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Numerical analysis of the ionization of gaseous methane induced by pulsed electron beams

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The contributions of beam electrons (the first term) and secondary electrons (the second term) accelerated by the electric field induced by two pulsed electron beams (Febetrons 705 and 706) to the total ionization of methane in the pressure range of 10 to 760 Torr were calculated by a numerical analysis. The fraction of the secondary electrons neutralized during the pulse duration was also evaluated. The computation result showed that, for a Febetron 705, the ionization is mainly due to the first term and that most of the secondary electrons produced are neutralized during the pulse duration. For a Febetron 706, the contribution of the second term is large even at 300 Torr and the secondary electrons recombine only by 20%–30% with ions during the pulse duration. For this beam, the effect of the induced electric field remains after the pulse. The mean secondary electron energy during the pulse also was estimated.

INTRODUCTION

The radiolysis of gaseous methane has been studied extensively,[1] but is still not completely clarified. In a recent paper,[2] we have shown from the investigation of irradiation temperature effect that the chain propagation leading to higher hydrocarbon products is mainly due to radical reaction. However, the reactions between ions and secondary electrons at an early stage are not fully understood. These reactions are thought to produce radicals.[1] Rebbert, Lias, and Ausloos[3] assumed that most of the major ions ($C_2H_5^+$ and CH_5^+) might recombine with secondary electrons during the pulse duration in the pulse radiolysis of gaseous methane.

In the previous papers,[4,5] we have shown from a numerical simulation that in the gas ionization induced by a pulsed electron beam from a Febetron 706 secondary electrons produced are accelerated by the longitudinal electric field of the pulsed beam, followed by a remarkable multiplication of secondary electrons (electron avalanche) and that the recombination of ions and secondary electrons hardly occurs during the pulse duration. These facts have never been considered in the pulse radiolysis in the past. In this paper, we attempt to examine the early stage of the pulse radiolysis of methane induced by pulsed electron beams from Febetrons 705 and 706, which are frequently used in the pulse radiolysis study, through the numerical simulation of the ionization process.

COMPUTATION METHOD

The computation was carried out for the ionization of methane induced by pulsed electron beams from Febetrons 705 and 706 over the pressure range from 10 to 760 Torr on the basis of the same model as in the previous paper.[5] This model had successfully explained the beam behavior of a Febetron 706 in the various gases,[4,5] and its outline is as follows. A rapid change of the net current (I_{net}) in a gas chamber induces a large backward longitudinal electric field E_z. For the beam of a constant radius r_0 with a uniform electron density, E_z on the beam axis is given by

$$E_z = -\frac{2}{c^2}\left(\frac{1}{2} + \ln\frac{R}{r_0}\right)\frac{dI_{net}(t)}{dt} , \tag{1}$$

where R is the gas chamber radius and c the light velocity. The net current is given by

$$I_{net}(t) = I_b(t) + I_{back}(t) , \tag{2}$$

where $I_b(t)$ is the beam current and $I_{back}(t)$ the plasma backward current given by Eq. (3),

$$I_{back}(t) = \pi r_0(t)^2 E_z(t)\sigma_e(t) , \tag{3}$$

where $\sigma_e(t)$ is the plasma conductivity expressed as

$$\sigma_e(t) = \frac{e^2 n_e(t)}{n_0(2m)^{1/2}Q_m(\bar{\epsilon})\bar{\epsilon}^{1/2}} . \tag{4}$$

In Eq. (4), m is the electron rest mass, e the electron charge, $Q_m(\bar{\epsilon})$ the momentum transfer cross section for electrons with mean kinetic energy $\bar{\epsilon}$, n_0 the number density of neutral molecules, and $n_e(t)$ the number density of secondary electrons produced in the beam channel. Secondary electrons are pushed out of the beam channel till the space-charge neutralization time t_N. The t_N is shorter than 0.2 ns for methane above 10 Torr so that the beam-charge is effectively neutralized at the beginning of the pulse for the both beams in the above pressure range. After t_N, secondary electrons are accelerated by the above induced electric field (E_z) in the opposite direction to the beam coordinate z for $dI_{net}/dt > 0$. The production rate of secondary electrons can be expressed as

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$$\frac{dn_e(t)}{dt} = \frac{n_0\sigma_{ion}(E_b)}{e}\cdot\frac{I_b(t)}{\pi r_0^2} + \frac{n_e(t)}{t_i(t)} - \alpha_r n_e(t)n_i(t) - \alpha_{rd}n_e(t)n_d(t)\,, \quad (5)$$

(term 1) (term 2) (term 3) (term 4)

where n_i and n_d are the number density of monomer ions and dimer ions, respectively, and α_r and α_{rd} are the recombination coefficients (cm^3/s) between electron–monomer ion and electron–dimer ion, respectively. The total ionization cross section $\sigma_{ion}(E_b)$ for the beam electrons with energy E_b can be estimated with Rieke–Prepejchal's parameters.[6] The mean ionization time t_i for secondary ionization by E_s can be estimated by

$$t_i = 1/w(\alpha - \eta)\,, \quad (6)$$

where w is the electron drift velocity, α the first Townsend ionization coefficient, and η the electron attachment coefficient.

The main primary species in the methane radiolysis are thought to be CH_4^+ (46%) and CH_3^+ (40%) from the data of mass spectrum of methane.[7] The CH_4^+ and CH_3^+ ions react with methane to produce CH_5^+ and $C_2H_5^+$ ions, respectively,

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + \dot{C}H_3\,, \quad (A)$$

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2\,. \quad (B)$$

The CH_5^+ and $C_2H_5^+$ ions scarcely react with methane[8,9] and are assumed to be neutralized by secondary electrons, for the yields of higher hydrocarbon products, which receive H^+ from these ions, are negligible at earlier stage.

The rate constants are almost the same for reactions (A) and (B)[10,11] and the recombination coefficients with secondary electrons also are very similar for CH_3^+ and CH_4^+.[12] Although α_r of $C_2H_5^+$ is not known, its value is considered to be similar to that of $C_2H_3^+$ from the data of various ions by Mull and McGowan.[12] We adopted the α_r of $C_2H_3^+$ as that for $C_2H_5^+$. Although α_r of CH_5^+ is rather similar to that of CH_4^+[12] than $C_2H_3^+$, we assumed that the α_r of CH_5^+ is equal to that of $C_2H_5^+$ so that the CH_3^+ and CH_4^+ ions can be treated as the monomer ions and the CH_5^+ and $C_2H_5^+$ as the dimer ions in Eq. (5) in the calculation. In addition, only CH_3^+, CH_4^+, and secondary electrons were assumed to be produced in the primary ionization of methane. From these simplification, the production rates of monomer and dimer ions for CH_4 are given as

$$\frac{dn_i}{dt} = \frac{n_0\sigma_{ion}(E_b)}{e}\,\frac{I_b(t)}{\pi r_0^2} + \frac{n_e}{t_i} - \alpha_r n_e n_i - k_d n_i n_0\,, \quad (7)$$

$$\frac{dn_d}{dt} = k_d n_i n_0 - \alpha_{rd} n_e n_d\,, \quad (8)$$

where k_d is the rate constant (1×10^{-9} cm^3/s)[10,11] for reactions (A) and (B). The term of $k_d n_i n_0^2$ in Eqs. (8) and (9) in Ref. 5 has been replaced by $k_d n_i n_0$ in Eqs. (7) and (8) of this paper, because the dimer ions in methane are produced by biomolecular reactions [reactions (A) and (B)]. These basic equations described above can be solved numerically by the aid of an electronic computer as indicated in the paper by Swain.[13]

In the present computation, the beam radius was assumed to be fixed at 0.6 cm for a Febetron 706 and 1.5 cm for a Febetron 705. We used the wave form for a Febetron 706 beam current that had been used in the previous paper (Fig. 1 of Ref. 4) and that for a Febetron 705 adopted the beam current wave form observed by Miller, Gerardo, and Poukey.[14] The pulse duration was assumed to be 5.2 ns for a Febetron 706[4] and 100 ns for a Febetron 705,[14] respectively. The mean energy of the beam electrons was assumed to be 480 keV for the former beam and 1.5 MeV for the latter beam. The hollowness of the beam from a Febetron 705 was ignored in the computation.

In the computation, literature values were used for the following parameters: w,[15–17] α/p,[18] D_L/μ,[19] and Q_m,[20,21] where D_L/μ is the lateral diffusion coefficient to the electron mobility. For methane, η in Eq. (6) is negligibly small,[22] and was assumed to be zero. The value of $\bar{\epsilon}$ was estimated by the next equation[23] from data on D_L/μ on the assumption of the Maxwellian,

$$\bar{\epsilon} = \tfrac{3}{2}eD_L/\mu \quad (e\text{: electronic charge})\,. \quad (9)$$

In addition, we assumed that the variation of α_r and α_{rd} with $\bar{\epsilon}$ is expressed from the data of Ref. 12 as

$$\alpha_r = 6.0\times10^{-8}\bar{\epsilon}^{-0.7} \quad \text{for } \bar{\epsilon} \le 0.8 \text{ eV}\,,$$

$$\alpha_r = 5.5\times10^{-8}\bar{\epsilon}^{-0.93} \quad \text{for } \bar{\epsilon} > 0.8 \text{ eV}\,,$$

$$\alpha_{rd} = 9.5\times10^{-8}\bar{\epsilon}^{-0.6} \quad \text{for } \bar{\epsilon} \ge 1 \text{ eV}\,,$$

$$\alpha_{rd} = 9.5\times10^{-8}\bar{\epsilon}^{-0.75} \quad \text{for } \bar{\epsilon} > 1 \text{ eV}\,.$$

Furthermore, the loss of the secondary electrons due to the diffusion out of the beam channel was neglected because of the shortness.

RESULTS AND DISCUSSION

The computation was carried out for CH_4 at selected pressures from 10 to 760 Torr. First, the representative results for the secondary electron density $[n_e(t)]$, the monomer ion density and the dimer ion density will be briefly shown below.

Figure 1 shows the calculated results for 10 and 100 Torr with a Febetron 706 beam as functions of time. The results for 30 and 300 Torr have been published in Fig. 11 of Ref. 5. The computed results for 760 Torr are almost the same as those for 300 Torr. The number density of secondary electrons during the pulse duration is on the order of 10^{15} cm^{-3} as shown by these data, and the yield of the dimer ion becomes remarkably large with an increase of pressure. Even at 30 Torr, dimer ions are predominant as a result of reactions (A) and (B).

In Fig. 1, at 100 Torr, the concentration of monomer ion has two maxima around 2 and 5 ns. The first maximum corresponds to the ionization due to the electric field E_s induced by the rapid increase of the beam current at the early period of the pulse. This peak becomes smaller as the pressure is increased as shown in Fig. 1 of this paper and Fig. 11 of Ref. 5. The second peak is due to the ionization induced by the rapid decrease of the beam current at the later part of the pulse. However, this peak is obscured at pressures

lower than 30 Torr. Below 30 Torr, the change of beam current is canceled by the plasma backward current to be kept almost constant as seen in Fig. 3 of Ref. 5 so that the induced electric field is not so large as to give enough ionization. On the other hand, above 300 Torr, reactions (A) and (B) occurs violently due to the increase of pressure so that the second peak becomes small again. As seen in Fig. 1, the neutralization between ions and secondary electrons is not so completed during the pulse duration as has been assumed at high dose rates by Rebbert, Lias, and Ausloos[3] as described in the introduction.

Figure 2 shows the calculated number densities of secondary electrons, monomer and dimer ions for 10, 30, 100, and 300 Torr with a Febetron 705 beam as functions of time. The results for 760 Torr are almost the same for those of 300 Torr. For this beam, dimer ions are predominant even at 10 Torr. This is due to the longer pulse duration (100 ns) of this beam. The number densities of these species during the pulse duration are on the order of 10^{14} cm^{-3}.

The figures shown so far give the temporary concentration of the species at each time, and do not give the total ionization or recombination during the pulse duration. In order to clarify these points, the total secondary electron yield per unit volume per pulse is estimated. Figure 3 shows the results for a Febetron 706. The chain lines and the dotted lines indicate the contribution of the

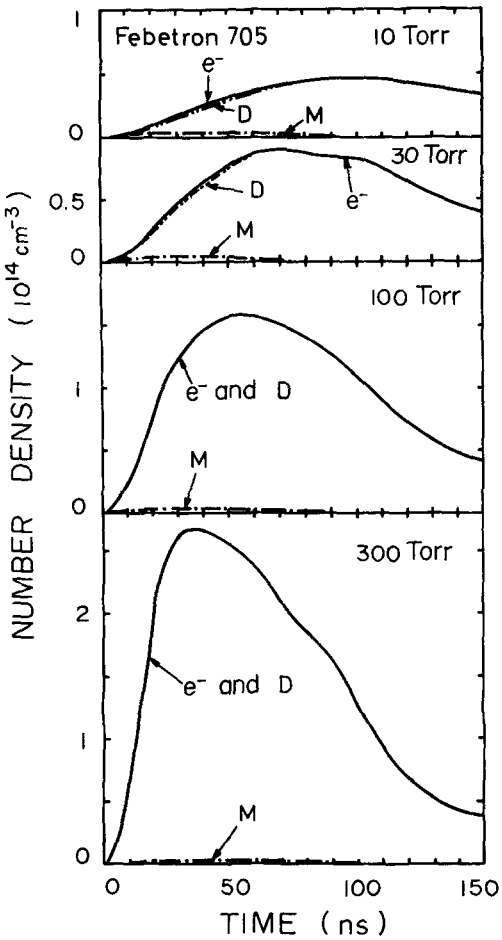

FIG. 2. The calculated number densities of secondary electrons e^-, monomer ions and dimer ions as functions of time at 10, 30, 100, and 300 Torr of CH_4 with a Febetron 705 beam; M represents the monomer ions ($CH_3^+ + CH_4^+$) and D the dimer ions ($CH_5^+ + C_2H_5^+$). Only these five species were assumed to be produced by ionization.

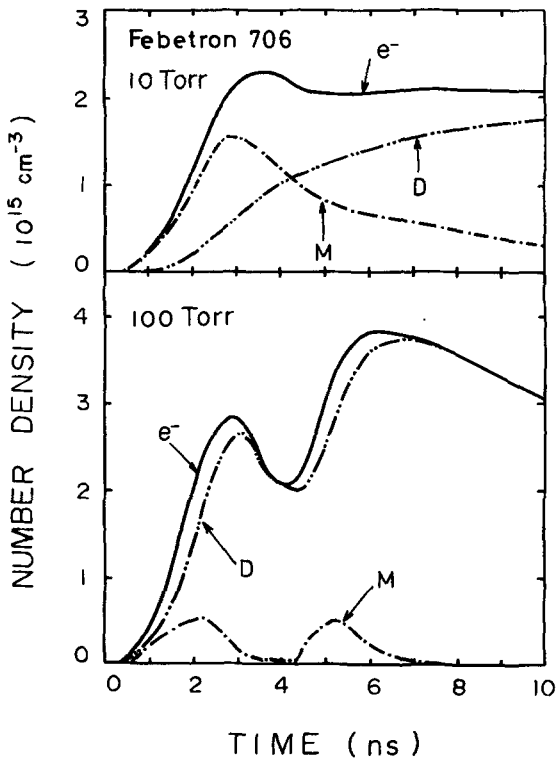

FIG. 1. The calculated number densities of secondary electrons e^-, monomer ions, and dimer ions as functions of time at 10 and 100 Torr of CH_4 with a Febetron 706 beam; M represents the monomer ions ($CH_3^+ + CH_4^+$) and D the dimer ions ($CH_5^+ + C_2H_5^+$). Only these five species were assumed to be produced by ionization.

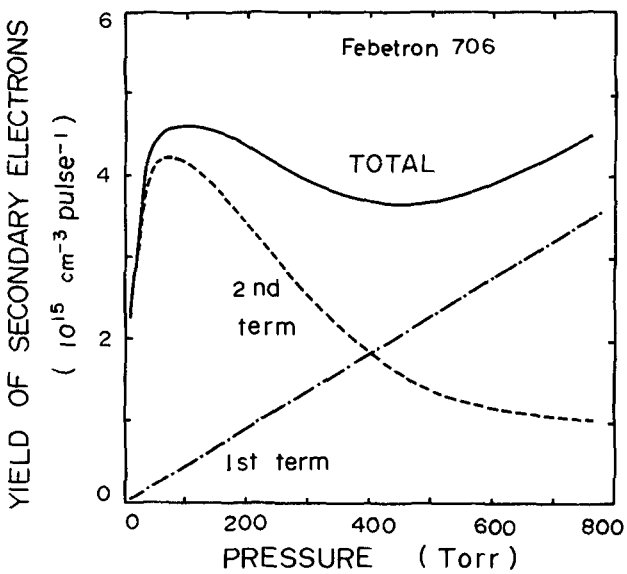

FIG. 3. The calculated secondary electron yield per unit volume (cm^{-3} $pulse^{-1}$) as functions of the pressure of methane with a Febetron 706 beam. The chain lines and the dotted lines indicate the contributions of the first and the second terms in Eq. (5) to the total secondary electron yield.

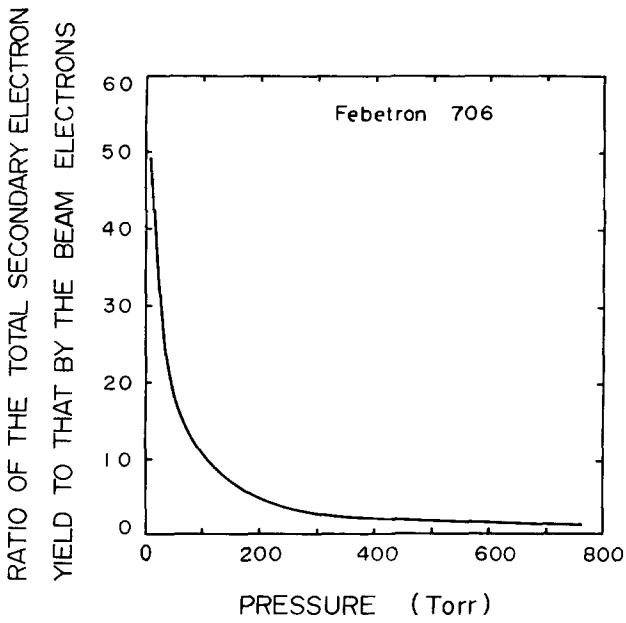

FIG. 4. The calculated ratio of the total secondary electron yield per pulse to that by the beam electrons (the first term) as a function of the pressure of methane with a Febetron 706.

first and second terms of Eq. (5), respectively. As seen in Fig. 3, the total secondary electron yield increases largely with pressure at low pressures and reaches a maximum around 100 Torr. At pressures above 100 Torr, the yield decreases gradually with pressure, and increases again at pressures above 500 Torr. At pressures above 500 Torr, the yield increases approximately in proportion to the pressure. Such a pressure dependence of the yield is analogous to that of the nitrogen yield from N_2O produced by a Febetron 706 by Willis, Boyd, and Miller.[24] From the data in Fig. 3, the large yield at low pressures is mainly due to the second term of Eq. (5), i. e., from secondary electrons accelerated by the induced electric field. This is clearly seen in Fig. 4 where the ratio of the total secondary electron yield to that by the first term is shown as a function of time. On the other hand, for a Febetron 705, the contribution of the second term is only 0. 5% of that by the first term even at 10 Torr from the present computation, indicating that the ionization is mainly due to the first term.

These differences of the contribution of the first and second term between Febetrons 705 and 706 are due to the difference in the beam characteristics. For a Febetron 706, the change of beam current with time is very large (the pulse duration: about 5 ns), while for a Febetron 705 the rate of change of current is much rather slowly and the pulse duration is much longer (100 ns). For a Febetron 706, a high electric field (about 20 000 V/cm) is induced, while for a Febetron 705, only a low electric field (at largest, 400 V/cm) is induced. In any case, for a Febetron 706, the contribution of the second term is predominant at low pressures. This effect continues for a certain period after the pulse end, especially at low pressures.

In Fig. 5, the total electron yield per cm per pulse along the beam path, which is estimated by multiplication of the beam cross section by the total secondary electron yield per cm^3 per pulse, is compared for Febetrons 705 and 706. For a Febetron 705, the total electron yield increases in proportion to the pressure, while for a Febetron 706, the total electron yield does not so change with pressure.

In order to estimate the neutralization between secondary electrons and ions during the pulse duration, the fraction of secondary electrons neutralized during this period is shown in Fig. 6 as functions of pressure for a Febetron 706. The contributions of the third term and fourth term in Eq. (5) are shown by chain lines in this figure.

As seen in Fig. 6, only 20%–30% of ions are neutralized even at 760 Torr. The fraction of the secondary electrons neutralized shows a maximum around 30–50 Torr and decreases with pressure, followed by an increase above 300 Torr. The total curve is determined by term 4 of Eq. (5) ($\alpha_{rd} n_e n_d$). In fact, the total curve is quite similar to the total curve of n_e in Fig. 3. The value of α_{rd} increases with a decreasing mean secondary electron energy or the reduced electric field E_s/p (p: gas pressure) which decreases with an increasing pressure as shown in Fig. 8 of Ref. 5. Therefore, the above change of the fraction with pressure may be explained as follows: (1) At pressures lower than 30 Torr, the yields of secondary electrons and ions per pulse increase largely with pressure as seen in Fig. 3. This may enhance the recombination rate with pressure in this pressure region. (2) On the range 50–300 Torr, the yields of secondary electrons and ions decrease gradually with an increase in pressure as shown in Fig. 3. This may lower the recombination efficiency with pressure.

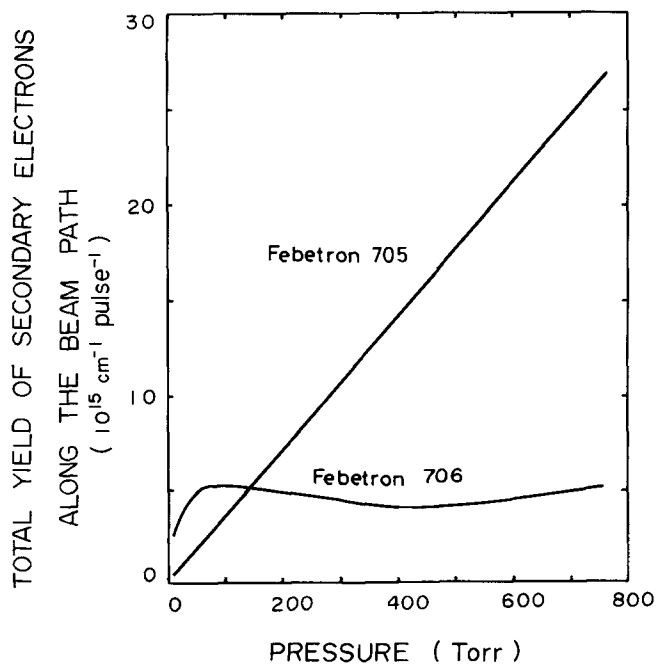

FIG. 5. The calculated total secondary electron yield, (cm^{-1} $pulse^{-1}$) as functions of the pressure of methane with Febetrons 705 and 706.

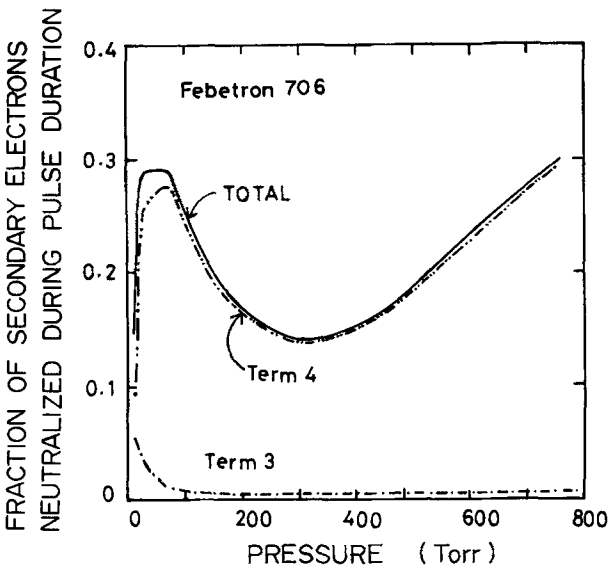

FIG. 6. The calculated total fraction of the secondary electrons neutralized during the pulse duration as functions of the pressure of methane with a Febetron 706 beam. The chain lines indicate the contribution of the third and the fourth term in Eq. (5).

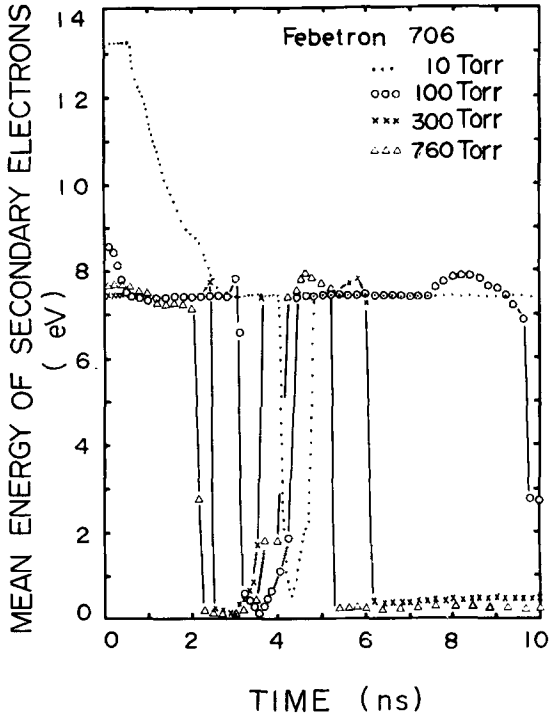

FIG. 8. The mean secondary electron energy estimated from field E_s/p by Eq. (9) during the pulse duration as functions of time for 10, 100, 300, and 760 Torr with a Febetron 706 beam.

(3) At still higher pressures, above 300 Torr, the fraction increases again. This is mainly due to the decrease of the mean secondary electron energy because of the increase of pressure.

The result shown in Fig. 6 is concerned with the neutralization within the short pulse duration (5.2 ns). After the pulse, the secondary electrons will be rapidly slowed down to the thermal energy, especially at higher pressures. This may enhance the recombination rate effective after the pulse. For a Febetron 705, more than 90% of the ions were estimated to recombine with secondary electrons during the pulse duration at above 200 Torr. This high recombination fraction as compared with that for a Febetron 706 is due partly to the longer pulse duration (100 ns) of this beam and partly to the low mean energy of secondary electrons owing to a small E_s/p described already. For this beam, the mean secondary electron energy estimated from E_s/p is below 0.3 eV except for lower pressures as shown in Fig. 7. In contrast to this, the mean secondary energy for a Febetron 706 is higher than 7 eV except for a short period where the induced electric field changes the sign, as shown in Fig. 8.

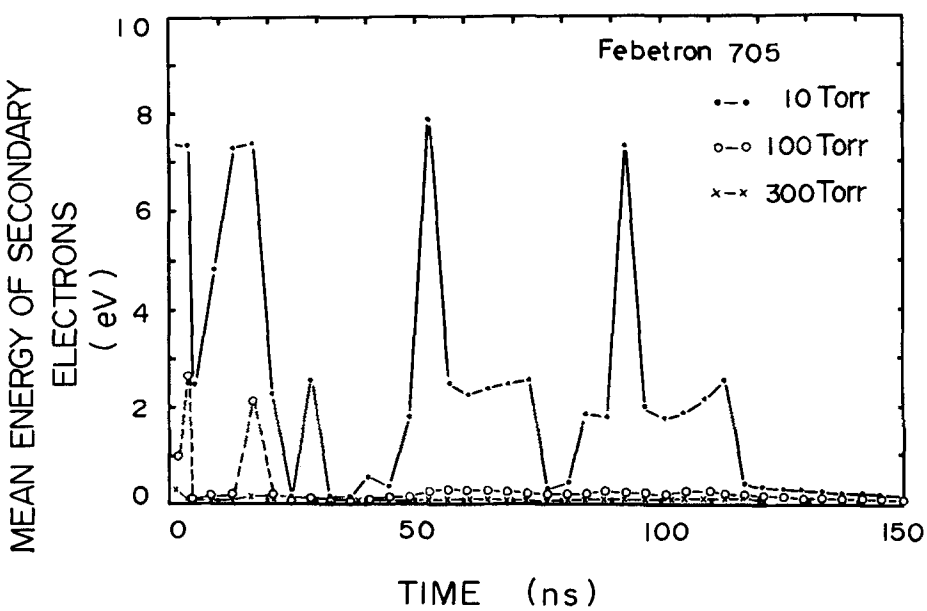

FIG. 7. The mean secondary electron energy estimated from the reduced electric field E_s/p by Eq. (9) during the pulse duration as functions of time for 10, 100, and 300 Torr of methane with a Febetron 705 beam.

CONCLUSION

In this paper, we have analyzed the ionization process of gaseous methane by pulsed electron beams during the pulse duration through a numerical simulation on a rather simple model. Although we neglected the radial distribution of the beam electron density and the beam radius variation with time in this model, the obtained results may represent the feature of the processes during the pulse duration.

The main conclusions obtained from this paper are as follows:

(1) For a Febetron 706, the ionization due to the second term (secondary ionization by secondary electrons accelerated by the induced electric field) is large, even at 300 Torr. The fraction of the secondary electrons neutralized during the pulse duration is small due to the high mean secondary electron energy.

(2) For a Febetron 705, ionization is mainly due to the beam electrons and about 90% of secondary electrons recombine with ions during the duration of the pulse.

In the computation, only ionic species were taken into account. However, in order to clarify the total processes occurring at an early stage of radiolysis of methane so as to elucidate the product yield, the radical and excited nuetral species should also be considered together. This will be a subject of a further study.

Willis, Boyd, and Miller[24] observed anomalous large yields of N_2 from N_2O, H_2 from H_2S, and CO from CO_2 at low pressures by a Febetron 706 beam. This phenomenon can be explained by the effect of the induced electric field as described in the text. The anomaly for a Febetron 705 beam is rather small according to the study by Boyd, Armstrong, Willis, and Miller.[25] As shown in the present paper, the effect of the induced electric field on ionization is negligibly small for this beam. The anomaly due to this beam may be due to the action of secondary electrons accelerated by the beam charge before the beam charge is neutralized by the accumulated ions. (After this time, this effect becomes negligibly small.) The anomaly may be partly due to the induced electric field caused by the hollowness of the beam.[14] The hollowness may cause a higher induced electric field and so produce more ionization. This problem will require a further study on an advanted model.

In addition, even for a Febetron 705 beam, the secondary electrons are accelerated to some extent by the induced electric field during the pulse duration as shown in Fig. 7. This should be taken into account in the simulation of the radiolysis by this beam. This has been neglected in the simulation of various gases in the past,[26-28] where the mean secondary electron energy was assumed to be thermal.

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