

# Electrical characterisation of a double DBD in He at atmospheric pressure used for surface treatments

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This study is focus on the double discharge formation and its properties with respect to the influence of various factors such as dielectric material and the parameters of the applied high voltage. A secondary discharge was induced at the end of a slow falling voltage flank, when a semi-sine uni-polar pulse voltage excites the DBD. The secondary discharge is always formed and its amplitude, as well as the amplitude of the main discharge depends on surface properties of the dielectric barrier and on the electrical parameters of the applied voltage. The most efficient treatment of a polymer sample in DBD plasma is made if the polymer is placed on the ground electrode. Moreover, the polymer site which is found towards the ground electrode is three times roughness than the other one.

(Received February 15, 2005; accepted August 22, 2007)

**Keywords:** Atmospheric pressure glow discharge, Pulsed dielectric barrier discharge, Secondary discharge, Polymer surface treatment, AFM

## 1. Introduction

The dielectric barrier discharge (DBD) produces non-equilibrium highly collisional plasma at rather high gas pressure by a high voltage pulse applied to a special system of electrodes [1-3]. Changing shape of the electrodes and the gap distance, gas composition, magnitude, excitation frequency and/or pulse duration of the applied voltage can produce different discharge modes of the DBD. There are two main modes: filamentary and homogeneous discharge (also named diffuse mode), respectively. Moreover, the homogeneous discharge can appear in two forms: glow discharge and Townsend discharge [4].

Usually, the so-called classical DBD driven by a sine wave voltage [5] is primarily used for applications. But, it was emphasized [6-11] that in any application (ozone generation, pollutant destruction, surface treatment, excimer lamp) [9, 12-15] the pulsed DBD is more efficient than that classical one. Moreover, it was found that in some experimental conditions of the pulsed barrier discharge, besides the main peak current a second current pulse with inverse polarity is induced at the decreasing applied voltage flank [7, 8-10, 12]. According to the results reported by Liu [6-9], the secondary discharge can be produced in a large range of the gas mixture and pressure, different types of electrodes and geometry as long as unipolar square voltage pulses are applied to the reactor. In our experimental conditions, secondary discharge in helium and helium with reactive gasses mixture (He+N<sub>2</sub> [15] and He+O<sub>2</sub> [16]) was produced during a semi-sine unipolar voltage pulse with slow rising and falling flank (15  $\mu$ s), in plane-parallel geometry [17]. The secondary discharge was formed for both modes, glow and filamentary. In latter case, both the primary and the secondary discharges consist of multiple current pulses.

In a previous paper [18] we have studied the influence of water vapour on acetaldehyde removal efficiency by BDB.

In the present paper a pulsed barrier discharge in helium at atmospheric pressure, in a glow mode, is discussed because it is suitable for surface treatments. The electrical diagnosis was used to study the atmospheric pressure DBD plasma in He. The study is focus on the secondary discharge formation, due to the fact that the secondary discharge might appear without supplementary energy from the outside electric circuit. The influence of the surface properties of the barrier material and the parameters of applied high voltage on the development of the both primary and secondary discharges was studied.

## 2. Experimental set-up

The dielectric barrier discharge (DBD) was produced in two similar reactors with two identically plane-parallel electrodes, as in Fig. 1, but different surfaces  $1.6 \times 6.5$  1 cm<sup>2</sup> and  $1.6 \times 3.2$  1 cm<sup>2</sup>, respectively. The copper electrodes are centred on the dielectric plates. Three different dielectric materials have been used as barriers: glass, ZrSnTiO ceramic (ZST) and polyethylene terephthalate (PET). Properties of the dielectric barriers studied in this paper are given in Tabel 1. The gas gap is always maintained constant at 3 mm. The high voltage power supply generates monopolar semi-sine pulses of 1 to 10 kV, pulse duration between 10  $\mu$ s to 45  $\mu$ s and frequency in the range 10 Hz to 10 kHz (TERAFLUX). A mass flow controller regulates the helium mass flow rate,  $Q_{He}$ . The flowing gas was injected into the discharge gap via a tank with multiple holes disposed along the gap and parallel to the electrodes, as in Fig. 1.

The experiments are made at room temperature, in spectral helium (Linde Gas, purity 4.6) without preliminary vacuum pumping. Consequently, the helium gas is mixed with impurities desorbed from the dielectric surfaces or inner surface of the pipes, tank and discharge chamber even if it works in clean laminar flowing gas.

This mode of operation is motivated by the conditions used in industrial system for plasma surface treatment of the materials.

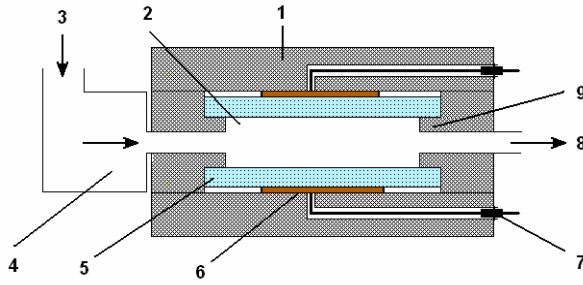


Fig. 1. Cross section of the DBD system; 1- chamber, 2 - gap space and discharge chamber, 3 - gas inlet, 4 - tank, 5 - dielectric barrier, 6 -Cu electrode, 7 - electrical contact, 8- gas outlet, 9- space holder.

The voltage  $U_a$  applied on the electrodes and the total current,  $I_t$ , through the entire reactor were stored using a 350 MHz digital oscilloscope (LeCroy WaveSurfer 434). The total current,  $I_t$ , was measured as voltage drop across the non-inductive resistor of  $150 \Omega$ , connected series to the ground, while the applied voltage on the electrodes was measured by the non-inductive resistance system.

### 3. Results and discussion

#### 3.1. Electrical characterisation of double DBD

The electrical circuit is basically a capacitive one [17]. The displacement current,  $I_d$ , was measured as circuit current without plasma between the electrodes. Therefore, the plasma current,  $I_p$ , is calculated subtracting the displacement current,  $I_d$ , from the total current,  $I_t$  measured with plasma formed between the electrodes (equation 1). Using the electrical model of homogeneous DBD proposed by Liu et al. [7], both the plasma voltage,  $U_p$ , and the dielectric voltage,  $U_d$ , of the DBD system in helium were calculated (equations 2-3). The plasma capacitance,  $C_p$ , was assumed to be constant and equal to the electrical capacitance before discharge ignition. The capacitance of the dielectric barrier,  $C_d$ , and the plasma capacitance,  $C_p$ , were calculated taking into consideration the reactor geometry. Thus, when the surface of each electrode is  $S_e = 5.04 \text{ cm}^2$ , we obtained that the plasma capacitance is  $C_p = 1.5 \text{ pF}$ . The dielectric capacitances of the two barriers,  $C_d$ , and the equivalent electrical capacitance of the DBD system,  $C_{DBD}$  (being calculated by using equation 4), are given in Tabel 1.

$$I_p(t) = I_t(t) - I_d(t) \quad (1)$$

$$U_p(t) = \frac{1}{1 + C_p/C_d} U_a(t) - \frac{1}{C_p + C_d} \int_0^t I_p(\tau) d\tau \quad (2)$$

$$U_d(t) = U_a(t) - U_p(t) = \frac{1}{1 + C_d/C_p} U_a(t) + \frac{1}{C_p + C_d} \int_0^t I_p(\tau) d\tau \quad (3)$$

$$\frac{1}{C_{DBD}} = \frac{1}{C_d} + \frac{1}{C_p} \quad (4)$$

The temporal evolution of the applied voltage,  $U_a$ , total current,  $I_t$ , plasma voltage,  $U_p$ , plasma current,  $I_p$ , and dielectric voltage,  $U_d$ , are presented in Fig. 2, for helium pulsed discharge in glow mode, and glass as barriers. The plasma voltage varies proportional in time with applied voltage, until the primary discharge turns on (points 1-2 in Fig. 2). The voltage across the dielectrics,  $U_d$ , starts increasing significantly only after the primary discharge breakdowns (marked 2 in Fig. 2). The rise of the  $U_d$  is due to the charges from the plasma volume being accumulated on the surface of the dielectric barriers. So, the primary discharge current charges the dielectric capacitance,  $C_d$ . After the primary discharge extinguishes (marked 3 in Fig. 2),  $U_d$  begins to decrease with a small rate (points 3-4 in Fig. 2) in comparison with that of the falling front of  $U_a$ , while the  $U_p$  decreases drastically (points 3-4 in Fig. 2). This fact is easily explained by taking into account the equation 3. It must be noticed that  $U_p$  presents a negative pulse (marked 4 in Fig. 2) when the applied voltage,  $U_a$ , decreases, even if the falling flank of  $U_a$  is not very fast. This negative pulse of  $U_p$  is produced by the electrical charges previously accumulated on the dielectric barriers. In this way a secondary discharge (point 5 in Fig. 2) with reversed polarity takes place at the falling flank of the applied voltage pulse due to the charges accumulated during the primary discharge [8-10] on the dielectric surface. Only after the secondary breakdown occurs, the  $U_d$  decreases significantly.

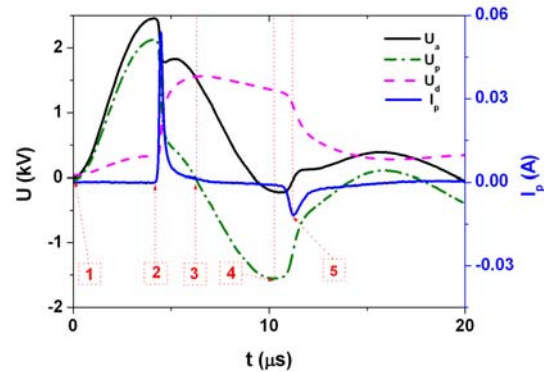


Fig. 2. Time evolution of applied voltage,  $U_a$ , and calculated values of plasma voltage,  $U_p$ , plasma current,  $I_p$ , and dielectric voltage,  $U_d$ , using glass as barriers.  $S_e = 5 \text{ cm}^2$ ,  $Q_{He} = 50 \text{ sccm} = \text{const}$ .

#### 3.2. Influence of the parameters of the applied high voltage over the secondary discharge

The influence of amplitude (Fig. 3) and duration (Fig. 4) of the applied voltage pulse on secondary discharge was investigated. The first, the delay time,  $\tau_d$ , was defined as duration between the primary and secondary current pulses. It was found that the  $\tau_d$  decreases when the applied voltage amplitude,  $U_a$ , grows (Fig. 3) and increases when pulse width,  $\tau_p$ , grows (Fig. 4).

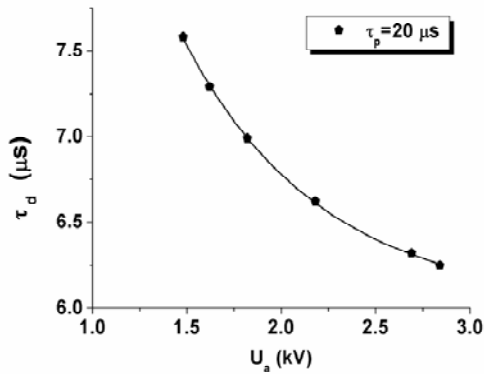


Fig. 3. Variation of delay time,  $\tau_d$ , versus applied voltage,  $U_a$ , for a constant pulse duration,  $\tau_p \approx 20 \mu s$ .  $S_e = 10 \text{ cm}^2$ ,  $Q_{He} = 90 \text{ sccm}$ .

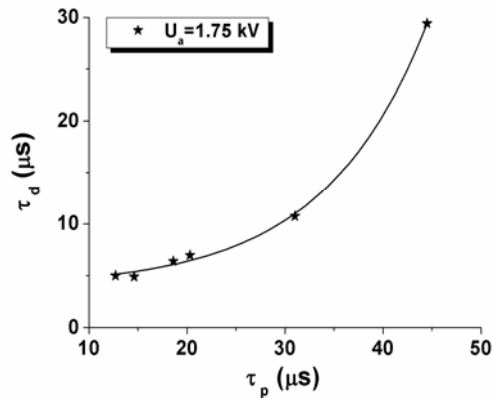


Fig. 4. Evolution of delay time,  $\tau_d$ , versus pulse duration,  $\tau_p$ , for a constant applied voltage,  $U_a = 1.75 \text{ kV}$ .  $S_e = 10 \text{ cm}^2$ ,  $Q_{He} = 90 \text{ sccm}$ .

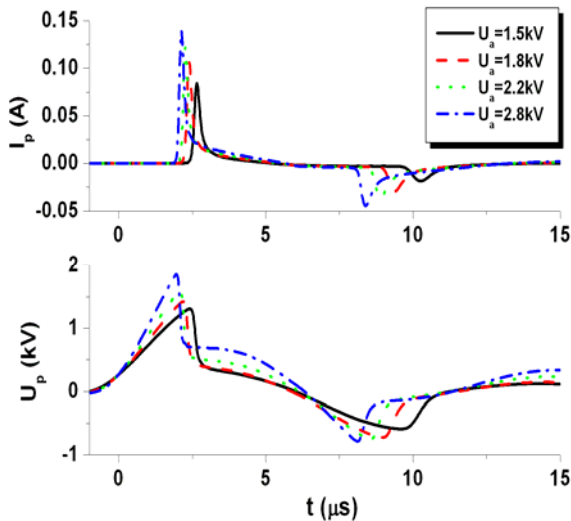


Fig. 5. Time evolution of plasma current,  $I_p$ , and plasma voltage,  $U_p$ , for different values of applied voltage.  $\tau_p \approx 20 \mu s$ ,  $S_e = 10 \text{ cm}^2$ ,  $Q_{He} = 90 \text{ sccm}$ .

Increasing the amplitude of the applied voltage pulse the discharge current increases too for both the primary and secondary discharge (Fig. 5). Due to the higher

electric field intensity in the gas gap, the breakdown of the both primary and secondary discharges is earlier. Larger intensity of the primary discharge more electric charges within the plasma system and more electric charges accumulate at the dielectric surface. The surface electrical charges accumulated on the dielectric conduct to polarity inversion of the plasma voltage earlier with the increase of the applied voltage. Consequently, when the applied voltage grows, the secondary breakdown is produced earlier (Figs. 3 and 5). Opposite situation has been observed with increasing of the pulse width (Fig. 4).

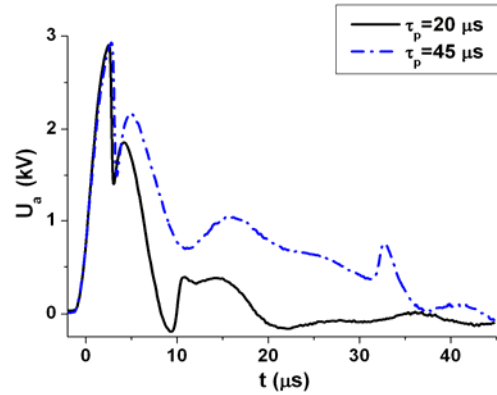


Fig. 6. Time evolution of applied voltage,  $U_a$ , for different values of pulse duration,  $\tau_p$ .  $S_e = 10 \text{ cm}^2$ ,  $Q_{He} = 90 \text{ sccm}$ .

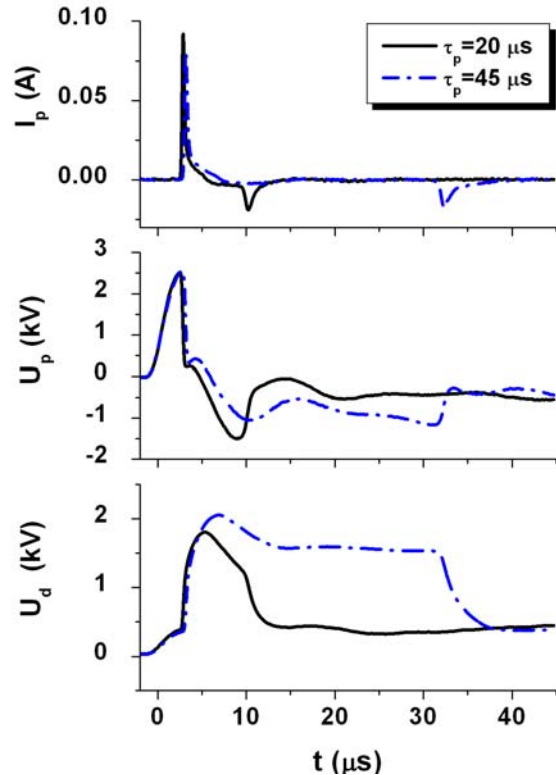


Fig. 7. Time evolution of plasma current,  $I_p$ , plasma voltage,  $U_p$ , and dielectric voltage,  $U_d$ , for different values of pulse duration.  $U_a = 2.9 \text{ kV}$ ,  $S_e = 10 \text{ cm}^2$ ,  $Q_{He} = 90 \text{ sccm}$ .

Increasing of the pulse duration pulse but constant amplitude of the applied voltage (Fig. 6) makes later appear of the secondary peak current (Fig. 7). This delay can be explained by slower decrease of the applied voltage with increase of the pulse width (Fig. 7). More exactly, taking into account the equation 3 and the fact that the time evolution of the dielectric voltage is little affected by the variation of the applied voltage pulse duration, we can note that the temporal evolution of the plasma voltage is governed by that of the applied voltage pulse.

Therefore, the double discharge phenomenon is produced for a large range of applied voltage values (Fig. 3). Furthermore, even if the values of the voltage pulse duration is triple and the rate of falling flank of the applied voltage pulse diminishes very much (about four times), the secondary discharge is still formed (Fig. 4), in spite of those reported by Liu et al [8].

### 3.3. Influence of the dielectric barrier type over the secondary discharge formation

The influence of the dielectric barrier type over the secondary discharge formation was studied. Three different dielectric materials were used as barriers: glass, ZST ceramic ( $\text{ZrSnTiO}$ ) and polyethylene therephtalate (PET). The parameters of the dielectric plates used as barriers are given in Tabel 1 as following the thickness,  $d_d$ , the electrical permittivity,  $\epsilon_r$ , the dielectric capacitance,  $C_d$ , and the equivalent electrical capacitance of the DBD system,  $C_{DBD}$ . In our conditions of the experiment, the secondary discharge is formed for any type of the dielectric used as barrier (Fig. 8. a).

However, the experimental results show that the dielectric materials play an important role over the discharge parameters. This role can acts in two ways. First way is a rather passive one and it is given by the contribution in establishing the value of the  $C_d$  and consequently the plasma voltage,  $U_p$ . The second role is an active one related to the nature of the dielectric surface, which can fix the flux of the primary electrons at the cathode due to secondary electron emission by ion bombardment. This active role of the surface was emphasized comparing the results obtained by using as dielectric barriers ZST plates (named, DBD-ZST) and polyethylene therephtalate (named, DBD-PET), respectively. The thickness of the dielectric plates, ZST and PET, were selected in such a way that the dielectric capacitance,  $C_d$ , has approximately the same value (see Tabel 1).

Tabel 1. Parameters of the dielectric barriers.

| Type of Dielectric Barriers | $d_d$ (mm) | $\epsilon_r$ | $C_d$ (pF) | $C_{DBD}$ (pF) |
|-----------------------------|------------|--------------|------------|----------------|
| PET                         | 0.2        | 3            | 33.45      | 1.43           |
| glass                       | 1.1        | 6            | 12.16      | 1.33           |
| ZST                         | 2.5        | 36           | 32.11      | 1.42           |

Moreover, the distance between the dielectrics being the same in all experiments, the plasma capacitance,  $C_p$ , was constant for both DBD systems. On the other hand, the electric reactance of the DBD systems without plasma between the plates, is pure capacitive, while after the discharge ignition the reactance is changed being no more pure capacitive.

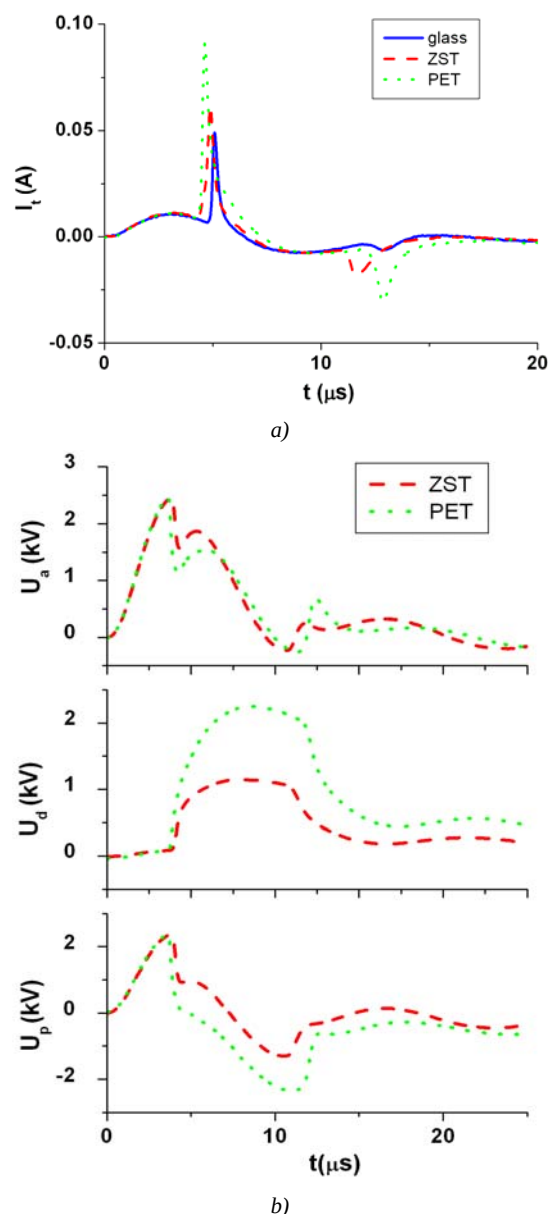


Fig. 8. Time evolution of the electrical parameters, for various types of dielectric barriers;  $Q\text{He}=50$  sccm=const.,  $U_a \cong 2.5$  kV,  $Se \approx 5$  cm<sup>2</sup>a) discharge current,  $I_t$ , and b) applied voltage,  $U_a$ , dielectric voltage,  $U_d$ , and plasma voltage,  $U_p$ .

For a constant value of applied voltage,  $U_a$ , the dielectric voltage is higher for the DBD-PET system than the other case (Fig. 8. b), in spite of the fact that the

dielectric capacitance has the same value in both DBD systems. This can be explained only by different values of the impedance corresponding to the plasma region and by the appearance of a mechanism which produces supplementary electrical charges in the DBD-PET system with respect to DBD-ZST one. This supplementary source of electrical charges, which can explain the increasing of the discharge current of the DBD-PET system, might be related to the polymer surfaces due to their higher secondary electron emission at the ion bombardment. So, we can clearly conclude that the surface processes are also very important in the discharge mechanism.

### 3.4. Surface Treatments by DBD Plasma

It is well known that the metastable atoms are very important for producing surface modifications by plasma treatment [19]. In the previously experiment it was found that higher concentration of metastable atoms, both helium and oxygen, is produced close to the ground (cathode) electrode [19,20]. This result was also confirmed in our experiment by measuring higher concentration of the metastable atomic oxygen close to the former cathode, which become anode during the second discharge pulse. It must note that the concentration of the atomic oxygen metastables is much lower than that of the primary discharge. Based on these results, which show that the highest density of oxygen metastables is localised near the ground electrode, the polymer sample used for surface treatment was placed on the ground electrode (cathode), in order to obtain efficient plasma treatment of polymer surface.

The Atomic Force Microscope working in tapping mode was used for investigation of the polymeric surface morphology. AFM measurements were made on each site of the sample treated under the same conditions when it is placed on the ground electrode (cathode). Moreover, it was obtained that the surface of the polymer sample facing the cathode is more roughness than the surface of the sample facing the other electrode (anode) (see Fig. 9). Probably this is due to the fact that between the polymer and the ground electrode, where the polymer was placed, a supplementary discharge was created, which leads to a supplementary plasma treatment of that site which is found towards the ground electrode. Works are in progress in order to clarify this interesting phenomenon.

Furthermore, a more efficient plasma treatment is obtained for higher value of the applied voltage and for a shorter duration of applied voltage pulse due to the fact that this leads to a higher power injected into the DBD

system and consequently to the more energetic electrons and excited species.

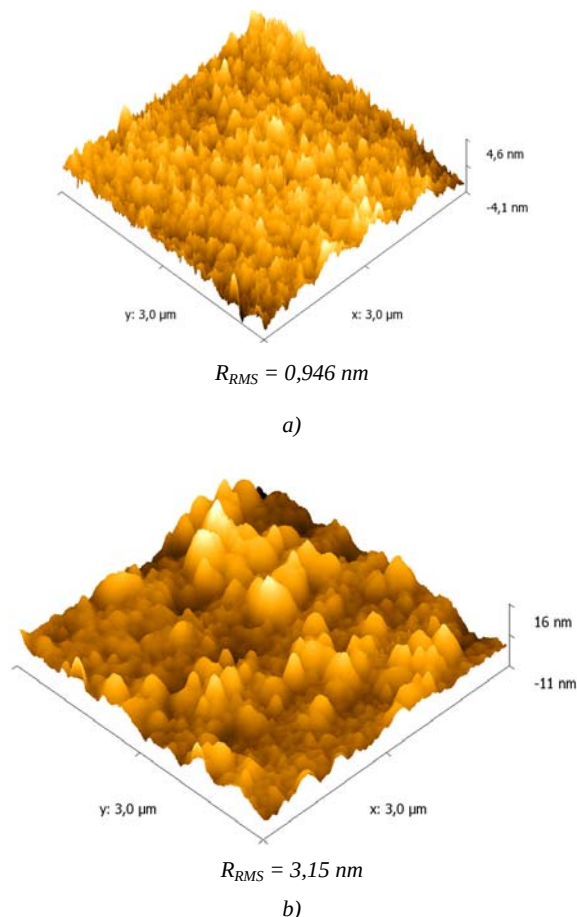


Fig. 9. 3D AFM images for PET sample treated when is placed on the ground electrode (cathode) (a) the site which is found towards the high voltage electrode, b) the site which is found towards the ground electrode.

## 5. Conclusions

Besides the main discharge, a secondary discharge was induced at the end of a *slow* falling flank (15  $\mu$ s) of a *semi-sine* unipolar voltage pulse for a dielectric barrier discharge in helium at atmospheric pressure, in plane-parallel geometry, with dielectric barriers on the both electrodes. The existence of a fast falling front of the applied voltage pulse is not a necessary condition in order to obtain the secondary discharge. On the other hand, the presence of dielectric barriers which have special surface properties (such as electret property and/or high secondary electron emission at ions bombardment) leads to appearance of a more intense secondary discharge.

The secondary discharge is always formed, for any type of the dielectric used as barrier, for any value of applied voltage and for any values of the voltage pulse width between 20-45  $\mu$ s, in our experimental conditions.

Besides the increasing of electrical energy injected into the DBD system, the most efficient treatment of a polymer sample in DBD plasma is made if the polymer is placed on the ground electrode (cathode).

### Acknowledgement

The Romanian Ministry of Education and Research supported this work under grants CEEEX RoEcoPlas 15098/2007.

### References

- [1] U. Kogelschatz, B. Eliasson and W. Egli, The XXIII<sup>th</sup> International Conference on Phenomena in Ionised Gases – ICPIG XXIII, Toulouse, France, July 17-22, 1997, 1.
- [2] U. Kogelschatz, The 7<sup>th</sup> International Symposium on High Pressure Low Temperature Plasma Chemistry - HAKONE 7, Greifswald, Germany, September 10-13, 2000.
- [3] H.-E. Wagner, R. Brandenburg, K. V. Kozlov, A. Sonnenfeld, P. Michel, J. F. Behnke, *Vacuum* **71**, 417 (2003).
- [4] F. Massines, P. Segur, N. Gherardi, C. Khamphan, A. Ricard, *Surface and Coatings Technology* 174-175, **8** (2003).
- [5] N. De Geyter, R. Morent, C. Leys, *Plasma Sources Sci. Technol.* **15**, 78 (2006).
- [6] S. Liu, M. Neiger, *Proc. of the 13<sup>th</sup> Int. Conf. on Gas Discharges and their Applications*, Glasgow, Great Britain, 3-8 September **1**, 263 (2000).
- [7] S. Liu, M. Neiger, *J. Phys. D: Appl. Phys.* **34**, 1632 (2001).
- [8] S. Liu, M. Neiger, *J. Phys. D: Appl. Phys.* **36**, 3144 (2003).
- [9] S. Liu, M. Neiger, *J. Phys. D: Appl. Phys.* **36**, 1565 (2003).
- [10] M. Laroussi, X. Lu, *Journal of Applied Physics* **96**(5), 3028 (2004.).
- [11] X. Pei, M. Laroussi, *J. Phys. D: Appl. Phys.* **39**, 1127 (2006).
- [12] K. Okazaki, T. Nozaki, *Pure Appl. Chem.* **74**(3), 447 (2002).
- [13] A. S. Chiper, N. Blin-Simiand, F. Jorand, S. Pasquiers, G. Popa, C. Postel, The 17<sup>th</sup> International Symposium on Plasma Chemistry, Toronto, Canada, August 7-12, 2005
- [14] F. Vollkommer, L. Hitzschke, *Proc. 8. th. Int. Symp. Sci. Tech. Light Sources*, Greifswald, Germany, 51, August 1998
- [15] A. S. Chiper, N. Apetroaei, G. Popa, *Journal of Optoelectronics and Advanced Materials* **7**(5), 2561 (2005).
- [16] R. Cazan, A. S. Chiper, G. Popa, The 5<sup>th</sup> International Conference on Global Research and Education, Inter-Academia 2006, Iasi, Romania, September 25 – 28, 2006, 623.
- [17] A. S. Chiper, V. Anita, C. Agheorghiesei, V. Pohoata, M. Anita, G. Popa, *Plasma Process. Polym.* **1**(1), 57 (2004)
- [18] A. S. Chiper, N. B. Simiand, F. Jorand, S. Pasquiers, G. Popa, C. Postel, *J. Optoelectron Adv. Mater.* **8**(1), 208 (2006).
- [19] G. Placinta, F. Arefi-Khonsari, M. Gheorghiu, J. Amouroux, G. Popa, *J. of Appl. Polym. Sci.* **66**, 1367 (1997).
- [20] A.S. Chiper, R. Cazan, V. Pohoata and G. Popa, , 28<sup>th</sup> ICPIG, Prague, Czech Republic, July 15-20, 2007, 1058.

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