We have completed installing our upgraded Multi-Technique Spectrometer/Diffractometer (Slides 3-6), together with a newly completed five-axis variable-temperature sample manipulator (Slides 7-9), other mechanical upgrades to improve spectrometer rotation and provide a sixth axis of sample rotation (Slide 10) and to improve angular resolution (Slide 11) on bend-magnet beamline 9.3.1 at the Advanced Light Source, which provides photons between about 2.3 keV and 5.5 keV (slide 2). This permits doing materials-science based hard x-ray photoemission (HXPS, HAXPES) for the first time at the ALS, and this effort represents only the second possibility for broad-based materials-related HXPS in the U.S., together with beamline X24A at NSLS, also situated at a bend magnet. For more on the 9.3.1 beamline, see next slide and W. Stolte at: http://ssg.als.lbl.gov/ssgbeamlinesbeamline9-3-1. Allowing for ring current and topoff, the ~10^{11} measured fluxes from 9.3.1 are comparable to those from both X24A and the HIKE beamline at BESSY (other successful bend-magnet HXPS facilities).

In the first hard x-ray photoemission results that follow (Slides 12-18), the spectrometer contribution to linewidth should be 0.20 eV. The 9.3.1 beamline contribution derives from a resolving power $E/\Delta E$ that is approximately constant at ~6,800 over its full range, which has now been verified by us in photoemission, and will thus yield for two of the energies used here 0.42 eV at 2842 and 0.66 eV at 4500 eV. The spectrometer should thus be contributing only a small amount to linewidth for both photon energies. These resolution values are thus over the full range better than typical monochromatized laboratory XPS systems using Al Kα at 1487 eV, and can be compared to optimum practical working resolutions of 0.20-0.30 eV in our prior measurements at the best undulator beamlines in the world (SPring-8, DESY-Petra III). See last slide with list of prior publications based on HXPS from other facilities.
A non-monochromatized Al Kα or MgKα x-ray source is also available in the system (Slide 6) for lower-energy measurements at 1487 eV or 1254 eV, with the usual ultimate resolutions of ca. 0.9 and 0.8 eV, respectively.

The hard x-ray measurements involve much greater information depths than typical XPS at 1.5 keV, by ca. 1.6x at 2842 eV and 2.3x at 4500 eV. As another comparison to typical UPS or ARPES measurements between 20 and 150 eV, the information depths in the hard x-ray measurements will be greater by ca. 9-30x at 2842 eV and 13-50x at 4500 eV. Thus, surface effects are minimized and bulk or buried-layer properties are more directly accessible.

The Berkeley system is also fully automated for angle scanning, with first standing-wave rocking curves in multilayer samples now obtained (Slides 14-15), and it has also demonstrated its ability to do hard x-ray angle-resolved photoemission (HARPES—See Gray et al., Nature Materials 10, 759–764 (2011) – Slides 16-17), including a sixth tilt axis that has been demonstrated in core-level photoelectron diffraction and angle-resolved photoemission (Slides 18-19).

Being able to rotate the spectrometer in-plane by ca. 50 degrees (see configuration in Slides 5 and 6) also permits doing variable surface sensitivity angle-resolved XPS (ARXPS) with a fixed grazing x-ray incidence angle at which intensities are a maximum, or doing HARPES with fixed photon-sample relationship. Other hard x-ray photoemission systems suffer severe losses in intensity when going away from grazing incidence to do ARXPS (see e.g. Slide 14(a)).

Website with slide-show details:
Beamline 9.3.1 is a double Si (1,1,1) crystal monochromator with a 2.2 to 5.3 keV energy range, covering the K-edges of:

- The optical design includes two identical, but oppositely deflecting, toroidal mirrors positioned symmetrically before and after the monochromator. This approach yields two benefits: high resolution by providing parallel x-rays for diffraction by the Si crystals, and a small beam spot by means of 1:1 focusing of the storage ring source with a minimum of aberrations.
- The beamline delivers approximately $2 \times 10^{11}$ photons/s over most of its photon energy range, with a resolving power of $\sim 6800$ over the entire range.
- The minimum beam size is better than 500 x 1000 microns, and the usual position stability is less than ±200 microns. Beam motion in scanning energy over the full range is very small, in the ±5 micron range for vertical and ±10 micron range for horizontal.

W. Stolte, ALS, [http://ssg.als.lbl.gov/ssgbeamlines/beamline9-3-1](http://ssg.als.lbl.gov/ssgbeamlines/beamline9-3-1)
Oxidized Si, 4500 eV photons

Si 2p and Si 1s core spectra

Si 0 2p

Si 0 1s

Si +4 2p

Si +4 1s

ΔE: ~4.0

ΔE: ~16.4

ΔE: 0 ~4.4

ΔE: ~16.8

with Mark West, Wayne Stolte, Alexander Saw, Aru Rattachanata, Daria Eiteneer, Aaron Bostwick, Catherine Conlon, Naoyuki Maejima, Armela Perona, Alex Gray, Alexander Kaiser, Giuseppina Conti, John Thomson, David Hemer, Zahid Hussain, Dennis Lindle. Chuck Fadley
Hard X-Ray Photoemission at the LBNL Advanced Light Source—First Results, March, 2012

Oxidized Si, 2834 eV and 4500 eV photons

More bulk sensitive, Si\(^{+4}\) oxide reduced

Slavomir Nemsak, Gunnar Palsson, Mark West, Wayne Stolte, Alexander Saw, Aru Rattachanata, Daria Eiteneer, Aaron Bostwick, Catherine Conlon, Naoyuki Maejima, Armela Perona, Alex Gray, Alexander Kaiser, Giuseppina Conti, John Thomson, David Hemer, Zahid Hussain, Dennis Lindle. Chuck Fadley
Permits using all relevant spectroscopies on a single sample: XPS (incl. Al and Mg Kα), HXPS, XPD; XAS (e− or photon detection), soft XES/RIXS
Hard X-ray Photoemission at the Advanced Light Source: The Multi-Technique Spectrometer/Diffractometer (MTSD)

Sample prep. chamber: LEED, Knudsen cells, QCM, electromagnet,...

Loadlock for sample introduction

Soft x-ray spectro-meter: Scienta XES 300

5-axis automated sample manipulator

Diff. seal

Chamber rotation

Electron spectro-meter: Scienta SES 2002

XPS: Al/Mg Kα

Diff. seal
Custom-built five-axis sample goniometer with cryogen flowing directly to sample base via helical capillaries

- Cam for selecting contact arm options
- Primary sample ~ 30 K to 2000 K
- 3 ref. Samples on carrousel
- $\phi$ rot’n. (±200°)
- Double helix cryo-capillary, for $\phi$ motion
- Contact arms for current, HV, temp. measurement
- Double helix cryo-capillary, plus helical conductor leads, for $\theta$ motion
- LHe/LN flow system
- S. Nemsak, M. West, J. Pepper, ...
Custom-built five-axis sample goniometer with cryogen flowing directly to sample base.

Primary sample
~ 30 K to 2000 K

3 ref.
Samples on carrousel

Primary sample

LHe/LN flow system:

VCR couplings

ϕ rot’n. (±200°)

Θ rot’n. (±200°)
Custom-built two-axis sample goniometer with cryogen flowing directly to sample base.

Primary sample
~ 30 K to 2300K

3 ref. samples on carrousel
• Non-torquing rotation mechanism for the main analysis chamber

Other recent upgrades

• Sample tilt mechanism 5-axis → 6-axis sample holder

M. West, S. Nemsak, J. Pepper, ...
Recalibration of the angular resolution for hard x-ray photoelectron diffraction or HARPES measurements

Resolution: 0.03-0.04 degrees over 2.5-5.5 keV

S. Nemsak, P. Karlsson (VGScienta)
First survey from 1.4 nm LNO on STO, \( h\nu = 4000 \) eV

Simulation (SESSA)

Expt.
First survey from 1.4 nm LNO on STO, \( h\nu = 4000 \text{ eV} \)

Expt.

\begin{align*}
\text{Ni}\text{2p} & \quad \text{Sr}\text{3p} \\
\text{Sr}\text{3s} & \quad \text{C}\text{1s} \\
\text{C}\text{1s} & \quad \text{Sr}\text{3d} \\
\text{Sr}\text{3d} & \quad \text{Ni}\text{3s} \\
\text{Ni}\text{3p} & \quad \text{Sr}\text{4s} \\
\text{Sr}\text{4p} & \quad \text{La}\text{3p} \\
\text{La}\text{4p} & \quad \text{La}\text{3d} \\
\text{Ni}\text{3p} & \quad \text{Ti}\text{3p} \\
\text{Ti}\text{3s} & \quad \text{La}\text{4s} \\ 
\text{La}\text{4s} & \quad \text{Ni}\text{3s} \\
\text{Ti}\text{3p} & \quad \text{Sr}\text{4s} \\
\text{Sr}\text{4s} & \quad \text{La}\text{4s} \\
\text{La}\text{4s} & \quad \text{La}\text{3p} \\
\text{Sr}\text{4p} & \quad \text{La}\text{3p} \\
\text{VB} & \quad \text{SESSA simulated spectrum} \\
\end{align*}
First standing-wave rocking curves from a test Si/Mo multilayer: photon energy 2300 eV

(a) Si 1s
(b) Si 1s-zoom

1st order Bragg:
\[ \lambda_x = 2d_{ML} \sin \theta_{Bragg} \]
\[ \lambda_{SW}(|E^2|) = \frac{\lambda_x}{2 \sin \theta_{inc}} \approx d_{ML} \]

X-ray Photo-Electron \( \sim 0.1 \) mm spot

\( \theta_{Bragg} \approx 4.0 \) nm

XPS Intensity [arb.u.]

Incidence angle [°]

Si1s (main) Si1s (oxide)

Incidence angle [°]

Si1s (main) Si1s (oxide)
First standing-wave rocking curves analysis for a Si/Mo multilayer: photon energy 4000 eV-expt. and x-ray optical modeling (YXRO)

(a) Si 1s
(b) Mo 2p\(_{3/2}\)
(c) O 1s
(d) C 1s

Core-level rocking curves:


<table>
<thead>
<tr>
<th>Oxide</th>
<th>Best Fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2)</td>
<td>13.2</td>
</tr>
<tr>
<td>Si</td>
<td>20</td>
</tr>
<tr>
<td>MoSi(_2)</td>
<td>6</td>
</tr>
<tr>
<td>Mo</td>
<td>4</td>
</tr>
<tr>
<td>MoSi(_2)</td>
<td>8</td>
</tr>
<tr>
<td>Si</td>
<td>16.4</td>
</tr>
</tbody>
</table>
First hard x-ray angle-resolved photoemission (HARPES) from test-case W(110): photon energy 2500 eV, T \approx 90K: expt.-multiple stitched images (Nemsak)

Incidence angle 2°; Expt’l. electron emission angle over 29° range, sample tilt 1.25°
First hard x-ray angle-resolved photoemission (HARPES) from test-case W(110): photon energy 2500 eV, $T \approx 90$K: expt.-multiple stitched images (Nemsak) versus free-electron final-state calculations (Plucinski)

Incidence angle 2°; Expt’l. electron emission angle over 29° range, sample tilt 1.25°
First 2D hard x-ray photoelectron diffraction (HXPĐ) making use of the new tilt mechanism: SiC(0001)- hv = 3100 eV

First 2D hard x-ray angle-resolved photoemission (HARPES) making use of the new tilt mechanism: SiC(0001) - $h\nu = 3100$ eV

First 2D hard x-ray angle-resolved photoemission (HARPES) making use of the new tilt mechanism: SiC(0001)- $h\nu = 3100$ eV
The LBNL Advanced Light Source and The Fadley Group, via the LBNL Materials Sciences Division, are supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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Wayne Stolte and other Beamline 9.3.1 activities are also supported through the University of Nevada Las Vegas, by National Science Foundation Grant No. PHY-05-55699 and by the ALS.
Background references to prior group papers on hard x-ray photoemission systems at other facilities
See also http://www.physics.ucdavis.edu/fadleygroup/ for other group activities and papers