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The role of precise energy input in atmospheric pressure plasma polymerization: the case of biomedical coatings

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Abstract: Atmospheric pressure plasma-enhanced chemical vapor deposition (AP-PECVD) of biomedical coatings is carried out in a dielectric barrier discharge (DBD) reactor. Argon is used as the inert carrier gas, entraining volatile organic precursors into the discharge zone. Precise measurements of the energy dissipated per discharge cycle, E_g, are carried out, supported by an equivalent electric circuit model.

Keywords: DBD, discharge energy, plasma polymerization, biomaterials

1. Characterization of Electrical Energy Input

A special *Debate* issue of *Plasma Processes and Polymers* (vol. 7, No. 5, 2010) dealt with film growth mechanisms in low-pressure plasma polymerization. A key role is played by the *specific energy* parameter, W/F (power input per unit of gas flow, or average energy transferred per monomer molecule during its residence time in the active plasma zone). This so-called Becker parameter goes back to the 1920s, but a modified version later became known as the Yasuda parameter, W/FM, the energy per mass of monomer [1]. Whatever views one may hold about reaction mechanisms, no one questions the importance of knowing power transfer to the plasma with the greatest possible precision, as also confirmed in a recent review paper by Friedrich [2]. While most workers in low-pressure plasma processing science pay close attention to power input, this seems less to be the case in atmospheric pressure plasma-enhanced CVD (AP-PECVD): so-called *Q-V plots*, also known as Lissajous figures, are used by many workers as a standard measurement technique for dielectric barrier discharges (DBD) since first proposed in 1943 [3]. As shown by Pipa *et al.* [4] and by this laboratory [5], that method can readily lead to false values of the DBD capacitance, C, and to other sources of error, for example, if one ignores the important contribution of displacement current.

Now, the electrical properties of a DBD reactor can be described by means of an equivalent circuit model, from which C can be experimentally determined from a.c. current and voltage measurements without plasma, the technique that we have adopted. This then allows precise determination of the electrical energy dissipated per discharge cycle, E_g, particularly in atmospheric pressure glow discharge (APGD) plasmas in noble gases or in nitrogen. Fig. 1 portrays the equivalent electrical circuit model that we use, the dashed rectangular box representing the actual DBD reactor. V_{ps} and V_m correspond to the voltage signals respectively measured by high and low voltage probes, R_m being a precision 50 Ω resistor (see abstract by M. Archambault-Caron *et al.*, this symposium).

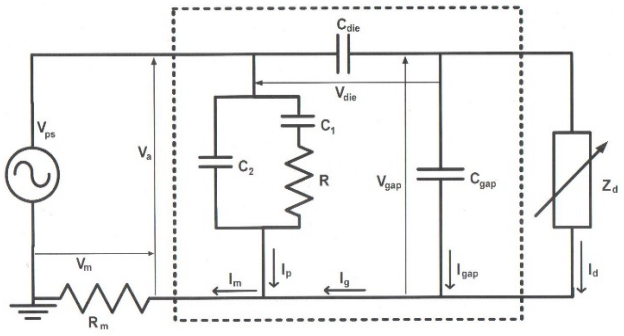


Fig. 1. Equivalent electrical circuit diagram; the portion in the dashed rectangle represents the DBD reactor.

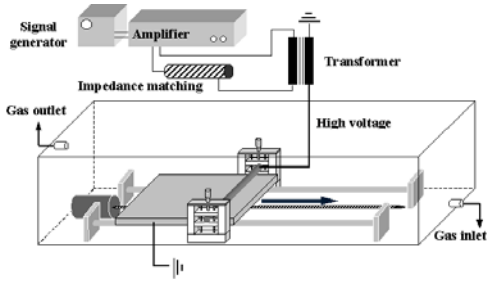
We can now perform precise measurements of the energy dissipated per discharge cycle, E_g, in the DBD reactor described below. This approach appears to be without precedent in the context of AP-PECVD.

Fig. 2a shows a schematic view of the DBD reactor system used in this study, while Fig. 2b is a photographic image of the planar high-voltage electrode assembly that replaces the original simple ceramic-coated cylindrical electrode shown in Fig. 2a.

2. Atmospheric Pressure Plasma Polymerization of Biomaterials: Method and Results

It is, of course, well known that plasma polymerization enables the use of organic compounds that cannot be conventionally polymerized; we therefore refer to them as *precursors*, in contradistinction with the term *monomers*. Nevertheless, it is possible to generate polymer-like materials, the chemistry and surface properties of which closely resemble classical polymeric counterparts, while the physical properties, such as solubility and crosslinking are drastically different. In AP-PECVD of the type we

(a)



(b)

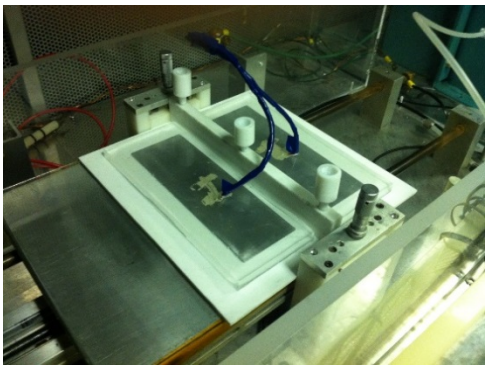


Fig. 2. a) Schematic view of the DBD reactor system; the original cylindrical high-voltage electrode was replaced by the planar pair shown in (b). b) Photographic image of the planar DBD electrode assembly, comprising Macor® machinable ceramic as the dielectric. The two high-voltage electrodes are encased in poly(dimethylsiloxane) (PDMS). In the center, one notes the three injection ports of the feed-gas diffuser. The mobile, glass-covered grounded electrode is at the lower left.

carry out here, argon (Ar) is used as the inert carrier gas; it is bubbled through the (liquid) precursors and entrains them into the discharge zone shown in Fig. 2b. Contrary to low-pressure PECVD, where undiluted organic precursors are normally used, one obviously has to account for energy absorption by Ar and transfer from the excited Ar* to the organic precursor molecules. Since the latter are heavily diluted in Ar (typically at the parts per thousand level), the measured E_g value primarily relates to Ar; we compare power absorption of the fixed flow of Ar carrier with and without the presence of the precursors, and find that the latter have a relatively minor effect on total power absorption when other discharge parameters (voltage, frequency, geometry, etc.) are kept constant.

AP-PECVD of thin organic coatings opens new routes to generate materials for specifically targeted applications. The target materials here are of biomedical interest, consisting of carboxylic- and/or amine-enriched polyester matrices, for example. Fig. 3 shows some of the precursors used in this research.

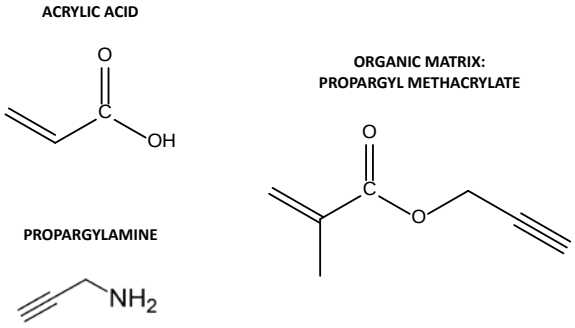


Fig. 3. Organic precursors used in this study.

A set of Fourier Transform Infrared (FTIR) spectra, shown in Fig. 4, clearly illustrates the impact of power absorbed by the plasma on the retention of the chemical functionalities of one of those precursors, acrylic acid, deposited at atmospheric pressure in the DBD reactor (Fig. 2).

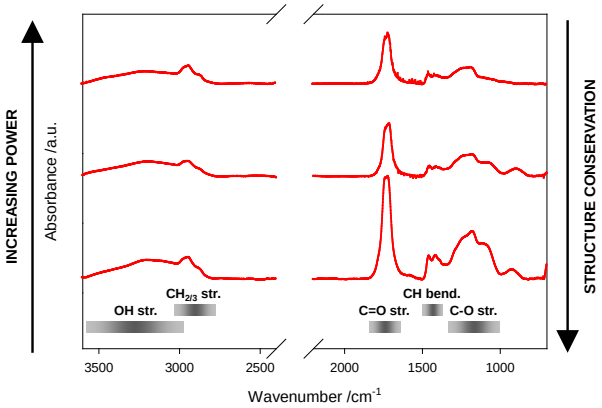


Fig. 4. IRRAS-FTIR spectra of plasma polymerized acrylic acid. The spectra are normalized with respect to the $CH_{2/3}$ stretching band.

As expected, a significant decrease in the C=O and C-O (stretching - str.) bands is observed with rising power input, on account of greater precursor fragmentation. This underlines drastic reduction of the deposited coatings' *acrylic acid character*. Chemical structure characterizations using X-ray Photoelectron Spectroscopy (XPS) and FTIR bear witness to the strong correlation between conservation of the precursors' chemical functionalities, on one hand, and E_g, on the other hand.

3. Acknowledgements

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