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Surface Dielectric Barrier Discharge in Closed-Volume Air

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ABSTRACT: The postdischarge kinetics of reactive species produced by a surface dielectric barrier discharge (SDBD) ignited in closed-volume air for decomposition of organic molecules in aqueous solutions was investigated. A SDBD with surface of 6 cm^2 was operated in a closed volume (0.5 L) of air at atmospheric pressure. The voltage across the plasma gap, the charge transferred through the plasma, and the dissipated power were computed from the charge-voltage diagram to values of 3900V, 0.2 μC, and 6W, respectively. The reactive species produced by the SDBD in a closed volume of air were active for decomposition of methylene blue molecules in small volumes of aqueous solution for a relatively long period of time after the discharge was cut off. The lifetime in gaseous phase of the species active for decomposition of organic molecules was approximately 11 minutes. However, SDBD operation in closed-volume air shortened the lifetime of polyimide dielectric of the discharge microelectrode system due to the increased humidity and reactivity of the active species generated by plasma. Measurement of relative humidity revealed that the discharge enhanced water evaporation. Atomic force microscopy investigations of dielectric surface in the discharge region revealed drastic modifications of surface morphology with an important increase of surface roughness as the result of SDBD operation.

KEY WORDS: surface DBD, reactive species kinetics, methylene blue degradation, dielectric degradation

I. INTRODUCTION

In recent years, interest in medical applications of atmospheric pressure plasmas has grown significantly.[1] Among various atmospheric pressure plasmas, the surface dielectric barrier discharge (SDBD) plasma has proven its potential as an important candidate for plasma treatments in wound healing,[2] drug administration,[3] sterilization,[4,5] and removal of contaminants from air[6] or water.[7] Most SDBD studies have been devoted to discharges working in open air or in closed vessels through which air or rare gases flowed.[8] The effluents then generated by plasma are transported and used for treatments. Very few studies of SDBD plasma treatments have been performed in closed-volume air.[7,9] The present study is devoted to SDBD operated in closed-volume air at atmospheric pressure for treatment of contaminant organic molecules in aqueous solution. Oehmigen et al.[7] studied the kinetic of chemical reactions taking place in liquid as result

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of active species produced in the discharge plasma and their diffusion into liquid. In their experimental arrangement, the plasma faced the liquid surface at a small distance (5 mm) and the volume of air available for the discharge was very small (14 mL) compared to the volume of treated liquid. In the present study, the plasma does not face the liquid surface, and the volume of air enclosed in vessel is much larger (0.5 L) than the volume of treated liquid (5 mL). Therefore, in the present study, the plasma treatment can be considered totally indirect; the treatment is determined by the plasma-generated active species in the gas phase and their free diffusion from the gas phase in water. The active plasma species involved in treatment of water or aqueous solutions are reactive oxygen species (ROS) and reactive nitrogen species (RNS).[9] Among them, O_3, OH^-, H_2O_2, NO_2^-, and NO_3^- are the most important active species, with important roles in treatments for removal of organic contaminants from water, inactivation of bacteria, or for inducing biologic reactions in living tissue.[10] Oh et al.[11] showed that these species are generated immediately in water once the atmospheric-pressure plasma is ignited and, if not consumed in reactions with organic molecules, they survive for long time. In the present study, kinetics of active species generated by SDBD operated in closed-volume air is investigated indirectly by analyzing the decomposition rate of methylene blue (MB) molecules in a small amount of water exposed to plasma effluents. Methylene blue is frequently used in studies of decomposition organic contaminant molecules in water.[12] ROS such as O_3, H_2O_2, and OH are the main active species for the degradation process of MB molecules in water, while RNS such as NO, NO_2, and NO_3^- are somehow detrimental to the MB degradation process due to consumption of oxygen in their generation processes.[13] Therefore, exposure of small amounts of MB aqueous solution to SDBD plasma effluents generated in closed-volume air gives information on the concentration of ROS and their lifetime in postdischarge medium. These plasma-generated species have a long lifetime (> 10 minutes), they were available for reactions in liquid phase for relatively long period (~30 minutes) after the discharge had been cut off. Thus, compared with operation in open air or gas flow, the operation of SDBD in closed-volume air increases the efficiency of treatment. However, the operation of the SDBD in closed-volume air has also drawbacks. Active plasma species promote water evaporation, which results in a faster increase of water vapor in the air during the discharge. The high concentration of active species in gas phase and the increase of humidity determine erosion of the dielectric polymer of the SDBD electrode system due to numerous reactions of the reactive plasma species with the dielectric material.

II. EXPERIMENTAL SETUP

The SDBD was generated in atmospheric air in a glass vessel with the volume of 0.5 L. Figure 1 presents schematically the experimental setup. The SDBD microelectrodes used in the present study had a sandwich structure (area = 2.3 × 3 cm^2) formed by two copper electrodes (18 μm thickness) deposited on the two sides of a polyimide foil (Kapton® with 14 μm thickness and relative dielectric permittivity of 3.4). The upper (hot) electrode was structured as 23 equidistant and parallel stripes (0.2 mm wide and 30

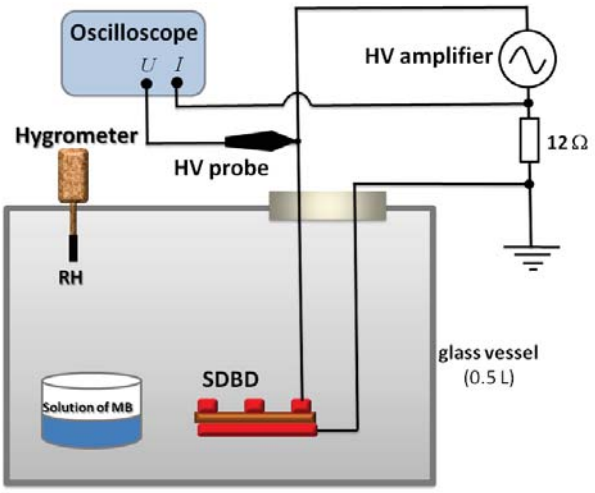

FIG. 1: Schematic representation of the experimental setup

mm long) with a gap width of 0.8 mm. In the glass vessel, side by side with the SDBD electrodes, there was placed a Petri dish (40 mm in diameter) with a small volume (5mL or 3 mL) of methylene blue (MB) solution (400 ppm) in deionized water. The SDBD was powered by a sinusoidal wave high-voltage amplifier. The voltage and intensity of discharge current signals were collected by specialized voltage probes and monitored by a digital oscilloscope (DPO 2024 from Tektronix, USA). The electric characterization of the discharge is provided in the next section. Decomposition of MB in solution was determined by measurements of optical absorbance in the region 400–800 nm (with a peak in absorption at 664 nm) by a UV-VIS spectrophotometer (Evolution 300 from Thermo Scientific). The humidity in the glass vessel has been monitored by a precision hygrometer (HM34C, Vaisala Oyj, Finland). The topography images and roughness of the dielectric before and after operation of SDBD in open and closed-volume air have been obtained by atomic force microscopy (AFM) measurements performed by a commercial AFM apparatus (XE 100 from Park, South Korea) working in noncontact mode. The measurements were performed with a silicon AFM probe (HQ:NSG 35 from NT-MDT, Russia) with a sharpened tip (nominal curvature radius of 8 nm) and a stiff cantilever (nominal resonant frequency and force constant of 150 kHz and 5.4 N/m, respectively).

III. ELECTRIC CHARACTERIZATION OF DISCHARGE

Figure 2a shows the typical waveforms of the applied voltage and intensity of the electric current through the SDBD during one oscillation period. The peak values of the applied voltage and current intensity are approximately 1900 V and 35 mA, respectively. As shown in Fig. 2b, the current intensity presents the typical pattern of a mul-

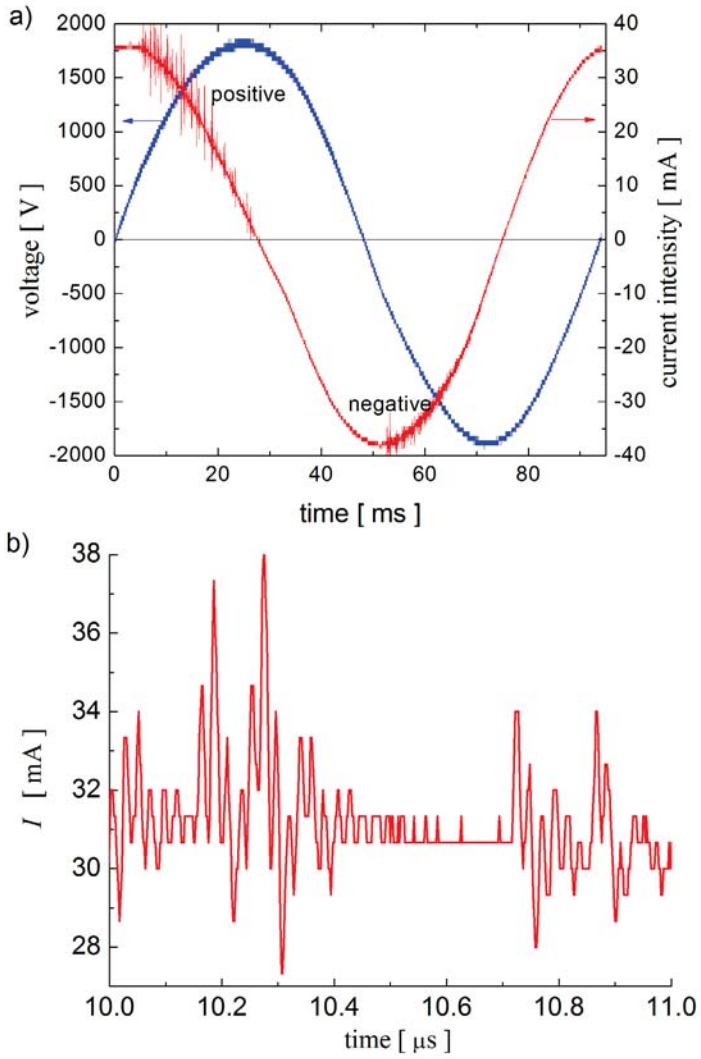

FIG. 2: (a) Typical waveforms of voltage and current intensity during a period of SDBD. (b) Detailed image showing current intensity variation at a smaller scale of time (1 μs).

tifilamentary discharge[14] with spikes with an amplitude of approximately 5 mA and a lifetime of approximately 20 ns. The amplitude and number of current intensity spikes are larger during the positive discharge than during the negative discharge. Several electrical parameters of the discharge are important as the energy dissipates during one oscillation period: discharge power, electric charge transferred to dielectric surface during one cycle of the discharge, Q_{dis}, and the voltage across the gas gap, U_b. All of these can be determined from charge-voltage Lissajous diagrams. Figure 3 shows a sketch of the measuring circuit of SDBD that indicates the capacitances involved in the discharge

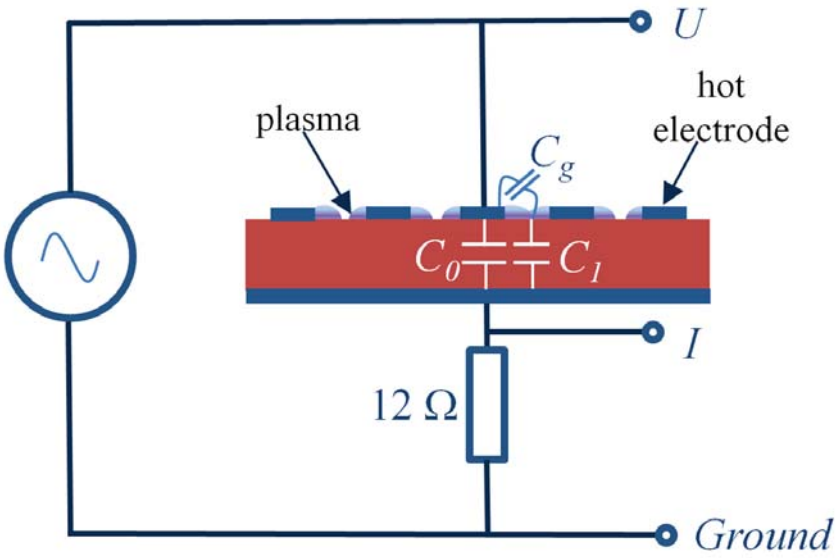

FIG. 3: Sketch of the SDBD circuit. The current intensity, *I*, signal is collected on a 12 Ohms resistor and the discharge voltage, *U*, is collected by a high-voltage probe connected to the top electrode. The bottom electrode has been grounded. Capacitance C_0, C_1, and C_g are shown schematically.

mechanism. The capacitance C_0 accounts for the capacitor formed by the dielectric between the top and bottom electrodes and does not change during the discharge. The capacitance C_1 accounts for the dielectric capacitor formed between the bottom electrode and the bare surface of the dielectric. The gap capacitance accounts for the air capacitor formed between the top electrode and the bare surface of the dielectric. During the multifilamentary discharges, the air gap is partially shortcut by the low impedance of air plasma. If *f* is the fraction of bare dielectric area covered by plasma, the impedance of SDBD circuit during positive and negative discharge periods is approximately

$$C_d \cong C_0 + f \cdot C_1 . \tag{1}$$

While the discharge is off, the capacitance of the SDBD electrode system is

$$C'_d = C_0 + \frac{C_1 \cdot C_g}{C_1 + C_g} . \tag{2}$$

The value of C_0 has been determined to be approximately 309 pF using the plane capacitor formula:

$$C_0 = \frac{\varepsilon_0 \varepsilon_r \cdot S}{d}, \tag{3}$$

where S is the area of the upper electrode (S = 140 mm^2), d the thickness of the dielectric (d = 14 μm), ε_r the relative electric permittivity of the dielectric (ε_r = 3.4), and ε_0 the electric permittivity of vacuum (ε_0 = 8.85 10^{-12} F/m). The same formula was used to compute a value of 1324 pF for C_1.

The changes in circuit capacitance from C_d' to C_d during the discharge cycles determine the changes of the slope in the Q-U diagram, which typically have a parallelogram shape. Figure 4 presents the Q-U diagram of the SDBD used in the present work. The regions AB and CD show a smaller slope, which corresponds to capacitance C_d' when the discharge is off, while the regions BC and DA show a larger slope, which corresponds to capacitance C_d when the discharge is on. From the Q-U diagram, C_d' = 260 pF and C_d = 390 pF. The values of C_d and C_1 show that, on average, only 10% of the bare dielectric surface is covered by conductive plasma. The value of C_d' determined from the Q-U diagram is close to the value of C_0 computed using the plane capacitor formula. To determine the relevant parameters of the discharge, the Q-V diagram of the

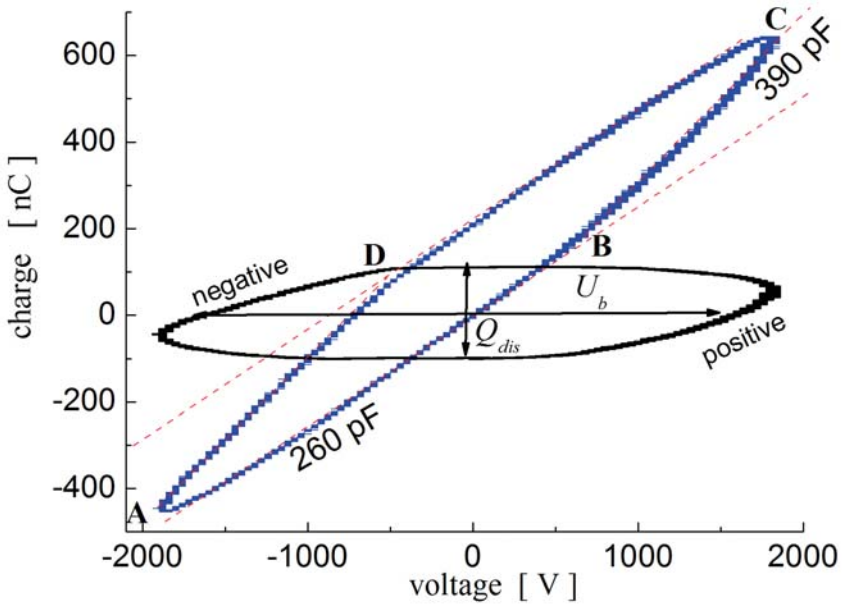

FIG. 4: Q-U diagram of SDBD showing typical parallelogram shape (ABCD) before (diagonal) and after (horizontal) extraction of contribution of displacement current through the capacitance C_d'. The slopes of quasi-linear parts of the diagram compute the capacitances C_d and C_d'.

discharge[15] was computed by extracting the contribution of the displacement current $I_d = C_d'dU/dt$ flowing through the dielectric (capacitance C'_d). The Q-V diagram of the discharge allows for determination of voltage across the plasma, U_b, and the charge Q_{dis} transferred through the plasma to values of 3900 V and 0.2 μC, respectively. These values determine the energy dissipated in one cycle to be approximately 0.5 mJ and the discharge power to be approximately 6 W.

IV. RESULTS AND DISCUSSION

A. Degradation of Methylene Blue Solution

Figure 5 shows the variation of MB concentration in the solution exposed to the action of reactive species produced by SDBD plasma. Due to dielectric failure, the SDBD electrodes could not be operated more than 10 minutes in closed-volume air (Fig. 5, discharge on plot). The discharge was then operated for only 4 minutes, and the time evolution of MB concentration in the solution exposed to active species generated by SDBD plasma was investigated during the discharge and after the discharge was cut off. As explained in the introductive section, ROS are the main active species for the degradation process of MB molecules in water, while RNS are more or less detrimental to the degradation process. The degradation of MB molecules in small volumes of aqueous

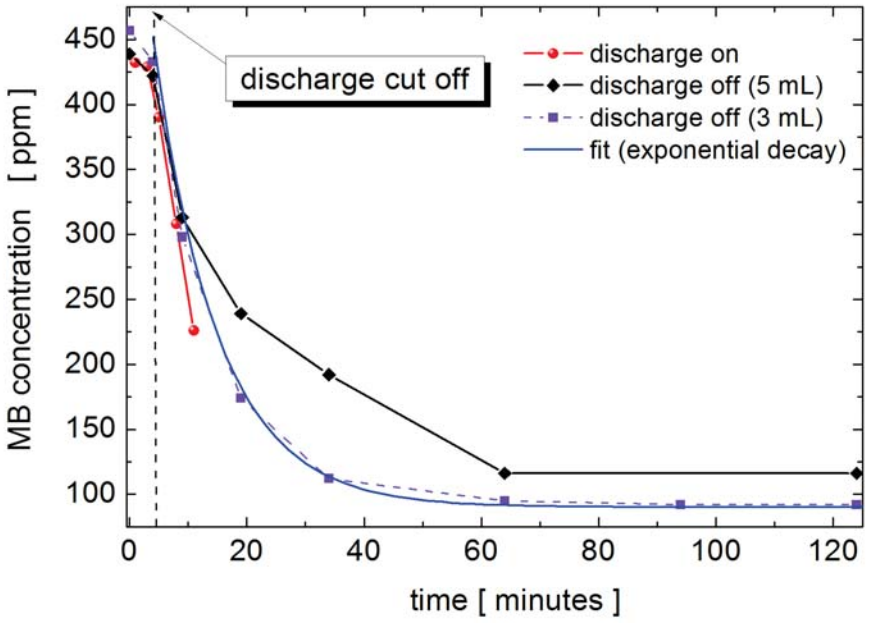

FIG. 5: Time variation of concentration of MB in water during SDBD plasma operation and after SDBD has been cut off

solution (5 mL) exposed to plasma effluents in a relatively large volume of air (500 mL) yields information on the concentration of ROS in the gas phase. The decay of MB concentration in the solution shows that the ROS generated by SDBD plasma have a long lifetime and decompose MB molecules for approximately 30 minutes after the SDBD is cut off. Thereafter, no further decomposition of MB occurs. The time variations of MB concentration show that, for smaller amounts of solution (less than 3 mL), the amount of the decomposed MB molecules is independent of the volume of the solution used in the experiments. This finding indicates that the decomposition process is limited by the flux of active species coming from air and dissolved in solution. Therefore, the time evolution of the decomposition rate of MB molecules in aqueous solution is an indicator of the time variation of the concentration of active species in the gaseous phase. The fit of the time variation of MB concentration with the exponential decay (Fig. 5) determines the decay time for the active species in the closed-volume air, which is approximately 11 minutes. This decay time may depend on the volume and surface of the glass vessel that contain the discharge gas. Also, the air humidity may affect the production and consumption of ROS. Therefore, we monitored the relative humidity (RH) of the air during the discharge and found that the SDBD enhances the evaporation of water from the MB solution, probably due to the contribution of radical species generated by plasma and the ultrasound produced by the SDBD dielectric.

Figure 6 shows the comparative increase of RH in the closed-volume air without and with SDBD. The evaporation of water under a closed-volume air condition raises the RH from the initial value of ambient air toward saturation. This process is relatively slow in the absence of SDBD plasma and faster in its presence. Therefore, SDBD enhanced the evaporation of the liquid water exposed to active plasma species. When SDBD is operated for relatively long time (10 minutes), this may contribute to the electric failure of the dielectric material because water is absorbed on the dielectric surface and modify its electric properties. Also, the content of water vapor in the discharge gas has a great impact on the discharge current and ultimately on the discharge power.[16]

B. Degradation of the Dielectric Material

The dielectric materials used in surface dielectric barrier discharge (SDBD) devices are inevitably exposed to plasma of the discharge filaments forming at their surface. These discharges determine the erosion and degradation of dielectric material because the action of active high-energy plasma species (i.e., electrons, ions, UV photons, and radical and metastable molecules) can cause dielectric failure. The increase in humidity during SDBD may also contribute to the degradation of the dielectric material.

In SDBD, plasma filaments form on the bare dielectric surface at the edge of the hot electrode. Therefore, we investigated the evolution of dielectric surface topography at this position using atomic force microscopy (AFM). We expected the operation of SDBD in open air to degrade the dielectric less because in this case the active species formed in plasma are diluted and transported in the environmental air. Therefore, we compared the changes of the dielectric surface morphology during SDBD operation

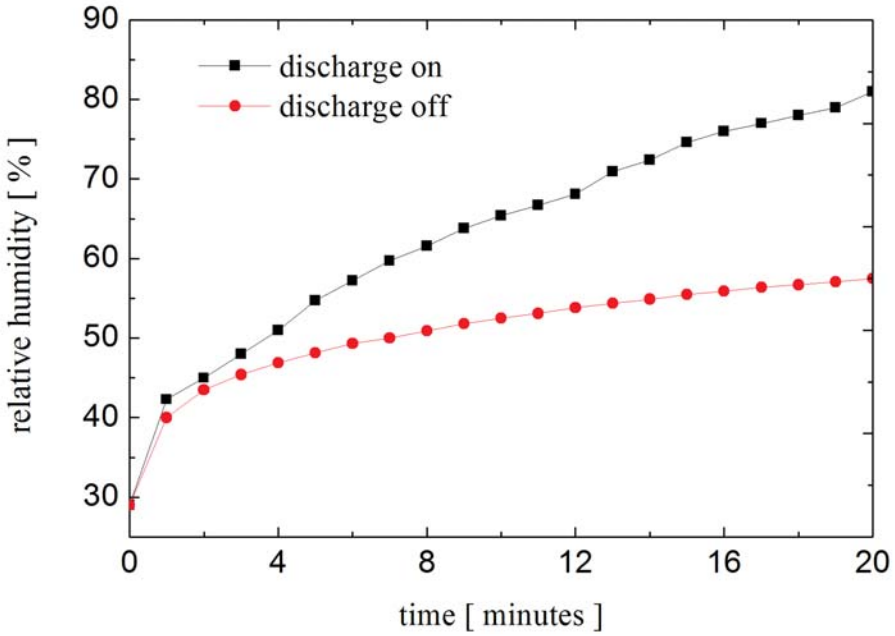

FIG. 6: Variation of relative humidity in closed-volume air during SDBD operation (squares) and without SDBD (dots)

in open and closed-volume (0.5 L) air. Figure 7 shows the comparative AFM topography images of the dielectric surface before operation (a) and after 4 minutes of SDBD operation in open (b) and closed-volume air (c). The AFM topography image of the dielectric surface before operation shows a relatively smooth surface (root mean square [RMS] roughness of ~20 nm). The AFM topography images of the dielectric surface after 4 minutes of operation revealed drastic changes consisting of surface buckling at the nanoscale. After 4 minutes of SDBD operation, the RMS roughness of the dielectric surfaces was 73 nm for operation in open air and 95 nm for operation in closed-volume air. Figure 8 shows the evolution of RMS roughness of dielectric surface as result of SDBD operation. The difference between RMS roughness values observed in these two cases is not very large for operation times less than 7 minutes. However, at longer operation times, the difference increases significantly, probably due to the effect of increased humidity in the closed-volume air.

V. CONCLUSION

In summary, we investigated the postdischarge kinetics of reactive species produced by SDBD plasma ignited in closed-volume air at atmospheric pressure to determine the decomposition of methylene blue molecules in aqueous solutions. The SDBD electrode system consisted of a dielectric foil of polyimide covered on one face with a planar cop-

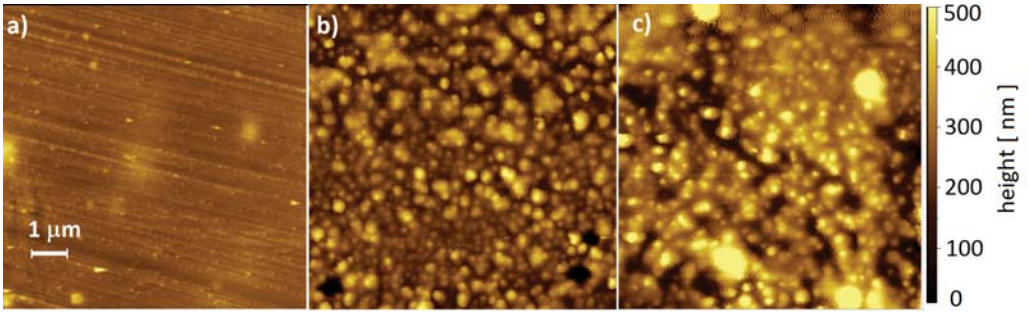

FIG. 7: Atomic force microscopy images of the dielectric surface before (a) and after 4 minutes of operation of SDBD in open air (b) and closed-volume air (c)

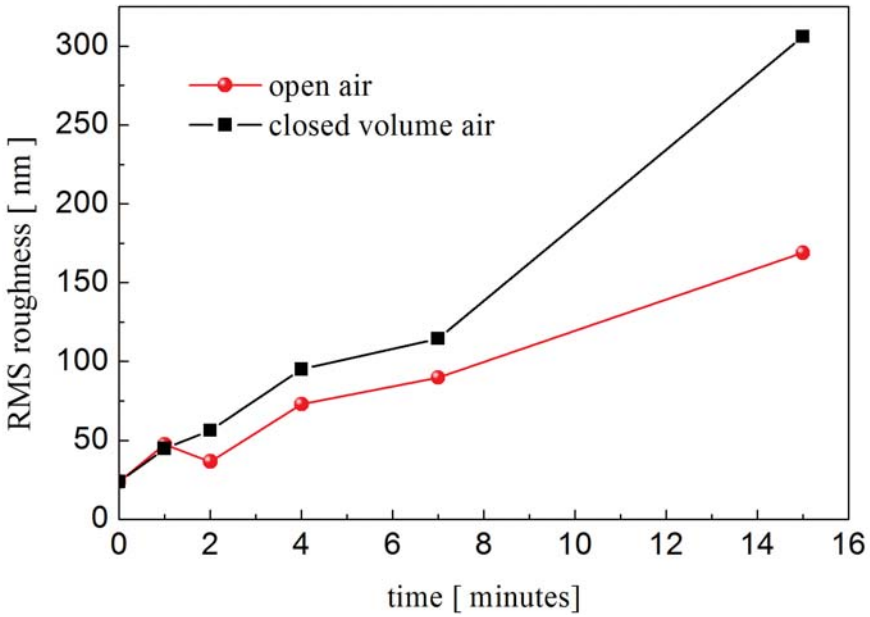

FIG. 8: Changes of root mean square (RMS) roughness of the dielectric surface during SDBD operation in open and closed-volume air

per electrode (grounded) and on the other face with a striped cooper electrode (connected to an high-voltage amplifier). The voltage across the plasma gap, the charge transferred through the plasma, and the dissipated power were determined from the charge-voltage Lissajous diagrams. After operation for 4 minutes, the discharge was turned off. However, the decomposition of methylene blue molecules continued for approximately 30 minutes, which indicates that the reactive species produced by SDBD were active for a relatively long period of time. The decomposition rate of methylene blue molecules in solution after the discharge was cut off determined the lifetime of active species in gas-

eous phase to be approximately 11 minutes. The operation of SDBD in closed-volume air in the presence of water shortened the lifetime of the polyimide dielectric of the discharge microelectrode system due to increased humidity and reactivity of the active species generated by the plasma. Atomic force microscopy was used to observe the changes in the surface morphology of the dielectric material during the discharge operation. The AFM topography images of the dielectric surface revealed drastic changes consisting in surface buckling at nanoscale, with formation of grains after only 4 minutes of operation. These surface-morphology transformations were indicated by the surface RMS roughness, which increased from approximately 20 nm for the dielectric surface before operation to approximately 90 nm for the dielectric surface after 4 minutes of operation. Operation of SDBD in closed-volume air resulted in larger modifications of dielectric surface morphology, especially for long operation times (compared with operation in open air). This effect is probably due to the increased humidity observed during SDBD operation in closed-volume air.

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