MICROWAVE PLASMAS AT ATMOSPHERIC PRESSURE: NEW THEORETICAL DEVELOPMENTS AND APPLICATIONS IN SURFACE SCIENCE

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Key words: plasma, atmospheric pressure, microwave, filaments, argon, oxygen

Abstract: Specificity of microwave plasmas created at atmospheric pressure is presented. Plasma is created in a quartz tube placed in a microwave cavity. The cavity is powered with a MW generator at the frequency of 2.45 GHz. Interesting results are obtained using a pulsed discharge with the frequency of few kHz. New phenomena such as filamentation are presented and described together with possible applications of such sources of reactive plasma particles.

Mikrovalovna plazma pri atmosferskem tlaku: sodobni teoretični pristopi in uporaba za modifikacijo površin

Kjučne besede: plazma, atmosferski tlak, mikrovalovi, niti, argon, kisik

Izvleček: Prikazujemo specifične značilnosti mikrovalovne plazme, ki jo vzbujamo pri atmosferskem tlaku. Plazmo ustvarimo v kvarčni cevi, ki je nameščena v mikrovalovni resonator. Resonator vzbujamo z MW generatorjem s frekvenco 2.45 GHz. Zanimive rezultate dobimo predvsem pri uporabi pulzne razelektritve s frekvenco nekaj kHz. Prikazujemo nekatere nove pojave, kot je na primer pojav drobnih razelektritvenih niti. Poleg razlage tega pojave predstavljamo tudi možnost uporabe tovrstne plazme kot izvira reaktivnih plazemskih radikalov.

1 Introduction

Microwave plasmas at atmospheric pressure can be easily implemented to get sources of active species for surface treatment. Contrary to the Dielectric Barrier Discharges, radiofrequency discharges /1-2/ and other microwave surfatrons /3-6/ which operate at low temperature, typically even at lower pressures, microwave plasmas in continuous mode make it possible to reach very high treatment temperatures /7-9/.

In this paper, we will situate the microwave plasmas among other sources at atmospheric pressure and describe the different aspects, both theoretical and applied, of microwave plasmas, including the micro-microwave plasmas newly proposed.

2 Design of sources

Several possibilities have been used to design microwave sources operating at atmospheric pressure (see Fig. 1). Sources like surface wave excited plasmas /11-15/, waveguide-based microwave torches /8, 16-21/ and resonant cavities /9, 22-26/ are widely used. Even split-ring resonator microplasma were recently proposed /27/ to create small-scale plasmas (the gap size can be as low as 45 µm). The choice of the microwave frequency (433, 915 or 2450 MHz among others) affects not only the size of the plasma, but also its mean electron density, leading to steeper gradients when the frequency increases. Of course, this choice strongly modifies the plasma properties. For example, it is possible to observe filamentation of a neon plasma at 2450 MHz but not at 433 MHz /28/.

Attention has been paid recently to the linear extension of these sources /29/ in order to obtain a plasma "curtain" that could be used over large dimension in continuous flow process but current solutions only apply under reduced pressure. A simpler solution would consist in multiplying the number of sources. However, such an approach would suffer from the lack of inhomogeneity in concentration at the boundary between two adjacent sources.

3 Theoretical study

New phenonema, like filamentation and contraction, have been recently studied using microwaves sources. In the first case, a reduction of the plasma diameter is observed in surface wave driven plasmas. The origin of this contraction is yet controversial. In the second case, the filamentation process is shown to depend on different time scales. The wave propagation conditions are defined by the dispersion equation and the boundary conditions of the problem.

3.1 Contraction

Contraction is defined as the compression of a plasma into a filament located at the discharge axis. This compression is due to a weaker ionization rate. According to /15/, it

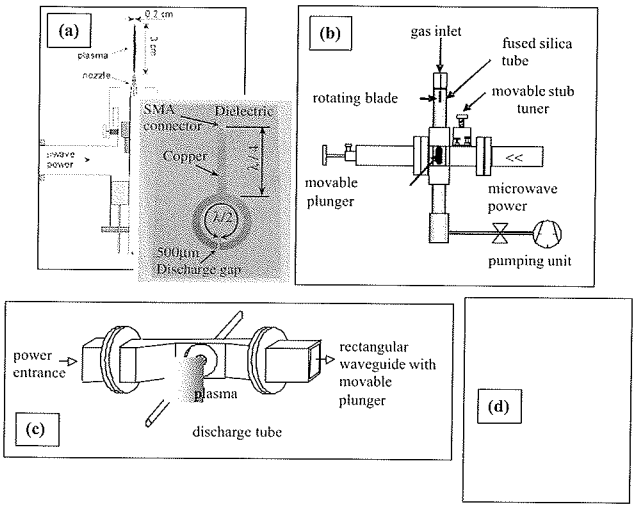

Fig. 1: Some possible designs of microwave sources operating at atmospheric pressure. (a) The "Torche à Injection Axiale" /7/, (b) resonant cavity /22/, (c) surfaguide wave launcher /11/ and (d) the split-ring resonator microplasma /27/.

could be due to a lower electron density caused by a decrease in the reduced electric field (E/N) due to a radial non-uniform heating of the gas. The decrease of the gas temperature changes the nature of the main dominating ion, since at high temperature, atomic ions prevail whereas dimmer ions are dominant at low temperature. Different works /30-31/ suggest that this lower electron density could result from a weak heating of the tail of the electron energy distribution function by electron-electron collisions.

3.2 Filamentation

When the discharge is sustained by a high frequency electric field, for certain operating conditions, another effect appears in addition to radial contraction - the breaking of the single plasma filament into two or more filaments of smaller diameters. We refer to this to as filamentation. The discharge filamentation is strongly connected to the contraction phenomenon. In these discharges that are controlled by ambipolar diffusion, we can think that the origin of filamentation is due to an inhomogeneity in the electron density or, but to a lesser extent, in the temperature. In Fig. 2, we observe a more intense light emission at the junction between the two filaments, suggesting a higher electron density as the possible source of the initial instability.

The filamentation process appears when the skin effect becomes important, i.e. at high electron density (typically ~10^{15} cm^{-3} in argon). The appearance of a second filament enables the better absorption of the power and a decrease in the mean electron density per filament. The presence of several filaments requires new microwave modes to satisfy the dispersion equations of the microwaves /32/.

We also showed recently that in pulsed mode, the growth of a filament could happen over different time scales. This is clearly evidenced in Fig. 3.

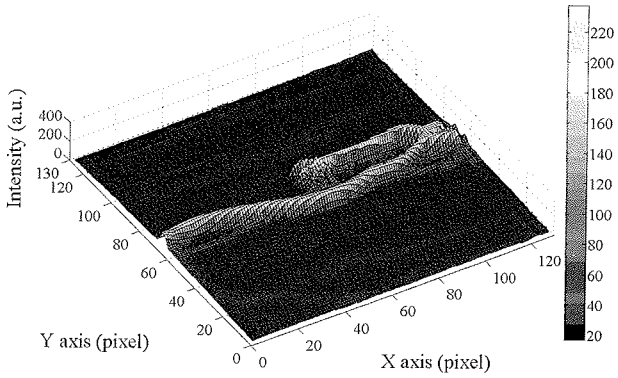

Fig. 2: Light intensity emitted by an argon plasma during the filamentation process. Two visible filaments are present in this image. Discharge sustained with a pulse frequency of 2 kHz. The pulse has a rectangular shape and the operation duty cycle is 41%. The absorbed power is ~70 W.

This memory effect is likely due to a post-discharge that remains active when the plasma is turned off.

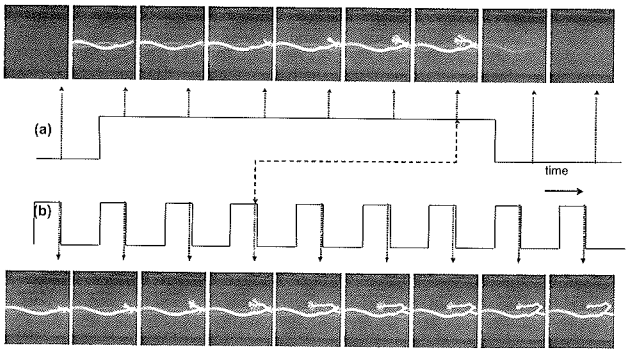

Fig. 3: Photographic sequence of atmospheric pressure discharges for a pulse frequency of 2 kHz. The pulse has a rectangular shape and the operation duty cycle is 41%. The absorbed power is ~70W. The resonant cavity is set up to resonate without plasma to ensure maximum electrical field, making the breakdown possible at each pulse. The integration time is 10 µs. (a): Selection of photographs taken every 31 µs during one period. (b): set of photographs taken at the end of each pulse after 9 pulses.

3.3 Modelling

Obviously, the lack of data on kinetic schemes occurring at high temperature requires specific works to improve the quality of the models /24, 33/ describing the behavior of these non-thermal plasmas. For example, the question of the dimmer ions dissociation rate as a function of the temperature is not solved yet since commonly used data only rely on estimation and not on measurements. This important question is essential to confirm the recent theory on contraction where the relative importance of atomic and molecular ions must be known accurately.

Another important aspect deals with the non-locality of the electron energy dissipation. Indeed, we have shown in /24/ that if the Boltzmann equation could be treated locally in helium, it is clearly not possible in argon, as it is yet commonly assumed. A more accurate treatment of the electron energy distribution function, as done for example in /13/, is necessary.

4 Surface treatments

Because of their high temperature (typically, above 1000 K and up to 5000 K), the microwave plasmas at atmospheric pressure can be use in many metallurgical applications like surface cleaning or Plasma Enhanced Chemical Vapor Depostion (PECVD). Micro-plasmas could also be used in small-scale materials processing or in micro chemical analysis systems /34,35/.

4.1 Surface preparation

Surface cleaning could be achieved with microwave sources at atmospheric pressure, by exploiting the high temperature of these sources, plasma processes being considered as environmental-friendly solutions. Many plasma processes (DBD, torches, corona discharges, etc.) are already proposed commercially to clean surfaces. However, a few is know on cleaning mechanisms. Two main problems arise: on the one hand, the oxidation of the surface can be enhanced in oxygen-containing plasma mixtures with respect to low pressure processes that usually operate at low temperature /36/. On the other hand, the cross-linking of radicals synthesized by the interaction of active species coming from the plasma with the contaminants can lead to the synthesis of a passive film that cannot be removed by the plasma. Under reduced pressure, this passive layer can be removed by sputtering. At atmospheric pressure, this step is no longer possible and a better understanding of the cleaning mechanisms is then required /37/.

4.2 PECVD

The main task to deal with in atmospheric PECVD is the control of the precursor flux with respect to the flux of active species from the plasma. Precursor dissociation and subsequent formation of intermediates must occur in the vicinity of the surface of the substrate. Diffusion being strongly limited at high pressure, one can only play on the convective flows of the precursors. The important time scale to be controlled is the residence time required for active species to reach the surface. For a long time scale, homogeneous nucleation leads to powder formation and deposition rates decrease. Transport of species through the boundary layer requires a minimum time that depends on the temperature and concentration. For shorter times, deposition rates decrease.

V. Hopfe and collaborators made huge progress in this field recently /38/. They succeeded in reaching deposition rates in the range 15-100 nm s^{-1} (static) and 0.3-2.0 nm m s-1 (dynamic) with properties of the silica thin films close to those of bulk silica. These very high values of the deposition rate make it possible to deposit thin films in continuous flow processes with moving substrate past the plasma source at several meters per minute.

However, deposition over large area with a high homogeneity in thickness and composition is still a difficult task to reach.

4.3 Other applications

Other possible applications deal with the development of small-scale microwave plasmas operating at high temperature. In general, microplasma sources capable of creating controlled small-sized discharges are desirable for applications such as bio-MEM sterilization, small-scale materials processing, micro chemical analysis systems, displays and micropropulsion. These microplasma sources can be integrated into small-scale portable devices that offer the same advantages of size, cost and reliability of microfabricated integrated circuits.

At high temperature, only some of these applications can be considered. We have developed recently a remote micro-plasma based on a resonant cavity by simply drilling a small hole (600 µm in diameter) on one side of the cavity. The microjet obtained like this can be a straight beam of active species over a relatively long distance (more than 10 cm - see Fig. 4).

This situation can only be reached at low flow rate to keep a laminar flow downstream the discharge which reaches ~2000 K /39/. The flow of this jet is controlled by the total

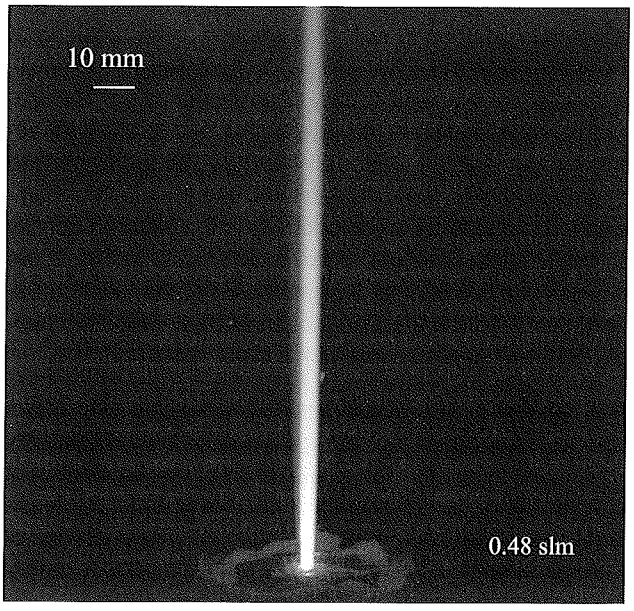

Fig. 4: Photograph of the atmospheric jet (Ar-20vol.%O_2) through a hole (600 µm in diameter) for a total flow rate of 0.48 slm. Power: 70 W.

flow rate of an Ar-20vol.%O_2 gas mixture. Three flow regimes are observed: one at low flow rates where the flow is laminar, one at intermediate flow rates where the flow is turbulent and transonic, and one at high flow rate where the flow is turbulent and supersonic.

With such a jet, thin film deposition by PECVD could be localized over a region as small as 1 mm^2. And more, such devices can be directly employed for the nanostructuring metals with oxygen plasma, where plasma radicals and surface heating is needed /40-46/. This will enable faster processing of materials and the growth of different nanostructures.

5 Conclusions

Atmospheric microwave plasmas are high-temperature non-equilibrium media where complex phenomena occur that are still under study. Resorting to atmospheric microwave plasmas can provide industrial solutions in the field of surface treatment. However, a lot must yet be done to improve the homogeneity of the surface treatments performed with such small-scale plasmas. We can hope also to be able to reach nanoscale using a top-down CVD approach as already performed under vacuum /47-55/. One difficulty to overcome will have to be the development of new plasma characterization diagnostics based on existing techniques in order to analyze these small-scale plasmas and their interactions with surfaces /56-65/.

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