Photo-Assisted Etching of Si in Cl- and Br-Containing Plasmas

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Photo-assisted etching (PAE) of p-Si in Cl_2/Ar plasmas was first reported in Ref. [1]. The PAE rate was substantial compared to the ion-assisted etching rate, causing complications for processes that require low ion energies, such as etching with atomic layer resolution or highly selective and anisotropic etching of nano-features.

Absolute etching rates (solid symbols) are shown in Fig. 1, calibrated by relative intensity of optical emission of the Si 2882 Å line (proportionality constant is given in parenthesis in figure label), and measured absolute etching rates (hollow stars), as a function of $E^{1/2}$ (E=ion energy), in different continuous wave argon/halogen plasmas. Pulsed dc bias at 10 kHz and 50% duty cycle was applied on the sample stage. Double headed arrow lengths indicate photo-assisted etching rates obtained by subtracting any isotropic (chemical) etching rate from the total sub-threshold etching rate. PAE is fastest in Cl_2/HBr, slower and nearly the same for Cl_2 and Cl_2/Br_2, still slower for HBr, and slowest for Br_2-containing plasmas, all diluted with 50% Ar. PAE rates correlated somewhat with the Ar 750.4 nm intensity as well as the total XPS halogen atom percent on the Si surface. However, the PAE rates correlated closely with the product of emission intensity and total halogen surface coverage.

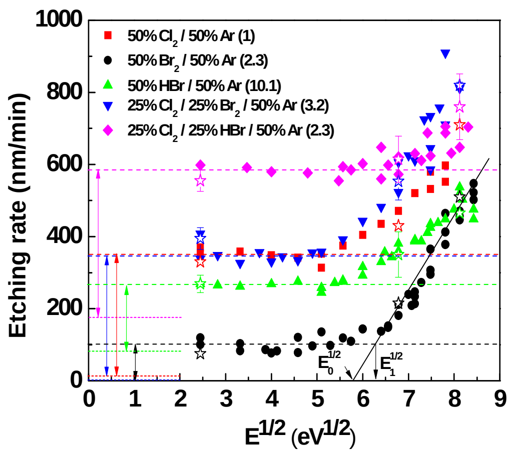


Fig. 1. Si etching rates in different Cl- and Br-containing plasmas.

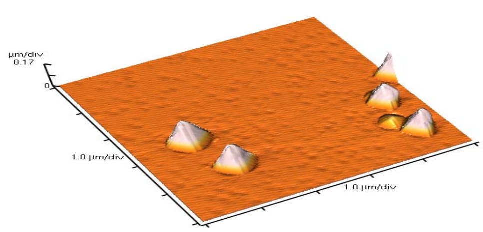


Fig. 2 AFM image of p-Si etched in 50% Cl_2/50%Ar plasma under PAE conditions.

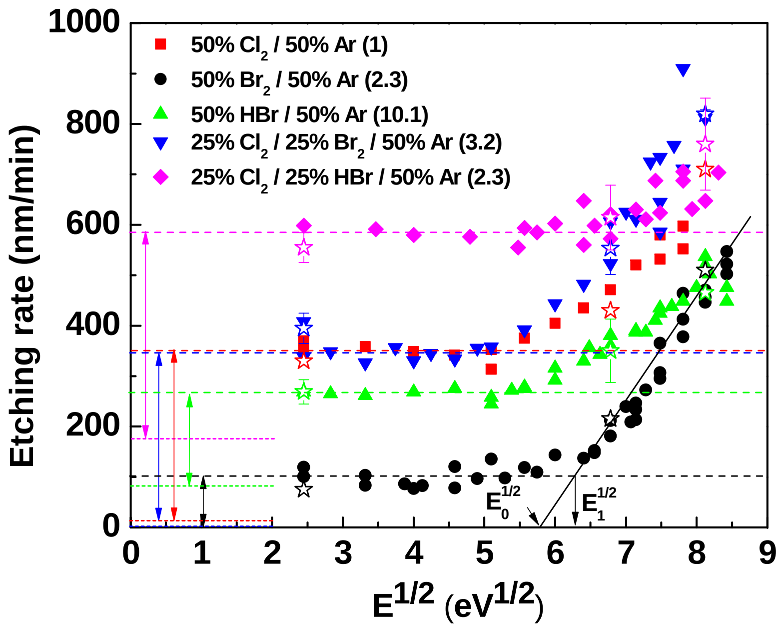
Etched blanket Si (100) samples were examined by AFM. Samples etched under PAE conditions in 50%Cl_2 /50%Ar plasma were found to have relatively smooth surfaces, except for a few interspersed pyramid-shaped hillocks (Fig. 2). XPS analysis of pre-etched blanket samples revealed 3-5% O, presumably due to native oxide which was not completely removed after HF treatment, and 3-5% of C. These contaminants likely acted as micromasks during etching. It appears that PAE rates, at least in chlorine, depend strongly on the crystallographic plane. Specifically, {100} planes etch much faster than {110} planes, leaving behind micro-masked pyramids with four {110} facets.

Reference

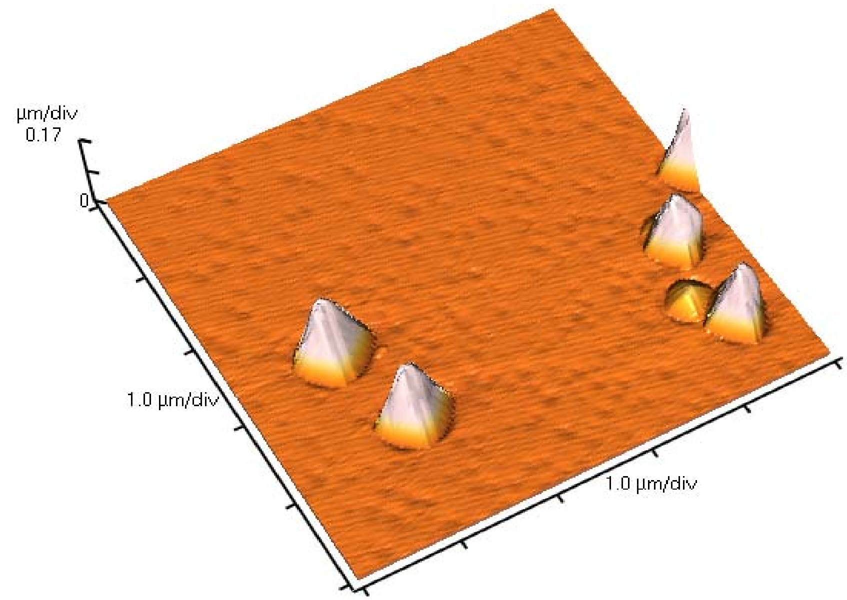
[1] H. Shin, W. Zhu, D. J. Economou and V. M. Donnelly, J. Vac. Sci. Technol. A, **30**, 021306 (2012).

PHOTO-ASSISTED ETCHING (PAE) OF SILICON IN Cl- AND Br-CONTAINING PLASMAS

- **Below a threshold energy, Si etching rate is independent of E (PAE regime).**
- **PAE rate of Si varies by gas mixture: Cl_2/HBr ≥ Cl_2, Cl_2/Br_2 > HBr/Ar > Br_2/Ar Double headed arrow lengths indicate photo-assisted etching rates.**
- **Pyramidal structure formation during PAE of Si (100) implies that {100} planes etch much faster than {110} planes.**



- **Si etching rates in Cl- and Br-containing plasmas.**



- **AFM image of p-Si etched in 50%Cl_2-50%Ar plasma under PAE conditions.**

UNIVERSITY of HOUSTON

HIGHLIGHT

Center for Predictive Control of Plasma Kinetics: Multi-Phase and Bounded Systems

PSC Department of Energy Plasma Science Center

DOE Plasma Science Center
Control of Plasma Kinetics

'NO$_x$ Box': A Novel Antimicrobial Plasma Source

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Previous research on antimicrobial effects from air plasma (e.g. when air plasma products are dissolved in water to make 'plasma-activated water' or PAW) focused on dielectric barrier discharges. [1] In another previous project, we showed that combining PAW and UVA photons could accelerate the antimicrobial effect by exploiting photolysis of nitrite (NO_2^-) in solution.[2] In this project, we tested a different type of air plasma using an air, sparking discharge. Since previous research suggested that nitrogen oxides (NO and NO_2 or 'NO_x') are important components of PAW, we tried to increase their rate of production by using a higher temperature spark discharge. We discovered this is an efficient way to create these antimicrobial species; furthermore, the least expensive power supplies are most efficient.

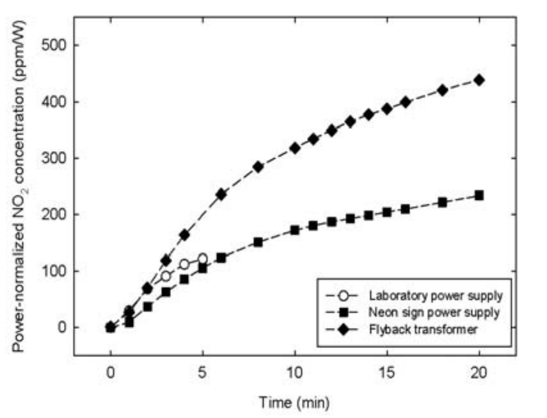


Fig. 1 – NO_2 production over time, normalized by plasma power consumption. A homemade flyback transformer was the least expensive power supply tested and produced NO_2 most efficiently.

Gaseous and aqueous chemistry were investigated by producing NO_x with three different power supplies: a Trek high-voltage amplifier (the "laboratory" power supply), a transformer designed as a power supply for neon signs, and a homemade 'flyback transformer.' The high-voltage transformer produced the greatest gaseous and aqueous concentrations of NO_x but consumed considerably more power than the neon sign power supply and flyback transformer circuit. When normalized by power consumption, the least expensive and least power-intensive transformers produce NO_x much more efficiently, as shown in Figure 1.

NO_x dissolves in aqueous solution to form nitrite (NO_2^-) and nitrate (NO_3^-). A ll three power supplies yielded high aqueous concentrations of nitrate and nitrite efficiently and without the need for separate mixing or agitation.

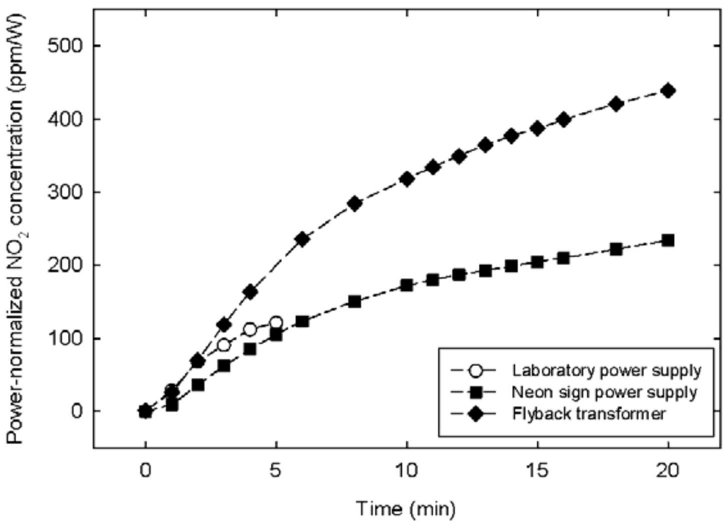
E. coli on surfaces and in aqueous suspension were inactivated with NO_x. All three power sources inactivated the bacteria to beyond the detection limit of our assay: 99.99% reduction for surfaces and 99.999% reduction in liquid, within 5 minutes. NO_x-based disinfection could be a useful disinfection strategy for non-autoclavable (temperature-sensitive) instruments and devices or where standard medical disinfectants are unavailable.

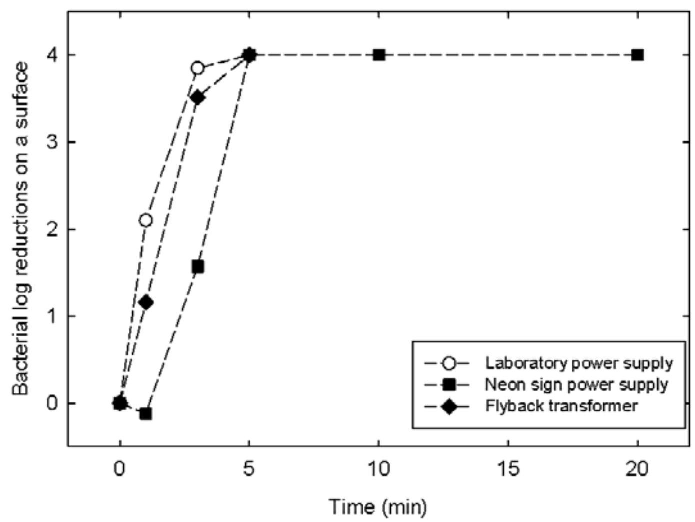
References

[1] Matthew J Traylor *et al.*, J. Phys. D: Appl. Phys. **44** 472001 (2011).
[2] Mathew J. Pavlovich *et al.*, Plasma Processes and Polymers, DOI: 10.1002/ppap201300065, (2013).

NOVEL ANTIMICROBIAL PLASMA SOURCES

- Air plasma can rapidly create high concentrations of highly antimicrobial oxides of nitrogen (‘NO_x’) using simple electrode designs.
- NO_x production normalized to power consumption is relatively insensitive to the type of power supply. Inexpensive power supplies work well.
- These devices offer promise of many novel applications, including non-autoclavable medical instrument or device sterilization, among many others.





- NO_2 production over time
- NO_x rapidly disinfects surfaces

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