Energy spectra of Penning electrons in non-local plasma at middle and high pressures

M Stefanova\textsuperscript{1,3}, P Pramatarov\textsuperscript{4}, A Kudryavtsev\textsuperscript{2} and R Peyeva\textsuperscript{1}

\textsuperscript{1}Acad. G. Nadjakov Institute of Solid State Physics, Bulgarian Academy of Sciences, 72 Tsarigradsko Chaussee, 1784 Sofia, Bulgaria
\textsuperscript{2}St. Petersburg State University, 7-9 Universitetskaya Nab., 199034 St. Petersburg, Russia

E-mail: mstef@issp.bas.bg

\textbf{Abstract.} A recently-developed collisional electron spectroscopy (CES) method enabled us to measure the energy spectra of groups of fast non-local electrons in a collisional mode at high pressures, where no collisional energy relaxation of electrons in the different groups takes place in the volume, and the different groups of electrons behave independently of each other. We recorded the energy spectra of groups of fast electrons created via Penning ionization of Ar and N\textsubscript{2} impurities by metastable He atoms at He pressures of 30 and 200 Torr. The experiments were conducted in the non-local negative glow plasma of a short dc microdischarge. The Penning electrons’ energy spectra were recorded by means of an additional electrode – a sensor located at the boundary of the discharge volume, in contrast with the classical Langmuir probe. The spectra are characterized by the appearance of maxima at characteristic energies corresponding to the energy of the electrons released via Penning reactions. Using the Penning electrons’ energy spectra, one can detect and identify the presence of different atomic and molecular admixtures in He at high pressures.

1. Introduction

The plasma electron spectroscopy (PLES) method, developed in 1994 by Kolokolov et al. [1], represents a new approach to studying elementary plasma processes and atomic constants. It makes use of the relation between the electron energy distribution function (EEDF) and the characteristics of the different elementary processes. On the basis of the PLES method, a new method for identification of gas impurities was proposed by Kudryavtsev [2], whereby gas impurities are identified by recording groups of fast non-local electrons released via Penning ionization of the impurity particles by metastable He atoms. A further development of the PLES method for identifying unknown species in a gas phase was reported in [3]. In [1-3], standard Langmuir probes were used for EEDF measurements in the positive-column afterglow plasma at low pressures (0.5 – 3.5 Torr). The main disadvantages of this method are a low sensitivity due to the small probe size and a large plasma volume due to the low working pressures. Moreover, the measurements in the afterglow plasma require a temporal resolution of the recording system, which further complicates the measurements.

\textsuperscript{3} To whom any correspondence should be addressed.
In this work we used the new collisional electron spectroscopy (CES) method, whose basic principles were presented in [4-6]. The CES method is based on measuring the energy spectra $R(\varepsilon)$ of fast non-local electrons released in Penning ionization of the impurity atoms or molecules by the metastable atoms of the main gas:

$$A^* + B \rightarrow A + B^* + e \{\varepsilon_p\}. \tag{1}$$

The Penning electrons’ energy is $\varepsilon_p = \varepsilon_m - \varepsilon_i$, where $\varepsilon_m$ is the excitation energy of the metastable particles $A^*$ and $\varepsilon_i$ is the ionization energy of the particles $B$. The use of helium as a main gas is convenient, since the metastable He levels have high excitation energies (19.8 eV and 20.6 eV).

The CES method enables one to measure the energy spectra of groups of fast electrons in a collisional mode at high pressures, where the energy relaxation of the electrons in the different groups does not occur by collisions in the volume, and the different groups of electrons behave independently from each other. This has to do with the fact that the electron loses only a small portion $\delta < 10^{-4}$ of its initial kinetic energy $\varepsilon_p$ in one elastic collision with a He atom. As a result, the electron energy relaxation length, $\lambda_e$, exceeds considerably the electron mean free path $\lambda$. In the case of He, the ratio is $\lambda_e / \lambda \approx 70$, and the parameter $\lambda_e p$ is $\approx 5$ cm Torr, where $p$ is the gas pressure of the main gas.

When $\lambda_e$ is greater than the specific plasma length $L$

$$\lambda_e > L, \tag{2}$$

the EEDF is formed in a non-local mode and the electrons move in the restricted plasma volume with conservation of their full energy $\varepsilon = w + e\Phi(r)$ (kinetic plus potential) [7]. If the Penning electrons’ energy is $\varepsilon_p > e\Phi_w$ (where $\Phi_w$ is the potential between the discharge axis and the wall), these electrons reach the wall in a free diffusion. In the absence of an electric field, or when it has a small value (e.g., negative glow plasma, afterglow plasma, where the electron temperature $T_e$, and hence, $e\Phi_w$, are small), the Penning electrons’ energy spectrum exhibits sharp peaks near the $\varepsilon_p$ energies, reproducing the spectrum $R(\varepsilon)$ of reactions of type (1) [1].

The inequality (2) is known as the condition for non-locality. Over the specific plasma length $L$, the EEDF depends weakly on the local plasma parameters and is the same at any point of the plasma. As a result, the non-local plasma has an important feature: by measuring the EEDF at the plasma boundary, one acquires information on the whole plasma volume. In non-local plasma, each group of Penning electrons reaches the plasma boundary with its initial energy and, hence, the EEDF can be recorded by means of an additional electrode – a sensor located at the boundary of the plasma volume. Thus, in contrast to the classical Langmuir probe, a sensor with a large collecting area can be used in order to enhance significantly the sensitivity of Penning electrons measurements.

The negative glow plasma of a short dc microdischarge is the most suitable medium for non-local formation of the EEDF. The important characteristics of the non-local negative glow plasma are: high metastable atom density, high rate of Penning ionization, equipotentiality, small dimensions, stable operation at high pressures, low operating voltage, simple design and simple power supply. Temporal resolution of the recording system is not required, which further simplifies the device.

2. Experimental

The experiments were carried out in the non-local negative glow plasma of a short (without a positive column) dc glow discharge. A schematic view of the discharge device is shown in figure 1. It consists of a plane disk-shaped (4 mm in diameter) cathode and an anode placed at a distance of 1 or 2 mm. A ring-shaped additional electrode, the sensor, is located coaxially between the anode and the cathode. The sensor is made of 0.4-mm molybdenum wire, 4 mm in diameter. It has a large collecting area, comparable to that of the anode. The plasma volume is reduced

![Figure 1. Schematic view of the microplasma discharge device.](image-url)
dramatically; it is about 0.01 cm$^3$, which is more than two orders of magnitude less than the one used in previous works [1-3]. The small size of the plasma volume allows a significant increase in the operating pressures.

The energy spectra of the Penning electrons were obtained by measuring the second derivative of the probe $VA$-characteristic ($d^2I/dV^2$) with respect to the scanning voltage applied, which, according to the Druyvesteyn’s relation, is proportional to the EEDF [8]. The so-called “modulation method” [8] was used. The recording system is typical for the probe measurements [5].

The Penning electrons’ energy spectra were obtained in He as the main gas with small admixtures of Ar and N$_2$. The total gas pressure ranged from 30 Torr to 200 Torr, with the discharge current being varied from 0.5 mA to 12 mA.

2. Results and discussion

A typical shape of the sensor’s $VA$-characteristic is shown in figure 2. It should be noted that, despite the high pressure (200 Torr), the essential parts of a Langmuir probe characteristic are well seen. The second derivative of the sensor current with respect to the scanning voltage applied, i.e. the EEDF, was obtained in the voltage range $-20$ V $- 5$V.

The energy spectra of the Penning electrons recorded at high pressures of the main gas are similar to those obtained in our earlier papers [5, 6] at intermediate pressures. Maxima appear in the EEDF at characteristic energies corresponding to Penning ionization of Ar or N$_2$ admixtures by metastable He atoms.

The electron energy spectrum measured when a small amount (0.2 %) of Ar is added to 200 Torr He is illustrated in figure 3. Two well-expressed characteristic Ar maxima are seen at about 4 eV and 4.8 eV. The slow part of the EEDF (reduced 50 times) is shown in figure 3 as well. The fine structure of the Ar maximum is the result of the existence of two metastable He atom states (triplet He($2^3S_1$) and singlet He($2^1S_0$)), having an energy difference of 0.79 eV. Fast electrons with energies of 4 eV and 4.8 eV are released in Penning reactions of Ar atoms with triplet and singlet metastable He atoms (reactions (3) and (4)), which form the two Ar peaks in the electron energy spectrum:

$$\text{He}(2^3S_1) + Ar(0) \rightarrow \text{He}(0) + Ar^+ (2P_{3/2}) + e \ (4.06 \text{ eV}),$$

$$\text{He}(2^1S_0) + Ar(0) \rightarrow \text{He}(0) + Ar^+ (2P_{3/2}) + e \ (4.85 \text{ eV}).$$

The Ar peaks in figure 3 have comparable amplitudes. As the cross sections for Penning ionization of Ar with singlet and triplet metastable He atoms ($16.4 \times 10^{-16}$ cm$^2$ and $5.3 \times 10^{-16}$ cm$^2$, respectively [9]), differ by about a factor of three, one can conclude that, at the particular discharge conditions, the density of singlet metastable He atoms is about three times as low as the density of triplet metastable He atoms.

The characteristic Ar maxima were easily obtained due to the large sensor surface.

Thus, the measured energy, $\epsilon_p$, at which the recorded Ar maxima appear in the EEDF allows one to detect and identify the presence of Ar atoms in the plasma at high pressures.

Except Penning reactions, fast electrons are produced by supper-elastic collisions of slow electrons with triplet...
and singlet metastable He atoms, which in non-local plasma form maxima in the EEDF as well. The peak at about 20 eV in figure 3 corresponds to electrons arising from such processes:

\[ \text{He}(2^3S_1) + e \rightarrow \text{He} + e \{19.82 \text{ eV}\} \]
\[ \text{He}(2^1S_0) + e \rightarrow \text{He} + e \{20.61 \text{ eV}\}. \]

At high He pressures, it can be observed at currents exceeding 10 mA only. This peak can be used for absolute calibration of the energy scale and for determination of the metastable He atoms density.

The Penning electron energy spectrum obtained in 200-Torr pure He is shown in figure 4. A maximum appears at about 4.2 eV due to a Penning reaction between N\(_2\) molecules present in the plasma as residual air impurities and triplet metastable He atoms leading to the formation of molecular nitrogen ions in ground state \[1, 5, 6\]:

\[ \text{He}(2^3S_1) + \text{N}_2(0) \rightarrow \text{He}(0) + \text{N}_2^+(X^2\Sigma) + e \{4.2 \text{ eV}\}. \]

The characteristic He maximum at about 20 eV (reactions (5) and (6)) is seen in figure 4 as well. It is weak and appears only at discharge currents over 8 mA.

The characteristic N\(_2\) maximum recorded in pure He illustrates the capability of the CES method to identify the presence of very low densities of N\(_2\) impurities by measuring the Penning electron energy spectrum.

Figures 5 illustrates the Penning electron energy spectra at 34 Torr He with admixture of 1 % N\(_2\). Well-expressed characteristic N\(_2\) maxima at 1.8 eV (figure 5a) and at 4.2 eV (figure 5b) are observed. The N\(_2\) maxima correspond to Penning reactions of N\(_2\) molecules with triplet and singlet metastable He atoms (reactions (7) and (8), respectively):

\[ \text{He}(2^1S_0) + \text{N}_2(0) \rightarrow \text{He}(0) + \text{N}_2^+(B^2\Sigma) + e \{1.8 \text{ eV}\}. \]

The maximum at 1.8 eV is superimposed over the steep rise of the tail of the bulk electrons distribution. It appears at a low discharge current (1 mA) and low modulating voltages. The peak at 4.2 eV is well expressed at discharge currents above 2 mA, while the peak at 1.8 eV is immersed in the slow part of the EEDF at this current. The rate constant for reaction (8) with singlet metastable He
atoms is about twice as high as than that for reaction (7) with triplet metastable He atoms [1], while the density of singlet metastable He atoms is lower than that of the triplet metastable He atoms.

4. Conclusions
The recorded energy spectra of Penning electrons at He pressures of 30 and 200 Torr, illustrated above, are characterized by the appearance of maxima at characteristic energies corresponding to the energy of the electrons released in Penning reactions involving Ar and N₂ impurities. Well-expressed maxima in the electron energy spectra are easily obtained as a result of the high number of Penning electrons collected by the large sensor surface. The non-local negative glow plasma of a short dc microdischarge is a suitable medium for recording electron energy spectra and for detection and identification of gas impurities.

To the best of our knowledge, no observation has so far been reported of maxima in the EEDF at high pressures due to electrons produced in Penning reactions of metastable He atoms with impurity atoms or molecules.

The maxima observed in the EEDF demonstrate the possibility to detect and identify the presence of different atomic and molecular admixtures in He at high pressures.

Acknowledgments
The authors wish to thank Mrs. Ts. Rankova for the preparation of the microplasma discharge device.

References
[1] Kolokolov N B, Kudryavtsev A A and Blagoev A B 1994 Physica Scripta 50 371
[2] Kudryavtsev A A 1999 Int. Workshop Results of Fundamental Res. for Investment; Russian Technol. for Industrial Appl. (May 1999 St. Petersburg Russia) Abstract Book p 94
[3] Sheverev V A, Khromov N A and Kojiro D R 2002 Anal. Chem. 74 5556
[4] Kudryavtsev A A and Tsyganov A B 2007 US Patent 7309992; Kudryavtsev A A, Tsyganov A B and Chirtsov A S 2011 Patent of Russian Federation 2422812 (in Russian)
[5] Kudryavtsev A, Pramatarov P, Stefanova M and Khromov N J Instrumentation IOP 2012 7 PO7002
[6] Kudryavtsev A A, Pramatarova M, Pramatarov P, Khromov N, Peyeva R and Patrikov T 2012 Contributed Papers 7th Int. Conf. Plasma Phys. Plasma Technol. vol 2 pp 628–31 (Sept. 2012 Minsk Belarus)
[7] Tsendin L D 1995 Plasma Sources Sci. Technol. 4 200
[8] Godyak V A and Demidov V I 2011 J. Phys. D: Appl. Phys. 44 233001
[9] Schmeltekopf A L and Fesefeld F C 1970 J. Chem. Phys. 53 3173