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DEVELOPEMANT OF AMBIENT PRESSURE HARD X-RAY PHOTOELECTRON SPECTROSCOPY

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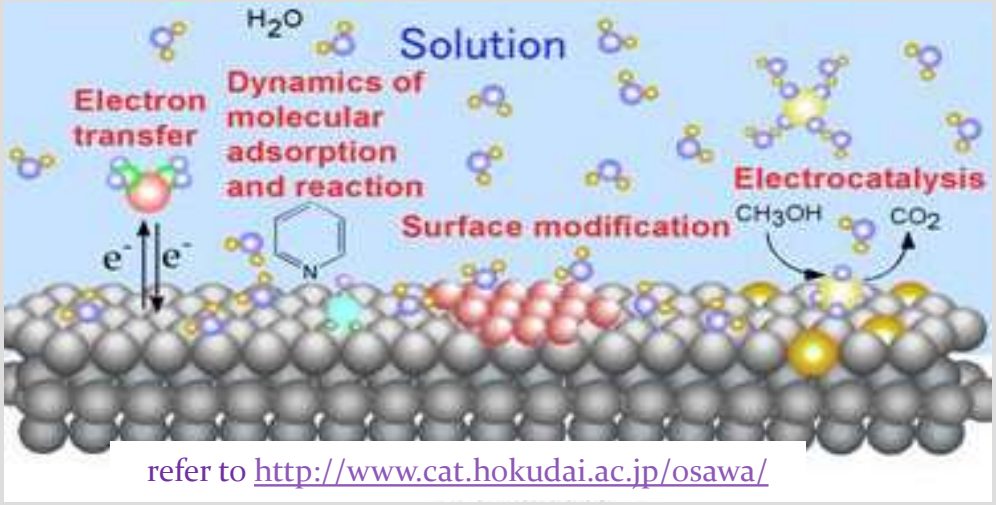
1. Introduction



refer to http://www.cat.hokudai.ac.jp/osawa/

There are many interesting processes at solid-gas as well as solid-liquid interfaces such as catalytic reactions and the adsorption of water on oxide surfaces under environmental conditions.

However, the conventional XPS is obviously not applicable for these studies, due to necessity of high vacuum in the analyzer.

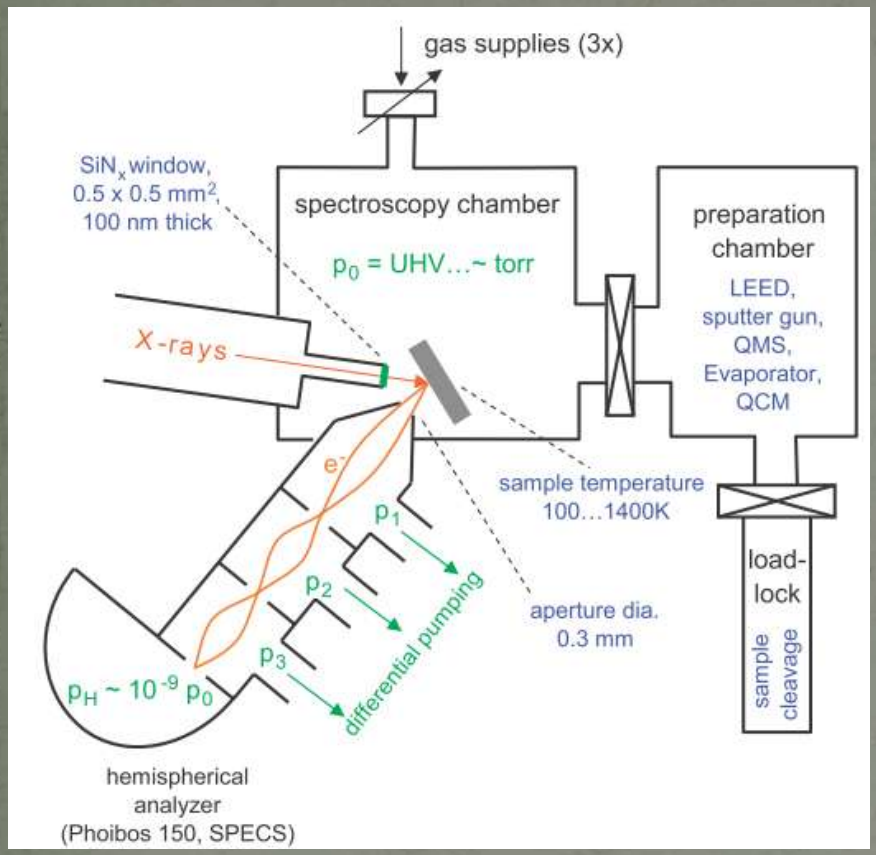
There are two possible ways to solve the difficulty.

One is to use differential pumping technique.

Another way is what we are going to present here, that is, HAXPES using environmental cells with very thin windows for photoelectrons.

2.Differential pumping type ambient pressure XPS(AP-XPS)

APPES -2 at ALS



In order to keep high pressure in this sample chamber without disturbing the high vacuum in the analyzer system, 3 stage differential pumping is used. Photoelectrons are introduced into analyzer lens through aperture of 300 μm. This APXPS system has limited the practical working pressure of upto 1000 Pa by using with the aperture size of 300 μm.

X-ray beam spot on sample : 7×10 μm

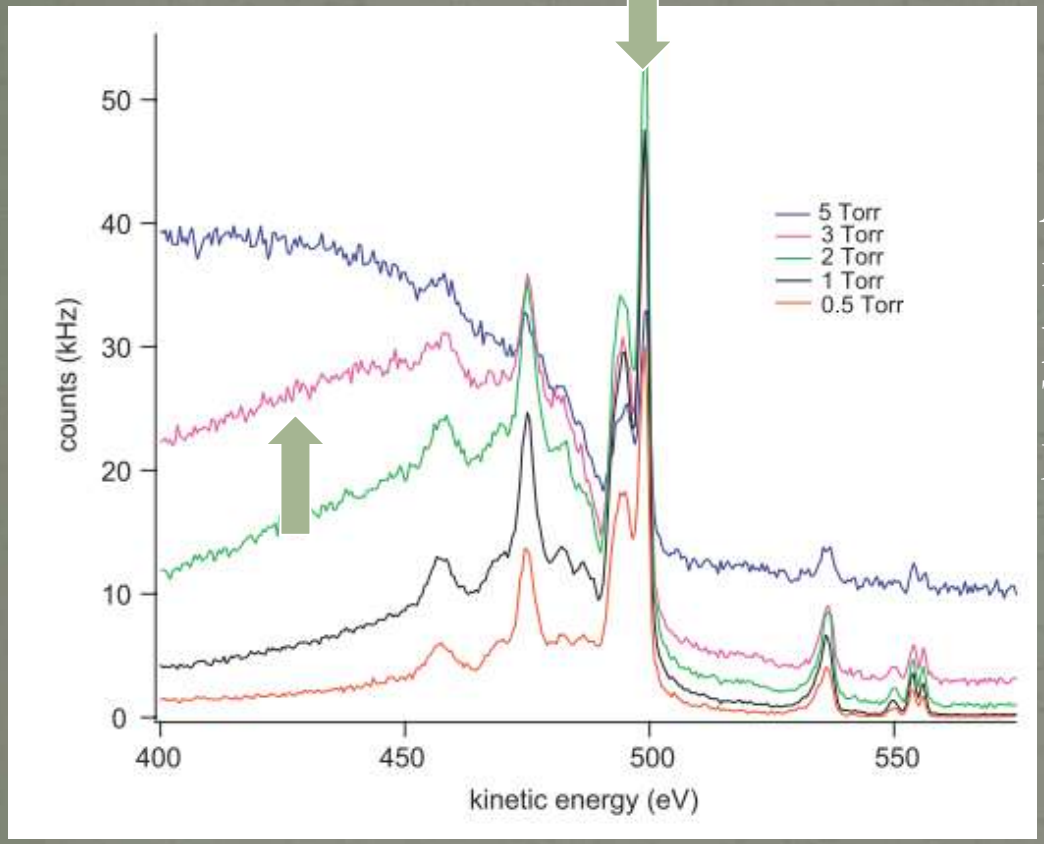
- current performance
  - working distance > several mm
  - aperture size > 0.3 mm
  - working pressure ～ 1000 Pa (7.5 Torr)

- future performance
  - aperture size ～ 15 μm
  - working pressure ～ 20 kPa (150 Torr)

Nucl. Instr. Meth. A601 (2009) 151

2.Differential pumping type ambient pressure XPS(AP-XPS)

Water vapor spectrum



Ambient pressure XPS intensity of water vapor at pressures from 0.5 Torr to 5 Torr.

X-ray energy : 568 eV

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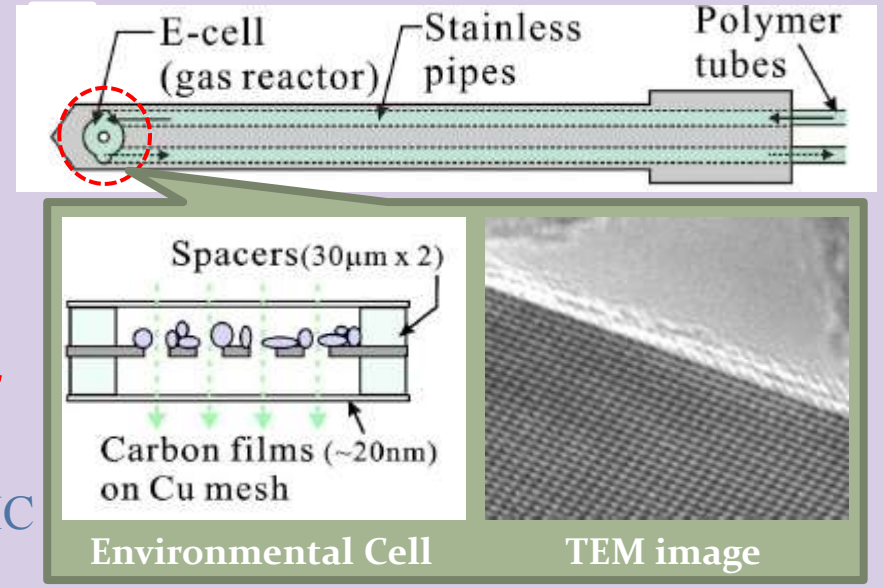
As pressure increases, the peaks are attenuated, and the background due to inelastic scattering increases significantly.

3. Improvement of windowed type environmental-cell

Windowed type environmental-cell transmission electron microscope(TEM)

Recently, Kawasaki et al successfully developed environmental cell with very simple structure, for TEM-observation, using amorphous carbon membranes for windows to penetrate electrons. Membranes of 10 nm, were expected to withstand pressure differences of greater than 2 atm.

T. Kawasaki et al., REVIEW OF SCIENTIFIC INSTRUMENTS **80, 113701 2009**



In case of HAXPES, the photoelectron can penetrate easily **form 10 to 20 nm** of membranes consist of light elements such as carbon, nitride, oxygen, and silicon. This allows us to realize much more simple apparatus for the AP-XPS.

We designed environmental cells for HAXPES by modifying the TEM cell structure to fit to HAXPES measurement.

3. Improvement of windowed type environmental-cell

Comparison of characteristics of membrane materials

		amorphous Silicon	Silicon oxide	Silicon nitride
ultra thin membrane		○ (>5nm)	△ (>20nm)	○ (>5nm)
thermal stability		～600℃	～1000℃	～1000℃
chemical stability		○	◎	◎
electrical conductivity		△	×	×

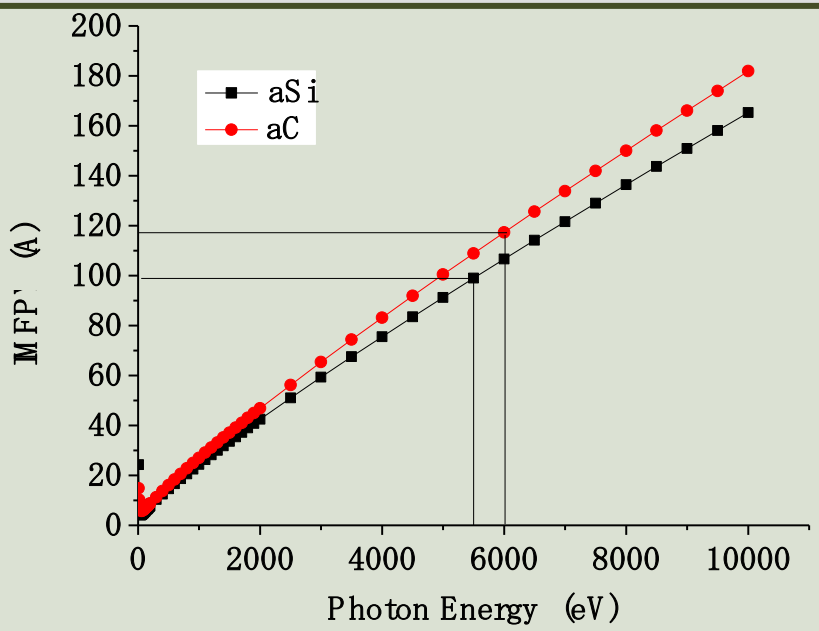
based on the collaboration with Dr. Kawasaki at Prof. Tanji's lab. of Nagoya University

refer to *ALLIANCE Biosystems* WEB site

Chemical-stability-wise, silicon nitride and silicon oxide are preferable, however, it is difficult to fabricate thin silicon oxide membrane.
In case chemical and thermal stability are not required, amorphous carbon is most preferable since it is conductive, thus charging effects would not serious.

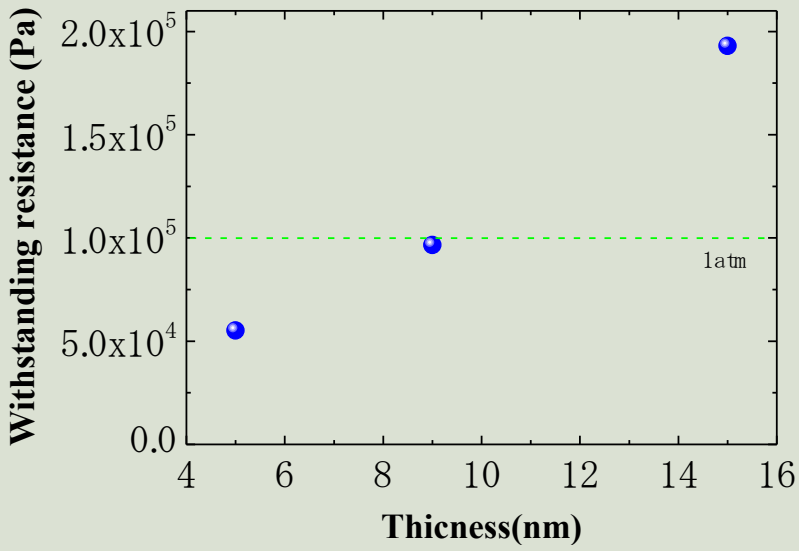
3. Improvement of windowed type environmental-cell

Inelastic mean free path (IMFP) depending on kinetic energy of photoelectrons



In amorphous silicon and amorphous carbon, inelastic mean free path of photoelectron kinetic energy 5-6 keV is about 10 nm.

Thickness dependence of the withstanding pressure (amorphous silicon).

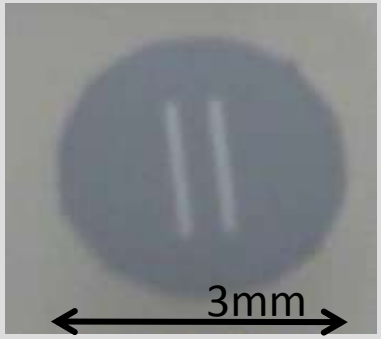


From the results , membrane with 12-15 nm thicknesses, withstand pressure differences greater than 1atm.

3. Improvement of windowed type environmental-cell

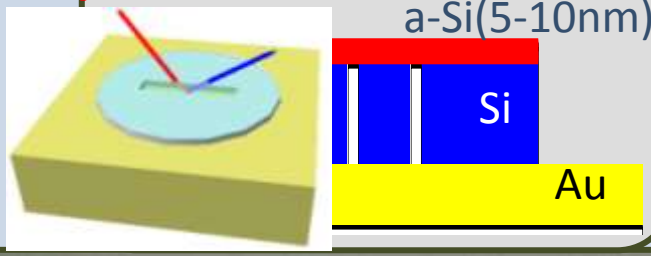
Study of window material and thickness

Picture of the aperture

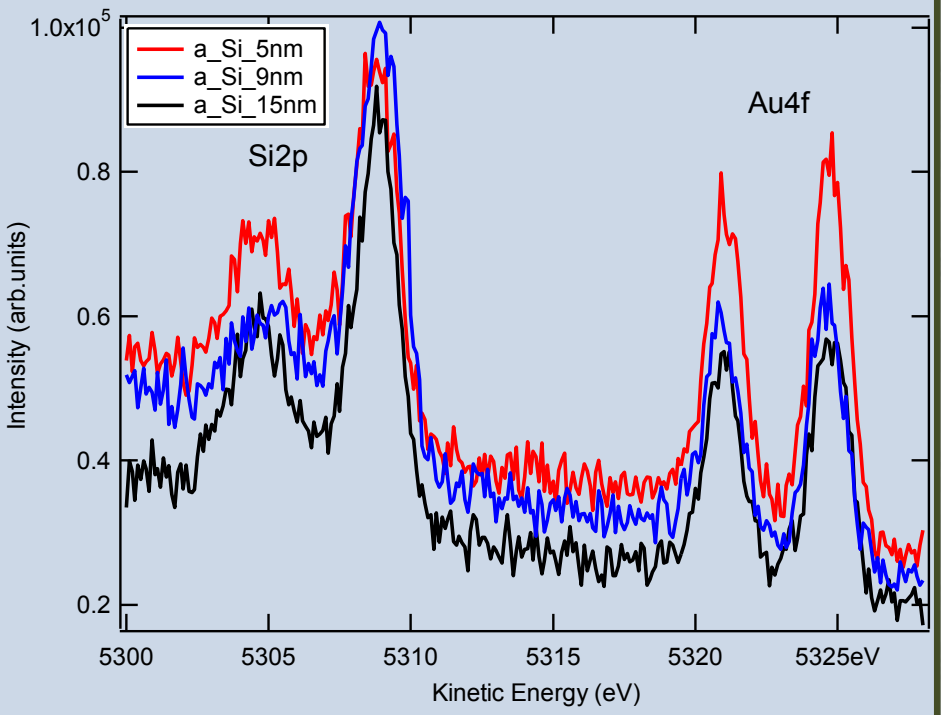


1500μm×100μm,
thickness:5-15nm

Schematic diagram of the sample



Thickness dependence of the a-Si in the Au4f spectrum



It is clear that sufficient signals can be obtained through a 15 nm thickness of window material of a-Si.

3. Improvement of windowed type environmental-cell

Results *comparison of characteristics of membrane materials*

	carbon	amorphous Silicon	Silicon nitride
ultra thin membrane	○ (>5nm)	○ (>5nm)	
thermal stability	～400℃	～600℃	
chemical stability	○	○	
electrical conductivity	○	△	
Thickness for withstand the pressure differential above 1.2 atm	>15nm (100μm×500μm) ※	12-15nm (100μm×1500μm) ※	(100μm×1500μm) ※
Transmission	○	◎	

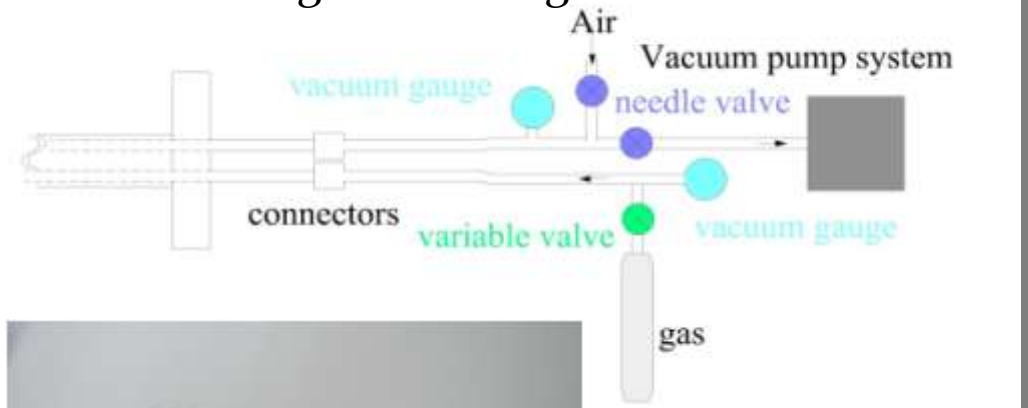
※Shape of the window

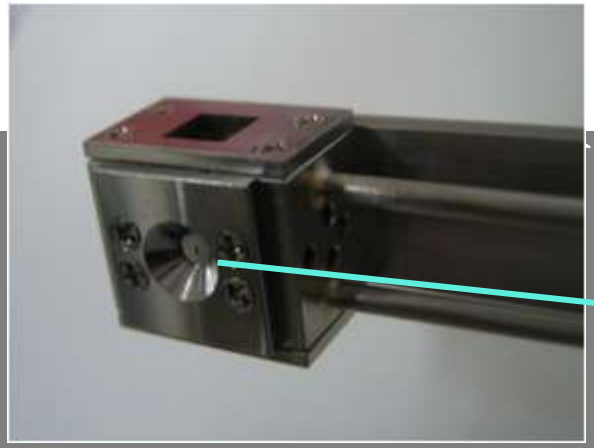
Basing upon above mentioned results, we have made a gas flow type cells for the observation of solid-gas interface reactions.

3. Improvement of windowed type environmental-cell

The gas flow type cell

Schematic diagram of the gas unit



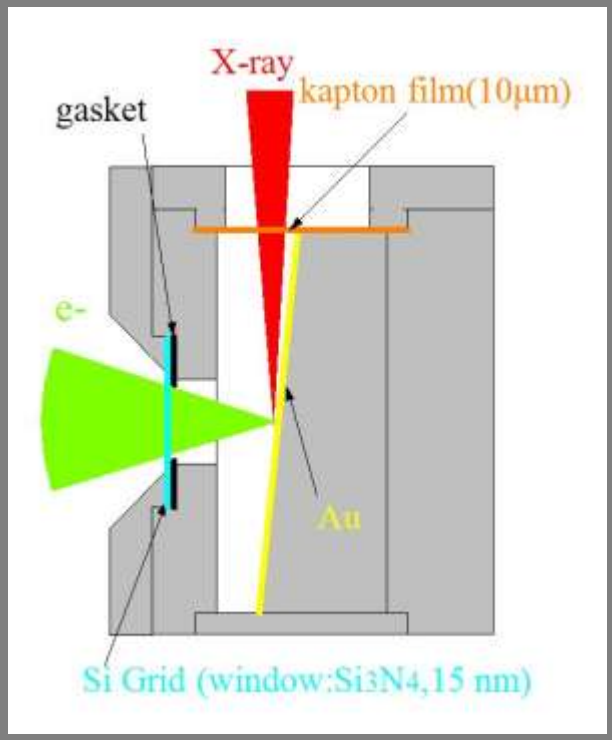


Si_3N_4(15nm)
(100μm×1500μm)

Photograph of the gas flow type cell

The flow rate can be controlled by a variable needle valve

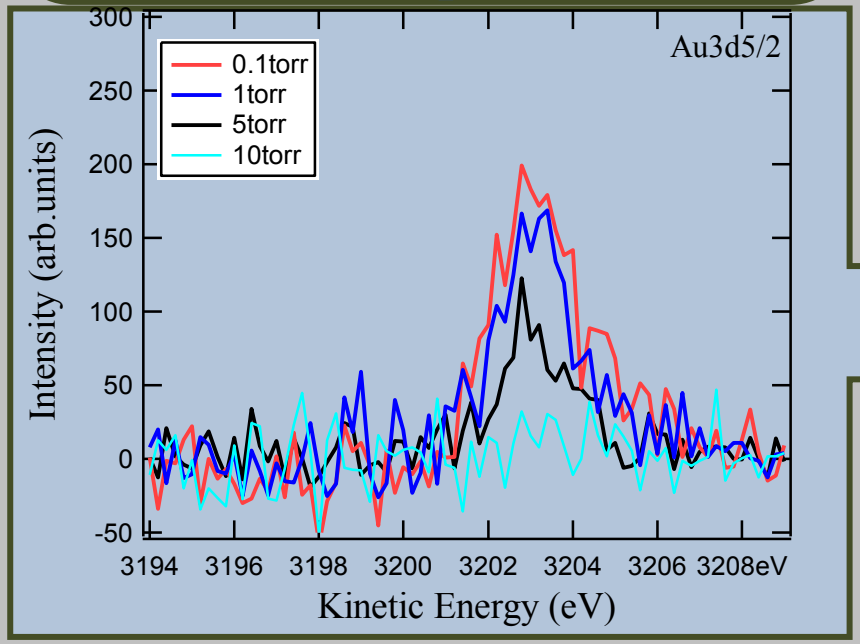
Cross section of a flow type cell



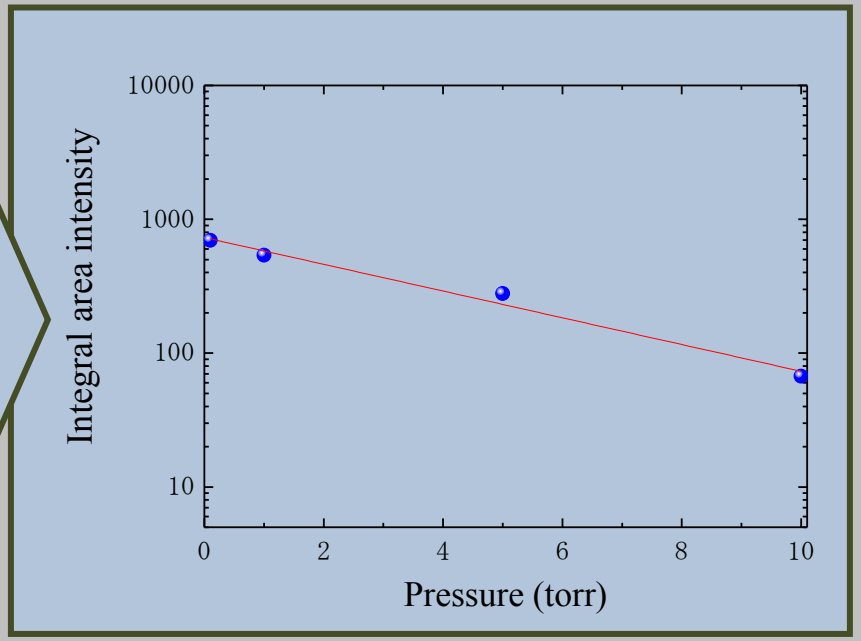
The distance between the Au sample surface and the membrane was 2.5 mm, in this test device.

3. Improvement of windowed type environmental-cell

Gas pressure dependence of the Au3d spectra



Gas pressure dependence of the integrated intensity



As shown in the right figure, integrated intensity of the spectrum decreases exponentially with pressure dependence.
In this experiment, the gap between the window and Au samples is too large, approximately 2 .5 mm, as mentioned above.

This long distance causes significant photoelectron attenuation, which limits the highest pressure of 10 torr for photoelectron observation from the sample surface.

4. Comparison of ambient pressure XPS techniques

	differential pumping + soft X-ray PES	ultra-thin membrane + hard X-ray PES
target	・surface molecule adsorption ・surface modification ・molecule or cluster	・interface reaction at the solid-gas or solid-liquid interfaces ・measurement of electrochemical reaction
high pressure	～10^3 Pa / 7.5 Torr ～10^4 Pa (in future)	～10^5 Pa / atmospheric pressure
interfering spectra		
R&D	・focused X-ray beam ・differential pumping system ・input lens of XPS machine	・ambient pressure XPS cell with a membrane and manipulator ・interlock system against breakage of a membrane

At present, the highest pressure is almost the same, however, we expect the highest pressure would reach 1 atm if we reduce the gap between the sample surface and the aperture membrane .

The present cell method has several additional advantages, such as

1) Low background,

2) Static pressure condition is accessible, and

3) Small and simple experimental configurations.

5. Summary

In summary, here we reported the successful feasibility test experiments on gas flow cell for the HAXPES measurements using HEARP Lab system.

We are making efforts to improve the cell toward realization of “ambient” pressure photoelectron spectroscopy.

Temperature control and external field application to the sample inside the cell also are targets for the further development.

The present flow cell is compatible to the SR beam line, thus we expect promising future in varieties of applications.

Thank you for your attention.