Influence of the Condition of the Exposed Electrode Edge in the SDBD on the Discharge Operation Mode in Argon

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Abstract. The paper is devoted to the phenomenological study of the operating modes of a surface barrier discharge in argon in the case of treated by the discharge and new aluminum and copper electrodes. It is shown that without preliminary treating of the edges of the electrodes in the case of copper and aluminum electrodes, the discharge has a different spatial structure determined by the self-organization of the DBD. After erosion cleaning of the electrode edges, the identical operating modes are established. Such effects confirm the former assumption that the key factor determining the mode of the discharge operation for various electrode materials is the surface charge built on the oxides deposited on the edge. The different dynamics of oxides in the case of copper and aluminum electrodes is determined by the resistance of the oxides of these metals to sputtering, which is indirectly confirmed by the estimation of the binding energy for these materials.

1. Introduction

The dielectric barrier discharge (DBD) is widely used in various applications, for example, surface treatment [1,2], plasma chemistry [3–5], plasma medicine and biology [6,7], plasma aerodynamics [8–11].

The output performance characteristic of the DBD-based device is obviously determined by the parameters of the discharge and the mode of its operation. For a long time, it was believed that the properties of the discharge in the air are determined only by the geometry of the electrode system and the parameters of the supply voltage, however, in recent works it has been shown that the choice of the material of the corona electrode can have a great influence on the discharge [12,13]. In the work [13], discharge in the air with corona electrodes made of aluminum and copper was considered. It was demonstrated that during the long-term operation of electrode systems upon modification of such electrodes, significant changes are observed in the discharge operating modes (in particular, the self-organization of the discharge changes).

In the case of an aluminum corona electrode, the discharge looks like a region of diffuse glow, while in the case of a copper one, distinguish plasma channels are observed, located regularly along the span of the electrode (figure 1a, b). Such changes lead to significant changes in the magnitude of energy input averaged over time and the electrode span [13]. In [14] it was demonstrated that after long-term operation of such electrodes, significant changes in the characteristics of individual microdischarges (MDs), their spatial and temporal statistics are observed. MDs transfer less average charge. On the aluminum electrode, their active wandering along the edge is observed, on the copper
electrode, on the contrary, stabilization of the cathode spots of MDs occurs (due to which such differences are observed in the integral images of the discharge on such electrodes).

![Discharge images on (a) aluminum and (b) copper electrodes. SEM-images of aluminum (c) and copper (d) edges after exposure to a barrier discharge [13].](image)

**Figure 1.** Discharge images on (a) aluminum and (b) copper electrodes. SEM-images of aluminum (c) and copper (d) edges after exposure to a barrier discharge [13].

This drift of the discharge parameters is assumed to be due to the different dynamics of the oxides formed on the exposed edge.

The aluminum electrode is covered by a homogeneous oxide layer (figure 1c) [13]. This layer has a thickness of several microns and charges and breaks during the discharge operation. On copper electrodes, craters with bare metal, surrounded by the redeposited oxide, are formed (figure 1d) [13].

Presumably, the dynamics of oxides on the corona-forming edge is determined by the ratio of the processes of accumulation of the oxidized electrode material and its sputtering in the cathode spots of microdischarges.

It was demonstrated in [13] that the balance between the action of these competing mechanisms depends on the repetition rate of micro-discharges (the so-called “streamer frequency”), i.e. on the amplitude and frequency of the supply voltage in the case of a sinusoidal DBD. However, when initiating a discharge in an oxygen-containing atmosphere, it is not possible to separate the processes of oxidation and erosion cleaning.

The purpose of this work is to study the discharge operation modes in the absence of oxidative processes at the edges of aluminum and copper electrodes.

2. Experimental setup

In this work, the classical configuration of the edge-plane surface barrier discharge was studied. The configuration is shown in figure 2.

The corona electrode was made in half of copper and aluminum foils 20 µm thick, glued to a dielectric barrier with an adhesive sublayer thickness of 2–4 µm. Alundum ceramics 1 mm thick was used as a barrier (ε = 10.4). The electrode system was powered by AC sinusoidal voltage with a frequency of 20 kHz and an amplitude of 500–4500 V.

Discharge was operated in argon. The use of argon made it possible to completely eliminate the chemical interaction of atoms and ions of the plasma-forming gas with the electrode edges. The gas pressure was varied from 0.1 to 0.5 bar, which made it possible to change the ion's energy and the intensity of cathode sputtering. To exclude the influence of gradual air inflow into the chamber, the working volume was periodically refilled with argon. The pressure was monitored using a DM-5002m digital manometer with an error of no more than 0.5%.
To measure the supply voltage, Tektronix P6015A HV probe was used; to record electrical signals, we used a LeCroy HDO6104AR oscilloscope with a bandwidth of 1 GHz.

For optical registration of the discharge, a CCD camera was used, images were taken with an exposure of 1/30 s.

3. Results and discussion
The first stage of the experiment was a registration of the discharge operating modes in argon on new (not previously used) electrodes. The discharge was initiated with a supply voltage amplitude of 1300 V at an argon pressure of 0.5 bar and was recorded by CCD camera. The exposure of the obtained images was much longer than the period of the supply voltage (30 ms and 50 μs, respectively). Figure 3a shows the resulting images.
When the discharge is first initiated on copper and aluminum electrodes, the same qualitative differences are observed as in an oxygen-containing medium: on the copper edge, the microdischarges are stable at times much longer than the supply voltage period; on the aluminum electrode, it looks like a diffuse glow region with discontinuities along the edge. Presumably, the stochastic behavior of microdischarges on the aluminum edge is caused by the charge buildup on the nanometer-thick oxide film. As in the case of coating an electrode with a thick oxide layer, this layer is recharged, which affects the memory effect and leads to the wandering of the cathode spots of microdischarges [13], [14]. It can be assumed that ions energy in the cathode layer at atmospheric pressure is insufficient to cause the oxide sputtering.

Before the second step, the oxide depositions were removed from both electrodes. The oxide was removed by erosion cleaning in the cathode spots of microdischarges. To increase the energy of the ions bombarding the electrode, the argon pressure was reduced to 0.1 bar. The supply voltage was reduced to 500 V, since at high values a transition from a glow discharge to a spark occurred. This mode was maintained until the formation of a uniform electrode layer along the entire edge (see figure 4). It is assumed that this energy was sufficient for the sputtering of the Al₂O₃ layer on the Al electrode.

At the second stage, the optical registration of the discharge was repeated under the same conditions (argon, 0.5 bar, 1300 volts). The results are shown in figure 3b. After removal of oxide formations, the discharge structure is non-homogeneous and stable on both copper and aluminum, and discharge operating modes on both electrodes are absolutely identical.

![Figure 4. Electrode treatment in low-pressure discharge.](image)

Thereafter, the electrode edge was modified by the barrier discharge in the air. The chamber was refilled with dry air, and a voltage of 4500 V was applied to the electrodes. This mode was maintained for 2 hours. The results of processing the edge of the electrode with such discharge parameters were mentioned in the introduction in figure 1 and are described in detail in the works [13], [14].

At the third stage, the chamber was again filled with argon, and the optical registration of the discharge was repeated under the same conditions (0.5 bar, 1300 volts). After processing the electrode in air, the discharge in argon on the aluminum electrode looks like a diffuse glow region (see figure 3c), the discharge on the copper electrode has many separate stationary cathode spots. Thus, the discharge structure in air and argon is similar on modified electrodes.

We assume, that the different behavior of the discharge for electrodes made from different materials is due to different dynamics of oxides at the edge. Analysis of the properties of aluminum
and copper, as well as their oxides, showed that the main fundamental difference is the resistance of copper and aluminum oxides to sputtering.

This statement follows from the estimate of the binding energy of CuO, Cu2O and Al2O3. The formation of oxides can occur in the reactions:

\[
\begin{align*}
Cu + \frac{1}{2}O_2 & \rightarrow CuO, \ t < 200^\circ C \\
2Cu + \frac{1}{2}O_2 & \rightarrow Cu_2O, \ t > 200^\circ C \\
2Al + \frac{3}{2}O_2 & \rightarrow Al_2O_3.
\end{align*}
\]

Other reactions require either high temperatures (> 600 °C) or sufficient concentration of other compounds (N2O, NO). Presumably, the conditions for their course are not created.

The binding energy can be estimated as

\[
\begin{align*}
\varepsilon(CuO) &= \Delta_f H^0(Cu) + \frac{1}{2}\Delta_f H^0(O_2) - (-\Delta_f H^0(CuO)), \\
\varepsilon(Cu_2O) &= 2\Delta_f H^0(Cu) + \frac{1}{2}\Delta_f H^0(O_2) - (-\Delta_f H^0(Cu_2O)), \\
\varepsilon(Al_2O_3) &= 2\Delta_f H^0(Al) + \frac{3}{2}\Delta_f H^0(O_2) - (-\Delta_f H^0(Al_2O_3)).
\end{align*}
\]

where \(\Delta_f H^0(XX)\) is the thermal effect of the formation of species \(XX\), for simple compounds \(\Delta_f H^0(XX)\) is taken equal to 0, \(\Delta_f H^0(CuO) = 162 \text{ kJ/mol, } \Delta_f H^0(Cu_2O) = 173.2 \text{ kJ/mol, } \Delta_f H^0(Al_2O_3) = 1675 \text{ kJ/mol.}

Substituting all the data and representing them in eV per molecule, we get:

\[
\begin{align*}
\varepsilon(CuO) &= 1.67 \text{ eV/mol,} \\
\varepsilon(Cu_2O) &= 1.79 \text{ eV/mol,} \\
\varepsilon(Al_2O_3) &= 17.31 \text{ eV/mol.}
\end{align*}
\]

One can see that the dissociation energy of the Al2O3 is an order higher than the same value for Cu oxides. The obtained energy values must be spent to dissociate all molecules. Obviously, during cathodic sputtering, the molecules do not disintegrate completely, but single atoms are pulled out of the formed oxides. Nevertheless, such an estimate allows us to conclude that the intensity of sputtering of aluminum and copper oxides also differs by an order of magnitude.

The significant difference in the dissociation energy between Al and Cu oxides leads to the different behavior of the oxides at atmospheric pressure. For Al, the oxide is not removed from the surface at atmospheric pressure (or 0.5 bar). As one reduces pressure, ion's energy increases and effective erosive cleaning occurs. Copper oxides are removed from the electrode at MDs positions. Finally, one can see that in the oxygen-free mixture, the discharge mode is similar on Cu and Al electrodes.

4. Conclusions
The condition of the electrode edge has a great influence on the operating mode of sDBD, including even in inert gases. If the edges have not been pretreated, they initially contain oxide formations, with their charging affects the spatial organization of the discharge for long (significantly longer than the supply voltage period) times.
The removal of oxides during the erosion cleaning of electrodes in argon leads to the same discharge operation modes on the copper and aluminum edges - microdischarge channels are stable, their electrode spots are formed on the same sections of the electrode edges and do not shift over time much longer than the period supply voltage. It means that in the absence of the oxide on the electrode edge, the key “memory effects” in the discharge do not depend on the electrode properties. On contrary, oxide formation on the edge is one of the key factors determining the mode of operation of the discharge.

The key difference between copper and aluminum electrodes, responsible for the different dynamics of oxides at the electrode edges, is the resistance of the oxides to sputtering in the cathode spots of microdischarges. According to estimates of the binding energy of molecules, aluminum oxide is more resistant to sputtering than copper oxides. At atmospheric pressure, the energy of the ions is insufficient to cause the sputtering of Al₂O₃.

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