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Collisional electron spectroscopy method for gas analysis

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Abstract. Recently developed collisional electron spectroscopy (CES) method, based on identification of gas impurities by registration of groups of nonlocal fast electrons released by Penning ionization of the impurity particles by helium metastable atoms, is verified experimentally. Detection and identification of atoms and molecules of gas impurities in helium at pressures of 14 - 90 Torr with small admixtures of Ar, Kr, CO2, and N2 are carried out. The nonlocal negative glow plasma of short dc microdischarge is used as most suitable medium. Records of the energy spectra of penning electrons are performed by means of an additional electrode - sensor, located at the boundary of the discharge volume. Maxima appear in the electron energy spectra at the characteristic energies corresponding to Penning ionization of the impurity particles by helium metastable atoms.

1. Introduction

The plasma electron spectroscopy (PLES) method, developed by Kolokolov *at al.* [1] represents a new approach for studies of elementary plasma processes and atomic constants. On the base of the PLES method a new method for identification of gas impurities is proposed by Kudryavtsev [2]. It is based on identification of gas impurities by registration of groups of nonlocal fast electrons, released in reaction of Penning ionization of the impurity particles by helium metastable atoms. Further development of PLES method for identification of unknown species in a gas phase is reported in [3]. In [1-3] the nonlocal afterglow plasma of positive column at low pressures (0.5 – 3.5 Torr) is used, and temporal resolution of the registration system is applied, which complicates the devices.

In this paper the new method of collisional electron spectroscopy (CES), whose basic principles are patented by Kudryavtsev *at al.* [4] is experimentally veryfied. The CES method is based on measurements of energy spectra $R(\varepsilon)$ of fast electrons released in Penning ionization of the impurities atoms or molecules by metastable atoms of the main gas:

$$A^* + B \rightarrow A + B^+ + e\{\varepsilon_p\} \qquad (1)$$

The energy of penning electrons is $\varepsilon_p = \varepsilon_m - \varepsilon_i$, where, ε_m is the excitation energy of metastable particles A^* and ε_i is the ionization energy of particles B. When EEDF is formed in nonlocal regime [5], i.e. electron energy relaxation length λ_ε is greater than the characteristic discharge dimension L, $\lambda_\varepsilon > L$, the electrons move in discharge volume with conservation of their full energy $\varepsilon = w + e\varphi(r)$ (kinetic plus potential). If the energy of penning electrons is $\varepsilon_p > \Phi_w$ (where Φ_w is the potential between axis and discharge wall), these electrons reach the wall in a free diffusion. In the absence of electric field or when it has a small value (e.g., negative glow plasma, beam plasma), where T_e, and hence $e\Phi_w$ are small, the energy spectrum of penning electrons represent sharp peaks near energies ε_p, reproducing the spectrum $R(\varepsilon)$ of reactions of type (1) [1-3]. Using the measured penning electrons spectra $R(\varepsilon)$ and the well known rate constants for Penning reactions one can identify the impurities and determine their concentrations. The CES method enables identification of gas impurities in a main gas in collisional regime of movement of the particles, where the different groups of electrons do not relax in energy by collisions in the volume and behave independently of each other. This opportunity is associated with the fact that in one elastic collision with a helium atom, the electron loses only a small portion δ of its initial kinetic energy ε_p, $\delta < 10^{-4}$. As a result the electron energy relaxation length λ_ε , considerably exceeds its mean free path λ. In particular for helium,$\lambda_\varepsilon /\lambda \approx 70$, and the parameter $\lambda_\varepsilon p$ has value: $\lambda_\varepsilon p = 3 \div 5$ *cm.Torr,* where p is the gas pressure.

It is convenient to use helium metastable atoms as A^* particles in (1), because their high excitation energy (19.8 *eV, 20.6 eV*) is sufficient to ionize any other atom or molecule (except neon) and to produce characteristic electrons having kinetic energy of several *eV*.

Since, in nonlocal plasma, each group of penning electrons reaches the plasma boundary with its initial energy, the registration of the EEDF is possible by means of an additional electrode - sensor, located at the boundary of the discharge volume. Thus, it is possible to use a large collecting area of the sensor and to enhance significantly the sensitivity of fast electrons registration.

Over the characteristic length L, the EEDF does not depend essentially on the local plasma parameters and it is the same at any point of the plasma. As a result, the nonlocal plasma has an important property: measuring the EEDF at plasma boundary, we get information from the whole plasma volume.

In this paper a new design of microplasma gas analyzer is proposed and experiments are carried out to detect and identify gas admixtures in helium.

2. Experiment

The design of microplasma gas analyzer used to demonstrate the practical realization of the CES method for gas analysis is shown in figure 1. The negative glow plasma of a short dc microdischarge is employed as most suitable medium for nonlocal formation of the EEDF and for creation of a compact gas analyzer. It consists of plane, disk-shaped (4 mm in diameter) cathode and anode, disposed at 1.7 and 4 mm distance. A ring-shaped additional electrode - sensor is placed coaxially between anode and cathode. It is used to collect the electrons under investigation and to record its VA-characteristics. The sensor is made of 0.4 mm molybdenum wire and has 4 mm diameter. The sensor has large collecting area compared to the classical Langmuir probe – it is comparable to that of the anode. The plasma volume is reduced dramatically; it is about 0.02 - 0.05 cm^3, which is more than two orders of magnitude less, compared to the previous works [1-3]. The small size of the plasma volume permits a significant increase in the operating pressures. Experiments are carried out in the negative glow plasma of a short (without a positive column) dc glow discharge. The gap between the cathode and the anode is chosen in such a manner to fulfill the condition for nonlocal formation of the EEDF at the pressures used in this work.

Records of electron energy spectra are carried out in helium with small admixtures of known gas impurities - argon, krypton, carbon dioxide and nitrogen. The total gas pressure is ranged from 14 to 90 Torr and the discharge current is varied from 0.5 to 5 mA. The identification of atoms and molecules of the impurities is performed by registration of the second derivative of the probe VAcharacteristic d^2I/dV^2, which, according to the Druyvesteyn relation [1], is proportional to the EEDF, i.e. to the energy spectra of penning electrons.

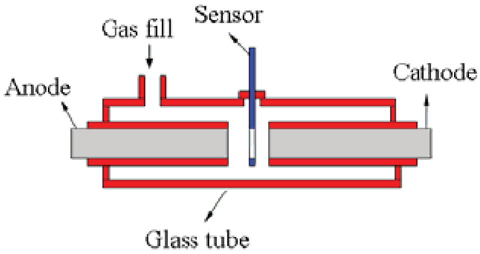

Figure 1. Schematic view of the microplasma gas analyzer.

The "modulation method" [1] is chosen to obtain the second derivative of the sensor current on the applied scanning voltage. Modulating signal of the type $\Delta V = V_0 \cos \omega t$ is used. For that purpose sinusoidal voltage of amplitude $2V_0 = 0.2$ - 1.2V (peak to peak) and frequency ω = 1362 Hz is mixed with the retarding sensor voltage. Registration system, conventional for probe measurements, is used.

3. Results and discussion

Typical electron energy spectra in helium-krypton gas mixture at two values of the modulation voltage are shown in figure 2 and figure 3. Well expressed maxima are seen. According to equation (1) the maxima recorded in the second derivative are due to electrons released in Penning ionization of krypton atoms by helium metastable atoms. At 1.2 V modulating voltage the characteristic krypton maximum appears at about 6.2 eV (figure 2), while at 0.5 V modulating voltage the characteristic krypton maximum has fine structure (figure 3). Maxima at 5.1 eV, 5.8 eV and 6.6 eV are resolved. The fine structure of the krypton maximum is due to the Penning reactions of triplet $He(2\ ^3S_1)$ and singlet $He(2\ ^1S_0)$ helium metastable atoms with krypton atoms producing krypton ions in two ground states $Kr^+(^2P_{3/2})$ and $Kr^+(^2P_{1/2})$, having energy difference of 0,67 eV. The fine structure components have comparable values. Cross section for Penning ionization of Kr with singlet helium metastable atoms $He(2\ ^1S_0)$ is $28.2.10^{-16}$ cm^2 while for triplet helium metastable atoms $He(2^3S_1)$ it is $7.7.10^{-16}$ cm^2 [6]. Therefore one can conclude for the presence of high enough density of helium singlet metastable atoms in the plasma volume. Besides the krypton maximum at 5.8 eV, another maximum at 19.8 eV is recorded (figure 2). This maximum corresponds to the electrons released in reaction of deactivation of helium metastable atoms $He(2^3S_1)$ by super-elastic collisions with slow electrons. The maximum at 1.8 eV in figure 3 is associated to the presence of residual nitrogen traces in the discharge chamber.

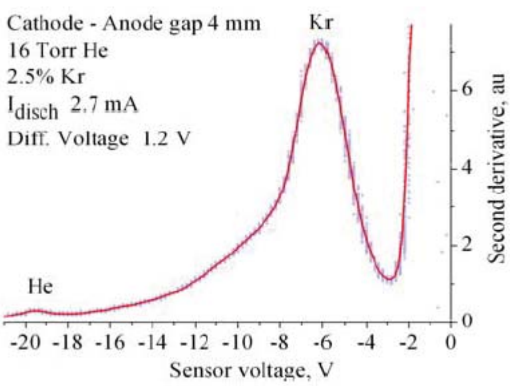

Figure 2. Electron energy spectra in He-Kr mixture.

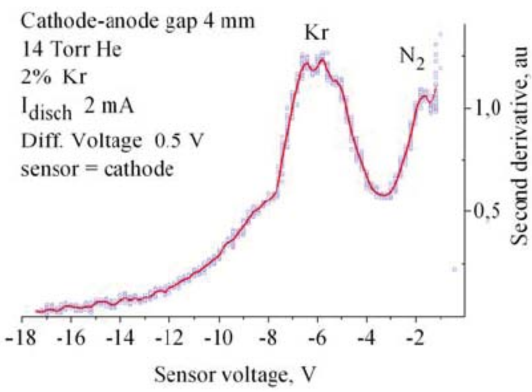

Figure 3. Fine structure of the electron energy spectra in He-Kr mixture.

Hence, the measured energy at the maximum in the EEDF allows to identify the presence of krypton atoms in the plasma.

The electron energy spectrum, when a small portion of argon (1%) is added to 90 Torr helium, is shown in figure 4. Well expressed maximum is seen at 4.1 eV. The characteristic argon maximum is easily obtained at low discharge currents – 2 mA. The argon maximum is due to the Penning reactions of triplet helium metastable atoms with argon atoms.

Figure 5 demonstrates the electron energy spectrum in mixture of 15 Torr helium pressure, 3.3% carbon dioxide and 0.5% nitrogen. Two peaks at 6.8 eV and 4.3 eV are recorded, representing penning electrons released according to reactions of carbon dioxide and nitrogen with singlet and triplet helium metastable atoms:

$$He(2^1S_0) + CO_2(0) \rightarrow He(0) + CO_2^+(X^2\Pi g) + e\ (6{,}81\ eV)$$

$$\mathrm{He}(2^3\mathrm{S}_1) + \mathrm{N}_2(0) \rightarrow \mathrm{He}(0) + \mathrm{N}_2^+(^2\Sigma^+) + \mathrm{e}\ (4{,}24\ \mathrm{eV})$$

It should be noted that the cross section for Penning ionization of CO_2 by $He(2^1S_0)$ is $84.6.10^{-16}$ cm^2, while the cross section of Penning ionization of nitrogen by $He(2^3S_1)$ is $5.2.10^{-16}$ cm^2 [6]. This explains the difference in the measured amplitudes of the two peaks.

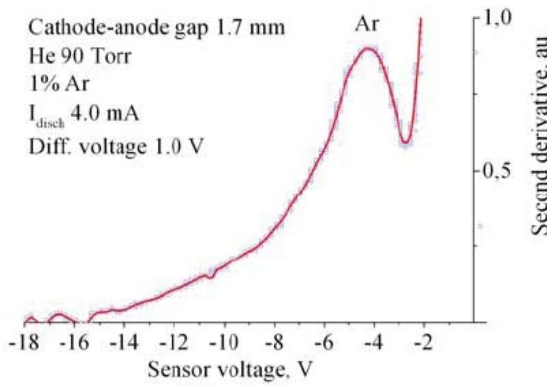

Figure 3. Electron energy spectra in He-Ar mixture.

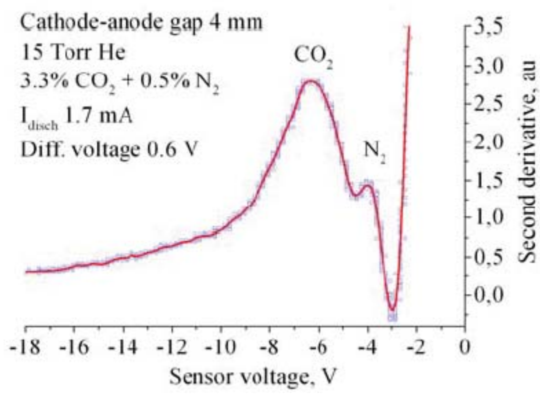

Figure 4. Electron energy spectra in He-CO_2-N_2 mixture.

The recorded maxima in the EEDF demonstrate the possibility to identify the presence of different atomic and molecular admixtures in helium in nonlocal negative glow plasma of a short dc microdischarge at high pressures.

The large sensor surface area collects sufficient number of penning electrons and well expressed maxima in the electron energy spectra are easily obtained at high pressures and low discharge currents. This contributes to significant enhancement in the measurements sensitivity. Temporal resolution of the registration system is not required, which further simplifies the device.

To our knowledge, measurements of maxima in the EEDF at high pressures (14 – 90 Torr) due to electrons produced in Penning reactions of helium metastable atoms with impurity atoms or molecules are not made till now.

4. Conclusions

The CES method gives the opportunity to develop a compact microplasma gas analyser simple in technical performance, whose dimensions are dramatically reduced compared to the traditional methods for gas analysis. All these advantages make it attractive for practical applications.

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