Modeling the extraction of sputtered species out of a pulsed hollow cathode discharge

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1. INTRODUCTION:

The field of nanotechnology is one of the emerging fields of technology; it has many applications including electronics, aviation, biomedical materials, and material science. It is expected to offer new materials with unique properties (electrical, thermal, optical ...etc) which do not exist for conventional materials. That development is expected to have a great impact on all fields of technology (it has already started to have that impact in some fields). That is why the scientific community is putting effort and money investigating all aspects of nanotechnology.

One of the fields which is vital for the nanotechnology is the science of generating nanostructures or nanoparticles. Due to the tiny size of those particles, special techniques are required to provide the ability of controlling the formulation and characteristics of nanoparticles. A large portion of those techniques is offered by plasma science; such as chemical vapor deposition (CVD) and arc discharges. In this work one of those techniques for generating nanoparticles on a substrate will be investigated, using hollow cathode discharge as the mechanism of generating nanoparticles.

The aim of this work is to build a theoretical model which will be used to link the input discharge parameters (mainly applied voltage, geometry, pressure gas flow, and the characteristics of the used materials and the discharge gas) to the parameters in the region of growth of nanoparticles. The model aim is to provide input data for models of grain formation in the chamber, these will eventually be used to optimize and tailor growth rate of nanoparticles on a substrate’s surface.
2. BACKGROUND:

The hollow cathode geometry is one of the geometries used in gas discharge; in that configuration a hollow (usually cylinder) geometry is used as the cathode. Such a configuration has a major advantage which is a long trapping time of the electrons. Since power is mainly consumed in heating electrons, longer trapping time means higher probability of collisions before electron loss, which means that energy is coupled to heavy species more efficiently than in planar cathode geometries.

In addition to the previous point, the hollow cathode geometry lowers the losses of ions to plasma outside hollow cathode because of small opening areas, which means they will contribute in the sputtering process more efficiently than in planar cathode geometries.

In the case under study, the cathode is made of aluminum and the discharge chamber is filled with argon gas. Since the analysis might be extended to include any metal other than Al, the word ‘metal (M)’ has been used as synonym with ‘aluminum’ in this work where both words are used interchangeably. The applied voltage is a negative pulse, the voltage current characteristic are shown in figure 1.

The parameters and the geometry of a reference discharge to be used in this work are shown in figure 2 and table 1:

![Figure 1: voltage pulse and discharge current](image1)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency</td>
<td>500 Hz</td>
</tr>
<tr>
<td>Duty cycle</td>
<td>1.5 %</td>
</tr>
<tr>
<td>Pulse Voltage</td>
<td>600 V</td>
</tr>
<tr>
<td>Initial Pressure</td>
<td>1 torr</td>
</tr>
<tr>
<td>Input flow rate</td>
<td>100 sccm</td>
</tr>
<tr>
<td>Discharge gas</td>
<td>Ar</td>
</tr>
<tr>
<td>Cathode material</td>
<td>Al</td>
</tr>
</tbody>
</table>

Table 1: parameters of the reference discharge
As shown in figure 2, the discharge chamber consists of 4 parts:

1. Hollow Cathode: the applied voltage is applied to the cathode which causes the ionization process to take place in that volume. The input gas flows through the hollow cathode.
2. Expansion zone: this zone is surrounded by a bounding barrier that can be put at bias potential.
3. Expansion Chamber: the main chamber with large dimensions, the wall is connected to ground.
4. Substrate tray: the plate at which the substrate is put.
3. FORMULATION OF THE PROBLEM:

In order to build a model for the formation of the grains, it is a must to determine the densities and the temperatures of different species involved in the discharge as functions of space and time, both inside the hollow cathode and in the expansion zone. In order to get that information one has to build a model to describe the plasmas behavior.

In the reaction we follow 6 different species involved, those species are: argon gas (Ar), argon ions (Ar⁺), metastable argon (Arᵐ), metal atoms (M), metal ions (M⁺), and electrons (e). Those species interact according to certain reactions; the majority of reactions take place in the hollow cathode volume because of the high density of the different species and the high temperature of the electrons.

The physical behavior might be divided into 2 stages; pulse on behavior and pulse off behavior. When the pulse is on, the ionization process starts, electrons start to heat and interact with heavy species. Those processes continue as long as the pulse is switched on, when the pulse is switched off, ionization process and electrons heating stop, while energy exchange between heavy species continue.

The transport of heavy neutrals (Ar atoms and metal atoms) is dominated by convection and diffusion driven by temperature and density gradients created mainly due to heating of the processed gas by sputtered atoms. Transport of charged species is in addition affected by electric fields. The exact mechanisms of transport will be investigated in subsequent sections.

The physical phenomena involved in the analysis are described generally by the following set of equations:

\[
\vec{E} = -\nabla V \\
\nabla \cdot \vec{E} = \frac{q_e}{\varepsilon_0} (n_{Ar^+} + n_{M^+} - n_e) \\
\frac{\partial n_i}{\partial t} + \nabla \cdot (n_i \vec{u}_i) = S_i - L_i \\
m_i n_i \left( \frac{\partial \vec{u}_i}{\partial t} + \vec{u}_i \cdot \nabla \vec{u}_i \right) = \pm q_e n_i \vec{E} - \nabla P_i + \eta \nabla^2 \vec{u}_i - \sum_j m_j n_j v_{c_{oll(i,j)}} (\vec{u}_i - \vec{u}_j) \\
m_i n_i C_v \left( \frac{\partial T_i}{\partial t} + \vec{u}_i \cdot \nabla T_i \right) = Q + \kappa \nabla^2 T_i - P_i \nabla \cdot \vec{u}_i \\
P_i = n_i k_B T_i \\
\vec{j} = \sigma \left[ \vec{E} + \frac{1}{q_e n_e} \nabla (n_e k_B T_e) \right]
\]

The index 'i' runs over all species (6 species); equations (1) and (2) describe the electric field in the sheath (see [1]); they describe the voltage in the sheath and the field driving transport process of charged species during the pulse. Equation (3) is the continuity equation; the terms 'S' and 'L' stand for 'Sources' and 'Loss', those terms depend on the species for which the equation is written. Equation (4) is the momentum equation; it includes the electric field (for charged species), the viscosity, the pressure...
gradient, and the momentum exchange between different species. Equation (5) is the energy equation (the heat equation); it includes the convection heat transport, volumetric heat sources (including Ohmic heating for charged species), the heat conductivity and the pressure work effects. Equation (6) is the equation of state of ideal gas which relates pressure with density and temperature for each species (for equations 3-5 see [2]). Equation (7) is the generalized Ohm’s law which is used to calculate the electric field in the plasma, it relates electric field in plasma to the drawn current (see [1]).

Having that set of equations, one has to determine how to formulate the different terms such that they describe the physical situation under investigation. The formulation is different depending on the part of discharge geometry. Once the formulation has been done, the resultant system of equations is a set of highly nonlinear coupled partial differential equations which is impractical to solve, so the complete model will be subdivided into simpler sub models such that each one of the sub models is solved independently of the others, then the result of the solved one will be used as initial data to the next sub model. The complete model has been divided into three sub models which are:

a. Hollow Cathode Model (HCM): this model computes the densities and the temperature evolution of different species within the hollow cathode volume; it includes heating due to the applied pulse, reactions between different species, sputtering yields, and losses to the walls of the hollow cathode.

b. Background expansion model: this model computes the velocity of the neutral gas flow both due to the time constant feed through the hollow cathode of argon gas, and the pressure pulse which evolves due to the heating of the gas mixture in the hollow cathode volume in discharge pulses. It basically deals with thermodynamic aspects of the complete model.

c. Puff model: this model is used to compute the flow during the discharge pulse (and a short time after it) of different species out of the hollow cathode volume. It should be noted that modeling the electric field at the hollow cathode exit is out of the scope of this work and that we here limit the task for making different assumptions of that electric field to see how it influences the particle extraction.

The validity of division of the complete model will be justified and investigated as the analysis is done. A detailed analysis of each of those models will follow.
4. MODEL CALCULATION FOR A ‘REFERENCE CASE’:

4.1. Inside the cathode:

4.1.1. Refill gas flow and pressure gradient inside HC:

In this model the steady state flow pattern will be computed in the hollow cathode volume and in the expansion zone. From now on all the computations have been done based on the reference case parameters given in table 1. Referring to table 1 the input flow rate is given as 100 sccm which is a unit of flux, converting it to the standard mass flux unit (kg/(m².s)) it corresponds to (for the argon gas with the given diameter of the hollow cathode):

\[ \Gamma_o = 0.15207 \frac{kg}{m^2 s} \]

The geometry in which the flow pattern will be computed is shown in figure 3:

![Figure 3: solution domain of the steady flow problem](image)

The system of equations being solved here is:

\[ \nabla \cdot (n\vec{u}) = 0 \quad (8) \]

\[ mn\vec{u} \cdot \nabla \vec{u} = -\nabla P + \eta \nabla^2 \vec{u} + \frac{\eta}{3} \nabla (\nabla \cdot \vec{u}) \quad (9) \]

\[ mnC_p\vec{u} \cdot \nabla T = \nabla \cdot (k\nabla T) + Q \quad (10) \]

Equations 8, 9 and 10 are basically the same as equations 3, 4 and 5 with small changes. The former three equations (8, 9 and 10) are the stationary versions of 3, 4 and 5; also they are solved for argon solely,
which implies the absence of any term corresponding to interaction with other species. Thus the right hand side of equation 3 is set to zero, and the collisions term in equation 5 is set to zero. The terms in equations (8, 9 and 10) and not in 3, 4, 5 are the compressible flow term in 9 and the volumetric heat source in 10.

The gas flows from the entrance of the hollow cathode at the given input flux, and the bounding barrier is modeled as wall (i.e. it doesn’t allow gas flow). The wall condition is applied to the walls of the hollow cathode as well. The exit of the system (the opening at the end of the expansion zone) is defined as open boundary at a constant pressure of 1 torr (133.32 Pa) the same as the initial pressure in the chamber.

The system was solved using COMSOL Mutiphysics (finite element based solver) giving the steady state velocity and the pressure in the whole geometry shown in figure 4:

Figure 4: Steady state velocity and pressure in the hollow cathode volume and the expansion zone

Figure 4 shows an expected behavior of gas flowing through a pipe, in such a situation the pressure decreases and the velocity increases in the direction of flow. At this point attention will be paid to the hollow cathode volume; the analysis of gas behavior in expansion zone will be treated in section 4.3. As figure 4 shows there is no significant variation in the radial direction in the hollow cathode volume neither in velocity nor in pressure. Thus a plot of the velocity and the pressure along the axis of the hollow cathode is sufficient to give a complete description of their behavior. The velocity and the pressure along the axis of the hollow cathode are shown in figures 5 and 6. The figures show that the change is almost linear as function of z coordinate in the hollow cathode volume. The difference in velocity between the entrance and the exit is almost 10 m/s and the difference in the pressure is 0.35 torr. The sudden change in velocity at the entrance and the exit is due the change in diameter of the geometry in which the gas is flowing, that is obvious for the exit but for the entrance it is implicitly implied by the boundary conditions.
It is difficult to define inlet boundary condition (the boundary condition at the entrance of the hollow cathode volume) in terms of flux; however it is possible to define the input pressure. In the case under study the input pressure has been chosen such that it drives a flux of 0.152 kg/(m².s) (for an exit pressure of 1 torr). The input pressure was 1.35 torr. The flux along the axis of the hollow cathode is shown in figure 7.
Figure 7: The mass flux along the axis of the hollow cathode
4.1.2. Plasma chemical model (HCM):

MODEL DISCRIPTION: The Ionization Region Model (IRM) was originally developed to compute the densities and temperatures of different species in planar sputtering magnetron geometry (see [3]), and has in this work been converted to hollow cathode geometry. We call this revised model the Hollow Cathode Model (HCM).

Once the voltage pulse has been applied, it starts to energize electrons (increase the electron temperature). That makes the electrons capable of inducing chemical reactions between different species, which causes changes in population of different species. The following table includes the induced reactions between the different species and the type of reaction:

<table>
<thead>
<tr>
<th>Reaction number</th>
<th>Reaction Formula</th>
<th>Reaction type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ar + e → Ar⁺ + 2e</td>
<td>Argon ionization</td>
</tr>
<tr>
<td>2</td>
<td>Ar + e → Ar⁺⁺ + e</td>
<td>Argon excitation</td>
</tr>
<tr>
<td>3</td>
<td>Ar⁺⁺ + e → Ar⁺ + e</td>
<td>Argon dexcitation</td>
</tr>
<tr>
<td>4</td>
<td>Ar⁺⁺ + e → Ar⁺ + 2e</td>
<td>Ionization from metastable Ar</td>
</tr>
<tr>
<td>5</td>
<td>M + e → M⁺ + 2e</td>
<td>Metal ionization</td>
</tr>
<tr>
<td>6</td>
<td>M + e → M⁺ + e</td>
<td>Elastic collision reaction</td>
</tr>
<tr>
<td>7</td>
<td>Ar⁺ + e → Ar⁺ + e</td>
<td>Elastic collision reaction</td>
</tr>
<tr>
<td>8</td>
<td>Ar⁺⁺ + M → Ar⁺ + M⁺⁺ + e</td>
<td>Penning ionization</td>
</tr>
<tr>
<td>9</td>
<td>Ar⁺⁺ + M → Ar⁺ + M⁺⁺</td>
<td>Charge exchange reaction</td>
</tr>
</tbody>
</table>

Table 2: The reactions taking place in hollow cathode volume

A basic assumption in IRM is that the volume of interaction is split into three volumes: IRM model accounts for two of them which are: the sheath region which is the outermost layer of the plasma (in contact with wall), and the ionization region, which is assumed to be characterized by almost uniform densities and temperatures for different species, and in which most of the ionization occurs. The third region is the surrounding bulk plasma. In the HCM, the ionization region corresponds to the inside of the hollow cathode while the bulk plasma is in the expansion zone. Due to the assumed uniformity one can use an average based description instead of the exact description; that will make the model a 0 D model (the only changing parameter is time) which will make the system easier to solve and follow (see [4]). Although it was shown in section 4.1.1 that a pressure gradient exists along the hollow cathode, we assume that the pressure in the hollow cathode volume is constant; the validity of the assumption will be tested at the end of this section. We will also assume that the gas to which the model is applied is stationary, as one could see from the previous section that the average velocity in the hollow cathode volume is 60 m/s, for a pulse duration of 30 μsec that means the gas has traveled 1.8 mm which is negligible compared to the length of the hollow cathode.

Starting from the standard continuity equation:

\[
\frac{\partial n}{\partial t} + \nabla \cdot (n\vec{u}) = S - L \Rightarrow \frac{\partial n}{\partial t} = S - L - \nabla \cdot (n\vec{u}) \Rightarrow \frac{\partial n}{\partial t} = S - L - \nabla \cdot \vec{I} \tag{11}
\]

To compute the average over volume, the equation has to be integrated over the volume of the ionization region:
Gauss’s law was implemented; assuming that the majority of the flux leaving or entering the surface is normal to the surface; that reduces the dot product to a simple product. $S_{HC}$ is the surface area inside of the hollow cathode. After dividing by volume the equation becomes:

$$\frac{\partial n}{\partial t} = S - L - \frac{R_{SHC}}{V}$$

(13)

Source and losses terms are represented by chemical reactions; they have the same form but they differ in sign; those terms can be written as:

$$S \ (or \ L) = k_{reaction}n_1n_2$$

(14)

Such that $k_{reaction}$ is the rate coefficient; $n_1$ and $n_2$ are the densities of the two species that interact.

In a similar approach, energy equations (or temperature equations) can be constructed, starting from the standard heat equation in terms of pressure with no internal degree of freedom (no molecules involved):

$$\frac{3}{2} \frac{dP}{dt} = Q - \nabla \cdot \bar{q} - \frac{5}{2} P \nabla \cdot \bar{u}$$

(15)

Following the averaging volume procedure; the equation can be written as:

$$\frac{3}{2} \frac{dP}{dt} = Q - \bar{q}S_{HC} - \frac{5}{2} P \bar{u}S_{END}$$

(16)

Having the previous formulation done, one can write the continuity equations and the energy equation for all the species. Since that was done in IRM (see [3]); only the modifications of IRM will be discussed in this work.

The physical reasons for the modifications are two. First, the IRM is a collision free case, while the hollow cathode is collision dominated. Second, in the IRM typically 70% of the surface of the ionization region faces the bulk plasma, while in the hollow cathode that is a few percent. Due to the previously mentioned reasons three modifications have been done to the IRM. The first modification of IRM is due to the collisionality. It concerns the flux across the boundaries. Flux is defined as density multiplied by the velocity, to define flux in an averaged volume model one has to relate the density in the ionization region volume to the density at the ionization region/ sheath interface, where the later density is used to compute the flux leaving the ionization region volume. That relation is given by what is called correction factors, those factors are computed from sheath calculations. Such factors are given in literature (see [5]). In the case under study the only needed correction factor is the radial correction factor which is defined as:

$$h_R = \frac{n(R_s)}{n(0)}$$

(17)

$R_s$ is the radius at which ionization region/ sheath interface exist ($R_s \approx \phi_{hc}/2$) and that radius is specified by sheath calculations. The values of the radial correction factors that relate mean free path $\lambda_{col}$ to characteristic scale length $l_c$ are given in table 2.
<table>
<thead>
<tr>
<th>Condition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low pressure ($\lambda_{\text{coll}} \gg l_c$)</td>
<td>$h_R = 0.4$</td>
</tr>
<tr>
<td>Intermediate pressure</td>
<td>$h_R = 0.8 \left( 4 + \frac{R}{\lambda_i} \right)^{-0.5}$</td>
</tr>
<tr>
<td>High pressure ($\lambda_{\text{coll}} \ll l_c$)</td>
<td>$h_R = \frac{0.8}{\left[ 4 + \frac{R}{\lambda_i} + \left( \frac{0.8 R u_B}{\chi_0 J_{1(\chi_0)} D_a} \right)^{2} \right]^{0.5}}$</td>
</tr>
</tbody>
</table>

Table 2: Radial correction factors for different regimes [5]

$R$ and $L$ are the physical radius and length of the hollow cathode; $\lambda$ is the mean free path between collisions, $u_B$ is the Bohm velocity, $D_a$ is the ambipolar diffusion coefficient, and $\chi$ is the first zero of the 1st order Bessel function. In the case under study the mean free path is found to be 0.3 mm approximately. That makes the regime under study here classify as the intermediate pressure regime, while the IRM model is for the low pressure regime. Note that the expressions given in table 3 are the radial correction factors for charged species; for neutral species the radial correction factor is simply (see [6]):

$$h_R = \frac{1}{4}$$

In the formulation of continuity equations for the 6 species the flux through the exit of the hollow cathode has been neglected. We motivate that by stating that the exit surface area is much smaller than the side surface area, which causes the flux through the exit during the pulse to be small compared to fluxes to the walls during the pulse duration for the reference case. Aside from the previous assumption, continuity equations are basically the same as in the IRM except for one difference in the Ar equation. In the IRM, the recombined Ar ions (i.e. neutral argon atoms) that return from the cathode are assumed to be lost to the bulk plasma. However, due to the cylindrical geometry of the hollow cathode and the fact that the length of the hollow cathode is much larger than its radius, in the HCM it is assumed that all the argon ions lost to the wall recombine and stay inside the hollow cathode as Ar atoms, which represents a source term for Ar atoms. Thus the second modification of the IRM is adding a new term to the equation of Ar atoms. The new equation of Ar atoms contains that extra term, the last term in equation 18:

$$\frac{dn_{\text{Ar}}}{dt} = -k_{iz} n_e n_{\text{Ar}} - k_{ex} n_e n_{\text{Ar}}^m + k_{dex} n_e n_{\text{Ar}}^m + k_p n_M n_{\text{Ar}}^m + k_{\text{chexc}} n_M n_{\text{Ar}}^m + \frac{r_{\text{Ar}+\text{HC}}}{V_{IR}}$$ (18)

Lastly, the energy equations will be discussed. The equation for electrons temperature is the same as it is in the IRM (refer to the appendix). For convenience the effect of the pulse in the electron temperature equation will be discussed here (it is the same in both the IRM and the HCM). When the pulse is applied it causes electrons to heat (because they are easier to be affected by the electric field due to their small mass), the heating term due to the pulse is given in the electron temperature equation by:

$$P_{\text{pulse}} = F_{pwr} V(t) I_{dch(t)}$$ (19)
In equation 19, $P_{\text{pulse}}$ is the power dissipated in the ionization region causing the plasma to heat. $V(t)$ is the pulse voltage, $I_{\text{dch}(t)}$ is the discharge current, and finally $F_{\text{pwr}}$ is a unitless parameter called power efficiency parameter (has a value between 0 and 1). Since it is known from the discharge physics that the majority of the applied external power is dissipated in the sheath region, only a small portion of the applied power is dissipated into the ionization region. That portion is represented by the power efficiency parameter. Since the analysis of the sheath is not covered either in IRM or in HCM, the value of $F_{\text{pwr}}$ will be pre specified. The pre specified value of $F_{\text{pwr}}$ will be obtained by adjusting its value to match the modeled current with the experimental current. The modeled current during the pulse as computed from the charged species fluxes at the cathode’s inner surface as:

$$I(t) = q_e((1 + \gamma_{(V(t))})\Gamma_{Ar^+} + \Gamma_{M^+})S_{HC}$$

(20)

$\gamma_{(V(t))}$ is the secondary emission coefficients for electrons due to argon ions bombardment.

The third modification of the IRM concerns the temperature equations for the other species. The temperature equations for the other species have to be constructed to replace a kinetic treatment used in the IRM. Following a similar procedure as for electrons, an equation for the temperature of heavy species can be constructed. Due to high collision frequency between different heavy species, we assume that they have the same temperature, which will be called from now on the Heavy Temperature. There is only one volumetric heat source which is elastic collisions with electrons; that term can be written as:

$$Q_{\text{reactions}} = \sum_{i=M,Ar} E_{i,\text{elastic}}k_{i,\text{elastic}}n_enn_i$$

(21)

Regarding the flux term; again it consists of summation of all species fluxes, each multiplied by the average energy it is carrying in or out. There are many fluxes playing a role in heavy species heating; those fluxes can be summarized as follow:

1. Flux of recombined Ar atoms (gain term).
2. Flux of sputtered metal atoms due to Ar ions bombardment (gain term).
3. Flux of sputtered metal atoms due to metal ions bombardment (gain term).
4. Fluxes due to energy exchange with walls (loss term).

After manipulation and simplification the equation can be written as (with $T_{\text{heavy}}$ in eV):

$$\frac{3}{2}(n_{Ar} + n_{M} + n_{Ar^+} + n_{M^+} + n_{Ar^{m}}) \frac{dT_{\text{heavy}}}{dt} =$$

$$E_{elas,Ar}k_{elas,Ar}n_enn_{Ar} + E_{elas,M}k_{elas,M}n_enn_{M} + \frac{w_{M,M}Y_{self}\Gamma_{M^+}S_{HC}}{v} + \frac{w_{M,Ar}Y_{self}\Gamma_{Ar^+}S_{HC}}{v} + \frac{w_{Ar,rec}\Gamma_{Ar^+}S_{HC}}{v} - \frac{3}{2}(T_{\text{heavy}}-T_{\text{wall}})\Gamma_{Ar^+}S_{HC}$$

(22)

By having equation 22, a complete set of equations is ready for being solved (6 equations of continuity and 2 equations of energy/temperature). The last thing which has to be determined is the average energy carried in/out by mass fluxes in the heavy temperature equations ($w_{Ar,rec}$, $w_{M,M}$ and $w_{M,Ar}$). A typical value of energy of recombined argon atoms in similar discharges is 2 eV [7]; so this value will be assumed in running the simulation. The other two energies can be computed using Thompson’s formula (see [8]). To read in more details about the complete set of equations and the different terms the reader is advised to read the appendix.
MODEL RESULTS: the pressure was assumed to be 1 torr in the hollow cathode, the value of Fpwr has been set to 0.3. After solving the system of 8 equations, the temperatures of electrons and heavies is shown in figure 8:

Figure 8: Electron and heavy temperatures (in eV) as function of time. The pulse in green is the voltage pulse in (V)

Figure 8 shows how temperatures of electrons (figure 8a) and heavy species (figure 8b) evolve, as it is well known in pulse discharge that pulsed power is mainly absorbed by electrons; then electrons start to lose that power by interacting with heavy species. As one can see from figure 9 for electron temperature; once the pulse has been applied the power is absorbed by the electrons causing the sharp increase in the electron temperature. After a while the electrons temperature is given by the balance between the pulse heating term (equation 19) and collisional losses. The most influential reactions in which electrons lose their energy are excitation reactions, then ionization reactions (electron impact ionization) and lastly elastic collisions reactions. Those effects are illustrated in figure 9a. For heavy species (figure 8b) the temperature raises as the pulse is applied, the main mechanism of heating is energy carried by sputtered atoms. The sputtering process continues as long as the pulse is applied but once the pulse is switched off sputtering stops. Heat exchange with walls dominates causing the heavy species to cool. Those effects are shown in figure 9b.
Figure 10 shows the evolutions in time of densities of Ar and M, it is clear to see that the density of argon atoms (figure 10a) starts to decrease when the pulse is applied, which is expected because the applied pulse increases the electrons energy which makes them capable of ionizing argon. The loss due to ionization continues until the pulse is switched off, when that happens the ionization process stops; which makes the recombination process to dominate, that causes argon atoms density to rise on the expense of argon ions density. The gas rarefaction in the hollow cathode due to ionization is only in the order of 1% in contrast to the case in sputtering magnetrons where it can be 50% to 90% [9] due to losses to bulk plasma.

The same applies as well to the losses of metal atoms (figure 10b), but the difference is that metal atoms has an extra source during the pulse which is sputtering; sputtering dominates over ionization loss which explains why the metal atoms density peaks at the end of the pulse. Once the pulse has been switched off, no sputtering occurs. The ionization potential for metal atoms is much lower than it is for argon atoms, which means that ionization (specifically charge exchange ionization) continues for longer time than electron impact ionization (reaction number 5 in table 2).
By looking at figure 11 one can see that the behaviors of metal density (figure 11a) and argon ions density (figure 11b) are similar. Once the pulse has been switched on electrons gain enough energy to initialize ionization processes, when the pulse has been switched off the ionization process almost stops and loss mechanisms start to dominate. It should be noted that metal ions has a larger relative degree of ionization (metal has lower ionization energy than argon) but they have lower loss rate for two reasons; the first is low ionization potential and the second is the continuity of penning ionization after the pulse has been switched off. The electrons density (figure 11c) is evolving in a way to conserve quasi neutrality condition in the ionization region.
The density of metastable argon (figure 12a) starts to evolve as expected when the pulse is applied, the difference in the case of metastable argon is that it arrives at a maximum peak which can’t be exceeded, what happens at that point is that gain and loss rates of metastable argon are very close of being equal (see figure 12a), that causes metastable argon to change around a certain value (unlike other species which peaks at the end of the pulse), when the pulse is switched off, electrons start to cool which causes losses terms to dominate over gain terms, the loss of metastable argon occurs at high rate compared to other species because of dexcitation reaction.
For the aspects of particle extraction to the expansion zone and particle growth one of the important parameters is the percentage of ionization of metal atoms which is shown in figure 13. When the pulse is switched on the ionization process starts, it continues to occur rapidly (the rising rate of percentage is high) as long as the pulse is running, when the pulse is switched off one can notice a small change in the slope of the curve (at a time of 31 μsec). That change happens because the mechanism of ionization is changed. During the pulse the ionization of metal atoms is dominated by electron impact ionization. However, once the pulse has been switched off, that ionization mechanism drops sharply while penning ionization continues for a while. The continuation of penning ionization causes the rising rate of ionization percentage of metal atoms to decrease, and it also causes the sharp decrease in densities of metastable argon (figure 12a) and metal atoms (figure 10b) just after the pulse. Finally it plays a role in making the decrease in metal ions density slow compared to decrease of argon ions after the pulse. It is also important to note that although the percentage almost reaches 100% after 40 μsec that doesn’t mean all metal atoms have been ionized, metal atoms exist but with a lower order of magnitude than metal ions, which makes it difficult to show in ionization percentage.
The modeled current and the experimental current are shown in figure 14 ($F_{\text{par}} = 0.3$). Because the modeled current has been computed using equation 20 which is based on the assumption that the pulse is on and the cathode is negatively biased, equation 20 is valid only during the pulse. During pulse off time the cathode is not biased, and the experimental current is determined by the path of the electrons and the ions between the anode and the cathode. The current shown in figure 14 computed after 31 μsec therefore has no physical meaning.

Figure 13: Percentage of ionization for metal atoms

Figure 14: Experimental current vs. Modeled current as function of time, the later is only valid to 30 μsec
Finally, the validity of constant pressure assumption will be tested. As shown in figure 6 the pressure varies almost linearly in the hollow cathode; it has a peak value of almost 1.35 torr at the entrance and 1 torr at the exit. The possible error introduced by assuming constant pressure in the HCM will be assessed based on calculation of the ionization percentage of metal atoms, the electron temperature, and the value of $F_{pwr}$. For comparison purposes the system was solved for 3 different pressures, 1.35 torr (entrance pressure), 1.175 torr (average pressure) and 1 torr (exit pressure). Figure 15 shows the effects of changing pressure. It is clearly noticed that the change is minor, which means that assuming a constant pressure in the hollow cathode volume is a valid assumption.

![The temperature of electrons](image)

![Ionization percentage of metal atoms](image)

![The modeled current for Fpwr of 0.3](image)

Figure 15: Comparison of behavior for different pressures.
4.2. At the cathode exit:
4.2.1. Pulse associated gas flow:

MODEL DISCRIPTION: this model takes into consideration the thermodynamic effects of the discharge, as it was possible to see from the heavy temperature curve (figure 8b) that the temperature rises to 0.11 eV which corresponds to 1267 K. Compared to the standard room temperature in the expansion zone, that temperature gradient is going to generate convection flow. Since argon gas represents the dominant species in population (98% at least as shown in figure 16), we assume that thermodynamic effects only affect the argon gas, which at the same time serves as background for the other species.

![Graph](image)

Figure 16: Percentage of argon gas

It should be noted that this model is a COMSOL model similar to the model discussed in section 4.1.1. The difference in this case is that the effect of generated heat due to the pulse will be taken into consideration. This model is basically the solution of the fluid flow problem of argon gas as it is heated in the different reactions followed by the HCM. The main quantities of interest here are the flow velocity and the temperature both as function of space and time where the flow velocity depends on the temperature and the density of the gas. The system of equation which has to be solved to compute the velocity has been introduced in section 3 (equations 3, 4 and 5).

As was mentioned in the introduction of this section, the system of equations will be solved solely for argon, thus all terms representing interactions with other species will be neglected. Also all the physical parameters in the flow equations (viscosity, heat conductivity and heat capacity at constant pressure) were taken from literature for argon gas [10]. Their values are temperature dependent. The geometry in which the system will be solved is shown in figure 3. The third equation (heat equation) is basically the same as heavy species energy equation but in the general most form. In order to match the two other equations one has to formulate the terms in heavy species energy equation as heat fluxes and sources in the general heat
equation. There are 4 fluxes of energy (heat): recombined argon flux (influx), sputtered metal atoms due to metal ions bombardment (influx), sputtered metal atoms due to argon ions bombardment (influx), and finally energy exchange with wall (outflux), these fluxes are coming from the walls of the hollow cathode. The fluxes and the energy they are carrying were obtained from the HCM. After some manipulation it is possible to write the heat flux as:

\[
\tilde{q} = -\kappa \nabla T = q_e \left( w_{MM} Y_{self} \Gamma_{M^+} + w_{M,Ar} Y_{sput} \Gamma_{Ar^+} + w_{Ar,rec} \Gamma_{Ar^+} - (T_{heavy} - T_{wall}) \Gamma_{Ar} \right) \tag{23}
\]

The heat flux is introduced into the heat equation (equation 5) by Fourier’s conduction law (see [2]):

\[
\nabla \cdot \tilde{q} = -\kappa \nabla^2 T \tag{24}
\]

Similarly, the volumetric heat sources are elastic collisions terms with electrons; after some manipulation, volumetric heat sources can be written as:

\[
Q = 3q_e m_e T_e n_e \left( \frac{k_{elas,M} n_M}{m_M} + \frac{k_{elas,Ar} n_{Ar}}{m_{Ar}} \right) \tag{25}
\]

A mass flux is introduced at the upper end of the hollow cathode; that flux is given as 100 sccm (equivalent to an entrance velocity of 26.3 m/s). The boundary condition at the end of the expansion zone is defined as outflow, which means that it acts as if it is an open boundary with an outside pressure of 1 torr. The initial pressure and velocity field in the hollow cathode and the expansion zone are the results of the steady flow problem discussed in section 4.1.1.
MODEL RESULTS: the model was run for 4000 µsec, which includes two pulses. A first figure to look at is the average velocity along the exit of the hollow cathode; it is shown in figure 17.

![Average downward velocity along the exit of the hollow cathode](image)

Figure 17: Downward flow speed as function of time

The velocity at 0 µsec is the average velocity given by steady flow pattern, afterwards the pulse is applied which heats the gas in the hollow cathode causing temperature and pressure gradients which causes a flow. The maximum flow velocity (almost 200 m/s) occurs at time of 50 µsec, which is 20 µsec after the pulse has ended, which supports the assumption made in HCM that loss due to flow through hollow cathode exit might be neglected during the pulse. When the gas flow peaks, a reversed pressure imbalance (lower pressure inside the hollow cathode) is induced between the expansion zone and the hollow cathode volume. That imbalance causes the flow to decelerate to velocities lower than the initial velocity; the lowest velocity in the case under study is 21.51 m/s (at 563 µsec). This effect might have an important effect on the extraction process for low flux rates (low values of scfm flow). At a certain limit the effect of pressure imbalance causes reversal of flux through the exit of the hollow cathode which means a portion of the gas which was blown away just after the pulse is sucked back into the hollow cathode volume. Since the blown gas carries the sputtered species, the sucking back effect is an undesirable effect. Figure 17 shows also that the flow speed reaches steady state velocity before the second pulse has been applied, which means that there is no overlapping effect in the generated flow pattern due to the pulse, at least at the exit of the hollow cathode. The temperature and velocity are plotted for different times in the next two pages.
Figure 18: Temperature and absolute velocity outside the hollow cathode ($t = 0$)

Figure 19: Temperature and absolute velocity outside the hollow cathode ($t = 31 \, \mu\text{sec}$)

Figure 20: Temperature and absolute velocity outside the hollow cathode ($t = 100 \, \mu\text{sec}$)
Figure 21: Temperature and absolute velocity outside the hollow cathode (t = 500 μsec)

Figure 22: Temperature and absolute velocity outside the hollow cathode (t = 1000 μsec)

Figure 23: Temperature and absolute velocity outside the hollow cathode (t = 2000 μsec)
Figures 18 to 23 show how the velocity and the temperature change as functions of space and time. Focusing at temperature, one can see from figure 19b that the temperature in the hollow cathode volume hasn’t raised enough at the end of the pulse to induce much convective flux into the expansion zone. It shows that the temperature just beside the wall is very high while the temperature along the axis is close to the standard temperature, after few μseconds temperature is uniformly distributed in the hollow cathode volume, which induces convective flow. As shown in figure 20b the hot gas starts to expand in the expansion zone which causes the temperature in the hollow cathode volume to decrease. In figure 21b it is shown clearly that the hot puff of gas which expanded out of the hollow cathode forms a ‘cloud’ at the exit of the hollow cathode. Figures 22 and 23 show the motion of the hot cloud, the initial velocity of the cloud is determined by the maximum flow velocity leaving the exit of the hollow cathode (see figure 17). Pressure imbalance causes the cloud to decelerate, thus while the cloud is moving away from the exit of the hollow cathode its velocity is significantly decreasing and its temperature is decreasing as well due to heat conduction.

![The temperature along the axis of the expansion zone](image-url)

Figure 24: The motion of the hot cloud of gas blown away of the hollow cathode

Figure 24 shows the motion of the hot cloud. The motion of the hot cloud gains its importance from the fact that it represents a puff of the gas heated inside the hollow cathode, which means that it carries certain amounts of the different species. It is an indicator of the distance which the carried species have traveled due to convection. More details will be investigated in the next section.

Looking at figure 19a, it can be seen that the heat pulse started to induce velocity along the exit of the hollow cathode at the end of the pulse (31 μsec), figure 20a shows two different behaviors of the velocity, the first one is the velocity of the pressure wave (the half circular light blue ring far from the exit of the hollow cathode), that velocity propagates isotropically in all directions. The other behavior of the velocity is shown at the exit of the hollow cathode, that velocity is directed along the axis of the expansion zone.
because it is driven by the steady state flow pattern. Focusing at the pressure wave behavior; later figures (21a to 23a) show that the pressure wave velocity has been deformed, it can be seen from those figures that the velocity has been increased along the axis of expansion zone while the velocity to the sides has been decreased. The pressure wave has lost its isotropic behavior because it was influenced by the steady flow pattern. That pattern affects it from two perspectives: the first one is accelerating the wave front propagating along the axis of expansion zone; the second one is the reflection of the wave front propagating off the axis due to circular flows in the expansion zone. Those circular flows are shown in figure 25.

![Arrow: Velocity field](image)

**Figure 25: Normalized velocity field of steady flow pattern**

The circular flow redirects the pressure wave front to the axis of the expansion zone. That effect also plays a role in limiting the radial expansion of the hot cloud as it moves forward. So the reflection due to the circular flow and the sucking back effect combined reform the wave front of the propagating pulse to become a narrow longitudinal flow. Plotting the velocity along the axis shows a similar effect to what was shown in figure 24.

Figure 26 shows the velocity along the axis of the expansion zone, it can be seen that the local maxima of velocity at each time almost coincide with the location of the hot cloud (figure 24), which indicates they represent the velocity of propagation of the hot clouds. So the cloud left the hollow cathode volume at time of 50 µsec, it propagated about 22 mm in 2000 µsec, which gives an average velocity of 11.28 m/s. That value might be used in building averaged based model of flow.
An important thing to be determined is whether the consecutive pulses will raise density gradient in the expansion zone or not (specifically around the cloud). Due to the large difference between temperatures of the cloud due to the first pulse and the cloud due to the second pulse, it is not possible to show both of them on a single graph. However, the curve of 2000 μsec in figure 24 shows that the center of the cloud is located at 22 mm and that the length of the cloud (corresponds to the width of the hill in the curve) is 40 mm. The tail of the curve (i.e. at z = 0) has the same temperature as the temperature of the background gas, which implies that the background gas has filled the volume located between the cloud and the exit of the hollow cathode. That means the second cloud and the first cloud will be separated by a cloud of background gas which means that the accumulation of the clouds will not occur. It should be kept in mind that the drawn conclusion here is an estimate based on the temperature of the background gas.
4.2.2. Extraction of sputtered species:

In the previous section, the fluid flow of argon gas was studied, since the majority of the gas mixture is composed of argon; the other species were not treated in the previous section, in this section the flow of the other species will be treated, the most important species to which attention will be paid are metal atoms, metal ions and electrons, those species play an important role in nucleation process which is the first step of the grain formation process. The model developed in this section will be used to study the flow of the previously mentioned species and to compute extraction efficiencies as functions of time.

MODEL DESCRIPTION: In this model the 2D convection diffusion equation close to the exit of the hollow cathode (i.e. in the expansion zone only) for each species is solved. The temperature of heavy species is assumed to be the same as the temperature of background gas. The convection velocity is the background’s gas velocity. The only collision frequency taken into consideration in this model is collision frequency with background gas. The surface area of the exit of the hollow cathode will be modeled as the inlet of the different species; it will be defined by the time varying densities of the different species computed from the HCM. The species are divided into two categories: neutrals (metal atoms) and charged species (metal ions, argon ions and electrons). The temperature of electrons as function of space and time will be solved for. For the sputtered species (metal atoms and ions) a figure of merit of the extraction process will be computed. We call that ‘the extraction efficiency’, it is defined as:

$$\eta_{M,M^+} = \frac{S_{\text{exit}} \Gamma_{M,M^+}(\text{exit})}{S_{\text{HC}}(\Gamma_M + \Gamma_{M^+})} \times 100\%$$

(26)

$S_{\text{exit}}$ and $S_{\text{HC}}$ are the surface areas of the exit and the walls of the hollow cathode respectively, $\Gamma_{M,M^+}(\text{exit})$, $\Gamma_M$ and $\Gamma_{M^+}$ are the metal atoms or the metal ions flux through the exit, metal atoms flux to the walls, and metal ions flux to the wall respectively. The flux through the exit has been computed in this section while the fluxes to the walls have been computed in section 4.1.2.

It should be noted that the extraction efficiency is defined for short time interval (i.e. from 0 to 100 μsec) because the majority of the different transport processes takes place during that interval. In addition, the analysis of the extraction efficiency was done based on an assumption that the densities of the sputtered species in the hollow cathode volume are not affected by the flux of the sputtered species through the exit of the hollow cathode.
METAL ATOMS: the convection diffusion equation is given as follow:

\[
\frac{\partial n_M}{\partial t} = -\nabla \cdot (-D \nabla n + n \vec{v}_{conv})
\]  

(27)

Equation 27 will be solved only in the expansion zone (the analysis of metal atoms in the hollow cathode volume has been already covered in section 4.1.2). The temperature (needed to compute diffusion coefficient) and the velocity (needed to compute convection term) in expansion zone have been computed in section 4.2.1.

![Figure 26: Metal atoms density at t =1000 μsec](image)

METAL ATOMS SOLUTION: the first thing which should be noted is that the cloud shown in figure 26 is wider than what it would be in reality, because of the previous assumption that the source is the surface area of the exit of the hollow cathode. In a solution taking into consideration the radial variation of densities within the hollow cathode volume the shape of the metal atoms cloud is expected to be similar to the shape of the hot argon cloud shown in figure 22b with greater radial expansion due to the effect of diffusion. Also when comparing figure 26 with figure 22b one can see that the metal atom cloud and hot argon cloud exist at the same point, which means that the main puff of metal atoms are blown away with hot argon gas. That is shown clearer in figure 27.
Figure 27: Comparison of locations of hot argon and metal atoms clouds at $t = 1000 \, \mu\text{sec}$

Figure 27 shows that the metal atoms cloud is slightly ahead of the hot argon cloud. That is explained by the fact that diffusion accelerates the flow of the metal atoms cloud. As one can see from figure 10b, the density of metal atoms peaks at $31 \, \mu\text{sec}$ which causes the metal atoms to start flowing before the main thrust of argon gas (at $50 \, \mu\text{sec}$) comes. Also one can see from figure 27 that the metal atoms cloud (although its maximum is a little bit ahead of the maximum of hot argon cloud) is almost completely carried by the hot argon cloud.

Having the flux at the exit of the hollow cathode obtained, one can compute the extraction efficiency. The extraction efficiency of metal atoms is shown in figure 28 as function of time. Figure 28 shows that the extraction efficiency of metal atoms is low on average. The efficiency drops as function of time. That occurs because of the ionization process. From a physical point of view ionization causes an increase in the flux to the walls of the hollow cathode. Once a metal atom is ionized it will be driven accelerated in the presheath until its velocity becomes equal to the Bohm speed (the flux to the walls is meant here). This means that ionization process might be thought of as if it accelerates metal atoms and consequently increases their flux. Since the expression of the extraction efficiency of the metal atoms includes the flux of metal ions in the denominator (equation 26), the ionization process causes the denominator to grow causing the efficiency to decrease with time. One can also see that the change of the dominant mechanism of ionization at the end of the pulse (shown in figure 13) is also shown in figure 28. At $33 \, \mu\text{sec}$ the extraction efficiency becomes negative, which indicates that the flux has reversed its sign. By looking at the components of the flux (shown in figure 29) one can see that the diffusive flux reverses its direction at the end of the pulse. What happens at that time is that the density of metal atoms drops in the hollow cathode volume (see figure 10b) and at the same time the main portion of metal atoms is located at the
exit of the hollow cathode forming the cloud of metal atoms. Because of the density difference (the cloud
has higher density than the hollow cathode volume), metal atoms start to diffuse back into the hollow
cathode volume. The reversed flow occurs simultaneously with the main flow of background gas flow
(which drives a convection flow of metal atoms). At that time the convective and the diffusive flows have
opposite directions. The diffusive flow becomes greater after the pulse is off, which can be told from the
extraction efficiency curve.

Figure 28: Extraction efficiency for metal atoms.

Figure 29: Flux components of metal atoms through the exit of the hollow cathode.
CHARGED SPECIES: the analysis of the extraction of the charged species will be focused on metal ions and electrons. Argon ions will be involved in the computation because they affect the other species. A fundamental difference between charged species and neutral is that they are affected by the electric field, and thus there are two different cases when dealing with extraction of charged species: during the pulse and after the pulse, the difference is the externally applied voltage. As was mentioned earlier the computation of the effective electric field can be calculated from the current density using generalized Ohm’s law (equation 7) but that computation is out of the scope of this text. Instead, two different cases will be investigated with respect to the electric field. The governing equation for convection diffusion equation for charged species is given in equation 28:

\[
\frac{\partial n}{\partial t} = -\nabla \cdot \left( -D \nabla n + n \vec{v}_{\text{conv}} \pm \mu \vec{E} \right)
\]  

The sign of the contribution of the electric field depends on the species. For electrons the convection term will be neglected due to their small mass. But it will be kept for ion species. Since we have three charged species (two ions and electrons) that means three fluxes will contribute in the extraction process. Computing the diffusivity and mobility of the three fluxes has to be done by computing the diffusion tensor and the mobility tensor which are in such situation density dependent (see [11]), which makes the problem highly nonlinear and difficult to handle numerically. To avoid that complexity we here assume the existence of an equivalent ionic species which has a particle mass equal to the average of the masses of argon and metal ions and a density equal to the sum of the ions species densities.

Concerning the effective electric field, there are two scenarios regarding its direction:

1. Inward electric field: In such a case the effective electric field is directed inward (pointing toward the hollow cathode volume), the direction of such a field matches the direction of the externally applied electric field, in such a case the flux of ions will be suppressed because the electric field attracts them back.
2. Outward electric field: A field of this type might arise in cases where density of electrons has a steep change in space (a high density gradient); the high density gradient causes the field direction to be reversed, which increases the extraction of ions. Such a case will be desirable in our case (see [12]).

For the analysis in this work two cases will be investigated:

1. Ambipolar diffusion: In this case the effective electric field is pointing outward, and adjusts for such a value that ion and electron fluxes are equal. Also it means that no current is drawn. The importance of this case comes from the fact that it provides an upper limit estimate of the extraction efficiency of metal ions.
2. Zero electric field: In this case the analysis will be done for the ions and electrons as if they are neutrals. In this case current is drawn. The importance of this case comes from the fact that it reveals the direction of the effective electric field, it also tests the validity of the ambipolar diffusion case, and lastly it gives an estimate of the extraction efficiency.

Starting by zero electric field, the electrons and equivalent ions will be treated as if they were uncharged; such a treatment implies that they will be treated independently of each other.
ZERO ELECTRIC FIELD SOLUTION: Since the electric field is not involved, it is possible to solve for metal ions without the need to refer to the equivalent ionic species. The spatial distribution of metal ions is shown in figure 30.

Figure 30 shows that metal ions (in case of zero electric field) behave exactly as metal atoms, which can be seen by looking at figure 30 and figure 26. Because both species have the same mass and they are influenced by the same temperature and velocity fields. The only difference is the order of magnitude which comes from the HCM results. The same conclusions regarding the location of the hot argon cloud and the metal ions cloud hold here. It is worth to remind the reader that this case is not physical; it gives an estimate of the extraction efficiency. The computation of the extraction efficiency for this case has been postponed to compare it with extraction efficiency of metal ions in the ambipolar diffusion case.

The zero electric field case of electrons is an important indicator of the direction of the effective electric field in the plasma. To compute the diffusion if the electrons the electrons temperature has to be computed in the expansion zone. The electron temperature can be obtained by solving the convection diffusion equation for the electrons energy density:

$$\frac{\partial n_e}{\partial t} = -\nabla \cdot \left(-D_{en} \nabla n_e + n_e \vec{v}_{conv}\right)$$  (29)

$n_e$ is the electron energy density, $D_{en}$ is the diffusion coefficient for the electron energy density. Equation 29 is just a different form of the equation for electrons temperature, for more information about that formulation the reader is advised to check [13]. Now, the electron density in the expansion zone can be computed by solving equation 27 and equation 29 for the electrons.
Figure 31: The electron temperature for the zero electric field case.

A comparison of the drawn current to the electron flux in the zero electric field case is shown in figure 32:

Figure 32: Comparison of the drawn currents (experimental vs. zero E field electrons current)
Figure 32 shows a difference by several orders of magnitude in the currents. The big difference implies that the direction of the electric field in reality is pointing in the direction of the flow (outward direction with respect to the hollow cathode). That direction also implies that the extraction of metal ions is higher than it is given by the extraction efficiency of the zero field case during the pulse.

The reversal of the direction of the current drawn by freely diffusing electrons occurs because the diffusive flux reverses its direction. Due to the extremely high diffusion coefficient of electrons (it has a value of $1.5 \cdot 10^5$ (m$^2$/s) just after the pulse at the exit of the hollow cathode), the electrons diffuse very rapidly and would if $E = 0$ distribute evenly in the expansion zone within less time than the pulse duration. At the end of the pulse the expansion zone would be full of electrons with high energy (see figure 31). It was shown in figure 8a that the electron temperature drops sharply at the end of the pulse. When that happens the electrons temperature in the expansion zone is higher than it is in the hollow cathode (the densities in the expansion zone and the hollow cathode are of the same order of magnitude), which causes the flux to reverse its direction. Due to the small mass of electrons compared to the mass of argon atoms, they are not affected by the gas flow of the background gas, thus no convection flow of electrons is induced.

It should be pointed out that the computation of the electron flux for the zero electric field is unphysical. Having such a large flux of electrons in the expansion zone would create large negative space charge and strong electric field. That field would be directed so as to prevent this from happening, i.e. outwards at the cathode exit. Therefore the zero electric field is unphysical situation and the computations provided in the next section are likely to approximate the real case.
AMBIPOLAR DIFFUSION SOLUTION: For the ambipolar diffusion case, the equivalent ion flux and the electron flux are equal; the expression for the flux is given in literature (see [1]). The presence of the background flow pattern induces a convection flux of equivalent ion species. For electrons to conserve the equality of flux they have to follow the flux of the equivalent ion species. The equivalent ions are driven by convection due to the background flow and at the same time they are dragged forward by the E field created by the electron pressure of the electrons while they are moving. The electrons behave as if they were affected by the convection flow of background gas. The dragging effect is described in the flux equation by introducing a correction factor to the convection term. After some manipulation the expression for the flux is given by equation 30:

\[ \tilde{I}_i = -D_a \nabla n + \left( \frac{\mu_e}{\mu_e + \mu_i} \right) n \tilde{v}_{conv} \equiv -D_a \nabla n + n \tilde{v}_{conv} \]  

(30)

In order to compute the ambipolar diffusion coefficient the electrons temperature equation has been solved. The solution is shown in figure 33.

Figure 33: Electron temperature at 31 μsec (at the end of the pulse) for ambipolar diffusion case.
Figure 33 shows the electron temperature in the expansion zone. It should be noted that no heating or cooling mechanism has been introduced, which means that the electron temperature in the expansion zone is rising because of the energy carried by the energetic electrons coming out of the hollow cathode volume. The electron temperature propagates isotropically into the expansion zone, which reveals that the dominant mechanism of transport is diffusion. One can also note that at the time the pulse ended, the hot electrons have traveled a significant distance into the expansion zone, indicating that the diffusion process has started at the beginning of the pulse. At the beginning of the pulse the diffusion process is driven by the temperature gradient (the ratio of electron temperature in the hollow cathode to the electron temperature in the expansion zone is 70 at that time). Gradually the electrons temperature drops, and the density of electrons increases. So the driving force of diffusion process changes from being temperature gradient to density gradient. The relatively high temperature of electrons causes the ambipolar diffusion coefficient to be large, which causes the electrons to spread rapidly in the expansion zone. Figure 35 shows that electrons at 1000 μsec have been distributed evenly in the expansion chamber. By the definition of the ambipolar diffusion case the density of electrons given in figure 34 is the same as the density of the equivalent ion species. The fluxes of the electrons and the equivalent ion species are equal as well.

With respect to the extraction efficiency, the flux of electrons through the exit of the hollow cathode is equal to the flux of the equivalent ion species. A criterion has to be defined to split the flux of equivalent ion species into its components (metal ions flux and argon ions flux). That was done here by multiplying the flux of equivalent ion species as function of time by the percentage of metal ions to the total ions. The percentage is computed from HCM (section 4.1.2). Having that done it is possible now to compute the
Extraction efficiency of metal ions. Extraction efficiencies of metal ions for the zero field case and for the ambipolar diffusion case are shown in figure 35.

![Extraction efficiency of metal ions](image)

Figure 35: Comparison of extraction ratios of metal ions

The extraction efficiency for the zero field case will be investigated at first. During the pulse the temperatures of the electrons and the heavy species increase. The increase in the temperatures causes an increase in both fluxes (to the walls and through the exit of the hollow cathode). Once the pulse is switched off the temperatures of the electrons and the heavy species start to decrease causing the fluxes to decrease as well. Simultaneously the flow velocity of the background gas (i.e. argon atoms) increases. The increase of the flow velocity of the background gas causes the flux through the exit of the hollow cathode to decrease slower than the fluxes to the walls, which explains why the extraction efficiency rises after the pulse. At 70 μsec the extraction efficiency becomes negative indicating that the total flux reverses its sign. The situation here is similar to the situation in the case of metal atoms. The diffusive flux reverses its direction because of the reversed density gradient (now pointing from the cloud at the exit to the hollow cathode volume). The difference in this case is that the convective flux is higher than it is in the case of metal atoms, which makes the time required for the net flux to be reversed longer. The longer time means that the cloud has moved away for a longer distance, which means that the effect of the reversed diffusive flux in the case of metal ions is much less than it is in the case of metal atoms. The components of the flux through the exit are shown in figure 36.
The extraction efficiency for the ambipolar diffusion case looks similar to the curves of the ionic species (see figure 10). Since the flux of metal ions to the walls is much greater than the flux of metal atoms to the walls, attention will be paid only to the flux of metal ions. The flux to the wall of metal ions depends heavily on the electron temperature as it influences the Bohm speed (the speed at which metal ions leave the ionization region). Once the pulse is on, the electron temperature rises sharply (see figure 8a), which causes the flux to the wall to increase. Although the density at the beginning in the hollow cathode volume doesn’t differ greatly from the density of electrons in the expansion zone, the temperature is very different, which causes the diffusion process to start early. As the pulse is running the flux to the walls decreases (because the electrons temperature drops) and the flux through the exit increases (because of the growing density gradient). That causes the extraction efficiency to increase during the pulse. Once the pulse is switched off, the electron temperature drops causing both fluxes (to the walls and through the exit) to drop. Figure 35 shows that the extraction efficiency of metal ions for ambipolar diffusion experiences a sharp drop just after the end of the pulse. The rate of falling changes (around 36 μsec). That happens because the diffusive flux has dropped to a level where the convective flux starts to influence the extraction efficiency. The effect of convective flux is obvious in the curve of extraction efficiency particularly after 50 μsec. The curve has a shape similar to the shape of the curve of the convective flux. See figure 37.
Unlike the situation for metal atoms and metal ions with zero electric field, the diffusive flux in the ambipolar diffusion case of metal ions doesn’t reverse its direction. That is explained by the fact that the ambipolar diffusion coefficient is relatively high, which implies that the ions and the electrons leaving the hollow cathode volume diffuse in the expansion zone in a short time. Thus no high density cloud forms at the exit of the hollow cathode.

An alternative approach of evaluating the efficiency of the extraction process might be defined by evaluating the ratio of the number of extracted particles of each species to the number of particles lost to the walls of the hollow cathode. We call that ratio the extraction ratio; it is defined in equation 31:

$$
\zeta = \frac{\int_0^T \Gamma_{\text{exit}} \cdot S_{\text{exit}} \cdot dt}{\int_0^T \Gamma_{\text{wall}} \cdot S_{\text{HCD}} \cdot dt}
$$

(S31)

$S_{\text{exit}}$ is the surface area of the exit of hollow cathode, $\Gamma_{\text{exit}}$ is the flux of a certain species through the exit of the hollow cathode, $\Gamma_{\text{wall}}$ is the flux to the hollow cathode walls, and ‘$T’$ is some specific time. Here ‘$T$’ will be taken as the pulse duration (30 $\mu$sec). The values of extraction ratio for metal atoms, metal ions for both cases and for the sputtered species (metal ions and atoms combined) are given in table 3.

<table>
<thead>
<tr>
<th>Species</th>
<th>Number of extracted particles</th>
<th>Extraction ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal atoms</td>
<td>$1.0434 \times 10^{12}$</td>
<td>4.153 %</td>
</tr>
<tr>
<td>Metal ions (zero field)</td>
<td>$3.9382 \times 10^{12}$</td>
<td>2.425 %</td>
</tr>
<tr>
<td>Metal ions (ambipolar diffusion)</td>
<td>$3.6225 \times 10^{13}$</td>
<td>22.31 %</td>
</tr>
<tr>
<td>Sputtered species (zero field)</td>
<td>$4.9816 \times 10^{11}$</td>
<td>2.65 %</td>
</tr>
<tr>
<td>Sputtered species (ambipolar diffusion )</td>
<td>$3.7268 \times 10^{13}$</td>
<td>19.87 %</td>
</tr>
</tbody>
</table>

Table 3: Extraction ratios of sputtered species
Table 3 shows that the extraction ratios are relatively high. It also shows that the difference between the ratios in the zero field case and in the ambipolar diffusion case is a factor of 10. In the real case the extraction ratio lay within the range defined by the extraction ratio of zero field case and the extraction ratio of the ambipolar diffusion case (close to the value of ambipolar diffusion case). The table also shows that the extraction ratio of the sputtered species is determined mainly by the metal ions. That is expected because the density of the metal atoms is much less than the density of metal ions because of the high ionization rate.

Finally it should be noted that the extraction ratio (defined by equation 31) and the extraction efficiency (defined by equation 26) are relative indicators of the number of the extracted particles. Although the number of extracted particles has been computed in table 3, it is not possible to compare that number with the number of particles confined in the hollow cathode volume. Because the obtained number of extracted particles was computed by integrating the flux out of the hollow cathode over a certain time interval, while the number of the confined particles in the hollow cathode is a function of time. Due to that difference there is no universal criteria of evaluating the efficiency of the extraction exists.
5. INTRODUCTION TO GRAIN FORMATION PROCESS:

Having determined the electron temperature, the heavy temperature (background gas temperature) and the fluxes of metal atoms and ions to the expansion zone, it is possible to start modeling the grain formation process as all the required information is available. Grains are clusters of particles (metal particles) combining together by different mechanisms, those grains represent the embryos of the nanoparticles which will eventually reside on the surface of the substrate.

Describing the grain formation process is a diverse field. Most of the research done in this field nowadays is done by following an approach called ‘Aerosol synthesis of nanoparticles’ (see [14] and [15]). Aerosols are small particles held (or suspended) in gas such as smoke or dust particles, while those particles are floating in the gas and they interact with each other. Those interactions are described by what is called ‘Aerosol general dynamics equation’ (see [16]), according to that equation the dynamics of aerosols are affected by three major factors: chemical composition, concentration and particles size. Particle size is described through the size distribution function (it gives the number density of particles with certain size), the concentration is defined for a set of particles with certain size, and finally the chemical composition plays a role in the conversion of a particle with a certain size to a larger size particles.

The main parameter of interest in the description of aerosol particles is the concentration of particles having a certain size, equation 32 is the equation describing that quantity:

\[
\frac{\partial n_k}{\partial t} + \nabla \cdot n_k \vec{v} = \nabla \cdot D \nabla n_k - \nabla \cdot n_k \vec{c} + S - L
\]  

(32)

Equation 32 is a continuity equation (written in diffusion convection form) but it has been modified to describe particles instead of individual atoms or ions. The variable \(n_k\) is the number density of particles with size property \(k\), \(D\) is the diffusion coefficient (depends on particle size), \(v\) is the convection velocity, \(c\) is the velocity due to some external force (i.e. electric field), and finally \(S\) and \(L\) stand for the sources and losses terms. Particles of certain size are generated or lost by different processes. The main processes are:

1. Nucleation: this process is the first step of particles formation. Nucleation represents an interaction in which single atoms or ions come together to form a particle, which is why this process is associated with the term ‘gas to particle conversion’. Nucleation is described by Classical Nucleation Theory (CNT see [17]). There are two types of nucleation: homogenous nucleation (uniform in space) and heterogeneous nucleation (occurs close to surfaces). In general nucleation process depends on many factors including temperature, density and pressure.

2. Coagulation: due to mutual forces exerted between different particles (due to Brownian motion or some other force) they come in contact with each other which causes them to form larger particles, which causes a decrease in the number of the particles and increase in their size. Once the particles have grown large enough they start to be affected by inertial forces causing them to deposit and thus they are lost. Coagulation depends on many factors including particles density; gas viscosity and temperature (see [16]).
3. Surface Reaction: this process might be included in nucleation (specifically heterogeneous nucleation), in this process particles grow is assisted by surface interaction (see [17] and [18]).

That was a brief introduction to the processes involved in creating or losing particles with certain size. Each one of those processes has multiple mechanisms. In the scope if this text it is not possible to get into more details of those processes. But a detailed explanation is given in the references listed in this section.
6. REFERENCES:


[10] Materials library of COMSOL v4.1


7. Appendix: Introduction to Ionization Region Model (IRM):

In this appendix we will explain in some details the physical background and the equations describing IRM. As was stated in section 4.1.2 the IRM consists of 7 ordinary differential equations, six of them describing time evolution of densities of different species and the seventh describe the electron temperature. Starting by Ar ions, Ar ions are involved in reactions 1 and 4 as resultant and reaction 9 as reactant (refer to table 2), so the equation can be written as:

\[
\frac{dn_{Ar^+}}{dt} = k_{iz} n_e n_{Ar} + k_{m,iz} n_e n_{Ar^m} - k_{chem} n_M n_{Ar^+} - \frac{\Gamma_{Ar^+ \text{HC}}}{v^2} - \frac{\Gamma_{Ar^+ \text{exit}}}{v^2} \tag{A1}
\]

In the previous equation terms involving ‘k’ are terms due to chemical reactions; terms including ‘\(\Gamma\)’ represents losses due to fluxes to the wall and through the exit of hollow cathode. Because of the mentioned reasons in section 4.1.2 the last term in equation A1 was neglected. The flux in equation A1 is defined as:

\[
\Gamma_{Ar^+} = n_{Ar^{+}(R_s)} u_{Ar^+} = h_R n_{Ar^+} u_{Bohm} \tag{A2}
\]

The Bohm speed is given by:

\[
u_{Bohm} = \sqrt{\frac{k_B T}{m}} \tag{A3}\]

Similarly, the equation for metal ions can be constructed:

\[
\frac{dn_{M^+}}{dt} = k_{chem} n_M n_{Ar^+} + k_p n_M n_{Ar^m} + k_{m,iz} n_e n_M - \frac{\Gamma_{M^+ \text{HC}}}{v^2} \tag{A4}
\]

The 3 terms to the left in the right hand side equation represent reactions number 5, 8, and 9 in table 2. The flux has the same definition of Ar\(^+\) flux (but for metal ion quantities).

For electrons, as quasi neutrality condition holds in the ionization region, the equation for electrons density is:

\[
\frac{dn_e}{dt} = \frac{dn_{M^+}}{dt} + \frac{dn_{Ar^+}}{dt} \tag{A5}
\]

For metastable argon, the equation can be constructed as follow:

\[
\frac{dn_{Ar^m}}{dt} = k_{ex} n_e n_{Ar} - k_p n_M n_{Ar^m} - k_{m,iz} n_e n_{Ar^m} - k_{dex} n_e n_{Ar^m} - \frac{\Gamma_{Ar^m \text{HC}}}{v_{IR}} \tag{A6}
\]

The first 4 terms to the left in the right hand side equation correspond to reactions number 2, 3, 4 and 8 in table 2. Flux definition is different from the previous species because the metastable argon is a neutral species. The flux is defined as:

\[
\Gamma_{Ar^m} = n_{Ar^{+}(R_s)} u_{Ar^+} = \frac{1}{4} n_{Ar^m} u_{Random}, u_{Random} = \sqrt{\frac{k_B T}{\pi m}} \tag{A7}
\]
For Argon atoms, the continuity equation is constructed in similar way to the previous equations, it is given by:

$$\frac{dn_{\text{Ar}}}{dt} = -k_{iz}n_{e}n_{\text{Ar}} - k_{ex}n_{e}n_{\text{Ar}} + k_{dex}n_{e}n_{\text{Ar}}^m + k_{p}n_{\text{M}}n_{\text{Ar}}^m + k_{chex}n_{\text{M}}n_{\text{Ar}} + \frac{\Gamma_{\text{Ar}}n_{\text{HC}}}{V_{IR}}$$  \hspace{1cm} (18)

The 5 terms to the left in the right hand side of the equation represent reactions number 1, 2, 3, 8 and 9 in table 2, the last term in the equation is the recombinated argon flux, it was explained in section 4.1.2.

Finally, the equation for metal atoms will be constructed. As ion species are accelerated in the sheath they hit the wall with high energy causing metal atoms to be sputtered of the walls of the hollow cathode causing an increase in the population of the metal atoms, thus the equation can be written as:

$$\frac{dn_{\text{M}}}{dt} = \frac{S_{\text{HC}}}{V} \left[ Y_{\text{Self}} \Gamma_{\text{M}} + Y_{\text{Sput}} \Gamma_{\text{Ar}} \right] - k_{p}n_{\text{Ar}}^m n_{\text{M}} - k_{chex}n_{\text{Ar}} + n_{\text{M}} - k_{m,iz}n_{e}n_{\text{M}} - \frac{\Gamma_{\text{M}}S_{\text{HC}}}{V_{IR}}$$  \hspace{1cm} (A8)

It should be noted that recombined metal ions are not counted because they reside in the walls as they are captured by a molecular binding energy in the wall. The terms involving ‘k’ in the right hand side of the equation correspond to 5, 8 and 9 in table 2. The flux in the last equation is defined as it was defined for Ar atoms.

The last equation is the electrons temperature equation, as electrons have higher mobility than ions. The applied pulse heats electrons which in their turn heat heavy species by collisions and acceleration of ions. Because the majority of the applied power is lost in sheath region, only a small portion of power contributes in heating electrons in the bulk plasma volume, thus the applied pulse serves as a volumetric heat source which has the following expression:

$$P_{\text{pulse}} = F_{\text{pwr}}V(t)I_{\text{dch}(t)}$$  \hspace{1cm} (19)

$I_{\text{dch}(t)}$ is the discharge current; $F_{\text{pwr}}$ is a coefficient representing portion of power delivered to the ionization region. Another volumetric source is energy lost due to reactions, in ionizing reactions electron losses ionization energy, in excitation reaction electrons loss excitation energy and finally in elastic collisions reaction electrons exchange energy with heavy species; since electrons have higher energy than heavy species do, elastic collisions are considered losses for electrons. According to the previous discussion the volumetric source corresponding to reaction can be written in the form:

$$Q_{\text{reaction}} = \sum_{i} E_{i}k_{i}n_{1i}n_{2i}$$  \hspace{1cm} (A9)

The index ‘i’ runs over all reactions in which electrons are involved; $E_{i}$ is the energy gained/lost per reaction; $k$ is the reaction rate, $n_{1}$ and $n_{2}$ are the densities of reactant species.

<table>
<thead>
<tr>
<th>The reaction</th>
<th>Ar ionization</th>
<th>Ar excitation</th>
<th>Aluminum excitation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy required (eV)</td>
<td>15.6</td>
<td>11.8</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Table A1: Energy required for different reactions involved in IRM

The flux term in the previous equation represents energy carried out of the ionization region, that energy is carried mainly by ion species as they are accelerated in the bulk plasma region (specifically in what is called presheath region), the flux of energy term is simply the mass flux multiplied by the average energy carried by each ion (kinetic energy corresponding to Bohm speed), so it can be written as:
\[ q = E_{\text{kinetic}} (\Gamma_{Ar^+} + \Gamma_{M^+}) \]  

(A10)

Thus the equation for electron temperature is ready to be constructed; after some manipulation and simplification it can be written as (Te is in eV):

\[
\frac{3}{2} n_e \frac{dT_e}{dt} = \frac{P_{pow} U_D}{eV} - \frac{1}{2} \frac{1}{v} \left( \Gamma_{Ar^+} + \Gamma_{M^+} \right)s_{HC} - \left( E_{ix} + \frac{3}{2} T_e \right) k_{ix} n_e n_{Ar^+} + E_{de} k_{de} n_e n_{Ar^+ m} - \left( E_{exc,ix} + \frac{3}{2} T_e \right) k_{exc,ix} n_e n_{Ar^+ m} - \\
\left( E_{M,ix} - E_{ex} + \frac{3}{2} T_e \right) k_{p} n_{M} n_{Ar^+ m} - \left( E_{M,ix} + \frac{3}{2} T_e \right) k_{M,ix} n_e n_{M}
\]  

(A11)