Electrode microwave discharge: areas of application and recent results of discharge physics

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Abstract. The first paper on the electrode microwave discharge (EMD) appeared in 1996. Presently many problems of EMD physics and applications have already been solved. Several examples of EMD application are discussed: diamond growth, deposition of CN_x films and nanotubes, deposition of metal films (Cu, Al), deposition of TiN and TiO_2 films, generation of O_2(2^3P), and EMD as a plasma cathode. Results of EMD experiments and modeling give rise to the assumption that an EMD consists of a self-sustained domain (near-electrode plasma region with overcritical plasma density) which is surrounded by a region of a non-self-sustained discharge (ball shaped region with undercritical plasma density). We assumed that the layer of charge separation and of induced electrostatic field originated at the outer EMD boundary was one of the reasons for the abrupt decrease of the plasma density which leads to the formation of a compact plasma structure. Recent modeling results of the strongly nonuniform electrode microwave plasma based on a quasi static, 1D spherically symmetric model showed that such a layer can be generated at the point where a sudden increase of the total ionization rate takes place.

1. Introduction
The intensive study of the electrode microwave discharge (EMD) started in 1996 [1] and now we have a lot of knowledge about the discharge physics and about the discharge applications [1–26]. The EMD is interesting due to its distinctive features and its promising applications. We call a discharge an EMD if the plasma is ignited near the tip of the powered electrode/antenna and the luminous plasma region is less than dimensions of the discharge chamber. The EMD turns into the ordinary discharge mode [2] at smaller distances between the electrodes.

The distinctive EMD features are: Extremely low maintaining discharge power (1–2 W) and a wide range of operating pressures; generation of compact plasma structures, of plasma active particles in large vessels and near the treated surface, and of plasmas in a chosen point of space (localization of plasma region; the area of plasma region being controlled by the electrode shape).

2. Experiment and modelling
A detailed description of the experimental set-up has been presented in [4,5,10,21,26]. Stainless steel cylindrical discharge chambers with diameters of discharge vessel of R_1 = 7 cm and R_2 = 4.2 cm have been used for the experiments. The plasmas in both arrangements revealed similar features, thus the properties of the described plasmas seem to be typical for electrode microwave discharge systems.
Plasma gases were Ar, Ne, H₂, N₂, O₂, CH₄, C₂H₂, air, and their mixtures at pressures 0.5—400 Torr. A gas flow system provides a total gas flow rate of less than 1000 sccm. A “gas feeding-pumping” system gives the possibility to operate with gas mixtures of 3 gases and introduces the input gas mixture through the channel inside the electrode or through the upper cover of the chamber. The latest modification of the setup (stand EMD-3) is shown in figure1.

![Figure 1a. Experimental set-up EMD-3. 1 – electrode (antenna), 2 – isolator, 3 – impedance transformer, 4 – plasma, 5 – coaxial-to-waveguide converter, 6 – shorting plunger, 7 – discharge chamber, 8 – optical windows](image)

Tubular and solid stainless steel and copper electrodes of different shapes (direct or bent rod and tube cylinder electrodes, trident electrode, spiral electrode, etc.) with diameters of 0.5–6 mm have been used as antennas. This set-up gives the possibility of breaking the galvanic coupling between antenna/electrode and the body of the discharge chamber. The latter property makes it possible to investigate the effect of external static fields on the properties of EMD plasma.

Most of results have been obtained when the discharge is ignited at the tip of a cylindrical electrode (antenna). The microwave power (2.45 GHz) was transmitted from magnetron generators with output powers of 2.5 kW or 150 W. The power absorbed in the system is measured by a directional coupler. For a given value of the input power the power absorbed in the plasma is obtained by subtracting the power losses in the empty chamber from the power losses in the chamber with plasma.

The discharge emission, which leaves the chamber through the lateral or bottom quartz windows, is focused by quartz lenses, collected by the optical fibre, and recorded with spectrometers (monochromators MDR-4 and MDR-23, spectrograph AvaSpec-2048, AvaSpec-3648, AvaSpec-2048-4-RM). The optical fibre can be moved both in the longitudinal and radial directions by means of a two-coordinate micrometric table with a spatial resolution of 150 μm. The discharge visualization is made by a video camera (the exposition time ranged between 1/20 and 1/8000 s), by a digital photo camera, and by electron-optic high time resolution digital cameras K008 and K011.

The set-up contains the devices for the spectral analysis of the microwave radiation (spectrum analyzer C4-27, stroboscopic oscilloscope C7-11) and for the registration of the time variation of the microwave power and of the integral plasma emission in the visible range (oscilloscope Tektronix TDS2012B).

The EMD had spherical symmetry at small flow rates. A few photos of the EMD are shown in figures 2, 3. The ball-like structure is deformed and the plasma expands along the electrode channel axis at flow rates higher than 50 sccm.
Methods used for the experimental study:

- Photometry of the discharge (study of EMD structure).
- Double probe method (determination of the local values of the electron temperature and density, electric field strength) [4,5,7–10].
- Emission spectroscopy in the visible range of the spectrum with spatial resolution (determination of plasma particles concentrations, gas temperature, electric fields, etc) [6,12–14,16,17,21,26].
- Electrodynamic measurements (determination of the absorbed power, frequency and microwave spectrum, time variation of the power).

Methods for EMD simulation:

- 0D kinetic numerical code [17,24].
- Self-consistent 1D modelling in quasi-static approximation [11,20,22,25].
- Self-consistent 2D modelling with the Maxwell equation [15,16,18,23].

**Figure 2.** View of the air discharge at the tip of a 6 mm electrode in nitrogen (1 Torr)

**Figure 3.** View of the air discharge with a needle electrode exploding (diameter – 1 mm, 50 Torr)

3. Brief summary on physics of the EMD in molecular gases and their mixtures with noble gases

3.1. General features and peculiarities of the EMD

I. General discharge properties (like spatial profiles of electron and ion densities, plasma emission) are independent of the diameter of the plasma chamber.

II. The discharge consists of (figure 2):

- a bright thin (1–1.5 mm) near electrode plasma region which covers the tip of the electrode;
- a ball-like emissive plasma region;
- a dark external conductive space.

III. The ball dimension increases with microwave power and decreases with pressure.

IV. There exists an upper limit for the microwave power. If the input power exceeds this value the discharge runs away from the tip of electrode towards the microwave generator.

IV. Thin electrodes can be destroyed due to melting and can even explode for high microwave powers and pressures (figure 3).

The structure of the EMD is clearly seen in figure 4.

3.2. Discharge boundary

The plasma ball has a sharp external boundary. Probe measurements showed an abrupt decrease of the electron concentration in a thin boundary layer even in diffusion controlled regime [7,8]. The only
reason, why the spread of charged particles out of the plasma ball is suppressed, is the existence of a local electrostatic field. A double layer has the necessary property. This boundary reveals an elastic property in case of contact with an external body, e.g. with the probe. In case of two plasma balls ignited at two closely placed electrodes/antennas the increase of the microwave power at first leads to growing ball diameters. At higher microwave powers the shape of the plasma balls changes into ellipsoids, which are always separated by the dark space.

![Color marked visualization of the total plasma emission of a nitrogen EMD together with the axial and radial distributions of the emission intensity (1.33 Torr).](image)

3.3. EMD dimensions
What is the largest plasma dimension of an EMD and the highest power absorbed in the plasma? The answer to these questions was given by the 2D model, which included the Maxwell equations [18].

It was shown that at small levels of the input power the discharge is initiated in a thin region of high electric field at the tip of antenna. The size of the plasma region increases with the input power and the discharge grows in size. The discharge center is still fixed near the tip of the electrode. At a certain power value (the upper limit) the discharge gets detached from the tip of the antenna and runs towards the generator. In this case the stationary discharge is maintained at the entrance of the discharge chamber. This value of the input power determines the largest size of the EMD. It is shown that the largest size of the plasma ball can not exceed the quarter of the generator’s wave length. Thus in order to increase the plasma size one needs to decrease the field frequency.

3.4. Gas temperature
The gas temperature in the hydrogen EMD plasma was determined from the relative intensities of rotational lines of the electron excited molecules $H_2(d^3\Pi_u)$. Calculations are based on the intensities of Q and R-branches emission for diagonal ($\nu' = \nu'' = 0, 1, 2$) bands of Fulcher $\alpha$-system $H_2(d^3\Pi_u \rightarrow a^3\Sigma_g)$. The rotational temperature of the ground state of $H_2$ is calculated taking into account the ratio of the rotational constants of the ground and excited states. The temperature had a flat radial distribution and does not exceed 1000 K at pressures below 10 Torr [13].

To determine the rotational temperature of the nitrogen plasma the analysis of non-resolved spectra of the 1<sup>st</sup> negative and 2<sup>nd</sup> positive system of the nitrogen emission has been used. In our conditions this temperature is assumed to be equal to the gas temperature. Gas temperature was less than 1000 K and the radial temperature profile was flat [21,26].
Since the discharge is a non-uniform gas dynamic system, there is a possibility of generating vortex flows that intensively mix the gas. Non-uniform gas dynamics can be caused both by gas feeding system and by the non-uniform heating of the electrode tip. This results in a non-uniform distribution of the gas temperature in the entire volume of the spherical plasma.

3.5. The EMD as “self-sustained-non-self-sustained” system
The analysis of the publications on the experimental results of microwave discharges and the modeling results of the EMD allows us to formulate the conception of “self-sustained-non-self-sustained” mechanism of the discharge. The discharge consists of the near-electrode region of self-sustained discharge, with an overcritical plasma density, surrounded by a ball-shaped region of non-self-sustained discharge, with an under-critical plasma density [19,21,23,26]. A layer of charge separation (similar to the double layer) exists on the outer plasma ball boundary and can be responsible for the abrupt decrease of the plasma density there. This layer might be a consequence of the self-consistency of plasma properties.

3.6. After-effects of EMD non-uniformity
The EMD is strongly non-uniform and this is a consequence of the electric field heterogeneity: the highest field exists near the electrode [11,15,16,29,23]. The strong heterogeneity of the electric field in the EMD leads to different physical processes in different parts of it [20,21,23,26]. Electron impact is the main channel for heavy particles excitation and ionization near the electrode, while secondary processes with the participation of excited particles determine the processes in the plasma ball region. In the nitrogen plasma this leads to the fact that the $^2$N$^+$ nitrogen band emissions prevail over others in the near-electrode region with main power consumption while the $^1$N$^+$ nitrogen band emissions give the principal part of the emission in the spherical part of the EMD. The behaviour of the ion profiles is an illustration for this effect: the N$^+_2$ ion is the dominant one near the electrode, while N$^+_4$ prevails over others in the ball region. The near-electrode region is the source of excited particles for spherical part of plasma. The non-uniformity also leads to changes of the channels of charged particles losses along the radius (figure 5).

3.7. Generation of layers of charge separation
Recent simulations showed that charged layers can be created in the plasma with a sudden increase of the electric field and of the ionization rate. A one-dimensional, quasi-static model for a stationary microwave nitrogen discharge inside spherically symmetric system of electrodes has been used [20]. The model consists of the microwave field equation in quasi-static approximation, the Poisson equation, the balance equations which describe the kinetics of the charged (e, N$^+_2$, N$^+_4$) and neutral (N$^2$(A$^3\Sigma^+u$), N$^2$(B$^3\Pi_g$), N$^2$(C$^3\Pi_u$), N$^2$(a$^1\Sigma^+_u$)) plasma components, and the time-independent homogeneous Boltzmann equation for electrons obtained in the two-term approximation. The kinetic scheme involves direct electron impact ionization, step and associative ionization, volume and wall recombination of charged and neutral particles, ion-molecular reactions, and excitation and de-excitation processes for molecules. Processes with vibrationally excited molecules are accounted for by using the well-known analytical expression for the vibrational distribution function (VDF) obtained in the diffusion approximation [27]. This condition is satisfied in strongly non-uniform microwave discharges in the plasma resonance region (figure 6). The charge separation ($\Delta n = (\Sigma N^+_i - n_0)$) induces the static electric field and this can be considered as one of the possible reasons for the sharp external boundary of the EMD.
4. EMD applications

The EMD gives the possibility: to study and to produce plasma chemical processes, to intensify physical-chemical processes in gas phase, including the burning process, to study the interaction of plasma with solids, to study the behavior of solids surrounded by a plasma with gas flows, and to study the interaction of plasma formations with gas flows.

Notwithstanding the fact that our knowledge on EMD physics is not complete, we have some examples of successful and promising EMD applications. It is necessary to mention some obvious disadvantages of the EMD, which can be important in research perspectives of this type of discharge. The considerable non-uniformity of the plasma leads to low spatial homogeneity of plasma-surface processing. We also indicate a low level of plasma absorbed power.

4.1. Diamond growth

The EMD have been used for diamond growth and the deposition of diamond-like films [1,3,28]. The process is held at a 15 Torr pressure in the mixture H\textsubscript{2} + (1–10%) CH\textsubscript{4} with a stainless steel electrode [1,3] and at a 20 Torr pressure in the mixture H\textsubscript{2} + 0.4% CH\textsubscript{4} with a graphite electrode [28]. Several results are shown in figures 7, 8 [3]. Deposition is made on silicon wafers at temperature of 1000 °C. It is known that the quality of the deposit is increased by adding oxygen and this is illustrated by curves 1 and 2 in figure 8. Deposition rate was of 1 \(\mu\)m/h. It is shown that the risk of contamination of the plasma vessel and of the treated surfaces in EMD by products from electrode erosion is small [1,3]. The method of electron spectroscopy for chemical analysis showed no traces of products from electrode erosion in plasma-treated substrates in experiments on the diamond growth when the electrode was heated up to the red-heat temperatures and the temperature of the substrate, located at the distance of 1 cm from it, was 1000 °C. The problem of electrode erosion is very important for RF and DC discharges. As the field frequency increases, the thickness of the electrode sheath decreases (the electron density is high enough to exceed the critical density) and the energy of the ions bombarding the electrode decreases as well. This fact is also a distinctive feature of the EMD plasma. The role of the electrode is only in the formation of the microwave field structure.

The EMD is a strongly non-uniform system and the deposition rate depends both on the distance of substrate from the electrode \((d_0)\) and the distance from the center of the substrate. Experimental deposition rates can be approximated as \(K(r) \approx \alpha (d_0^2 + x^2)^{-1}\) where \(r\) is the distance from the point on the substrate from the center of plasma ball [28]. It is important that deposits on the substrate were
observed also outside the luminous plasma ball. This means that the dark discharge region is active and the above formula reflects the distribution of active particles around the electrode.

**Figure 7.** Microphotograph of the substrate after deposition [3].

**Figure 8.** Raman spectra of deposits. Curve 1 – 400 sccm H$_2$ + 16 sccm CH$_4$, curve 2 – 400 sccm H$_2$ + 16 sccm CH$_4$ + 1 sccm O$_2$ [3].

There are three methods to increase the size of homogeneously treated surfaces. The first is obvious: one has to decrease the microwave frequency. The second one relies on using a discharge system with several electrodes [28]. The third relies on using a dilative, conical electrode. Figure 9 shows that the radial distribution of the ion probe saturation current for a conical electrode is flatter than that for cylindrical one (the plane of measurements is placed at the distance of 5 mm below the tip of the electrode and perpendicular to its axis) [5].

**Figure 9.** Double probe ion saturation current in the hydrogen EMD for a cylindrical and for a conical electrode [5].

**Figure 10.** Microphotograph of a silicon substrate after CN–film deposition [30].

### 4.2. Coating deposition

Mixtures of different plasma gases with hydrocarbons are used for deposition of amorphous and polycrystalline coatings. The EMD with a graphite electrode in the mixture 0.9 Torr H$_2$ + 0.1 Torr CH$_4$ has been used for the deposition of nanotubes on a heated Ni substrate at an incident power of 250 W [29]. The density of the deposit was inhomogeneous over the substrate surface.
The possibility of deposition of CN_x-films with a mixture of N_2 and C_2H_2 at a pressure of 1 Torr (power consumption 2–40 W) on silicon, glass, Al, paper and polymer films have been demonstrated in [30]. The temperature of substrates is varied between 30 and 700 °C. The deposit is non-uniform and the highest thickness is observed under the electrode. Coatings on silicon wafers have a columnar structure and columns are oriented perpendicular to the surface. The tops of the vertical columns are seen in figure 10 along with a few columns deliberately placed on the surface for illustration. The hardness of the coating decreases with the content of C_2H_2 in the mixture. The nitrogen content in the deposit does not exceed 10 atomic percent. The nitrogen content in the polymer-like films deposited on thermal-sensitive substrates does not exceed 5 atomic percent.

Melting Cu and Al electrodes at high microwave powers have been used for the deposition of Cu and Al films on Pyrex and stainless steel substrates in hydrogen plasmas. Deposits include droplets of the metals [29]. Mixtures of hydrogen with nitrogen or oxygen have been used for the deposition of TiN and TiO_2 films on stainless steel substrates [29].

4.3. The EMD as a source of O_2(a^1Δ)

The study of the conditions for the generation of the oxygen O_2(a^1Δ) singlet is of interest for researchers in the frame of numerous tasks in organic chemistry, plasma chemistry, and laser physics [31]. Gas discharges are one of the sources of O_2(a^1Δ). The process of O_2(a^1Δ) generation has been tested for the EMD on the base of a 1D quasi-static model for oxygen discharges at different pressures [25]. Several results are presented in figure 11. At a pressure of 1 Torr the calculated concentration of O_2(a^1Δ) is close to the theoretical limit (25%) and the radial distribution concentration is close to homogeneous. A pressure increase leads to a reduction of the concentrations and its homogeneity becomes worse. This model gives a good description of the EMD, so we can expect that an EMD at low pressures would be an effective generator of O_2(a^1Δ) for different applications.

4.4. The EMD as a plasma cathode

The installation shown in figure 1 allows the operation in the absence of galvanic coupling between the antenna and the chamber and thus to study the EMD properties in the external, static field. This field can be produced by an external DC power source. The DC voltage-current characteristics of the EMD have been studied in [22] (see figure 12). It was shown that the dark space of the discharge is a conductive medium. The DC current grows with the microwave power at constant pressure and falls with pressure at constant power. In the range of voltages shown in figure 13 the EMD does not change.
its structure. At higher positive DC voltages with respect to the chamber the DC current increases by two orders of magnitude and a secondary surface discharge (non-self-sustained) appears near the walls of the chamber. However, the magnitudes of these voltages are still not enough for the generation of an ordinary DC discharge. At high negative electrode voltage the EMD can become extinguish.

The peculiarity of this DC circuit is that the conductivity of the dark part of EMD is much less than that for the active part of the EMD with effective microwave ionization. This is why the external DC voltage is applied to the outer dark part of the discharge but not to the active part. The voltage-current characteristics in figures 12 are determined by the dark space and the sheath near the discharge walls. This fact is confirmed by simulations (figure 13) [22].

![Figure 12](image12.png)

**Figure 12.** Experimental DC voltage-current characteristics of the nitrogen EMD at different powers (a) and pressures (b) [22].

![Figure 13](image13.png)

**Figure 13.** Calculated DC voltage-current characteristic of the EMD (a) and radial distribution of DC field E in nitrogen EMD at different applied voltages (b) [22].

The EMD plays the role of a plasma cathode. Thus the low power microwave source and the external DC voltage can activate the medium in a large volume and gives a possibility to process the internal surface of details with large dimensions. The danger of wall atomization is small because the secondary surface discharge is a low voltage one and is non-self-sustained.

5. Conclusion

Non-equilibrium electrode microwave discharges attract the interest because of its unique physical peculiarities and of its promising applications. This type of discharge is representative of strongly non-uniform discharges and thus combines the properties of quite different discharges. Physical processes
in the EMD are different in various regions of the discharge. The plasma content (excited and charged particles) is also different. This discharge can be attributed to the class of “self-sustained-non-self-sustained” ones. Although experiments and modeling already gave answers to plenty of questions, many problems are still unsolved and a detailed study of the nature of the abrupt external discharge boundary, of the behavior of the EMD in external fields and in gas flows, etc., is needed. The EMD can be effectively used in plasma chemistry for the treatment of surfaces, for coating deposition or as a plasma cathode. The search for new applications of the EMD is also a subject for further studying.

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References
[1] Bardos L, Barankova H, Lebedev Yu A, Berg S and Nyberg T 1996 Proc. 7th European Conf. on Diamond, Diamond-like and Related Materials, Tours, France, 4.1
[2] Brandt A A and Tikhomirov Yu V 1974 Plasma multiplators of frequency (Moscow: Nauka, in Russian)
[3] Bardos L, Barankova H, Lebedev Yu A, Nyberg T and Berg S 1997 Diam. Relat. Mat. 6 224
[4] Bardos L and Lebedev Yu A 1998 Tech. Phys. 43 1428
[5] Bardos L and Lebedev Yu A 1998 Plasma Phys. Rep. 24 956
[6] Lebedev Yu A, Mokeev M V and Tatarinov A V 2000 Plasma Phys. Rep. 26 272
[7] Lebedev Yu A and Mokeev M V 2000 High Temp. 38 338
[8] Bardos L and Lebedev Yu A 2000 High Temp. 38 528
[9] Bardos L and Lebedev Yu A 2001 Plasma Phys. Rep. 27 418
[10] Lebedev Yu A and Mokeev M V 2002 Tech. Phys. 47 135
[11] Lebedev Yu A, Tatarinov A V and Epstein I L 2002 Plasma Sources Sci. Technol. 11 146
[12] Lebedev Yu A and Mokeev M V 2003 Plasma Phys. Rep. 29 251
[13] Lebedev Yu A and Mokeev M 2003 Plasma Phys. Rep. 29 1059
[14] Lebedev Yu A and Mokeev M 2003 High Temp. 41 725
[15] Lebedev Yu A and Tatarinov A V 2004 Plasma Sources Sci. Technol. 13 1
[16] Lebedev Yu A, Mokeev M V, Tatarinov A V and Epstein I L 2004 Plasma Phys. Rep. 30 91
[17] Lebedev Yu A and Shakhatov V A 2006 Plasma Phys. Rep. 32 58
[18] Lebedev Yu A, Tatarinov A V and Epstein I L 2006 High Temp. 44 317
[19] Lebedev Yu A, Epstein I L, Tatarinov AV and Shakhatov V A 2006 J. Phys.: Conf. Ser. 44 30
[20] Lebedev Yu A and Epstein I L 2007 Plasma Phys. Rep. 33 63
[21] Lebedev Yu A, Solomakhin P V and Shakhatov V A 2007 Plasma Phys. Rep. 33 157
[22] Lebedev Yu A, Tatarinov A V and Epstein I L 2007 High Temp. 45 283
[23] Lebedev Yu A, Tatarinov A V and Epstein I L 2007 Plasma Sources Sci. Technol. 16 726
[24] Shakhatov V A and Lebedev Yu A 2008 High Energ. Chem. 42 207
[25] Lebedev Yu A, Tatarinov A V and Epstein I L 2008 High Temp. 46 645
[26] Lebedev Yu A, Solomakhin P V and Shakhatov V A 2008 Plasma Phys. Rep. 34 614
[27] Gordietz B, Osipov A and Shelepin L 1980 Kinetic Processes in Gases and Molecular Lasers (Moscow: Nauka)
[28] Taniyama N, Kudo M, Matsumoto O and Kawarada H 2001 Jpn. J. Appl. Phys. 40 L698
[29] Eto A, Kimura S and Kando M 2003 Microwave Discharges: Fundamentals and Application ed Ohl A (Greifswald, INP) 65
[30] Bardos L, Barankova H and Lebedev Yu A 1999 42nd Ann. Conf. of Soc. of Vac. Coaters, Chicago, IL, Proc. SVC TC paper E-7
[31] Ionin A A, Kochetov I V, Napartovich A P and Yuryshev N N 2007 J.Phys.D: Appl.Phys. 40 R25