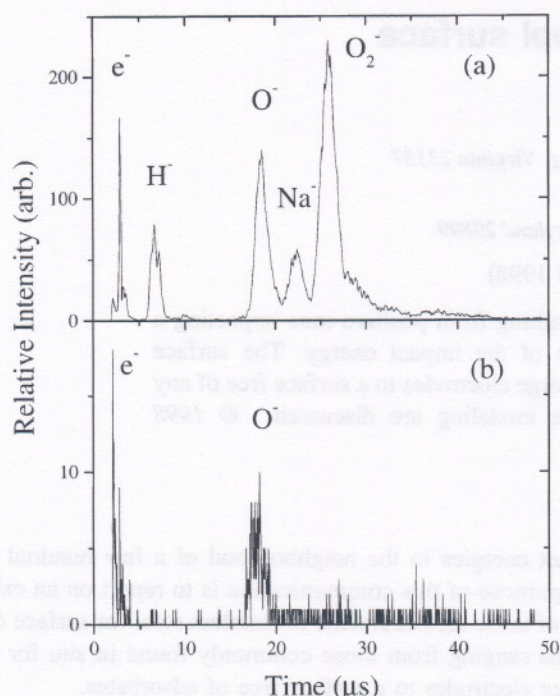


FIG. 1. TOF mass spectrum of the secondary negative ions sputtered with 250 eV Na^+ ions from (a) a technical stainless steel surface and (b) the sputter-cleaned stainless steel surface.

anion emission) indicates some sodium accumulation on the T surface. If the surface is cleaned with a single cycle of heating and sputter cleaning, the only negative ion species remaining is O^- , as is seen in Fig. 1(b).

Absolute yields (the number of emitted particles per incident ion) for both electrons and anions are shown in Fig. 2 as a function of ion impact energy for the three surface conditions. The estimated uncertainty for the yield measurements is 10%. For the technical surface, anion emission is quite large and exceeds that for electron emission for almost the entire energy range of the experiment. For surface condition H the ion yield decreases considerably, but still exceeds that of electrons for impact energies below 250 eV. It is only after condition S is achieved that both the electron and ion emission approach zero. It is well known that the presence of alkali metals on a surface can alter both the work function and the emission properties of a metallic substrate.^{7,8} With the exception of the technical surface, the integrated sodium dose to the surface is quite small and there is no appreciable sodium accumulation on the surface during the course of the yield measurements. This is verified by a TOF spectrum taken for surface condition H (not shown in Fig. 1) which reveals no secondary Na^- or H^- implying that heating removes adsorbed sodium and water. Kinetic energy spectra of 250 nm-generated photoelectrons reveal that the work function is constant (4.8 ± 0.1 eV) as the surface conditions are varied between H and S. The large variation in yields observed as the surface conditions are altered is not due simply to an adsorbate-altered work function.

It is clear that secondary electron and anion emission, initiated by ion impact, can be quite large and depend very strongly upon the surface conditions for a stainless steel sur-

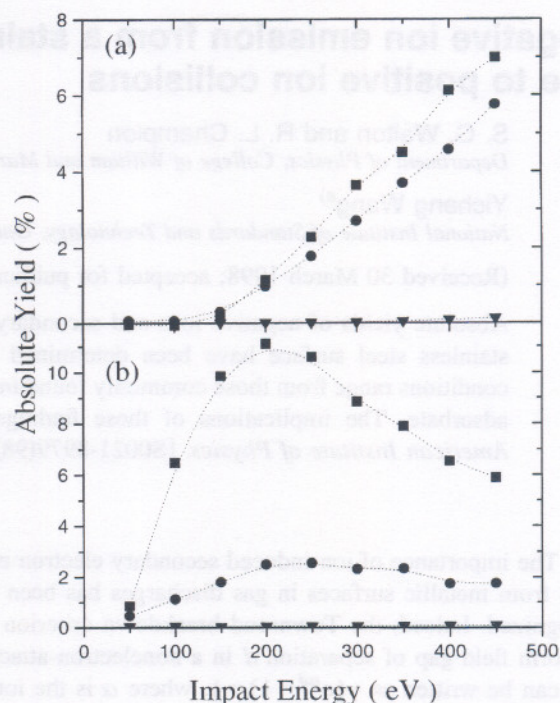


FIG. 2. (a) Absolute secondary electron and (b) negative ion yields as a function of Na^+ impact energy. Squares are for a technical stainless steel surface; circles are for the stainless steel surface cleaned by resistive heating; triangles are for the sputter-cleaned stainless steel surface.

face. The absolute yields can be large even for a surface which has been cleaned by heating. Moreover, the probability for anion emission—predominately O^- and O_2^- —is found to exceed that for electron emission for a large range of impact energies. This finding could have significant implications in modeling rf discharges in gases typically used in the semiconductor industry. A sound understanding of various negative ion formation mechanisms is essential in understanding discharges in electronegative gases. For example, negative ions are known to play a dominant role in particulate formation.⁹ Also, the density of negative ions in an O_2 plasma exceeds that for electrons by orders of magnitude.³ A large secondary negative ion yield from electrode surfaces clearly influences the charge balance and the electrical characteristics of the discharge in such a gas.

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