

# Scaling of unsaturated bonds and radicals in bioactive films with plasma parameters

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**Abstract:** Previously, we showed significant differences between the reactivity of amine plasma polymers deposited in capacitively coupled plasma discharge at the RF electrode and floating potential. However, a direct comparison was hindered because the plasma reactors were different. In the current study, we investigate the scaling of different bonds and radical density at different substrate potentials for otherwise comparable conditions.

## 1. Introduction

Plasma polymers with amino groups (amine plasma polymers in short) are of particular interest for many bioapplications, for example, the construction of immunosensors due to their ability to bind antibodies [1], DNA sensing thanks to binding single-stranded DNA probes [2], and for tissue engineering because they provide hydrophilic surfaces allowing efficient cell attachment and proliferation [3,4]. Better optimization of bioactive amine plasma polymers (amine PPs) needs an understanding of the key reasons for their reactivity. Previously published works provide hints that unsaturated C-to-N bonds, such as nitriles [1], and radicals trapped in the films [5] contribute significantly to the reactivity, besides the concentration of primary amines that are the main suspects because of the well-known reaction between two amino acids forming a peptide bond.

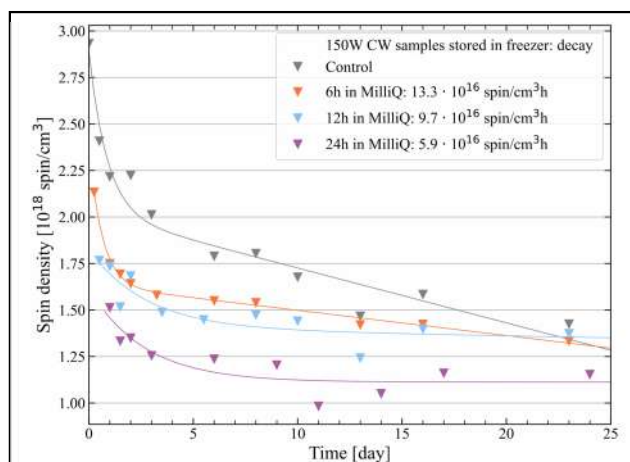
Here, we determined how the density of nitrile/imine bonds and radicals trapped in the amine PPs vary with the RF power for the films deposited at the RF electrode that acquires a negative DC self-bias and at the floating potential. We used continuous and pulsed modes of the capacitively coupled plasma (CCP) and assessed the scaling with the overall energy input (power invested into the bulk plasma and ion energy flux).

## 2. Methods

The amine PP films were deposited in RF discharge with capacitive coupling from cyclopropylamine (CPA) vapors mixed with Ar. The RF (13.56 MHz) discharge was operated continuously or pulsed. Details of the plasma reactor configuration and deposition procedure are described in our previous publications [3,4]. The on-time RF power varied between 30 and 150 W, and the pressure was 50 Pa. The substrates were placed on the RF electrode, which acquires a negative DC self-bias, either directly or on the thick glass plate. The latter ensured that the substrate was at the floating potential.

## 3. Results and Conclusion

We assessed the density of nitrile groups in the films by infrared spectroscopy. It decreased with the average RF power,  $P_{av}$ , calculated as the on-time power multiplied by the duty cycle. Similar scaling was obtained for the nitrogen content in the films, but the comparison of saturated and unsaturated C-to-N bonds (from XPS)



**Fig. 1.** Spin density in the amine PP film deposited at 150 W in the continuous discharge at the RF electrode. The initial density (“Control” at the time 0 days) is compared to the density after immersion in MilliQ water for 6, 12 and 24 hours. The time dependence shows the radical recombination (spin density decrease) with the aging time in the freezer.

revealed a bond rearrangement confirming a decrease of unsaturated bonds (nitriles and imines) with increasing  $P_{av}$ . The density of radicals trapped in the films was determined by EPR. The highest values were obtained for the deposition at the RF electrode and highest RF power (Fig. 1). However, the spin density scaled with the on-time power, not  $P_{av}$ .

## Acknowledgement

This work was supported by the Czech Science Foundation (project 24-12321S) and the Czech NanoLab project LM2023051 (MEYS CR).

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