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著者	飯塚　哲
journal or publication title	Applied Physics Letters
volume	63
number	12
page range	1619-1621
year	1993
URL	http://hdl.handle.net/10097/35450

doi: 10.1063/1.110714

Effect of electron temperature on negative hydrogen ion production in a low-pressure Ar discharge plasma with methane

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(Received 4 January 1993; accepted for publication 12 July 1993)

Production of negative hydrogen ions (H^-) is continuously controlled in a low-pressure Ar discharge plasma with methane by using a pin-hollow cathode. The electron temperature is changed by varying the pin length. An enhanced production of negative hydrogen ions is observed with a decrease in the electron temperature.

Weakly ionized reactive plasmas have widely been used for many kinds of material processing. In such plasmas, an electron temperature T_e should have large effects on the production of various radicals and charged particles on which material processing strongly depends. Therefore, control of T_e is of crucial importance in order to clarify and choose the most suitable conditions for material processing. Generally speaking, however, it is difficult to change T_e if the geometry and gas (including its pressure) used are fixed. To solve this difficulty, a so-called "pin-hollow" cathode has been developed for low-pressure discharges at Tohoku University.[1] With an increase in the length of pins installed in the hollow cathode, T_e decreases continuously by an order of magnitude.

In this letter, this method of T_e control is applied to an investigation of negative hydrogen ion (H^-) production in a low-pressure Ar discharge plasma with a small amount of methane (CH_4), which is important to clarify in conjunction with material processing for hydrogenerated amorphous and diamondlike carbon films.[2] The production of negative ions is dependent on chemical processes in weakly ionized reactive plasmas. In other ways, negative ions largely influence the chemical processes that occurred there. They also affect electrostatic potential profiles determining the kinetic energy of positive ions hitting substrates. Needless to say, a dependence of negative ion production on T_e is one of the key problems in the field of negative-ion beam generation.[3] In our experiment, negative hydrogen ions are produced as a result of methane dissociation and their density is continuously controlled by changing T_e. The results show a drastic increase of negative hydrogen ion production with a decrease in T_e.

A pin-hollow cathode of 20 cm diam is used in this experiment. The hole diameter of the cathode front is 17 cm. 48 pins are installed, with equal spacing on a circle of 16 cm diameter, in the hollow cathode. The pin length δ is externally varied in the range 0–7 cm. A 35-cm-diam ring anode with a 10-cm-diam hole is set at a distance of 10–20 cm from the cathode front. We also have an axially movable 20-cm-diam target at a distance of 30–40 cm from the cathode front. A weak magnetic field of 120–150 G is applied in the axial direction. An Ar discharge is triggered by applying a negative potential ($\simeq -400$ V) to the cathode with respect to the anode, which is grounded together with the stainless-steel vacuum chamber.

The Ar plasma produced is guided through the anode hole into a region between the anode and the target, which is grounded or floated. When there is no pin in the hollow cathode ($\delta=0$), we have a glowing plasma with $T_e=2$–3 eV in the region from the cathode up to the target, although the plasma diameter is smaller in the anode-target region than in the cathode-anode region, as shown in Fig. 1(a). As δ is increased, however, the glow structure changes. Between the cathode and the anode, with an increase in δ, the glow gradually becomes weak in the radially inner part of the plasma. For $\delta=7$ cm, the inner core part is completely dark and the glow is limited only in the radial region almost outside the circle on which the pins are located. Between the anode and the target, we have this core part of the plasma, which passes through the anode hole, as shown in Fig. 1(b). The outer glowing part is terminated by the anode. According to the probe measurements, T_e is continuously decreased by increasing the pin length in the region between the anode and the target and also in the radial core part between the cathode front and the anode. Typical conditions and parameters here are as follows: Argon pressure=5–10 mTorr with a flow rate of 98 sccm, discharge current=300 mA, plasma density $\simeq 9 \times 10^8/\mathrm{cm}^3$, $T_e=2$–0.4 eV, depending on the pin length $\delta=0$–7 cm.

A small amount of methane gas with a flow rate of 2 sccm is introduced into the argon plasma mentioned above. The Langmuir probe characteristics obtained at the radial center of the plasma between the anode and the target are demonstrated for $\delta=0$ and 6 cm in Figs. 2(a) and 2(b), respectively. Curves "1" and "2" correspond to the discharges without and with the methane, respectively. As clearly seen from the probe characteristics "1" in Figs. 2(a) and 2(b), $T_e \simeq 2$ eV for $\delta=0$ decreases to $T_e \simeq 0.4$ eV for $\delta=6$ cm in the absence of the methane. When we introduce the methane for $\delta=0$, little change appears in the probe characteristics. As δ is increased to 6 cm, however,

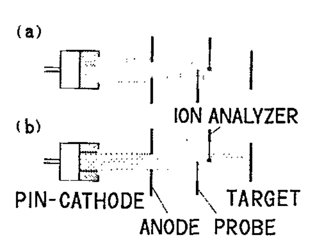

FIG. 1. Discharge structures for pin length (a) $\delta=0$ and (b) 7 cm.

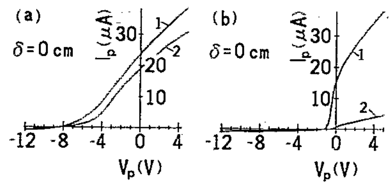

FIG. 2. Langmuir probe characteristics for pin length (a) $\delta=0$ and (b) 6 cm in a plasma without ("1") or with ("2") methane.

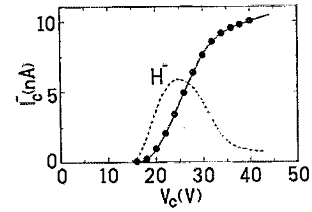

FIG. 4. Collector current I_C^- as a function of collector voltage V_C. A dotted curve shows dI_C^-/dV_C.

the electron saturation current is found to decrease drastically, although there is not such a change in the ion saturation current [see "2" in Fig. 2(b)]. Since there is a charge neutrality in the plasma, this result is due to a production of negative ions. Therefore, in our experiment, there is a clear effect of T_e on negative-ion production, yielding a lot of negative ions at $T_e \simeq 0.4$ eV.

In order to make direct measurements of negative ions, we use an ion mass analyzer of 12 mm in diameter and 18 mm in length, which is schematically shown in Fig. 3(a). The analyzer is immersed at the radial center of the plasma between the anode and the target as shown in Fig. 1. The first electrode with a 1-mm-diam hole at the center is biased at V_a, yielding negatively charged particles to pass through the hole. The second cylindrical electrode is biased at V_C to accelerate charged particles which move across the magnetic field B with a Larmor radius r_M. A collector current I_C^- biased at V_C appears only when r_M becomes larger than a threshold Larmor radius r_0 (=5.5 cm), as can be seen in Fig. 3(a). When $r_M < r_0$, the ions are absorbed by the second electrode, therefore, we detect no current I_C^-. Figure 3(b) presents temporal evolutions of I_C^- at $V_C=20$ V with δ as a parameter when the methane gas is introduced into the argon plasma at t (time)=0 with time duration of 30 s. For $\delta=0$ cm, a small increase in I_C^- is observed after the methane feeding. With an increase in δ, there appears a drastic enhancement of I_C^-, which increases in time up to an almost saturated value with a rise time of about 10 s. It decays within about 10 s after stopping the CH_4 feeding. An electron contribution to I_C^- is checked by turning off the discharge at $t=50$ s. There appears no appreciable variation in I_C^- when the discharge is turned off. Therefore, the electron current in I_C^- is negligible.

By changing the acceleration energy V_C, I_C^- is measured as a function of V_C. Differentiating the I_C^--V_C curve with respect to V_C, we can obtain dI_C^-/dV_C numerically as a function of V_C, which should have peaks corresponding to the ion mass numbers M. Here, M is obtained from the relation $M=er_0^2B^2/2m_HV_{C0}$, where m_H is the mass of hydrogen atom and V_{C0} is the collector voltage at the peak of the dI_C^-/dV_C curve. The I_C^- and dI_C^-/dV_C curves for negative ions are shown in Fig. 4. One peak is found at $V_{C0} \simeq 25$ V in the dI_C^-/dV_C curve. Using $r_0=5.5$ cm, $B=140$ G, and $V_{C0}=25$ V, we obtain $M=1.01\simeq 1$. Therefore, the H^- is the main species.

In Fig. 5, I_C^- is plotted, together with T_e, as a function of the pin length δ. I_C^- is found to increase with a decrease in T_e. There appears a drastic increase in I_C^- for $T_e<1.0$. I_C^- at $T_e\simeq 0.4$ eV ($\delta=6$–7 cm) is about 9× the value at $T_e\simeq 1.9$ eV ($\delta=0$). In this case, the negative ion density $\simeq 7\times 10^8$ cm^{-3} is estimated from the reduction of the electron saturation current in the presence of the methane in Fig. 2(b), where the plasma density $\simeq 9\times 10^8$ cm^{-3} before the methane feeding. The result yields an efficient negative ion formation with a conversion rate of 70%–80%.

A mechanism of the H^- production is explained as follows. As shown in Fig. 1 the pin length δ inside the cathode is very important for changing the T_e profile in the radial direction, which is essential for the continuous control of H^- production. When δ becomes large, the glow discharge with a higher discharge-current density takes place locally in the radial edge region between the cathode and the anode as shown in Fig. 1(b). In this narrow region, there are many high-energy electrons of $T_e=2$–3 eV, which dissociate the methane, producing CH_3 as well as H_2 ($CH_4+e\rightarrow CH_3+H+e$, $CH_4+e\rightarrow CH_2+H_2+e$).[4] According to Hiskes's works,[5] the high-energy electrons also excite the H_2 to form vibrationally excited hydrogen molecules $H_2(v'')$ with higher energy levels v''. These $H_2(v'')$

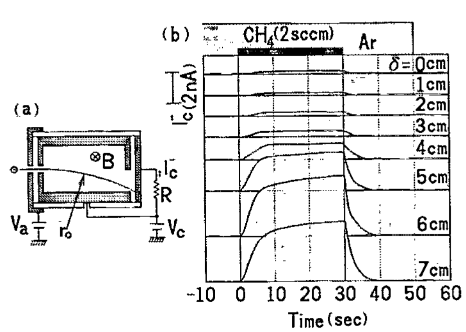

FIG. 3. (a) Schematic of ion analyzer. (b) Temporal evolutions of collector current I_C^- with pin length δ as a parameter. Methane is introduced at t (time)=0 with a duration of 30 s. Discharge is turned off at $t=50$ s.

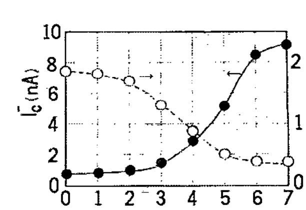

FIG. 5. Collector current I_C^- and electron temperature T_e as a function of pin length δ.

particles diffuse, escaping from a further effect of the high-energy electrons, into the inner core region of the plasma where T_e is quite low for large values of δ, as shown in Fig. 5. Cold electrons have a large cross section of dissociative attachment with the excited hydrogen $H_2(v'')$: $H_2(v'') + e \rightarrow H^- + H$,[6] resulting in an enhancement of the negative H^- ion production in the core plasma region. When $\delta = 0$, however, a high T_e plasma occupies the whole plasma column [see Fig. 1(a)]. The electron bonding energy in H^- is only 0.75 eV, so that as T_e rises from 0.4 to 2.3 eV there are more energetic electrons available to detach the electron and thus the H^- ion is destroyed. Therefore, H^- density is reduced because of the decrease in the dissociative attachment for H^- production in the high T_e region,[5] where electron detachment is also enhanced by high-energy electrons.

In summary, measurements have been made on an effect of T_e on negative hydrogen ion production in a low-pressure Ar discharge plasma with methane gas. In order to control T_e, we have employed a pin-hollow cathode technique which yields a continuous decrease of T_e with an increase in the pin length. Production of negative hydrogen ions is found to be enhanced by decreasing T_e. The density of negative hydrogen ions becomes comparable to that of low-temperature electrons, even if the methane gas introduced is quite small, showing a big influence of the electron temperature on the reactive processes concerned. An essential point of our work is a *continuous control of H^- density* by means of the pin-hollow cathode.

This work is supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture of Japan. The authors are indebted to H. Ishida for his technical support.

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