

## Fundamental study of atmospheric pressure Ar-N<sub>2</sub> postdischarges and their application for metallic surfaces cleaning and activation.

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Surface wave discharges (SWDs) are at the forefront of technological advances, playing a key role in the development of new applications, particularly in surface modification of materials [1]. Surfatron is one of the better-known electromagnetic field applicators for SWDs generation. When nitrogen gas is introduced into an argon discharge generated with the surfatron device, the discharge shortens and changes its color from white to pink (Fig. 1), suggesting a modification of the excited species existing in the plasma. Moreover, the appearance of a fainter orangish region upstream, commonly known as remote plasma, afterglow or postdischarge, is observed. However, the absence of a visible postdischarge after an Ar discharge does not imply its nonexistence, but rather that it is not emitting radiation in the visible spectrum domain.

In the discharge region, charged species, excited species, and neutrals coexist. However, in the postdischarge there is no energy input, so mostly metastable states with longer lifetimes are present. Another feature of postdischarges is the significant decrease in the gas temperature along the afterglow, even reaching room temperatures.

So, postdischarge are an exceptional tool for the treatment of materials avoiding thermal damage and ion bombardment. Moreover, the ability to work at atmospheric pressure makes this processes to be more manageable and affordable, eliminating the requirements of vacuum pumps. To optimize industrial applications, understanding behavior and internal kinetics is essential, but no deep fundamental studies concerning Ar-N<sub>2</sub> postdischarges exist up to date. First step is the identification of the species present in this region. Optical emission spectra of Ar and Ar-N<sub>2</sub> postdischarges appears in Fig. 2. When nitrogen is injected into the plasma, the emission spectra is modified, resulting in a significant drop of the emission of argon lines, together with the appearance of molecular bands: First Positive System (FPS) and Second Positive System (SPS) of the nitrogen molecule, as well as a few intense signal coming from the First Negative System (FNS) of the nitrogen molecular ion. In the postdischarge, reaction pathways are more limited compared to the discharge, where electrons play a fundamental role in internal kinetics, so the existence of excited species is caused by long-lived metastable states. In the case of Ar, the pooling of Ar metastables (4s levels) gives rise to the formation of Ar<sup>+</sup> and Ar<sub>2</sub><sup>+</sup> ions [2]. Recombination of these ionic species, either by three-body recombination or by dissociative recombination, leads to the production of excited species. Moreover, in Ar-N<sub>2</sub> postdischarges, Ar metastables can participate in excitation transfer reactions producing N<sub>2</sub>(C) excited molecules from the ground state [3], subsequently giving rise to FPS and SPS emissions via fast radiative decay. Regarding FNS emissions, N<sub>2</sub><sup>+</sup> ions can be generated via atomic nitrogen metastables pooling [2]. The presence of these active species in postdischarge region would enable the treatment of thermosensitive materials, as well as metallic materials in situations where high temperatures or charge effects should be avoided, such as in microelectronic devices.



Fig. 1: Ar and Ar-N<sub>2</sub> plasmas generated with surfatron device.

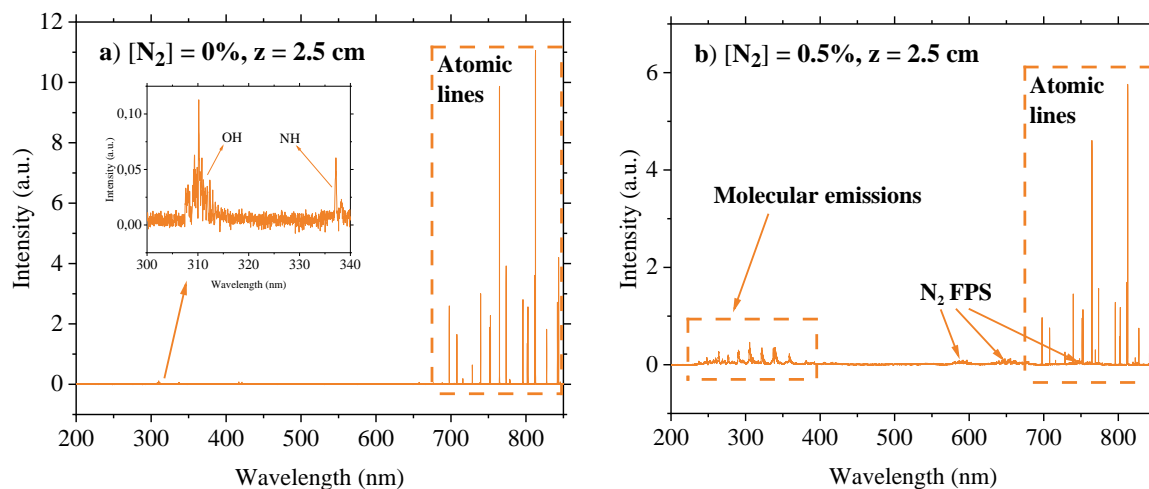


Fig. 2: Emission spectra of an Ar postdischarge (a) and Ar-N<sub>2</sub> ([N<sub>2</sub>] = 0.5 %) postdischarge (b) sustained with a surfatron at atmospheric pressure.  $z$  is the distance between the end of the discharge and the optical fiber position at the postdischarge.

When an Ar or Ar-N<sub>2</sub> ([N<sub>2</sub>] = 0.5 %) postdischarge is applied over a metallic surface, notable changes in the water contact angle (WCA) are observed (Fig. 3). The untreated surfaces of aluminum and steel display an averaged WCA of 61° and 54°, respectively. Following treatment with an Ar postdischarge, these values decrease to 32° and 21°, while treatment with an Ar-N<sub>2</sub> postdischarge results in averaged WCA values of 26° and 20° for aluminum and steel, respectively. These results may be attributed to modifications in surface roughness or to changes in the chemical composition of the surface. To investigate potential modifications in surface roughness and topography that may cause the

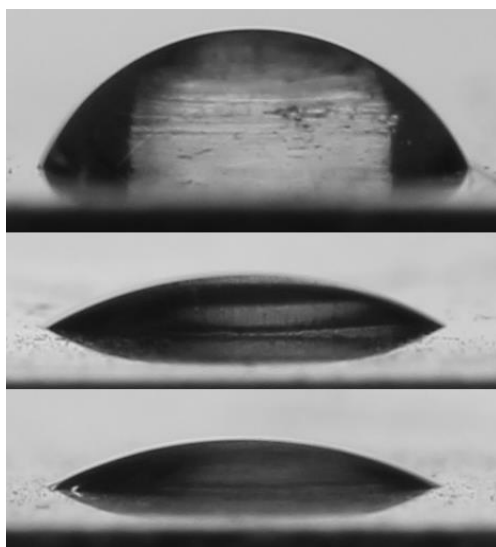


Fig. 3: Aluminum surfaces: (a) Untreated (b) after Ar postdischarge treatment and (c) after Ar-N<sub>2</sub> postdischarge treatment.

observed changes, a Confocal and Interferometric Microscopy analysis of the surfaces has been conducted, revealing that there are no significant changes in surface roughness or in the mean values of the maximum peak height or the maximum valley depth, and other parameters derived from this analysis, such as root mean square roughness. X-Ray Photoelectron Spectroscopy (XPS) analysis has been then conducted to assess physicochemical changes in the plates, showing a reduction in surface carbon content, suggesting the removal of the outer hydrocarbon layer [1]. Additionally, there is an increase in oxygen proportion, possibly attributed to the incorporation of hydrophilic radicals such as OH or NO, explaining the decrease in the WCA of the metallic surfaces. This induced change in surface wettability facilitates the development and implementation of innovative applications, such as enhancing the adhesion of functional dyes or depositing graphene dispersions to improve surface corrosion resistance.

[1] J. Muñoz, *Applied Surface Science*, **407** (2017) 72-81.

[2] J. Henriques, *Journal of Applied Physics*, **109** (2011) 023301.

[3] J. Henriques, *Journal of Applied Physics*, **109** (2011) 023302.

**Aknowledgments:** This work was partially supported by Grant TED2021129261AI00 funded by MCIN/AEI/10.13039/501100011033 and by the European Union NextGenerationEU/PRTR. The predoctoral contract of F.J. Morales-Calero was granted by a MOD-2.2 from Plan Propio de la Universidad de Córdoba (2020).