AMBIENT-PRESSURE X-RAY PHOTOEMISSION SPECTROMETER FOR SURFACE ANALYSIS OF PLANETARY SURFACE.

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Introduction: *We present an update to our development of a low-mass, low-power ambient-pressure X-ray photoemission spectrometer (XPS) for the quantitative analysis of the composition and chemical state of elements on planetary surfaces.* The exposed outcrops and chemical sediments of Mars retain clues to its past history—the rock weathering processes, the presence and perseverance of liquid water, and possible biological habitability.This instrument targets high priority science objectives for Mars such as understanding geochemical processes especially with respect to the role of water, past habitability, oxidants, organic degradation, and dynamic atmosphere/mineral interactions. It is also suitable for other environments including Europa and small bodies.

XPS provides both quantitative elemental and chemical state information through the energy analysis of photoelectrons emitted from a sample that is irradiated with soft X-rays. The key strengths of XPS lie in the return of detailed chemical bonding information, quantitiative chemical analysis, and sensitivity to the first 5 to 10 nm of the surface of the sample. XPS can provide direct chemical information on all elements, except H, in rocks and soils. In addition to quantifying the distribution oxidation states in a sample, XPS provides direct information on the chemical bonding, allowing the identification of chemical compounds. It is well suited for identifying and distinguishing the various possible chemical states of elements of importance to understanding the Martian outcrops and chemical sediments such as O, N, P, Mg, Ca, Cr, S, Fe, Cl, Br, and C. XPS has not previously been considered for planetary exploration because laboratory XPS systems are large (>1000 kg) power consuming instruments.

The particular implementation of XPS presented here has been dubbed “ChemStat”, a contraction in reference to the chemical state information this technique will provide.

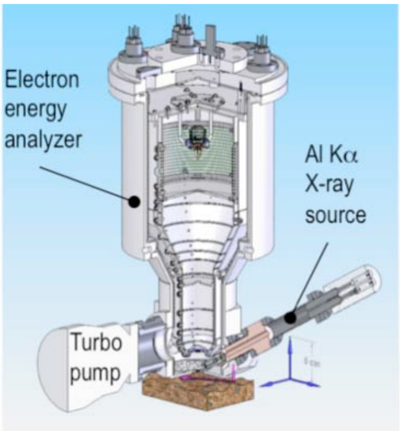

Figure 1: *Ambient XPS concept probes near surface region, including atmospheric species interacting with the surface.*

Key Technologies and Science Enabled: Two new technology advancements enable the miniaturization of XPS for planetary applications: i) a new electron energy analyzer and ii) a dual-layer X-ray and electron transmissive membrane. Collectively, these two advancements enable a new XPS system that is ~100 times less massive and power consuming, without sacrificing spectral or spatial resolution. The sample remains outside the spectrometer vacuum chamber, eliminating the need for prepare and transport the sample into the spectrometer. **Figure 1** shows a schematic of the analyzer design and spectrometer concept.

Keeping the sample in its ambient environment enables one to probe in real time dynamic chemical changes on the sample surface as a result of atmosphere/solid surface interactions. This promises new insight into such phenomenon as weathering processes, oxidant formation, photolytic or chemical degradation of organic compounds, including, for example, possible biomarkers and polycyclic aromatic hydrocarbons from meteoritic infall.

Electron Energy Analyzer. Commercial XPS systems use dispersive electron energy analyzers, which are not amenable to miniaturization because sensitivity and energy resolution depend upon the size of the concentric hemispheres typically used. In contrast, the new electron energy analyzer discussed here does not spatially disperse electrons according to their energy, but instead uses high-pass and low-pass filters to illuminate the detector with a narrow range of electron energies. This approach is amenable to miniaturization without sacrificing performance and was developed to the breadboard stage by Apparati, Inc. via a NASA SBIR. [1]

Dual-Layer Membrane. Only recently has ambient-pressure XPS emerged as a laboratory instrument and such instruments depend upon extensive differential pumping. The ChemStat implementation uses a dual-layer silicon nitride membrane as a gas isolator film. A dual-layer membrane is required because both X-rays and electrons must be transmitted. X-rays can easily penetrate many microns of Si_3N_4, but electrons are unable to transmit through films thicker than 5–6 nm. Such ultra-thin films cannot be made over the required mm-size areas.

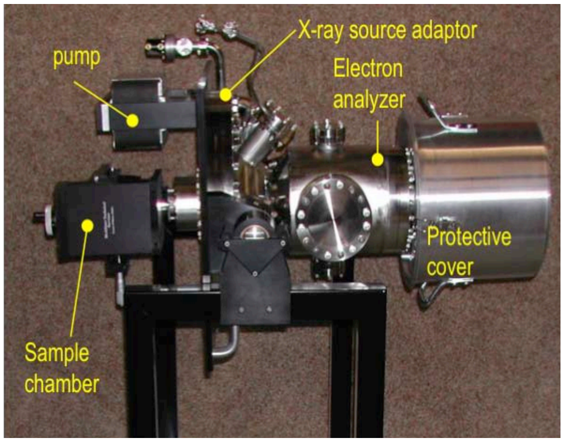

Figure 2. *Prototype ChemStat system with sample environment chamber to simulate Mars ambient and development stand to permit full spectrometer rotation for access.*

Our solution was to develop a dual-layer that consists of arrays of ultra-thin (2.5 to 5 nm) Si_3N_4 windows on a supporting thin (0.5 to 1 μm) Si_3N_4 membrane, which, in turn, is fabricated on a supporting thick (300 to 500 μm) Si frame. [2] We have successfully tested dual-layer membranes with 3.5-nm ultrathin windows fabricated over a 5-mm area against 35 psi pressure differential while demonstrating theoretically predicted electron transmission properties.

Spectrometer System Characteristics. Current performance chacteristics estimated for a flight version of ChemStat are as follows: 7 kg, 10 W, 0.8 eV spectral resolution, 100 μm spatial resolution, and operating pressure for sample of $<10^{-6}$ to 10 torr.

Development Update: Effort in the last year focused on two fronts: (i) optimizing the dual-layer membranes for maximum electron transmission while maintaining membrane robustness against bursting, and (ii) integrating a prototype spectrometer with a sample environmental chamber to simulate Mars ambient pressure.

The prototype ChemStat spectrometer is shown in **Figure 2** on a special stand to allow access to the sample environmental chamber and dual-layer membrane component. The spectrometer has been adapted to accept a commercial Al Kα X-ray source (a source more suitable for a planetary instrument is under parallel development via a SBIR contract). The sample chamber has been designed to hold the sample ~1 mm from the dual-layer membrane. This distance is dictated by the mean-free path of the photoelectrons, which must traverse from the sample into the spectrometer analyzer through the Mars ambient-pressure maintained in the sample chamber.

Many designs for the dual-layer membrane were investigated (**Figure 3**). Burst pressures of 30 to 90 psi were obtained for membranes over a range of nitride stress conditions and thicknesses suitable for this spectrometer concept.

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References:

[1] Bryson C., Kelly M., Wu W. (2006), SBIR report for Contract NNC04ACA20C, 28 Feb 2006

[2] Bryson C., Grunthaner, F., Grunthaner P., (2004) US Patent No. 6,803,570 B1

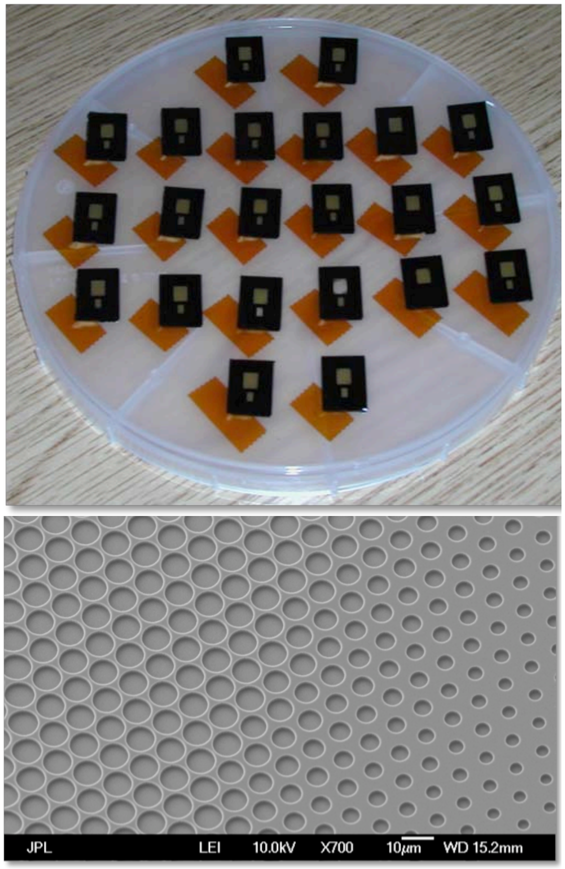

Figure 3. *Top: Photo of test die to investigate membrane burst pressures for a series of different membrane designs. For a given die, the small membrane transmits X-rays to the sample and the larger membrane transmits photoelectrons to the analyzer. Bottom: SEM shows ultra-thin nitride window array for electron transmission.*