# Defect-Assisted Radical Adsorption in Plasma-driven Atomic Layer Etching of Silicon Dioxide

A. Osonio[1], T. Tsutsumi[1,2], K. Ishikawa[1,2] & M. Hori[1]
[1]*Center for low-temperature Plasma Sciences, Nagoya University, Nagoya, Japan*
[2]*Graduate School of Engineering, Nagoya University, Nagoya, Japan*

**Abstract:** In this report, the adsorption dynamics of $CF_2$ radicals on Ar plasma-treated $SiO_2$ were examined to assess ion-induced surface modifications. Ex-situ electron spin resonance (ESR) and surface characterization revealed enhanced $CF_2$ adsorption after Ar plasma exposure at low ion energy of 34.9 eV. This increase is linked to ion-induced defects, indicated by a rise in dangling bond density. The results highlight the pivotal role of surface defects in promoting $CF_2$ radical interactions. These insights underscore tbe critical role of surface defects in facilitating $CF_2$ radical interactions.

## 1. Introduction

Within the domain of atomic layer etching (ALE) process, a key aspect of the etching mechanism involves the formation of dangling bonds on a substrate's surface, which play a crucial role in influencing surface chemical reactions.[1-2] Once formed, these dangling bonds significantly shape surface chemical reactions. With the growing complexity of device architectures, understanding the surface mechanisms and optimizing PEALE for silicon dioxide ($SiO_2$) is a crucial step toward enabling next-generation nanoscale fabrication. A common approach involves cyclic exposure to fluorocarbon plasmas followed by low-energy argon (Ar) ion bombardment. This study examines plasma-induced defect density and its relationship with $CF_2$ radical adsorption to advance ALE process optimization.

## 2. Methods

A custom-designed capacitively coupled plasma system was used in this work. Argon plasma was generated by applying a 60 MHz power supply to the upper electrode, irradiating am $SiO_2$ film on a Si substrate. The surface was subsequently exposed to $CF_2$ radicals produced by pyrolyzing hexafluoropropylene oxide (HFPO) at 390°C. The adsorption behavior of $CF_2$ radicals post-plasma irradiation was then analyzed. In-situ spectroscopic ellipsometry (SE) (M2000F, J.A. Wollam) in the wavelength range of 400 to 1000 nm was used to monitor film thickness. ESR at room temperature measured dangling bond density using a $CuSO_4 \cdot 5H_2O$ reference.

## 3. Results and Discussion

Results demonstrate the defect-assisted radical adsorption in the PEALE of $SiO_2$, as evidenced by ESR spectra (Figure 1) showing that Ar plasma irradiation for 30s and 60s increases the E' center signal, corresponding to dangling bonds formed by three oxygen-bonded Si atoms in the $SiO_2$ film. SE measurements confirm that, under identical plasma conditions, no sputtering occurs, and the film thickness remains nearly constant. Compared to the pristine sample and the sample exposed to only 30 s of Ar plasma, $SiO_2$ samples treated for at least 60 s show an increased $CF_2$ deposition rate of 1.5 Å over 10 minutes of continuous exposure. These results suggest that Ar ion irradiation, which serves as the desorption step in ALE, also creates surface defects that significantly enhance radical adsorption, improving process efficiency in subsequent cycles.

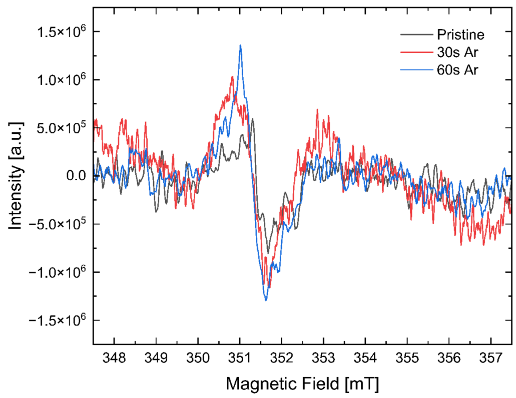


**Fig. 1**. ESR spectra of pristine and $Ar^+$-treated $SiO_2$ thin films following 30 s and 60 s plasma exposure.

## 4. Conclusion

Ion bombardment of $SiO_2$ with Ar plasma enhanced defect-mediated $CF_2$ radical adsorption. ESR analysis revealed a higher dangling bond density in plasma-treated $SiO_2$ compared to pristine samples, confirming the role of ion-induced defects. In-situ ellipsometry further demonstrated increased $CF_2$ film deposition and subsequent etch enhancement in $SiO_2$. The formation of dangling bonds due to ion bombardment plays a crucial role in facilitating radical adsorption, directly influencing the atomic layer etching process.

## References

[1] K. Ishikawa, et al. Appl Phys Lett., **81(10),** 1773-1775 (2002).
[2] M. Inayoshi, et al. J Vac Sci Technol A, **16(1)**, 233-238 (1998).