Electron-Beam Activation of Rarefied Gases

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Abstract. The energy and spatial distribution function of primary and high-energy secondary electrons is studied on the basis of Boltzmann equation. Highly anisotropic distribution function of primary electrons is considered in a small angle scattering approximation with the energy losses in inelastic collisions. The distribution function of almost isotropic secondary electrons is studied on the basis of integral Boltzmann equation. The Green function for secondary electrons $G(|\vec{r}-\vec{r}\,'|, e)$ is obtained, which permits one to obtain the distribution function of high-energy secondary electrons.

Keywords: Electron beams, energy degradation, secondary electrons, Boltzmann equation, argon.
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1. INTRODUCTION

Electron beams with energy E_b~1-100 keV are widely used for gas activation in plasma chemistry, for creation of laser active media for electro-ionized lasers, cleaning of smoke fumes, for production of plasma in E-beam sustained discharges, and for electron-beam diagnostics in rarefied gases. In recent decades, E-beams have been used for plasma-chemistry applications, e.g. for thin film deposition with the help of E-beam assisted CVD method [1-3].

In this paper it is shown that for plasma-chemistry applications the use of electron beams with relatively low initial energies in the range of 100-1000 eV is preferable. A comprehensive description of E-beam generated plasma should include the consideration of energy degradation and scattering of primary beam electrons, production and degradation of secondary electrons, formation of exited atoms, molecules, and ions. High-energy secondary electrons produced in gas ionization by electron beams play an important role in gas ionization, dissociation, excitation of electronic, vibration and rotation states of molecules. Rate constants of these processes can be much higher than the rate constants caused by high energy primary electrons due to specific energy dependence of cross sections of electron molecule collisions.

In recent decades, calculations of the degradation spectrum of electrons have been made by several authors, for example, see [4]. Spatial-dependent aspects of electron degradation were considered with the help of the Monte Carlo simulation method [5]. However, the disadvantage of the Monte Carlo method is that it requires large amounts of computer time, and simulation results can be communicated only as a great quantity of numerical data. Numerical results given in such forms are not very useful in establishing the general principles of E-beam activation of gases.

In this paper, a theoretical consideration of electron-beam degradation, spreading, and secondary electron production around the primary low-current electron beams (J_b~1-100 mA) is given for low and moderate gas pressures in the range 10^{-2} – 10 Torr on the basis of the Boltzmann equations for primary and high-energy secondary electrons. The numerical calculations have been made for pure argon.

2. DISTRIBUTION FUNCTION OF PRIMARY ELECTRONS

Rate constants of molecule excitation, ionization, dissociation, and formation of secondary electrons in a gas are the functions of energy and spatial distribution of primary beam electrons. Energy losses and scattering of primary electrons of low-current E-beam in a gas should be considered on the basis of the Boltzmann equation. This equation is rather complex and its simplification is connected with the analysis of differential cross sections for high energy electrons, which experience small angles scatterings (forward scattering) in collisions with gas atoms. We split the problem into two separate problems: energy losses with zero-angle scattering, and spreading of electron beam in small-angle scattering approximation (for mean electron energy depending on the length of penetration into gas).

2.1. Energy Degradation of Primary Electrons

We consider a cylindrical electron beam moving initially in z-direction in the gas with density $N_g=const$. Let us introduce the distribution function for primary electrons $\bar{f}_b(z,e) \approx \left\langle f_b(z,r,e,\vec{\Omega}) \right\rangle_r d(\vec{\Omega}-\vec{\Omega}_0)$, averaged over the beam radial profile χ_0(r) and normalized as follows

$$\sqrt{E_0}\int_0^{E_0}\frac{de}{\sqrt{e}}\bar{f}_b(z,e)=n_b(z)/n_b(0), \tag{1}$$

where E_0 is the initial energy of primary electrons at z=0. The normalization (1) is convenient for mono-directional beam of primary electrons. The electron flux, J_n, and the mean energy, $\bar{E}(z)$, then will be read as

$$J_n(z)=\sqrt{E_0}\int_0^{E_0}de\bar{f}_b(z,e)=const \qquad n_b(z)\bar{E}(z)=\sqrt{E_0}\int_0^{E_0}de\sqrt{e}\bar{f}_b(z,e), \tag{2}$$

where $n_b(z)$ is beam density at the length of penetration z averaged over the radial distribution. The energy losses for primary beam electrons can be considered in one-dimensional approach for the highly anisotropic distribution function of primary electrons depending on the length of penetration z. In a small angle scattering approximation, the distribution function satisfies the Boltzmann equation:

$$\begin{aligned}\frac{\partial\bar{f}_b(z,e)}{\partial z} &= N_g\sum_j\left[s_j(e+e_j)\bar{f}_b(z,e+e_j)-s_j(e)\bar{f}_b(z,e)\right]- \\ &-\int_0^{(e-I)/2}des_i(e)q(e,e)\bar{f}_b(z,e)+\int_0^{e}des_i(e+I+e)q(e+I+e,e)\bar{f}_b(z,e+I+e),\end{aligned} \tag{3}$$

where $\sigma_j(e)$ is cross section for excitation of j[th] atomic level by an electron impact, ε_j is the excitation threshold (energy loss) in this process, $\sigma_i(e)$ is the cross section of ionization by electron with energy e, I is the ionization potential of atoms. Cross sections for energy excitation of argon were taken from [7]. $q(E,e)$ is the spectrum of generation of secondary electrons with energy ε in the ionization of atoms by primary electron with energy E [8],

$$q(e,e)\approx\left[\bar{e}arctg((e-I)/2\bar{e})\right]^{-1}\left(1+e^2/\bar{e}^2\right)^{-1}, \qquad \int_0^{(E-I)/2}q(E,e)de=1. \tag{4}$$

where $\bar{e}\approx 0.8I$, (for argon, $\bar{e}(Ar)\approx 12.5$ eV).

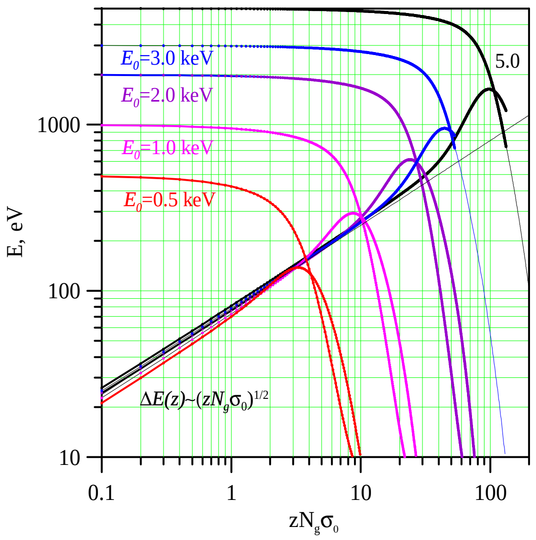
The first two terms in the right side of equation (3) present discreet energy losses by primary electrons in excitation of electronic states of molecule, the third term presents continuous energy losses in ionizing collisions with the production of secondary electron, and the last term describes the primary electrons, which get into the energy interval de after molecule ionization with the generation of secondary electron of energy ε distributed according to the spectrum $q(e+I+\varepsilon,\varepsilon)$.

In Fig. 1, the mean energy, $\bar{E}(z)$, and the root-mean-square energy $\Delta E=\sqrt{\overline{E^2}-\bar{E}^2}$ are presented for initial beam energy E_0 depending on the non-dimensional penetration length $zN_g\sigma_0$ ($\sigma_0=10^{-16}$ cm^{-2}). It is seen that for small $\bar{z}=zN_g\sigma_0<Z_c(E_0)$ the root-mean-square energy ΔE depends linearly on $\bar{z}^{0.5}$, and $\Delta E \ll \bar{E}(z)$. Thus, the energy width of electron distribution in the beam is much narrower than the mean energy. However, for $\bar{z}>Z_c(E_0)$, the root-mean-square energy ΔE departs from linear dependence on $\bar{z}^{0.5}$. The mean energy $\bar{E}(z)$ decreases more rapidly, and, for some $z_c N_g\sigma_0=Z_c(E_0)$, $\Delta E(Z_c)$ becomes equal to the mean energy $\bar{E}(z)$.

For argon, the value $Z_c(E_0)$, can be approximated for $E_0>0.15$ keV by the expression

$$Z_c(E_0)=z_cN_gs_0\approx(2.25+100(E_0/1keV)^3)^{1/2}. \tag{5}$$

This is the condition of electron beam “collapse”. Somewhat before this point, a noticeable part of “primary” electrons achieves a low energy region (e.g., energy lower than 100 eV) where they do not differ from high energy secondary electrons, see, Fig.2 (for E_0=1 keV). For this condition, the radial-angle distribution of beam electrons becomes very wide, the beam is spread intensively in space, and transforms into an electron cloud (plasma).



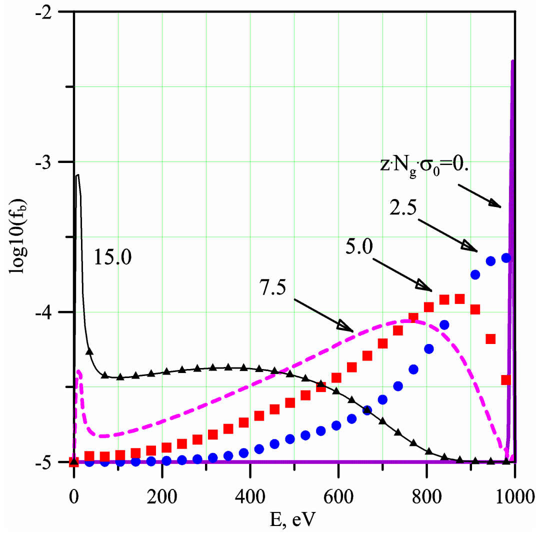


FIGURE 1. Mean energies $\overline{E}(z)$ of primary beam electrons, and root-mean-square energies ΔE for different initial energy of E-beam electrons that passed the distance $zN_g\sigma_0$ in argon.
FIGURE 2. Energy distribution function of primary electrons $f_b(E,z)$ for different distances $zN_g\sigma_0$ in argon.

2.2. Radial Spreading of Electron-Beam

The radial and angle distribution of electrons in the beam can be evaluated from the exact Boltzmann equation in a small angle scattering approximation and based on the assumption that electrons at the distance z have mean energy $\overline{E}(z)$. Here we use the analytical results obtained in [6]. Differential cross sections for electrons have rather complex angle dependence with maximums and minimums. However, for the energy range from 100 eV to 10^4 eV, small-angle scatterings become dominant. Bromberg [7] has shown that for a number of gases in this energy region, the differential cross section, total cross section, and the root-mean-square angle can be presented in the form

$$\sigma(E,\theta)=\sigma^0(E)\exp(-\xi\sqrt{E}\theta),\qquad \sigma_t(E)=2\pi\sigma^0(E)/\xi^2E,\qquad \langle\theta^2\rangle=6/\xi^2E, \tag{6}$$

where σ^0 and ξ are some constants. Bromberg connects σ^0 and ξ with parameters of a long-range polarization potential of electron-atom (molecule) interaction ($\xi\approx0.5$ for Ar). Cross sections in the form (6) offer one considerable convenience and were used below for the evaluation of electron beam spreading [6].

Radial distribution of electrons in the beam passing the distance z in gas can be presented in the form

$$n_b(r,z)=n_b(0)\int_0^\infty d\nu\,\nu J_0(\nu r/b)w_0(\nu)\exp(-B(z,\nu)),\qquad w_0(\nu)=\int_0^\infty da\,aJ_0(\nu a/b)\chi_0(a/b)/b^2 \tag{7}$$

where $\omega_0(\nu)$ is the Bessel transformation of initial electron-beam radial profile, $\chi_0(a/b)$, b is the characteristic radius of electron beam at z=0, and the function

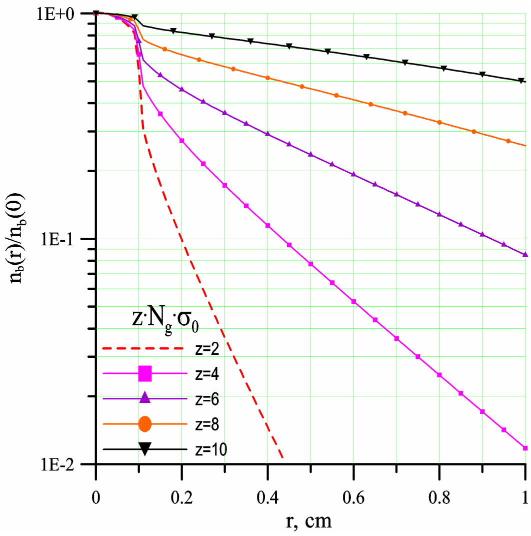
$$B(z,\nu)=\int_0^z dz'\sigma_t(E')N_g(z')\left\{1-\left[1+(z-z')^2\nu^2/b^2\xi^2E(z')\right]^{-3/2}\right\} \tag{8}$$

contains information about electrons scattering on the path from z=0 to z.

In Fig. 3, the normalized radial distribution of electron beam density $n_b(r,z)/n_b(0,z)$ calculated according to (7-8) (for initial energy E_0=1 keV and b=0.1 cm) depending on penetration length z is presented. It is seen that exponential wings in the distribution for $r>b$ appear for small z, and $n_b(r=b,z)/n_b(0,z)<1$. For some value of z, the density in wings reaches the value of density on the beam axis. For larger penetration length z, $\sigma_t(E)N_gz\geq1$, the radial distribution becomes Gaussian one with mean-square radius:

$$\langle r^2\rangle=\left(b^2+N_g\sigma_t\langle\theta^2\rangle z^3/3\right). \tag{9}$$

Spreading of the beam becomes noticeable in the range of penetration $zN_g\sigma_0>Z_c$ where the mean electron energy becomes lower than 100 eV, i.e. in the range of "complete" energy degradation of beam electrons. For large distances, the mean width of a beam becomes proportional to the square root of gas density and to the power 3/2 of penetration depth. The angle distribution of the electron flux can be also obtained from Boltzmann equation. For $N_g s_t(\bar{E})z \geq 1$, it becomes the Gaussian one, with the root-mean-square angle equal to $<\Theta^2>=N_g\sigma_t(E)z<\theta^2>$, where $<\theta^2>$ is the root-mean-square angle for a single collision according to (6). This formula is equivalent to the Molière expression, in which the exponential cross section is used instead the Rutherford cross section.



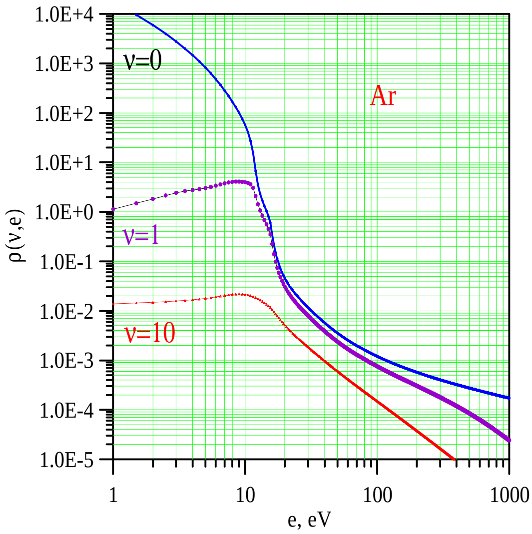


FIGURE 3. The radial distribution of normalized E-beam density for different penetration length, z. Initial energy E_0=1 keV; initial radius of E-beam is b=0.1 cm.

FIGURE 4. Dependence of the function $r(n,e)$ for secondary electrons on energy for ν=0, 1, and 10.

3. INTEGRAL BOLTZMANN EQUATION FOR SECONDARY ELECTRONS

For determination of EDF for secondary electrons spatial dependence in steady state conditions, it is necessary to solve the Boltzmann equation for electron distribution function with a source term describing secondary electrons generated in a gas by a primary electron beam. We will assume for simplicity that all collisions are isotropic, with cross sections equal to momentum cross sections. The integral Boltzmann equation for isotropic part of distribution function $f_s(\vec{r},e)$ of secondary electrons can be written in the form [6]:

$$f_s(\vec{r},e) = a\int \frac{d^3\vec{r}'}{4p}\frac{\exp(-s_t(e)a\,|\vec{r}-\vec{r}'|)}{|\vec{r}-\vec{r}'|^2}\Big\{c(\vec{r}')q(E_b,e)+s_{el}(e)f_s(\vec{r}',e)+ \\ +\sum_j s_j(e+e_j)f_s(\vec{r}',e+e_j)+\int_{e+I}^{2e+I} q(e,e-e-I)s_i(e)f_s(\vec{r}',e)de+\int_{2e+I}^{(E_b-I)/2} q(e,e)s_i(e)f_s(\vec{r}',e)de\Big\}, \qquad (10)$$

where $c(\vec{r}) = n_b(\vec{r})/n_b(0)$ is the dimensionless function of primary electron beam profile, $n_b(0)$ is a characteristic number density of primary electrons on the beam axis (axis "OZ"), $\alpha=N_g b\sigma_0$, b is the characteristic radius of electron beam. The integral Boltzmann equation (10) for secondary electron generated in an electron beam has a sufficient clear meaning: the first term in figure brackets describes the generation of secondary electrons in point $\vec{r}'$ under gas ionization by a primary electron beam; the next two terms describe elastic and inelastic isotropic collisions of secondary electrons with the energy $e+e_j$ in point $\vec{r}'$ after which the electron obtains energy *e*; the last two terms describe continuous energy loss of secondary electron in molecule ionization, and generation of the tertiary electron with energy *e* in ionization by secondary electron. The factor before brackets reflects the flying away of the secondary electrons from the point of generation or the point of last collision $\vec{r}'$ to the point $\vec{r}$. Finally, integration over the whole space collects all contributions in the point $\vec{r}$. The distribution function of secondary electrons in (10) is normalized as follows

$$s_i(E_b)\sqrt{E_b}\int_e^{E_m} f_s(\vec{r},e)/\sqrt{e}de = n_e(\vec{r})/n_b\,. \qquad (11)$$

Then the excitation rate of j-th molecular state will be equal to

$$F_j^s(\vec r) = F_i^p(0)\int_{\varepsilon_j}^{E_m} f(\vec r,\varepsilon)\sigma_j(\varepsilon)d\varepsilon,$$

where $F_i^p(0) = N_g n_b(0) v_b \sigma_i(E_b)$ is the ionization rate by the primary electrons on beam axis.

With the help of Fourier-Bessel transformation of the spatial distribution function, $f_s(\vec r,\varepsilon)$ can be presented in the form:

$$f_s(\vec r,\varepsilon) = \int \frac{d^3\vec r'}{4\pi}\chi(\vec r')G(|\vec r-\vec r'|,\varepsilon), \qquad G(|\vec r-\vec r'|,\varepsilon) = \frac{2}{\pi}\int_{-\infty}^{\infty} d\nu\nu\frac{\sin[\nu|\vec r-\vec r'|]}{|\vec r-\vec r'|}\rho(\nu,\varepsilon), \tag{12}$$

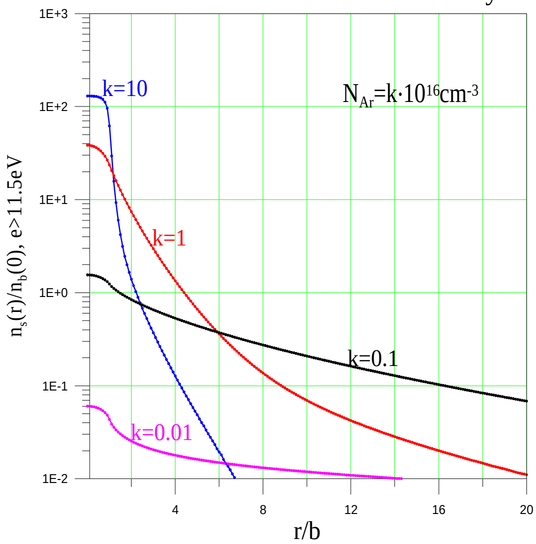
where $G(|\vec r-\vec r'|,\varepsilon)$ is the Green's function of the initial Boltzmann equation.

The function $\rho(\nu,\varepsilon)$ is the Fourier-Bessel image or a "spectral function" of the distribution function $f(\vec r,\varepsilon)$ and must be determined from the equation

$$\sigma_t(\varepsilon)\rho(\nu,\varepsilon) = A(\nu,\varepsilon)\cdot\Big\{q(E_b,\varepsilon)+\sigma_m(\varepsilon)\rho(\nu,\varepsilon)+\sum_j \sigma_j(\varepsilon+\Delta\varepsilon_j)\rho(\nu,\varepsilon+\Delta\varepsilon_j)+$$

$$+\int_{\varepsilon+I}^{2\varepsilon+I} q(\varepsilon,\varepsilon-\varepsilon-I)\sigma_i(\varepsilon)\rho(\nu,\varepsilon)d\varepsilon+\int_{2\varepsilon+I}^{(E_b-I)/2} q(\varepsilon,\varepsilon)\sigma_i(\varepsilon)\rho(\nu,\varepsilon)d\varepsilon\Big\}, \quad A(\nu,\varepsilon)=\frac{\alpha\sigma_t(\varepsilon)}{\nu}\mathrm{arctg}\frac{\nu}{\alpha\sigma_t(\varepsilon)} \tag{13}$$

The expression (12) with the Green's function represents "exact" solution of the Boltzmann integral equation (10) for an arbitrary spatial secondary electrons source of generation. Thus, *ρ(ν,ε)* is universal function for the given kind of gas, which does not depend neither on gas density nor source spatial distribution, and for a given electron-molecule collision cross sections can be easily calculated numerically.



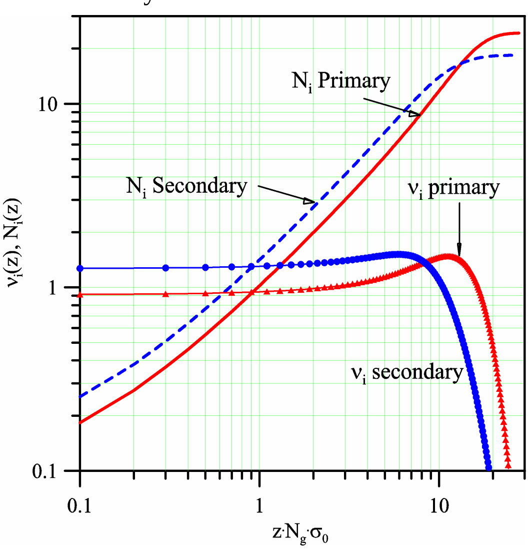


FIGURE 5. Radial distribution of density of secondary electrons with energy e>11.5 eV produced in argon by E-beam (E_0=1 keV; b=0.1 cm) at different argon densities N_{Ar}=k·10^{16}cm^{-3} (k=10, 1, 0.1, 0.01).

FIGURE 6. The yield of electron-ion pairs creation and ionization rates for primary and secondary electrons (arbitrary units), depending on penetration length. Initial E-beam energy is E_0=1 keV.

In Fig.4, the dependence of *ρ(ν,ε)* on the energy of secondary electrons calculated for argon is presented. In Fig.5, the radial dependence of secondary electrons densities with energy higher than 11.55 eV is given for different argon densities. It is seen that for relatively narrow beams under low density conditions secondary electrons formed a wide halo around an electron beam, and E-beam plasma occupies a much wide region than a primary beam. While gas density is increasing, the spatial profile of high energy secondary electrons is approaching the profile of E-beam. In Fig.6, the yields of electron-ion pairs created by an E-beam that passed the length z and by secondary electrons are presented for initial energy E_0=1 keV. It is seen that at small z ionization is mainly produced by secondary electrons because they have higher cross sections of ionization than those of primary electrons. The "price" of pair birth for argon (both by primary and secondary electrons) obtained in this paper is 25.5 eV, that is almost equal to the value obtained in [4] by Monte Carlo method.

For some limiting cases, integrals (12) can be substantially simplified, and it is possible to obtain analytical solutions. For ν=0, the equation (13) coincides with the Boltzmann equation for the spatially uniform source term ($c(\vec{r}) = const$), i.e. $\rho(\nu=0,e)$ presents EEDF for a spatially uniform infinitely wide electron beam. In the general case, if parameter $\alpha=N_g b\sigma_0$ tends to infinity, then the small values of ν will give noticeable contribution to the integral (12), and we have $f_s(\vec{r},e) = c(\vec{r}')\,\rho(0,e)$. The limiting case $\alpha=N_g b\sigma_0$>>1 has evident interpretation: under a high gas density or very wide source, spatial distribution function is determined by the local generation rate of electrons in the point $\vec{r}$ due to a small free length of scattering, and energy spectrum is determined by energy losses of secondary electrons (inelastic collisions) only. For presenting a certain practical interest cylindrical electron beams, a general solution (12, 13) can be simplified restricted to the one-fold integration of spectral function.

$$f(r,e) = \int_0^\infty d\nu\nu J_0(\nu r) w_0(\nu)\,\rho(\nu,e), \tag{14}$$

where $\omega_0(\nu)$ was defined in (7). This formula was used for determination of spatial-energy distribution of high energy secondary electrons in molecular gases [6].

4. CONCLUSIONS

The developed theory of collimated low-current electron beam propagated through gas includes the model of primary electron energy degradation in non-elastic collisions with gas atoms, multiple scattering of primary electrons in a small-angle approximation, and creation of secondary electrons in ionizing collisions. These processes lead to the spreading of beam electrons in coordinate and energy space, and formation of electron-beam plasma. An integral linear transport equation for secondary electrons generated in a region of E-beam has been considered. With the help of Fourier-Bessel transformation, integral Boltzmann equation was reduced to a much simpler equation for the "spectral" function, which is a universal function depending on the sort of gas only. The Green's function of initial integral equation has been found. The developed theory can estimate space and energy distribution function of secondary electrons with energy higher than the lowest threshold of non-elastic collision.

The "losses" of electrons in non-elastic collisions into energy region $e<I$ lead to formation of low-energy secondary, which turn out to be in the "dead" energy region. In this energy region, electrons can experience only elastic collisions with small energy losses. The balance of these electrons can be maintained only due to the ambipolar diffusion of electrons and ions in a self-consistent electric field to the chamber walls, or in the process of volume recombination. The accumulation of low-energy electrons around the electron beam, especially in the region of electron beam "collapse" is the ground for the formation of electron-beam plasma. The increase of electron beam current leads to the increase of electron beam density, and, for some currents (say, J_b>10 mA, for pressures p>1 Torr), Colombian collisions of primary and high energy secondary electrons with low-energy secondary electrons lead to the increase of energy thermalization in electron beam plasma and faster spreading of the beam. Thus, for increased beam current, Colombian collisions should be included into the model.

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