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Direct Characterization of the Electronic Structure of Shocked and Heated Materials

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Physics & Advanced Technologies Directorate
Chemistry & Materials Science Directorate

Final report for LDRD Project 01-ERD-019

Detailed knowledge of how materials respond to strong shocks or other extreme conditions on rapid timescales (such as laser heating) are required to support LLNL missions of national security and stockpile stewardship. This project started in FY01 to develop and demonstrate a new pump-probe characterization capability for investigating ultrafast changes in the chemical and electronic structure of materials under extreme conditions with picosecond time resolution.

The LLNL COMET (Compact Multipulse Terawatt) [1] is a compact 15 TW laser facility operating at 1054 nm wavelength, and utilizes the technique of chirped pulse amplification to produce two high power beams at a rate of 1 shot every 4 minutes. A short pulse length varied from 500 fs to 25 ps and a long 600 ps (FWHM) pulse is focused in a high intensity line focus with a traveling wave geometry to generate an intense Ni-like Pd ion $4d - 4p$ x-ray laser (XRL) line at 14.7 nm (84.5 eV). Total energy in the two beams is of order 3 – 7 J to produce lasing where the peak-to-peak delay between the laser pulses is found to be optimal at 700 ps with the short pulse arriving after the long pulse. Typical COMET x-ray laser characteristics are summarized in Table 1.

High photon flux/shot, high monochromaticity, and picosecond pulse duration when combined with small source area and beam divergence properties of the 14.7 nm line [2] give ultra-high peak brightness $\sim 10^{24} - 10^{25}$ ph. mm⁻² mrad⁻² s⁻¹ (0.1% BW)⁻¹. Overall, the 14.7 nm peak brightness is 5 – 6 orders of magnitude higher than 3rd generation synchrotron undulator sources. However, third generation synchrotron undulator sources still have higher average brightness of $0.5 - 6 \times 10^{18}$ ph.mm⁻² mrad⁻² s⁻¹ (0.1% BW)⁻¹ at 50 – 10 nm, respectively. The technique of electron time-of-flight (e-ToF) spectroscopy requires a monochromatic, ps pulsed source for efficient x-ray laser induced photoelectron spectroscopy (PES).

TABLE 1. COMET x-ray laser source parameters

Source Parameters	COMET X-ray Laser	Importance ^b
Laser Pump Energy (J)	5 - 10	
X-ray Laser Energy (μJ)	25	
Photons/Shot	2×10^{12}	x
Shot Rate (Hz)	0.004	
Wavelength (nm)	12 – 47	
/	$< 10^{-4}$	x
Source Size (μm^2)	25×100	
Divergence (mrad^2)	2.5×10	
XRL Pulse Duration (ps)	2 – 10	x
Peak Brightness, B ^a	1.6×10^{25}	x
Average Brightness, B ^a	1.3×10^{11}	

^a [Units of ph. $\text{mm}^{-2} \text{mrad}^{-2} \text{s}^{-1} (0.1\% \text{ BW})^{-1}$].

^b “**x**” denotes considered important x-ray laser source parameter.

The focus of the first year was to implement and interface the necessary instrumentation in order to give a proof-of-principle demonstration of the x-ray laser probe/time-of-flight photoelectron spectroscopy technique. This involved installing a UHV beamline and chamber on the COMET laser facility. The UHV chamber and beamline design allows the interface of the x-ray laser beamline from high (10^{-5} mbar) to ultra-high vacuum (10^{-8} mbar) and includes a differential vacuum pumping station, pinhole/filter isolation, and a means for introducing new samples remotely without breaking vacuum. In addition, the first photoelectron spectrometer (PES) was obtained from LBNL and subsequently re-built. This spectrometer was a large aperture paraboloidal mirror analyzer (PMA).

The 3rd COMET laser arm was also completed and tested for high contrast, frequency doubled output. This arm will be used as the optical pump in the dynamic experiments for creating sample melt. The present capability of 1.2 J in a 500 fs pulse at 527 nm wavelength exceeds the requirements for this project. This beam can be delivered simultaneously with the other two laser arms generating the x-ray laser probe. All three laser beams come from a common oscillator and estimated jitter between timing of optical pump and the x-ray laser probe is < 5 ps.

The routing of the x-ray laser probe beam to the sample for surface analysis while discriminating against broadband spontaneous x-rays from the plasma requires the use of special Mo:Si multilayer coated flat and spherical mirror optics. These were fabricated at LLNL (courtesy of T. Barbee, Jr. and J. Nilsen) and successfully tested on COMET to relay and focus the 147 Å (85 eV) x-ray

laser beam. The beam properties of near-field exit footprint, far-field pattern, divergence (2 mrad) and pointing angle stability ($\sim 100\mu\text{rad}$) were determined and found to satisfy the requirements of the project. The beam is partially coherent (measurements made in collaboration with Jorge Rocca of Colorado State University), exhibits a few tens of spatial modes and has a 5x diffraction limited output as shown in Figure 1.

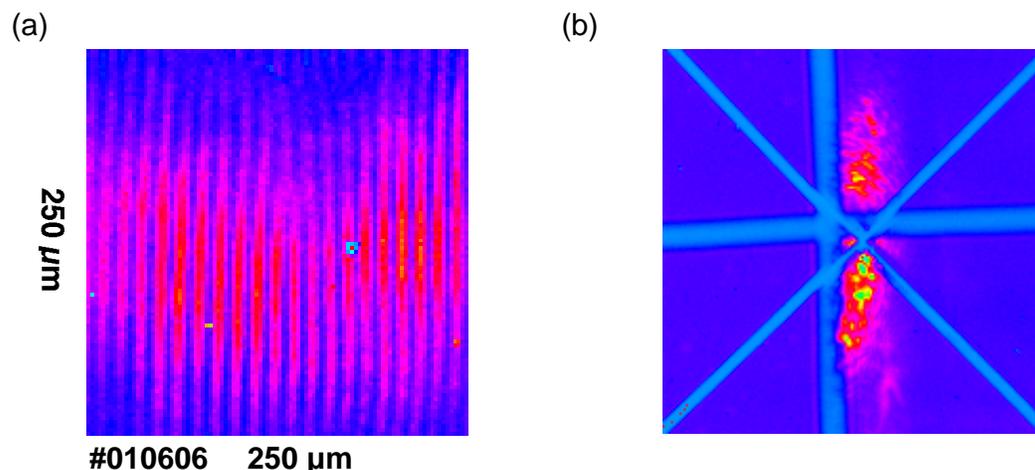


Figure 1. X-ray laser coherence and pointing (a) spatial coherence is demonstrated by the high fringe visibility (0.7) measured by interferometry, (b) near-field x-ray laser pattern aligned on 250 μm crosshairs through beamline.

Figure 2 shows a schematic of the x-ray laser photoelectron spectroscopy experimental setup. The 3rd COMET laser arm is focused onto the sample to produce rapid heating and induce phase changes. As previously mentioned, the x-ray laser probe is collimated by a normal incidence Mo:Si multilayer spherical mirror and relayed along the beamline by a 45° Mo:Si multilayer flat mirror. The narrow reflectivity window of the mirrors selects the x-ray laser wavelength and minimizes other plasma x-rays reaching the sample. A pinhole or thin filter isolates the beamline from the experimental ultra-high vacuum (UHV) chamber, operating below 10^{-8} mbar pressure. The x-ray laser probes the material surface being heated by the optical laser pump, at various times and induces photoemission. These low energy photoelectrons, with K.E. < 84.5 eV, emitted from the valence band and shallow core levels are detected by the time-of-flight spectrometer.

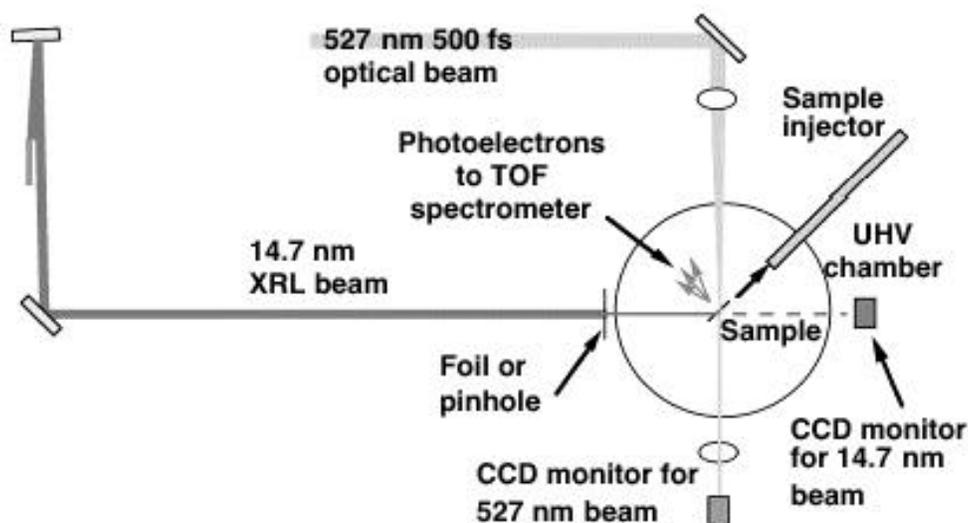


Figure 2. Schematic for the optical pump – x-ray laser probe of material surfaces.

In the second year, we overcame several major scientific and technical challenges to successfully validate the x-ray laser PES technique by measuring tantalum 4f and tungsten 4f core- and valence electron spectra from room-temperature bulk materials. We installed an argon ion gun in the dedicated x-ray laser beam line ultrahigh-vacuum chamber for sputter cleaning samples in-situ to remove surface oxides and contaminants. This improved the surface purity and corresponding core-level and valence-band photoemission intensity. To meet the novel requirements of single pulsed x-ray induced PES spectra, we improved the data-acquisition electronics for fast time resolution by optimizing the ToF analyzer performance using fast (3 GHz), transient, digitizing oscilloscopes.

Figure 3 shows the photoelectron time-of-flight spectra of the native oxide on the W and Ta reference samples acquired with the paraboloidal mirror analyzer and illuminated with $10^8 - 10^9$ x-ray laser photons. Since the mean escape depth of the photoemitted electrons is on the order of $\sim 5-10 \text{ \AA}$ for this kinetic energy, the spectra should be more indicative of the oxide layer without sputter cleaning.

The photoelectrons are ejected with discrete kinetic energy $E_k = h\nu - E_b - \phi$, where $h\nu$ is the energy of the incident photon (84.5 eV), E_b is the binding energy of the photoelectron relative to the Fermi level and ϕ is the work function of the material ($\phi = 4.5 \text{ eV}$ for W and 4.1 eV for Ta). The Fermi level is used as the zero binding energy level by definition. Each photoelectron has a discrete energy representative of the element from which it was emitted thus allowing one to identify the atomic species present. Furthermore, the binding energy of an electron is influenced by its chemical environment and thus can be used to identify the chemical state of a given atom in the sample.

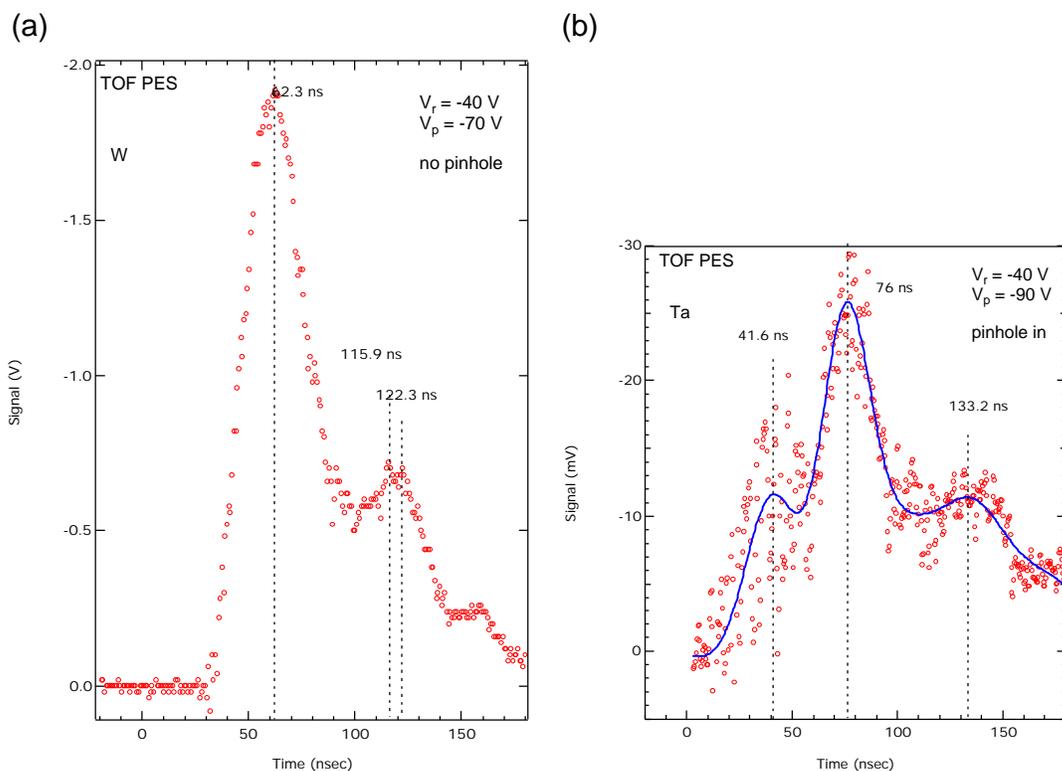


Figure 3. First spectra demonstrating COMET X-ray laser induced time-of-flight photoelectron spectroscopy showing the 4f core-level and valence band for (a) tungsten (W) and (b) tantalum (Ta). The blue line in (b) is the best fit to all the data points.

Peaks corresponding to valence band and core-level emission are observed in the spectra. The broad background originates from secondary electron emission that represents elastically scattered electrons with kinetic energies near that of the W and Ta *d* electrons, multiply scattered electrons reflected to the surface after passing through a thick layer of target material, and low energy electrons which are formed as a result of excitation of loosely bound atomic electrons.

In the third year, we redesigned the entire UHV chamber for installation of a new electron time-of-flight (e-ToF) analyzer [3] designed and built by Oliver Hemmers at the University of Nevada, Las Vegas. (Figure 4) The new e-ToF analyzer incorporated further improvements to the microchannel plate detector and data acquisition electronics (impedance matching), both factors that contribute directly to increased e-ToF energy resolution. To achieve higher kinetic-energy resolution, improvements were also implemented in the retarding-lens systems. The enhanced resolution and performance of this new electron-ToF spectrometer and easy *in-situ* analyzer alignment is described in detail elsewhere. [3]

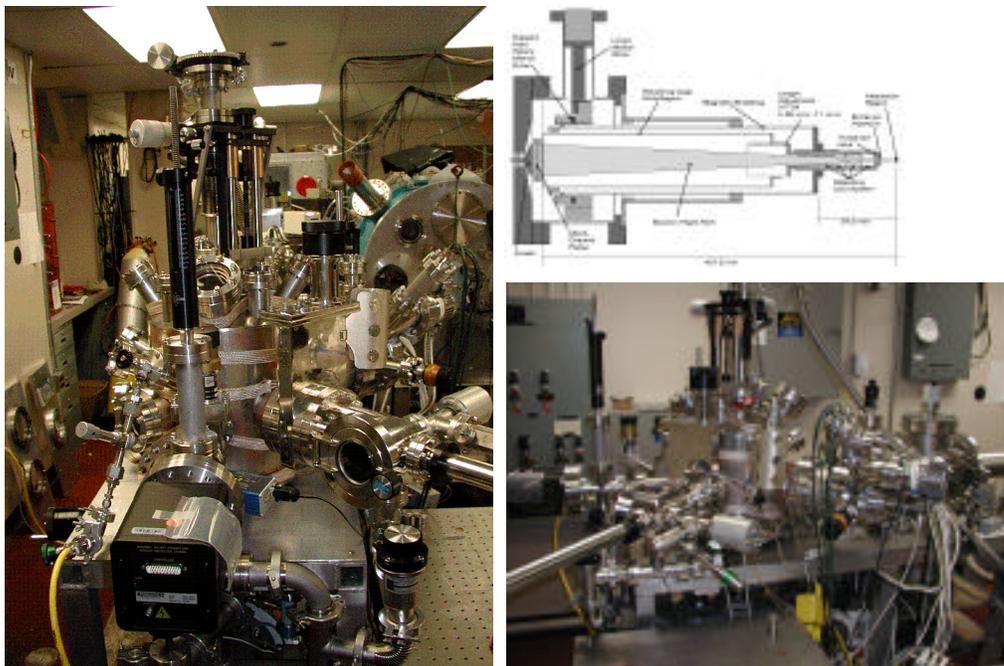


Figure 4. Photograph showing the redesigned ultrahigh vacuum chamber with UNLV e-ToF analyzer. This system is installed on the COMET XRL beamline.

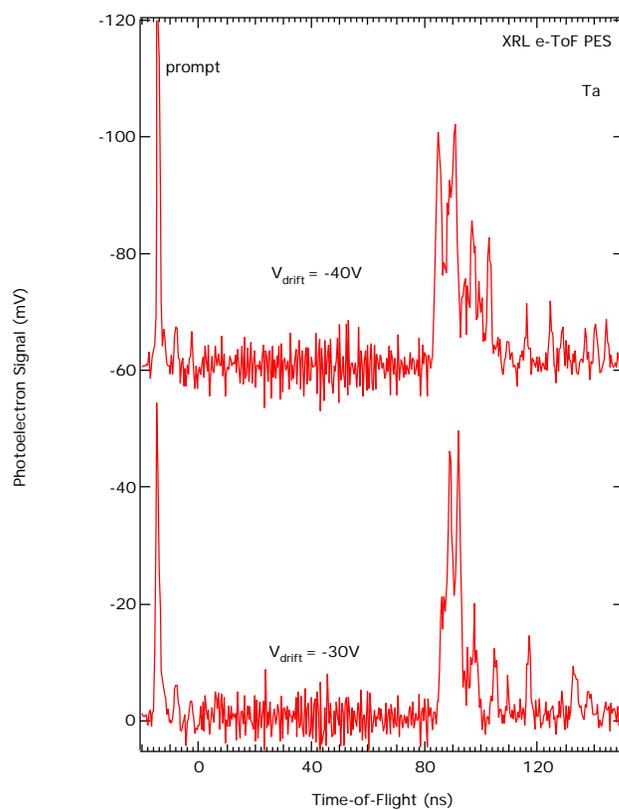


Figure 5. COMET X-ray laser induced time-of-flight photoelectron spectroscopy of Ta with new UNLV e-ToF analyzer.

Figure 5 shows the photoelectron time-of-flight spectra of the Ta reference sample acquired with the new UNLV e-ToF analyzer and illuminated with $10^8 - 10^9$ x-ray laser photons. The peak labeled prompt at -10 ns is due to x-ray photons scattered from the sample surface hitting the detector and represents a timing fiducial for the time-of-flight photoelectron peaks measured after 80 ns. Increasing the drift voltage gives better separation of the photoelectron peaks and therefore better energy resolution (Fig. 5 upper trace) in the spectrum

The upper valence band of oxidized Ta is composed primarily of Ta $5d$ and $6sp$ occupied states that hybridize with O $2p$ states. [4] These valence band electrons will have the highest kinetic energies and thus will be the first events in the spectrum. The Ta $4f_{7/2,5/2}$ spin-orbit pair with kinetic energies of 58.4 eV and 56.4 eV, respectively, are the next expected events in the spectrum. Note also that the photoionization cross-sections for Ta $5d$ and $4f$ states at this photon energy are 0.4606 Mb and 1.722 Mb, respectively. [5]

We have successfully validated x-ray laser induced time-of-flight photoemission by measuring the valence band and shallow core-level photoemission in room temperature bulk materials. Single-shot spectra have been achieved showing that the incident photon number is more than enough for this application. Surface oxides and contaminants will be a limiting effect on the technique, and thus *in-situ* sputter cleaning will be required. In addition, further refinements to the e-ToF analyzer will be required to improve alignment and overcome stray magnetic fields. Future work will include demonstration of the optical pump-X-ray probe characterization capability to observe the evolution of changes in chemical and electronic structure with picosecond time resolution during dynamic processes.

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Appendix: Publications related to LDRD work

Journal Publications

1. R.F. Smith, V.N. Shlyaptsev, J. Dunn, J. Nilsen, J.R. Hunter, J.J. Rocca and J. Filevich, M.C. Marconi, **Refraction Effects on X-ray and UV Interferometric Probing of Laser Produced Plasmas**, JOSA B, Vol. 20 Issue 1 Page 254 (January 2003). UCRL-JC-149100.
2. R.F. Smith, J. Dunn, J. Nilsen, V.N. Shlyaptsev, S. Moon, J. Filevich, J.J. Rocca, M.C. Marconi, J.R. Hunter, T.W. Barbee, Jr., **Picosecond X-ray Laser Interferometry of Dense Plasmas**, Phys. Rev. Lett., **89** (6), pp. 065004-1 (2002). UCRL-PRES-148431.
3. Joseph Nilsen, James Dunn, Raymond F. Smith, and Troy W. Barbee, Jr., **Two-dimensional imaging and modeling of the 14.7 nm Ni-like Pd X-ray laser**, JOSA B, Vol. 20 Issue 1 Page 191 (January 2003). UCRL-JC-147816.
4. R.F. Smith, J. Dunn, J.R. Hunter, J. Nilsen, S. Hubert, S. Jacquemot, C. Remond, R. Marmoret, M. Fajardo, P. Zeitoun, L. Vanbostal, C.L.S. Lewis, M.-F. Ravet, F. Delmotte **Longitudinal Coherence Measurements of a Transient Collisional X-ray Laser**, Opt. Lett. **28**, 2261 (2003). UCRL-JC-149593-REV-1

Conference Proceedings and Presentations

1. A.J. Nelson, J. Dunn, T.W. Van Buuren, J. Hunter, and R.F. Smith, **Time-of-flight x-ray photoelectron spectroscopy with an x-ray laser source**, presented at 8th International Conference on X-ray Lasers Aspen, Colorado, May 27 - 31, 2002. UCRL-JC-147929-ABS.
2. J. Dunn, R.F. Smith, J. Nilsen, A.J. Nelson, T.W. Van Buuren, S.J. Moon, J.R. Hunter, J. Filevich, J.J. Rocca, M.C. Marconi, and V.N. Shlyaptsev, **Small-scale soft x-ray lasers for probing matter**, presented at the APS Laser Science XVIII Symposium on "Frontiers of Laser Sources", Orlando, Florida, Sept. 29 - Oct. 3, 2002. UCRL-JC- 149091-ABS.
3. R.F. Smith, J. Dunn, J. Nilsen, H. Fiedorowicz, A. Bartnik, V.N. Shlyaptsev, **Recent x-ray laser characterization experiments at LLNL**, Technical Digest of Applications of High Field and Short Wavelength Sources IX 2001, ed. T. Ditmire and R. Freeman, Palm Springs, CA, 21 – 24 October, 2001, Optical Society of America (2001). UCRL-JC-148030.
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IX 2001, ed. T. Ditmire and R. Freeman, Palm Springs, CA, 21 – 24 October, 2001, Optical Society of America (2001). UCRL-JC-145740

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6. J. Dunn, A.L. Osterheld, A. Ya. Faenov, T.A. Pikuz, and V.N. Shlyaptsev, **Injector-Amplifier Design for Tabletop Ne-like X-ray Lasers**, Proc. of 8th International Conference on X-ray Lasers Aspen, Colorado, May 27 - 31, 2002, ed. by J.J. Rocca, J. Dunn and S. Suckewer (AIP). UCRL-JC-149105.
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