

ASSESSING THE SELF-CLEANING CAPABILITY OF A COPLANAR BARRIER DISCHARGE WITH DIFFERENT BARRIER SURFACE COATINGS AND ELECTRODE GEOMETRIES

Z. SZALAY, J. RÁHEĽ, Z. MACHALA, K. HENSEL

Bratislava, Brno

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Deposit formation from air-toluene mixture was evaluated on a coplanar dielectric barrier discharge at atmospheric pressure. Alumina ceramics, alumina with TiO_2 coating and alumina with high permittivity layer coating were examined at various electrode configurations. In general higher discharge input power led to reduction of solid deposition on the ceramics surface. TiO_2 -coated alumina exhibited substantially smaller deposit formation rate. This is explained by the presence of TiO_2 photocatalytic effect and by the change of discharge microfilament dynamics.

1. Introduction

The Diffuse Coplanar Surface Barrier Discharge (DCSBD) is a specific type of dielectric barrier discharge (DBD), employing a set of parallel strip electrodes embedded in the dielectric near to its surface. DCSBD has the unique ability to generate a thin layer of macroscopically homogenous layer of non-thermal plasma with high power densities ($\approx 100 \text{ W/cm}^3$). The discharge consists of numerous H-shaped microdischarges with pronounced areas of diffuse afterglow plasma above the surface

Comenius University, Faculty of Mathematics, Physics and Informatics, Department of Experimental Physics, Bratislava, Slovakia

Masaryk University, Faculty of Science, Department of Physical Electronics, Brno, Czech Republic

Comenius University, Faculty of Mathematics, Physics and Informatics, Department of Astronomy, Earth Sciences and Meteorology, Bratislava, Slovakia

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E-mail address: szalay@gimmel.ip.fmph.uniba.sk

of dielectric. The effective thickness of such plasma is around 0.3 mm. DCSBD was developed to suit the needs of industry for material treatment [Šimor *et al.*, 2002].

Beside research focused on treatment of various materials [Černák *et al.*, 2009], the chemical activity of DCSBD was studied on VOC abatement [Machala *et al.*, 2009]. During the operation of DCSBD in air polluted with toluene vapours, the formation of organic deposit was observed, which eventually quenched the discharge on ceramics surface. Using ceramic with TiO₂ functional coating its discharge area remained free of deposit. This self-cleaning effect, first observed by Machala *et al.* [2009], was later confirmed using a more advanced experimental setup [Szalay *et al.*, 2010]. We define the self-cleaning by absence of deposited plasmachemical products in the area of plasma. Aim of this study is to investigate the mechanism of this effect on TiO₂-enhanced ceramics and the influence of electrode geometry and a high permittivity coating on the self-cleaning efficiency. The insight to the processes responsible for the self-cleaning effect contributes to optimization of DBD plasma polymerisation and VOC abatement applications.

2. Experimental

2.1. Reactor design and measurement methodology

For this study a simplified electrode arrangement was used. Each DCSBD electrode element consists of a square shaped plate (101×101×0.635 mm) of alumina (96 % Al₂O₃) with screen-printed silver electrodes in circular concentric geometry (Figure 1a) on one side. Interelectrode gaps of 1.5, 2, and 3 mm were used. Some of the ceramics were coated with sol-gel made TiO₂ (1–3 layers) fired at various temperatures to alter the rutile/anatase phases ratio of final TiO₂ layer. The TiO₂ layers (1 ml of TiO₂ sol per layer) were spin-coated on cleansed ceramics at rotational speed of 1100 rpm. After setting the prepared ceramics were fired in oven at 350, 700 and 900 °C for duration of 1 hour each. One ceramic plate was coated with a high permittivity ($\epsilon_r = 120$) dielectric layer using ESL 4113-H screen printing paste.

The electrode was mounted into PVC enclosure (Figure 1b), equipped with gas feed system and insulation oil cooling system. Circulating synthetic transformer oil insulated the screen-printed silver electrodes, eliminating any unwanted electrical breakdown between them and stabilizing the temperature of investigated electrode elements. The discharge was generated above the electrodes on the surface of the ceramics. The device was sealed with translucent cylindrical PMMA lid with embedded ducts for inlet and outlet tubes (right and left positioned above the ring electrode, mutual distance 3 cm). The discharge chamber volume was adjusted to the effective thickness of plasma. The plasma reactor was driven by a LIFETECH VF700 power supply (10 kV, 38.5 kHz sinusoidal voltage).

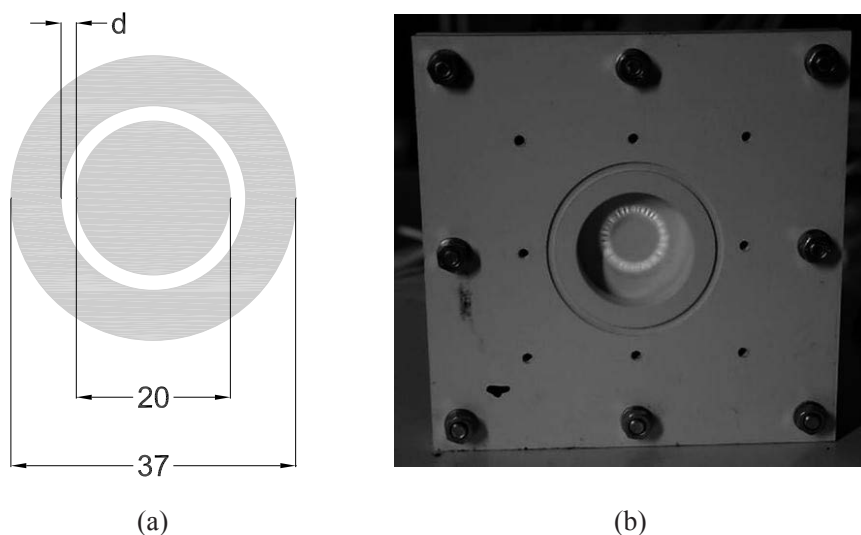


FIGURE 1. (a) Depiction of used arrangements (d – interelectrode gap, all measures in mm) (b) Front view of reactor (without front lid) during discharge operation.

Atmospheric air as carrier gas was bubbled through liquid toluene to get enriched by its vapours. Using two air flow controllers with maximum ranges of 1 and 2.5 (5) l/min respectively we have set the total flow rate of gas mixture (0.5–3 l/min) as well the exact concentration of toluene (500–8000 ppm). Temperature was controlled to ensure constant concentration of toluene saturated vapours in the mixture. Toluene vapours were diluted with air in mixing chamber and led to the discharge chamber. The gaseous products of toluene decomposition were continuously transported through the outlet tube into a glass gas cell of 10 cm length equipped with KRS-5 windows, residing inside FTIR spectrometer. The presented experimental setup is identical to the one we used in our previous work [Szalay *et al.*, 2010].

The products of toluene decomposition were analyzed by Fourier Transform infrared (FTIR) spectroscopy using BRUKER Vector 22 spectrometer. Absorption spectra were obtained in continuous flow regime from sets of 10 scans per sample from spectral range of $4000\text{--}500\text{ cm}^{-1}$ with 1 cm^{-1} resolution. The removal efficiency of toluene was measured from the decrease of absorbance of the toluene absorption band at 3040 cm^{-1} , corresponding to C–H stretching vibrations in the aromatic ring.

Using Tektronix P6015A HV probes and Pearson current monitor Model 4100 we obtained voltage and current waveforms of the discharge, which were processed by Tektronix TDS 2024 (200 MHz, 2.5 GS/s) digital oscilloscope. The discharge power was then calculated by time integration of the U-I product using Tektronix Wavestar software.

To demonstrate the difference in self-cleaning capabilities between uncoated ceramics with different interelectrode gaps d (Figure 1a) and ceramic with high permittivity coating, the fixed total flow rate of 0.5 l/m and toluene concentrations ranging from 500 to 8000 ppm were chosen. The inlet was by default positioned on the right side. During these tests FTIR spectrometer and probes were disconnected. We measured the power consumption of the whole system with a plug-in wattmeter. Deposition rates and distribution on ceramics were examined on the base of photography comparison.

2.2. Chemical effects of DCSBD and self-cleaning ability of TiO_2 -coated electrode

Toluene was decomposed mainly to CO_2 and lower amounts of CO, HCOOH and water. The other compounds HNO_3 , N_2O_5 , NO_2 , N_2O and O_3 are typical products of discharge in pure air. FTIR spectrum of toluene in DCSBD is shown elsewhere [Szalay *et al.*, 2010]. The discharge power of Al_2O_3 electrode ($d = 1.5$ mm) was 13 ± 1 W, on TiO_2 coated ceramics ($d = 1.5$ mm) 14 ± 1 W.

We have previously shown that TiO_2 -coated ceramics exhibit better toluene removal rates than alumina and have generally less organic deposit on the discharge area [Szalay *et al.*, 2010]. TiO_2 was chosen due to its UV photocatalytic properties [Fujishima *et al.*, 2008] as it was expected to improve decomposition efficiency. The primarily investigated TiO_2 -coated alumina with 700 °C firing temperature achieved enhanced self-cleaning performance with increasing number of TiO_2 layers. On alumina with 3 layers of TiO_2 no deposit formation was observed in the discharge area during DCSBD operation in toluene vapours for the test duration of 4 hours. From the subsequent self-cleaning tests using ceramics with TiO_2 fired at 350 °C and 900 °C it appears that the firing temperature of the sol-gel layer has no relevant impact on self-cleaning.

In this study we have investigated the toluene decomposition rate together with the levels of C-containing gaseous products and ozone (Figure 2) for 500 ppm and 1000 ppm toluene. Ozone levels were peaking around 500 J/l energy density for Al_2O_3 and 700 J/l for TiO_2 , then they began to fall. It is accountable for the temperature rise in discharge chamber with increasing energy densities. This decrease of ozone levels almost to 0 indicates, that above cca 1500 J/l the O radicals involved in ozone formation are predominantly contributing to plasmochemical conversion of toluene, as suggested by Machala *et al.* [2009]. For 500 ppm toluene there was no deposit formed in discharge area for any of used electrodes. TiO_2 ceramic was capable of removing up to 95 % of toluene. More efficient oxidation of toluene was evident from the higher CO_2 levels and lower CO production for TiO_2 -coated ceramics. Decreasing formic acid levels indicate slightly more solid deposit for TiO_2 at higher energy densities.

Results for 1000 ppm are of greater importance, as this concentration was used for deposition tests (at 1500 J/l for Al_2O_3 and 1620 J/l for TiO_2) in our previous

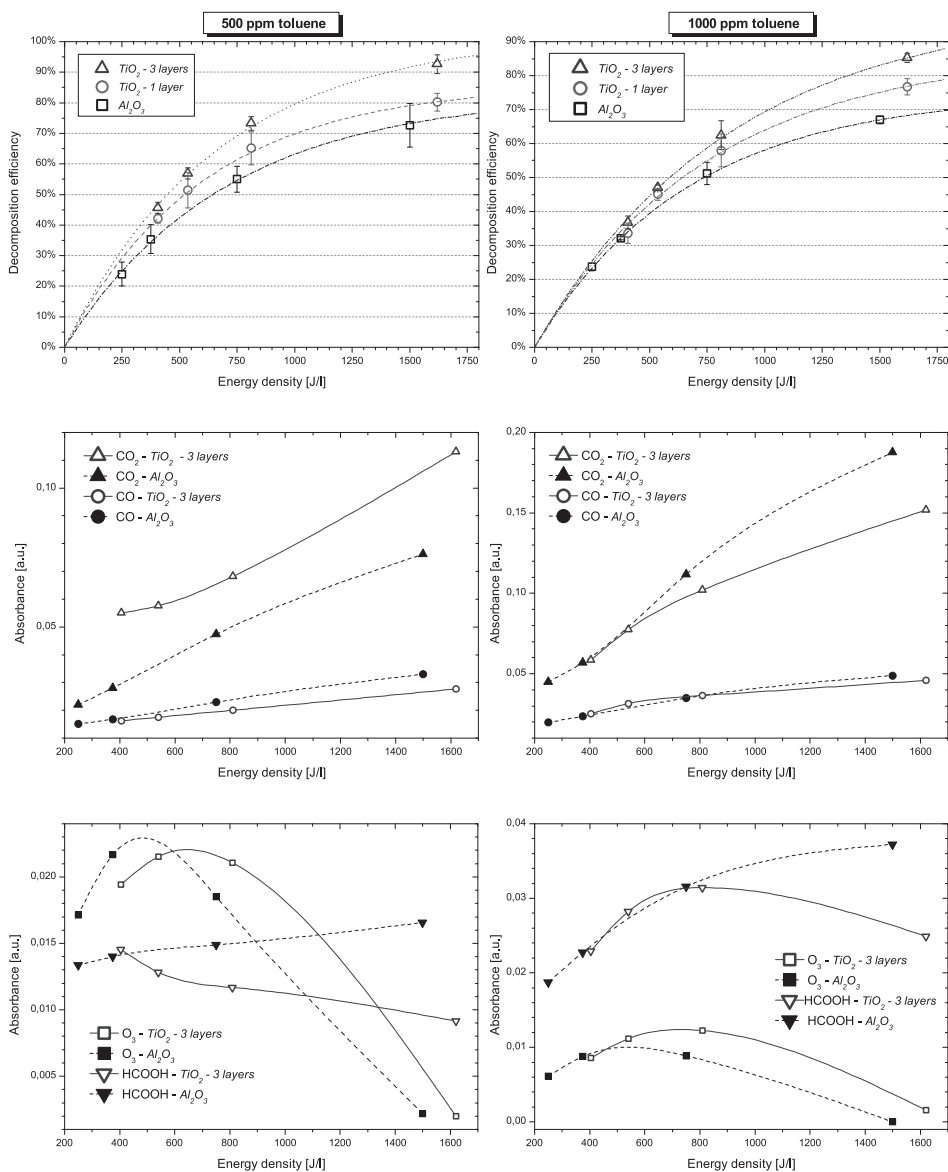


FIGURE 2. Comparison of decomposition efficiency and gaseous products of toluene between Al_2O_3 and TiO_2 (700 °C firing temperature). Plots in the left column refer to 500 ppm of toluene, right column refers to 1000 ppm of toluene.

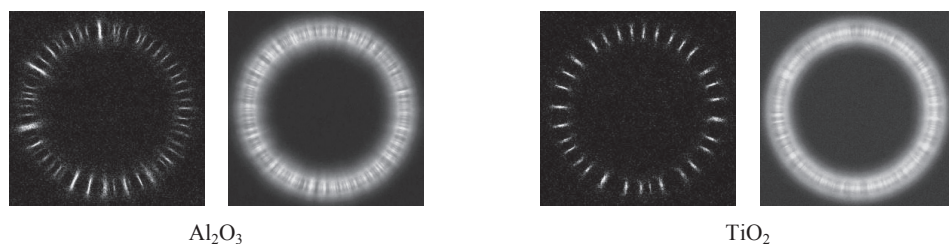


FIGURE 3. Structure of DCSBD on Al_2O_3 and TiO_2 (3 layers, 700°C) ceramics. Exposure times 1/1000 s (left) and 1/10 s (right).

work [Szalay *et al.*, 2010]. The toluene removal efficiency exceeded 85 % for TiO_2 . CO_2 levels for TiO_2 were rising slower than for Al_2O_3 with the increasing energy density, while CO levels were essentially the same for both ceramics. Formic acid and ozone had similar development curves for TiO_2 . Concentration of both products declined at higher energy densities. As there were less C-containing gas products for TiO_2 than for Al_2O_3 , we can conclude that for TiO_2 at 1000 ppm toluene is predominantly converted to heavier polymeric compounds leading to increased deposit generation. This contradicts our visual observations as the discharge area is still cleaner than on Al_2O_3 . The self-cleaning effect is therefore not achieved only by means of plasmachemical processes supported by photocatalytic properties of TiO_2 .

As FTIR analysis alone did not provide reasonable explanation of the self-cleaning, we have begun to investigate the microdischarge dynamics on these two barrier surfaces. The charges deposited on the dielectric by the discharge filaments have a strong impact on the discharge structure [Celestin *et al.*, 2009]. Every microdischarge deposits electric charge on the dielectric plate, which weakens the electric field from the electrodes and extinguishes the discharge filament. In the next half-period, this charge amplifies the outer field; hence successive filaments are likely to appear in filament traces. The ability to accumulate and retain the deposited charge is dependent on the properties of the dielectric.

We studied persistence and distribution of microdischarges in order to describe the self-cleaning mechanism. Photographs of the discharge on both Al_2O_3 and TiO_2 were taken (Figure 3). The average number of microfilaments on TiO_2 was 40 % lower than their number on Al_2O_3 . The biggest difference between both ceramics lied in the shorter residence time of microdischarges on TiO_2 . On Al_2O_3 the microdischarges tended to oscillate around the equilibrium locations which resulted in prolonged residence time up to one order of magnitude longer than on TiO_2 . This oscillation was accompanied by gradual expansion and successive shrinking of random filaments (look at the brighter filaments on Fig. 3) followed by their extinction. Such effect was not observed on TiO_2 . The greater microdischarge mobility on TiO_2 and generally lower probability of microdischarge appearing on the same spots rendered the plasma to appear more homogenous.

The organic polymer of toluene is being deposited outside the discharge area and in gaps between individual discharge filaments. The oscillating character of Al_2O_3 microdischarges allowed formation of a deposit layer in between them more easily than on TiO_2 , which in result locally increased the ignition voltage. As the discharge was quenched on these spots, “islands” of deposit were gradually formed, which essentially locked the microdischarges in place. On TiO_2 the rapid position change of microdischarges along the interelectrode gap in a given period of time ensured better coverage of discharge area with the DCSBD plasma. We expect that due to this fast microdischarge relocation the produced polymeric fragments have not enough time to condense in between filaments and adversely affect the discharge conditions. They are plasmochemically further processed and repulsed by microdischarges outside the discharge area where they finally condense.

2.3. Further examination on different ceramics

Aim of these tests was to validate the role of input power and interelectrode gap in achieving the self-cleaning of Al_2O_3 discharge ceramics. Both parameters are contributing to the total electrical charge transported by single microdischarge [Kogelschatz *et al.*, 2003, Jidenko *et al.*, 2010]. The increase of total charge was achieved also by employing Al_2O_3 with the high permittivity dielectric coating.

The measured power consumption was 57–61 W (high power) and 36–40 W (low power). At low power on electrode $d = 3$ mm and electrode with high permittivity coating only partial coverage of electrode gap with microdischarges was achieved. Tests with 8000 and 5000 ppm toluene were discarded shortly after seeing the ceramic completely covered with sticky deposit in less than 5 and 20 minutes respectively. From the photographs (Figure 4) we can conclude that the discharge cannot clean itself at higher than 1000 ppm toluene concentrations on uncoated Al_2O_3 . At 2000 ppm and 3000 ppm only partial cleaning was achieved, which was mainly due to partial relocation of microdischarges from the heavily contaminated areas to areas with less deposit (below the inlet duct), where a higher filament density was then achieved. All three electrode gaps provided similar level of self-cleaning. The filaments on high permittivity layer appeared mostly near the inlet and generated there a dark thin deposit layer with generally dry and fine consistence. This is the opposite we observed on Al_2O_3 and TiO_2 . The self-cleaning performance of this layer seems to be better than Al_2O_3 . Even though we did not investigate the decomposition efficiency and chemistry related to this layer, we can assume a different self-cleaning mechanism. Using 2000 ppm toluene we confirmed, that higher discharge power improves the self-cleaning performance regardless of electrode geometry.

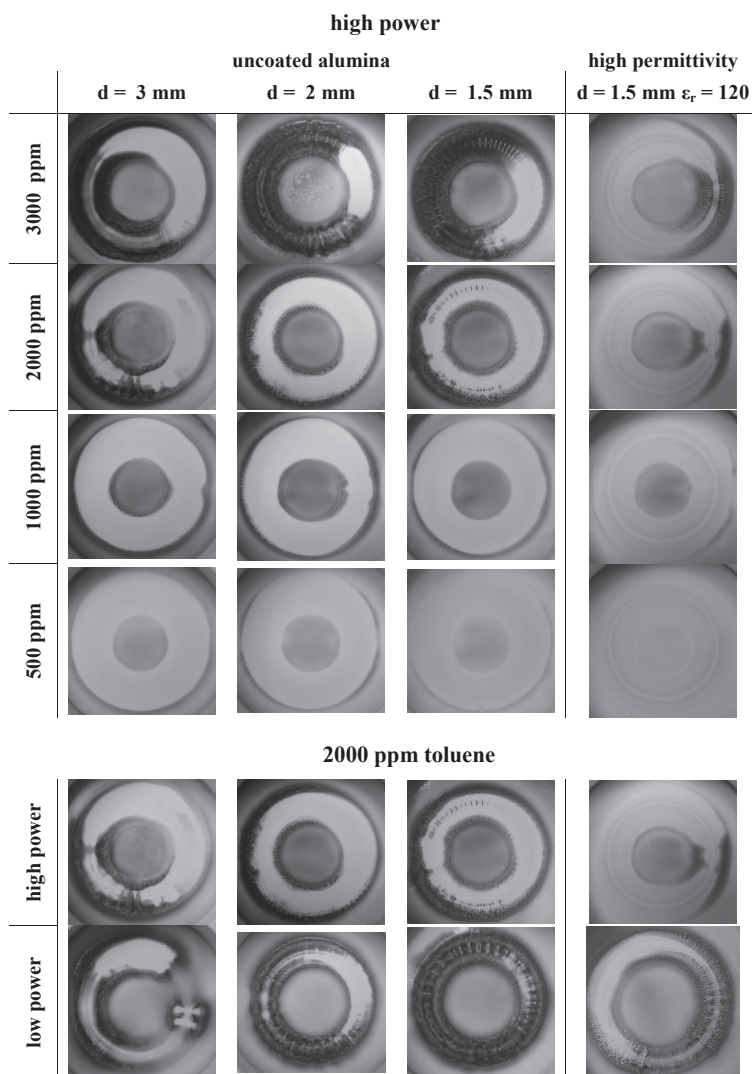


FIGURE 4. Photographic comparison of deposit formed at different configurations.

3. Conclusion

In this paper we investigated the self-cleaning capabilities of DCSBD employing three different barrier surfaces, namely alumina, alumina with TiO_2 coating and alumina with high permittivity dielectric layer, and three different electrode arrangements on alumina. We have shown that simply by increasing the discharge power we can improve the self-cleaning capabilities of any used electrode. By coating the ceramics we improved the self-cleaning in comparison to bare alumina. According

to our findings microdischarge dynamics play more important role in the process of the self-cleaning of TiO₂ electrode than its photocatalytic effect. Even though the employed type of DBD is still not economically feasible for commercial VOC abatement, the self-cleaning effect by itself is a remarkable phenomenon and holds great potential for future industrial applications.

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