Vol 10 No 7, July 2001
1009-1963/2001/10(07)/0639-06

Chinese Physics

© 2001 Chin. Phys. Soc.
and IOP Publishing Ltd

ELECTRON TRANSPORT BEHAVIOURS IN THE NITROGEN DIRECT CURRENT GLOW DISCHARGE*

Zhang Lian-zhu(张连珠),† Yu Wei(于 威), Wang Jiu-li(王久丽),
Han Li(韩 理) and Fu Guang-sheng(傅广生)
Department of Physics, Hebei University, Baoding 071002, *China*

(Received 19 August 2000; revised manuscript received 2 March 2001)

A Monte Carlo simulation is presented to describe the electron transport behaviours in the nitrogen direct current glow discharge. The energy and angular distributions of the electrons at different positions of the cathode dark space are calculated; their energy and density distribution features throughout the entire discharge are discussed. The influence of molecular vibrational excitation, typical for electron–molecule collisions, has been studied and the elementary process of active species generation has been illustrated. The simulated results reveal that, in the cathode dark space, the high-energy electrons are mainly forward scattering and behave as a high-energy 'electron beam'. The sharp increase of the number of secondary electrons plays an important role in producing active species at the interface between the cathode dark space and the negative glow region. The vibrational excitation enhances the energy loss of electrons in the negative glow region.

Keywords: Monte Carlo simulation, nitrogen direct current glow discharge, mechanism of active species generation
PACC: 5265, 5280, 5220F

I. INTRODUCTION

Glow discharge is used in a large number of application fields, such as in microelectronics for plasma etching, thin-film deposition, modification of surfaces, and in flat plasma display, spectrochemical analysis, etc. For understanding the fundamental processes of glow discharge, in the past years, much experimental and theoretical work has been carried out on inert gases such as Ar and He.[1−6] Recently, as an effective means of producing active nitrogen species in plasma processing, especially in the new functional and mechanical materials such as GaN, CN deposition, nitrogen glow discharge has received extensive attention. Many techniques such as optical emission spectroscopy, electronic probes and mass spectroscopy have been used to study the behaviours and the reaction processes of the plasma particles.[7,8] To attain better results in these application fields, theoretical calculation and analysis of their internal mechanisms are required.

The molecular glow discharge, which involves dissociation and vibrational excitation plasma processes, is quite different from the atomic glow discharge. The density and energy distributions of the plasma species produced in the molecular glow discharge have their special features. Since the behaviours of the species in the nitrogen glow discharge are more complex than those in atomic gas (e.g. Ar and He), it is necessary to find a proper way to describe the discharge processes. Previously, a number of models have been proposed such as the fluid model,[9,10] the kinetic (Boltzmann) model,[11,12] and the Monte Carlo model.[13−15] Among these models, the Monte Carlo simulation is most accurate, because it deals with particles on the lowest microscopic level. The cathode dark space (CDS) is the most important region of direct current (dc) glow discharge, characterized by a high electric field. We choose the Monte Carlo method to simulate the main plasma species (e^-, N_2^+, N^+, N_{2f}) in the CDS of the nitrogen direct current glow discharge. The heavy species (N_2^+, N^+, N_{2f}) have been investigated in our previous work.[16] The production and the initial distributions of these heavy species are directly determined by the electron transport behaviours. Thus, the electrons play the most import role in the glow discharge.

In this paper, the Monte Carlo simulation is used to describe the electrons in a N_2 dc glow discharge.

*Project supported by the Natural Science Foundation of Hebei Province, China (Grant No. 597058).
†Address: Hebei Normal University.

The basic description of the model is given in section II. The model assumptions are presented in subsection A and the simulation method is described in subsection B. The corresponding collision cross sections are provided in subsection C. The results and a discussion are given in section III.

Ⅱ. DESCRIPTION OF THE MODEL

A. Model assumptions

The model assumptions are the same as those used for heavy species in Ref.[16]. Only the collisions of electrons with neutral ground-state nitrogen molecules (N^0_{2s}) are incorporated. The other processes, such as heavy species collisions and the combination process, are not included in our simulation. The collisions taken into account are vibrational excitation, electronic excitation, ionization, dissociation, dissociative ionization and elastic collision. Secondary electrons produced by ionization and dissociative ionization have been followed as well.

The electric field is assumed to vary linearly with the distance from the cathode in the CDS:[4]

$$\varepsilon(z) = 2(V_C/d_c)(1 - z/d_c), \tag{1}$$

where V_c is the voltage applied to the cathode, d_c is the length of CDS and z is the axial position of the electron. In the negative glow region (NG), the electric field is assumed simply to be zero.

B. Monte Carlo simulation

The Monte Carlo procedure is similar to that used to describe the heavy particles in the CDS.[16] The simulated electrons start at the cathode. Their initial energy is assumed to be 4eV (actually the energy is distributed between 0 and 6 eV with a maximum at 4eV.[17]) The initial angular distribution is assumed to be isotropic between 0 to $\pi/2$. Every electron is followed until its energy becomes lower than the vibrational excitation threshold and the secondary electrons are simulated in the same way. The new energy (E) and direction (θ') after a collision depend on the type of collision.

For elastic collisions, the new energy is determined by the formula:

$$E = E_0[1 - 2(m_e/m)(1 - \cos\chi)], \tag{2}$$

where E_0 is the electron energy before the collision, m_e and m are, respectively, the mass of the electron and the nitrogen molecule. χ is the scattering angle of the electron after the collision.

For vibrational excitation, electronic excitation and dissociation, the new energy can be written as follows:

$$E = E_0 - E_{vib}, \tag{3}$$

$$E = E_0 - E_{exc}, \tag{4}$$

$$E = E_0 - E_{dis}, \tag{5}$$

where E_{vib}, E_{exc}, E_{dis} are the vibration excitation, electronic excitation and dissociation threshold (taken as 1.2eV, 9eV and 13eV) respectively.

If an electrons participates in an act of ionization or dissociative ionization, the new energy of the primary and secondary electrons are determined by random numbers (r_1 and r_2) uniformly distributed between 0 and 1:

$$E_{pri} = (E_0 - E_i)r_1, \tag{6}$$

$$E_{sec} = (E_0 - E_i)(1 - r_1), \tag{7}$$

$$E_{pri} = (E_0 - E_{d,i})r_2, \tag{8}$$

$$E_{sec} = (E_0 - E_{d,i})(1 - r_2), \tag{9}$$

where E_i and $E_{d,i}$ are the ionization and dissociative ionization thresholds (taken as 15.6eV and 30eV respectively). The above energy thresholds of different collisions are obtained from the corresponding experimental cross-section data.[18−23]

The new direction after each type of collision is assumed to be anisotropic.[7] The new direction after a collision can then be deduced from:

$$\cos\theta' = \cos\theta\cos\chi + \sin\theta\sin\chi\cos\phi, \tag{10}$$

where θ and θ' are, respectively, the angles with respect to the axial direction before and after the collision. The azimuthal angle ϕ is distributed between 0 and 2π and is also determined by a random number.

In our simulation procedure, the secondary electrons produced by ionization and dissociative ionization are treated in the same way as the primary electrons. For statistical reasons, a sufficiently large number of electrons (e.g. 10^5) have been followed.

C. Collision cross sections

According to the experimental data, we combine the ten main electronic excitation processes into one composite excitation process with an energy threshold of 9eV.[19] The vibrational excitation cross section is the mean value derived from the various vibrational excitation processes.[18] The ionization cross section is obtained from Refs.[20,21]. The total dissociation and

dissociative ionization cross sections are taken from Refs.[22,23]. The total cross sections are taken from Refs.[24,25,26]. All of the cross sections used in our simulation have been fitted into analytical formulae.

Ⅲ. RESULTS AND DISCUSSION

The external parameters used in the calculations (133 Pa and 500V) are obtained from typical discharge conditions.[7,27] We assume that the electrode distance is 2 cm and that the CDS length is 0.35cm.

The spatial variation of electron energy and angular distribution in the CDS are presented in Fig.1. The electron energy is distributed between 0 and 250eV at a position of about 0.1cm from the cathode with the maximum at the higher-energy end. The incident angle at this position is much less than 10° plus a minor fraction of backscattering. With an increased distance, such as at z=0.22cm, the electron energy distribution spreads into two peaks at 430eV and 70eV which correspond to the primary electrons having not suffered any inelastic collision and the secondary electrons arising from ionization and dissociative ionization, respectively. The majority of the incident angles is still less than 10°. At the CDS–NG interface the electrons are mostly concentrated at the low-energy end, but a few electrons which have not experienced any inelastic collision are still visible at the high-energy end. The incident angles of most electrons remain small. We only follow the electrons to the interface, so no electrons are backscattered to the CDS from the NG, and accordingly, all scattering angles are less than 90°.

These distributions are related to the relative contributions of the energy gain due to electric field acceleration and the energy loss due to inelastic collisions. Furthermore, the cross sections of various electron collisions change with the electron energy. Electrons possessing energies corresponding to the high inelastic collision cross sections will participate in various inelastic collisions and lose a large part of their energy. But others having higher energies will be too fast for efficient collisions and will maintain their energies.

The electrons in the CDS behave as a strongly forward scattering 'electron beam'. Even those having encountered several collisions still have small scattering angles. These results are in good agreement with the experimental results. This becomes more evident as the discharge voltage increases and the gas pressure decreases. Fig.2 shows the energy distribution at different gas pressures.

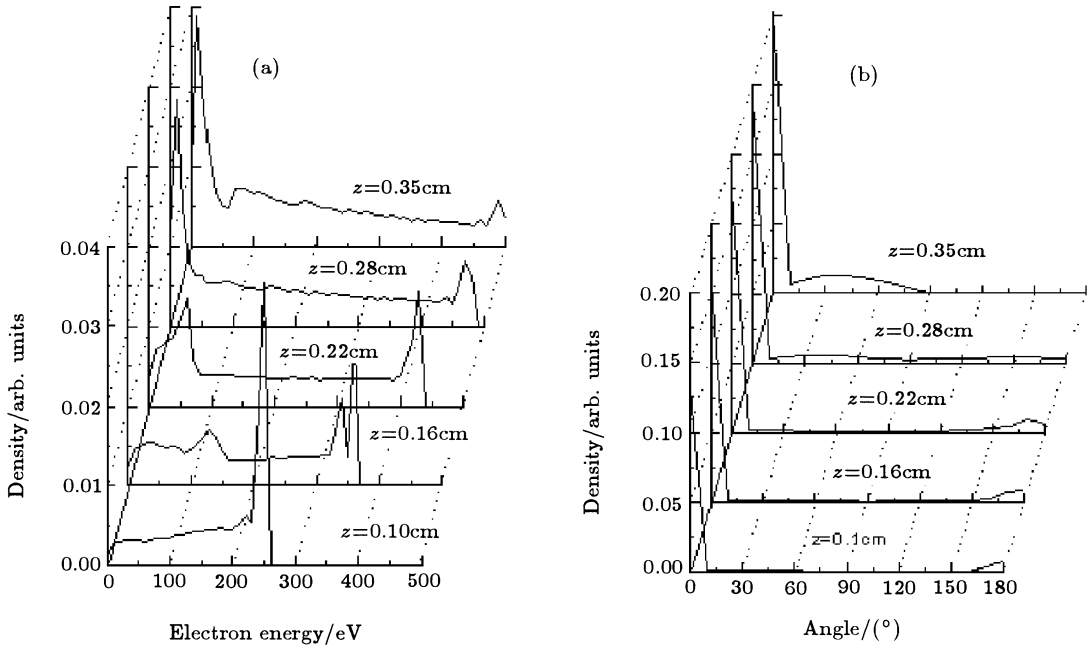


Fig.1. Energy distribution (a) and angular distribution (b) of the electrons in the CDS at different positions from the cathode.

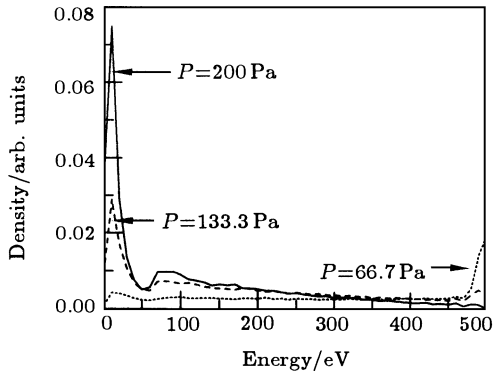


Fig.2. Energy distribution of electrons at the CDS–NG interface at different gas pressures.

Figure 3 represents the energy and the angular distribution of the electrons bombarding the anode. Although in the CDS the electrons possess high energy and transport nearly parallel to the electric field, after travelling through the NG, the energy of most electrons is less than 1.4eV, and their incident angles become larger. The electrons reflected from the anode and the secondary electrons arising from the electron bombardment are neglected, because they can only affect the electron distribution in the vicinity of the anode but not that throughout the discharge space.

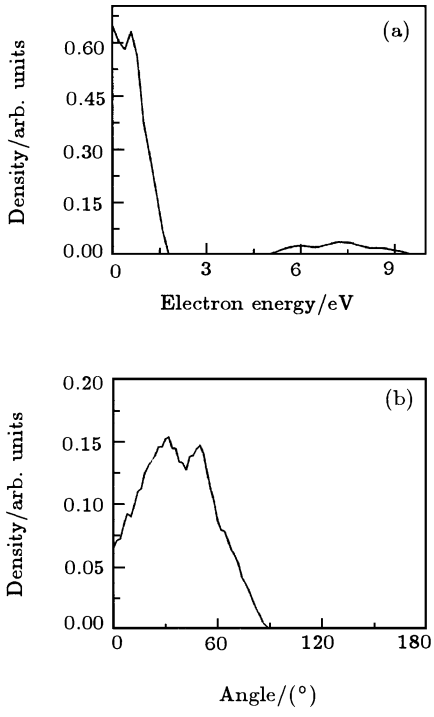


Fig.3. Energy distribution (a) and angular distribution (b) of the electrons bombarding the anode.

Figure 4 shows the electron density and mean energy distribution in the entire discharge space. The electron density that is very small within the CDS increases sharply at the CDS–NG interface and a maximum value can be found in the NG (Fig.4, curve *a*). The reason is that when the electrons travel through the CDS–NG interface the collisions between the electrons and N_{2s} become more frequent, leading to the dramatic increase of the number of the secondary electrons (electron avalanche). Accordingly,, curve *b* of Fig.4 shows that the mean energy of the electrons increases rapidly near the cathode and decreases sharply in the vicinity of the interface. This is because of the higher electric field and less inelastic collisions within the CDS compared with the nearly zero electric field in the NG and more inelastic collisions near the interface.

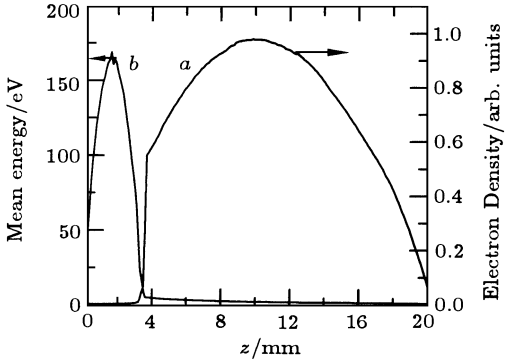


Fig.4. Spatial dependence of the distributions of electron density (curve *a*) and electron mean energy (curve *b*) in the entire discharge space.

In the NG region, owing to the low-energy threshold of the electron vibrational excitation typical of molecular discharge, the density of the electrons traced decreases and drops almost to zero near the anode since the majority of the electrons have been transferred to the slow group. The corresponding mean energy of the electrons in this region drops off greatly and cannot become stable until it drops to the vibrational excitation energy threshold (Fig.4, curve *b*). These transport electrons with low energy are the dominant current carriers in the discharge space. A more detailed study of their transport behaviour in this low-energy range should be carried out together with additional processes, such as the combination of electrons with ions in this region.

The above results lead to a framework for understanding electron–molecule collision processes in the N_2 glow discharge. The electrons are mainly accelerated by the electric field in the CDS region and act as the dominant current carriers in the NG region where

the lower energy vibrational excitation collision is a mainly relevant process to electron energy loss. At the CDS–NG interface, many active atomic or molecular species such as N_2^*, N_2^+, N^*, N^+ will be created by various electron–molecule collisions. Figure 5 illustrates our simulated relative distribution of the $N_2(C\,^3\Pi_u)$ state along the axis due to electron–molecule excitation collisions and the corresponding experimental result of nitrogen optical emission spectroscopy (emission wavelength λ=357.7 nm).[7] We can see that the result of Monte Carlo simulation is generally in agreement with the experimental result.

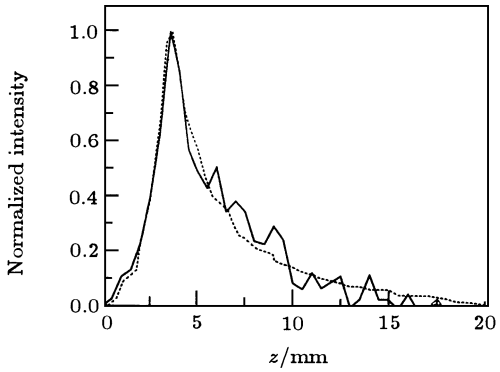


Fig.5. Normalized computed distribution of $N_2(C\,^3\Pi_u)$ (full lines) and experimental result (dotted line).

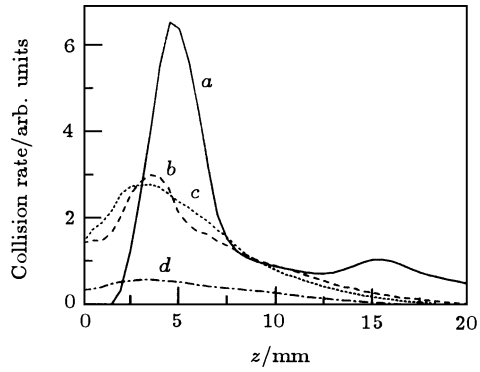


Fig.6. Collision rate distribution of different kinds of collisions as functions of distance from the cathode: *a*, vibrational ionization; *b*, dissociation; *c*, ionization; *d*, dissociative ionization.

Figure 6 illustrates the different collision coefficients as functions of position from the cathode. It shows that the ionization, dissociation and dissociative ionization collisions reach their maxima near the CDS–NG interface, which are related to the highest creation rates of the active species (N^0, N^+, N^*) at this region. The rates of these collisions drop to nearly zero at about 1.5 cm from the cathode. The vibrational excitation collision with the low-energy threshold of 1.2eV also goes through the maximum at the CDS–NG interface, but a secondary peak appears in the NG region, as the electrons are slowed down further after crossing the CDS–NG interface. This is believed to be characteristic of the molecular discharge compared to the atomic discharge.

IV. CONCLUSIONS

A Monte Carlo model is presented to describe the dc glow discharge in molecular N_2. The aim of our work is to provide a reasonable description of the molecular gas discharge. In this paper, the energy, angular distributions, mean energy and density of electrons as functions of distance from the cathode have been calculated. The rates of various kinds of collisions in the entire discharge space are discussed. The influence of vibrational excitation and dissociation collisions characteristic of the molecular discharge is investigated. The main results are the following:

(1) In the CDS of the nitrogen dc glow discharge, the forward-transporting electrons behave as a high-energy 'electron beam'. The number of high-energy electrons decreases gradually while the number of electrons within the 'electron beam' increases gradually with the increase of the distance from the cathode. These transport characteristics depend on the discharge conditions.

(2) The number of secondary electrons increases sharply at the CDS–NG interface and a large number of electrons transfer to the slow group in NG.

(3) The electron–N_2 dissociation, ionization and dissociative ionization collisions play important roles for the production of active nitric particles.

References

[1] Chuchi M and Kubota T 1983 *J. Phys. D: Appl. Phys.* **16** 1705

[2] Farouki R T, Harmaguchi S and Daluie M 1991 *Phys. Rev.* A **44** 2664

[3] van Straaten M, Gijbels R and Vertes A 1992 *Anal. Chem.* **64** 1855

[4] Gottsho A R, Mitchell A and Scheller G R 1989 *Phys. Rev.* A **40** 6407

[5] Boeuf J P and Marode E 1982 *J. Phys. D: Appl. Phys.* **15** 2169

[6] Bogaerts A, van Straaten M and Gijbels R 1995 *Spectrochim. Acta.* **50B** 179

[7] Liu J H, Ding H B, Wang W C, Tang S K and Yang X F 1999 *Proc. 9th Nat. Symp. Plasmas Science and Technology* (Dalian, China: PSPST) p 49

[8] Mogen K S, Eskildsen S S and Mathiasen C 1998 *Surf. Coat. Technol.* **102** 41

[9] Boeuf J P 1987 *Phys. Rev.* A **36** 2782

[10] Passchier J D P and Goedheer W J 1993 *J. Appl. Phys.* **74** 3744

[11] Carman R J and Maigland A 1987 *J. Phys. D: Appl. Phys.* **20** 1021

[12] Abril I 1988 *Comp. Phys. Commun.* **51** 413

[13] Sun J Z, Gong Y and Wang D Z 1993 *J. Phys. D: Appl. Phys.* **26** 436

[14] Bogaerts A 1999 *Plasma. Sources. Sci. Technol.* **8** 210

[15] Chen Y Z, Chen Q M, Li J, Lai J J and Qiu J L 1998 *Acta Phys. Sin.* **47** 1665 (in Chinese)

[16] . Yu W, Zhang L Z, Li X W, Han L, Chen Y M and Fu G S 1999 *Acta Phys. Sin.* **48** 1701 (in Chinese)

[17] Chapman B 1980 *Glow Discharge Processes* (New York: Wiley)

[18] Dube L and Herzenberg A 1979 *Phys. Rev.* A **20** 194

[19] Cartwright D C 1977 *Phys. Rev.* A **16** 1041

[20] Mark T D 1975 *J. Chem. Phys.* **63** 3731

[21] Rapp D and Golden P E 1965 *J. Chem. Phys.* **43** 4081

[22] Zipf E C and Mclaughlin R W 1978 *Planet Space Sci.* **26** 449

[23] Donald R, Paula E G and Donald D B 1965 *J. Chem. Phys.* **42** 4081

[24] Baldwin G C 1974 *Phys.Rev.* A **9** 1225

[25] Kennerly R E 1980 *Phys. Rev.* A **21** 1876

[26] Cheng X J and Fan X W 1992 *Acta Phys. Sin.* **41** 885 (in Chinese)

[27] Bastien F, Wu J H, Goguillon P and Marode E 1990 *J. Phys. D: Appl. Phys.* **23** 813