

## Metal-Insulator Transitions in an Expanding Metallic Fluid: Particle Formation Kinetics

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Core-level photoemission spectroscopy provides a local probe of expansion dynamics and associated transient chemical properties as a highly pressurized, metallic fluid expands into vacuum following impulsive heating of a semiconductor by an intense, ultrashort laser pulse. Transient photoemission peak shifts reveal that metal-insulator transitions occur rapidly following laser heating. These experiments probe constituents species and solidification kinetics occurring in the early moments of material ejection and provide insight into how particles arise in the current laser ablation regime.

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An intense, ultrashort laser pulse can rapidly heat matter to extreme temperature and pressure creating transient material states of fundamental interest. Impulsive superheating, for instance, may allow one to study metal-insulator transitions as matter passes near a liquid-vapor critical point or similar transitions driven purely by volume expansion. A rapidly superheated material will expand into vacuum (ablation) and this expansion is of considerable practical importance since ablation is used to synthesize organic and inorganic microparticles and films [1]. Significant uncertainties remain regarding transient chemical properties of the ejecta and about the underlying dynamics of particle formation [2]; direct probes of the rapid, complex material evolution are essential.

Experimentally, it has proven difficult to directly probe transient material states in the early moments of vacuum expansion. Material is only a few  $\mu\text{m}$  from the bulk surface so absorption/reflection spectroscopies interact with the residual surface and do not distinguish surface dynamics from material-ejection dynamics. Careful optical experiments have provided important insight into the ejecta dynamics of near threshold femtosecond ablation [3,4], yet suffer some limitations since the probe interacts with the residual bulk surface and the optical response depends on generally unknown proportions of liquid, gas, and vapor phases. Core-level photoemission spectroscopy (CPS) should offer distinct advantages. As a *local* probe CPS is well known for providing chemical sensitivity [5] and, significantly, one probes solely the ejecta since the electron escape depth ( $\approx 1$  nm [5]) is short compared to typical ablation depths ( $> 10$  nm [6]). To date CPS has primarily probed static chemical properties. Here we report the first application of time-resolved CPS to probe the early-time vacuum expansion of an impulsively superheated material. CPS is extended to the picosecond time domain and reveals metal-insulator transitions which

accompany structural phase transitions as a highly pressurized metallic fluid expands into vacuum. These experiments demonstrate an ability to probe constituent species and solidification kinetics occurring early in the vacuum expansion of an extreme material and provide insight into how particles arise in the current ablation regime.

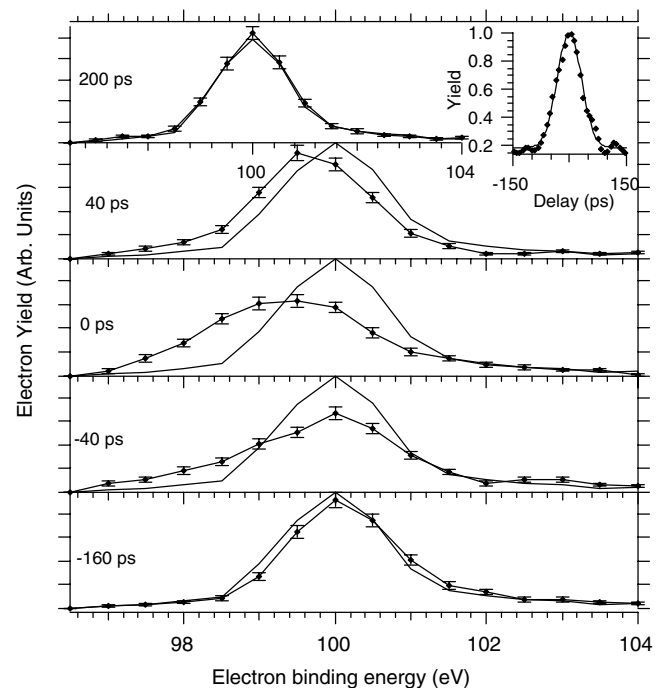


FIG. 1. Temporal sequence of photoemission spectra ( $12 \text{ J/cm}^2$ ) at specified pump-probe delays (line with markers). Positive delay: x rays probe before the laser pump. A reference spectrum at  $+240$  ps is also shown (no markers). Inset: Electron counts (97–99 eV, vicinity of shift) as a function of pump-probe delay. This curve ( $80 \pm 10$  ps FWHM), a convolution between the 80 ps x-ray pulse and the transient duration, indicates a photoemission transient  $< 50$  ps.

Laser-pump and x-ray-probe photoemission experiments are performed at the Advanced Light Source (ALS) using a laser system (800 nm, 200 fs, 1 kHz) synchronized to the ALS storage ring. Femtosecond laser pulses impulsively heat a silicon wafer to produce a hot, pressurized fluid which expands into vacuum (initial temperature and pressure estimated at 20 000 K and 40 GPa;  $T_{\text{critical}} \sim 5000$  K). Vacuum expansion is probed by time-delayed synchrotron pulses (400 eV) with  $2p$  core spectra recorded using a hemispherical analyzer. The synchrotron fill mode isolates a single x-ray pulse whose photoelectrons are electronically gated so measurements at a fixed pump-probe delay reflect spectral evolution over a time-window set by a single x-ray pulse ( $\sim 80$  ps via streak camera). Photoemission transients shorter than 80 ps can be observed although better noise statistics are required for shorter transients. Current noise levels (10–20%) allow one to see photoemission peak shifts lasting longer than  $\sim 10$ –20 ps (10–20% of 80 ps). A sample region is exposed to multiple pump-probe cycles so that the initial (unheated) material is either microcrystalline or amorphous. Static spectra show only a small ( $< 0.2$  eV) peak shift and no peak-shape distortion between a “fresh” silicon surface and a laser-exposed surface.

A temporal sequence of Si  $2p$  spectra (Fig. 1,  $12$  J/cm<sup>2</sup>) reveals a transient peak shift; an initial shift to lower binding energy (200 to 0 ps) following by a subsequent return to higher binding energy (0 to  $-160$  ps). The total yield is constant to within  $\sim 10\%$  and the dynamics are revealed in greater detail by plotting electron counts (97–99 eV, vicinity of shift) as a function of delay (Fig. 1 inset). The measured width ( $\sim 80$  ps) of this curve, a cross correlation between the 80 ps x-ray pulse and the transient duration, indicates a spectral transient shorter than the x-ray pulse while error bars ( $\sim 10$  ps) indicate an upper limit of  $\sim 50$  ps. Significantly, since the spectrum is perturbed for a time ( $< 50$  ps) less than the x-ray duration, a perturbed spectrum at a fixed delay must contain at least the following two peaks: one corresponding to transiently perturbed material and another to unperturbed material (which, depending on delay, is either recovered or not yet excited).

Consider (Fig. 2) the maximally perturbed spectrum, deconvolved assuming the simplest (i.e., two-peak) deconvolution: one peak at the original position (unperturbed material) with the original width and a second peak of the same width but with adjustable position and height (perturbed material). A good fit to data is obtained for Gaussians of approximately equal amplitude and a photoelectron peak shift of  $\sim 1.3$  eV. While better time and energy resolution are required to demonstrate the uniqueness of this deconvolution, the shifted peak position is consistent with a fluid phase of silicon (discussed below).

CPS probes the local state-of-aggregation through shifts in peak position with material phase. While the

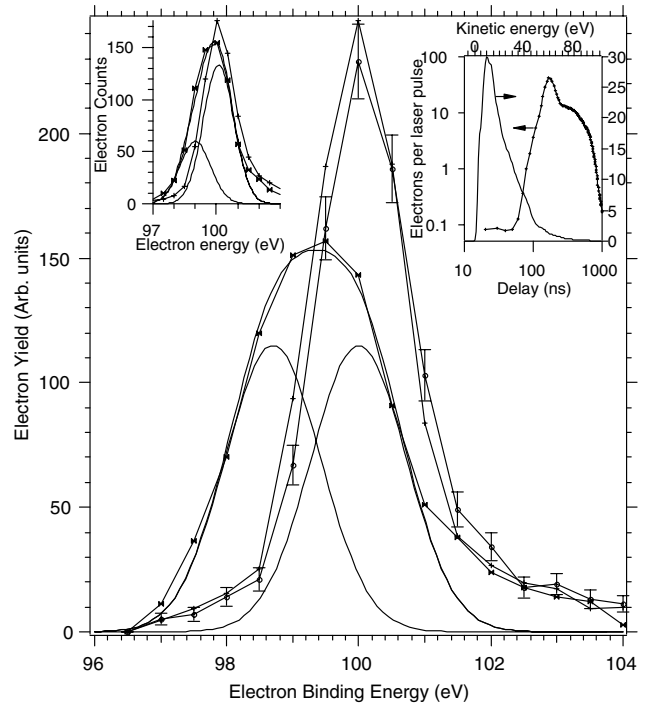


FIG. 2. X-ray spectra ( $12$  J/cm<sup>2</sup>) for delays of  $-160$  ps (circles,  $1.7$  eV FWHM peak width),  $240$  ps (crosses,  $1.7$  eV width) and  $0$  ps (bow ties,  $2.7$  eV width). The broadened peak is decomposed into two Gaussians of width  $1.7$  eV: a “perturbed” peak (at  $98.7$  eV with amplitude 115) and an “unperturbed” peak ( $100$  eV with amplitude 115). The sum of these two Gaussians is also shown. Left inset: X-ray spectra ( $4$  J/cm<sup>2</sup>) for delays of  $240$  ps (crosses,  $1.7$  eV width) and  $0$  ps (bow ties,  $2.3$  eV width). The broadened peak is decomposed into two Gaussians ( $100.1$  eV with amplitude 133,  $99$  eV with amplitude 60). The sum of these two Gaussians is also shown. Right inset: Both vertical axes indicate detected number of laser electrons per pulse. The time-integrated spectrum ( $0$ – $1$   $\mu$ sec; top and right axes) is shown as is the time history of electron emission (energy integrated; bottom and left axes). The initial ( $0$ – $10$  ns) measured yield of  $\sim 0.1 e^-$ /shot indicates space charge contributions to this figure and Fig. 1 are  $< 0.1$  eV (see text).

spectral transient is consistent with a phase transition (see below), we have considered alternative explanations. It was determined that surface photovoltage transients [7] are not observed, while a 1 eV Doppler shift from material expansion would require an unrealistically high ( $500\,000$  K) lattice temperature. Finally, space charge effects from laser electrons are estimated at  $< 0.1$  eV by assuming electrons are emitted in a sphere comparable to the laser spot size ( $\sim 50$   $\mu$ m) and calculating that  $> 10^4 e^-$ /shot in a subnanosecond pulse (the transient duration) are required to produce a 1 eV shift. By contrast, we determine the yield of laser electrons as  $< 10^3 e^-$ /shot in  $0$ – $10$  ns based on the yield of detected electrons ( $0.1 e^-$ /pulse, Fig. 2 inset) and our detection efficiency ( $10^{-3}$ – $10^{-4}$ ).

The current fluence exceeds the threshold fluence [8] for melting silicon so a fluid is produced upon laser heating. We now show the spectral transient is consistent with solid-fluid-solid phase transitions as initially laser-heated material melts and resolidifies after vacuum ejection. CPS is known for providing chemical sensitivity and the approach is to compare measured peak shifts with expectations based on model calculations. To our knowledge calculations of the solid-fluid shift in silicon are not available; relevant estimates, however, can be found for germanium [9]. Qualitatively, the solid-fluid transition in both silicon and germanium is an insulator (solid) to metal (fluid) transition [10]. An x-ray core hole is more efficiently screened by the mobile electrons of a metal than by the immobile electrons of an insulator [5] and this difference in core-hole screening (relaxation) is the principle factor causing a peak shift to lower binding energy in the metal.

For a quantitative estimate there are three contributions to solid-fluid peak shift: (i) change in initial state energy, (ii) change in final state energy (relaxation), and (iii) possible change in surface potential (i.e., reference level [11]). Experiments and calculations on germanium indicate that final state (extra-atomic) relaxation dominates the solid-fluid shift; the  $K$ -absorption edge is observed to shift by 1.3–1.4 eV upon melting and changes in final state relaxation are calculated at  $\sim 1.2$  eV [9]. We take this number (1.2 eV) as an estimate of the solid-fluid shift in silicon. In doing so we assume (i) that final state relaxation dominates in silicon as well as in germanium and (ii) that final state relaxation is of comparable magnitude in silicon and germanium. The first assumption is reasonable for insulator-metal transitions since relaxation shifts can be large ( $\sim 1$  eV) while initial state modification should be comparatively small. Initial state modification reflects changes in the local potential due to neighbor atoms; the *solid-atom* shift in silicon (reflecting presence vs absence of neighbors) has been calculated at  $\sim 1$  eV [12]. The corresponding *solid-fluid* shift should be comparatively small since it results from the more modest rearrangement of neighbors. Similarly, the surface potential is small ( $\sim 0.2$  eV [13]) and possible solid-fluid variations are neglected. As for the second assumption, it is reasonable to assume that relaxation, reflecting the polarization energy between a core hole and the induced charge distribution [5], is comparable in silicon and germanium. The metallic fluids have nearly identical carrier density ( $2 \times 10^{23}/\text{cc}$ ) [10] so the polarizabilities should be similar. Further, the solids have similar dielectric constants ( $\epsilon = 11.9$  for Si and  $\epsilon = 16$  for Ge [14]); the (macroscopic) polarization energy scales as  $(1-1/\epsilon)$  and this factor varies by  $<10\%$ . While core-hole size differs in the Ge ( $1s$ ) and Si ( $2p$ ) cases, Bechstedt [15] calculates only modest changes in relaxation energy with hole-size ( $<10\%$  difference in moderately polarizable media between Si  $1s$  and  $2p$  holes). While detailed theoretical

calculations from the community are strongly encouraged, the solid-fluid shift in Ge (1.2 eV) provides a reasonable estimate for the corresponding shift in silicon.

The transient shift can therefore be understood as reflecting a transient fluid phase of the ejecta. Initial laser heating produces a metallic fluid and the accompanying insulator-metal transition should produce a peak shift of  $\sim 1.2$  eV; we observe a  $\sim 1.3$  eV shift (deconvolution Fig. 2). We emphasize that we are probing dynamics within the ejecta rather than at the bulk surface since both lattice heating and material ejection occur rapidly ( $\ll 10$  ps); 80 ps probe pulses render us insensitive to the very earliest moments of surface heating and material ejection and the ejecta shield the underlying bulk surface. Since the bulk surface is known to stay molten for a long time ( $\gg 1$  ns [16]), the observation (discussed below) of rapid ( $< 50$  ps) solidification supports this conclusion.

CPS is sensitive to the local chemical environment and here provides insight into some basic features in the vacuum expansion of an extreme material. We comment on insights into the *local* expansion dynamics which determine the phase of the ejecta and associated phase transition kinetics. We conclude by comparing these findings on energetic short-pulse ablation to previous findings on long-pulse ablation.

Consider the ejecta phase. Lattice heating in silicon occurs rapidly ( $\sim 1$  ps [17]) so for high initial temperature atoms quickly have energy above the cohesive energy and are loosely speaking “unbound.” Material will be ejected in vapor form if upon ejection the interatomic spacing is increased so that neighbor atom wave functions no longer overlap. A condensed form is preserved if expansion is largely inhomogeneous; the *average* density drops but the *local* density remains high. Importantly, we find that spectral weight is preserved in the transient (solid-liquid) peak and this suggests that ejected material exists primarily in condensed rather than vapor form. This finding is supported by an absence of spectral weight at the vapor phase position. The atom-solid peak shift can be estimated since estimates can be found for the initial state shift ( $\sim 1.4$  eV [12]), the change in (extra-atomic) relaxation (4.7 eV [15]), and the value of the surface potential ( $\sim 0.2$  eV [13]). Accordingly, vapor particles (isolated atoms) should be shifted  $\sim 3.5$  eV to higher binding energy relative to the solid. Given the absence of spectral weight at this location and  $\sim 10\%$  accuracy on the data we conclude that vapor particles comprise  $<10\%$  of the ejecta. Since the current spectra indicate that a condensed phase dominates the ejecta, it seems that in the current ablation regime expansion is microscopically inhomogeneous; wave function overlap is maintained and a vapor phase is suppressed.

As a second point, metallic core-hole screening (i.e., fluid Si) is observed to persist for  $<50$  ps and we take this as evidence that the ejected material has solidified on this rapid time scale. Rapid solidification suggests a highly

nonequilibrium phase transition. (Quasi) equilibrium phase transitions occur via nucleation and growth. We estimate that such a transition would take  $\sim 25$  ns given the measured solidification interface velocity (25 nm/ns [18]) and estimates of our probe volume ( $10^9$  nm<sup>3</sup>) and size of a critical nucleus ( $\sim 1$  nm [19]). This time is nearly 3 orders of magnitude greater than the observed solidification time and suggests that the solid phase nucleates throughout a substantial fraction of the probe volume on a  $< 50$  ps time scale. Phase transition by homogeneous nucleation (rather than by interface propagation) has been referred to as phase explosion [20] and signatures a highly undercooled material phase. In quasistatic experiments silicon quench rates of  $\sim 10$  K/s were obtained with an associated undercooling of  $\sim 240$  °C and a (solid-phase) nucleation rate of  $\sim 10^4/\text{cm}^3 \cdot \text{s}$  [21]. At this low nucleation rate less than one critical nucleus would be produced within our probe region in 50 ps indicating that rapid cooling accompanying vacuum expansion leads to significantly enhanced undercooling (vs quasi static case). Enhanced undercooling is of interest from a materials processing perspective since it may allow one to “trap” metastable material states.

Finally, with regard to particle formation, the relative absence of vapor particles indicates that in the current regime particles do not arise by condensation of a dilute vapor. This stands in contrast to nanosecond silicon-ablation experiments where vapor condensation is observed to be an important mechanism in the formation of particles [22]. In long-pulse ablation material is ejected into an intense laser field and it is likely that secondary laser-ejecta interactions contribute to the production of vapor particles. Secondary laser interactions are eliminated in short-pulse ablation so the nascent particle-size-distribution is determined by vacuum expansion. The sudden expansion of energetic matter is of interest to a number of scientific disciplines and simulations have established that strain associated with gradients in the expansion velocity leads to material fracture and an associated size distribution of “fragments” [23,24]. We therefore expect the nascent particle-size distribution in short-pulse ablation to be determined primarily by an initial fragmentation process. Recent simulations have probed the role of fragmentation in laser ablation [24].

The current experiments demonstrate an ability to probe transient material states and metal-insulator transitions occurring early in the vacuum expansion of an extreme material. Foreseeable improvements in energy (10–100 meV) and time ( $\sim 100$  fs [25]) resolution can reveal fine structure in the photoemission spectra and, with close coupling to theory, will provide detailed insight into the chemical evolution of extreme materials.

Such insights will play an important role in unraveling and eventually controlling the complex dynamics by which nanoparticles form via laser ablation. For instance, fine structure in the photoemission spectra can provide information regarding transient particle size and composition on the nanometer length scale.

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