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著者	飯塚　哲
journal or publication title	Applied Physics Letters
volume	64
number	14
page range	1786-1788
year	1994
URL	http://hdl.handle.net/10097/35451

doi: 10.1063/1.111808

Enhanced methyl-radical production in an Ar-CH_4 pin-hollow cathode discharge

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(Received 17 August 1993; accepted for publication 16 January 1994)

A methyl-radical formation is observed to be enhanced in an Ar-CH_4 discharge plasma using a hollow cathode with movable pins inside. In the discharge with pins, high energy electrons in the radial edge region of the plasma column produce methyl radicals. They diffuse toward the central region of the plasma column, increasing their density, where the electron temperature is so low ($\simeq$0.4 eV) that there occurs no reaction to decrease the methyl-radical density.

In recent years there has been growing interest in plasma chemical vapor depositions of hydrogenerated amorphous carbon films and diamondlike films because of their advantages of large thermal conductivities, chemical inertness, and high electrical resistivities.[1] Various methods have been reported for the production of such films.[2,3] It has commonly been recognized that methyl radicals are quite essential for the film deposition,[4] promoting measurements of the methyl-radical density by using quadrupole mass spectroscopy[5] and infrared absorption spectroscopy.[6]

The production of radicals strongly depends on the electron energy. Therefore, it is important to control the electron temperature T_e and choose the most suitable condition necessary for material processings. For this purpose we have developed a so-called "pin-hollow cathode."[7,8] The pin length changes a local discharge structure, yielding a T_e control in the central region of the plasma column. Here, we report a methyl-radical production depending on the local structure of T_e.

The plasma is produced by applying negative dc voltage of $-(350-400)$ V to a 20-cm-diam pin-hollow cathode of 7 cm long with respect to a 35-cm-diam grounded anode with a 10-cm-diam hole at the center. The 48 pins are set inside the hollow cathode with equal spacing on a circle of 15 cm in diameter. The pin length δ can externally be changed in the range of 0–7 cm. When the pins are inserted in the cathode, the discharge takes place mainly in the radial edge region (A), as schematically shown in Fig. 1. Here, the axial magnetic field is strong enough for confining electrons radially. Therefore, the radial structure of T_e in the cathode region does not diffuse in the radial direction, persisting along the magnetic field into the plasma column. Then, the electrons of 2–3 eV are locally distributed in the region of $r \gtrsim 7.5$ cm and there are only low-energy ($\simeq$0.4 eV) electrons in the central region (B) of the plasma column. When the pins are pulled out, however, the discharge appears even in the central region and T_e is 2–3 eV in the regions of (A) and (B).

Typical experimental conditions are as follows: discharge current $I_d=0.1-1.0$ A, Ar pressure $P_{Ar}=5-10$ mTorr with flow rate 98 sccm, axial magnetic field B=120–150 G, and the anode-cathode distance is 10 cm in the experiment. The CH_4 gas with a flow rate 2 sccm is introduced into the Ar plasma. The plasma density and electron temperature are measured by a heated wire probe of 0.1 mm in diameter and 3 mm long.

The methyl radicals CH_3 are measured by a quadrupole mass spectrometer. The neutral particles sampled at the radial center $r=0$ cm are introduced through a 1-mm-diam orifice into a subchamber which is differentially evacuated. The threshold ionization technique (appearance mass spectrometry)[5,9] is quite useful for the radicals which exhibit no optical emission. This technique is employed here to evaluate the methyl-radical density n_{CH_3}. The sampled gas is ionized by an electron beam before entering the quadrupole electrodes. If the beam energy is set at about 15–16 eV, a little higher than the appearance energy ($\simeq$14.3 eV) for CH_3^+ ion generation due to dissociative ionization of CH_4 and the appearance energy ($\simeq$9.8 eV) for CH_3^+ ion generation due to direct electron-impact ionization of CH_3, both the CH_4^+ ion current $I_{4\,off}^+$ and the CH_3^+ ion current $I_{3\,off}^+$ are detected even when the discharge is turned off, as shown in Fig. 2(a). When the plasma is turned on, the CH_4 is dissociated to produce the CH_3 in the plasma, which is also introduced into the subchamber. Then, two components appear in the CH_3^+ ion current $I_{3\,on}^+$: One is due to the direction ionization of CH_3 and the other is due to the dissociative ionization of CH_4.

A fraction of CH_4 dissociated in the discharge is evaluated by the ratio $\alpha=(I_{4\,off}^+-I_{4\,on}^+)/I_{4\,off}^+ =(n_{CH_4off}-n_{CH_4on})/n_{CH_4off}$, because these currents are expressed as $I_{4\,off}^+=A\sigma_{44}n_b n_{CH_4off}$ and $I_{4\,on}^+=A\sigma_{44}n_b n_{CH_4on}$ where A is determined by the measuring system, n_{CH_4on} and n_{CH_4off} are the methane densities when the plasma discharge is turned on and off, respectively, n_b is the electron beam density in the mass spectrometer, and σ_{44} is the ionization cross section of CH_4 for producing the CH_4^+. α is indepen-

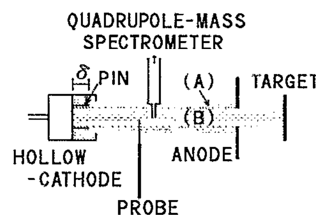

FIG. 1. Schematic drawing of discharge structure using a hollow cathode with pins inside, where (A) and (B) show high and low electron temperature regions, respectively.

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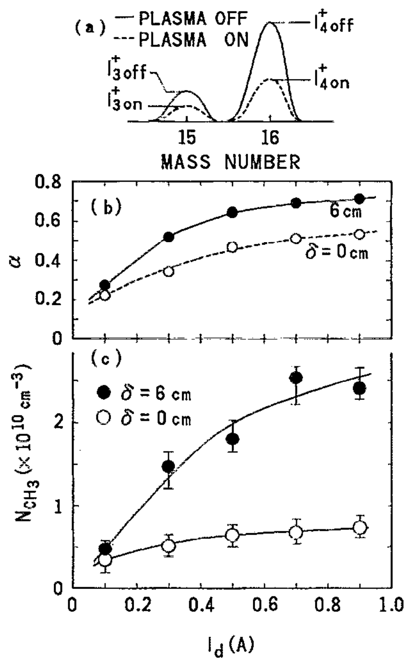

FIG. 2. (a) Typical output signals of quadrupole mass spectrometer at mass numbers of $M=15$ (CH_3) and 16 (CH_4) when the discharge is turned off (solid curve) and on (dotted curve). The currents, $I^+_{3\,off}$, $I^+_{3\,on}$, $I^+_{4\,off}$, and $I^+_{4\,on}$ indicate corresponding peak values, respectively. (b) Dependences of dissociation ratio α on discharge current I_D with pin length δ as a parameter. (c) Methyl-radical density n_{CH_3} as a fuction of discharge current I_d with pin length δ as a parameter at the radial center. Total pressure$=5\times10^{-3}$ Torr.

dent of the electron beam energy. Figure 2(b) shows a variation of α as a function of I_d with δ as a parameter. The methane dissociation increases with an increase in I_d. As δ is increased, the dissociation increases even for I_d=constant. This means that the variation of discharge structure due to the pin length is important for an efficient methane dissociation.

From the output signals of the quadrupole spectrometer shown in Fig. 2(a), the CH_3 density in the plasma n_{CH_3} ($\equiv n_{CH_3 on}$) is estimated from the relation $n_{CH_3}/n_{CH_4 off}=(\sigma_{44}/\sigma_{33})(1-\alpha)(I^+_{3\,on}/I^+_{4\,on}-I^+_{3\,off}/I^+_{4\,off})$, where $I^+_{3\,on}=A\sigma_{43}n_b n_{CH_4 on}+A\sigma_{33}n_b n_{CH_3 on}$, $I^+_{3\,off}=A\sigma_{43}n_b n_{CH_4 off}$, σ_{43} and σ^{33} are the dissociative ionization cross sections of CH_4 to yield the CH_3^+ and the direct ionization cross section of CH_3 to yield the CH_3^+, respectively. The dissociations from other products C_mH_n into the CH_3^+ and CH_4^+ are negligible for such a low electron-beam energy as in our case. When the beam energy is set at 15 eV, for example, $\sigma_{33}\simeq0.56\times10^{-16}$ cm^{-2} and $\sigma_{44}\simeq0.2\times10^{-16}$ cm^{-2}.[10,11]

Variations of n_{CH_3} as a function of I_d are shown with δ as a parameter in Fig. 2(c). For δ=6 cm we find an enhanced production of the CH_3, which increases with I_d, and when I_d=0.9 A, n_{CH_3} is 2.5×10^{10} cm^{-3}. However, for δ=0 cm, an increase in n_{CH_3} is relatively small compared to the case of δ=6 cm. These variations are quite similar to the dissociations shown in Fig. 2(b).

A dependence of n_{CH_3} on δ is shown in Fig. 3. It is found that n_{CH_3} starts increasing at δ=2–3 cm and attains

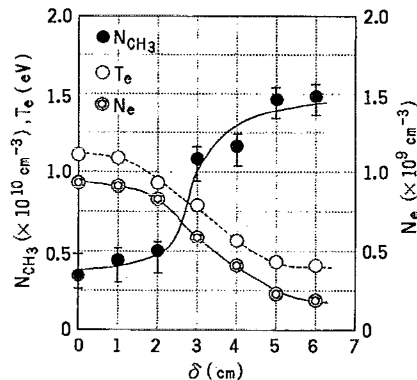

FIG. 3. Methyl-radical density n_{CH_3}, electron temperature T_e and electron density n_e as a function of pin length δ at the plasma center. Total pressure$=5\times10^{-3}$ Torr and a discharge current=0.3 A.

approximately 1.5×10^{10} cm^{-3} at δ=5–6 cm. In order to investigate the relation to the plasma parameters, T_e and n_e at r=0 cm are also plotted in Fig. 3. T_e is found to decrease with δ and becomes 0.43 eV for δ=6 cm. Therefore, the higher n_{CH_3} is observed in the very low T_e plasma. As δ is increased, n_e also decreases from δ=2–3 cm and at δ=6 cm, it becomes about 20% of that of δ=0 cm. This is due to an enhanced production of negative hydrogen ions H^-.[12] In spite of the decrease in n_e, n_{CH_3} increases as δ is increased. Therefore, we presume that the CH_3 is produced not in the low T_e region but in the high T_e region surrounding the low T_e region. It is to be remarked that n_{CH_3} is more sensitive to T_e rather than n_e.

The CH_3 density in the central region is determined by a balance between the production rate (or inward diffusion from the plasma periphery where the CH_3 is produced) and the loss rate from the central region with different electron temperature. The CH_3 is produced by the electron impact dissociation ($e+CH_4\rightarrow CH_3+H+e$) in the high T_e region, although a small amount of the CH_3 might be produced by an ion-molecule reaction ($CH_4^++CH_4\rightarrow CH_5^++CH_3$).[4] On the other hand, candidates for loss channels of the CH_3 are the volume recombinations ($CH_3+CH_3\rightarrow C_2H_6$, $CH_3+H\rightarrow CH_4$), ion-molecule reactions ($CH_3^++CH_4\rightarrow C_2H_5^++H_2$), and surface reactions [CH_3^+ (or CH_3)$\rightarrow$CH(s)+H_2, where (s) indicates an adsorbed species] on the chamber wall and the electrodes.[4,5,13] Under our experimental conditions, however, the CH_3-CH_3 combinations would be negligibly small because the CH_3 density is relatively low ($\simeq10^{10}$ cm^{-3}) and the time scale of the radical density decay [$\tau\simeq1/(n_{CH_3}\kappa)$] is more than 10 s because the rate coefficient κ is of the order of 10^{-11} cm^3/s. The surface reaction rates are also supposed to be small.[4,5] Therefore, the remnant ion-molecule reaction is a dominant loss process of the CH_3[13] in our experiment. According to Ref. 4, the rate coefficient of this reaction is of the order of 10^{-9} cm^3/s, larger by two orders of magnitude than κ mentioned above.

On the basis of these considerations, we can explain the mechanism of the CH_3 density increase with a decrease in T_e in the central region. When δ is large under a fixed discharge

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current, the glow discharge appears in the radial edge region (A) of the plasma column, where electrons of T_e=2–3 eV are produced.[8] In this narrow region, the CH_4 is dissociated to produce the CH_3. The CH_3 moves into the inner region (B) where $T_e \simeq 0.4$ eV and n_e decreases drastically as shown in Fig. 3. In this region the ionization of the CH_3 is quenched and we can neglect the ion-molecule reaction mentioned above. In the region (B), therefore, there is no furious chemical reaction decreasing n_{CH_3}. This is the reason why an increase in n_{CH_3} is observed as δ is increased.

When δ approaches zero, however, the high T_e and n_e plasma occupies the whole plasma column.[8] In this case, the CH_3 is produced in the whole plasma column through the electron impact dissociation. The CH_3 is also ionized to yield the CH_3^+ which in turn reacts with the CH_4 to decrease the n_{CH_3}, balancing with the CH_3 production.

In our experiment, n_{CH_3} ($\simeq 1\times 10^{10}$ cm^{-3}) is rather low compared with that in other works where $n_{CH_3}=10^{11}$–10^{12} cm^{-3} for pure CH_4 radio-frequency plasmas with CH_4 pressure of 10–50 mTorr.[5,14] In our work, the net CH_4 partial pressure in a CH_4–Ar plasma is 0.16 mTorr, roughly less by two orders of magnitude than the values in those works. The density ratio $n_{CH_3}/n_{CH_4 off} \simeq (0.7-1.0)\times 10^{-3}$ at δ=0 cm, however, gives an almost similar value to those in Refs. 5 and 14. The value of $n_{CH_3}/n_{CH_4 off}$ is enhanced by increasing δ, as shown in Fig. 3. Our work clearly shows that a local decrease in the electron temperature provides a key mechanism for sustaining a higher methyl radical density.

In summary, an effect of local structure of the electron temperature on the methyl-radical production has been clarfied in an Ar-CH_4 discharge plasma produced by using a pin-hollow cathode. The methyl radical density is estimated using the quadrupole mass spectroscopy. A region of low electron temperature is very effective for sustaining a higher methyl-radical density in the discharge plasma.

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

[1] A. Aisenberg and R. Chalbot, J. Appl. Phys. **42**, 2953 (1971).
[2] P. J. Kung and Y. Tzeng, J. Appl. Phys. **66**, 4676 (1989).
[3] L. Holland and S. M. Ojima, Thin Solid Films **38**, L17 (1989).
[4] L. E. Kline, W. D. Partlow, and W. E. Bies, J. Appl. Phys. **65**, 70 (1989).
[5] H. Toyoda and H. Kojima, and H. Sugai, Appl. Phys. Lett. **54**, 1507 (1989).
[6] J. Wormhoubt, J. Vac. Sci. Technol. A **8**, 1722 (1990).
[7] S. Iizuka, K. Koizumi, and N. Sato, *Proceedings of the 1989 International Conference on Plasma Physics*, New Delhi, India, edited by A. Sen and P. K. Kaw (India Academy of Science, Bangalore, 1989), Vol. 3, p. 1193; N. Sato and S. Iizuka, *Proceedings on the International Seminar on Reactive Plasmas*, Nagoya, Japan (Nagoya University, Nagoya, Japan, 1991), p. 371.
[8] N. Sato, S. Iizuka, T. Koizumi, and T. Takada, Appl. Phys. Lett. **62**, 567 (1993).
[9] B. Robertson, D. Hils, H. Chatham, and A. Gallagher, Appl. Phys. Lett. **43**, 544 (1983).
[10] B. Adamczyk, A. J. H. Boerboom, B. L. Schram, and J. Kistemaker, J. Chem. Phys. **44**, 4640 (1976).
[11] F. A. Baiocchi, R. C. Wentzel, and R. S. Freund, Phys. Rev. Lett. **53**, 777 (1984).
[12] S. Iizuka, T. Koizumi, T. Takada, and N. Sato, Appl. Phys. Lett. **63**, 1619 (1993).
[13] S. A. Studniarz and J. L. Franklin, J. Chem. Phys. **49**, 2652 (1968).
[14] S. Naito, N. Ito, T. Hattori, and T. Goto, *Proceedings of the 10th Symposium on Plasma Processing*, Osaka, Japan (Japan Society of Applied Physics, Tokyo, Japan, 1993), p. 53.

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