Approaches for ultrafast imaging of transient materials processes in the transmission electron microscope

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The growing field of ultrafast materials science, aimed at exploring short-lived transient processes in materials on the microsecond to femtosecond timescales, has spawned the development of time-resolved, \textit{in situ} techniques in electron microscopy capable of capturing these events. This article gives a brief overview of two principal approaches that have emerged in the past decade: the stroboscopic ultrafast electron microscope and the nanosecond-time-resolved single-shot instrument. The high time resolution is garnered through the use of advanced pulsed laser systems and a pump–probe experimental platforms using laser-driven photoemission processes to generate time-correlated electron probe pulses synchronized with laser-driven events in the specimen. Each technique has its advantages and limitations and thus is complementary in terms of the materials systems and processes that they can investigate. The stroboscopic approach can achieve atomic resolution and sub-picosecond time resolution for capturing transient events, though it is limited to highly repeatable ($>10^6$ cycles) materials processes, e.g., optically driven electronic phase transitions that must reset to the material’s ground state within the repetition rate of the femtosecond laser. The single-shot approach can explore irreversible events in materials, but the spatial resolution is limited by electron source brightness and electron–electron interactions at nanosecond temporal resolutions and higher. The first part of the article will explain basic operating principles of the stroboscopic approach and briefly review recent applications of this technique. As the authors have pursued the development of the single-shot approach, the latter part of the review discusses its instrumentation design in detail and presents examples of materials science studies and the near-term instrumentation developments of this technique.

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1. Introduction

Since its inception, the transmission electron microscope (TEM) has been used to observe materials dynamics. The earliest observations of displacements (linear defects in crystalline materials) were made during \textit{in situ} straining experiments of metallic foils in the TEM by Peter Hirsch in the early 1950s (Hirsch, 1980; Hirsch et al., 1956). These experiments illustrated the advantage of using electrons to observe microstructural features: contrast from dynamical electron scattering effects allows the visualization of microscopic defects, making the TEM a powerful materials characterization tool (Hirsch et al., 1960; Howie and Whelan, 1961, 1962). The motion of dislocations in the strained metal was recorded on film using a standard camera with millisecond temporal resolution. These observations verified theoretical models of dislocation structure, interaction dynamics, and sources, providing fundamental understanding into the relationship between microstructure and mechanical behavior (Hirsch et al., 1956). In general, the aim of \textit{in situ} TEM is to relate structural features and dynamics observed on the Ångström to micron length scales to macroscopic behavior.

Since these seminal dislocation experiments, a myriad of TEM holders and specialized instrumentation have been developed for \textit{in situ} materials studies under various applied conditions: high temperatures, specific load conditions (nanoindentation, tensile and compressive loading (Marks et al., 2008; Minor et al., 2004;
Oh et al., 2009; Warren et al., 2007; Ye et al., 2008), externally applied magnetic (Tanase and Petford-Long, 2009) and electrical (Tan et al., 2001) field gradients, ultra-high vacuum (Tromp and Ross, 2000), in gaseous (Crozier et al., 2008; Gai, 1999, 2002), liquid environments (Creemer et al., 2008; Grogan and Bau, 2010), etc. Beyond these technological advancements to provide unique environmental conditions and external stimuli, the spatial resolution of in situ TEM techniques has greatly improved due to innovative electron optics (Batson et al., 2002) (e.g., high-quality, low-aberration lenses and aberration correctors), drift correction, and environmental enclosures that allow, for example, the observation of atomic motion across a phase boundary or the growth of nanostructures in the environmental TEM. Though in situ TEM techniques have progressed greatly in recent years and have provided valuable insights into materials, these techniques are still limited to the same temporal resolution (millisecond) as the first dislocation dynamics studies.

In most cases, video acquisition rates (33 ms) commonly used for in situ TEM observations lack the temporal resolution needed to fully interpret the evolution of the materials process occurring in the specimen. Using the dislocation experiments as an example, a typical goal for these in situ experiments is to acquire images of an evolving microstructure in which dislocations nucleate at sources, move at specific velocities, and interact under a given loading condition. For the interpretation of the dislocation dynamics, the acquisition system must capture and dissociate individual events. The ability to capture these processes depends on the temporal resolution of the recording system and its capability to spatially resolve features of the event at a given velocity. That is, the motion blur of these mobile features must be less than the desired spatial resolution, e.g., to have a motion blur less than 10 nm with 33-ms video rates requires the moving feature of interest to be slower than \( \sim 3 \times 10^{-7} \text{m/s} \). These speeds are slow when compared to the velocities common to many dynamic processes such as phase fronts in martensitic and even many diffusional transformations (Porter and Easterling, 1992) and dislocation speeds during plastic deformation under nanoindentation (Minor et al., 2004, 2006) (see Fig. 1). The next frontier for in situ TEM instrumentation lies in improving temporal resolution such that salient features of rapid materials dynamics can be captured.

The motivation to develop high time resolution microscopy techniques is by no means a recent thrust. It was evident from these first in situ experiments that higher time resolution than can be afforded by video rates was needed to understand a broader class of deformation conditions and materials reactions. Over the past four decades, many groups have pursued and developed time-resolved techniques (Bostanjoglo et al., 2000; Bostanjoglo and Rosin, 1976; Domer and Bostanjoglo, 2003; LaGrange et al., 2006, 2008; Lobastov et al., 2005; Reed et al., 2009; Spivak et al., 1988; Zewail, 2010). The first known example in the literature can be traced back to experiments conducted in the USSR in the mid-1960s by Spivak et al. (1966), in which they used a gated electron source synchronized with an applied magnetic field near the specimen to observe domain wall motion on microsecond timescales. Though the technological limitations of the era in TEM optics and electronics did not permit imaging of the domain wall dynamics with high spatiotemporal resolution, it is the first known application of the stroboscopic approach in a TEM.

High time-resolved TEM imaging may be achieved with either a single-shot (Armstrong et al., 2007a; Bostanjoglo, 2002; Bostanjoglo et al., 1987, 2000; Campbell et al., 2010; Domer and Bostanjoglo, 2003; King et al., 2005; LaGrange et al., 2006, 2008; Reed et al., 2009) or a multi-shot signal accumulation (stroboscopic) approach (Bostanjoglo and Rosin, 1976, 1980; Lobastov et al., 2005; Spivak et al., 1966; Takaoka and Ura, 1988; Zewail, 2010). The choice of the approach depends on the desired processes to be observed. If the process is unique and irreversible, then a single-shot approach is required to observe the dynamics (LaGrange et al., 2007, 2008), though the resolution of this technique is limited by electron–electron interactions (Armstrong et al., 2007a,b; LaGrange et al., 2006, 2008). However, electronic system dynamics and phase transitions that are highly repeatable require a stroboscopic technique with sub-picosecond temporal resolution (Barwick et al., 2008; Carbone et al., 2009a,b; Flannigan et al., 2009, 2010; Kwon et al., 2008a,b; Park et al., 2010, 2011). The stroboscopic approach captures rapid material dynamics with 0.1 nm spatial resolution on sub-picosecond timescales by accumulating the signal from millions of nominally identical pump–probe experiments from the same region on the sample, thus requiring that the process be highly repeatable and reset between pump–probe cycles (Lobastov et al., 2005; Zewail, 2010). The instrumentation requirements are thus quite different between the two approaches. The single-shot approach requires significant modification to the conventional TEM electron optics to operate in high-current mode (mAs of current), while the stroboscopic approach uses the standard electron optics and configurations of the TEM manufacturer (LaGrange et al., 2008; Reed et al., 2010). In both cases, high time resolution requires that the electron source be based on laser-driven photoemission and the TEM be modified to provide laser access to the electron source and the sample. Laser-based photoemission is the only way to generate pulses with the required brightness and short duration needed for high time-resolved electron microscopy (Armstrong et al., 2007a; LaGrange et al., 2006).

Both techniques have their advantages and limitations, and they are complementary in many ways and can be used to study materials behavior with unprecedented temporal and spatial resolution. Zewail et al. (Barwick et al., 2009; Lobastov et al., 2005; Zewail, 2010) have recently pushed the stroboscopic...
method to the extreme with a modern implementation employing femtosecond lasers and a field-emission TEM equipped with a high-energy-resolution electron energy loss spectrometer, allowing both sub-picosecond time-resolved imaging and spectroscopy. They have used their 4-D ultrafast electron microscope (4-D UEM) to observe mechanical resonance and photoexcited changes in binding between graphitic layers on picosecond timescales (Barwick et al., 2008; Carbone et al., 2009a,b; Flannigan et al., 2009; Zewail, 2010). The single-shot technique and technology have been advanced by the authors at Lawrence Livermore National Laboratory in the development of the Dynamic Transmission Electron Microscope (DTEM), which uses intense electron pulses to image transient materials states with nanometer/nanosecond resolution (Armstrong et al., 2007a; LaGrange et al., 2006, 2008; Reed et al., 2010). The DTEM has been used to capture rapidly evolving microstructures, phase transformations, and chemical reaction fronts in unexplored regimes at nanosecond scales (Campbell et al., 2010; Kim et al., 2008, 2011; Kulovits et al., 2011; LaGrange et al., 2006, 2007, 2008, 2009; Masiel et al., 2010; Nikolova et al., 2010; Taheri et al., 2009). This article details the state-of-the-art instrumentation of each approach and provides a brief discussion of how the single-shot and stroboscopic approaches have been applied to materials science investigations. Since the authors have been involved in the development of DTEM, the instrumentation and application will be discussed in detail.

2. Stroboscopic ultrafast electron microscopy (4-D UEM)

The advent of ultrashort laser systems and with them the development of advanced optical spectroscopy and electron scattering techniques that utilize ultrashort optical, X-ray, or electron pulses have burgeoned the fields of femtochemistry and femtobiology (observing chemistry and biological systems at timescales <10–12 s) to probe photo-stimulated, transient chemical and structural changes in molecules and materials. The stroboscopic TEM method (4-D UEM) developed in the lab of Prof. A. Zewail at CalTech adapts previous versions with modern laser and TEM technology (Lobastov et al., 2005; Zewail, 2010). In 4-D UEM, the specimen is cyclically pumped by one optical line of a femtosecond laser operating at a high repetition rate (MHz or faster) while another optical branch of the same laser is used to create a pulse train of electrons (through photoemission) that probes the specimen at some particular point in its pump cycle. Each electron pulse has on average only one electron, thereby eliminating space charge effects and enabling imaging resolution equivalent to that of conventional TEM. This method has frequently been referred to as single-electron imaging (Zewail, 2010). Images are built up from millions of single-electron pulses that are precisely time-correlated with the optical pulse generating the observable process in the specimen by using a simple optical delay line. Using this method, temporal and spatial resolution can be maintained at the optimum levels, but the fact that the specimen must be laser-pumped millions of times means that the process being studied must be perfectly reversible—the sample must recover from the excited state back to the ground state between shots.

The femtosecond 4-D UEM stroboscopic imaging and spectroscopy techniques are able to capture ultrafast reversible electronic processes on the scale of Ångström, femtoseconds, and fractions of an electron volt. They can be used to explore the dynamics of plasmonic and excitonic resonances in nanoscale systems and to study the influence of the structure and defect content on ferroelectric, ferromagnetic, and antiferromagnetic transitions in magnetic materials that are technologically important for microelectronics (Barwick et al., 2009; Carbone et al., 2009a,b; Park et al., 2010, 2011; Zewail, 2010). Existing optical probes of these processes miss essential details and cannot interrogate structural transitions or chemical changes to correlated changes in reflectivity. Stroboscopic instruments can probe these processes in real-space images, diffraction space, and electron energy loss spectroscopy with the requisite spatial, temporal, and energy resolution to truly follow the evolution these reversible processes in detail.

Recent studies (Barwick et al., 2008; Carbone et al., 2009b; Kwon et al., 2008b) using the femtosecond stroboscopic approach have been applied to the lattice dynamics and structural transitions in graphite films. Photoexcitation and heating of the electron system of the graphic foil with a femtosecond laser pulse is thought to shock the material, causing a structural transition as confirmed from large c-axis lattice expansion within a few picoseconds after the heating pulse. The lattice expansion is thought to be much too large to result from just thermal expansion and to correspond to a bonding hybridization change from sp2 to sp3 diamond. The bonding transition was confirmed using time-resolved, femtosecond electron energy loss spectroscopy (FEELS)1 (Carbone et al., 2009a,b). The excited “diamond-like” state persists for several picoseconds and then relaxes back to graphite. From observed variations in the bend–contour contrast and using cross-correlation image processing, nanoscale variations in vibration resonance and global resonance frequencies were observed, from which the in-plane elastic modulus of a single graphene sheet in the graphitic foil was measured. Using the standard toolbox of analytical microscopy techniques, the Zewail group has been able to divulge the subtle details of the complex evolution of transient states across large temporal (femtosecond to microsecond) and length scales (sub-nanometer to micron), noting the coupling of structural changes to photoexcited changes in the density of states and bonding.

The power of this technique lies in its ability to make connections between dynamical changes in atomic structure, morphology, chemical ordering, and electronic structure on the sub-picosecond timescales in nanoscale systems.

The major limitation of this technique is that processes studied must be completely reversible for millions of pump–probe cycles and reset within the repetition of the laser, which limits 4-D UEM to the study of the perfectly reversible chemical and materials processes. Many of the phase transformations and morphological changes that are important in processing engineered materials and relevant for catalytic reactions or biological processes are irreversible and cannot be interrogated with this technique. Furthermore, there is a misconception in the literature that the 4-D UEM stroboscopic approach will advance bio-imaging (Flannigan et al., 2010; Zewail, 2010). In fact, this technique suffers from the same radiation damage effects and irreversible changes that degrade soft-matter, biomaterials and reduce image resolution in standard cryoEM techniques. That is, radiation damage is an irreversible processes and it cannot be imaged by a single-electron, stroboscopic approach. In most cases, femtosecond stroboscopic imaging cannot arrest the dynamics or specimens’ movements to produce a sharp image if the motion is random and the dynamics of the processes never unfold the same way twice. For instance, imaging of cellular reactions in TEM environmental fluid holders would be impossible, as rapid Brownian motion of particles would blur the images. In order to observe the dynamics of irreversible processes, a single-shot approach must be used. However, electron–electron interactions make high spatial resolution imaging on ultrashort timescales rather difficult (Armstrong et al., 2007a; King et al., 2005; LaGrange et al., 2006; Reed et al., 2009).

1 FEELS has also been used to study multi-photon absorption, optical, and plasmon resonant modes. It is a powerful technique that allows the study of spatially correlated changes in electronic structure in nanostructured materials (Barwick et al., 2009; Park et al., 2011; Zewail, 2010).
3. Single-shot imaging (DTEM)

The single-shot approach was pioneered by Bostanjoglo and coworkers (Bostanjoglo, 2002; Bostanjoglo et al., 1987, 2000; Domer and Bostanjoglo, 2003), who demonstrated a spatial resolution of ∼200 nm with pulse duration of ∼10 ns. The first instruments used gated electron sources and laser-induced thermal emission to achieve microsecond resolution. Later evolutions of the instrument used nanosecond pulsed, UV lasers to generate intense electron pulses for high-time-resolution, single-shot imaging via photoemission. These instruments also included a high-speed deflector and multichannel plate acquisition system to collect three frame sequences of the transient dynamics with nanosecond switching times. Though the instruments constructed in Bostanjoglo’s group pioneered the single-shot method, they were built on an antiquated TEM platform (Elmskop 1A) with a non-optimal electron-optic and photo-gun design, limiting the spatial resolution.

Since all the information is obtained in a single specimen drive event, this technique is able to measure irreversible and unique material events that cannot be studied by the stroboscopic approach. The limitation is that the method requires high beam currents. High-brightness photoemission sources must be used for low-noise imaging on nanosecond timescales, requiring unique modifications of the electron optics and gun in the TEM. The electron-optic design should preserve the high-brightness electron pulse and minimize space-charge and electron–electron–scattering effects that can degrade the resolution (Armstrong et al., 2007a; King et al., 2005; LaGrange et al., 2006, 2008; Reed et al., 2009). The key is therefore to choose microscope components and operating parameters that optimize the tradeoff between spatial and temporal resolution. The following section details the recent electron optical modifications to the TEM column of the Dynamic Transmission Electron Microscope (DTEM) at Lawrence Livermore National Laboratory (LLNL) that allow for high-quality, real-space images of materials dynamics with 15-ns exposure times.

3.1. Single-shot DTEM at LLNL

In its current state, the LLNL DTEM can capture transient states in irreversible materials processes with 15-ns temporal resolution using a single-shot approach—one specimen pump and one probe pulse (see Fig. 2) (Campbell et al., 2010; LaGrange et al., 2008; Reed et al., 2010). To achieve the 15-ns exposure times, the single-probe pulse has enough electrons to capture a complete image or diffraction pattern of the transient state in the material. The electron bunch in the probe pulse is generated via photoemission by irradiating a Ta disk cathode with a 211-nm-wavelength laser pulse. High-quality images and diffraction patterns are produced with electron bunches containing $10^9$ and $10^7$ electrons, respectively. With these high currents enable by a unique electron-optical configuration, the LLNL DTEM can acquire images with a better than 10-nm spatial resolution, which is more than an order of magnitude improvement over the single-shot instrument developed by Bostanjoglo. The electron-bunch duration on nanosecond timescales closely corresponds to the UV laser pulse width, e.g., in LLNL DTEM, a 12-ns UV pulse generates a 15-ns electron bunch. A second laser synchronized to the photoemission laser drives specific reactions in the specimen, and a snapshot image or diffraction pattern of the reaction is obtained after a defined time interval, e.g., 10 ns, 100 ns, etc. By combining several of these snapshot images or diffraction patterns from repeated experiments on “fresh” sample regions at different delays, it is possible to create a time sequence of the on-average evolution of the reaction. This allows us to observe the intrinsic details of how a dynamic reaction evolves, rather than merely inferring the extremely complex reaction pathway from postmortem analysis.

Two core aspects of the DTEM technology at LLNL have undergone considerable development and evolution from the original designs of the single-shot instrument developed by the Bostanjoglo group—the laser-driven photo-gun and the electron-optic configuration of the TEM column. Increased time resolution comes at the expense of reduced signal (number of electrons in a pulse) and electron beam coherence, which is ultimately governed by the finite brightness of the photoemission source. Operating with high-current electron pulses has the additional expense that space-charge effects and associated lens aberrations can further reduce the effective brightness of the gun. The key advancement of DTEM technology at LLNL was the choice of microscope components, electron-optic settings, and laser operating parameters that optimize the tradeoff between spatial and temporal resolution and preserve the finite brightness of the photo-gun through the entire electron optical system.

Custom laser systems and laser transport optics were constructed to maximize the photoemitted current, and the electron optics were modified to provide higher signals on the sample and CCD camera (LaGrange et al., 2006). More current is generated from larger emission areas but with reduced spatial coherence. The amount of charge emitted from an area on the cathode is proportional to the electric field strength applied to the cathode (Child-Langmuir, space-charge limit) (Jansen, 1998; Kruit and Jansen, 1997). Newly emitted electrons exert an electric field that retards the further emission of electrons (image charge), and these space-charge forces are balanced by the applied electric fields in the gun. Thus, high electric fields applied to the cathode allow the generation of bright photoemitted beams. The equipotential lines of the electrical field should be smooth, such that the photoemitted bunch of electrons have a uniform spatial and temporal distribution and the space-charge effects do not spatially broaden the electron bunch, producing aberrations and reducing gun brightness. The photo-gun geometry and laser-system parameters were thus optimized to obtain a high, smooth electric field and high photoemitted current from a small emission region, e.g., flat photocathode with a small Wehnelt-cathode gap and 300-μm 1/e2 diameter laser spot. Optimization of the gun configurations alone did not provide the number of electrons per pulse required for high-contrast bright-field imaging. To make the additional tradeoff between beam coherence and signal, the removable and fixed apertures were removed from the condenser lens system, which allowed for high convergence angles and higher currents on the specimen. The high convergence angles and large-diameter pulsed beam coupled with the spherical aberrations of the objective lens significantly reduced the image resolution (30 nm), making it difficult to resolve microstructural features (Armstrong et al., 2007a; LaGrange et al., 2006). Further improvements in the spatial resolution to <10 nm were achieved by increasing the gun brightness through the optimization of the laser spot profile, e.g., relay imaging of a spatial filter to produce a small flat-top beam on the cathode (LaGrange et al., 2008). Appropriate laser beam spatial profiles are critical for source brightness and the reduction of space-charge-induced aberrations that reduce brightness.

Though the laser system and gun were optimized to maximize photoemission current, the spatial coherence of the electron beam was sacrificed to obtain the necessary signals for imaging by modifying the DTEM’s condenser system to accept much wider (higher emittance) electron beams than a conventional TEM. Removing fixed apertures and weakening the C1 lens made small improvements in signal on the camera and image quality. However, the cathode laser mirror positioned above the C1 lens was the limiting aperture and blocked 90% of the electrons. To increase the dose on the specimen and CCD camera, a very weak, large-bore lens...
(dubbed the C0 lens, since it precedes C1) and a long (~20 cm) drift space were added above the laser mirror (LaGrange et al., 2008; Reed et al., 2010). This allowed the beam to be refocused and pass through the 1-mm-diameter hole in the mirror and into the center of the C1 lens without introducing excessive aberrations. The better coupling of the photoemitted beam into the condenser optics produced a twentyfold improvement in beam current compared to the DTEM without the C0 lens (Reed et al., 2010).

With this electron-optic configuration, the signal and spatial resolution are limited by the source brightness rather than by the lens and aperture designs. To increase spatial resolution, the source brightness must be improved. The spatial resolution with 15-ns pulses is expected to be ~1 nm, which is primarily limited by random electron scattering events in high-strength lens crossovers below the specimen that produce an irreversible loss of high-resolution spatial information encoded in an electron pulse. However, the current resolution of LLNL DTEM is still limited to ~10 nm, and two orders of magnitude increase in brightness is required to reach the “stochastic” spatial resolution limit of 1 nm (Armstrong et al., 2007b; Reed et al., 2009). In order to achieve this increased brightness, the photo-gun and electron accelerator need a radical change from conventional TEM designs and operating principles, and efforts are underway to design a new, high-brightness photoemission gun for the next-generation DTEM instruments (Reed et al., 2009).

Given the limited source brightness, a compromise can be made that improves spatial resolution, but it comes at the expense of temporal resolution. Since not all experiments require nanosecond time resolution, longer electron pulse can be used. Longer pulses have reduced space-charge effects and thus can have higher electron doses that enable the acquisition of images with higher spatial resolution, e.g., with a 1-μs electron pulse, images with sub-nanometer resolution can be acquired (Armstrong et al., 2007b; LaGrange et al., 2008; Reed et al., 2009). In situ experiments at these longer pulses are still four orders of magnitude higher in temporal resolution than conventional TEM, and the temporal resolution is sufficient, for example, to study some catalytic reactions, crystallization, and dislocation dynamics, which can benefit from the added electron dose and increased spatial resolution. To enable a flexible platform to tailor the laser parameters for a given experiment, an arbitrary waveform generation laser (AWG) was constructed that can temporally shape laser pulses, thus allowing easy changes to the pulse duration. The AWG is comprised of a waveform generator that drives a fiber-based electro-optical modulator, which temporally shapes a continuous-wave fiber laser seed pulse, and a series of free-space diode laser heads that amplifies the modulated waveforms to energies >1 J. The AWG cathode drive laser allows for continuously variable and controlled electron pulse durations from 250 μs down to 10 ns and the production of electron pulse trains, an essential element of the planned DTEM “Movie Mode” of operation.

3.2. Movie Mode DTEM

The ability to acquire high-time-resolution movies, dubbed Movie Mode Dynamic Transmission Electron Microscope, expands
the DTEM’s science capabilities by providing detailed histories of unique material events on the nanometer and nanosecond scales. Prior DTEM hardware only allowed single-pump/single-probe operation, building up a process’s typical time history by repeating an experiment with varying time delays at different sample locations. The Movie Mode DTEM upgrade enables single-pump/multi-probe operation. It provides the ability to track the creation, motion, and interaction of individual defects, phase fronts, and chemical reactions, providing invaluable information of the chemical, microstructural, and atomic-level features that influence the dynamics and kinetics of rapid material processes. While a single pump–probe snapshot provides statistical data about these factors, a multi-frame movie of a unique event allows all of the factors to be identified and the progress of nucleation-and-growth processes to be explored in detail. It provides unprecedented insight into the physics of rapid material processes from their early stages (e.g., nucleation) to completion, giving direct, unambiguous information regarding the dynamics of complex processes.

The two core components of the Movie Mode technology (Fig. 3) are the arbitrary waveform generator (AWG) cathode laser system and a high-speed electrostatic deflector array. The AWG cathode drive laser produces a series of laser pulses with user-defined pulse durations and delays that stimulates a defined photoemitted electron pulse train. Each pulse captures an image of the sample at a specific time. A fast-switching electrostatic deflector located below the sample directs each pulse (image) to a separate patch on a large, high-resolution CCD camera. At the end of the experiment, the entire CCD image is read out and segmented into a time-ordered series of images, i.e., a movie. The current technology produces 9-frame movies but the near-term modification to the system should enable up to 25-frame movies with interframe times as low as 25 ns. This frame rate is six orders of magnitude faster than modern video-rate in situ TEM. Future versions of Movie Mode may also include fast-framing CCD technology, which can capture hundreds of frames within a few microseconds. The operating principle of these devices is that the photoelectron CCD data from multiple frames is stored in on-chip buffers that are read out at the end of the acquisition.

3.3. Applications

3.3.1. Complex laser-driven crystallization of amorphous Ge films

The crystallization of amorphous Ge (a-Ge) films induced by laser heating is quite complex, creating an exotic microstructure that forms over timescales ranging from a few nanoseconds to several microseconds after pulsed-laser excitation (see Fig. 4) (Bostanjoglo, 1982; Bostanjoglo and Endruschat, 1985; Bostanjoglo et al., 1992; Nikolova et al., 2010; Sharma et al., 1984). High-quality information on the final postmortem structure can be obtained.
with a variety of techniques. However, structural characterization of short-lived nonequilibrium states has shown to be very challenging. Revealing the dynamics of the structural transformations in materials requires direct observations with at most nanosecond temporal resolution and a spatial resolution of few nanometers. We used the single-shot nanosecond imaging capabilities of the DTEM to capture the complex crystallization behavior of a-Ge films and determine the nucleation and growth mechanism of the crystallization process.

During crystallization, three distinct microstructural regions form: (1) nanocrystalline region, (2) radial dendritic-like grains, and (3) layered structure with nanocrystalline grains and large grains oriented tangential to the growth front (see Fig. 4). Crystallization initiates at times less than 20 ns and Zone (1) fully crystallizes within 55 ns. The crystallization rate was determined by estimating the mean size and number of newly formed crystallites apparent in the amorphous matrix as a function of time after the laser heating pulse (Nikolova et al., 2010). Assuming that linear growth of isolated, active nuclei occurs during crystallization and that parabolic grain growth is the predominant mode of coarsening after complete crystallization, the change between these growth modes at the intersection between the fits on the plot in Fig. 5 indicates the timescale for complete crystallization, ~55 ns. By counting the number of crystals per unit area for each time delay, the nucleation rate was estimated. The number of crystals per unit of area increased for delays up to 50 ns, then decreased due to coalescence and coarsening reactions, which is in good agreement with the estimated 55 ns for full crystallization. The maximum nucleation rate, i.e., the rate calculated from 0 and 20 ns, has been estimated to be $1.6 \times 10^{22}$ nuclei/cm$^2$ s. These data obtained from DTEM observations are the first known report that uses direct imaging of nanosecond crystallization events in a-Ge to quantify nucleation rates.

The large dendritic grains in Zone (2) emerge from the nanocrystalline Zone (1), which act as nuclei, and grow at rates exceeding 10 m/s to lengths of several microns (see the time-resolved images in Fig. 6). The striated grain structure at the transition zone suggests an oscillatory instability between the two crystallization modes, nanocrystallization (Zone (1)) and dendrite formation (Zone (2)). Perhaps after a certain volume has crystallized and is heated by the exothermic crystallization reaction, the temperature is sufficient to catalyze the growth of large dendrites (Mullin–Sekerka instability). The roughening of the crystallization front (dendritic protrusions) also suggests localized heating. After delays longer than 1 μs from the laser heating pulse, the growth mode at the periphery of the laser-irradiated zone changes from radial along the direction of heat diffusion to tangential, perpendicular to the thermal gradient, forming Zone (3) that consists of “tangential” layers comprised of large faceted crystals (light gray contrast) and nanocrystals (dark gray). The time-resolved images in Fig. 7 clearly show this tangential growth mode that develops over a period of ~10 μs. The complexity of the growth dynamics reveals the underlying importance of interfacial energy anisotropies on the crystallization kinetics. Future studies will attempt to correlate these observed growth dynamics with calculated heat evolution and temperature profiles, as well as simulation of the anisotropic dendritic and oscillatory growth.

### 3.3.2. Quantifying nucleation behavior in amorphous NiTi film crystallization

The crystallization processes of as-deposited, amorphous NiTi (a-NiTi) thin films has been studied in great detail using techniques such as differential scanning calorimetry and in situ TEM (Chen and Wu, 2001; Jiang et al., 2001; Kim et al., 2000; Lee et al., 2005; Ramirez et al., 2006; Vestel et al., 2003; Wang and Vlassak, 2006). The kinetic data from these experiments have been analyzed using semi-empirical models such as the Johnson–Mehl–Avrami–Kolomogrov (JMAK) formulae (Avrami, 1939; Johnson and Mehl, 1939). The kinetic parameters determined from this analysis have been useful in defining process control parameters for tailoring microstructural features and shape-memory properties for device applications. Laser-based annealing has been used to spatially control the microstructure evolution down to submicron levels. Nanosecond pulsed-laser annealing is particularly attractive since it limits the amount of peripheral heating and unwanted microstructural changes to underlying or surrounding material. Such laser-processing techniques are quite common for producing a-Si and a-Ge thin-film-based microelectronics. However, the complex crystallization processes of NiTi intermetallics are difficult to discern and control under heating conditions of pulsed-laser irradiation, which occur at temperatures far above the glass transition ($T_g$) and are extremely short (<100 μs).

The limited data on the crystallization kinetics of NiTi under pulsed-laser irradiation is primarily due to the high crystallization rates intrinsic to high-temperature annealing far above $T_g$ and the spatial and temporal resolution limitations of standard TEM and DSC techniques (LaGrange et al., 2009). The high time and spatial resolution capabilities of the DTEM afford the direct observation of rapid nucleation events occurring from pulsed-laser irradiation and the quantification of nucleation rates. Fig. 8 shows an example of a series of nanosecond, time-resolved DTEM images of the pulsed-laser-induced crystallization process in the a-NiTi film. The middle image is taken 1.5 μs after the pump laser irradiates the sample; the center of the pulsed laser spot (135 ± 5 μm 1/e$^2$ diameter) is located in the upper left-hand corner of the image. Note the semi-circular pattern of the newly formed crystallites (light contrast) in the amorphous matrix (dark background) that radiates outward from the center of the laser-irradiated zone. Crystallization initiates first in this region at a radius corresponding to a temperature of 1200 K (middle image of Fig. 8). The surrounding regions crystallize with varying nucleation, growth rates and times proportional to the temperature gradient across the Gaussian laser-heated zone governed by the thermodynamically driving forces and kinetics. Fig. 9 shows the variation in crystallite density with crystallite size observed at delay of 1.5 μs from initial laser heating pulse (e.g., data taken from the middle image in Fig. 8). This variation is driven by thermal gradients across laser irradiated area giving rise to an
equal gradient in thermodynamic driving forces and kinetics leading to a variation in nucleation behavior, growth rates and grain sizes. At radial distances close to the center of the laser-heated zone, where temperatures approach an estimated 1500 K, the nucleation rates are quite low ($<5 \times 10^{16}$ nuclei/cm$^3$ s), though, the crystalized grain are large (>1 $\mu$m) due to high growth rates. At 25 $\mu$m from the center, where temperature are estimated to be around 1200K, the nucleation rates are quite high ($10^{18}$ nuclei/cm$^3$ s) and the growth rates are moderate producing sub-micron grain sizes (500–700 nm). At temperatures between 900 and 1100 K, the nucleation rates are high, exceeding ($>10^{20}$ nuclei/$\mu$m$^3$ s) that produce grain sizes below 100 nm. Below 900 K, no nucleation is observed. Though the temperature in this region is above reported values for $T_g$ (700 K) (Chen and Wu, 2001), the combination of low temperatures and high cooling rates ($>10^6$ K/s) does provide the sufficient conditions (limited kinetics) to drive crystallization.
This crystallization behavior can be described qualitatively by classical phase transformation theory as the competition between thermodynamic driving force and kinetics, which can be further illustrated by the transient crystallized microstructure shown in Fig. 10. The plot in Fig. 10A shows the curve for 90% crystallization as a function of time for pulsed-laser annealing. Note that the high rates of crystallization occur at temperatures around 1200 K (the nose of the C-curve). At temperatures above 1200 K, the thermodynamic driving force for nucleation decreases (increased entropy), but growth rates are kinetically enhanced at the higher temperatures, leading to large grains. At temperatures below 1200 K, the nucleation rates are high due to higher driving forces but the crystallite growth is kinetically limited (diffusion-controlled), leading to fine-grained microstructures. The time-resolved DTEM image in Fig. 10B, taken at a delay of 6 μs, displays a direct measurement of this C-curve behavior, where the crystallization fronts are propagating inwards and outwards, and the radial variation in grain size. The direct measurement of nucleation and growth rates as a function of temperature allows prediction and control of grain size, which is necessary for fabrication of devices. Using the DTEM, rapid nucleation and growth phenomena occurring under steep thermal gradients can be directly observed and quantified with nanosecond time resolution. This allows us to gain insight into the subtle details of materials processes in previously unexplored regimes and far-from-equilibrium conditions.

3.3.3. Observing liquid–solid interface instabilities in rapidly solidifying metallic films

How microstructures evolve during solidification is of great scientific and technological importance. Laser-based melting and joining of metallic thin films are widely used in the fabrication of microelectronic circuits, where the control of structure-sensitive properties is important for device performance. Much is still unknown about the kinetics and mechanisms that govern the laser-induced rapid solidification in metal thin films to produce high-aspect-ratio grain structures with large defect concentrations. Though there are many theoretical models, virtually no experimental data exist to validate computational predictions of the process kinetics and structural evolution of the liquid–solid interface. Time-resolved optical methods that facilitate measurement of rapid solidification kinetics in Si or Ge (Bassler et al., 1997) cannot be applied to the study of solidification in metals, since most metallic liquids and solids have the same optical reflectivity.

To validate finite element models of the heat evolution during solidification, the first experiments studied the rapid solidification of laser-melted zones in pure metals systems having well-known thermodynamical properties (Kulovits et al., 2011). The specimens were nanocrystalline, 80-nm-thick Al films deposited on 100-nm-thick amorphous Si3N4 membranes. The DTEM experiments were performed by first melting the Al films with a single 12-ns, 1064-nm-wavelength laser pulse. Different delays between the laser heating and electron pulses were used to acquire images and diffraction patterns (DP) of the liquid–solid interface dynamics and observe microstructural evolution during rapid lateral solidification. Before melting, the low-magnification image of the as-deposited thin film shows a weak, speckled contrast of the nanocrystalline microstructure (Fig. 11A). The corresponding DP shows a ring pattern characteristic of the nanocrystalline Al film superimposed on the diffuse background from the amorphous Si3N4 substrate, as identified by the diffuse peaks situated underneath sharper Al diffraction maxima in the radial average intensity (RAI) plot. After heating the sample with laser fluences of ~510 mJ/cm², the Al layer rapidly melts, as indicated by the disappearance of the nanocrystalline grains in the bright field (BF) image, the diffuse rings in the DP, and broad peaks in the RAI plot (Fig. 11B). After 5 μs, the solidification front transits across the field of view, exhibiting a distinctly smooth morphology free from local protrusions that would suggest growth of thermal dendrites. Though the liquid–solid interface is elliptically shaped on the micron length scale, it is smooth on the scale of the film thickness (80 nm), indicative of a stable planar liquid–solid solidification front, producing large elongated grains (Fig. 11C). After solidification, the DP showed a reduced diffuse background and distinct diffraction spots instead of diffraction rings, since the number of grains in the field of view was significantly reduced (Fig. 11D). By tracing the progress of the solid–liquid interface during the transformation, we estimate a solidification front velocity of ~3–4 m/s. The velocity and planar front morphology correspond to solidification inward from a cold solid into a superheated liquid that is 100 K over the melting temperature (T_m > 100 K) (Porter and Easterling, 1992). These data will be used to calibrate heat transfer and thermal profile simulations of the solidification, which, in turn, will be used to interpret solute effects on morphological instabilities in alloys.

We have also extended our studies of rapid solidification to alloy systems. Preliminary investigation of the Al–Cu system showed that the liquid–solid interface transitions from a "stable" planar front to an unstable wavy front as the Cu content increases. Fig. 12 shows select DTEM bright-field images of delay time sequences for a dilute Al–5 at.%Cu and a concentrated Al–33 at.%Cu alloy. The dilute alloy exhibits a planar solidification front that propagates at a
velocity of $\sim 3.5$ m/s, similar to the pure Al films. These films exhibit a distinct band of fine-grained microstructure near the edge of the melt-solidified zone that differs from the larger, elongated grains in the center of the zone. The band suggests a compositional instability during the initial stages of solidification that causes remelting from the heat of mixing (Al and Cu) and recrystallization. This instability can also be created by competing constitutional supercooling effects from Cu solute pushed to the solidification front. The concentrated Al–33 at.\%Cu alloy exhibits a wavy solidification front and instabilities perturbed by compositional variations at the front, typical for dendritic growth during alloy solidification. Solidification front velocities are typically less than 1 m/s and nucleation within the melt has been observed, likely due to constitutional supercooling effects. Future work will include detailed investigation of the dependence of the interfacial stability on chemical composition of the Al–Cu alloys, in order to provide experimental data for theoretical model verification.

4. Summary

Table 1 summarizes the operational parameters, technical capabilities, limitations, and advantages of the stroboscopic and single-shot instruments presented in this article. Both techniques provide a fundamentally new capability for the characterization
of dynamics at the nanoscale and offer many orders of magnitude increase in time resolution over conventional electron microscopy techniques. These techniques should be viewed as complementary. Each technique possesses unique capabilities designed to study specific materials dynamics. Instruments operating in the stroboscopic mode can study highly repeatable photoexcited processes on sub-picosecond timescales with atomic resolution. The single-shot approach can study irreversible processes with nanosecond/nanometer resolution. In the past decade, these novel instruments have made fundamental contributions toward many scientific fields by providing novel insights from the study of photoexcited, nanoscale mechanical instabilities and phase transformations; photoexcited electronic transitions; martensitic phase transformations; rapid chemical reactions in multilayer thin films; and rapid laser-driven crystallization and solidification processes occurring under extreme driving forces. These techniques hold enormous potential for the way scientists perform in situ electron microscopy experiments. As this burgeoning field matures, we envision many more applications, new techniques and instrumentation, and exciting new insights to the salient behavior of materials as we delve into these unexplored regimes.

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References


Table 1

<table>
<thead>
<tr>
<th></th>
<th>Stroboscopic</th>
<th>Single shot</th>
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<tr>
<td>Example</td>
<td>4-D UEM</td>
<td>DTEM</td>
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<tr>
<td>Electrons/pulse</td>
<td>~1–10⁶</td>
<td>~10⁷–10⁹</td>
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<td>Time resolution</td>
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<tr>
<td>Energy spread</td>
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<td>~10eV</td>
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<td>Spectroscopy</td>
<td>Yes</td>
<td>Not demonstrated</td>
</tr>
<tr>
<td>Main strength</td>
<td>Spatiotemporal resolution</td>
<td>Capture unique, irreversible events in real space</td>
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<tr>
<td>Main weakness</td>
<td>Limited to the study of extremely repeatable processes</td>
<td>Resolution</td>
</tr>
</tbody>
</table>

Fig. 12. Time-delay sequence of time-resolved bright-field DTEM images showing the morphological and structural evolution during rapid solidification of two Al–Cu thin films. In the top images, the laser was centered on the far left, 10μm outside the images. In the bottom row of images, the center of the Gaussian laser spot was positioned near the lower right-hand corner.


