

## CALCULATION AND ANALYSYS OF ELECTRON TRANSPORT COEFFICIENTS IN TRIES-N<sub>2</sub> GAS MIXTURES

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ARTICLE INFO		ABSTRACT
Received:	07/11/2022	The electron transport coefficients in gases or gas mixtures are important data for plasma modeling. The pure triethoxysilane (TRIES) and pure N <sub>2</sub> are widely used in various plasma processing such as doping plasma, plasma etching and plasma-enhanced chemical vapor deposition. In order to improve the quality of plasma processing, the TRIES-N <sub>2</sub> mixture was suggested. Therefore, the determination of the electron transport coefficients in TRIES-N <sub>2</sub> mixtures with different mixing ratio are necessary. In this study, the electron transport coefficients, which include the electron drift velocities, the density-normalized longitudinal diffusion coefficients and the Townsend first ionization coefficients in TRIES and its mixture with N <sub>2</sub> , were firstly calculated and analyzed using a Boltzmann two-term calculation. This study was carried out in the E/N (ratio of the electric field E to the neutral number density) range of 0.1-1000 Td (1 Td = 10 <sup>-17</sup> V cm <sup>2</sup> ) based on the reliable electron collision cross section sets for TRIES and N <sub>2</sub> molecules. These results are necessary for plasma processing using the TRIES-N <sub>2</sub> mixtures.
Revised:	30/11/2022	
Published:	30/11/2022	
<b>KEYWORDS</b>		
TRIES-N <sub>2</sub> mixtures		
Electron transport coefficient		
Boltzmann equation		
Plasma processing		
Triethoxysilane		

## TÍNH TOÁN VÀ PHÂN TÍCH CÁC HỆ SỐ CHUYỂN ĐỘNG ELECTRON TRONG HỖN HỢP KHÍ TRIES-N<sub>2</sub>

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THÔNG TIN BÀI BÁO		TÓM TẮT
Ngày nhận bài:	07/11/2022	Các hệ số chuyển động electron trong các chất khí hoặc hỗn hợp các chất khí là những dữ liệu quan trọng cho việc mô hình hóa plasma. Triethoxysilane (TRIES) và N <sub>2</sub> nguyên chất được sử dụng rộng rãi trong các quá trình xử lý plasma như plasma pha tạp, khắc plasma, lắng tụ hơi hóa học tăng cường plasma. Để nâng cao chất lượng của xử lý plasma, hỗn hợp khí TRIES-N <sub>2</sub> được đề xuất. Do đó việc xác định các hệ số chuyển động electron trong hỗn hợp khí TRIES-N <sub>2</sub> là cần thiết. Trong nghiên cứu này, các hệ số chuyển động electron bao gồm vận tốc dịch chuyển electron, hệ số khuếch tán dọc và hệ số ion hóa Townsend thứ nhất trong phân tử khí TRIES và hỗn hợp của nó với N <sub>2</sub> được tính toán lần đầu tiên sử dụng chương trình Boltzmann bậc hai. Nghiên cứu này được thực hiện trong khoảng E/N (hệ số giữa cường độ điện trường E và mật độ) 0.1-1000 Td (1 Td = 10 <sup>-17</sup> V cm <sup>2</sup> ) dựa trên các bộ tiết diện va chạm electron đáng tin cậy của phân tử TRIES và N <sub>2</sub> . Các kết quả này là cần thiết cho quá trình xử lý plasma sử dụng hỗn hợp khí TRIES-N <sub>2</sub> .
Ngày hoàn thiện:	30/11/2022	
Ngày đăng:	30/11/2022	
<b>TỪ KHÓA</b>		
Hỗn hợp TRIES-N <sub>2</sub>		
Hệ số chuyển động electron		
Phương trình Boltzmann		
Xử lý plasma		
Triethoxysilane		

DOI: <https://doi.org/10.34238/tnu-jst.6889>

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## 1. Introduction

The pure triethoxysilane (TRIES) and pure N<sub>2</sub> gases are widely used in various plasma processing such as doping plasma, plasma etching and plasma-enhanced chemical vapor deposition (PECVD) [1] – [8]. Y. Shin *et al.* [3] studied the silicon dioxide (SiO<sub>2</sub>) films, which were deposited by the low plasma-enhanced chemical vapor deposition using the TRIES and tetraethoxysilane (TEOS). They suggested that TRIES is a good candidate for SiO<sub>2</sub> films. Y. Kudoh *et al.* [4] have been proposed a new plasma chemical vapor deposition (CVD) technology with reaction gases of TRIES and oxygen (O<sub>2</sub>). This technology improves the step coverage of SiO<sub>2</sub> films and quality of SiO<sub>2</sub> films deposited on the step sidewalls. The gas can be used in the form of pure. However, the gas mixtures are commonly used to improve the quality of plasma processing. The database of electron transport coefficients in the pure TRIES and N<sub>2</sub> molecule has been published. However, the electron transport coefficients in TRIES-N<sub>2</sub> mixtures both in experiments and theories are not available. Therefore, the determination of the electron transport coefficients in TRIES-N<sub>2</sub> mixtures with different mixing ratio are necessary.

For these purposes, the Boltzmann two-term calculation was applied to calculate and analyse the electron transport coefficients in the TRIES-N<sub>2</sub> mixture for the first time. These coefficients include the electron drift velocities  $W$ , the density-normalized longitudinal diffusion coefficients  $ND_L$ , the ratio of the longitudinal diffusion coefficient to the electron mobility  $D_L/\mu$  and the first ionization coefficients  $\alpha/N$ . The calculations were carried out in the  $E/N$  range of 0.1-1000 Td at a pressure of 1 Torr and a temperature of 300 K.

## 2. Analysis

As successfully used in many publications and also in our previous papers [9] – [13], the electron swarm method was applied for TRIES-N<sub>2</sub> mixture to calculate the electron transport coefficients. These coefficients can be derived by solving the Boltzmann equation in the two-term approximation [14]. The Boltzmann two-term calculation suggested by Tagashira *et al.* [14] has been presented briefly here.

The electron energy distribution function (EEDF),  $f(\varepsilon, E/N)$ , is normalized by:

$$\int_0^{\infty} f\left(\varepsilon, \frac{E}{N}\right) d\varepsilon \equiv 1 \quad (1)$$

The EEDF for gases can be found by solving the Boltzmann equation

$$\frac{\partial f}{\partial t} + \bar{v}\nabla_{\mathbf{r}} f + \bar{a}\nabla_{\mathbf{v}} f = \left(\frac{\partial f}{\partial t}\right)_{\text{coll}} \quad (2)$$

Where  $\mathbf{r}$  is positions,  $\mathbf{v}$  is velocities of electrons, and  $f = f(\mathbf{r}, \mathbf{v}, t)$  is the distribution function of  $\mathbf{r}$  and  $\mathbf{v}$ ,  $(\partial f/\partial t)_{\text{coll}}$  is the collision term. After finding the EEDF from equation 2, the electron drift velocity can be obtained as follows:

$$\mathbf{W} = -\frac{1}{3} \left(\frac{2}{m}\right)^{1/2} \frac{eE}{N} \int_0^{\infty} \frac{\varepsilon}{q_m(\varepsilon)} \frac{df(\varepsilon, E/N)}{d\varepsilon} d\varepsilon \quad (3)$$

where  $\varepsilon$  is the electron energy,  $m$  is the electron mass,  $e$  is the elementary charge and  $q_m(\varepsilon)$  is the momentum-transfer cross section. The density-normalized longitudinal diffusion coefficient is defined as

$$ND_L = \frac{V_1}{3N} \left( E \int_0^{\infty} \frac{\varepsilon}{Q_T} \frac{\partial}{\partial \varepsilon} (F_1 \varepsilon^{-1/2}) d\varepsilon + \int_0^{\infty} \frac{\varepsilon^{1/2}}{Q_T} F_0 d\varepsilon \right) - (\varpi_0 A_2 - \varpi_1 A_1 - \varpi_{02}) \quad (4)$$

where  $V_1$  is the speed of electron,  $Q_T$  is the total cross section, here  $F_n$  and  $\varpi_n$  ( $n = 0, 1, 2$ ) are respectively the electron energy distributions of various orders and their eigenvalues.  $V_1, \varpi_n, \varpi_0$  and  $A_n$  are given by

$$V_1 = \left(\frac{2e}{m}\right)^{\frac{1}{2}} \tag{5}$$

$$\varpi_1 = -\frac{V_1 E}{3N} \int_0^{\infty} \frac{\varepsilon}{Q_T} \frac{\partial}{\partial \varepsilon} (F_0 \varepsilon^{-1/2}) d\varepsilon + (\varpi_0 A_1 - \varpi_{01}) \tag{6}$$

$$v_0 = V_1 N \int_0^{\infty} \varepsilon^{1/2} q_i F_0 d\varepsilon \tag{7}$$

$$A_n = \int_0^{\infty} F_n d\varepsilon \tag{8}$$

$$\varpi_{0n} = V_1 N \int_0^{\infty} \varepsilon^{1/2} q_i F_n d\varepsilon \tag{9}$$

The Townsend first ionization coefficient is defined as

$$\alpha / N = \frac{1}{W} \left(\frac{2}{m}\right)^{1/2} \int_I^{\infty} f(\varepsilon, E / N) \varepsilon^{1/2} q_i(\varepsilon) d\varepsilon \tag{10}$$

where  $I$  is the ionization onset energy and  $q_i(\varepsilon)$  is the ionization cross section.

The sets of electron collision cross section are required input data for this calculation. Therefore, in order to obtain the accuracy electron transport coefficients, it is necessary to choose the reliable sets of electron collision cross section. The electron collision cross section is set for TRIES molecule determined by Tuoi *et al.* [12], and  $N_2$  molecule determined by Nakamura [15]. The electron collision cross section set for  $N_2$  [15] includes one momentum-transfer cross section  $Q_m$ , seven vibrational excitation cross sections  $Q_{v1-7}$ , seven electronic excitation cross sections  $Q_{ex1-7}$  and one ionization cross section  $Q_i$ . The electron collision cross sections for  $N_2$  molecule were shown in Figure 1 and their threshold energies were listed in Table 1. The electron collision cross section set for the TRIES [12] molecule includes one momentum-transfer cross section  $Q_m$ , the ionization cross section  $Q_i$ , the dissociation cross section  $Q_d$ , and two vibrational excitation cross sections  $Q_{v1,2}$ . The electron collision cross sections for TRIES molecule were shown in Figure 2 and their threshold energies were listed in Table 2. The reliability of these sets has been proven in [12] for TRIES and in [15] for  $N_2$ .

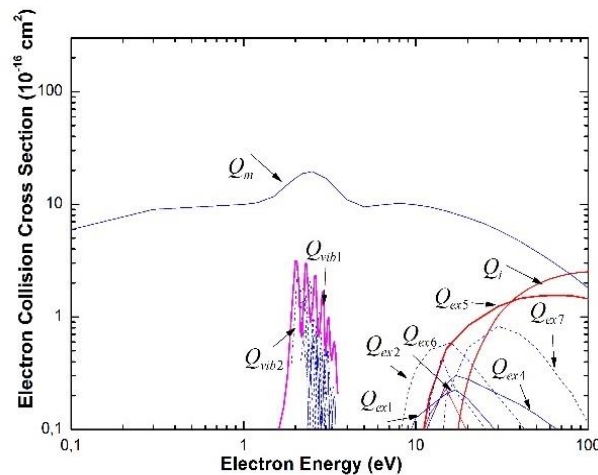
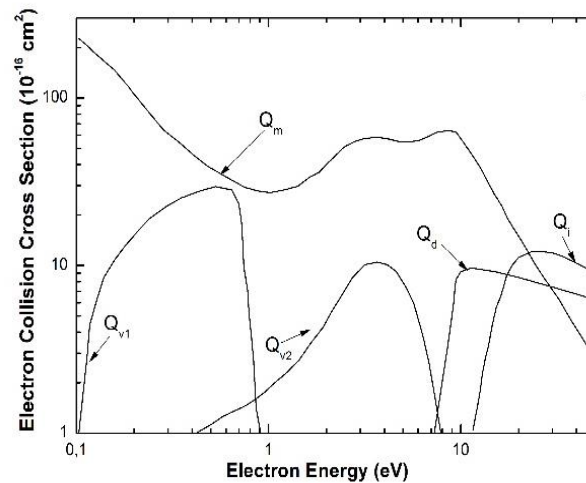


Figure 1. Set of electron collision cross sections for the  $N_2$  molecule



**Figure 2.** Set of electron collision cross sections for the TRIES molecule

**Table 1.** Threshold of electron collision cross sections for TRIES molecule [12]

Electron collision cross sections	Energy threshold (eV)
Vibrational excitation cross section $Q_{v1}$	1.13
Vibrational excitation cross section $Q_{v2}$	2.71
Ionization cross section	3.6
Dissociation cross section	10.6

**Table 2.** Threshold of electron collision cross sections for  $N_2$  molecule [15]

Electron collision cross sections	Energy threshold (eV)
Seven vibrational excitation cross sections $Q_{v1-7}$	0.288 to 2.18
Seven electronic excitation cross sections $Q_{ex1-7}$	6.169 to 12.579
Ionization cross section	15.5

### 3. Results and Discussions

The calculated electron transport coefficients in the E/N range of 0-1000 Td for the TRIES- $N_2$  mixtures with various mixing ratios are shown in Figures 3-6. The solid line and symbols display the calculated results for electron transport coefficients in 10%, 30%, 50%, 70%, and 90% TRIES- $N_2$  mixtures. The solid curves display the calculated results for the electron transport coefficients in the pure TRIES and pure  $N_2$  molecules. It is clearly that the electron transport coefficients in pure TRIES, pure  $N_2$  and their mixtures gases are as functions of the reduced electric field. Figure 3 shows the electron drift velocities  $W$  for the pure TRIES, pure  $N_2$  and their mixtures. At same the E/N, the  $W$  values in TRIES- $N_2$  mixtures lie between those of the pure gases (except in the 10% TRIES- $N_2$  mixture). The values of  $W$  in 10% TRIES- $N_2$  mixture are greater than those in pure gases for E/N range of 1.5-30 Td. Figure 4 displays the variation of the density-normalized longitudinal diffusion coefficient  $ND_L$  with the reduced electric field for various TRIES- $N_2$  mixtures. The curves of the  $ND_L$  for mixtures are located between those of the pure gases over all range of E/N. Figure 5 also displays the variation of the ratio of the longitudinal diffusion coefficient to the mobility  $D_L/\mu$ . The trends of  $D_L/\mu$  are the same as the trends of  $ND_L$  in the TRIES- $N_2$ . Figure 6 displays the variation of the Townsend first ionization coefficient  $\alpha/N$ . Unlike other coefficients, the variation of  $\alpha/N$  in 10% TRIES- $N_2$  and 30% TRIES- $N_2$  have different trends. The curves of  $\alpha/N$  in mixtures are higher than those in pure gases. Therefore, the curves of the calculated electron transport coefficients for TRIES- $N_2$  mixtures lie

between those of the pure gases over the all range of  $E/N$  (except for the first Townsend ionization coefficient).

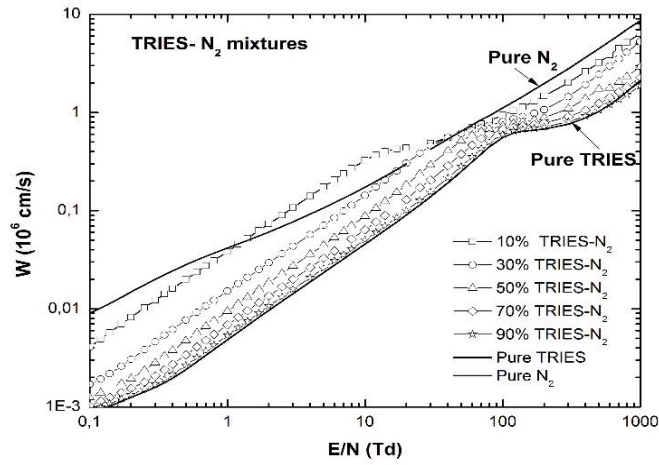


Figure 3. The electron drift velocity in TRIES- $N_2$  mixtures

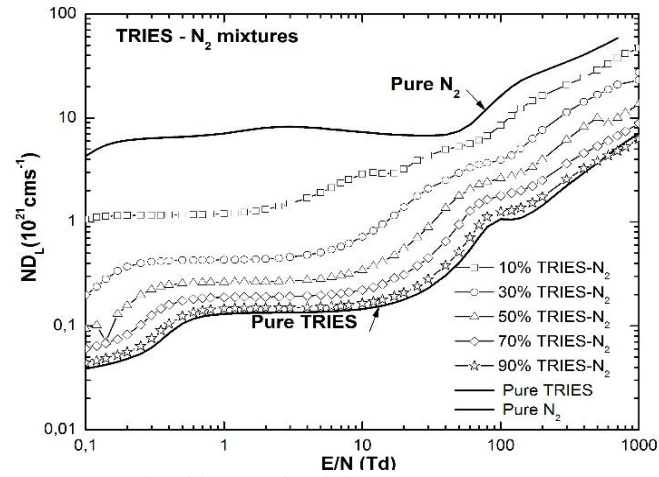


Figure 4. The density-normalized longitudinal diffusion coefficient  $ND_L$  in TRIES- $N_2$  mixtures

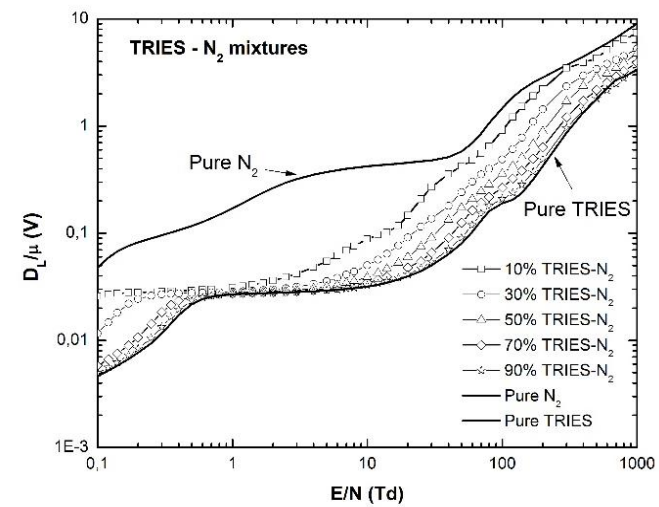
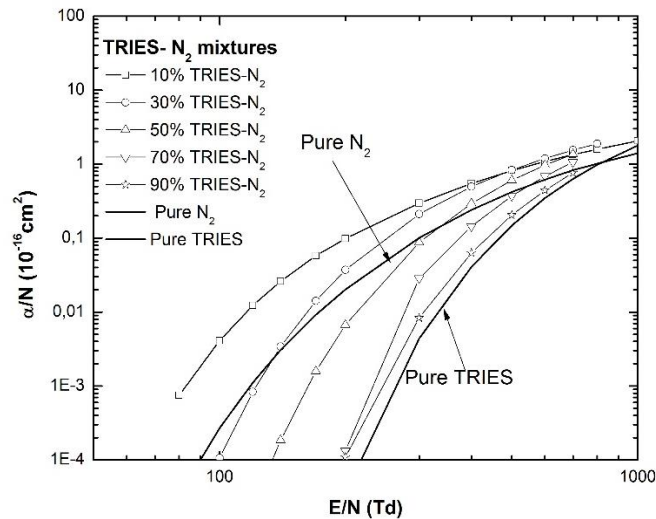


Figure 5. Ratio of the longitudinal diffusion coefficient to the electron mobility  $D_L/\mu$  in TRIES- $N_2$  mixtures



**Figure 6.** Townsend first ionization coefficient  $\alpha/N$  as functions of  $E/N$  for the TRIES- $N_2$  mixtures

#### 4. Conclusion

In this study, the electron transport coefficients for pure TRIES, pure  $N_2$  and their mixtures in the  $E/N$  range of 0.1-1000 Td by using the Boltzmann two-term calculation were calculated for the first time. We observe the variations of the electron transport coefficients of a pure TRIES,  $N_2$  and TRIES- $N_2$  gas mixture with  $E/N$ , which were affected by the concentrations of gas mixtures. At the same  $E/N$ , the values of the electron transport coefficients in the mixture lie between those of the pure gases over the all range of  $E/N$  (except for the first Townsend ionization coefficient in 10% TRIES- $N_2$  and 30% TRIES- $N_2$  mixtures). These coefficients were produced from reliable sets of electron collision cross section for TRIES and  $N_2$  molecules. Therefore, these results are useful and reliable data for expansion of choices of TRIES- $N_2$  mixtures in various industrial applications, especially in plasma etching, plasma-enhanced chemical vapor deposition and doping plasma.

#### Acknowledgement

This research was supported by Hung Yen University of Technology and Education, under grant number UTEHY.L.2022.19.

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