AGEING BEHAVIOR OF He DBD TREATED GLASS SURFACE

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Received November 9, 2011

This paper reports the ageing behavior of a 1.74 MHz cross-field He Dielectric Barrier Discharge (DBD) treated glass surface. The spectroscopic characterization identified the reactive species and confirmed the non-thermal and non-equilibrium character of the discharge. Water contact angle measurements and AFM topography demostrated the enhancement of hydrophilicity and cleaning of the surface.

Key words: dielectric barrier discharge, plasma treatment, glass, ageing.

1. INTRODUCTION

Several years ago plasma treatment of glasses was considered to be one of the most promising areas in glass manufacturing and applications [1]. Nowadays non-thermal plasmas have been widely used to alter the surface properties of various types of glasses without affecting their bulk properties. The majority of plasma assisted technologies were based on low pressure processes. In recent years, however, due to the lower operational and maintenance costs and simpleness of the equipments, non-thermal atmospheric pressure discharges have attracted considerable interest for use in surface modification techniques [2].

Specific surface properties like hydrophobicity, hydrophilicity, wettability, printability, biocompatibility, roughness, hardness or electrical conductivity can be modified to meet the specific requirements of specific applications. One of the most important requirement for a plasma modified material is to keep its new surface properties as long as possible. Several papers deal with this subject for plasma treated polymer surfaces [3-7].

Thus, the study of the ageing of a plasma exposed glass surface could offer important information about the durability in time of the treatment.

This paper presents preliminary results about the ageing behavior of a glass surface treated in a 1.74 MHz He Dielectric Barrier Discharge (DBD).

2. EXPERIMENTAL AND METHODOLOGY

In this study, a cross field DBD is generated in a parallelepipedic plasma chamber with a total volume of 160 cm^3 (Fig. 1). It contains two disk shaped metallic electrodes (24.5 mm diameter) covered with PTFE (1.5 mm thickness) as dielectric. The gap of the discharge space can be modified in the range of 0.5-2 cm. One of the electrodes is connected to the output of the drive generator and the other one is grounded. The chamber has an access nozzle through which helium gas (99.9995 % purity, Linde Gas Romania) with flow-rates lower than 5 slpm (standard liters per minute) is introduced. It flows perpendicularly to the electric field through the discharge space and is exhausted through two exit holes (3 mm diameter) placed on the opposite side of the chamber. The helium flowing is controlled with a digital mass flow controller (Aalborg Instruments & Controls, USA).

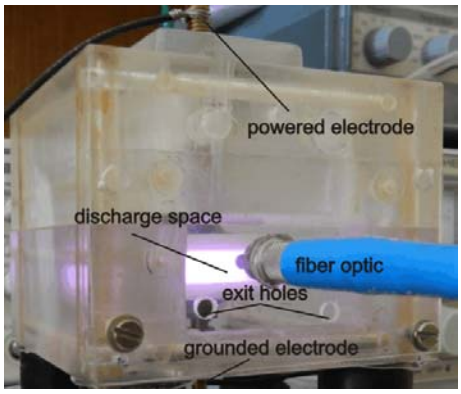

Fig. 1 – The cross-field DBD plasma chamber.

The laboratory made drive generator is based on the voltage-fed half-bridge series resonant inverter. Its schematic is shown in Fig. 2.

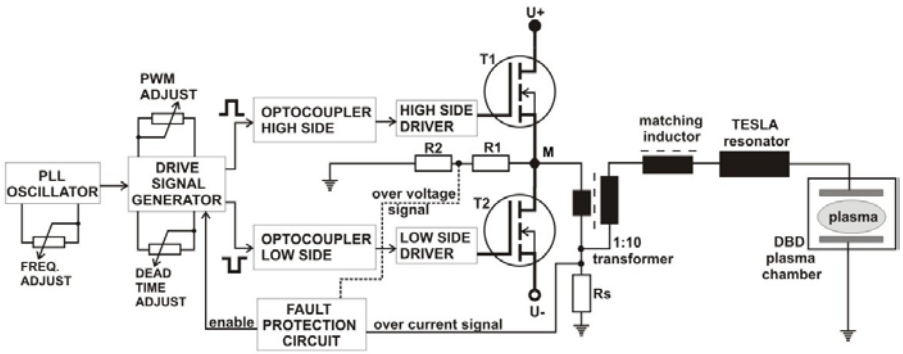

Fig. 2 – Schematic of the drive generator.

In the mid point of the half-bridge inverter (M) is connected the plasma chamber *via* a Tesla resonator, a matching inductor and a high-voltage transformer. When the circuit is driven with current pulses having the frequency equal to the self-resonant frequency of the circuit containing the Tesla resonator and plasma chamber (1.74 MHz), the power transferred to the load (the discharge) is maximized. The details on the running principle of drive generator are presented in [8]. For our applications the IRFP450 MOSFETs, are fed with symmetrical dc supply voltages in the range of 40-150 V and average currents lower than 1 A.

The plasma emission spectrum was monitored using two Ocean Optics HR 4000 spectrometers. Atomic and molecular emitting species identification was performed using appropriate software [9]. The same software was used to estimate the electron excitation temperature (T_{exc}), the temperature of excitation of vibrational states of N_2 molecule (T_{vibr}) using the molecular N_2 bands. The rotational temperature (T_{rot}) for OH was estimated by comparing the experimentally recorded spectra with the appropriate synthetic spectra generated by the LIFBASE 2.0 spectral simulation software [10]. The kinetic gas temperature was measured with a Pyrex-glass covered K-type thermocouple connected to a computer driven digital multimeter (MASTECH M345).

Glass wettability was tested by estimating the contact angle of bidistilled water droplets deposited on the glass samples. Glass samples of 15 mm x 15 mm were prepared by cutting microscope slides. Testing surfaces were degreased and cleaned by consequent washing with alcohol and distilled water, then dried. 3 μl of deionized water droplets as test liquid were deposited on the surfaces using a micropipette. The photos of each droplet deposited on the untreated and treated surfaces respectively, were taken using a commercial digital camera (Nikon Coolpix P500, 14 Mpx resolution) and the methodology presented in [11]. The images were processed by *Image J* freeware software [12] using the "contact angle" plug-in [13].

The occurent topographical changes induced by plasma treatment on glass surfaces was monitored by AFM measurements using an Ntegra Aura - NT MDT microscope.

3. RESULTS AND DISCUSSIONS

In order to identify the reactive plasma species produced, the optical emission spectra of the cross-field DBD (60 V dc power supply, 1.0 slpm He, developing stage [14]) were recorded in both UV and VIS ranges of the electromagnetic spectrum (Fig. 3 and Fig. 4, respectively) and the most important atomic and molecular components were identified.

Since our DBD system is an open-air one, bands resulting from the excitation of the back diffused air components are present in the UV spectrum, as expected: the second positive system of N_2 ($C^3\Pi_u \rightarrow B^3\Pi_g$, bandheads at 315 nm, 337nm,

353 nm, 357 nm, 371 nm, 375 nm and 380 nm) and the N_2^+ ($B^2\Sigma_u \rightarrow X^2\Sigma_g$, 391 nm) emission dominates the region as shown in Fig.3. No evidence of the NOγ system ($A^2\Sigma^+ \rightarrow X^2\Pi$, 200–300 nm) or of the OH molecular emission ($A^2\Sigma^+ \rightarrow X^2\Pi$, 306 – 312 nm) was detected.

The VIS spectrum (Fig. 4) presents an abundance of neutral helium lines corresponding to emission wavelengths between 500 nm and 750 nm (501 nm, 587 nm, 667 nm, 706 nm, 728 nm). Originating in the moisture content of back diffused air, the first three lines of the hydrogen Balmer series (H_γ 434 nm, H_β 486 nm and H_α 656 nm) and O atomic lines (777 nm and 844 nm) were observed in the spectrum.

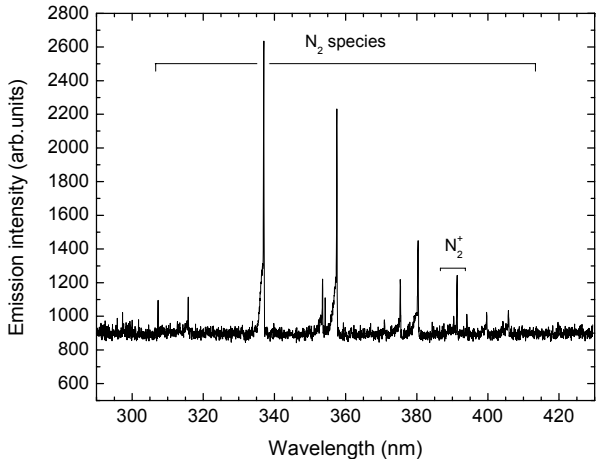

Fig. 3 – Fragment of the UV emission spectra of the He DBD.

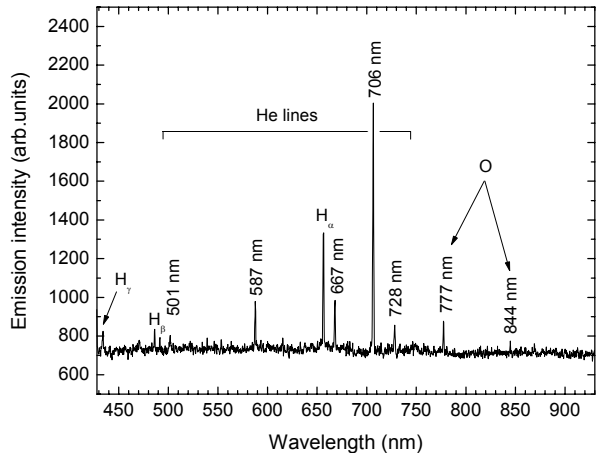

Fig. 4 – Fragment of the VIS emission spectra of the He DBD.

Analyzing the N_2^+ emission band around 391 nm, by the comparison technique, the rotational temperature was found to be about 416 K (Fig. 5).

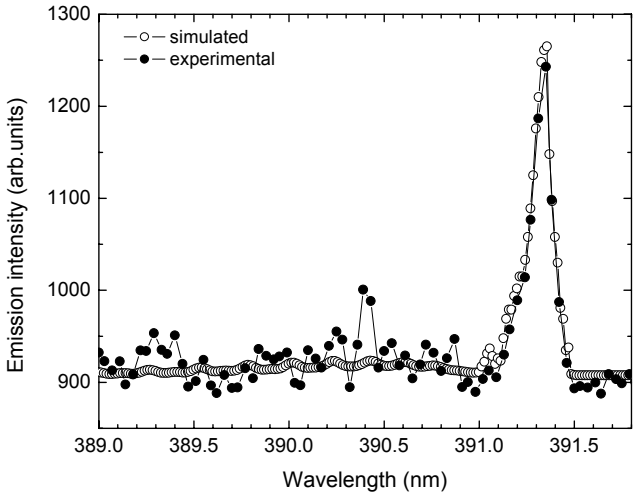

Fig. 5 – The N_2^+ emission band around 391 nm, simulated *vs.* experiment.

The atomic and vibrational excitation temperatures, estimated *via* Boltzmann plot method, were found to be 1346 ± 331 K for He, and 2813 ± 217 K for N_2 respectively. Thus, the estimated temperatures clearly demonstrate the non-equilibrium, non-thermal character of our cross-field DBD.

Several glass samples were treated at a 60 V dc supply voltage and 1.0 slpm He flow-rate, for different treatment durations, and the resulting changes of their surface property was investigated by contact angle measurements (Fig. 6).

Fig. 6 – Water droplet on a not treated (a) and a 5 s He DBD treated (b) glass surface.

As it can be observed in Fig. 7, the contact angle of the glass decreased from approximately 33° to 13° after 5 s of plasma treatment and did not vary much between the treatment duration of 2 s and 5 s. The considerable decrease in contact angles after plasma treatment suggests that the glass surface was successfully cleaned.

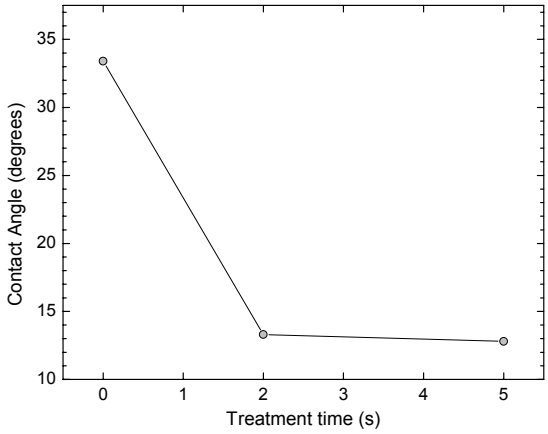

Fig. 7 – Effect of DBD treatment on glass surface.

The results of the topographical investigations, performed by AFM technique (Fig. 8), confirm the hypothesis of an intensive surface cleaning without any structural bulk change.

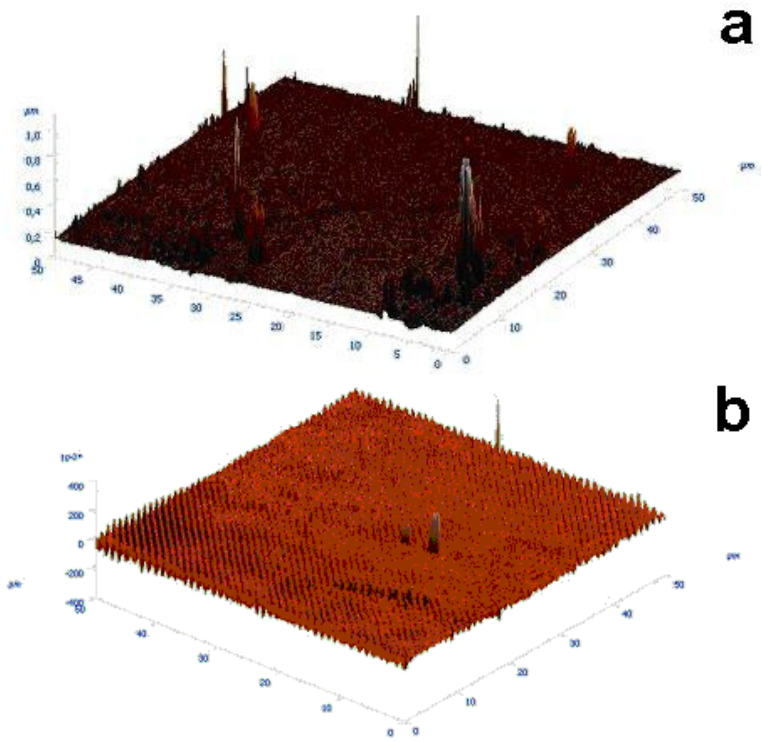

Fig. 8 – AFM images of a not treated (a) and a 5 s He DBD treated (b) glass surface.

In order to see whether the surface cleaning induced by plasma treatment is durable in time, an ageing test was performed. Glass samples, previously cleaned and than treated for 2 s in the plasma, were kept under clean (dust and grease free) conditions. From time-to-time contact angle measurements were performed and the results were compared to the original one for the untreated sample.

The results of the ageing are presented in Fig. 9 (error bars represents the standard deviation of 5 measurements).

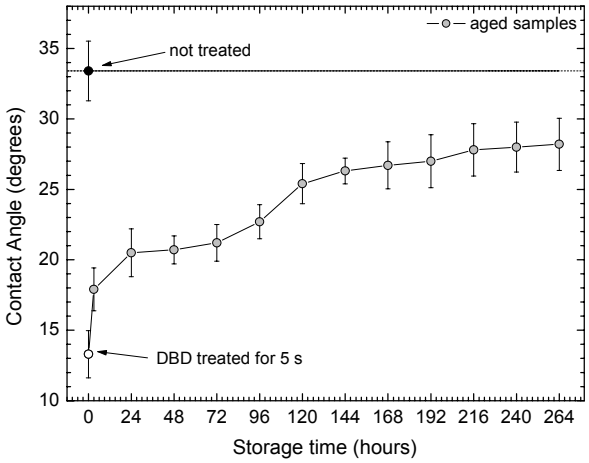

Fig. 9 – The ageing effect of the He DBD treatment.

As one can see, the values of the contact angles increase with the increasing storage time. This could be subscribed to the deposition of organic contamination on the glass surface from the surrounding ambient air, in content of the clean storage conditions.

4. CONCLUSIONS

A 1.74 MHz He DBD was used for surface treatment of glasses. Very short treatment times (2-5 s) were sufficient to clean the surface and make it hydrophilic. The spectroscopic characterization of the generated He DBD identified the reactive species and confirmed the non-thermal, non-equilibrium character of the discharge. The contact angle measurements performed on the not treated and on the DBD exposed glass surfaces confirmed the cleaning of the surfaces. AFM topography demonstrated the intensive plasma cleaning of the surfaces without changes in surface roughness. The hydrophilicity of the treated glass surfaces are subject to ageing, the water contact angles will increase with the duration of the storage time.

Due to this finding one can say that, the first three hours after DBD treatment are the most appropriate for surface involved applications (thin film deposition, painting, grafting, etc.).

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