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Nano-scale Dipole Electrodes for Subcritical Discharges

S. Popović and L. Vušković
Department of Physics, Old Dominion University
Norfolk, Virginia 23529

Abstract

We propose a concept for nanoscale initiation of subcritical microwave discharges using carbon nanotubes. We find arguments in favor of this concept by considering diffusion and the field emission processes around the tip of single-wall carbon nanotubes. This promising mechanism may enable generation of sub-microwave discharges at atmospheric conditions at non-prohibitive power levels.

1. Introduction

Employing carbon nanotubes (CNTs) in electric discharges is promising, but not obvious application of CNTs. CNTs have been declared as a potential candidates for the electrodes in fuel cells, or as the electrodes for diagnostics on molecular level, but seldom as cathodes or anodes in an electrical discharge. However, researchers at Samsung [1] have demonstrated a fully sealed 4.5x4.5 sq. inch, 2.4 mm thick display operating on the CNT field emission mechanism. Since then, several other groups have reported the development of devices based on field emission from nanotubes. The effect of the field emission has been studied using CNTs both as conductors and semiconductors, but not in the context of electrical breakdown and self sustained electrical discharges. In the following we are making the case for CNTs as nanoelectrodes for electric discharges, or as nano-scale initiators for sub-critical microwave discharges, operating at high E/N and with high field enhancement factors. In addition to the field enhancement at the cut-off tip of a CNT or a CNT rope, the seeding of electrons through field emission is potentially positive factor that further contributes to field enhancement.

Basis for present analysis lays in the fact that in the electric discharges the scaling parameter for length is actually N d, where d is a distance (for instance the gap distance, or the radius of the electrode tip) and N is the neutral particle density. In analogy, the scaling parameter for the electric field E is the reduced electric field, E/N. Therefore, if we want to increase the density, for instance, in the electric discharges at atmospheric pressures, we have to decrease the distance, d. Furthermore, if we want to increase the reduced electric field and generate electric breakdown, we would have to enhance locally the electric field. In the sub-critical microwave discharge, this has been accomplished by introducing the half-wavelength dipole initiators, where an additional scaling parameter is the sub-criticality factor, λ/d, where λ is the microwave wavelength [2]. Therefore, by reducing the size of the tip of electrode we can enable the increase of density N and the increase of the sub-criticality factor, λ/d. In order to clarify this, we will show in the following that the realization depends on several other factors.

First, in order to start the avalanche process, at least one primary electron has to be present in the volume during the time interval of the electric field enhancement. Having in mind the short pulse duration and miniature enhancement volume, the probability that a cosmic ray generate the primary electron is very low. Hence, breakdown is delayed by a statistical time lag. When the statistical time lag exceeds the pulse duration, the breakdown does not happen, and the discharge does not start. Therefore the electron seeding process has to be established in the form of simmer current, nuclear radiation, ultraviolet photons to extract photoelectrons from the surface, or the field emission.

Second, the diffusion of electrons has to be properly accounted for. Once an electron is injected into the field enhancement volume, there are no guaranties that it will stay there long enough in synchronism with the field pulse, to start the avalanche process. Also, the electron may undergo a variety of elementary processes with the surrounding atoms and molecules where it may be attached or recombined thereby reducing or eliminating the contribution to the avalanche process.

Third, the discharge is composed of a multitude of filaments each being individually attached to a single CNT electrode. The tip of the electrode has to endure the operation cycle without melting, ablating or changing some other vital characteristic. Above all, the electric conductivity and the thermal conductivity have to be as high as possible.

Fourth, the electrostatic effect of the neighboring CNT electrodes has to be eliminated. Therefore, the spacing between the electrodes has to be adjusted so that each of them has its own field enhancement volume, not interfering with the neighbor CNT electrode.

In the following we will make the case for carbon CNTs to meet all the requirements, and that, with a proper fabrication process, they can be made to operate in the deeply sub-critical regime, at atmospheric pressure with the very moderate electric field requirement outside the field enhancement volume. This means that the prohibitive equipment weight and cost for microwave discharges at atmospheric pressure can be eliminated.

Rosen et al [3] have demonstrated experimentally that presence of CNTs on molibdenum-based surfaces of surge protection devices reduced their mean breakdown voltage by about 25%. Application of single-wall CNTs especially decreased the run-to-run variability (by a factor of 4-20) of conventional gas discharge tube protectors (GDTs). The effect of field emission responsible for the electron seeding in the vicinity of the electrodes has produced observable results, although the tubes were facing the electric field side-on in this arrangement. Furthermore, the CNT electrode bundles were distributed randomly over the surface. The effect was observable in the terms of breakdown voltage and substantial in the terms of reduction of variability.

In this paper we propose a different approach. Our analysis requires the growth of CNT electrodes facing end-on the electric field, where field emission is increased in comparison to the side-on arrangement. Contrary to the relatively moderate effect obtained using CNT bundles, this arrangement is expected to enhance the electric field around the CNT electrode by orders of magnitude. Besides the field enhancement, the

free electron seeding by field emission will further reduce the statistical time lag. By comparison, referring to the experiment of Ref. [3], the enhancement of the field in the electrodes was minimal due to the side-on arrangement and due to the interference of the neighboring CNTs in the bundle. We intend to utilize a modification of the techniques for spatially-organized growth of CNT electrodes described in the literature [4-7] in order to obtain maximum field enhancement effect from an individual CNT.

2. Sub-critical microwave breakdown in air

In the linear approximation, when the process of dissociative recombination of electron and positive molecular ions can be neglected, the balance of electron population can be described as

$$\frac{\partial N_e}{\partial t} = D \cdot \Delta N + (\nu_i - \nu_a) N_e + \left(\frac{\partial N_e}{\partial t}\right)_{seed} \qquad (1)$$

where N_e is the electron density, $\left(\frac{\partial N_e}{\partial t}\right)_{seed}$ is the rate of electron seeding by photoelectric effect, photo ionization or field emission, D is the coefficient of ambipolar diffusion, ν_i is the rate of the ionization process $e + M_2 \rightarrow 2e + M_2^+$, and ν_a is the rate of the dissociative attachment process $e + O_2 \rightarrow O + O^-$. Dissociative recombination and three-body electron attachment processes are neglected, since we are dealing with low electron density around breakdown threshold, at very high E/N values. This assumption is justified in the initial stage of the breakdown. Ionization frequency is approximated [8] by

$$\nu_i = \nu_a \left(\frac{E}{E_0}\right)^{\beta}, \qquad (2)$$

where $\beta = 5.3$, E is the local value of field amplitude, and the amplitude of the breakdown microwave field is

$$E_0 = 30p\sqrt{2\left(1 + \frac{\omega^2}{\nu_c^2}\right)}, \qquad (3)$$

where p is the pressure and ω is the angular frequency of the field. According to Ref. [8], attachment frequency and momentum transfer frequency are given by $\nu_a = 6.4 \times 10^4$ p and $\nu_c = 4.0 \times 10^9$ p, respectively, (frequencies are in s^{-1} when p is in Torr).

We define the microwave breakdown criterion in the vicinity of a conductor as the condition when the electron density rate changes sign:

$$\frac{\partial N_e}{\partial t} = 0. \tag{4}$$

The Eq. (4) indicates that the electron losses, such as electron diffusion and attachment, are compensated by the electron gains from ionization and seeding.

3. Enhancement of Microwave Field

We will now compare the two generic electrode configurations, a sphere (nanoparticle) and an ellipsoid (CNT), and demonstrate the favorable effect of field enhancement on the tip of a CNT.

3.1. Spherical Conductor

When a conductive sphere of radius $R<<\lambda/2\pi$ is placed in the external microwave field of amplitude E_{ex}, the field in the direction of the external field, at a distance r from the center of the sphere can be expressed by

$$E = E_{ex}\left(1+\frac{2}{\left(\frac{r}{R}\right)^3}\right). \tag{5}$$

At the poles of the sphere facing and opposite with respect to the direction of the field it is $3E_{ex}$.

The diffusion Eq. (1) for electron density can be transformed into the Airy equation for the electron density distribution around the sphere:

$$\frac{\partial^2 \varphi}{\partial z^2} + \frac{z}{b^2 B^2}\varphi = 0, \tag{6}$$

where $\varphi=N_e\rho$, $\rho=r/R$, $z=bA-bB(\rho-1)$, $b=\nu_a R^2/D$, $A=(3\ \varepsilon)^{\beta}$, $B=2\beta(3\ \varepsilon)^{\beta}$, and $\varepsilon=E_{ex}/E_0$. Boundary condition at the surface of the sphere is $\varphi=0$ for $\rho=1$ because $N_e=0$ at the surface of the sphere. For simplicity, we assume that the sphere is not charged initially. Hence, the analytical solution of Eq. (6) can be expressed in the form of Bessel function:

$$\varphi = C\sqrt{z}\left[J_{\frac{1}{3}}\left(\frac{2z^{\frac{3}{2}}}{3bB}\right)+J_{-\frac{1}{3}}\left(\frac{2z^{\frac{3}{2}}}{3bB}\right)\right] \qquad \text{for } z>0, \text{ and} \tag{7a}$$

$$\varphi = C(-\sqrt{z})\left[J_{\frac{1}{3}}\left(\frac{2(-z)^{\frac{3}{2}}}{3bB}\right)+J_{-\frac{1}{3}}\left(\frac{2(-z)^{\frac{3}{2}}}{3bB}\right)\right] \qquad \text{for } z<0. \tag{7b}$$

At the boundary condition, Eq. (7a) gives

$$\frac{2z^{\frac{3}{2}}}{3bB} = 2.338. \tag{8}$$

Taking $z=bA$ at the surface, diffusion length for electron attachment $l_a = \sqrt{\frac{D}{\nu_a}}$ and assuming ambipolar diffusion coefficient to be $D=D_a=1.4\times10^4$ p (in cm^2/s when p is in Torr), we obtain the breakdown criterion for the external electric field so that the microwave breakdown takes place at the pole facing the direction of the field:

$$\frac{l_a}{R} = \frac{\left[(3\varepsilon)^\beta - 1\right]^{\frac{3}{2}}}{7.2\beta(3\varepsilon)^\beta}. \tag{9}$$

For a given radius of the sphere and the given pressure, the nonlinear algebraic Eq. (9) will give the subcritical, external electric field. Subcritical breakdown fields for spheres of different radii, given in Fig.1, illustrate why the conductive sphere is only a partial solution for the sub-critical microwave breakdown. The breakdown field is increasing as the sphere radius is decreasing. From Eq. (5) we see that the enhancement factor cannot be greater than three. Therefore, a nano-scale spherical conductor does not contribute to the field enhancement and it is not favorable to use it in subcritical microwave discharges.

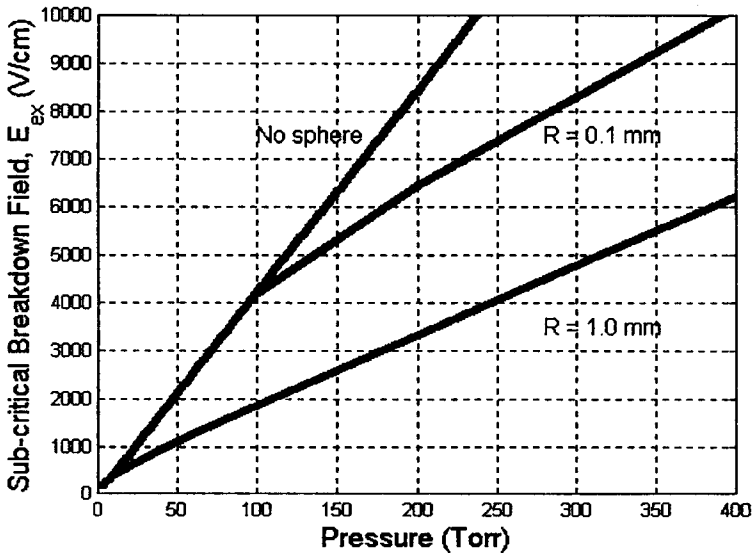

Figure 1. Subcritical breakdown with a conductive sphere.
Radius of a sphere, R is indicated.

3.2. Half-wavelength dipole conductor

Consider now a half-wavelength long dipole with a sharp tip parallel to the field. We will take the similar consideration as in Section 3.1 but instead of the sphere we will approximate the dipole with a narrow conductive ellipsoid. In the case of resonance when the length of the dipole is equal to one half of the microwave wavelength, we obtain enhancement factor for the field:

$$\varepsilon_d = \frac{E_{tip}}{E_{ex}} \approx 0.255\frac{\lambda}{R}, \tag{10}$$

where E_{tip} is the enhanced field at the tip of the dipole, λ is the wavelength of the field, and R is the radius of the curvature of the tip. In the absence of diffusion effect, this would be the field enhancement factor. However, at the atmospheric pressure this is not the case and the breakdown criterion, as in the case of the sphere, is defined as

$$\frac{l_a}{R} = \frac{\left[(3\varepsilon_{br})^{\beta} - 1\right]^{\frac{1}{2}}}{7.2\beta(3\varepsilon_{br})^{\beta}}, \tag{11}$$

where

$$\varepsilon_{br} = \frac{E_0}{E_{ex}}. \tag{12}$$

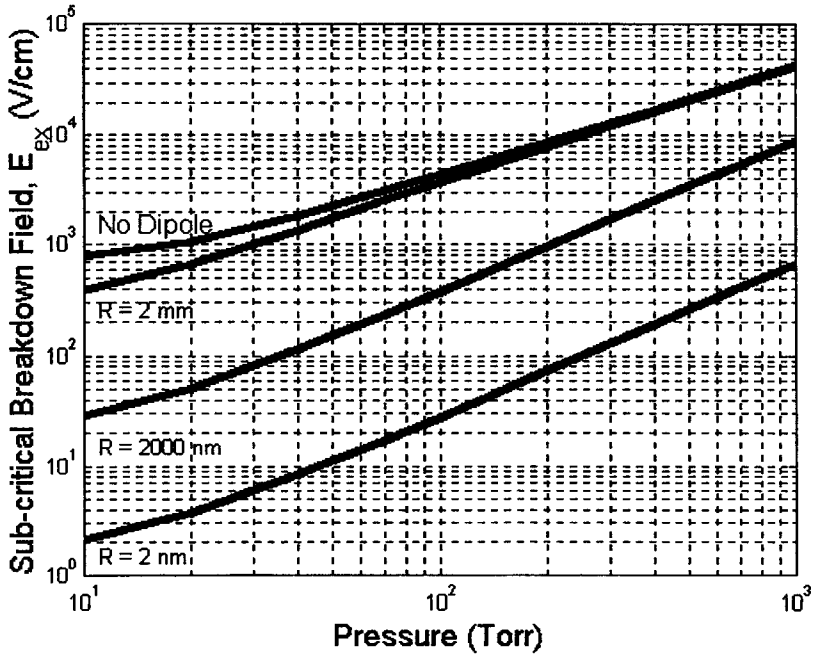

Figure 2. Subcritical breakdown with a cylindrical dipole.
Microwave frequency of 60 GHz was assumed.
Radius of the curvature of the tip, R is indicated.

As in the case of the sphere, the unknown external field E_{ex} defining breakdown for the given frequency, pressure, and the radius of the electrode tip is obtained by solving Eq. (11). The results are given in Fig. 2 for an extreme wavelength frequency of 60 GHz, which is interesting because of unusually high absorption by oxygen. For lower wavelengths corresponding to Ku-band or X-band the result would be even more favorable. In the other words, the electrode tip, designed to satisfy breakdown condition at 60 GHz and a given pressure, will easily satisfy the breakdown condition for all other frequencies of interest. The length of the half wavelength dipole should be adjusted accordingly.

4. CNT Electrodes in Subcritical Microwave Discharge

Relevant characteristics of the single-wall, conductive CNTs are given in Table I. This table is compiled on the basis of experimental results reported in Refs. [4-7,9-14].

Table I. CNT Characteristics.

Quantity	Reported Value	Estimated Limit
Electrical resistivity	10^{-4} Ωcm	
Current density	20 μA/0.5 mm^2	4 10^7 A/cm^2
Dissipated power	320 μW	
Volume	10^{-16} cm^3	
Power density	> GW/cm^2	
Thermal conductivity		2000 W K/m
Young's modulus	10^{12} Pa	

The CNTs have demonstrated high thermal conductivity and high tolerance for dissipated power. These properties, combined with the high current density limits are all favorable for the application in generation of sub-critical microwave discharges.

It can be demonstrated relatively easy that the field enhacement factor required for the field emission current from CNT is much smaller than the field enhancement factor in the microwave field, given by Eqs. (11) and (12). Therefore, it can be expected that a strong field emission current, of the order of 100 $\mu A/cm^2$, will provide the seeding electron fluence of about 10^8 $cm^{-3}s^{-1}$, which is more than most nuclear or photoemission seeding devices provide.

In order to eliminate the negative effect of electrostatic interference between individual nanotubes, the CNTs should be spatially distributed so that the every one tube is exposed to the applied field, E_{ex}, and the effect of the field enhancement due to the neighboring electrodes is negligible. This condition can be formulated as $E_{tip}(R/d)^3 = E_{ex}$ where d is

the distance of separation between the CNTs. Using the Eq. (11) for the field enhancement, we obtain $d/R \approx (\lambda/R)^{1/3} \approx 100$.

It is obvious that, for the best effect, the CNTs should not be implemented in bundles or any other densely packed structure. Separation distance should be of the order of 100 nm. This, relatively sparsely packed structure could still contain 10^9 CNTs per cm^2 and support relatively high current density and power dissipation, typically encountered in the discharges at atmospheric pressure.

5. Conclusion

Conductive carbon nanotubes can be used as elements of the initiators for subcritical microwave discharge. Using the standard diffusion approach to subcritical microwave breakdown, we found that the half-wavelength dipoles enhance the microwave field by more than two orders of magnitude when CNTs are imbedded on their surface. Therefore, by using CNTs in the initiators the power requirements for generating and sustaining the microwave discharge at atmospheric pressure would be less prohibitive.

Several properties of CNTs combine favorable to support this concept. Field emission current could be strong enough to eliminate the statistical time lag for the inception of the discharge, thereby providing an inherent seeding mechanism. Thermal and electrical conductivity indicate that CNTs could sustain the level of power dissipation encountered in a high pressure microwave discharge. In order to exploit fully their field enhancement and seeding mechanisms, an adequate spatial arrangement of CNTs is required.

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