

Dissociation Processes of SiCl_4 and Plasma Parameters measured by Transient Spectroscopy at the Beginning of a SiCl_4 –Helium dc Discharge*

Takeki Sakurai, Shigeru Kobayashi,^A Jun Ogura,^B
Yukio Inoue and Hirokazu Hori

Department of Electronic Engineering and Computer Science,
Yamanashi University, Kofu 400, Japan.

^A Present address: Olympus Optical Co. Ltd, Hachioji 192, Japan.

^B Present address: YHP, Hachioji 192, Japan.

Abstract

We propose that the excitation or the dissociation mechanism and plasma parameters in a discharge can be estimated by spectroscopic methods, such as the measurement of the transient behaviour of fluorescences at the beginning of a pulsed dc discharge. Fluorescences emitted from excited atoms and dissociated fragments from 270 to 640 nm in wavelength are measured as a function of time at the beginning of a discharge of a He– SiCl_4 gas mixture. The transient waveform of fluorescence is calculated by considering the experimental results of discharge current and voltage between electrodes measured as a function of time. From a comparison of the experimental and calculated waveforms of fluorescence it is concluded that the fragment emitting the light, SiCl_2 , is excited in a single-step from SiCl_4 by electronic collisions and the fluorescence-emitting fragments of SiCl_3 , SiCl , Cl_2 , Cl , Si and Cl^+ in a discharge can never be excited by electronic collisions in a single step. Furthermore, an average electron energy in the plasma at a steady state is simply estimated from a measurement of the transient behaviour of emission lines from helium excited states. The result is in fair agreement with the value measured by using an electric probe.

1. Introduction

Discharges are widely used in microelectronics technology. Especially, in plasma processing such as etching and deposition, discharges of gas including polyatomic molecules such as SiH_4 , CH_4 and SiCl_4 are of great interest because of their practical applications. Dissociated molecules and atoms have an important role in these processes. Methods such as optical emission spectroscopy and laser-induced fluorescence spectroscopy have come to be nonintrusive and sensitive diagnostic tools for these dissociated materials, and the absolute density and spatial distribution of radicals have been measured in SiH_4 and CH_4 discharges (Roth *et al.* 1984; Schmitt *et al.* 1984; Matsumi *et al.* 1986; Asano *et al.* 1987; Takubo *et al.* 1988; Mataras *et al.* 1989; Tachibana *et al.* 1990, 1991; Itabashi *et al.* 1990; Naito *et al.* 1993). However, there still remains the problem of understanding the exact dissociation and excitation mechanisms of these polyatomic molecules.

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In order to discuss the excitation and dissociation processes in a plasma it is necessary to know the values of plasma parameters. A plasma parameter is usually measured with an electric probe but this method is not always easy to use in an actual discharge. It is preferable to measure parameters by nonintrusive methods such as the spectroscopic method.

Discharges always start with a gas breakdown and at the beginning of the discharge all plasma parameters show transient behaviour before reaching steady-state values. As a result, measurable quantities such as fluorescence, discharge current and voltage applied between electrodes show their own time behaviours, and their transient waveforms include much important information concerning discharge parameters and various atomic and molecular processes. Therefore, analysis of these transient signals makes it possible not only to elucidate various excitation processes but also to estimate plasma parameters.

In this study we applied a pulsed dc discharge to a gas mixture of helium and SiCl_4 . The transient behaviour of the fluorescence emitted from the dissociated fragments of SiCl_4 is measured during the beginning of the discharge. From these experimental results the dissociation or the excitation process of various fluorescence-emitting fragments is clarified. In addition, we show that the approximate value of the electron energy in the plasma can be simply estimated from the nonintrusive measurement of the transient signal.

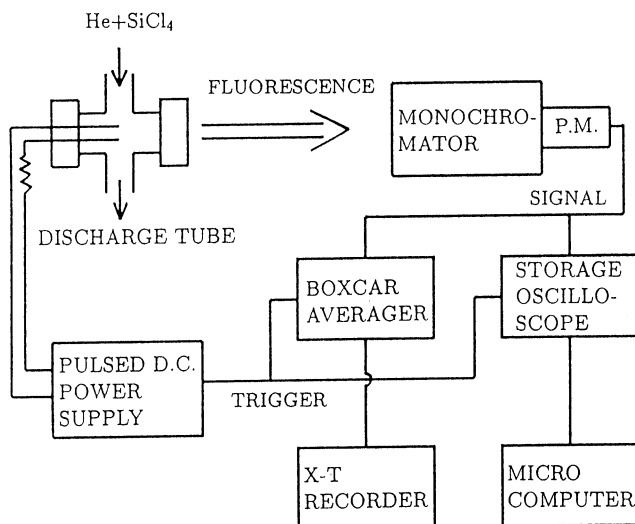


Fig. 1. Experimental arrangement.

2. Experiments

(2a) Apparatus

The experimental apparatus is shown in Fig. 1. A helium buffer gas mixed with SiCl_4 flowed slowly through a discharge tube with diameter of 30 mm. Most of the experiments were conducted with a helium pressure of 25 Torr, SiCl_4 pressure of 5 Torr and flow rate of 0.4 l/min (1 Torr $\equiv$ 133 Pa). A stainless steel cylindrical electrode of length 10 mm and diameter 1 mm was used, and the

distance between electrodes was 5 mm. A pulsed dc voltage with risetime 35 ns and decay time 50 ns was applied between the electrodes. The Debye length under the experimental condition of 100 mA is estimated to be about 0.1 mm and the sheath thickness is less than 0.5 mm. The glow was uniform around the electrodes. It was experimentally confirmed that the fluorescence intensity distribution measured with a spatial resolution of 1 mm was quite uniform across the gap except for the region of a cathode dark space, where the thickness was less than 1 mm.

Transient atomic and molecular fluorescences during the beginning of the discharge passed through the glass window of the discharge tube and a monochromator, were then detected by a photomultiplier and the output signal was recorded by a storage oscilloscope or a gated boxcar averager. In this experiment the time resolution of the detecting system was much faster than the time scale of the transient discharge. Since the system measuring the transient spectrum had no appreciable spatial resolution, the detected signal is the spatial average of the fluorescence emitted between the electrodes.

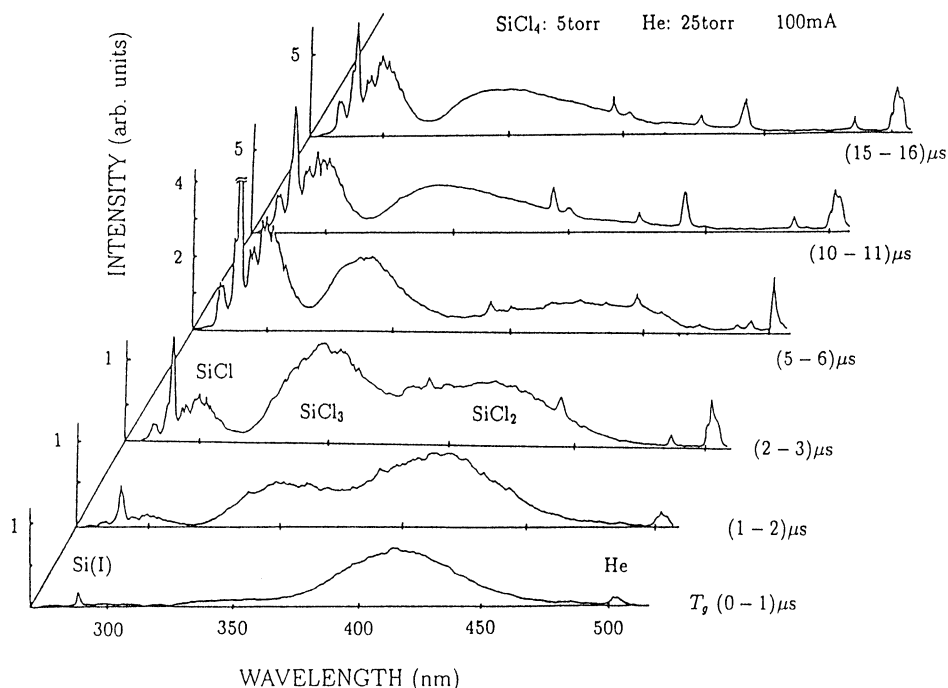


Fig. 2. Time-resolved fluorescence spectra emitted during the beginning of a pulsed dc discharge in a mixture of SiCl_4 and He.

(2b) Results of Fluorescence

Experimental results on the time-resolved fluorescence spectrum obtained under the condition of glow discharge at the steady-state discharge current of 100 mA are shown in Fig. 2. Here T_g is the gate width of the boxcar averager and

the discharge starts at time 0 μ s. Molecular spectra are observed in addition to He, Si and Cl atomic emission lines. The emission at a wavelength of around 300 nm is found to be due to the transition from B to X in the SiCl diatomic molecule (Pearse and Gaydon 1976). The spectrum in the range 330 to 470 nm has two peaks at wavelengths of about 340 and 420 nm, and these two components have different time behaviours. These fluorescences were originally thought to be emitted from SiCl₂ (Asundi *et al.* 1938). However, by analogy with emission spectra of SiF₂ and SiF₃ (Rao 1970; Wang *et al.* 1973), it was determined that emissions with the peaks at 340 and 420 nm originated from SiCl₃ and SiCl₂, respectively. The weak diatomic emission due to the transition from B to X in Cl₂ was also measured at a wavelength of around 580 nm, which is not shown in Fig. 2. In the same gas mixture, when the discharge became an arc mode at discharge current of 10 A, all molecular emission disappeared, and only atomic and ionic emission lines of He, Si and Cl were observed.

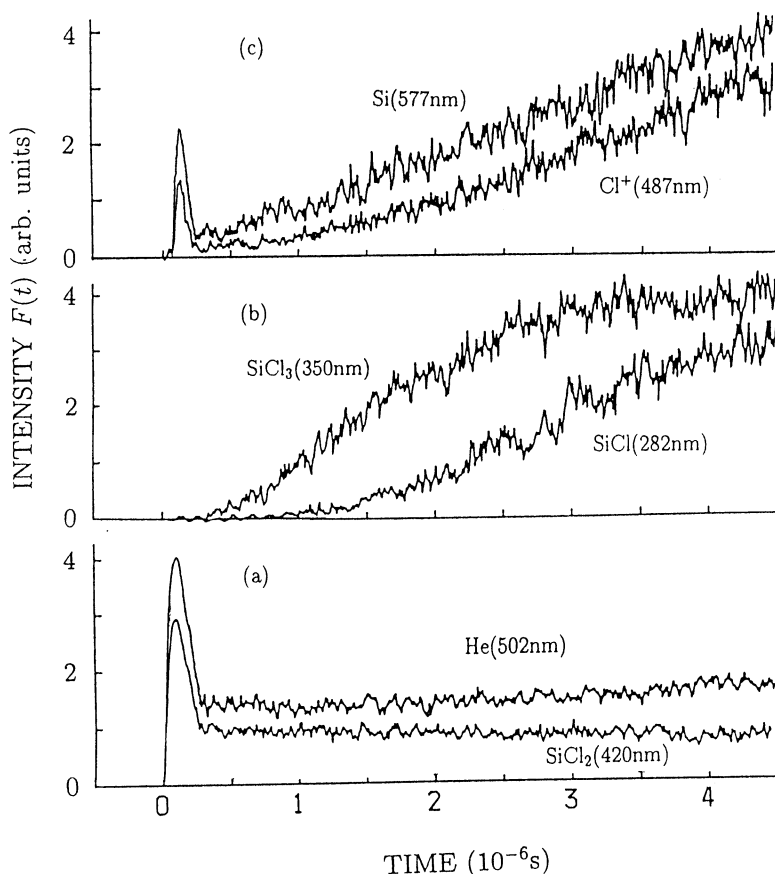


Fig. 3. Transient light intensities emitted from atoms and molecules under the same discharge conditions as shown in Fig. 2.

The exact transient behaviour of light intensities emitted from atoms and molecules was measured by a storage oscilloscope, as shown in Fig. 3. The line intensities of atomic helium at 502 nm, as well as molecular SiCl₂ at 420 nm, have

an initial peak followed by a constant value. We hereafter call this waveform type A. The emissions of SiCl at 282 nm and SiCl_3 at 350 nm gradually increase with time until about $5\ \mu\text{s}$ and reach a steady state at a time later than $5\ \mu\text{s}$. The gradually increasing waveform known as type B is obtained for the emission of Cl^2 at 601 nm, Si at 391 nm and Cl at 441 nm, none of which are shown in Fig. 3. The emission of Cl^+ at 487 nm has an initial peak followed by a gentle increase, and this waveform known as type C is a mixture of types A and B. The emission of Si at 288 and 577 nm also belongs to type C.

In order to analyse the excitation and dissociation processes, it is important to estimate the lifetime of the fluorescence-emitting fragments. For the purpose of estimating its order of magnitude, the light intensity was observed in an afterglow at the end of the pulsed voltage, and it was shown that the intensity decays exponentially. But these decay times are of the same order of magnitude as the decay time of the discharge, so an accurate value for the lifetime of the state could not be obtained from the experimental results. However, the measured fall time of the intensity can give an upper limit for the lifetime of the excited state of the fluorescence-emitting fragments, τ . The results indicate that τ for He(502), Si(391), Si(577) and SiCl (282) is less than 50 ns, τ for Cl(441), Cl^+ (487) and SiCl_2 (420) is less than 60 ns, and τ for Si(288) and SiCl_3 (350) is less than 100 ns, where values in parentheses show the fluorescence wavelength measured.

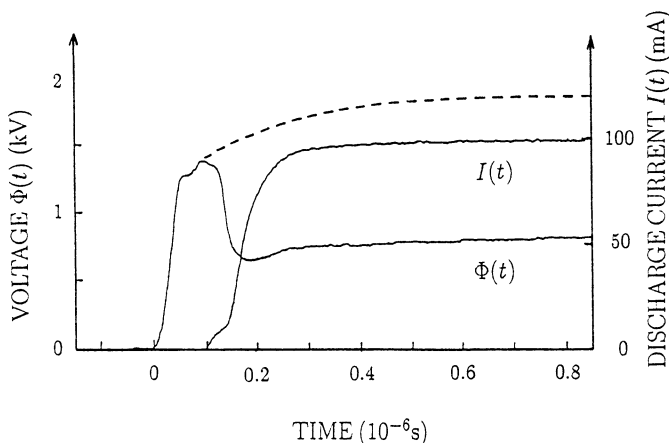


Fig. 4. Waveforms of the discharge current and the voltage between electrodes. The discharge conditions are the same as shown in Figs 2 and 3.

The waveforms of the discharge current $I(t)$ and the voltage between electrodes $\Phi(t)$ were measured simultaneously under the same discharge conditions, and the results are shown in Fig. 4. The dotted curve in Fig. 4 indicates the voltage when the discharge does not take place.

3. Discussion

(3a) Excitation Process of Fluorescence-emitting Fragments

If the upper state of fluorescence-emitting fragments is excited from a parent molecule by an electronic collision in a single step, the density of the state $n^*(t)$

is given by

$$\frac{dn^*(t)}{dt} = \langle \sigma v_e(t) \rangle n_e(t) N - \gamma n^*(t), \quad (1)$$

where σ is the cross section of the electronic collision, $v_e(t)$ is the electron velocity, $n_e(t)$ is the electron density, N is the density of parent molecules in the ground state, γ is the decay rate of the excited state and the angle brackets represent the thermal average. The same equation is also applied to the atom excited by a single-step electronic collision. In order to calculate the time behaviour of the emission intensity, equation (1) must be solved with time-dependent $v_e(t)$ and $n_e(t)$. The intensity as a function of time, $F(t)$, is proportional to $An^*(t)$ where A is the transition probability of the spontaneous emission.

The relative value of the electron density $n_e(t)$ at the discharge starting time is estimated from the relationship that the discharge current $I(t)$ is proportional to $n_e(t)v_d(t)$ where $v_d(t)$ is the electron drift velocity. The mean free time of electrons colliding with atoms is less than 1 ns under the experimental conditions, and the drift velocity $v_d(t)$ as a function of time is determined by the electric field $E(t)$ on a time scale of $0.1 \mu\text{s}$. For the case shown in Fig. 4 the space charge is rapidly increased until $0.1 \mu\text{s}$ and the electric field distribution between the electrodes changes considerably during this time. At around $0.1 \mu\text{s}$ the discharge current becomes measurable and the space charge approaches the steady-state value. At times later than $0.1 \mu\text{s}$ a large part of the voltage $\Phi(t)$ is applied to the cathode fall, however, the relative distribution of the voltage across the gap may be almost the same as that of the steady state. This indicates that the electric field $E(t)$ is proportional to $\Phi(t)$ in this time period. Then, the velocity $v_d(t)$ is assumed to be proportional to the voltage between the electrodes $\Phi(t)$ after the discharge current $I(t)$ becomes measurable on a mA scale and the voltage $\Phi(t)$ starts decreasing. Finally we have

$$n_e(t) \propto I(t)/\Phi(t). \quad (2)$$

The behaviour of $n_e(t)$ is estimated from the results shown in Fig. 4 by using (2). The electron density reaches a steady state at about 200 ns.

In order to obtain the transient behaviour of $n^*(t)$ from (1), it is not necessary to know the proportional constant in (2), but the term in angle brackets in (1) is very sensitive to the electron energy. The electron energy distribution is supposed to be in thermal equilibrium on a time scale of several tens of ns and the average electron energy $V_e(t)$ in a helium discharge is almost proportional to E/p in the region 0.1 to $1 \text{ V cm}^{-1} \text{ Torr}^{-1}$ (Warren and Parker 1962). By using the same relationship between the electric field and voltage as described in the last section, we again assume that the time dependence of the average electron energy $V_e(t)$ at a fixed gas pressure with the given discharge tube is proportional to the voltage between electrodes $\Phi(t)$. Then, $V_e(t)$ is given by

$$V_e(t) = V_{e0}\Phi(t)/\Phi_0, \quad (3)$$

where V_{e0} and Φ_0 are the average electron energy and voltage between electrodes,

respectively, in a steady state. In the calculation of the angle bracket in (1) it is also assumed that the electron energy distribution is Maxwellian and that the cross section for electronic collision as a function of electron energy V is given by the Fabrikant formula

$$\sigma = \sigma_m \frac{V - V_i}{V_m - V_i} \exp\left(\frac{V_m - V}{V_m - V_i}\right), \quad (4)$$

where V_i and V_m are the threshold energy and energy at the maximum, respectively. In an actual discharge the energy distribution may be slightly distorted from a Maxwellian. However, it is often helpful in practical applications to simply treat the electron energy distribution as a Maxwellian.

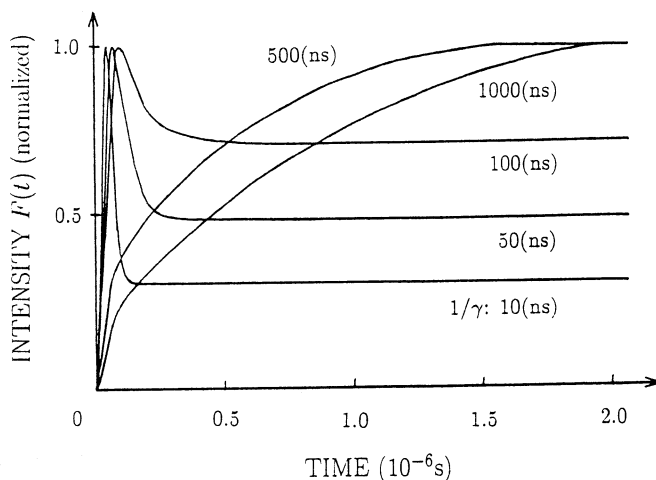


Fig. 5. Calculated time behaviour of the fluorescence intensity emitted from the state excited by electronic collisions in a single step under the experimental discharge condition. The parameter is the total decay rate of the state.

Now, the time behaviour of the state density $n^*(t)$ excited by electronic collisions in a single step is calculated from (1) with various values of the decay rate. The results are shown in Fig. 5. In the calculation the average electron energy at the steady state V_{e0} is 4 eV, which is estimated from the same optical analysis of the helium line at 502 nm, as described below in Section 3b. It is confirmed from the results shown in Fig. 5 that if the decay rate is larger than $1/(100 \text{ ns})$, the fluorescence intensity $F(t)$ which is proportional to the excited state density has an initial peak following the steady-state value and its time behaviour is very similar to the experimental result for fluorescences of type A. On the other hand, if the decay rate is less than $1/(500 \text{ ns})$, the intensity gradually increases with time and no clear initial peak appears. The experimental results described in the previous section show that the lifetime of fluorescence-emitting excited states for all species measured is less than 100 ns. Therefore, it is concluded that the state emitting fluorescence of type A is excited by an electronic collision in a single step, and the state emitting in type B cannot

be excited by a single-step electronic collision, but is excited by a multistep process. The state of type C may be excited by a mixture of single and multiple steps. Here, it is difficult to explain the exact meaning of the multiple steps. The multi-step process may include two- or multi-step excitations by electronic collisions or other various production mechanisms by radical- or ion-molecule reactions.

The first conclusion is confirmed from the fact that the helium fluorescences emitted from the states mainly excited in a single step are type A. The state SiCl_2^* emitting in type A may be excited from SiCl_4 by the processes $\text{SiCl}_4 + e \rightarrow \text{SiCl}_4^* \rightarrow \text{SiCl}_2^* + e$ and $\text{SiCl}_2^* + 2\text{Cl}$. The second dissociation process occurs very fast and on a time scale of ns SiCl_2^* seems to be excited by a single-step electronic collision.

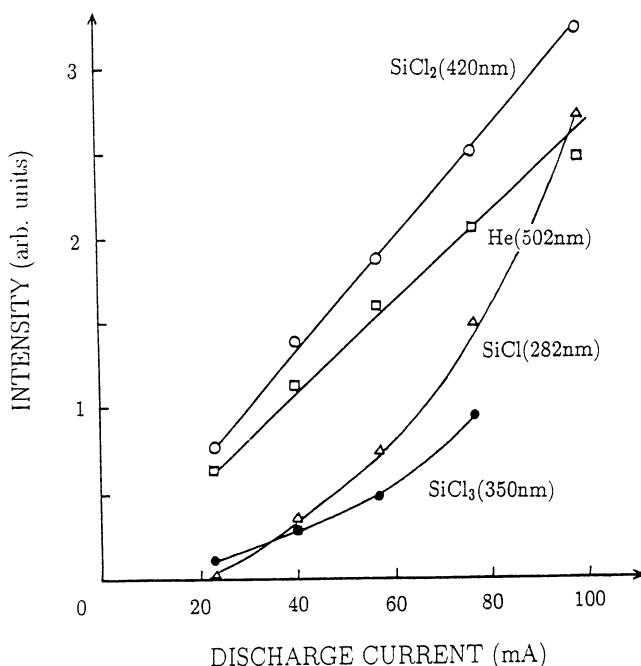


Fig. 6. Experimental results of the fluorescence intensities emitted from various species as a function of discharge current.

These excitation mechanisms have also been studied via the discharge current dependence of the fluorescence intensity. The fluorescences as a function of discharge current are shown in Fig. 6. The fact that the intensities of helium and SiCl_2 belonging to type A increased linearly with the discharge current is in marked contrast to the nonlinear increase in the intensity of SiCl_3 . In addition to SiCl_3 , all spectral lines belonging to type B show a nonlinearity. These results also confirm that the states of helium and $\text{SiCl}_2(420)$ emitting the fluorescence of type A are excited by a single-step electronic collision, and the states of $\text{SiCl}(282)$, $\text{SiCl}_3(350)$, $\text{Cl}_2(601)$, $\text{Si}(391)$ and $\text{Cl}(441)$ emitting in type B are excited by a multi-step collision.

(3b) Estimation of Electron Energy

The fluorescence intensity during the beginning of the discharge has a different time behaviour depending on the excitation and dissociation processes. In the previous section, it was stated that the excitation and dissociation mechanisms of the fluorescence-emitting fragments can be estimated from an analysis of the time behaviour of the fluorescences at a given electron energy. In this section we show that the approximate value of the average electron energy can be simply estimated from measurement of the time behaviour of the fluorescence emitted from an atom which is excited by electronic collisions in a single step with a known cross section.

Since highly excited states of helium are mainly excited by a single-step electronic collision under the experimental conditions, the measurements were made for emission lines at wavelengths of 501.6, 587.6 and 667.8 nm of He. In order to simplify the analysis the distance between the electrodes was set to 10 cm, which is much longer than that used in the previous section, and the fluorescence was measured at the centre of the positive column of a pure helium discharge. The average electron energy in the positive column in a steady state was also measured by a double-probe method for comparison with the result estimated by the spectroscopic method.

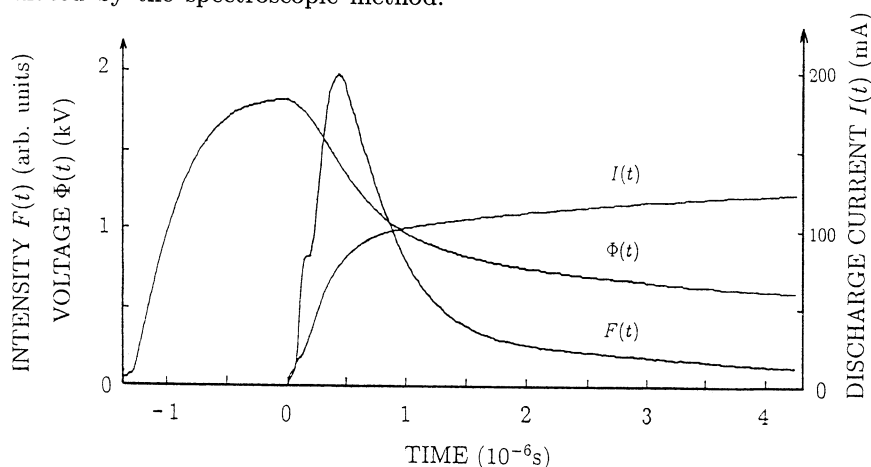


Fig. 7. Time behaviour of the fluorescence emitted from a helium excited atom, as well as the discharge current and voltage between electrodes of a pulsed dc discharge in pure helium. The distance between electrodes is 10 cm, which is much longer than that used in previous experiments.

The experimental result for the fluorescence $F(t)$ of the 502 nm helium line is shown in Fig. 7, as well as the voltage $\Phi(t)$ and discharge current $I(t)$. The initial peak in the fluorescence appears at about $0.5 \mu\text{s}$. The steady-state condition, which is not shown in Fig. 7, is reached at about $12 \mu\text{s}$. Other emission lines have a similar time dependence. The transient duration is much longer than that in the previous section. This is due to the change in the distance between electrodes, and the breakdown for a longer distance takes place slowly.

The time-dependent intensity $F(t)$ is calculated in the same way as described in the previous section by using (1)–(4) for various values of the average electron energy in the steady-state V_{e0} , which is the only unknown plasma parameter in

this case. In the calculation for the 3^1P state of helium the threshold energy V_i is 23 eV, the energy at the maximum V_m is 100 eV and the radiative decay rate A is $1.3 \times 10^7 \text{ s}^{-1}$ (Wiese *et al.* 1966). The radiative transition from the 3^1P to the ground state is neglected due to a resonance trapping at the gas pressure used. The total decay rate γ including the collisional decay is assumed to be $4 \times A$ at 5 Torr and 100 mA. This value is not so important in determining the transient intensity, because the observed time dependence is on a scale much greater than $1/\gamma \approx 20 \text{ ns}$. The electron energy distribution is, for simplicity, again assumed to be Maxwellian.

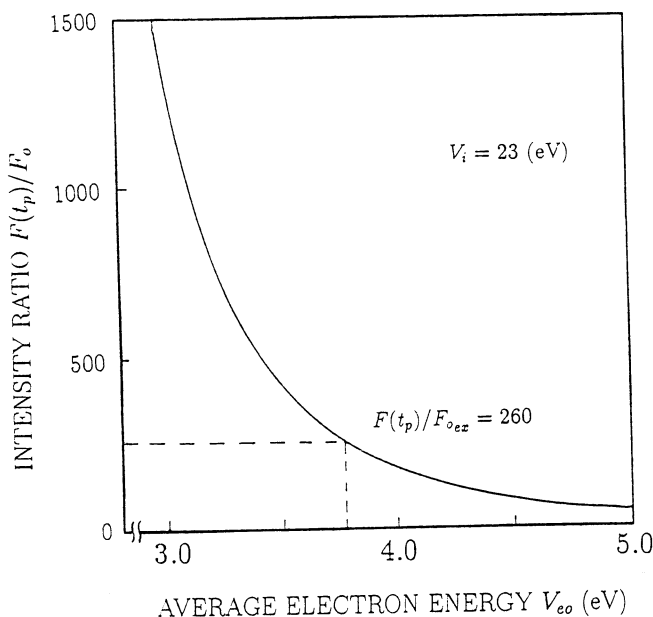


Fig. 8. Ratio between the peak value and steady-state value of the fluorescence calculated for the 502 nm helium line as a function of average electron energy V_{e0} .

The calculated ratio of the peak value and steady-state value of the fluorescence intensity $F(tp)/F_0$ is shown in Fig. 8 as a function of V_{e0} . The threshold energy V_i of the excitation in helium is much higher than the average electron energy, and the ratio $F(tp)/F_0$ is strongly dependent on the average electron energy V_{e0} at fixed value of V_i . The experimental value of $F(tp)/F_0$ obtained at 130 mA and 5 Torr is 250, and V_{e0} is estimated to be 3.8 eV. The calculated waveform of $F(t)$ at this value agrees with the experimental result.

The value of V_{e0} as a function of pressure measured from various emission lines is shown in Fig. 9. Results obtained by the double-probe method at the dc discharge are also plotted and almost agree with the results obtained by the spectroscopic method. However, it seems that the spectroscopic results show no pressure dependence. At higher pressures the excited state can be pumped by a stepwise excitation from the metastable state and a cascade transition from the upper levels in addition to the single-step electronic collision. In particular, the role of the stepwise excitation becomes important at times much later than

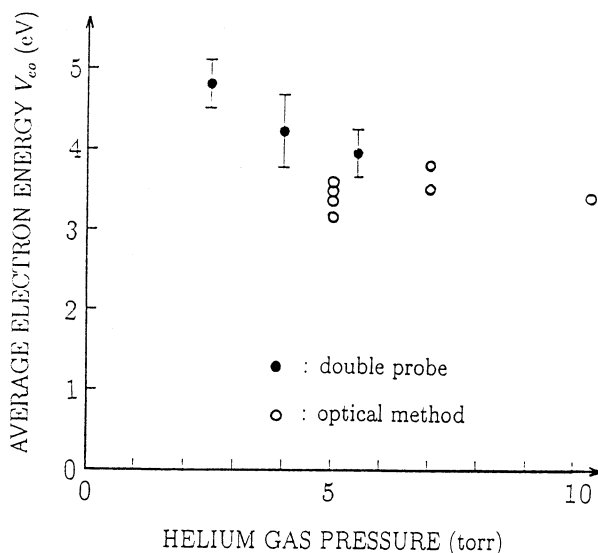


Fig. 9. Average electron energy in the steady state V_{e0} estimated from measurement of fluorescence during the beginning of the discharge. The results obtained by an electric double probe are also plotted.

the time of the initial peak, and the apparent experimental ratio $F(tp)/F_0$ is decreased. As a result the electron energy estimated by the spectroscopic method at higher pressures may be slightly higher than the actual one. The average electron energy in the steady state under the experimental conditions described in the previous section was estimated from the same spectroscopic method by measuring the 501.6 nm helium line.

4. Conclusions

The spectral intensities during the beginning of a dc discharge were measured in a mixture of SiCl_4 and helium. In addition to the atomic emission lines, molecular lines of SiCl , SiCl_2 , SiCl_3 and Cl_2 were observed. Each emission line at the discharge starting period shows a unique waveform.

First, this waveform is used to determine the excitation and dissociation processes of the fluorescence-emitting fragments. The waveforms are separated into three types. The emission lines from SiCl_2 and helium, denoted by type A, have an initial large peak followed by a small steady-state value, and the intensities from SiCl_3 , SiCl , $\text{Si}(391 \text{ nm})$ and $\text{Cl}(441 \text{ nm})$, denoted by type B, have no initial peak and gradually increase up to a steady-state value. The lines from $\text{Si}(288 \text{ and } 577 \text{ nm})$ and $\text{Cl}^+(487 \text{ nm})$, type C, have an initial peak and a gradual increase. The discharge current dependence on the intensities of these lines and the upper limit of the lifetime of each state are also measured. From a comparison of the experimental and theoretical waveforms it is determined that the upper state of the emission line of type A is excited by the electronic collision in a single step and the state emitting in type B can never be excited by a single-step electronic collision. The excitation of the state of type C is a mixture of single-step and multi-step processes.

Second it is shown that the emission in type A can be utilised for simply estimating the approximate value of the average electron energy at a steady state in a dc discharge. The values obtained by the spectroscopic method are almost in agreement with the average electron energy measured by an electric double probe.

It is concluded that the transient behaviour of the emission intensity during the beginning of a discharge is a characteristic waveform and includes much important information on excitation processes and plasma parameters. The spectroscopic measurement provides a simple and nonintrusive method of analysing the atomic and molecular process and diagnosing the plasma parameters.

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