Properties of electron swarms in CF$_3$I

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We report the electron swarm parameters, the drift velocity, and the ionization coefficients in CF$_3$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$_4$ to show that CF$_3$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$_4$. © 2009 American Institute of Physics. [doi:10.1063/1.3224197]

In the manufacturing process of semiconductor devices, fluorine compounds (CF$_x$I$_y$) have been utilized as dry etching gases. In particular, CF$_4$ has been widely used. However, these specified chlorofluorocarbons are currently the target for reduction to prevent ozone depletion and global warming. Thus, a substitute gas CF$_3$I was created, which possesses low values for ozone depletion and global warming potentials.

In this article, we present the experimental results for the electron swarm parameters in CF$_3$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$_4$I have been examined in detail by Christophorou and Olthoff, the experimental swarm parameters for CF$_4$I have not been reported in the literature. Therefore, we have made a comparison of the results with those of CF$_4$. As to the electron transport properties in CF$_3$I, several studies have been presented. For example, Naidu and Prasad, Shimozuma et al., Hunter et al., and Nakamura and Tomisawa have obtained the swarm parameters in CF$_3$I experimentally, while Itoh et al. (1993) have determined them computationally by the Boltzmann equation analysis. Furthermore, Christophorou and co-workers 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. $W_m$ 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:

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

where

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

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

$$N(z) = \int_0^{\infty} n(z,t)dt.$$
Drift velocity for CF4 by the other investigations, except for the SST experiment was 10–40 mm, and the gap length of the electrodes in the SST experiment was 10–150 mm, and the gap length of the electrodes was 2–15 mm. The drift length between the electrodes applied for the ATS experiment was 200–3000 Td and the gas pressure 0.1–1.0 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 CF4. The present $W_m$ values for CF3I at $E/N$ below 1000 Td are generally 10%–20% smaller than the drift velocity for CF4 by the other investigations, except for the drift velocity by Naidu and Prasad, which lies at notably higher values than the others.

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

The purity of CF3I gas sample used is above 99.99% (Tosoh F-Tech, Inc.). The reduced electric fields ($E/N$) applied for the ATS experiment was $E/N=200–3000$ Td and the gas pressure was 0.1–1.0 Torr at 0 °C-reduced temperature, while $E/N=400–5000$ 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 experimental result and Cal. the calculated result.

The effective first ionization coefficient ($\alpha/N=(\alpha-\eta)/N$) is shown in Fig. 2. Although the values of the coefficient for CF3I are much lower than those for CF4 at $E/N$ below 1000 Td, they exhibit an inclination to approach to the value for CF4 as $E/N$ increases. For the low $E/N$ region, the coefficient is specifically plotted in Fig. 3. The limiting $E/N$ is found to be about 440 Td, which is much greater than 140 Td for CF4. This suggests that the CF3I molecule has a high reactivity for electron attachment. In fact, the attachment cross section of CF3I has been estimated to be very large (particularly for electron energy below 1 eV). It should be noted that the limiting $E/N$ found here is also superior to that of SF6 (355 Td). 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 Gossseries plot. 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

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

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

In conclusion, as the electron swarm parameters in CF$_3$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 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 CF$_3$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 CF$_3$I through the discharges and the chemical stabilities.

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