



**PLATHINIUM**  
PLASMA THIN FILM INTERNATIONAL UNION MEETING

13-17 September 2021  
Antibes, French Riviera  
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## **Large volume liquid treatment with high-density microwave plasma**

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Plasma-liquid interaction has attracted much attention for various applications such as water purification, decomposition of liquid waste, biotechnology, agriculture, and material synthesis. For such purpose, dielectric barrier discharges, spark discharges, etc. have been used as the plasma source, because these atmospheric pressure plasma sources are compatible with liquid environment. These discharges also have merit of low power consumption with energy saving. However, some applications such as hydroponic culture, liquid waste management etc. requires large amount of liquid plasma treatment and efficient plasma treatment system is essential.

For efficient liquid treatment, pressure reduction is one of the solutions because the discharge ignition is much easier at reduced pressure condition, not only in the case of DC discharge but also in the case of RF discharge including microwave. Based on this, we made various approach to liquid treatment under reduced-pressure condition using microwave power. In the presentation, effectiveness of the reduced-pressure process will be shown. Furthermore, to realize sustainment of stable plasma close to the liquid surface, an alternative way of liquid treatment set-up is proposed, where reduced pressure is automatically formed by liquid flow with the aid of Venturi effect. This concept also has a merit of compatibility with the liquid treatment because the liquid can be treated with in-line process.

With using this concept, new microwave plasma treatment source will be presented. As an example of the water waste treatment, organic decomposition by the in-line liquid treatment system will be shown. Furthermore, the microwave liquid treatment system is applied to materials processing. Recently, silver nanoparticles have given much attention as silver “nano-ink” in printing electronics. For such application, silver nanoparticles are produced from silver nitrate or other related solutions by the in-line liquid treatment system. By optimizing liquid compound, conversion efficiency to silver nanoparticle was more than 5%, which is promising to suppress production cost of silver nano particles.



## Influence of the electron description on the modelling of scenarios with interest for plasma-based applications

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The adequate description of the electron kinetics is paramount to capture the behaviour of low-temperature plasmas, becoming a critical aspect of modelling in scenarios with interest for applications. In this talk, we present two examples where modelling results can be severely affected by the formulation adopted to describe the plasma electrons.

The first example focuses on the temporal evolution of the electron kinetics in dry-air plasmas (80%N<sub>2</sub>:20%O<sub>2</sub>), excited by electric-field pulses with rise-times 10<sup>-9</sup> and 10<sup>-6</sup>s, applied to a stationary neutral gaseous background at pressures 105 and 133Pa [2]. The study solves the electron Boltzmann equation (EBE) using the LisOn KInetics Boltzmann solver (LoKI-B) [1] and adopts either (i) a time-dependent formulation that considers an intrinsic time evolution for the electron energy distribution function (EEDF); or (ii) a quasi-stationary approach, where the time-independent form of the EBE is solved for different values of the reduced electric-field during the pulse. The simulations show that (i) gives solutions similar to (ii) for rise-times longer than the characteristic evolution time of the EEDF, i.e. 20ns at 105Pa and 20ms at 133Pa, meaning that a quasi-stationary description is possible in microsecond pulses at atmospheric pressure, failing for nanosecond pulses at both pressures considered here.

The second example addresses capacitively coupled radio-frequency discharges in N<sub>2</sub>-H<sub>2</sub> at low pressure (0.3–0.9mbar), low power (5–20W), and H<sub>2</sub> concentrations up to 5% [3]. Simulations use a hybrid code that couples a two-dimensional time-dependent charged-particle fluid module to a zero-dimensional kinetic module, that solves the EBE and includes a detailed surface chemistry for NH<sub>x</sub>. The code includes a dedicated module for fast electrons generated by secondary emission. The inclusion of these fast electrons results in an exponential growth of the electron density at higher powers, which is not captured by the fluid code for slow electrons and allows fitting the measurements by tuning the secondary emission coefficient

(SEC). The results highlight the relevance of plasma-surface interactions, given the role of SEC in the electrical parameters and the critical influence of the surface production of ammonia in the plasma chemistry.

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### References

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## **Novel methods for tuning film properties using nanostructures**

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We have developed three novel methods for tuning film properties using nanostructures: controlling nucleation in gas phase, nucleation on substrates, and nucleation under catalysts. They correspond to nanoparticle composite film deposition, inverse SK mode deposition and sputtering-assisted metal-induced layer exchange. The nanoparticle composite films are deposited using nanoparticles and radicals formed in reactive plasmas [1]. Chemical reactions on nanoparticles take place much faster than those on substrate surface, especially at low substrate temperatures, because nanoparticles of a low heat capacity become high temperature due to heating from plasma and they have a large surface to volume ratio. Utilizing this feature, we have succeeded high quality SiN<sub>x</sub> films at a low substrate temperature of 100 °C. The inverse SK mode is a new mode of hetero-epitaxial film growth, in which stress is relaxed in an atomically flat buffer layer consisted of nanocrystals aligned in-plane and out-of-plane and single crystal with a low defect density grows on the buffer layer [2]. To realize the buffer layer of this mode, we applied impurity-mediated sputtering. Nitrogen was employed as an impurity for ZnO film fabrication. We obtained single crystal ZnO on sapphire with a large lattice mismatch of 18%. The inverse SK mode opens great possibilities of single crystal hetero-epitaxy of multicomponent systems with a wide mixture range. The impurity-mediated sputtering provides an alternative method for amorphous film formation at high substrate temperatures. We applied this method to obtain amorphous ITO films with a high mobility. The metal-induced layer exchange is a well-known method of crystal film formation on glass and polymer. We reduced the processing time by 2-3 orders of magnitude and the processing temperature using a sputtering-assisted metal-induced layer exchange method [3]. By applying the method, we succeeded in crystalline Ge formation on polyamide films at 150 °C in a short processing time of 10 min. In addition to these film fabrication methods, we will show film properties and some device applications. In particular, by combining a novel inverse SK mode with a novel material of ZnInON, we demonstrated room temperature operation of an excitonic transistor, a novel ultra-low energy consumption and ultra-fast switching device with an optical input and output.

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## **A cocktail of active ingredients - benefits and challenges for plasma medicine**

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Low-temperature plasma discharges in or in contact with air produce a variety of reactive oxygen and nitrogen species (RONS). The reactive species produced by plasmas are the same molecules that the human body generates for signaling or antimicrobial effects. Plasma treatment of eukaryotic cells can thus cause a similar effect as an innate immune system oxidative burst and plasma at low doses can mimic an immune response to tissue damage, wounds or infection which could initiate a natural healing response. Utilizing plasma-generated RONS for plasma-aided wound healing or plasma oncology is therefore a promising alternative to conventional treatments and the effectiveness of plasma for wound healing and cancer treatment has been shown in vitro and in vivo. Yet, the mechanisms of action and the delivery of RONS to the target are currently still under investigation.

In this contribution we will explore the cocktail of active ingredients; the generation and transport of the reactive species O and OH from the gas phase through a liquid to a biological sample and investigate the role that the biological sample plays as part of the reaction pathway. Using the model biological sample cysteine, which is often found in proteins that play a key role in signaling, the differences between a more OH/H<sub>2</sub>O<sub>2</sub>-dominated chemistry and a more O-dominated chemistry is explored. The results indicate that the modifications caused by a OH/H<sub>2</sub>O<sub>2</sub>-dominated chemistry are similar to those that can be found in context of redox biology, whereas modifications caused by O-dominated chemistry differ significantly. Atomic oxygen is unknown in nature whereas OH and H<sub>2</sub>O<sub>2</sub> are well known and produced by organisms. The cocktail of active ingredients in a plasma and the variety of different plasma sources available makes it thus difficult to assess and generalize the impact of plasma on cells. On the other hand, the tunability of plasma and the possibility to tailor RONS production to certain outcomes provides a promising and powerful tool to aid the healing of chronic wounds or to develop new strategies in cancer treatment.



## Electrical diagnostics for Dielectric Barrier Discharges: from integrated measurements to spatially resolved measurements. Benefits for plasma processes at atmospheric pressure?

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Dielectric Barrier Discharges (DBDs) can be used in many processes as thin-film coating, sterilization, treatment of gases, aerodynamic flow control, and lighting devices [1]. Depending on the gas, electrical operation parameters and discharge geometry, the plasma operates in the classical filamentary mode or in a homogeneous regime [2]. Electrical measurements are a more convenient than optical measurements to characterize the discharge regime and to study the discharge behavior. However, and because of the dielectric presence, it is not possible to directly measure the electrical parameters of the discharge. Usually, the electrical parameters are calculated from the measured quantities under usage of an electrical equivalent circuit [4]. The key parameter for this approach is the determination of the discharge area, which is usually considered to be equal to the electrode surface as long as the discharge is homogeneous. However, even if the plasma seems to cover the electrodes uniformly, its electrical properties (current density, breakdown voltage, duration of discharge, ...) are not exactly the same at any time and at any point of the surface. For example, when a gas flow is injected from one side of the planar DBD arrangement, the species densities are not the same along the gas flow because of the kinetic processes and chemical reactions in the discharge [4]. Thus, the discharge current and the gas voltage are not uniform along the spatial DBD dimensions. Therefore, determination of discharge current and gas voltage from macroscopic parameters of the DBD is often inaccurate.

In order to have a more accurate characterization of the discharge behavior, a measurement of the local current density is required. To get a 2D mapping of the discharge electrical parameters, the ground electrode is prepared as a segmented electrode with 64 equally spaced square segments. The high voltage electrode still remained full. This electrode is a 3x3 cm<sup>2</sup> square, while each square of the segmented electrode has a 3.44 mm side length, a distance of 350 μm spaced each segments. A prototype, using a ground electrode divided into 64 identical squares and a data acquisition system has been developed [5]. This system can be used to study the spatial electrical behavior of a DBD. It has been successfully validated on planar DBD by the comparison with short exposure time photos taken by a camera from above the discharge cell [5]. It has been used to study the diffuse discharge (APTD) and shows the effect of a gas flow on the local electrical behavior of the discharge. In the case of diffuse DBDs with sinusoidal voltages at frequencies from 1 to 20 kHz, the temporal and spatial resolutions are high enough to characterize the behavior of the discharge with sufficient spatial information.

This electrode arrangement and measuring systems allows a 2D mapping of the discharge electrical parameters (discharge current, power dissipated, gas voltage, etc.) of Townsend but also for Glow discharges, hybrid or patterned regimes. Concerning the plasma processes for surface coatings, this system can be used to monitor the evolution of the local discharge power which defines the local deposition rate. If we use this segmented electrode as the high voltage electrode with adequate power supply, we could reconfigure the electrode and the power transfer to the discharge. Then this system could be used to realized patterns. All of this opens up new directions which will be discussed during the presentation.

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