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Plasma-assisted catalytic ionization using porous nickel plate

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Hydrogen atomic pair ions, i.e., H^+ and H^- ions, are produced by plasma-assisted catalytic ionization using a porous nickel plate. Positive ions in a hydrogen plasma generated by dc arc discharge are irradiated to the porous plate, and pair ions are produced from the back of the irradiation plane. It becomes clear that the production quantity of pair ions mainly depends on the irradiation current of positive ions and the irradiation energy affects the production efficiency of H^- ions. © *2011 American Institute of Physics*. [doi:10.1063/1.3637463]

INTRODUCTION

Hydrogen negative-ion production mechanisms can be classified in terms of the electron source.[1] In the surface effect, an electron at the Fermi level in the conduction band of a metal shifts by tunneling to the electron affinity level of an atom or molecule approaching the metal surface. The probability of an electron shift is increased as the effective work function of the metal surface decreases. Such an electron shift occurs in particle reflection and sputtering phenomena. Cesium has the lowest work function of all elements. A small admixture of cesium vapor in a hydrogen discharge significantly improves negative-ion production and decreases the current of coextracted electrons.[2–4] However, the use of cesium complicates the ion source operation and requires the careful stabilization of cesium injection and discharge parameters. There have been many attempts to develop negative-ion sources with acceptable negative-ion beam emittance but without a cesium admixture. In volume production, plasma electrons are the source of electrons.[5,6] A highly vibrationally excited hydrogen molecule effectively captures a low-energy plasma electron to form a negative ion through dissociative electron attachment. However, there is a relatively low current density of negative ions in volume production.

Hydrogen atomic pair ions, i.e., H^+ and H^- ions, are the lightest ions and have high response frequencies to electromagnetic fields. To generate a pair-ion plasma[7–9] consisting of only pair ions, the production of equal quantities of H^+ and H^- ions and the absence of impurities such as electrons and other ions are required. It is difficult to satisfy these requirements in surface production with a cesium admixture or in volume production. To overcome this difficulty, we have proposed a plasma-assisted catalytic ionization method.[10–12]

In our previous work, a Penning-ionization-gauge discharge plasma was used for positive-ion irradiation of a porous catalyst. Both the irradiation energy and the flux of positive ions depended on the discharge power. We found that the irradiation energy should be controlled independently of the irradiation flux. In this paper, the dependence of the production properties of the pair ions on the irradiation energy in the case of using a porous nickel (Ni) plate as a catalyst is discussed.

EXPERIMENT

A hydrogen plasma is generated by a dc arc discharge between filament cathodes and a wall anode in a cuboidal chamber with a cross section of 25 cm × 25 cm, i.e., a bucket plasma source. The cathodes are four horseshoe tungsten filaments of 0.7 mm diameter and 15 cm length, which are biased at a discharge voltage of $V_d = -70$ V, at which the plasma density is maximized. The plasma generated in a field-free region is surrounded by line-cusp magnetic fields near the grounded chamber wall. The diffusion of the plasma to the wall is thus reduced, resulting in the highly efficient generation of a uniform plasma. Figure 1 shows a schematic diagram of the experimental setup.

A commercially available Ni porous plate (CELMET, Sumitomo Electric Toyama Co., Ltd.) with a porous body of 22–24 cells/cm, a pore size of 0.45 mm, a thickness of 1.4 mm, a specific surface area of 5800 m^2/m^3, and a porosity of 96.6% is used as a catalyst. The porous catalyst is biased at a dc voltage of V_{pc}. The irradiation current applied to the porous catalyst is measured. Since the circular irradiation area is 19.6 cm^2 (diameter of 5 cm) and the other electrode is covered with a mica plate, the irradiation current density J_{ir} can be obtained. The porous plate is located at $z = 0$ cm, the discharge section corresponds to the region $z < 0$ cm, and the pair-ion production section corresponds to the region $z > 0$ cm. Plasma parameters are measured using Langmuir probes at $z = -7$ cm and 3 cm. The hydrogen pressure in the source during operation is about 0.2 Pa.

The hydrogen plasma in the region $z < 0$ cm is generated at a discharge power of 700 W. The probe characteristics are measured at $z = -7$ cm to obtain the plasma parameters. Positive ions are accelerated up to $e(\phi_s - V_{pc})$ (eV) in the sheath formed in front of the porous plate, where ϕ_s is the plasma potential and $V_{pc} < 0$ V. The dependences of the irradiation energy of positive ions $e(\phi_s - V_{pc})$ and the irradiation current density J_{ir} on V_{pc} are shown in Fig. 2. When V_{pc} is changed between -1000 V and $+50$ V, the plasma density, electron temperature, and ϕ_s remain approximately constant at 3×10^{11} cm^{-3}, 10 eV, and $+20$ V, respectively. The irradiation energy is proportional to V_{pc} because of constant ϕ_s. J_{ir}, which depends on plasma density, remains almost constant when V_{pc} < -100 V. On the other hand, J_{ir} rapidly decreases when V_{pc} increases to above -100 V because of the superimposed

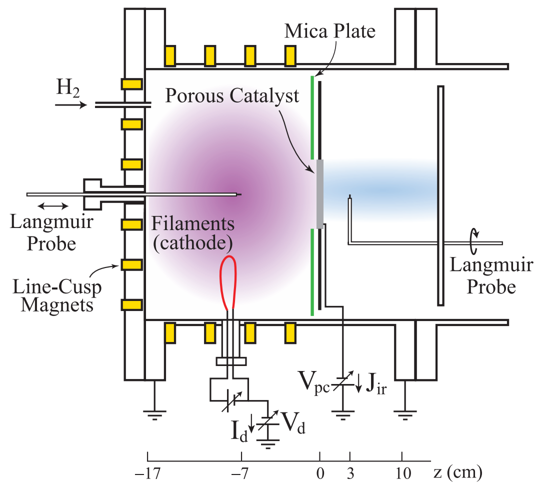

FIG. 1. (Color online) Diagram of experimental setup. Hydrogen plasma generated in a bucket source is irradiated to a Ni porous catalyst. Hydrogen atomic pair ions are produced from the back of the irradiation plane by plasma-assisted catalytic ionization.

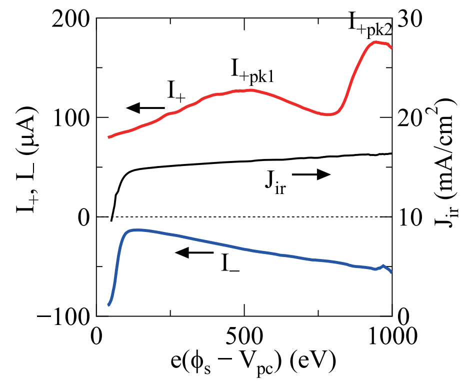

FIG. 3. (Color online) Probe saturation currents of positive and negative ions and the irradiation current density as functions of the irradiation energy.

current of electrons. Therefore, the irradiation energy can be controlled by adjusting V_{pc} to enable a constant irradiation current density when $V_{pc} < -100$ V.

Under positive-ion irradiation, pair ions are produced and an ionic plasma is generated in the region $z > 0$ cm. The positive- and negative-saturation currents of the probe, I_+ and I_-, are obtained at probe bias voltages of -120 V and $+120$ V, respectively. The dependences of $I_\pm$ and J_{ir} on the irradiation energy are shown in Fig. 3. The thermal cathodes are biased at $V_d = -70$ V, electrons can reach the porous plate when $V_{pc} \geq V_d$, and fast electrons of corresponding to the tail component in the Maxwellian distribution can also reach the plate when $V_{pc} > -100$ V. I_- is large when $V_{pc} > -100$ V because part of the irradiated electrons can pass through the porous plate without termination on the plate surface. Positive ions are only irradiated when $V_{pc} < -100$ V; thus, the irradiation energy is $e(\phi_s - V_{pc}) > 120$ eV.

The current ratio I_-/I_+ is less than 1 when $e(\phi_s - V_{pc}) > 120$ eV, indicating that the ionic plasma comprises only positive and negative ions without electrons. I_- increases proportionally with the irradiation energy under only positive-ion irradiation; that is, the production quantity of negative ions increases. I_+ also tends to increase with the irradiation energy, but there are some peaks at various different irradiation energies. These peaks only appear when the catalyst surface is in a state of activation. Furthermore, both I_+ and I_- increase proportionally with J_{ir}, and the production quantity of pair ions increases proportionally with the irradiation flux. J_{ir} can be varied by adjusting the discharge power because the plasma density in the region $z < 0$ cm depends on the power. The dependence of the peak energies on J_{ir} is shown in Fig. 4. There are at least two peaks at a given irradiation current density. The peak energies increase with J_{ir}. The peaks are a distinctive production property of positive ions and do not appear in the production of negative ions. It is not known exactly at this stage why the peak energies that depend on the irradiation current density exist.

The dependences of the normalized probe saturation current of negative ions I_- and the irradiation current density J_{ir} on the discharge power are shown in Fig. 5, where I_- and J_{ir} are normalized by their values at $P_d = 100$ W. I_- is increased by a factor of 1.85 at $P_d = 485$ W compared with its value at 100 W, and J_{ir} is increased by a factor of 2. The incremental modulus of I_- for J_{ir} is $\Delta I_-(J_{ir}) = 0.85$. As the same of Fig. 5, the dependences of the normalized I_- and J_{ir} on the irradiation energy are shown in Fig. 6, where I_- and J_{ir} are normalized at $e(\phi_s - V_{pc}) = 150$ eV. I_- and J_{ir} are

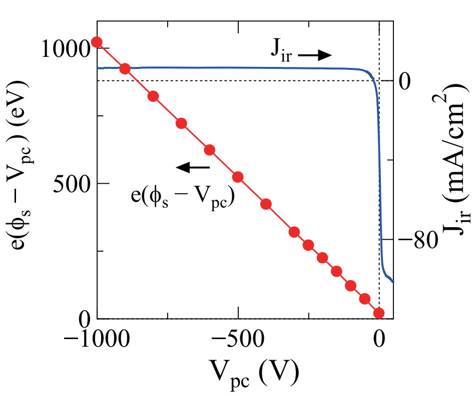

FIG. 2. (Color online) Dependences of the irradiation energy and the current density of positive ions on the dc bias voltage of the porous catalyst.

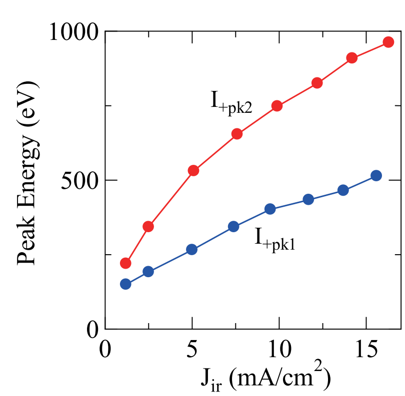

FIG. 4. (Color online) Dependence of peak energies appearing in positive-ion production on the irradiation current density.

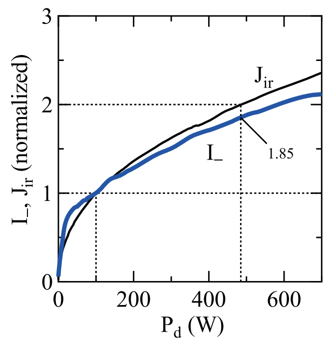

FIG. 5. (Color online) Normalized probe saturation current of negative ions and the irradiation current density as functions of the irradiation energy.

increased by factors of 1.55 and 1.04 at $e(\phi_s - V_{pc}) = 300$ eV compared with their values at 150 eV, respectively. The incremental moduli of I_- and J_{ir} for the irradiation energy are 0.55 and 0.04, respectively. The incremental modulus of I_- for the irradiation energy considering the compensation of J_{ir} increment is $\Delta I_-(e(\phi_s - V_{pc})) = 0.52$. The irradiation current density has a stronger effect on the production quantity of negative ions than the irradiation energy. The value of I_-/I_+ reflects in the production balance between positive and negative ions. On the whole, I_-/I_+ tends to increase in proportion to the irradiation energy, even though I_-/I_+ has peaks due to the I_+ peaks. Therefore, the irradiation energy affects the production efficiency of negative ions.

DISCUSSION

The surface production mechanism of pair ions on a porous catalyst is considered to be completely different from the conventional mechanism of surface production, which is based on contact ionization, i.e., the electronic transition of metals with low work functions. Hydrogen atoms, produced by dissociative adsorption, are covalently bonded with metal atoms on the surface, and can easily move along the surface, i.e., surface migration occurs. Dissociative adsorption and surface migration on catalysts are well-known fundamental phenomena. Hydrogen atoms migrate along the pore surface in the porous catalyst to the back of the irradiation plane.

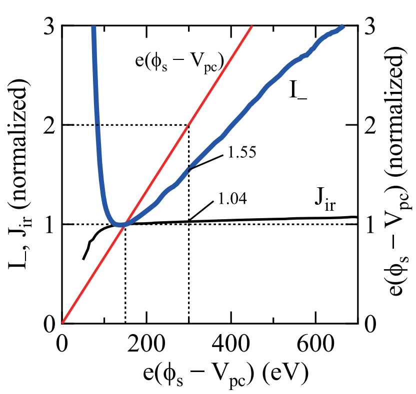

FIG. 6. (Color online) Normalized probe saturation current of negative ions, the irradiation current density, and the irradiation energy as functions of the irradiation energy.

If hydrogen atoms on the back surface are provided with sufficient energy, they can be charged and detach from the surface in face of image force as H^+ or H^- ions. In the case that two shared electrons shift to the surface metal atoms during desorption, H^+ ions are produced. H^- ions, on the other hand, are produced when the electrons shift to hydrogen atoms. Desorption ionization in the gaseous phase is known to occur in laser desorption/ionization.[13,14] When the kinetic energy of irradiated positive ions is partially transferred to hydrogen atoms on the back surface, desorption ionization occurs. The energy required for desorption ionization is much higher than the thermal energy supplied from the surface metal atoms. H^+ and H^- ions are not produced without the irradiation of positive ions. Moreover, the work function of Ni is 5.15 eV, which is relatively high.[15] The contact-ionization probability of H^- ions is infinitesimal. The effect of catalytic activity on hydrogen is important here, and the work function does not affect the ionization. Negative ions are produced from the irradiation plane in conventional converter-type production based on an electronic transition, whereas fast electrons and positive ions promote collisional detachment. It is highly beneficial that pair ions are produced from the back of the irradiation plane, because the production can prevent collisional detachment. We refer to this process involving positive-ion irradiation, dissociative adsorption, surface migration, and desorption ionization as plasma-assisted catalytic ionization.

The production quantity of positive ions from the catalyst surface is greater than that of negative ions in the case of using the Ni porous plate. The production balance between positive and negative ions will be mainly determined by the irradiation energy and catalyst material. Electronegativity describes the ability of an atom to attract electrons toward itself and it affects desorption ionization. The electronegativities of Ni and H are 1.8 and 2.2 in Pauling units, respectively. To increase the production quantity of negative ions, the electronegativity of the catalyst material should be decreased.

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[1] J. Ishikawa, "Negative ion sources," in *The Physics and Technology of Ion Sources*, 2nd ed., edited by I. G. Brown (Wiley-vch Verlag, Weinheim, 2004), p. 285.
[2] G. D. Alton, Surf. Sci. **175**, 226 (1986).
[3] K. N. Leung and K. W. Ehlers, Rev. Sci. Instrum. **53**, 803 (1980).
[4] Y. Okumura, M. Hanada, T. Inoue, H. Kojima, Y. Matsuda, Y. Ohara, Y. Oohara, M. Seki, Y. Suzuki, and K. Watanabe, *Proceedings of 16th Symposium on Fusion Technology*, Vol. 2 (North-Holland, Amsterdam, 1991), p. 1026.
[5] M. Bacal and G. W. Hamilton, Phys. Rev. Lett. **42**, 1538 (1979).
[6] O. Fukumasa and S. Mori, Nucl. Fusion **46**, S287 (2006).
[7] W. Oohara and R. Hatakeyama, Phys. Rev. Lett. **91**, 205005 (2003).
[8] W. Oohara, D. Date, and R. Hatakeyama, Phys. Rev. Lett. **95**, 175003 (2005).

[9]W. Oohara and R. Hatakeyama, Phys. Plasmas **14**, 055704 (2007).
[10]W. Oohara and O. Fukumasa, J. Plasma Fusion Res. SERIES **8**, 860 (2009).
[11]W. Oohara and O. Fukumasa, Plasma Fusion Res. **5**, S2106 (2010).
[12]W. Oohara and O. Fukumasa, Rev. Sci. Instrum. **81**, 023507 (2010).
[13]M. Karas, D. Bachmann, and F. Hillenkamp, Anal. Chem. **57**, 2935 (1985).
[14]K. Tanaka, H. Waki, Y. Ido, S. Akita, Y. Yoshida, and T. Yoshida, Rapid Commun. Mass Spectrom. **2**, 151 (1988).
[15]H. B. Michaelson, J. Appl. Phys. **48**, 4729 (1977).