On electron attachment effect on characteristics of the DBD in chlorine and its mixtures with xenon

S V Avtaeva
Novosibirsk State University, 2 Pirogova Street, Novosibirsk, 630090, Russia
E-mail: s_avtaeva@srd.nsu.ru

Abstract. The electron attachment effect on DBD characteristics in chlorine and its mixtures with xenon has been studied. Characteristics of the DBDs in pure chlorine and in xenon-chlorine mixtures with a chlorine fraction of 0.1-5% were modeled using the fluid model. It is shown that the electron attachment limits a magnitude of the DBD current, contributes to formation of multiple current spikes, appearance of a double layer near the dielectric surface and formation of XeCl* excimer molecules, and leads to a redistribution of the power deposited into the discharge: more power is deposited into ions and less power is deposited into electrons.

1. Introduction
The electron attachment in plasma of electronegative gases and their mixtures with electropositive gases made the plasma properties very different from that of electropositive plasma [1]. The properties of the electronegative plasma depend on electronegativity \( n_e/n_n \) and a whole series of other parameters. The theoretical and experimental studies of dc discharges and slightly less rf discharges show that the discharges in electronegative gases are structured with an ion-ion core and an outer electron-positive ion plasma [2, 3]. The electron attachment effects on property of the transient discharges quickly changing their characteristics in space and time as, for example, the dielectric barrier discharges (DBD) are much less studied. DBDs in inert gas-halide mixtures are widely used in excilamps to generate VUV radiation [4, 5] and can be applied for diverse surface treatment. The future development of the DBD plasma sources will depend on a better understanding the underlying physics. There we present some finding on the electron attachment effect on properties the DBD in Xe-Cl\(_2\) mixtures and in pure chlorine, which are revealed at fluid modeling of the discharges.

2. Model
Characteristics of the DBD in Xe-Cl\(_2\) mixtures were simulated using 1D fluid model described in detail elsewhere [6]. To decrease a time of simulation the simplified kinetic scheme of reactions was used [7, 8]. Characteristics of the DBD in pure chlorine were simulated using similar 1D fluid model of the DBD described in detail in [9]. We analyzed characteristics of a DBD between plane-parallel dielectric-covered electrodes to which a harmonic voltage with amplitude \( U_0 \) and frequency \( f \) is applied. The one-dimensional model of a homogeneous DBD is based on the continuity equations for charged components (electrons, negative and positive ions), balance equations for neutral components coupled via a set of reactions under the assumption of a local electric field, Poisson’s equation, and equation for the external electric circuit.
Set of partial differential equations with allowance for initial conditions, boundary conditions, and equation for the external circuit was solved by the method of lines. In this method, the spatial derivatives are discretized by the finite-difference method. As a result, the nodal values of each
dependent variable become unknown functions of time. Discretization was performed by the control volume method on a quasi-uniform mesh. The electron and ion fluxes were approximated by means of the Sharfetter–Gummel exponential scheme. The resulting set of coupled differential-algebraic equations was solved by the multistep backward differentiation method (the Gear method). The numerical algorithm was described in detail in [6, 10].

3. Results and discussion

Characteristics of the DBDs in pure chlorine and in xenon-chlorine mixtures (0.1-5% Cl₂) were modeled using the fluid model. The discharge gap length \( d_g \) is varied in a range 4-8 mm, electrodes are covered with dielectric layers. Two dielectric layers have an identical thickness \( d_b \) of 1-2 mm and a relative permittivity of 4 (glass). The harmonic voltage \( U_S = U_0 \sin(2\pi f t) \) with amplitude of 4.25-8 kV and frequency of 25-100 kHz was applied to electrodes. The gas pressure \( P \) was varied in a range of 15-300 Torr and gas temperature is assumed to be equal 300-400 K.

3.1. Xe-Cl₂ mixtures

The calculations show that, as the chlorine concentration in the mixture increases, the voltage drop across the discharge gap lifts, while the amplitude of the current spike decreases. The lower the chlorine concentration is, the greater the voltage drop across the discharge gap after the current spike is. The discharge accumulated at the surfaces of the dielectric layers decreases with increasing chlorine concentration in the mixture. These effects are explained by electron attachment to chlorine atoms, \( e^- + Cl_2 \rightarrow Cl + Cl^- \).

It was obtained both experimentally and theoretically that as the chlorine concentration \( n_{Cl_2} \) in Xe-Cl₂ mixtures increases, the radiation intensity of the second continuum of XeCl₂* decreases substantially, while the intensity of the XeCl⁺ (B→X) band increases. Already at \( n_{Cl_2} = 0.2\% \), the radiation of the XeCl⁺ (B→X) band with a head at 308 nm becomes dominant. The increase in the intensity of the XeCl⁺ (B→X) band with increasing chlorine concentration is observed only at \( n_{Cl_2} \leq 1\% \). The further increase in the chlorine concentration leads to the rapid decrease in both the intensity of the XeCl⁺ (B→X) band and the total intensity of discharge radiation. According to our experimental examination and fluid modeling, the chlorine concentration optimal for formation of the XeCl⁺ (B→X) band is 0.4-0.5% [11]. At this chlorine concentration about 81% of the discharge radiation falls on the XeCl⁺ radiation, 18% - on XeCl₂⁺ radiation and only 1% - on XeCl⁺⁺ radiation.

Consideration of the main processes influencing the formation and quenching of working XeCl⁺⁺ molecules during a various phases of voltage cycle shows that during short current spikes the harpoon reaction \( Xe^+ + Cl_2 \rightarrow XeCl⁺⁺ + Cl \) provides the greatest contribution into generation of XeCl⁺⁺ exciplex molecules while the ion-ion recombination \( Xe^+ + Cl \rightarrow XeCl⁺⁺ + Xe \) provides the greatest contribution during afterglow phase [12]. Quenching of XeCl⁺⁺ molecules is a result of the radiative decay \( XeCl⁺⁺ \rightarrow Xe + Cl + hv \) (308 nm). However during current spikes the dissociative ionization \( e^- + XeCl⁺⁺ \rightarrow Xe^+ + Cl + 2e^- \) also plays a dominant role in the quenching of XeCl⁺⁺ molecules.

Fig. 1. Gap-averaged instantaneous discharge power \( I \) and its distribution between electrons \( 2 \) and positive \( 3 \) and negative \( 4 \) ions during a cycle; \( U_0 = 5 \) kV, \( f = 100 \) kHz, and \( P = 200 \) Torr [12].
The discharge radiation power strongly changes during a cycle and correlate with the power deposited into electrons. It was observed that electrons adsorb discharge power in each period during small intervals of a time correlating with current spikes (Fig. 1). Between current spikes, discharge energy is mainly absorbed by ions. It is because of during periods between current spikes densities of electrons and Xe$^+$ ions strongly decrease because of attaching of electrons to chlorine atoms $e+Cl_2\rightarrow Cl+Cl$ and conversion of Xe$^+$ ions into Xe$_2^+$ ions $Xe^++2Xe\rightarrow Xe_2^++Xe$. However during current spikes the electron density strongly increases owing to ionization of gas and in the sheath near dielectric layers it exceeds densities of Cl$^-$ and Xe$_2^+$ ions.

![Image](image1.png)

**Fig. 2.** Time behavior (a), (c) of the source voltage $U_s$, voltage drops across the discharge gap $U_g$ and dielectric barriers $U_m$ and the total current density $J$, and (b), (d) the surface charge density on the dielectric layer adjacent to (1) the left (grounded) electrode and (2) the right (loaded) electrode at the voltage with $f=100$ kHz and $U_0=5$ (a, b) and 8 kV (c, d) in the DBD in Xe-Cl$_2$ (0.5% Cl$_2$), $P=200$ Torr; $d_g=4$ mm, $d_b=2$ mm [7].

In case of moderate $U_0$ (a low over-voltage) the charge deposited on dielectric surfaces during the current spike quickly decreases the dielectric surface charge up to zero, so $U_G$ and $U_m$ fall up to small values (Fig. 3 a, b) and it leads to a local collapse of the electric field in the area defined by the surface charge. After the current spike the surface charge again gradually increases owing to charge transferred by the plasma. Ionized gas in the gap is almost in quasi-neutral condition. The most part of a source voltage falls across the dielectric layers and smaller part falls across the gas gap. As a result, after the spike a voltage drop on a gap decreases with time, not having reached the breakdown voltage during the voltage half-cycle once again [7].

In case of high $U_0$ (a sizeable over-voltage) the charge deposited on dielectric surfaces during current spike is not sufficient for neutralization of the surface charge accumulated on the dielectric surfaces before the spike (Fig 3 c, d). Thus, after the current spike a residual charge with density $\sigma_{ris}$ $\approx 1–2$ nC/cm$^2$ remains on dielectric surfaces (Fig. 3 d). As a result, an electric field near to the
dielectric surface (the cathode fall) decreases not completely. After ‘primary’ spike across dielectrics and across the gas gap there are voltage drops having opposite signs. The great part of the source voltage $U_S$ falls on the gap. The gap voltage accelerates seed electrons to dielectric to neutralize the residual surface charge. Leaving of electrons from the plasma to the dielectric surface increases electric field in the sheath near the dielectric. The voltage drop across the gap promptly reaches the breakdown value once again. In the strong electric field a ‘second’ ionization wave is developed to create a ‘secondary’ current spike [7].

Thus, the reason of developing the ‘secondary’ current spike is that in case of the great over-voltage there is strong electric field across the gap and a great charge deposited on dielectric surfaces before the ‘primary’ current spike. At the same time, magnitude and time of the current spike depend on $U_0$ a little and are determined by the electron mean energy and density culminated at breakdown voltage, and by rates of ionization, recombination and electron attachment during the current spike. As a result, the charge, transferred during a current spike, depends on $U_0$ a little.

3.2. Pure chlorine

Fig. 3 shows the time dependences of the power supply voltage, the voltage drops across the discharge gap and the dielectric barriers, and the total current density of the DBD in chlorine over 1.5 voltage cycles. It can be seen that at a chlorine pressure of 15 Torr a breakdown occurs when the voltage drop across the discharge gap reaches a value of ~0.5 kV. Several weak current spikes, a number of which increases with decreasing pressure, are observed after the first spike. The peak current density in the spikes at the chlorine pressure of 15-100 Torr is about 4 mA/cm$^2$.

![Fig. 3. Time dependences of the (1) electrode voltage $U_s$, (2) voltage drop $U_g$ across the discharge gap, (3) voltage drop $U_m$ across the dielectric layers, and (4) total current density $J$ in the DBD in Cl$_2$ with $d_g=8$ mm, $d_b=2$ mm at $f = 100$ kHz, $U_0 = 8$ kV and $P= 15$ Torr [9].](image)

Two phases can be distinguished in the discharge dynamics: the active phase with multiple current spikes, which follows the breakdown of the discharge gap, and the passive phase. The active phase is characterized by the current spikes, a high current amplitude compared to that in the passive phase, small surface charge density on the dielectrics, and high voltage drop across the discharge gap. The passive phase (with no current spikes) is characterized by a low current amplitude, large surface charge density on the dielectrics, and small voltage drop across the discharge gap [9].

The chlorine plasma is electronegative, $n_n>n_e$, $n_n$ and $n_e$ are density of negative ions and electrons, correspondingly. During current spikes the electron density in both space charge sheaths (~0.5 mm) increases and a double layer appears near the electrode to which an ionization wave moves (the left electrode in Fig. 4): the positive space charge sheath adjoining the dielectric is followed by the negative space charge sheath extending up to the boundary of the quasi-neutral plasma. The appearance of a double layer is related to the fast increase in the electric field near the dielectric as it is approached by the ionization wave. The mean electron energy at the front of the ionization wave increases substantially, reaching 7 eV near the dielectric, and the dissociation and ionization rates of chlorine molecules, the rate constants of which increase with increasing $E/n$, also grow. At the same time, the rate constant of electron attachment to chlorine atoms depends weakly on $E/n$, and the rate of electron attachment to Cl atoms decreases after the mean electron energy reaches 5 eV. As a result, ionization of chlorine molecules near the dielectrics dominates over electron attachment; the density of
Cl$_2^+$ ions near the dielectric increases abruptly, forming a positive space charge; and the electrons escape onto the dielectric surface, thereby neutralizing the surface charge. Electron attachment dominates over ionization behind the front of the ionization wave, where the electric field is weak. In this case, the field of the positive space charge near the dielectric surface facilitates charge separation behind the front of the ionization wave by entraining negative ions and repelling positive ones. As a result, a double layer forms near the dielectric toward which the ionization wave propagates [9].

After first current spike, the surface charge on the dielectrics decreases. However, the electron density remains low, although it increases by two to three orders of magnitude. Since the mobility of Cl$^-$ ions is much lower than the electron mobility, the current spike is weak and rapidly terminates, because the electric field decreases due to a decrease in the surface charge density and mean electron energy in the course of ionization, dissociation, and excitation. As a result, the surface charge density decreases a little, and a large surface charge still remains on the dielectrics after termination of the current spike. This leads to a rapid growth of the electric field near the dielectric toward which the ionization wave propagates, thereby giving rise to a new current spike. This spike is also weak for the same reason as the preceding spike, and the process repeats again. Thus, there appear several successive current spikes, the amplitudes of which initially grow from spike to spike. When the voltage across the discharge gap drops to value that is lower the breakdown voltage the spikes disappear and the current gradually decreases as the surface charge accumulates on the dielectrics [9].

4. Conclusions
The electron attachment determines the DBD characteristics in chlorine and has the great effect on the DBD behaviors in Xe-Cl$_2$ mixtures. The modeling shows that the electron attachment limits a magnitude of the DBD current, contributes to formation of the multiple current spikes, appearance of a double layer near the dielectrics surface and formation of XeCl$^*$ excimer molecules, and leads to a redistribution of the power deposited into the discharge: more power is deposited into ions and less power is deposited into electrons. The reason of developing the multiple current spikes is that a charge, transferred by a current spike, weakly depends on a voltage, so at big voltage the charge is insufficient for neutralization of the dielectric surface charge. As a result, voltage drop across the gap promptly reaches the breakdown value once again and the ‘next’ current spike develops. At moving an ionization wave to the electrode covered by dielectric layer the electron attachment leads to appearance of a double layer near the dielectrics surface because of sharp changing an electric field, ionization and attachment rates and separated effect of the field on charged species.

References
[1] Franklin R N 2002 Plasma Sources Sci. Technol. 11 A31.
[2] Lichtenberg A J, Lichtenberg M A, Kouznetsov I G and Chung T H 2000 Plasma Sources Sci. Technol. 9 45.
[3] Ivanov V V, Klopovsky K S, Lopaev D V, Rakhimov A T and Rakhimova T V 1999 IEEE Trans. Plasma Sci. 27 1279.
[4] Kogelschatz U 2012 J. Opt. Technol. 79 484.
[5] Lomaev M I, Skakun V S, Sosnin E A, Tarasenko V F, Shitts D V, Erofeev M V 2003 Phys. Usp. 46 193.
[6] Avtaeva S V, Saghi B and Rahmani B 2011 *IEEE Trans. Plasma Sci.* **39** 1814.
[7] Avtaeva S V 2014 *IEEE Trans. Plasma Sci.* **42** 229.
[8] Saghi B, Avtaeva S V, Rahmani B, and Zissis G 2016 *IEEE Access* **4** 792.
[9] Avtaeva S V 2017 *Plasma Phys. Rep.* **43** 876.
[10] Avtaeva S V and Kulumbaev E B 2008 *Plasma Phys. Rep.* **34** 452.
[11] Avtaeva S V, Sosnin E A, Saghi B, Panarin V A, and Rahmani. 2013 *Plasma Phys. Rep.* **39** 768.
[12] Avtaeva S 2014 *Eur. Phys. J. D.* **68** 90.