CALCULATION AND ANALYSYS OF ELECTRON TRANSPORT COEFFICIENTS IN TRIES-N_2 GAS MIXTURES

Phan Thi Tuoi[1], Dao Van Da[1], Do Anh Tuan[2*], Pham Xuan Hien[3]
[1]*Hung Yen University of Technology and Education*
[2]*A Chau Industrial Technology Joint Stock Company, Ha Noi*
[3]*University of Transport and Communications*

ARTICLE INFO

Received: 07/11/2022
Revised: 30/11/2022
Published: 30/11/2022

KEYWORDS

TRIES-N_2 mixtures
Electron transport coefficient
Boltzmann equation
Plasma processing
Triethoxysilane

ABSTRACT

The electron transport coefficients in gases or gas mixtures are important data for plasma modeling. The pure triethoxysilane (TRIES) and pure N_2 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_2 mixture was suggested. Therefore, the determination of the electron transport coefficients in TRIES-N_2 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_2, 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^{-17} V cm^2) based on the reliable electron collision cross section sets for TRIES and N_2 molecules. These results are necessary for plasma processing using the TRIES-N_2 mixtures.

TÍNH TOÁN VÀ PHÂN TÍCH CÁC HỆ SỐ CHUYỂN ĐỘNG ELECTRON TRONG HỖN HỢP KHÍ TRIES-N_2

Phan Thị Tươi[1], Đào Văn Đã[1], Đỗ Anh Tuấn[2*], Phạm Xuân Hiển[3]
[1]*Trường Đại học Sư phạm Kỹ thuật Hưng Yên*
[2]*Công ty Cổ phần Kỹ thuật Công nghiệp Á Châu, Hà Nội*
[3]*Trường Đại học Giao thông Vận tải*

THÔNG TIN BÀI BÁO

Ngày nhận bài: 07/11/2022
Ngày hoàn thiện: 30/11/2022
Ngày đăng: 30/11/2022

TỪ KHÓA

Hỗn hợp TRIES-N_2
Hệ số chuyển động electron
Phương trình Boltzmann
Xử lý plasma
Triethoxysilane

TÓM TẮT

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_2 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_2 được đề xuất. Do đó việc xác định các hệ số chuyển động electron trong hỗn hợp khí TRIES-N_2 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_2 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^{-17} V cm^2) dựa trên các bộ tiết diện va chạm electron đáng tin cậy của phân tử TRIES và N_2. Các kết quả này là cần thiết cho quá trình xử lý plasma sử dụng hỗn hợp khí TRIES-N_2.

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

* Corresponding author. *Email: tuanda@acit.com.vn*

1. Introduction

The pure triethoxysilane (TRIES) and pure N_2 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_2) 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_2 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_2). This technology improves the step coverage of SiO_2 films and quality of SiO_2 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_2 molecule has been published. However, the electron transport coefficients in TRIES-N_2 mixtures both in experiments and theories are not available. Therefore, the determination of the electron transport coefficients in TRIES-N_2 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_2 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/μ and the first ionization coefficients α/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_2 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(ε, E/N), is normalized by:

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

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

$$\frac{\partial f}{\partial t} + \vec{v}\nabla_r f + \vec{a}\nabla_v f = \left(\frac{\partial f}{\partial t}\right)_{coll} \tag{2}$$

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

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

where ε 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

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

where V_1 is the speed of electron, q_T is the total cross section, here F_n and ϖ_n (n = 0, 1, 2) are respectively the electron energy distributions of various orders and their eigenvalues. V_1, ϖ_n, ϖ_0 and A_n are given by

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

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

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

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

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

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 $Q_{v1\text{-}7}$, seven electronic excitation cross sections $Q_{ex1\text{-}7}$ 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.

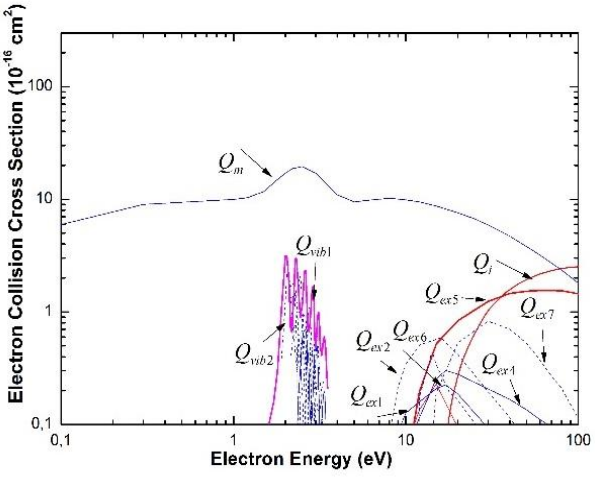

Figure 1. *Set of electron collision cross sections for the N_2 molecule*

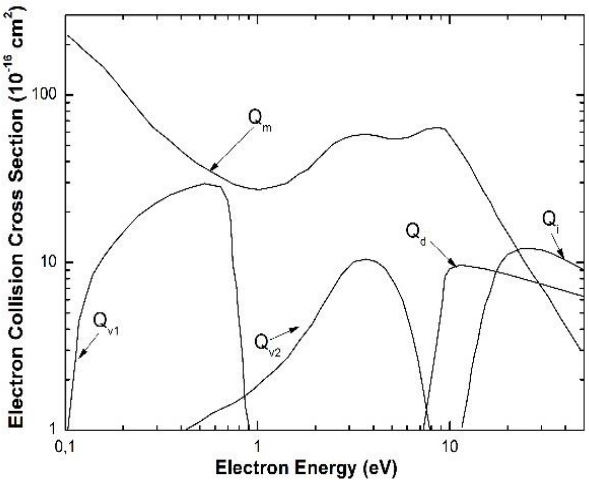

Figure 2. *Set of electron collision cross sections for the TRIES molecule*

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 $Q_{v1\text{-}7}$	0.288 to 2.18
Seven electronic excitation cross sections $Q_{ex1\text{-}7}$	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/μ. The trends of D_L/μ 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 α/N. Unlike other coefficients, the variation of α/N in 10%TRIES-N_2 and 30%TRIES-N_2 have different trends. The curves of α/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).

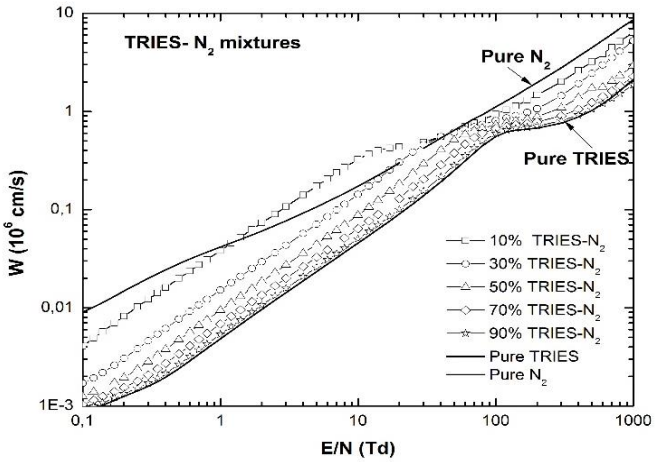

Figure 3. *The electron drift velocity in TRIES-N_2 mixtures*

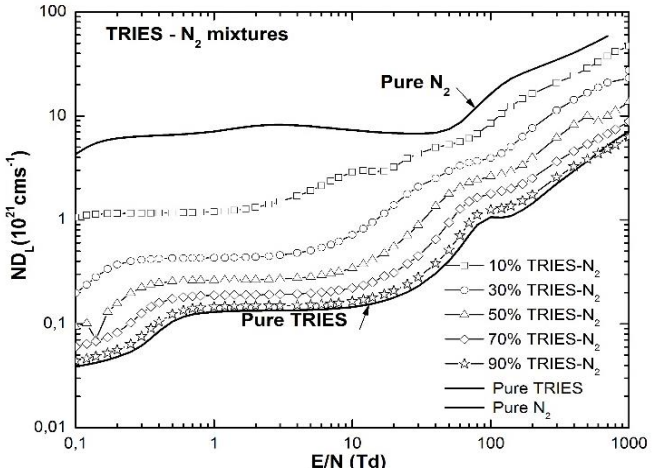

Figure 4. *The density-normalized longitudinal diffusion coefficient NDL in TRIES-N_2 mixtures*

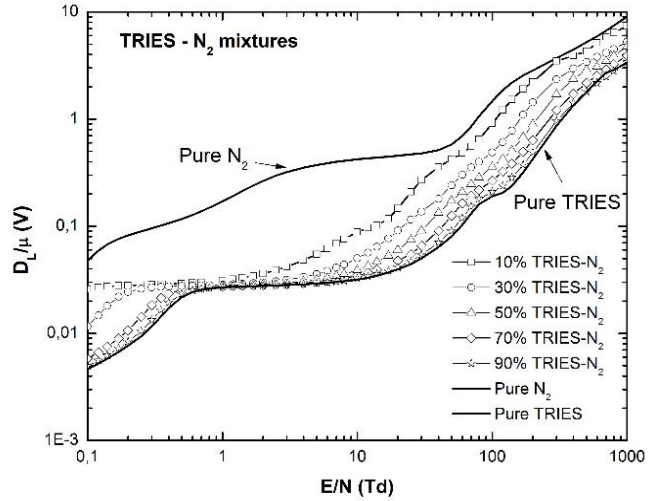

Figure 5. *Ratio of the longitudinal diffusion coefficient to the electron mobility D_L/μ in TRIES-N_2 mixtures*

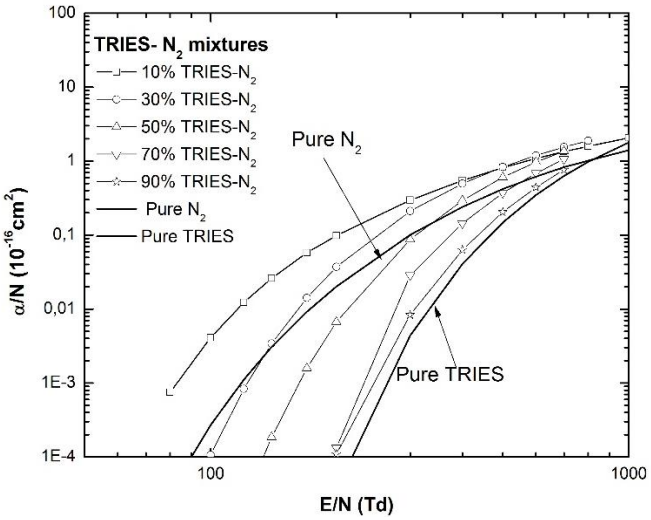

Figure 6. *Townsend first ionization coefficient α/N as functions of E/N for the TRIES-N_2 mixtures*

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.

TÀI LIỆU THAM KHẢO/ REFERENCES

[1] K. Yoshida, R. Sato, T. Yokota, Y. Kishimoto, and H. Date, "Electron Transport Properties in HSi (OC2H5) 3 Vapor," *Japanese Journal of Applied Physics*, vol. 50, no. 12R, 2011, Art. no. 120210.

[2] M. Abbasi-Firouzjah, "The effect of TEOS plasma parameters on the silicon dioxide deposition mechanisms," *Journal of Non-Crystalline Solids*, vol. 368, pp. 86-92, 2013.

[3] Y. Shin, Y. Akiyama, N. Imaishi, and S. Jung, "Silicon Dioxide Film Deposition by Afterglow-Plasma-Enhanced Chemical Vapor Deposition using Triethoxysilane and Tetraethoxysilane," *Engineering Sciences Reports, Kyushu university*, vol. 25, no. 1, pp. 1-6, 2003.

[4] Y. Kudoh, Y. Homma, N. Sakuma, T. Furusawa, and K. Kusukawa, "Directional plasma CVD technology for sub-quarter-micron feature size multilevel interconnections," *Japanese Journal of Applied Physics*, vol. 37, no. 3S, 1998, Art. no. 1145.

[5] H. J. Lee, "Plasma Diagnostics during Plasma-Enhanced Chemical-Vapor Deposition of Low-Dielectric-Constant SiOC (-H) Films from TES/O_2 Precursors," *Journal of the Korean Physical Society*, vol. 53, no. 3, 2008, doi: 10.3938/jkps.53.1468.

[6] M. J. Krečmarová, V. Petrák, A. Taylor, K. J. Sankaran, I. N. Lin, A. Jäger, V. Gärtnerová, L. Fekete, J. Drahokoupil, F. Laufek, and J. Vacík, "Change of diamond film structure and morphology with N_2

addition in MW PECVD apparatus with linear antenna delivery system," *Physica Status Solidi*, vol. 211, no. 10, pp. 2296-2301, 2014.

[7] H. C. Knoops, E. M. Braeken, K. de Peuter, S. E. Potts, S. Haukka, V. Pore, and W. M. Kessels, "Atomic layer deposition of silicon nitride from Bis(tert-butylamino) silane and N_2 plasma," *ACS Applied Materials & Interfaces*, vol. 8, no. 35, pp. 19857–19862, 2015.

[8] Z. Zang, A. Nakamura, and J. Temmyo, "Nitrogen doping in cuprous oxide films synthesized by radical oxidation at low temperature," *Materials Letters*, vol. 42, no. 1, pp. 188-191, 2013.

[9] A. T. Do and B. H. Jeon, "Electron collision cross sections for the tetraethoxysilane molecule and electron transport coefficients in tetraethoxysilane-O_2 and tetraethoxysilane-Ar mixtures," *Journal of the Physical Society of Japan*, vol. 81, no. 6, pp. 064301- 064301-8, 2012.

[10] A. T. Do, "Calculations of electron transport coefficients in Cl_2-Ar, Cl_2-Xe and Cl_2 –O_2 mixtures," *Journal of the Korean Physical Society*, vol. 64, no.1, pp. 23-29, 2014.

[11] X. H. Pham, T. T. Phan, C. N. Tang, and A. T. Do, "Studying effect of adding buffer gases to TRIES gas on the electron transport coefficients," *ICERA 2019, LNNS*, K.-U. Sattler et al. (Eds.), Springer Nature Switzerland, vol. 104, pp. 693–703, 2020.

[12] X. H. Pham, T. T. Phan, and A. T. Do, "Electron Collision Cross Sections for the TRIES Molecule and Electron Transport Coefficients in TRIES-Ar and TRIES-O_2 Mixtures," *Journal of the Korean Physical Society*, vol. 73, no. 12, pp. 1855-1862, Dec. 2018.

[13] A. T. Do "Analysis of insulating characteristics of Cl_2-He mixture gases in gas discharge," *Journal of Electrical Engineering & Technology*, vol. 10, no. 4, pp. 1735-1738, 2015.

[14] H. Tagashira, Y. Sakai, and S. Sakamoto, "The development of electron avalanches in argon at high E/N values. II. Boltzmann equation analysis," *J. Phys*. D., vol. 10, pp. 1051-1063, 1977.

[15] Y. Nakamura, *Private Communication*, Tokyo Denki Univ., Tokyo, Japan, Nov. 2010.