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The Influence of the Gas Mixing Ratio on Some Characteristics and Reaction Rate Coefficients of Ar/N_2 and He/N_2 DC Plasma35

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The aim of this study is to analyze the relation between the reaction rate coefficients, hence the production of active species, and the gas mixing ratio in a comparative way between Ar/N_2 and He/N_2 gaseous mixtures. The Ar and He contributions ranged from 0 to 100 % at a total gas pressure of 0.4 Torr and a reduced electric field E/N of 610 Td. Langmuir probe is employed to measure electron temperature. The results showed that adding Ar to N_2 plasma reduced both the discharge operating voltage and the electron temperature. However, an opposite action is obtained on Adding He. Also, Ar can induce the dissociation of molecular nitrogen and increase the production of nitrogen atoms, however it has an insignificant effect on the nitrogen ionization mechanism. On the other hand, He addition enhances the production of N_2^+, N^+ and N-atoms through ionization, ionization dissociation and dissociative reaction, however it has a decreasing effect on the dissociative recombination mechanism

Keywords*:* DC plasma/ Ionization/ Dissociation/ Rate coefficients

Introduction

Nitrogen plasma is known for its important technological applications in various fields of our life including metallic nitriding, surface modifications of different materials such as polymers and their composites, and sterilization of medical tools. Therefore, until now, a huge number of both theoretical and experimental studies came out investigating and characterizing nitrogen plasmas demonstrating its effects on different materials [1-4]. Some applications of N_2 plasma, such as surface etching and thin film nitriding, heating and biological sterilization count on the existence of nitrogen in its atomic form. Dissociation of N_2 into 2N is not that easy in case of pure nitrogen due to the strong N-N bond (945 KJ/mole) [5]. However, the process can be enhanced by adding noble gases such as He, Ar or Ne. Addition of such gases can affect the discharge characteristics (the electron temperature, electron / ion number density and electron energy distribution function), consequently, changes the excitation, ionization and dissociation rate coefficients, and hence, enhancing the concentration of active species.

Adding Ar or He into N2 plasma has been used to regulate the electron temperature and enhance the number of active species in an inductively coupled plasma [6]. K. Abbas et.al [7] added Ar to N2 in DC glow discharge and concluded that 60% Ar concentration in Ar/ N2 plasma is most suitable for the nitriding of silicon due to the production of a large number of active species which facilitate the nitrogen diffusion. Helium is considered one of the powerful Penning reagents for plasma species to be exited, ionized and dissociated through inelastic collisions. Also, due to its low mass, He-atoms are characterized by their lower efficiency of cathodic sputtering so that when added to another gas (N2 in the present paper) no increase in the impurity level would be expected [6, 8]. Naveed et. al [9] investigated the effect of changing He concentration in a capacitive RF He/N2 plasma on

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the N2 active species (N2(C 3Πu) and $N_2^+(B2\ \Sigma_u^+)$) and different plasma characteristics. They detected a considerable increase in the active species concentration upon increasing He percentage in the gas mixture.

In a previous study [10] the characteristics of Ar/N_2 and He/N_2 DC-plasma were measured using single cylindrical Langmuir probe. The study gave quantitative measurements of the electron temperature, T_e, electron number density, n_e, ion number density, n_i, plasma potential, V_p, electric field distribution, E, and electron energy distribution function, EEDF as a function of Ar and He fractions in the discharge. As a complement of this study, the present work aims to investigate the effect of changing He and Ar contents, in a DC N_2 plasma, on different reaction rate coefficients utilizing the previously obtained values of the plasma parameters.

Materials and Method

The schematic diagram describes the discharge unit is given in an earlier publication [11]. It consists of a Pyrex glass tube of 18 cm in length and 13cm in inner diameter. The tube contains two parallel copper electrodes of 5cm in diameter and 7cm separation distance. A continuous flow of He/N_2 and Ar/N_2 is allowed to enter the tube throw a needle valve after evacuating the tube to a base pressure 10^{-3} Torr. The total gas pressure is recorded by Pirani gauge and kept constant at 0.4 Torr during the measurements. The calculated reduced electric field E/N was fixed at about 610 Td.

The Lnagmuir probe, employed for plasma diagnostics, made of tungsten wire of 0.3 mm in diameter and 5 mm exposed length supported by a ceramic tube concentric in a Pyrex glass one. The probe is allowed to enter a discharge tube from an opening in its middle. The electron temperature, T_e, is determined at different Ar and He concentrations in the gas mixtures, from the slope of the ln (I)-V curve of the probe in the transition region between the floating potential and plasma potential by the following equation [12]:

$$T_e = e/(k_B\ dln\ (I)/dV)$$

Where e, K_B, I and V are the electronic charge, Boltzmann constant, probe current and probe voltage respectively.

The characterization of electrons, atoms, radicals, ions and molecules in Ar/N_2 and He/N_2 mixtures is needed to understand and control the behavior of these different plasma species for their relevance for technological applications. In cold plasma, the main primary reactions by electron impact on atoms and molecules are ionization, excitation to higher energy levels and dissociation. The rate coefficients, K_s, of these reactions can be obtained by integrating the product of electron velocity times the cross section of each process over an estimated Maxwellian distribution [13].

$$k_s = \langle \sigma(\upsilon)\upsilon \rangle_\upsilon = 4\pi \int_0^\infty \sigma(\upsilon)\upsilon^3 f(\upsilon) d\upsilon$$

Different reactions and their relate rate coefficients are obtained from the literature and listed in Table (1).

Table (1): Reactions and rate constants of N2 plasma

	Reaction mechanism	Rate coefficient (cm3/s)	Reference
R1	$N_2 + e \rightarrow N^+ + N + 2e$	$-5.68\times10^{-12}T_e + 8.57\times10^{-12}T_e^2 - 4.11\times10^{-12}T_e^3 + 7.26\times10^{-13}T_e^4 - 3.09\times10^{-14}T_e^5$	14
R2	$N_2 + e \rightarrow N_2^+ + 2e$	$1.01\times10^{-10}T_e - 1.13\times10^{-10}T_e^2 + 3.14\times10^{-11}T_e^3 - 7.52\times10^{-13}T_e^4 - 5.14\times10^{-14}T_e^5$	14
R3	$N_2 + e \rightarrow 2N + e$	$1.18\times10^{-8}\times T_e^{0.5}\times e^{-13.3/Te}$	15
R4	$N_2^+ + e \rightarrow N + N$	$2.8\times10^{-7}\times(0.026/T_e)^{0.5}$	16

Where R1, R2, R3 and R4 designated to the following reactions respectively: the ionization dissociation reaction with rate coefficient K_i^{diss}, the ionization reaction with rate coefficient K_i, the dissociative reaction with rate coefficient K_d, the dissociative recombination with rate coefficient K_d^r

Results and Discussion

The variations of discharge operating voltage as a function of Ar and He percentages at fixed current and pressure are depicted in Fig. (1). This figure shows a slightly decreasing voltage with increasing Ar percentage; however, an increasing behavior is obtained in case of He. These behaviors can be explained in the light of the fact that although Ar and N_2 have nearly the same ionization potentials ionization cross sections ($\approx 15.7\ eV\ and \approx 2.5X\ 10^{-20}$) [17], the decreasing behavior of the operating voltage with Ar contribution refers to the fact that in case of pure noble gas plasmas, the main ionization mechanism is the step wise one,

$$e + Ar \rightarrow e + Ar^{*} \quad , \quad e + Ar^{*} \rightarrow 2e + Ar^{+}.$$

Where Ar^{*} designated for the Ar metastable exited state. However, the situation for N_2, as a molecular gas, is different because there are some additional complexities for molecular processes due to the increased internal degrees of freedom i.e. electron energy loss channels, such as vibrationally and rotationally excited states in addition to the molecular dissociation mechanisms. This effect results in reduction in the operating discharge voltage needed to sustain the discharge. In contrary to Ar addition, He addition results in increasing the discharge voltage. The reason for this behavior is attributed to the fact that for T_e within the range 1-20 eV, helium has electron collision cross section of about 2 $x10^{-21}m^2$ in its ground state which is smaller than that of N_2 of $1.2x10^{-19}\ m^2$ [18]. So that in order to sustain the discharge, the voltage has to be increased.

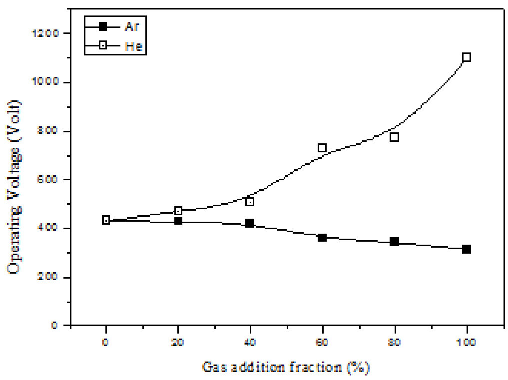

Figure (1): variation of discharge operating voltage as function of Ar and He percentage

Figure (2) demonstrates the variation of T_e with the addition percentage of both Ar and He in N_2 discharge. In spite of the similarity of ionization potentials and ionization cross sections of both Ar and N_2, T_e showed a slight decrease ranging from 4.5 to 1.5 eV, with an increase of Ar ranging from 0 to 100%. This result was interpreted as according to a previous work by the authors [10] as the measurements of the electron number density, n_e and EEDF showed that, argon addition resulted in increasing the values of n_e, and hence the electron-electron collision frequency is expected to be increased. This behavior, in turn, tends to deplete electrons in the “hot tail” and the EEDF relaxes to Maxwellian distribution, as a consequence, T_e decreases [19]. This result agrees with the measurements of F.U. Khan et.al [20,21], they showed that $T_{e\text{-}tail}$ obtained from EEPF and the electron temperature obtained from spectroscopic line–ratio technique decreases with the mixing ratio in Ar/N_2 inductivly coupled discharge and they attributed their result to the increase of total ionization cross sections (inelastic collisions). In H_2/Ar plasma, M. Sode et.al [22] obtained the same result with increasing the Ar contribution and attributed this behavior to the increase in the effective ionic mass from 2.7 amu (for H_2) to 40 amu (for Ar). In the proposed mixture, the effective mass increased from 28.02 amu (for N_2) to 40 amu (for Ar). Due to the same reason for increasing the operating voltage, increasing He content will reduce electron collision frequency, and this gives the electrons the chance to move in the electric field with a larger mean free path, consequently, increasing their kinetic energy and hence their temperatures. According to the current results, T_e increased from 4.5 to 8.9 eV through the whole range of He addition as shown in Fig. (2). Qing Xiong et.al [23] concluded that increasing of the electron temperature, in case of He being more than Ar and any other noble gas attributed to the existence of the metastable 2^1S in singlet state. Then electrons could have the ability to accumulate a high energy in the external electric field consequently, induce the ionization and/or excitation of He atoms through collisions. M.A. Naveed et.al [18], by using Langmuir probe and OES, demonstrated that the electron temperature, electron density and concentration of active species increase with increasing the helium contribution in RF He/N_2 plasma.

Ionization rate coefficients, K_i and K_i^{diss}, due to the reactions R1 and R2 as a function of Ar content are represented in Fig. (3-a). As can be seen from the figure, an increase in the Ar content results in a noticeable influence on the ionization rates due to R1 and R2. As the rate coefficients have a decreasing trend with increasing Ar content. However, a slight increase (nearly a saturation trend) in both rates at the concentration (Ar 40% for R1 and 50 % for R2) was observed. The ionization dissociation, due to R2, is about two orders of magnitude higher than the ionization rate due to R1. The deceasing behavior of K_i and K_i^{diss} with Ar % agrees with previous works in the literature [24,25]. As they concluded that argon addition does not affect the nitrogen ionization mechanism and attributed this conclusion to the fact that the energy of the Ar matastable atoms of $^3P_0$ (11.72 eV) and $^3P_2$ (11.55 eV) are lower than the threshold ionization energy of N_2 molecules (which is 15.57 eV for R1 and 24.5eV for R2).

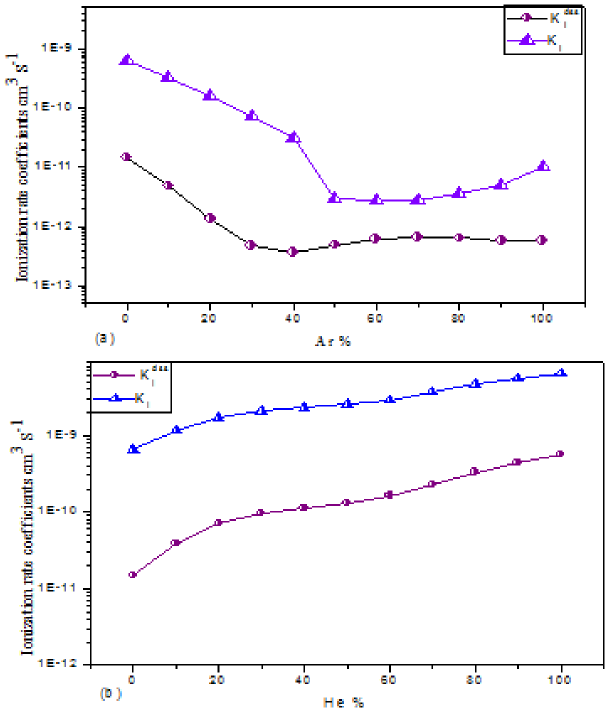

Figure (3): Ionization rate coefficients of N_2 as a function of Ar (a) and He (b) content in the mixture

On the other hand, Fig. (3-b) demonstrates that on increasing He fraction in the gas mixture k_i and K_i^{diss} showed a similar increasing trend due to both R1 and R2 with values due to R2 are one order of magnitude higher than that due to R1. This behavior can be interpreted as: with increasing He fraction in the gas mixture, the scattering of electrons with He atoms increases, in addition to the reduction of collision frequency because of the smaller helium collision cross section. Hence, the electron energy increases and it can ionize nitrogen molecules upon collision with it. The production of N_2^+in He/N_2 gas mixture is previously reported [26, 27] to be mainly due to Penning ionization of $N_2(X^2\Sigma_g^+)$ by metastable helium atoms. As the He atoms of metastable states 2^3S_1 and 2^1S_1 having the energies 19.8 eV and 20.6 eV respectively, both are higher than the threshold ionization energy of the N_2 molecule (15.57 eV).

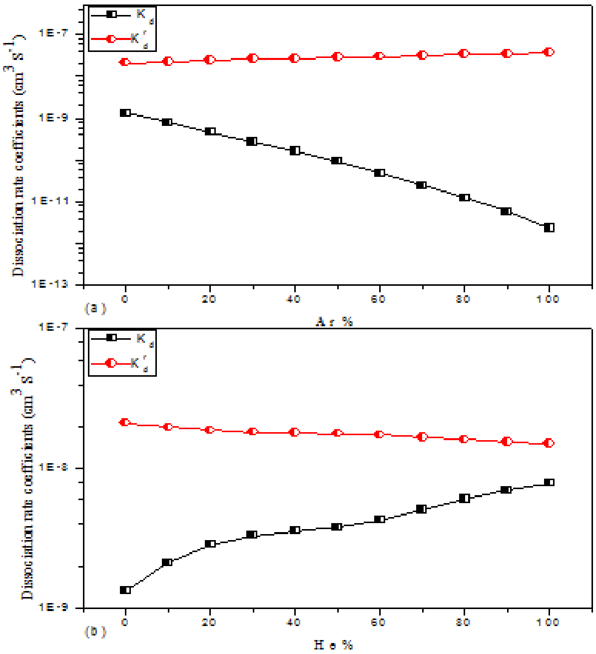

Figure (4): Dissociation rate coefficients of N_2 as a function of Ar (a) and He (b) content in the mixture

Dissociative rate coefficients, K_d and K_d^r, due to the reactions (R3, R4) for N_2 plasma as a function of Ar addition are presented in Fig. (4-a). The dissociation due to R3 showed a decreasing behavior, however due to R4, it slightly increased with increasing Ar fraction. Adding Ar to N_2 plasma may create additional destruction channels for charged particles. Because of the similar values of their ionization potential, charge transfer reaction may be possible $Ar^+ + N_2 \rightarrow Ar + N_2^+$. This reaction may be followed by dissociative recombination $N_2^+ + e \rightarrow N + N$ [28].

M.A. Song et. al. [29] investigated the effect of Ar fraction on the properties of low-pressure inductively coupled nitrogen-argon plasmas applying both Langmuir probe and OES techniques. In agreement with the present results, they observed that increasing the Ar % leads to a slight increase of the emission intensity from N-atoms, which is an indication of the increase of dissociation rate coefficient. They explained that this could be attributed to the fact that with an increase of Ar content, the Penning excitation and Penning dissociation, due to Ar metastables, increase the densities of the excited states of N-atoms.

Dissociative rate coefficients due to the reactions (R3, R4) for N_2 plasma as a function of He addition are presented in Fig. (4-b). It is clear from this figure that K_d has an increasing trend, however K_d^r, shows a slightly decreasing tendency. The obtained increasing behavior of K_d is partially in agreement with Maria Younus et. al [30]. They detected the increase of N-atoms intensity with increasing the He concentration above 56% in a RF He-N_2/Ar plasma and attributed this behavior to their measurements of the EEPF which showed that the density of both high and low energy electrons increased simultaneously with increasing He %. The high energy electrons enhance the production of N-atoms through the reaction R3 $(N_2 + e \rightarrow 2N + e)$, however, the low energy electrons enhance the production of N-atoms through the reaction R4 $(N_2^+ + e \rightarrow N + N)$. According to a previous work by the authors [10], the measured EEDF showed a decided shift of the distribution towards the higher energy and slight increase in the density of high energy electrons, however, the low energy electrons showed a decreasing density. This can explain the obtained result of the decreased K_d^r, and the increased K_d with He concentration.

Conclusion

The variations of discharge operating voltage and electron temperature of N_2 DC plasma was investigated as a function of plasma composition. It was found that the values of discharge voltage and electron temperature tend to decrease with increasing Ar %, however their values had an increasing behavior with increasing He%.

The effect of gas composition on the different reaction rate coefficients also had been investigated and according to the proposed experimental condition, argon can induce the dissociation of molecular nitrogen and increase the production of nitrogen atoms however, it has no touchable effect on the nitrogen ionization mechanism. On the other hand, helium addition enhances the production of N_2^+, N^+ and N^-atoms through ionization, ionization dissociation and dissociative reaction, however it has a decreasing effect on the dissociative recombination mechanism.

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