OVERVIEW OF ORGANIC COMPOUNDS APPLIED IN SEMICONDUCTOR TECHNOLOGY

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ABSTRACT

This paper attempts to give an overview of organic compounds used in semiconductor technology. Plasma processing technology is vitally important to several of the largest manufacturing industries in the world. Plasma-based surface processes are indispensable for manufacturing the very large-scale integrated circuits (ICs) used by the electronics industry. The electron transport coefficients in both pure gases and their mixtures are necessary data for the expansion of the choices of proper gases in plasma processing. The electron transport coefficients, which include electron drift velocities, density-normalized longitudinal diffusion coefficients and density-normalized effective ionization coefficients, were first calculated and analyzed using a two-term approximation of the Boltzmann equation in the E/N (ratio of the electric field E to the neutral number density).

Keywords: *semiconductor, electron transport coefficient, Boltzmann equation, plasma processing.*

1. INTRODUCTION

In this article, we present an overview of organic compounds applied in semiconductor technology. Organic compounds are molecules that are made up of carbon covalently bonded to other atoms, most commonly hydrogen, oxygen, and nitrogen. Compounds of an organosilicon group provide a large variety of possible reactants for either chemical vapor deposition (CVD) or plasma-enhanced CVD (PECVD) processes. They are generally sufficiently volatile near room temperature, relatively non-toxic and nonflammable, cheap and available from the commercial resource [1].

The fabrication of electronic components, especially microelectronic integrated circuits, have undoubtedly

found the widest and most demanding application for thin film depositions [2]. An important aspect of microelectronics technology involves the deposition of dielectric thin films such as silicon dioxide (SiO_2). Plasma processing has emerged as an important technology for the deposition and etching of thin solid films in the manufacture of microelectronic devices. Molecular gas plasmas are currently widely used in the microelectronics industry for the deposition and etching of thin solid films. Plasma processing is one of many techniques and processes used in the manufacture of integrated circuits [4]. Most of the important materials used in integrated circuit manufacture can be plasma etched in some gas. The most important applications, not surprisingly, are Si-containing materials: Si, SiO2 and Si_3N_4 [5]. Tetramethylsilane (TMS), $Si(CH_3)_4$, Tetraethoxysilane, $Si(OCH_2CH_3)_4$, Triethoxysilane (TRIES), $Hsi(OC_2H_5)_3$ which is the simplest organosilicon compound, it is widely used in plasma polymerization processes and plasma-enhanced chemical vapor applications [6-11]. Because of its physical and industrial importance, the consistent set of electron collision cross sections for TEOS, TMS, TRIES molecule and electron transport coefficients in the binary mixtures of compounds of an organosilicon group molecule with other molecules and atoms are necessary to quantitatively understand plasma phenomena. The electron transport coefficients include the mean-arrival time-drift velocity (W_m) and the density-normalized longitudinal diffusion coefficients, NDL, the ratio of the longitudinal diffusion coefficient to the electron mobility, DL/μ, and the Townsend first ionization coefficient. For evaluation of the plasma properties in applications using TEOS, TMS and TRIES molecules, the electron collision cross sections and the electron transport coefficient for the TEOS, TMS and TRIES molecules are necessary.

2. ANALYSIS

As successfully used in our previous papers [12-18], the electron swarm method was also applied in this study. The electron transport coefficients were obtained by solving the Boltzmann equation in the two-term approximation [19]. The sets of electron collision cross section are required input data for this calculation. The sets of electron collision cross section are required input data for this calculation. Therefore, to obtain the accuracy of electron transport coefficients, it is necessary to choose reliable sets of electron collision cross section. The electron collision cross section set for TRIES molecule determined by Tuoi *et al*. [12], and TEOS molecule determined by Tuan [14], TMS molecule determined by Hien[15]. To desire the electron transport coefficients, the Boltzmann

two-term calculation suggested by Tagashira [20] was applied.

The electron energy distribution function (EEDF), f(ε, E/N), is normalized by

$$\int_0^\infty f(\varepsilon, E/N)d\varepsilon = 1 \quad (1)$$

The EEDF can be obtained theoretically by solving the Boltzmann equation

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

where f = f(r, v, t) is the distribution function of the positions r and velocities of electrons v, is the acceleration due to external forces and (∂f/∂t)coll the collision induced rate of change of the number of electrons per unit volume of phase space. The electron drift velocity calculated from the solution of electron energy distribution function, f(ε, E/N), of the Boltzmann equation is defined as

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

$$ND_L = \frac{V_1}{3N}\left(E\int_0^\infty \frac{\varepsilon}{q_T}\frac{\partial}{\partial\varepsilon}\left(F_1\varepsilon^{-\frac{1}{2}}\right)d\varepsilon + \int_0^\infty \frac{\varepsilon_2^1}{q_T}F_0\,d\varepsilon\right) - (\varpi_0 A_2 - \varpi_1 A_1 - \varpi_{02}) \quad (4)$$

where ε is the electron energy, m is the electron mass, e is the elementary charge and qm(ε) is the momentum-transfer cross section. The density-normalized longitudinal diffusion coefficient is defined as where V_1 is the speed of electron, q_T is the total cross section, here F_n and ϖ_n are (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

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

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

$$\varpi_0 = V_1 N\int_0^\infty \varepsilon^{\frac{1}{2}} q_i F_0 d\varepsilon \quad (7)$$

$$\varpi_{0n} = V_1 N\int_0^\infty \varepsilon^{\frac{1}{2}} q_i F_n d\varepsilon \quad (8)$$

$$A_n = \int_0^\infty F_n d\varepsilon \quad (9)$$

$$\alpha/N = \frac{1}{w}\left(\frac{2}{m}\right)^{\frac{1}{2}}\int_0^\infty f\left(\varepsilon,\frac{E}{N}\right)\varepsilon^{\frac{1}{2}} q_i(\varepsilon)d\varepsilon \quad (10)$$

where q_i is the ionization cross section The Townsend coefficient is defined as where I is the ionization onset energy and $q_i(\varepsilon)$ is the ionization cross section.

Step 1: Modification of the low energy inelastic cross sections (mainly the vibrational excitation cross sections) in order for the calculated electron transport coefficients (mainly the W, ND_L, ND_T, D_L/μ, and D_T/μ) in the binary mixtures of the object gas with buffer gases to agree with those of the experiments.

Step 2: Modification of the elastic momentum transfer cross section for the

object gas so that the calculated electron transport coefficients (mainly the W, ND_L, ND_T, D_L/μ, and D_T/μ) in pure object gas would agree with those of the experiments when the inelastic cross sections determined in step 1 are not altered.

Step 3: Modification of the high energy inelastic cross sections except the vibrational excitation cross sections so that the calculated electron transport coefficients (mainly the α/N, η/N, and $(\alpha - \eta)/N$) in pure gas and mixture gases of object gas would agree with those of the experiments when the inelastic cross sections determined in step 1 are also not altered.

3. RESULTS AND DISSCUSION

The reliable sets of electron collision cross section for TEOS, TRIES and TMS molecules were shown in Figs. 1-3. These sets were obtained by applying three steps in part II.

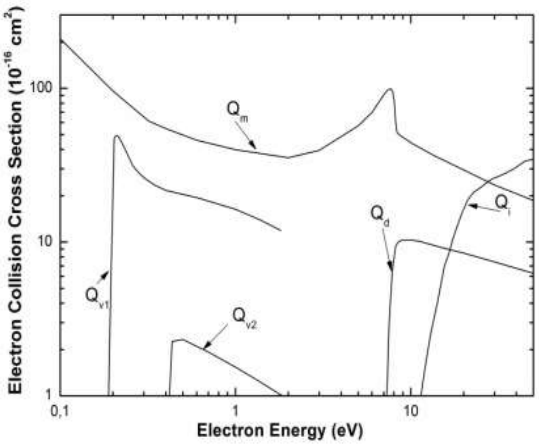

Fig. 1. *Set of electron collision cross sections for the TEOS molecule.*

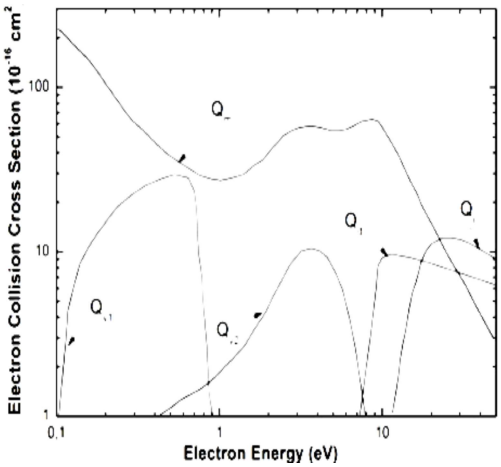

Fig. 2. *Set of electron collision cross sections for the TRIES molecule.*

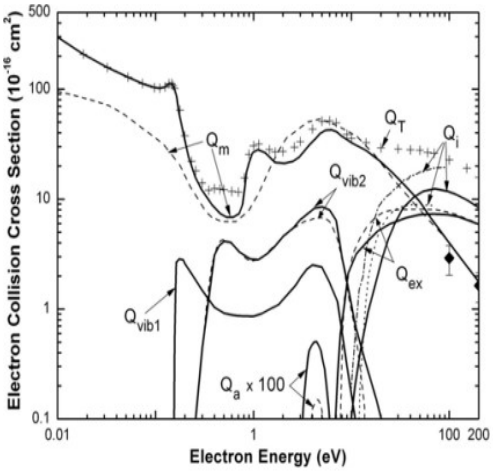

Fig. 3. *Set of electron collision cross sections for the TMS molecule.*

Based on the data of electron collision cross section set for TEOS, TRIES and TMS molecules, two-term approximation of the Boltzmann analysis was used to calculate the electron transport coefficients in their mixtures with O_2 or Ar gases. The electron transport coefficients in TEOS-Ar, TEOS-O_2, TRIES-Ar, TRIES-O_2, TMS-Ar, TMS-O_2 were shown in Figs. 4-17.

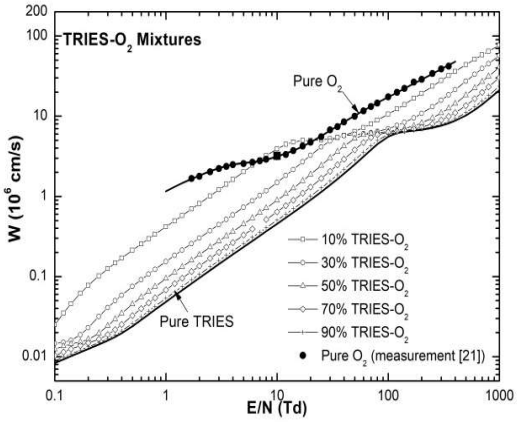

Fig. 4. *Electron drift velocity W as functions of E/N for the TRIES-O2 mixtures with 10%, 30%, 50%, 70%, and 90% TRIES.*

The solid line and symbols show present W values calculated using a two-term approximation of the Boltzmann equation for the TRIES-O2 mixtures. The solid curves show present W values calculated for the pure TRIES and O2 molecules. The solid circle symbols show the experimental values for the pure O2 molecule.

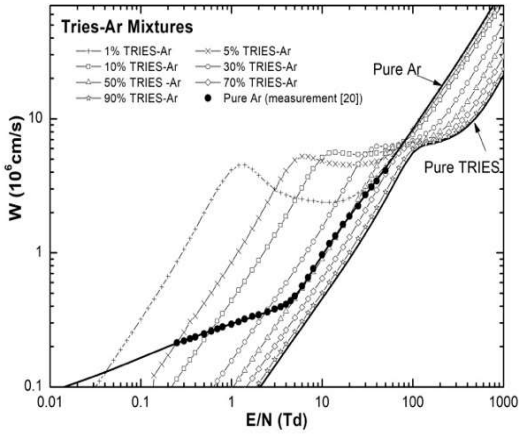

Fig. 5. *Electron drift velocity W as functions of E/N for the TRIES-Ar mixtures with 1%, 5%, 10%, 30%, 50%, 70%, and 90% TRIES.*

The solid line and symbols show the present W values calculated using a two-term approximation of the Boltzmann equation for the TRIES-Ar mixtures. The solid curves show present W values calculated for the pure TRIES molecule and pure Ar atom. The solid circle symbols show the experimental results for the pure Ar atom.

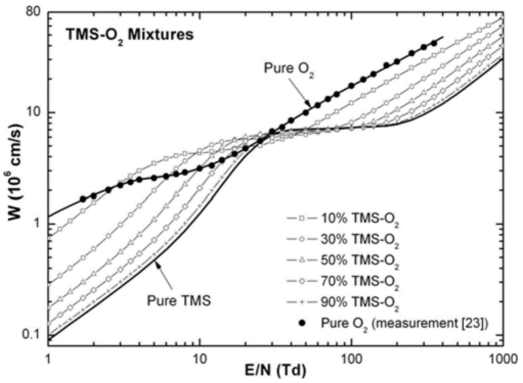

Fig. 6. *Electron drift velocity W as functions of E/N for the TMS-O_2 mixtures with 10%, 30%, 50%, 70%, and 90% TMS.*

The solid line and symbols show the present W values calculated using a two-term approximation of the Boltzmann equation for the TMS-O_2 mixtures. The solid curves show present W values calculated for the pure TMS molecule and pure O_2 molecule. The solid circle symbols show the experimental results for the pure O_2 molecule.

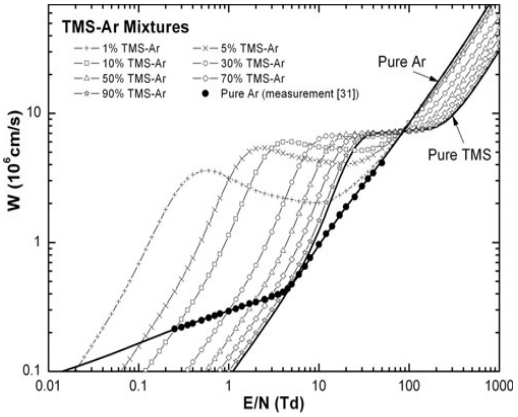

Fig. 7. *Electron drift velocity W as functions of E/N for TMS-Ar mixtures with 1%, 5%, 10%, 30%, 50%, 70%, and 90% TMS.*

The solid line and symbols show present W values calculated using a two-term approximation of the Boltzmann equation for the TMS-Ar mixtures. The solid curves show present W values calculated for the pure TMS molecule and the pure Ar atom. The solid circle symbols show the measured values for pure Ar.

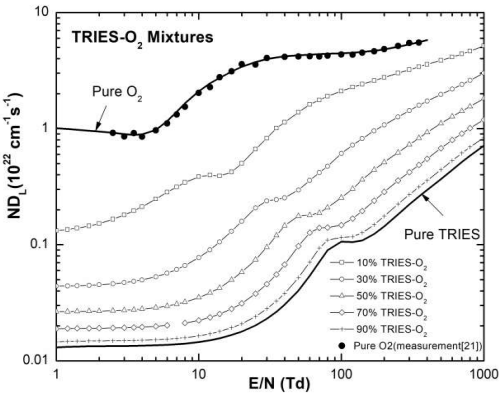

Fig. 8. *Density-normalized longitudinal diffusion coefficient NDL as functions of E/N for the TRIES-O2 mixtures with 10%, 30%, 50%, 70%, and 90% Tries.*

The solid line and symbols show present NDL values calculated using a two-term approximation of the Boltzmann equation for the TRIES-O_2 mixtures. The solid curves show present NDL values calculated for the pure TRIES and O_2 molecules. The solid circle symbols show the experimental results for pure O_2.

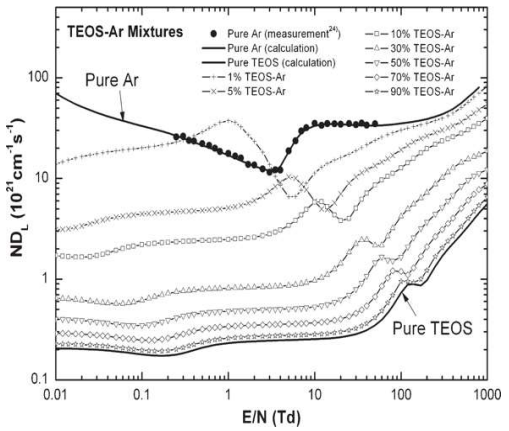

Fig. 9. *Density-normalized longitudinal diffusion coefficient NDL as functions of E/N for the TEOS-Ar mixtures with 10%, 30%, 50%, 70%, and 90% Tries.*

The solid line and symbols show present NDL values calculated using a two-term approximation of the Boltzmann equation for the TEOS-Ar mixtures. The solid curves show present NDL values calculated for the pure TEOS and Ar atom. The solid circle symbols show the experimental results for pure Ar.

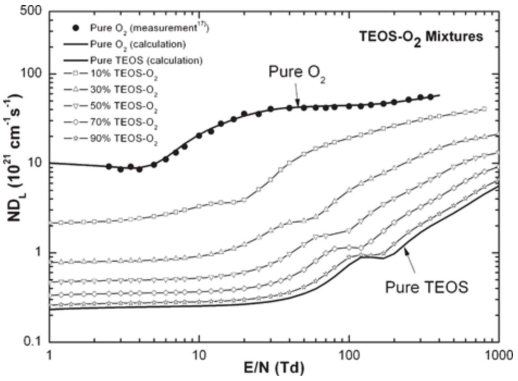

Fig. 10. *Density-normalized longitudinal diffusion coefficient NDL as functions of E/N for the TEOS–O_2 mixtures with 10, 30, 50, 70, and 90% TEOS.*

The solid line and symbols show present NDL values calculated using a two-term approximation of the Boltzmann equation for the TEOS– O_2 mixtures. The solid

curves show present NDL values calculated for thepure TEOS and O_2 molecules. The solid circle symbol shows the measurement value of the pure O_2.

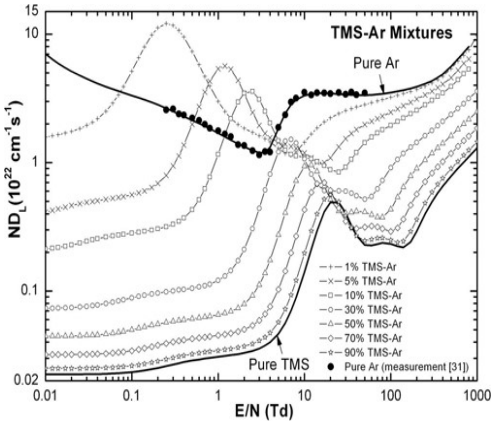

Fig. 11. *Density-normalized longitudinal diffusion coefficient NDL as functions of E/N for TMS-Ar mixtures with 1%, 5%, 10%, 30%, 50%, 70%, and 90% TMS.*

The solid line and symbols show present NDL values calculated using a two-term approximation of the Boltzmann equation for the TMS-Ar mixtures. The solid curves show present NDL values calculated for the pure TMS molecule and the pure Ar atom. The solid circle symbols show the measured values for pure Ar.

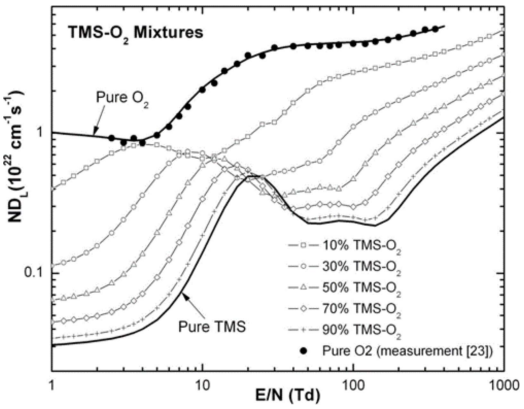

Fig. 12. *Density-normalized longitudinal diffusion coefficient NDL as functions of E/N for TMS-O_2 mixtures with 10%, 30%, 50%, 70%, and 90% TMS.*

The solid line and symbols show present NDL values calculated using a two-term approximation of the Boltzmann equation for the TMS-O_2 mixtures. The solid curves show present NDL values calculated for the pure TMS molecule and the pure O_2 molecule. The solid circle symbols show the measured values for pure O_2.

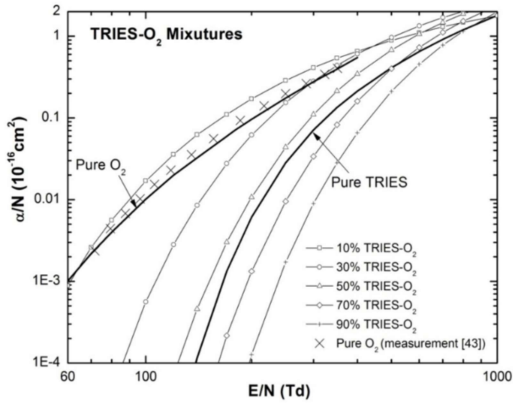

Fig. 13. *Townsend's first ionization, α/N in the TRIES-O_2 mixtures*

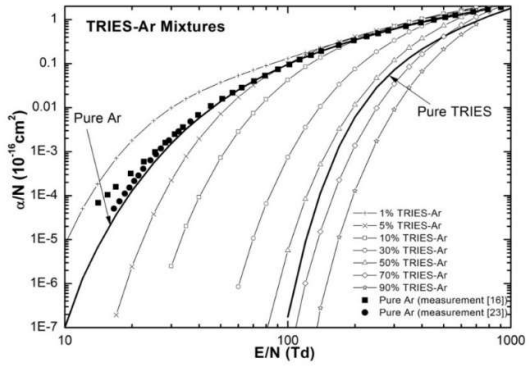

Fig. 14. *Townsend's first ionization, α/N in the TRIES-Ar mixtures*

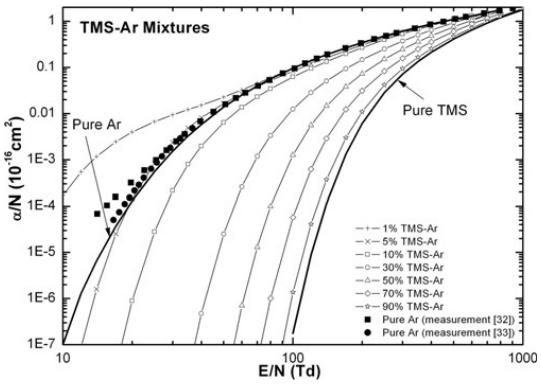

Fig. 15. *Townsend's first ionization, α/N in the TMS-Ar mixtures*

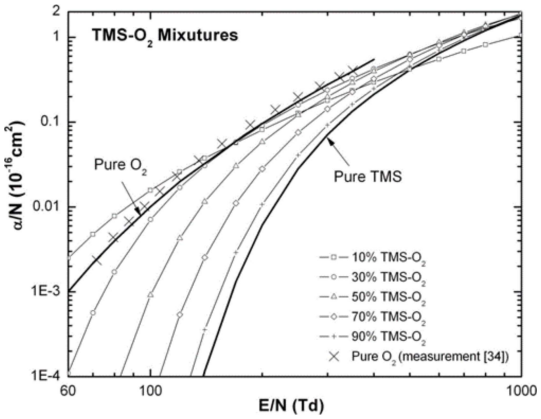

Fig. 16. *Townsend's first ionization, α/N in the TMS-O_2 mixtures*

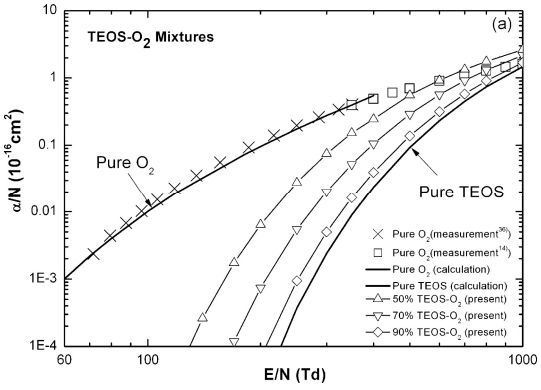

Fig. 17. *Townsend's first ionization, α/N in the TEOS-O_2 mixtures*

It is clear that the trend of W, NDL and α/N in TEOS, TRIES, and TMS both in pure and mixture with O_2 or Ar, are similar. These electron transport coefficients in these organic compound mixtures along with the electron collision cross section set are necessary data for the expansion of the choices of proper gases in application using the organic compound, especially in semiconductor technology.

CONCLUSION

In this study, the reliable sets of electron collision cross section for organic compound molecules such as TEOS, TRIES and TMS were presented. The electron transport coefficients, which include the electron drift velocity, the density-normalized longitudinal diffusion coefficient, the Townsend's first ionization coefficients, in TEOS-Ar, TEOS-O_2, TRIES-Ar, TRIES-O_2, TMS-Ar, TMS-O_2 mixtures, were also calculated and analyzed. Because of the lack of data on the electron collision cross section and the electron transport coefficients in pure and mixtures of organic compounds, the present theoretical results will be helpful for applications using the organic compounds mixture, especially in semiconductor technology.

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