Electron Swarm Parameters in Germane – Argon Mixtures Using Boltzmann equation

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ABSTRACT

A theoretical approach for calculating the electron swarm parameters in Germane – Argon (GeH₄-Ar) mixtures has been calculated by using two-term solution of the Boltzmann method in the range of E/N varying from 0.04 to 100 Td (1Td=10⁻¹⁷ V.cm²). These parameters namely, electron energy distribution function, characteristic energy, electron mobility. The ionization coefficients in addition to the electron drift velocity have also been calculated. The effect of the reduced electric field strength E/N on these parameters has been investigated, and compared with the available experimental data. Excellent agreements have been founded which suggest that the present approach is sufficient for computing the electron swarm parameters via two-term analysis.

1. INTRODUCTION

A lot of physical problems need to describe the non-stationary high discharge in non-isothermal spastically homogeneous plasma. Electron kinetics simulated by using two term solution of Boltzmann equation, taking into account anisotropy of electron energy, ie. Gas laser afterglow discharge, application of RF discharges and swarm method for calculation of electron atom/molecules cross section from swarm experimental swarm data calculated by using two–term solution of Boltzmann equation during the past decade (Huxley, 1974, Pichford, 1982, Rumble, 1981).

The study of the electron energy distribution function (EEDF) in ionized gases important for the quantitative understanding of gas discharges, plasma physics, laser physics. One of the most common techniques to obtain the distribution function is the solution of the Boltzmann equation using the Lorentz approximation (Zoltan and Nikolay, 2016). The role of electron swarm parameters is an important one because it provides a link excited state. Because of low ionization level of under 10⁻⁵, electron-electron and electron-ion are neglected. The plasma instabilities are less significance. When the plasma state reach to non-equilibrium, the transport parameters and electron collision cross section from swarm experimental swarm data calculated by using two-term solution of Boltzmann equation during the past decade (Huxley, 1974, Pichford, 1982, Rumble, 1981).
between electron gas collision cross section and gas breakdown and discharge phenomena. The swarm parameters may be directly calculated from a set of collision cross section by using either the Boltzmann equation or Monte Carlo simulation method (Yousfi and Benabdessadok, 1996).

A product of such calculations is the electron energy distributions also evaluated the percentage of energy loss by different collision processes. Once the validity of the swarm parameters are assured, they may be used to explain pre-breakdown and breakdown phenomena as well as providing sum information for understanding of discharge (Colonna and D’Angola, 1996, Bychkov et al., 2014).

Germane (GeH₄) is a colorless, flammable and high toxic gas, heavier than air. Its structure analogue to silane (SiH₄) and methane (CH₄) gas. Germane molecules has been used in depositing hydrogenated amorphous silicon-germanium (a-SiGe:H) thin films by metal organic vapor phase epitaxial or chemical beam epitaxial (Venkatasubramanian et al., 1989). Because of complex structure of the germane molecule the basic plasma processes have not been understood. In particular for germane molecules mixed with gases are the most fundamental in understanding the physics in plasma to fabricate thin film by etching and deposition in micro electron device fabrication (Gorur et al., 2012). Several industrial applications can be made using low-temperature plasmas such as the production of integrated circuits that involves deposition and etching (Mario et al., 2016).

Since (GeH₄) is mixed with Ar in semiconductor fabrication plasma processes, to study the electron swarm parameters for these mixtures under effect D.C. electric field, a set of elastic and inelastic cross section required. Modeling and simulation of discharge used for this processes (Soejima and Nakamora, 1993).

The calculated values are obtained by suitably averaging over the electron energy distribution function (EEDF), which is itself obtained by using the cross sections as input to a Boltzmann solver (Morgan and Penetrante, 1990). Theoretical method was used to study the plasma discharge in Ar-Cl₂ mixtures, using Boltzmann equation (Smith and Thomson, 1978). In present work we explained that a small amount of (GeH₄) effected the electron energy distribution function in GeH₄-Ar mixtures by two term solution of Boltzmann equation using the numerical NOMAD code, D.C. discharge is applied (Rockwood and Greene, 1980).

The drift velocity and longitudinal diffusion coefficient of electrons were measured in the 0.210% and 0.980% GeH₄-Ar mixtures for the first time (Soejima and Nakamora, 1993). We have extended our study to the mixtures (0.21%, 0.98%, 2%, 5% and 10% GeH₄-Ar mixtures for the second time.

The object of this paper is to calculate the (EEDF) and the electron swarm parameters in GeH₄-Ar mixtures in the range 0.04 Td to 100 Td where (1 Td = 1 X 10⁻¹⁷ V.cm²) and comparison with experimental results. The calculation was analyzed by using two term approximation of the Boltzmann equation.

2. Theory

The fundamental equation governing the electron distribution function is the Boltzmann equation. For spatially uniform gas in the presence of the steady electric field, the spatially homogeneous Boltzmann equation for electrons is given by (Morgan and Penetrante, 1990):

$$\frac{\partial f(v)}{\partial t} - \frac{eE}{m} \nabla_v f(v) = C$$

(1)

Where C is the collision integral, which, in the present study, accounts for the following processes: elastic scattering of electrons from atoms (the corresponding part of the collision integral is designated as Cₐ), excitation of electronic states and ionization of atoms by electron impact from the ground state (Cᵢₐ), as well as electron-electron collisions (Cₑ):

$$C = C_ᵢₐ + Cₐ + Cₑ$$

(2)

The conventional method of solving equation (1) is based on the expansion of the distribution function f(v) in Legendre polynomials, Pₙ(cosΘ). Retaining the two
first terms only we arrive at the two-term approximation:
\[ f(v) = f_0(v) + f_1(v) \]
\[ \cos \Theta, \]
(3)

Where \( v \) is the magnitude of the velocity, \( \Theta \) is the angle between \( v \) and \(-E\), \( f_0(v) \) is the symmetrical (isotropic) part of the distribution function and \( f_1(v) \) (the anisotropic part) describes the directed motion of the electrons along the electric field. In weakly ionized gases, most collisions occur between electrons and neutral atoms, the collisions between electron-electron and electron-ion are rare.

3. Transport Coefficients

The swarm parameters are defined in term of the collision cross section \( (Q) \) and the electron energy distribution function \( f(u, E/N) \) as follows: The relation between drift velocity and electron energy distribution function is (Al-Amin and Lucas, 1988):
\[ \nu_d = \frac{1}{3} \frac{(2e)}{m} E \int_0^\infty u \left( \sum_i \delta_i \right)^{-1} df u \]
\[ du \] (4)

where \( \delta_i = \frac{N_i}{N_s} \) represents the fractional concentration of the \( (s) \) species and \( N_s \) is the number of molecules of species \( (s) \) in the excited state \( (j) \). Where the energy distribution is constant in time and space and normalized by
\[ \int_0^\infty u^{1/2} f_0(u) du = 1 \]
(5)

The mobility is defined as the proportionally coefficient between the drift velocity of a charged particle and electric field. The mobility of electrons is:
\[ \mu = \frac{e}{m v_m} = \frac{v_d}{E} \]
(6)

\( v_m \) Represent the electron momentum transfer frequency, the electron mobility decreased with \( E/N \) increase; these occurrence energy loss results of an electron through the collisions between electrons and neutral molecules. From the computed drift velocity, the electron mobility \( \mu \) is obtained as (Ridenti et al., 2012):
\[ \mu N = \frac{1}{3} \frac{(2e^2)}{m} \int_0^\infty u \left( \sum_i \delta_i \right) \frac{df}{du} du \]
(7)

The diffusion coefficient \( D \) is given by (Al-Amin and Lucas, 1988):
\[ D_N = \frac{1}{3} \frac{(2e^2)}{m} \int_0^\infty u \left( \sum_i \delta_i \right) \frac{df}{du} du \]
(8)

If the distribution is not Maxwellian, the Einstein relationship is useful in defining a characteristic energy (Christophorou and Hunter, 1984)
\[ \epsilon_k = \frac{eD}{\mu} \]
(9)

Using the distribution function one can compute the electron mean energy (Morgan and Penetrante, 1990),
\[ \langle \epsilon \rangle = \int_0^\infty f(u) u^{1/2} du \ (ev) \]
(10)

For a Maxwellian energy distribution
\[ \frac{2}{3} \langle \epsilon \rangle = \frac{D}{\mu} \]

The primary ionization coefficient is a basic parameter in discharge physics and is defined as the number of ionizing collisions made by an electron in moving (1 cm) in the direction of the applied electric field. The coefficient is used in describing the behavior of a swarm of electrons traveling through a gas is the ionization coefficient (Frost and Phelps, 1964),
\[ \frac{1}{N} = \frac{1}{v_d} \left( \frac{2e^2}{m} \right) \int_0^\infty \left( \sum_i \frac{N_i}{N} \right) \frac{Q_i(\epsilon)}{\epsilon} f(u) u \ du \ (cm^3/s) \]
(11)

where \( e \) and \( m \) are the charge and mass of the electron, \( N_i/N \) the relative concentration of the k-component, \( v_d \) is drift velocity given by equation (4), \( I(\epsilon) \) is the ionization onset energy, and \( Q_i(\epsilon) \) are ionization cross-section. The values of \( f(u) \) are calculated from Boltzmann’s equation using all the collision cross sections.

4. Cross Section

We use the argon cross sections from our calculation for electron swarm parameters. The momentum transfer cross section was
The electron at high energy suffers inelastic collisions with Argon atoms, the Germane gas molecules causing these atoms and molecules to be excited to higher different electronic levels. However, electron kinetic is strongly affected by the electric field and also by inelastic collisions due to the inefficiency of elastic collision in the energy transfer. It is seen from the shift of the curve that the 10% GeH₄-90%Ar mixture reduce the mean energy of electrons. A significant shift of tails of EEDF on pure Argon towards higher energies results from different mechanisms of electron energy dissipation through the inelastic collision in this gas.

The best set of cross-sections for germane molecules used to calculate swarm parameters (drift velocity and diffusion coefficient) are shown by dashed lines in figures (2 and 3). This cross-sections are shown to give very good agreement between present calculation and measured drift velocity and diffusion (Soejima and Nakamora, 1993) in mixtures 0.21% and 0.98% GeH₄ in Argon. The calculated values in pure Germane and Argon are also shown in the same figure. Drastic changes in drift velocity were observed by adding small amounts of GeH₄ into Ar, because of momentum transfer and vibrational excitation sections of GeH₄ at low energy. As shown in figure (2), drift velocities showed negative differential conductivity over the E/N range 0.1 to 0.4 Td in the 0.21% mixture and over range 2.5 to 6 Td in the 0.29% mixture, the decrease was not smooth but contained a small hump when the concentration of GeH₄ in mixtures is small.

The calculated electron drift velocities in GeH₄-Ar mixture gases are shown in figure(4), the drift velocity values in GeH₄-Ar mixture gases are suggested to be between those of the pure gases over the range of E/N > 6 Td. In the range of E/N > 6 Td, the drift velocity values in these binary mixtures are higher than those of GeH₄, especially on E/N = 2 Td corresponding to electron energy of about 0.1015 eV. To the best of our knowledge, the electron drift velocity strongly depends on momentum transfer cross sections and vibrational excitation cross sections. In these cases, the reasons could be suggested.

5. Results and Discussions

Germane (GeH₄) has been widely used as an amorphous thin film in plasma processing, thus we need sets of electron collision cross sections for (GeH₄). Germane is an active the main attaching constituent in the mixtures, it different from argon gas that have two vibration and electronic levels in addition to the ionization with threshold energy 12.3 eV.

The electron swarm parameters as functions of E/N for the binary mixtures GeH₄-Ar have been calculated in the E/N range 0.04 Td < E/N < 100 Td by a two term solution of the Boltzmann equation.

The influence of different discharge parameters on the electron distribution function is shown in figure (1). The EEDF is strongly affected by a change of the gas mixture, the figure shows the change of distribution function with the growth of the portion of Germane (GeH₄) at the constant value of the electric field strength E/N. Therefore, for the distribution functions at E/N = 10 Td in two gases GeH₄ and Ar quite different and the distribution function for the mixture 10% GeH₄-90%Ar is different as shown in figure (1). This is because of the threshold energy at the vibration level 0.1015eV in the case of GeH₄ gas. For this reason, the inelastic collision of an electron with GeH₄ molecules occurs at low value of E/N. Therefore, the number of electrons at low energy increases at specified E/N value and they will also increase as a result of increase of GeH₄ gas concentration in the mixture.
Although electron mobility strongly depends on $E/N$ (0.01 to 1 Td), while the dependence of electron mobility decreases with increasing $E/N$. The behavior of the drift velocity. The electron drift velocities in the GeH$_4$–Ar mixtures are very sensitive to the mixture ratio of the GeH$_4$ molecule, especially in the low $E/N$ range. Small regions of the NDC in these binary mixtures are observed in the $E/N$ ranges of 0.3–4Td for 0.21%GeH$_4$–Ar, 0.6–6Td for 0.5%GeH$_4$–Ar, 1–10Td for 2%GeH$_4$–Ar, 2–20Td for 5%GeH$_4$–Ar and 4–20Td for the 10%GeH$_4$–Ar mixtures. The occurrences of these phenomena are due to the Ramsauer–Townsend minimum (RTM) of the elastic momentum transfer cross sections of the GeH$_4$ molecules, and the Ar atom. At a higher $E/N$, the electron drift velocities in 2, 5, and 10% GeH$_4$–Ar mixtures are closer to that in pure GeH$_4$. This is due to dominant inelastic collision processes in the swarm shifting from those proceed by the vibrational excitation of the GeH$_4$ molecule to those caused by electronic excitations of the majority Ar atom because the mean energy of the electrons is enhanced at a higher $E/N$.

The characteristic energy as a function of $E/N$ is shown in figure (5), the calculated values of characteristic energy for pure Germane are also shown in the same figure for comparison. The characteristic energy increases as a function of $E/N$, but at a specified value of $E/N$ the characteristic energy decrease by increasing GeH$_4$ in mixtures.

The electron mobility is also one of the important parameters of electron swarm behavior, like the drift velocity. The dependence of electron mobility on $E/N$ for different GeH$_4$ content in the mixture is shown in figure (6). The behavior of the electron mobility decreases with increasing GeH$_4$ concentration in the mixture at fixed $E/N$ (0.01 to 1 Td), while the dependence of electron mobility on the partial concentration of GeH$_4$ is reversed in the range 1 to 100 Td. For comparison, the calculated values for pure Germane are also shown in the same figure. Although electron mobility strongly depends on the amount of Germane in Argon and the parameter approximated to that in pure Germane at higher $E/N$, it depends on $E/N$. It should be noted that the hump in electron mobility occurred at roughly the same $E/N$.

The calculated ionization coefficients in GeH$_4$–Ar mixture gases are shown in figure (7). The variation of ionization coefficient $\alpha/N$, with $E/N$ for pure GeH$_4$ and Ar are also shown in the same figure, the $\alpha/N$ values in GeH$_4$–Ar mixture gases are suggested to be between those of the pure gases over the ranges of $E/N > 4$ Td. For pure Argon, the ionization coefficient is higher than the value of ionization coefficient in pure Germane over the same range of $E/N$. There are five further curves between the ranges mentioned later, with different mixtures of GeH$_4$ and Ar, i.e 0.21%, 0.98%, 2%, 5% and 10% GeH$_4$ in Argon, respectively. As shown in figure (7), the increase of GeH$_4$ content in mixture decreases the ionization coefficient. However, the growth of the inelastic collisions of electrons with germane molecules which are proportional to their concentration, reduce the number of fast electrons and causes lowering of ionization coefficient at higher concentration of the GeH$_4$ in the mixture.

6. Conclusion

The electron EEDF and transport coefficients (electron drift velocity, longitudinal diffusion coefficient, electron mobility, ionization coefficient) in binary mixtures of GeH$_4$–Ar was calculated by a two-term solution of the Boltzmann equation for the range (0.04 $\leq E/N \leq$ 100 Td) in the 0.21%, 0.98%, 2%, 5%, and 10% GeH$_4$–Ar mixture. Drastic changes in swarm parameters were detected by adding Germane into Argon. The drift velocity of electrons showed an unusual negative differential conductivity, with the decrease in the drift velocity not being smooth but having a small hump in both mixtures. These observed feature in the electron swarm parameters are due to the inelastic processes of germane molecules, possibly vibrational and electronic excitation. Models of gas discharge plasmas could be constructed using the binary mixture gases of GeH$_4$ gas with a high concentration of Argon.
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Figure (1): Comparison of calculated electron energy distribution function (EEDF) at $E/N=10\text{Td}$. Solid line $\text{GeH}_4$, dashed line $10\%\text{GeH}_4+90\%\text{Ar}$, dotted line pure Ar.

Figure (2): Electron drift velocity as a function of $E/N$ in GeH$_4$-Ar mixtures with comparison with experimental results.
Figure (3): Density-diffusion coefficient as a function of E/N in GeH$_4$-Ar mixtures with comparison with experimental results.

Figure (4): Electron drift velocity as a function of E/N for various GeH$_4$-Ar gas mixtures.
Figure (5): The characteristic energy as a function of E/N for various GeH₄-Ar gas mixtures.

Figure (6): The electron mobility as a function of E/N for various GeH₄-Ar gas mixtures.
Figure (7): The ionization coefficient as a function of E/N for various GeH4-Ar gas mixtures.