



|                  |  |
|------------------|--|
| Title            | Properties of electron swarms in CF3I  |
| Author(s)        | Hasegawa, H.; Date, H.; Shimozuma, M.; Itoh, H.  |
| Citation         | Applied Physics Letters, 95(10), 101504<br><a href="https://doi.org/10.1063/1.3224197">https://doi.org/10.1063/1.3224197</a>   |
| Issue Date       | 2009-09-07   |
| Doc URL          | <a href="http://hdl.handle.net/2115/39288">http://hdl.handle.net/2115/39288</a>  |
| Rights           | Copyright 2009 American Institute of Physics. This article may be downloaded for personal use only. Any other use requires prior permission of the author and the American Institute of Physics. The following article appeared in Appl. Phys. Lett. 95, 101504 (2009) and may be found at <a href="http://dx.doi.org/10.1063/1.3224197">http://dx.doi.org/10.1063/1.3224197</a> |
| Type             | article  |
| File Information | APPLAB9510101504_1.pdf   |



[Instructions for use](#)

## Properties of electron swarms in CF<sub>3</sub>I

H. Hasegawa,<sup>1</sup> H. Date,<sup>2,a)</sup> M. Shimozuma,<sup>3</sup> and H. Itoh<sup>4</sup>

<sup>1</sup>Tomakomai National College of Technology, Tomakomai 059-1275, Japan

<sup>2</sup>Faculty of Health Sciences, Hokkaido University, Sapporo 060-0812, Japan

<sup>3</sup>Hokkaido Institute of Technology, Sapporo 006-8585, Japan

<sup>4</sup>Muroran Institute of Technology, Muroran 050-8585, Japan

(Received 5 July 2009; accepted 19 August 2009; published online 11 September 2009)

We report the electron swarm parameters, the drift velocity, and the ionization coefficients in CF<sub>3</sub>I gas for relatively wide ranges of reduced electric fields ( $E/N$ ). The drift velocity is measured based on the arrival-time spectra of electrons for  $E/N=200-3000$  Td, and the first and second ionization coefficients are determined by the steady-state Townsend method for  $E/N=400-5000$  Td. The results are compared with those of CF<sub>4</sub> to show that CF<sub>3</sub>I has a high reactivity for electron attachment in a low  $E/N$  region resulting in a much higher limiting  $E/N$  value (440 Td) than that of CF<sub>4</sub>. © 2009 American Institute of Physics. [doi:10.1063/1.3224197]

In the manufacturing process of semiconductor devices, fluorine compounds (C<sub>x</sub>F<sub>x</sub>) have been utilized as dry etching gases.<sup>1</sup> In particular, CF<sub>4</sub> has been widely used.<sup>2</sup> However, these specified chlorofluorocarbons are currently the target for reduction to prevent ozone depletion and global warming. Thus, a substitute gas CF<sub>3</sub>I was created, which possesses low values for ozone depletion and global warming potentials.<sup>3,4</sup>

In this article, we present the experimental results for the electron swarm parameters in CF<sub>3</sub>I, obtained by the arrival-time spectra (ATS) method using the double-shutter drift tube and the steady-state Townsend (SST) method. In the ATS method, we have measured the drift velocity  $W_m$  (the mean arrival-time drift velocity) for the reduced electric field at  $E/N$  from 200 to 3000 Td, while the first and second ionization coefficients ( $\alpha$  and  $\gamma$ ) have been determined in the SST method at  $E/N$  from 400 to 5000 Td. Although electron collision data for CF<sub>3</sub>I have been examined in detail by Christophorou and Olthoff,<sup>4</sup> the experimental swarm parameters for CF<sub>3</sub>I have not been reported in the literature. Therefore, we have made a comparison of the results with those of CF<sub>4</sub>. As to the electron transport properties in CF<sub>4</sub>, several studies have been presented. For example, Naidu and Prasad,<sup>5</sup> Shimozuma *et al.*,<sup>6</sup> Hunter *et al.*,<sup>7</sup> and Nakamura and Tomisawa<sup>8</sup> have obtained the swarm parameters in CF<sub>4</sub> experimentally, while Itoh *et al.* (1993)<sup>9</sup> have determined them computationally by the Boltzmann equation analysis. Furthermore, Christophorou and co-workers<sup>1,2</sup> have assessed and integrated several investigations including some of those above.

The experimental techniques used in the present study are based on two methods: the ATS method and the SST method. These are described briefly here. To measure the drift velocity  $W_m$ , we have employed the ATS method.<sup>10</sup>  $W_m$  is determined from the distribution of arrival-time of electrons at fixed locations, which is a coefficient of the specific transport equation given by the interchange in space and time in the conventional continuity equation as follows:

$$\frac{\partial n}{\partial z} = \alpha^{(0)}n - \alpha^{(1)}\frac{\partial n}{\partial t} + \alpha^{(2)}\frac{\partial^2 n}{\partial t^2} - \alpha^{(3)}\frac{\partial^3 n}{\partial t^3} + \dots, \quad (1)$$

where

$$\alpha^{(0)} = \frac{1}{N(z)} \frac{dN(z)}{dz} = \bar{\alpha}, \quad (2)$$

$$\alpha^{(1)} = \frac{d\langle t \rangle}{dz} = \frac{1}{W_m}, \quad (3)$$

$$N(z) = \int_0^\infty n(z, t) dt. \quad (4)$$

Here,  $n(z, t)$  is the electron number density at a position  $z$  and time  $t$ ,  $\bar{\alpha}$  is the effective ionization coefficient, and  $\langle t \rangle$  represents the average of the arrival-time of electrons at every location. The coefficients in the right-hand side of Eq. (1) are the parameters describing the behavior of the ATS at the spatial location of the electrode capturing arrival electrons. The experiment is conducted using a double-shutter drift tube, where arriving electrons are collected by the electrode with shutter 2 at a certain distance from the cathode (with shutter 1 releasing initial electrons). The experimental apparatus and procedure for this method are the same as those described by Hasegawa *et al.*<sup>11</sup> The value  $W_m$  is determined by the derivative of the mean arrival-time  $\langle t \rangle$  with respect to the drift distance as in Eq. (3). On the other hand, to determine the effective ionization coefficient  $\bar{\alpha}$ , the SST method has been used. The experimental apparatus and procedure are basically the same as those by Hasegawa *et al.*<sup>12</sup> Since the theoretical equation for the current growth for the SST experiment is represented by

$$I = I_0 \frac{\frac{\alpha}{\alpha - \eta} \exp[(\alpha - \eta)d] - \frac{\eta}{\alpha - \eta}}{1 - \gamma_T \frac{\alpha}{\alpha - \eta} \{ \exp[(\alpha - \eta)d] - 1 \}}, \quad (5)$$

we can deduce the first ionization coefficient  $\alpha$  and the electron attachment coefficient  $\eta$  by fitting this equation to the experimental current growth curve. Here,  $I_0$  is the initial current value and  $\gamma_T$  is the secondary coefficient. If the second-

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic mail: date@hs.hokudai.ac.jp. Tel.: +81-11-706-3423. FAX: +81-11-706-4916.

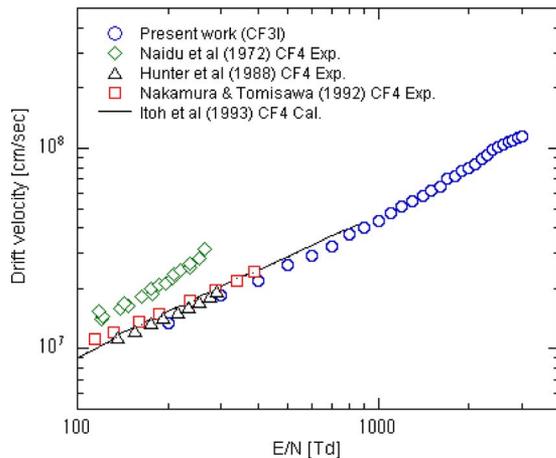


FIG. 1. (Color online) Comparison of the drift velocity. The point in the present work represents the mean arrival-time drift velocity  $W_m$ . In the figure legend, Exp. denotes the experimental result and Cal. the calculated result.

any effect appears significantly, the attachment process can be regarded as negligible (i.e.,  $\eta \cong 0$ ). Then, Eq. (5) is reduced to

$$I = I_0 \frac{\exp(\alpha d)}{1 - \gamma_T [\exp(\alpha d) - 1]} \quad (6)$$

In the fitting procedure of each equation to the experimental result, the linearized least-square-method was employed.

The purity of  $\text{CF}_3\text{I}$  gas sample used is above 99.99% (Tosoh F-Tech, Inc.).<sup>13</sup> The reduced electric fields ( $E/N$ ) applied for the ATS experiment was  $E/N=200\text{--}3000$  Td and the gas pressure was 0.1–1.0 Torr at 0 °C-reduced temperature, while  $E/N=400\text{--}5000$  Td and the gas pressure 0.2–4 Torr for the SST experiment. The drift length between the cathode and the double-shutter to collect electrons in the ATS experiment was 10–40 mm, and the gap length of the electrodes in the SST experiment (using the Harrison type electrodes) was 2–15 mm.

Figure 1 shows the drift velocity in comparison with the reported data for  $\text{CF}_4$ . The present  $W_m$  values for  $\text{CF}_3\text{I}$  at  $E/N$  below 1000 Td are generally 10%–20% smaller than the drift velocity for  $\text{CF}_4$  by the other investigations, except for the drift velocity by Naidu and Prasad,<sup>5</sup> which lies at notably higher values than the others.

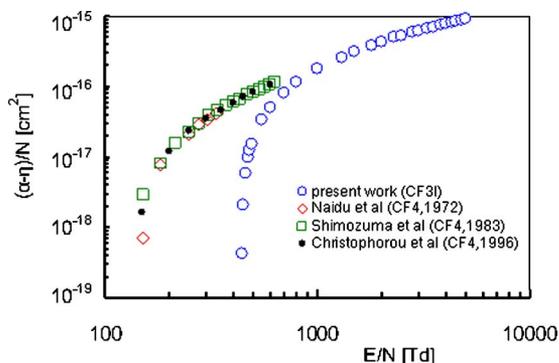


FIG. 2. (Color online) Comparison of the effective first ionization coefficient,  $\bar{\alpha}/N=(\alpha-\eta)/N$ . The data by Christophorou *et al.* (Ref. 2) ( $\text{CF}_4$ ) are recommended values.

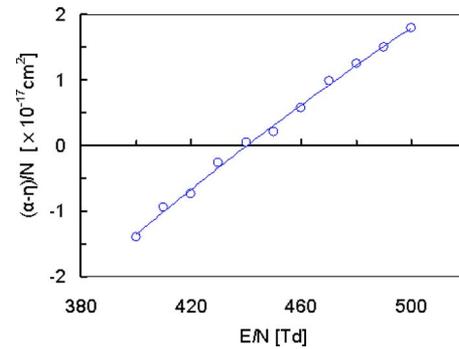


FIG. 3. (Color online) The effective first ionization coefficient,  $\bar{\alpha}/N=(\alpha-\eta)/N$ , in a low  $E/N$  region.

The effective first ionization coefficient (per gas density  $N$ ) is shown in Fig. 2. Although the values of the coefficient for  $\text{CF}_3\text{I}$  are much lower than those for  $\text{CF}_4$  at  $E/N$  below 1000 Td, they exhibit an inclination to approach to the value for  $\text{CF}_4$  as  $E/N$  increases. For the low  $E/N$  region, the coefficient is specifically plotted in Fig. 3. The limiting  $E/N$  (for  $\alpha-\eta=0$ ) is found to be about 440 Td, which is much greater than 140 Td for  $\text{CF}_4$ .<sup>6</sup> This suggests that the  $\text{CF}_3\text{I}$  molecule has a high reactivity for electron attachment. In fact, the attachment cross section of  $\text{CF}_3\text{I}$  has been estimated to be very large (particularly for electron energy below 1 eV).<sup>4</sup> It should be noted that the limiting  $E/N$  found here is also superior to that of  $\text{SF}_6$  (355 Td).<sup>14</sup> Figure 4 shows the total secondary ionization coefficient  $\gamma_T$ , which was measurable at  $E/N$ 's above 2000 Td.

The experiment in this study has been performed based on the assumption that energy distribution of electrons is in the equilibrium state (i.e., the hydrodynamic regime) that remains unchanged with a negligibly small effect of field distortion in the various gap lengths. In order to confirm the validity of the present experiment at the high  $E/N$  region in terms of the equilibrium, we attempted to draw the current growth by the Gosseries plot.<sup>15</sup> This plot represents the relationship between the reciprocal  $Y_d$  of the current at an electrode separation  $d$  and the reciprocal current measured at  $d+\Delta d$  as

$$Y_d = Y_{d+\Delta d} \exp(\alpha \Delta d) + \frac{\gamma_T}{I_0} [\exp(\alpha \Delta d) - 1], \quad (7)$$

which is derived from Eq. (6). A plot of  $Y_d$  against  $Y_{d+\Delta d}$  is linear only if both  $\alpha$  and  $\gamma_T$  are spatially independent and the initial current  $I_0$  is constant. Figure 5 shows the Gosseries plots for  $E/N=4000$  and 5000 Td. As is shown in the figure, the linearity is very good for the both cases, and this implies

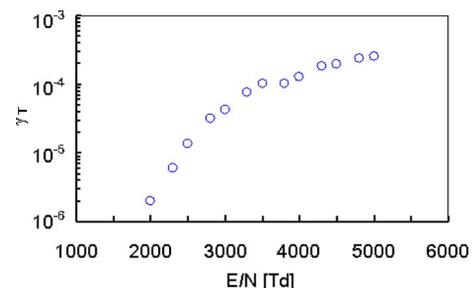


FIG. 4. (Color online) The secondary ionization coefficient as a function of  $E/N$ .

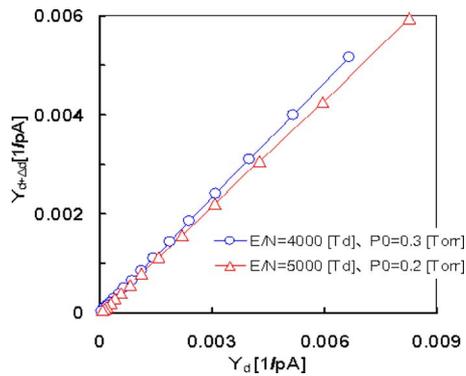


FIG. 5. (Color online) The Gosses plots for the SST experiment with  $\text{CF}_3\text{I}$  at  $E/N=4000$  and  $5000$  Td. Here,  $P_0$  (pressure at  $0^\circ\text{C}$ ) is  $0.3$  Torr and  $\Delta d$  is  $0.03$  cm at  $E/N=4000$  Td, and  $0.2$  Torr and  $0.05$  cm at  $E/N=5000$  Td.

that the experiments have been carried out under the equilibrium state for every gap length configured.

In conclusion, as the electron swarm parameters in  $\text{CF}_3\text{I}$  gas, we have determined the drift velocity ( $W_m$ ) by using a double-shutter drift tube for  $E/N$  from  $200$  to  $3000$  Td, and the first and second ionization coefficients ( $\alpha$  and  $\gamma$ ) by the SST method from  $E/N=400$  to  $5000$  Td. The results were compared with those of  $\text{CF}_4$ . The comparison showed that the parameters differ largely in low  $E/N$  region while they have a tendency to coincide with each other at high  $E/N$  above  $1000$  Td. The limiting  $E/N$  value was about  $440$  Td, and the secondary ionization coefficient ranged from  $10^{-6}$  to  $10^{-4}$  orders for  $E/N$  from  $2000$  to  $5000$  Td with a monotonic increase. These results suggest that  $\text{CF}_3\text{I}$  can be used not only as a dry etching gas in semiconductor fabrications but also as an effective insulation gas between high voltage gaps. For the latter application, further investigations are necessary

regarding disintegrations of  $\text{CF}_3\text{I}$  through the discharges and the chemical stabilities.

The authors are most grateful to Tosoh F-Tech Inc. for providing  $\text{CF}_3\text{I}$  gas. The authors are also indebted to Shibata N. and Narita S. for helping to perform the experiments. This work was financially supported in part by the Grant-in-Aid for Scientific Research in Japan.

<sup>1</sup>L. G. Christophorou and J. K. Olthoff, *J. Phys. Chem. Ref. Data* **28**, 967 (1999).

<sup>2</sup>L. G. Christophorou, J. K. Olthoff, and M. V. V. S. Rao, *J. Phys. Chem. Ref. Data* **25**, 1341 (1996).

<sup>3</sup>New Energy and Industrial Technology Development Organization (NEDO), Global Warming Countermeasures: Japanese Technologies for Energy Savings/GHG Emissions Reduction (Revised Edition) (2008) <http://www.nedo.go.jp/english/publications/reports/index.html>.

<sup>4</sup>L. G. Christophorou and J. K. Olthoff, *J. Phys. Chem. Ref. Data* **29**, 553 (2000).

<sup>5</sup>M. S. Naidu and A. N. Prasad, *J. Phys. D: Appl. Phys.* **5**, 983 (1972).

<sup>6</sup>M. Shimozuma, H. Tagashira, and H. Hasegawa, *J. Phys. D: Appl. Phys.* **16**, 971 (1983).

<sup>7</sup>S. R. Hunter, J. G. Carter, and L. G. Chistophrou, *Phys. Rev. A* **38**, 58 (1988).

<sup>8</sup>Y. Nakamura and Y. Tomisawa, Technical Paper of Electrical Discharge Committee Gas Discharges, Ed. 92–39 IEE Japan (in Japanese) (1992).

<sup>9</sup>H. Itoh, T. Matsumura, K. Satoh, Y. Nakao, and H. Tagashira, Proceedings of the 21st International Conference on Phenomena in Ionized Gases (ICPIG), Bochum, Germany, 1993 (unpublished), Vol. 1, pp. 385–386.

<sup>10</sup>K. Kondo and H. Tagashira, *J. Phys. D: Appl. Phys.* **23**, 1175 (1990).

<sup>11</sup>H. Hasegawa, H. Date, M. Shimozuma, K. Yoshida, and H. Tagashira, *J. Phys. D: Appl. Phys.* **29**, 2664 (1996).

<sup>12</sup>H. Hasegawa, Y. Sato, K. Murai, M. Shimozuma, and H. Tagashira, *J. Phys. D: Appl. Phys.* **18**, 1361 (1985).

<sup>13</sup>Tosoh F-Tech, Inc., <http://www.f-techinc.co.jp/pages/eindex.html>.

<sup>14</sup>M. Shimozuma, H. Itoh, and H. Tagashira, *J. Phys. D: Appl. Phys.* **15**, 2443 (1982).

<sup>15</sup>M. A. Folkard and S. C. Haydon, *J. Phys. B* **6**, 214 (1973).