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Study of the treatment's homogeneity in plasma assisted chemical vapour deposition by atmospheric pressure dielectric barrier discharge

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ABSTRACT

Dielectric Barrier Discharge (DBD) appears to be a promising technology to perform surface treatments at atmospheric pressure, particularly for the treatments of large-dimension flat objects for on-line industrial applications. Besides the fact of allowing short treatment times, the advantage of atmospheric pressure is the suppression of constraints correlated to the implementation of vacuum devices necessary for low pressure treatments. But at the present time, if this technology showed its ability for the surface cleaning, it is not still the case for thin film deposition over large surfaces, due to an insufficient homogeneity of the deposited layers. This lack of homogeneity is the main present problem limiting the use of DBD in PACVD. The study of the layer's uniformity leads us to search links between the internal physical phenomena inside the reactor and the layer's properties. This paper is focused to the study of the spatial homogeneity of SiO_x thin films deposited over large surfaces by using an atmospheric pressure DBD with N_2/O_2/HMDSO gas mixture. The results presented in this paper show that it is possible to understand the homogeneity variations of deposited layers by simultaneously making the link between the deposited power in plasma (taking into account both the energy per pulse and the pulse repetition frequency) and the gas hydrodynamics in the flow boundary layer.

1. Introduction

One of the great challenges is to find new technologies against metal corrosion being at the same time, non-destructive (cold techniques), clean and economically viable. Many low pressure plasma techniques have been developed in the recent years and their efficiency largely demonstrated [1–3], but these low pressure techniques require a large amount of expensive vacuum equipments. Thus, the development of a new plasma technology operating at atmospheric pressure which could be more costly-effective for on-line treatment of large surfaces, is a real industrial challenge. Among the different discharges already developed to produce stable plasmas at atmospheric pressure [4], the Dielectric Barrier Discharges (DBD) are particularly attractive because of their simplicity, cheapness, and great flexibility in terms of geometric shape, working gas mixture composition and operating parameters [5–7]. Thus, they are commonly used to produce transient non thermal plasmas usable for many applications such as ozone production, UV emission, flux gas treatment and surface modification [8–22]. Usually, the DBD operates in a filamentary mode, but under special conditions there also exist two different diffuse modes, the so-called Atmospheric Pressure Glow Discharge (APGD) generally obtained in rare gases, and the Atmospheric Pressure Townsend Discharge (APTD) which is realized in nitrogen at the condition that each discharge electrode was covered by a dielectric (double-DBD configuration). The conditions for operating the DBD in these diffuse modes were extensively studied by F. Massines et al. [11,15,16,18]. However, it should be mentioned that, despite their great interest for specific applications, these two modes (10^3–10^4 W/m^2) do not allow depositing a large amount of power density in the plasma, compared to the more classical filamentary DBD ($>10^5$ W/m^2). Moreover, they are very sensitive to small changes in the operating conditions and a transition from the diffuse modes towards the filamentary one can readily occurs.

High-speed on-line treatment of metallic surfaces requires both i) a high power deposition in an inexpensive buffer gas (nitrogen or air), and ii) that the surface to be treated is the grounded electrode of the discharge. In those conditions, at atmospheric pressure the filamentary discharge mode is unavoidable. It should be emphasized that despite the inhomogeneous character of the filamentary discharges, homogeneous treatments of surfaces can be obtained as previously shown [18–21]. This results from the spatial random distribution of the energetic filaments, for which the lifetime is of a few tens of nanoseconds, whereas the treatment duration is at least a few seconds. Usually the DBD were powered with a sinusoidal power supply. However, recent results have shown that a pulsed excitation

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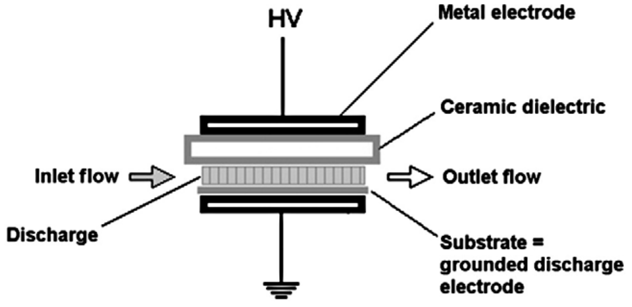

Fig. 1. Schematic representation of the experimental DBD reactor.

can provide many advantages. For ozone synthesis, a decrease of more than 30% of the energy consumption was demonstrated [19,20] when the sinusoidal excitation was replaced by a pulsed one. Moreover, a better efficiency of the radiation emitted by VUV excilamps was also achieved with pulsed excitation [20,21]. These higher performances mainly result from a better control of the injected energy into the plasma and of the resulting chemistry [18–23].

So, in this paper, we chose to study the application of pulsed filamentary DBD for atmospheric pressure PACVD (Plasma Assisted Chemical Vapour Deposition), in order to deposit thin SiO_x films on metallic sheets. While the design of a DBD reactor is generally quite simple [5–24], the optimization for the thin layers deposition at atmospheric pressure requires a large understanding of the processes conditioning the film growth mechanisms. At high pressure, the main challenge is to control the quality and the homogeneity of deposited layers. Due to the high density of reactive species, the volume chemical reaction rates are increased compared to low pressure processes, inducing more porous and less homogeneous layers on the substrate surface [24]. Our main interest was to find a mean to control the quality of the layers deposited over large steel surfaces. To do that, we investigated the correlations between the energy injected into the plasma, the flow hydrodynamics, and the properties of the deposited SiO_x films.

2. Experimental

A schematic drawing of the experimental set-up is shown in Fig. 1. The DBD reactor is constituted of a reaction chamber including two flat parallel electrodes, $225\times50\ \mathrm{mm}^2$, with a gap of 2 mm. In order to avoid the arc regime, a 3 mm alumina plate (Al_2O_3, $\varepsilon_r=10$, purity: 97.5%) is glued with silicone on one electrode (the high-voltage one). The other electrode (the grounded one) is simply the metallic sheet to be treated. It is made of black iron, 200 µm in thickness and about 400 nm in roughness. Before being placed in the reactor, this electrode is simply cleaned by immersion in an ultrasonic bath using Ethanol as a liquid solvent. The DBD is powered by a home made pulsed high-voltage power supply, allowing the application of peak voltage up to 20 kV at pulse repetition frequency in the range 10–100 kHz. The determination of the energy deposited into the plasma was performed through the measurement of the electrical parameters. An example of the discharge voltage $U_{\mathrm{m}}(t)$ and of the discharge current $I_{\mathrm{m}}(t)$ is presented in Fig. 2. They were determined by using high-voltage probes (Tektronix P6015A, ratio 1:1000, bandwidth: 75 MHz), home made Rogowski current probes (bandwidth higher than 100 kHz) and a digital Lecroy oscilloscope (bandwidth higher: 1 GHz). The shape of the electrical waveforms depends of the coupling between the reactor and the power supply. The second negative current pulse which appears in Fig. 2 is due to the saturation of the output transformer of the power supply, and its amplitude is a function of the transformer temperature. As previously demonstrated [18,23] from a modelling of the DBD circuit, the energy injected per pulse into the plasma can be directly determined from the measured voltage and current waveforms through the relation: $E_{\mathrm{inj}}=\int U_{\mathrm{m}}(t)I_{\mathrm{m}}(t);t$. It should be pointed out that, for a given primary voltage applied to the low-voltage stage of the power supply, the energy injected per pulse into the plasma changes by less than 10% when the repetition frequency varies in the range 20–80 kHz. By changing the primary voltage, the deposited energy can be continuously adjusted in the range 2–12 mJ per pulse. Accordingly, by changing both the pulse repetition frequency and the primary voltage the mean power deposited into the plasma can be chosen in the range 20 W–1000 W ($2\cdot10^3\ \mathrm{W/m^2}$–$10^5\ \mathrm{W/m^2}$).

Two configurations of the gas injection were used: a longitudinal gas injection and a transversal one as shown in Fig. 3. For the longitudinal injection, the gas mixture is introduced into the reactor through a duct, 16 mm in diameter, equipped with a porosity diffuser about 10 µm in order to limit the low turbulence effects due to the geometric discontinuities at the entrance of the reaction chamber. The exit port, without diffuser, has a diameter of 20 mm. In the transversal geometry, the gas flow is admitted though a port, 26 cm in length and 4 mm in height, also equipped with a diffuser. The exit port has the same geometry than the entrance port but does not include a diffuser. Whatever the geometry, the gas extraction is only produced by the gas flow without any pumping. So, the internal hydrodynamics is mainly conditioned by the geometry of the reaction chamber (hydraulic head loss), by the flow rate value (Reynolds number, Mach number) and the plasma (thermal disturbances and electro-hydrodynamic effects [25,26]). The internal static pressure is constant and equals to the atmospheric pressure. For all the experimental conditions used in the present work, the Mach number was lower than 0.3, in such a way, the fluid can be considered as an incompressible one. Moreover, the Reynolds numbers are in the range 10–100 leading a laminar gas flow.

The nitrogen flow rate is fixed to 1000 ml/min, the oxygen flow rate is limited to 5 ml/min (5000 ppm). HMDSO is injected in the gas mixture in vapour form by means of a controlled evaporator and its flow rate was chosen equal to 4 ml/min (4000 ppm). Research grade gases are used and their flows were regulated through mass flow-meters. Before being introduced in the discharge chamber, the gas flow goes through a mixing section assuring its chemical homogeneity. The calculated ratio between oxygen concentration and precursor concentration $R=[O_2]/[\mathrm{HMDSO}]$ is 1.25. At this value, we observed that the deposition growth rates are relatively high, a few tens of nm min^{-1} up to 900 nm min^{-1}, compared to a few nm min^{-1} with low pressure techniques [27]. Low variations of this ratio ($1<R<5$) slightly change the chemistry of layers by changing the carbonic content and the global growth rate; but it does not significantly change the non-uniformity of the deposited layers. So,

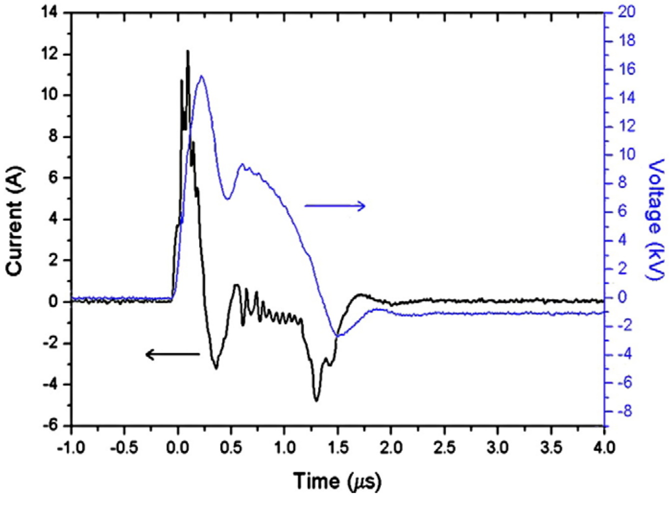

Fig. 2. Oscillogram of the current and the voltage applied to the DBD reactor. $F=55$ kHz, $U_{\mathrm{prim}}=250$ V, N_2: 1 l/min, HMDSO: 4000 ppm, O_2: 5000 ppm.