Kinetics of trapped radicals formation and recombination in amine plasma polymers

B. Beliančínová[1], L. Janů[1], V. T. Santana[2], D. Nečas[1], L. Zajíčková[1,3]

[1]Plasma Technologies, CEITEC – Central European Institute of Technology, Brno, Czechia
[2] Magneto-Optical and THz Spectroscopy, CEITEC, Brno, Czechia
[3] Dept. Condensed Matter Physics, Masaryk University, Brno, Czechia

Abstract: Amine plasma polymers exhibit a high concentration of free radicals that are trapped in the material for extended periods (6 months). The spin density increases with higher on-time power, indicating that radicals are primarily created during the on-time period due to the penetration effect of ions. Over time, the spin density decreases due to diffusion to the surface or recombination in the bulk.

1. Introduction

Plasma polymers (PPs) are thin organic films with variable properties that can be tuned by a simple variation of deposition conditions, such as the ratio of compounds in the gas mixture, power, plasma mode, and pressure. The ability to prepare finely tuned surfaces is essential for potential applications in biosensing and tissue engineering, among other fields [1].

Previously, amine PPs were successfully used for the design of biosensors [2]. However, they suffered from baseline drift, which was eliminated by immersion in PBS. This finding opened questions about potential free radicals trapped in the plasma polymer. Until then, the presence of amino groups and unsaturated bonds was considered a key factor in the excellent reactivity of PP films [3]. Free radicals can form by ion bombardment during deposition, and they have already been successfully employed to bind complex molecules such as proteins covalently [4].

Here, we determined the concentration and scaling of free radicals trapped in amine PPs and examined the kinetics of radical diffusion.

2. Methods

The amine PPs were prepared in a capacitively coupled radiofrequency (RF, 13.56 MHz) discharge by plasma-enhanced chemical vapor deposition (PECVD) at low pressure (50 Pa). The deposition mixture consists of cyclopropylamine vapor and argon. Amine PPs were prepared in continuous (CW) and pulsed (PW) plasma mode, wherein a 33% duty cycle was selected. The on-time RF power varied between 30 and 150 W. By multiplying the RF power by the duty cycle, the important scaling parameter P_{avg} was calculated. Electron paramagnetic resonance (EPR) was utilized to measure spin density.

3. Results and Conclusion

A chemical composition comparison of samples prepared in PW and CW discharges showed that the atomic concentrations (and also the nitrogen-to-carbon ratio) overlapped, i.e., P_{avg} can be used as a suitable scaling parameter when discussing the CW and PW modes.

Amine PPs contain a high amount of free radicals ($\sim 2 \cdot 10^{18}$ spin/cm^3) trapped in the layer for a long time (6 months). The spin density increased with increasing on-time power. A higher power resulted in a higher ion energy
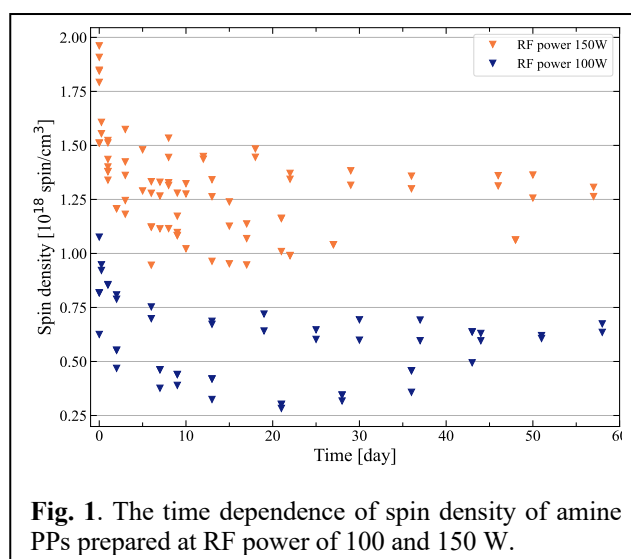
Fig. 1. The time dependence of spin density of amine PPs prepared at RF power of 100 and 150 W.

flux due to a higher ion density and a higher energy of ions that are accelerated in the plasma sheath by the DC self-bias proportional to the power. Since the films grow during the off-time with almost the same deposition rate, the results revealed an exciting detail about the creation of radicals because their density does not scale with P_{avg} but with the on-time power. This means that the radicals in the material grown during off-time are created during on-time due to the penetration effect of ions. The spin density was the highest after the deposition and decreased with storage time. The decrease was attributed to radical recombination in bulk or their diffusion to the surface of PP films.

References

[1] C. Karthik et al., *Biomedical Engineering*. 26, (2023).
[2] E. Makhneva et al., *Sensors and Actuators B: Chemical*. 276, 447-455 (2018).
[3] E. Makhneva et al., *Surface & Coatings Technology*. 290, 116-123 (2016).
[4] M.M. Bilek et al., *Proceedings of the National Academy of Sciences*. 108, 14405-14410 (2011).