Probing Liquid Surfaces under Vacuum Using SEM and TOFSIMS

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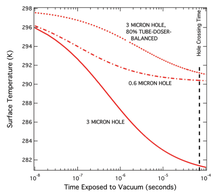
Introduction

- Applying vacuum-based molecular probes of liquid surfaces aids many environmental, biological, and industrial studies.
- Limitations of previous approaches: 1) too much water in main chamber; 2) severe cooling problems; 3) specially built instrument or inherently tethered to the instrument.
- It is a significant breakthrough to use microfluidic interface assembly to study liquid surface under vacuum conditions.
- It has been applied in time of flight secondary ion mass spectrometer (TOF-SIMS) for the first time.

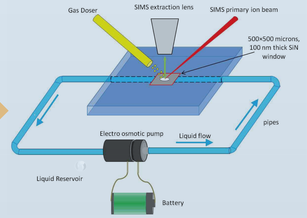
Design Considerations

- Aperture size
- Mean free path
- Aperture/reservoir gas load
- Surface tension
- Flowing or static
- Temperature drop
- Concentration changes
- Wetting issues
- Beam damage



Cooling From Evaporation

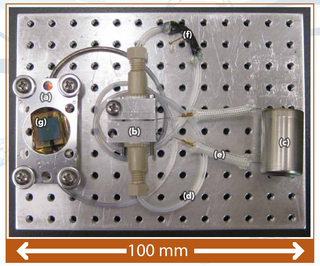
The schematic of a vacuum compatible liquid TOF-SIMS module

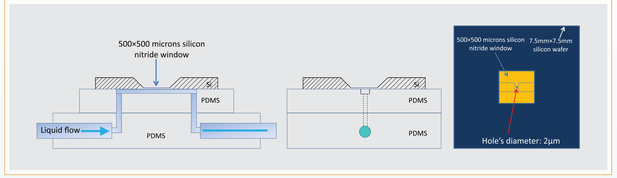


Experimental

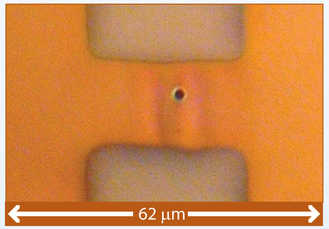
A photo of a vacuum compatible liquid SIMS module: Version I

(a) PDMS microfluidic block
(b) Electroosmotic pump
(c) Battery
(d) PTFE tubings
(e) UHV compatible fiberglass sleeving
(f) Viton tee containing the short capillary
(g) 500×500 μm² silicon nitride window at the center of a 7.5×7.5 mm² silicon wafer



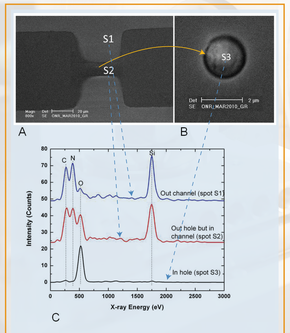


Optical photos of a 2 μm hole drilled by FIB on a silicon nitride widow



Results and Discussions

ESEM image of the micro channel and the micron-sized aperture above the channel and EDX spectra at different locations

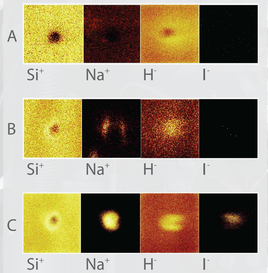


A 2 μm hole is drilled by FIB, and pure water was used

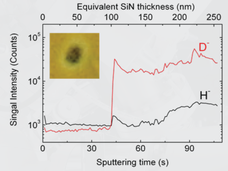
Atomic percentage at different locations (S1, S2 and S3)

Atomic Percent(%)	Outside channel (S1)	Outside hole but in channel (S2)	In hole (S3)
C	38	36	9
O	6	15	86
Si	14	12	2
N	41	37	3
Na	1	1	0
Cl	0	0	0

TOF-SIMS imaging of 10×10 μm² of silicon nitride membrane surfaces around the aperture.



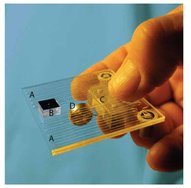
H⁻ and D⁻ signal profiles vs. Bi⁺ ion erosion time. Inserted is an optical image (10x10 μm²) of the drilled hole.



To avoid contamination during sample handling, we directly drill a hole by the SIMS Bi^+ beam. Heavy Water (D_2O) was added in the sealed channel.

Module Version II is being developed, and it offers improvements:

- It has less extra joints to avoid possible leaking.
- It is smaller and more integrated.
- Glass is used instead of PDMS and PTFE tubing to avoid gas permeability of them.



(a) Glass chip
(b) PDMS microfluidics block
(c) Electroosmotic pump
(d) Battery

Conclusions

- Developed a portable micro-environment and self-contained vacuum interface for studying high-vapor pressure liquid surfaces
- Demonstrated liquid surfaces in situ detection by time of flight secondary ion mass spectrometer (TOF-SIMS) and scanning electron microscope (SEM)
- Adaptable to other analytical platforms; and it opens new avenues for understanding interfacial reactions on liquid surfaces in the future

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