On particle formation graphite cathode Argon DC discharges

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Abstract: The formation of carbon dust in DC discharges with graphite electrode is investigated using a numerical model that combines a plasma module, a molecular cluster growth module and a solid particle growth module. The dynamic of particle formation is analyzed and the results are interpreted in terms of negative cluster and particle trapping in the potential well induced by field reversal in the negative glow.

Keywords: dusty plasma, modeling, cluster, carbon, DC discharge.

1. Introduction
Formation of carbonaceous dust particles was observed in argon DC discharges operated with a graphite cathode more than a decade ago [1]. To our best knowledge, there is presently no model that enables one interpreting the formation of these particles. We present in this paper a first model based on a three step scenario, i.e., sputtering of carbon atom and small molecules, molecular growth of these molecules, nucleation of dust and aerosol dynamic, to explain the production of dust in these conditions. We try to investigate whether the small field reversal that takes place at the boundary between the sheath and the negative glow can induce a significant dust formation.

2. Investigated discharge
The experiments are performed in argon DC glow discharge between two parallel electrodes of 10 cm diameter and separated by 14 cm. The argon pressure is $P_g = 0.6 \text{ mbar}$. The bias of the graphite cathode is $\sim -550 \text{ V}$, the current is imposed to 80 mA and the input power is $\sim 40 \text{ W}$[2]. The resulting carbon cathode sputtering allows the continuous injection in the plasma of carbon atoms. Nanoparticles are collected on the upper side of the anode. The discharge is maintained during 10 minutes in order to keep discharge current constant. Electron density in the negative glow is determined by langmuir probes to a few $10^{10} \text{ cm}^{-3}$. Dust particles are obtained with a density of $\sim 2.10^8 \text{ cm}^{-3}$ and an averaged size of 54 nm after 10 minutes of discharge[2].

3. Model
In this paper we are interested in the investigation of the very first phase of dust formation in a DC discharge when particle density is still small enough to make the discharge mainly governed by electron and ions. This means that we consider conditions at which the DC discharge parameters are not modified by the charged clusters and dust particles that may form in the plasma. Electron and electric field profiles can be then computed independently of the dust nucleation and transport.

The model developed for this study includes three modules. The first one describes the DC discharge in a dust-free plasma. We combines analytical models with a Monte-Carlo simulation to determine the electric field, the electron density and the non local ionization source term in the cathode sheath, the negative glow, the Faraday Dark space and the positive column [3]. Basically, the non-local approach developed by Kolobov and Tsendin is used to determine the sheath dimension and the absolute values of ionization rate in the sheath [4]. Monte-Carlo simulation is used to determine the relative evolution of the ionization profile over all the Argon discharge and to infer the position and dimension of the negative glow, the Faraday dark space and the positive column[3]. The absolute ionization rate in the sheath and the negative glow can be estimated by combining the non local model and the Monte Carlo simulation. The electron density in the negative glow and the Faraday Dark space is estimated from the electron ambipolar diffusion equation taking into account when necessary the non local ionization [4,5]. The electron density and temperature in the positive column are estimated from electron and power balance equations [6]. The position of the field reversal is determined from the condition of zero ion current as described in [4-5,7].

The electron density and electric field profiles are then used as input data for the other modules that describe
molecular growth of carbon clusters and particle nucleation and growth in the discharge column. Note that the only parameter in this model is the temperature of the cold electron in the negative glow.

The second module describes the molecular growth of carbon clusters. We are interested in cluster kinetics under fairly low temperature conditions and fairly low pressure. Cluster formation is mainly due to sputtering of a graphite cathode by energetic argon ions. This sputtering produces carbon atoms and small molecules, i.e., in C, C₂ and C₃, near the cathode [8]. The emission of positively charged carbon species should not affect carbon cluster growth and particle formation in the investigated discharge system. The emitted positively charged ions would indeed experience the sheath potential, few hundreds of eV, and return back to the cathode except if their energy exceeds the potential fall in the sheath which is unlikely to happen for the major part of the emitted carbon species. Then, the model takes into account neutral and negative cluster from C/C to C₃/ C₁₅ which are transported by drift/diffusion and undergo molecular growth reactions. We assume that the growth of clusters with more than 15 carbon leads to spontaneous nucleation and solid particulate formation. Their time evolution is described by drift-diffusion-reaction equations (one for each cluster) that express the balance between the density time-variation, a drift-diffusion flux divergence term and a cluster production source term [9].

In the estimation of the cluster production rate, we took into account the following collisional processes:

- Aggregation process

Since graphite sputtering mainly lead to C, C₂ and C₃, we assumed that molecular growth proceeds through addition of these species to the other clusters and neglected the aggregation between large clusters. The aggregation of negative clusters was also neglected. We therefore have the following aggregation processes [10]:

\[
C_n + C_x \leftrightarrow C_{nx+1}, \quad x=1-3, \ n>1 \quad (R1)
\]

\[
C_n^- + C_x \rightarrow C_{n+x}^-, \quad x=1-3, \ n>1 \quad (R2)
\]

\[
C_n^+ + C_x^- \rightarrow C_{n+x}^-, \quad x=1-3, \ n>1 \quad (R3)
\]

The aggregation constant was studied by many authors [10-13]. We made use of the results of Shweigert et al. [14] to express the overall reaction rate as function of the sizes of the collision partners using the kinetic theory and assuming activation energy of 0.225 eV. We also introduced a correction suggested by and Bernholc [14] and that allows taking into account the existence of magic numbers in the observed size distributions of the carbon clusters. Activation energy of 0.225 eV consistent with the value suggested by Shweigert [14] was used.

The kinetics of negative clusters involve three kinds of processes: electron attachment, electron detachment and charge transfer between clusters. The rate constants for attachment/detachment processes are estimated as indicated in [15], while charge transfer rate constants are estimated according to [10].

\[
C_n^- + C_x \rightarrow C_{n+x}^- + C_x \quad (R4)
\]

\[
C_n^- + C_x^+ \rightarrow C_{n+x}^- + C_x \quad (R5)
\]

The third part of our model describes the particle growth and transport in the discharge. The model allows estimating particle density, averaged size and averaged charge. The size and charge distributions are not directly considered in the numerical model. This does not enable one taking into account directly in the numerical model the existence of positively or neutral particles that result from charge fluctuation and play a key role in the coagulation process [16, 17]. The existence of these neutral or positively charged particles is taken into account using the approach suggested in [18] where the charge distribution can be inferred from the particle averaged charge and size, the electron density and the electron temperature. The fraction of particles that are neutral or positively charged can be therefore estimated without considering a detailed description of the charge distribution. The particle population is therefore described through three conservation equations for the particle number density, mass density and charge density. The particle average size is inferred from the calculated average number and mass densities assuming a solid density of 1000 kg/m³ for the carbon particles. The particle average charge is inferred from the charge and number densities.

The conservation equations for particle number and mass densities express the balance between the densities time-variation (mass or number), a drift-diffusion flux divergence term and a source term that involves nucleation from molecular cluster, coagulation, and growth through sticking. The nucleation rate was estimated on the basis of kinetic theory and assuming a sticking coefficient of 1.

The conservation equation for the charge density expresses the balance between the time-variation of the charge density, a drift-diffusion induced charge flux divergence term and a source term that involves the
charge production through nucleation or sticking of charged clusters, the charging by the plasma electron and ions currents [17,20]. The electron includes two components. The first one is due to the cold electron which represents the major part of the electron population and the current of which is estimated from the OML theory [17,20]. The second electron current component corresponds to the very fast electron emitted at the cathode. A rough estimation of the charging due to these electrons on the averaged charge of the particle shows that the corresponding current component can be neglected. The decrease of the electron density due to particle charging is taken into account in the estimation of the electron current.

4. Results
The discharge conditions correspond to the system investigated in [2]. The simulation parameters are the following : $T_e=0.1\text{eV}$ for the cold electron in the negative glow, $T_g=373.15\text{ K}$, a 0.5 torr pressure, a 550 V current and a sputtering yield at the cathode of $10^{-9}$. The Electric Field obtained in the discharge is shown in figure 2 where the cathode is positioned at 14 cm and the anode at the origin. The field strongly varies in the cathode sheath and becomes negative in the negative glow where it remains almost constant and decreases in the anode sheath. It appears therefore that the discharge is a short one without positive column and Faraday dark space and with only one field reversal. We can then expect that negative clusters and particles are trapped near the cathode. Figure 3 shows indeed the axial variation of the $C_{15}^-$ density at different simulation times. It appears that negative clusters are trapped in the negative glow just at the exit of the sheath where their density achieves a maximum value of $10^6\text{ cm}^{-3}$ for discharge duration of 1150 s. Taking into account that the densities of negative clusters show the same orders of magnitude, the total charge carried by the electron, i.e., a maximum of almost $10^{11}\text{ cm}^{-3}$ in the negative glow, remains much greater than the charge carried by the carbon cluster. The discharge properties can be therefore estimated neglecting the cluster charge density. It is worthy to notice here that the $C_{15}^-$ cluster density becomes significant, i.e., with a maximum density above $10^6\text{ cm}^{-3}$, only when the discharge is maintained for more than 500s which corresponds to the delay of the aggregation process to obtain a 15 carbon-cluster chain from the C, C$_2$ and C$_3$ sputtered from the cathode. At the end of the aggregation process, nucleation of the $C_{15}^-$ clusters leads to dust formation. The axial profile of particle density is shown in Figure 4 for different discharge durations. The particles are also trapped in the negative glow just at the exit of the sheath. The time variation of the particle density is however slightly different from that of the cluster density. Particle formation becomes significant only when discharge is maintained for more than 750 s and there is almost no particle, the particle maximum density is below $10^3\text{ cm}^{-3}$, produced below 350 s discharge duration. Note also that the particle density near the field reversal position remains almost constant for discharge duration smaller than 350s.

In fact during the first 350 s after the discharge ignition, the particles mainly experience an increase of their average diameter of that reaches a maximum of 34 nm at the field reversal position. Then, the enhanced nucleation kinetics that takes place once the large molecular carbon clusters are formed (see figure 3) result in the decrease of the average diameter down to a value of 26 nm reached for a discharge duration of 750 s. For longer discharge durations when the particle density starts to be significant, the molecular growth becomes limited since a large fraction of the molecular carbon clusters stick on the particles which also reduce the nucleation kinetics. As a result higher averaged diameter is obtained in this second period.

As far as the dust charge is concerned, nucleation of negative clusters leads to one negative charge. Sticking of these particle do not change directly this averaged charge because only neutral cluster can agglomerate to negative dust particles. But with a growing dust size, electron and ion current on the particle increase: the consequence is then a higher charge as can be seen at $t=350$s on figure 5. This current increases until the electrons are consumed by the dust and the clusters. Our model takes into account this electron consumption for the computation of the current on the dust which leads is the decreasing charge observed at 750s at the location of the negative cluster and dust concentrations.

5. Conclusion
The study presented in this paper clearly shows that the dust formation observed in DC discharge with graphite cathode can be well interpreted in terms of molecular growth, particle nucleation and growth. The field reversal that takes place at the exit of the sheath just before the negative glow plays a key role in trapping the negative clusters and particles. Although the present results should be considered as preliminary, it is worthy to mention that the particle density and diameter predicted in this paper are in good qualitative agreement. The model presented here can be used to investigate how particle formation is affected by discharge conditions. This is the scope of a more detailed future work.
Figure 2: Electric Field obtained at

Figure 3: negative cluster C15\textsuperscript{+} density

Figure 4: Dust density along the discharge

Figure 5: distribution of particle charges

References


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