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RASIRC
Lorenzo Diaz | Product Manager
Phone: 858-259-1220
E-mail: ldiaz@rasirc.com

Improved Surface Functionalization with H_2O_2

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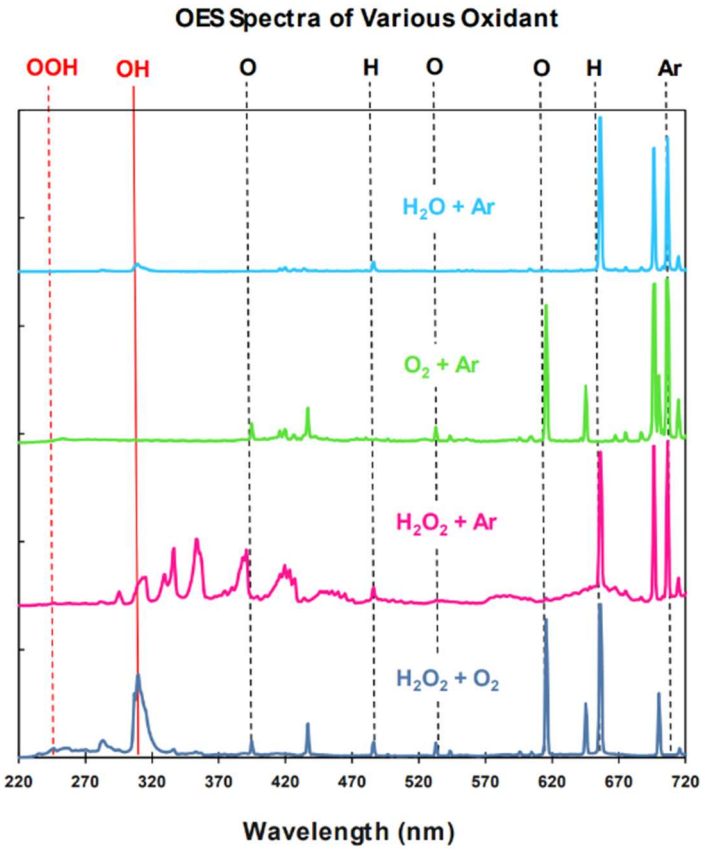
Introduction

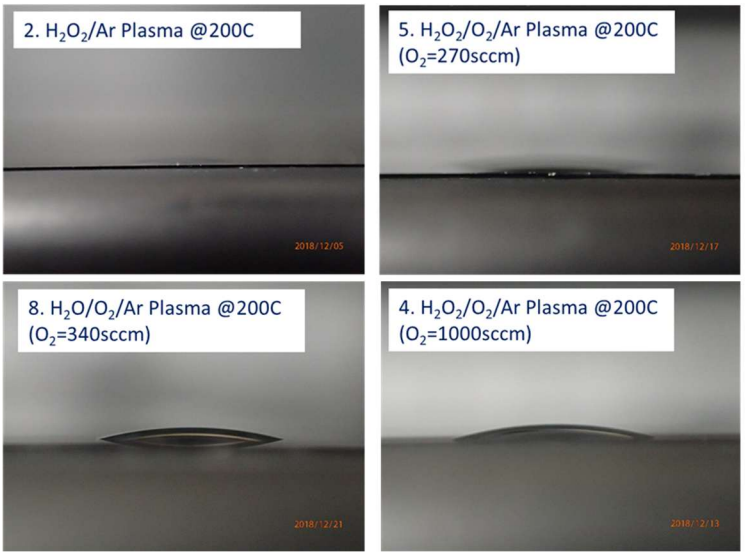
As semiconductor devices continue to shrink in size and increase in structural complexity, the need for precise and efficient surface treatments has become more critical than ever. Among these treatments, surface hydroxylation plays a central role, enabling strong interfacial adhesion, uniform thin-film deposition, and reliable wafer bonding. Traditionally, water (H_2O) has been employed to generate surface hydroxyl groups, but it is increasingly evident that hydrogen peroxide (H_2O_2) offers distinct advantages due to its higher oxidative potential. RASIRC's BRUTE® Peroxide and Peroxidizer™ technology exemplify the growing shift toward H_2O_2-based approaches, offering controlled delivery of H_2O_2 vapor with high purity and reactivity. Compared to H_2O, H_2O_2 produces significantly more reactive OH species under plasma or thermal activation, leading to superior surface functionalization. This enhanced reactivity enables improved performance in a variety of applications, including protein immobilization, wafer bonding, and area selective deposition (ASD). As such, H_2O_2 is rapidly emerging as the preferred reagent for next-generation surface engineering in semiconductor manufacturing.

OES Data

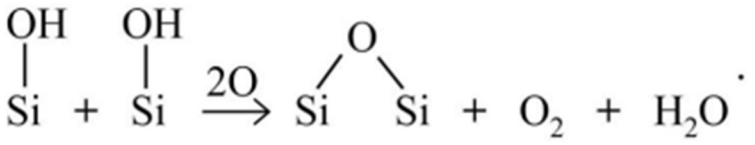


Optical emission spectroscopy reveals that the OH signal intensity, centered around ~309 nm, is significantly higher for the H_2O_2 + Ar plasma compared to the H_2O + Ar plasma, suggesting substantially greater OH radical generation. Visually estimating the area under the OH peak, the relative OH concentration appears to be approximately five times higher with H_2O_2. This observation aligns with the expected plasma chemistry: H_2O_2 decomposes into two OH radicals per molecule, whereas H_2O produces fewer under equivalent plasma energy conditions. The enhanced OH generation from H_2O_2 indicates its superior reactivity and potential for more effective surface hydroxylation. These measurements were conducted at the Tsukuba Laboratory of Taiyo Nippon Sanso Corporation using an MKS Remote Plasma Source and a Hamamatsu C10346-01 multiband plasma-process monitor.

Contact Angle Data

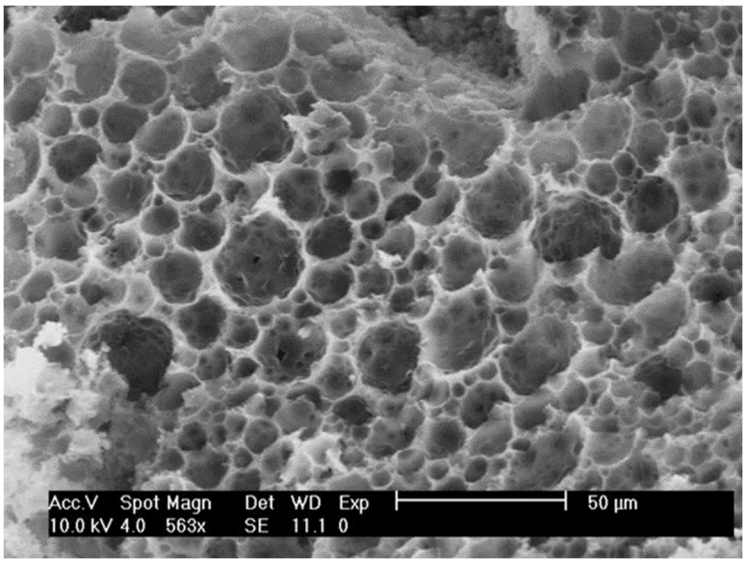


Gas Mixture	O_2 Flowrate (sccm)	Contact Angle
H2O2/Ar	0	< 4°
H2O2/Ar/O2	270	8.1°
H2O2/Ar/O2	340	16.2°
H2O2/Ar/O2	1000	21.6°



TNSC's experimental results further demonstrate that H_2O_2 plasma not only generates more OH radicals but also better preserves surface hydroxylation, unlike O_2 plasma, which promotes dehydroxylation through siloxane bridge formation4. As shown in literature, O atoms convert Si–OH to Si–O–Si, reducing hydrophilicity. In contrast, H_2O_2 supplies both O and OH species, enhancing reactivity and maintaining –OH coverage—critical for nucleation and bonding. This is supported by TNSC's contact angle experiments: as O_2 was added upstream to H_2O_2/Ar plasma, increasing O_2 flow led to a higher contact angle, indicating reduced hydroxylation and surface functionality.

Protein Immobilization Data



Item	H2O Bubbler	Peroxidizer	Note
H2O:H2O2 molar ratio	1:0	4:1	
g/min	0.75	1.00	
Carrier gas flowrate (slm)	10	10	
Exposure time	20 hr	4 hr	
BCA (mg/g particle)	3.1 (+.4, -.2)	13.3 (+.9, -.6)	Measured with flourospectrometer and BCA assay
			5 samples each

Building on the OES findings, the functional impact of increased OH radical generation was further validated through protein binding assays. The data strongly supports the conclusion that H_2O_2 generates significantly more reactive OH species than H_2O, resulting in enhanced surface activation and greater protein binding. As shown above, OES results show a ~5 times higher OH peak intensity for H_2O_2 + Ar plasma compared to H_2O + Ar, indicating substantially increased radical generation. This correlates closely with the results of the BCA assay, where the H_2O_2-rich treatment (Peroxidizer) yielded 13.3 mg/g of protein binding—approximately 4.3 times higher than the 3.1 mg/g observed with H_2O treatment. Notably, this increase was achieved despite a shorter exposure time (4 hours vs. 20 hours) and a higher flow rate, further underscoring H_2O_2's superior functionalization efficiency. The porous surface morphology observed via SEM suggests that H_2O_2 vapor can deeply diffuse into the internal structure, reacting with surface groups to introduce a higher density of functional moieties such as –OH and =O. These groups facilitate silanization and subsequent protein immobilization. Overall, H_2O_2 thermally activates more binding sites across both external and internal surfaces, leading to significantly improved biomolecule attachment, as evidenced by consistent trends across spectroscopy, surface chemistry, and protein quantification data.

Area Selective Deposition

In Area Selective Deposition (ASD), H_2O_2 plays a critical role in enabling tunable and robust surface preparation. Its strong oxidative properties lead to a high density of surface hydroxyl (-OH) groups, which promotes faster nucleation on growth surfaces by enhancing chemical reactivity and precursor adsorption.2 Additionally, H_2O_2 offers selective functionalization capability: it can hydroxylate specific materials preferentially, creating contrast between growth and non-growth regions and supporting more precise pattern definition.3 The resulting dense –OH layers also improve the adhesion and uniform coverage of inhibitor films, leading to better surface passivation in non-growth areas. Moreover, consistent and well-controlled surface chemistry contributes to improved nucleation control, yielding sharper pattern edges and reducing defectivity. Overall, H_2O_2 enables more effective surface differentiation and control in ASD, supporting the fabrication of advanced, high-resolution nanostructures.

Wafer Bonding

A high density of surface hydroxyl (-OH) groups plays a critical role in enhancing wafer bonding performance. OH-terminated surfaces are highly hydrophilic, readily absorbing ambient moisture and forming hydrogen bonds across the interface, which promotes initial adhesion. During subsequent annealing, these hydroxyl groups undergo dehydration reactions to form strong covalent Si–O–Si bonds, leading to durable and reliable wafer bonding. A higher initial density of hydroxyl groups not only facilitates bonding at lower temperatures—reducing thermal stress and improving process compatibility—but also ensures uniform adhesion across the entire wafer surface. Compared to H_2O or O_2, H_2O_2 is significantly more effective in generating surface hydroxyls due to its strong oxidizing properties.1 The reactive oxygen species produced by H_2O_2 interact more efficiently with silicon or oxide surfaces, resulting in higher and more uniform OH coverage. This makes H_2O_2 particularly advantageous in processes requiring low-temperature, high-uniformity of wafer bonding.

Summary

Hydrogen peroxide (H_2O_2) demonstrates superior performance as a surface activation agent compared to water (H_2O), as evidenced by optical emission spectroscopy, protein binding assays, and surface morphology analysis. Its ability to generate significantly more reactive OH species under plasma or thermal conditions leads to enhanced chemical functionalization, enabling higher protein immobilization efficiency even with shorter exposure times. These findings are further supported by its proven effectiveness in wafer bonding and area selective deposition, where high hydroxyl density, uniform coverage, and selective surface reactivity are critical. Overall, H_2O_2 offers a versatile and powerful approach to surface preparation, enabling improved performance in both biofunctional and semiconductor applications.

About RASIRC

RASIRC innovations convert low vapor-pressure liquid chemistries into safe and reliable gas flow for most processes. RASIRC technology delivers hydrazine gas and hydrogen peroxide gas in controlled, repeatable concentrations. RASIRC products include BRUTE® Peroxide, BRUTE® Hydrazine, Peroxider® and RainMaker® Humidification System. These products incorporate proprietary and patented technology that enables them to deliver gas to process with precision. BRUTE Peroxide generates ultra-dry hydrogen peroxide gas and can be used with or without a carrier gas. The Peroxidizer is the first commercial vaporizer capable of delivering concentrations greater than 5% H_2O_2 gas by volume from 30% H_2O_2 liquid source.

Reference

1. S. W. Park *et al.*, *Surf. Sci.* **652**, 322–333 (2016).
2. J. Park *et al., Ceram. Int.* **41**, 1839–1845 (2015).
3. S.W. Park *et al., J. Chem. Phys.* **146**, 052808 (2017).
4. S.B. Habib *et al., J. Vac. Sci. Technol*. A 28, **476** (2010).

P:858-259-1220, email ldiaz@rasirc.com or visit http://www.rasirc.com

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